

LIGNIN-BASED CARBON FIBER

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Thesis Advisor: Dr. Joseph M. Genco

An Abstract of the Thesis Presented
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This study was undertaken in support of the Biorefinery concept applicable to hardwood Kraft mills. The “near neutral hemicellulose extraction process” uses sodium carbonate and sodium sulphide (green liquor) to extract acetyl groups and carbohydrates from hardwood chips for conversion into acetic acid and five and six carbon sugars respectively. Lignin, although extracted in the process, is underutilized and is potentially a valuable by-product.

The objective of this study was to investigate methods of recovering lignin as a possible precursor material suitable for production of carbon fiber. Recovered hardwood lignin would serve as an alternative raw material to supplement commercial precursors such as polyacrylonitrile (PAN) and pitch from petroleum and coal. Previous lignin studies are reviewed that use a variety of lignin types and lignin-polymer blends as precursors for carbon fiber. Few however explore using pre-extracted lignin from a Biorefinery as a carbon fiber precursor. The most suitable method developed in the present study for recovery of pre-extracted lignin involved a four step procedure. Crude lignin is

precipitated from the wood extract by adding sulfuric acid to lower the pH value to 1.0. The crude lignin extract is then upgraded by using hydrolysis to cleave lignin carbohydrate bonds and to remove carbohydrates that contaminate the lignin. The precipitated lignin solids were separated by filtration, washed with water and then dried in an oven. This procedure was found superior to a technique predicated upon using ethanol to precipitate and remove carbohydrate contamination. Lignin recovered using the hydrolysis method developed here was found to be high in carbon, high in total lignin, low in inorganic contamination and low in insoluble material, but high in volatile material.

The recovered lignin could be readily spun into lignin fibers, but the spun fibers proved to be extremely brittle. Of all of the samples evaluated, Alcell lignin fiber was found to be the least brittle. This decrease in brittleness in the Alcell lignin fiber was attributed to a low glass transition temperature (T_g) measured as (108.6 °C) and found to be the lowest of any of the samples evaluated. The spun lignin fiber was stabilized thermally in air at 200 °C and converted into carbon fiber in an argon atmosphere at 1,000 °C. Micrographs obtained using scanning electron microscopy (SEM) illustrated numerous imperfections on the surface and in the interior microstructure of the carbon fiber when compared to micrographs taken of commercial carbon fiber manufactured using PAN and pitch. These imperfections were thought to be related to the high volatile material content in the samples and a heating rate that was too high in the carbonization process. To utilize pre-extracted lignin as a raw material for producing carbon fibers the brittleness problem must be overcome. Methods for solving this problem are discussed, including hydrogenation and acetylation of the lignin to reduce cross-linkages and lower its glass transition temperature (T_g).

THESIS/DISSERTATION/PROJECT

ACCEPTANCE STATEMENT

On behalf of the Graduate Committee for Jie Luo, I affirm that this manuscript is the final and accepted thesis/dissertation/project. Signatures of all committee members are on file with the Graduate School at the University of Maine, 42 Stodder Hall, Orono, Maine.

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TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	iv
LIST OF TABLES.....	x
LIST OF FIGURES.....	xii
Chapter	
1. BACKGROUND INFORMATION	1
1.1 Raionale for Study.....	1
1.2 Hemicelluloses Pre-extraction Process	2
1.3 Carbon Fiber	5
1.3.1 Properties of Carbon Fibers	11
1.3.2 Applications of Carbon Fiber	11
1.3.3 Commercial Precursor Materials for Carbon Fiber	12
1.3.4 Production Process for Carbon Fiber	12
1.4 Lignin	14
1.4.1 Structure of Lignin	14
1.4.2 Lignin-Carbohydrate Complex.....	17
1.4.3 Applications of Lignin	20
2. REVIEW OF PREVIOUS LITERATURE ON LIGNIN BASED CARBON FIBER.....	21
2.1 Carbon Fiber from Lignin for Transportation	22
2.2 Modified Lignin for Use in Carbon Fiber Production	24
2.3 Organosolv Lignin as Precursor	27
2.4 Carbon Fibers from Lignin – Synthetic Polymeric Blends	29

3. OBJECTIVE AND SCOPE	32
4. HEMICELLULOSE PRE-EXTRACTION EXPERIMENTS	35
4.1 Wood Components.....	35
4.2 Chemicals and Materials	38
4.3 Hemicelluloses Pre-extraction Experiments.....	38
4.4 Results and Discussion.....	39
4.4.1 Extract pH.....	43
4.4.2 Wood Extracted	43
4.4.3 Pressure and Temperature	44
4.4.4 Lignin Content in Extract	50
4.4.5 Total Solids and Organics Solids in Extract.....	50
4.4.6 Xylan and Acetate Concentrations in Extract.....	52
4.5 Conclusions	53
5. LIGNIN ISOLATION AND CHARACTERIZATION	55
5.1 ORNL Specifications for Lignin as a Carbon Fiber Precursor Material.....	55
5.2 Lignin Separation Methods	56
5.2.1 Method of Sun	56
5.2.2 Hydrolysis Method.....	58

5.3 Analysis of Recovered Lignin	59
5.3.1 Lignin Content	59
5.3.2 Ash Content at 900 °C.....	61
5.3.3 Volatile Material Content at 250 °C	61
5.3.4 Particulate Matter Content.....	61
5.3.5 Carbon Content	61
5.3.6 Statistical Experimental Analysis	62
5.4 Results and Discussion.....	63
5.4.1 Two-Sample t-Test Used to Compare the Lignin Isolation Techniques.....	66
5.4.2 Lignin Isolated by the Hydrolysis Method.....	67
5.5 Conclusions	77
6. LIGNIN FIBER SPINNING	80
6.1 Lignin Glass Transition Temperature	80
6.1.1 Factors Influencing the T_g Value	82
6.1.2 Glass Transition Temperature Determination	86
6.2 Lignin Molecular Weight	87
6.2.1 Molecular Weight Determination	89
6.3 Lignin Fiber Spinning	90
6.3.1 Polymer Fiber Spinning	90
6.3.2 Lignin Fiber Spinning	91

6.4 Results and Discussion.....	93
6.4.1 Lignin Glass Transition Temperature	93
6.4.2 Lignin Molecular Weight	97
6.4.3 Dependence of T_g upon Molecular Weight	100
6.4.4 Lignin Fiber Spinning	100
6.5 Conclusions	105
7. LIGNIN FIBER STABILIZATION AND CARBONIZATION	107
7.1 Lignin Fiber Thermal-stabilization	107
7.2 Lignin Fiber Carbonization	108
7.3 Lindberg/Blue M Tube Furnace	108
7.4 Carbon Fiber Surface Microstructure.....	109
7.5 Samples	110
7.6 Results and Discussion.....	110
7.6.1 Lignin Fiber Thermo-stabilization and Carbonization.....	110
7.6.2 Effects of Thermo-stabilization on Lignin Glass Transition Temperature.....	115
7.6.3 Carbonization of Lignin Fiber	117
7.6.4 Yield of the Thermo-stabilization and Carbonization Processes	118
7.6.5 Surface Microstructure of Carbon Fiber	123
7.6.6 Properties of Carbon Fiber	131
7.7 Conclusions	135

8. CONCLUSIONS AND RECOMMENDATIONS.....	137
8.1 Conclusions	137
8.2 Recommendations	141
REFERENCES.....	143
APPENDIX A ANALYSIS OF RAW EXTRACTS.....	149
APPENDIX B PRELIMINARY EXPERIMENTS.....	155
BIOGRAPHY OF THE AUTHOR	161

LIST OF TABLES

Table 2.1 Cost of Commercial PAN Based Carbon Fiber	23
Table 2.2 Summary of Physical Properties of Carbon Fibers from Lignin Literature Sources	25
Table 2.3 Physical Properties of Carbon Fibers from Lignin-PEO Blends	30
Table 2.4 Physical Properties of Carbon Fibers from Lignin Blends.....	31
Table 4.1 Summary of Green Liquor Pre-Extraction Data	42
Table 4.2 Chemical Analysis of the Raw Wood---Data Estimated by Dr. Haixuan Zou	42
Table 5.1 Lignin Specifications as a Precursor Material for the Production of Carbon Fiber	56
Table 5.2 Summary of the t-test Applied to the Properties of Lignin Isolated by the Two Methods	64
Table 5.3 Comparing the Lignin Samples Isolated by Different Methods.....	69
Table 6.1 Properties of Standard Polystyrene	94
Table 6.2 Glass Transition Temperatures T_g for Different Lignin Samples.....	95
Table 6.3 Lignin Glass Transition Temperatures Reported by Schmidl	97
Table 6.4 Lignin Molecular Weights by GPC	98
Table 6.5 Lignin Molecular Weight Measurements Reported by Schmidl	99
Table 6.6 Summary of Fiber Spinning Experiment	101
Table 7.1 Summary of Lignin Fiber Thermo-stabilization and Carbonization Process.....	113
Table 7.2 Lignin Glass Transition Temperature before and after Thermo-stabilization	116
Table 7.3 Carbon Content in Lignin before and after Carbonization.....	118

Table 7.4 Yields Values for Each Step in the Production of Carbon Fibers	120
Table 7.5 Properties of Carbon Fiber	131
Table 7.6 Relative TEA Values of Carbon fibers	134
Table B.1 Summary of Lignin Separation from the 6% Green Liquor Extracts	158
Table B.2 Summary of Composition Data for the Recovered Solid Samples	160

LIST OF FIGURES

Figure 1.1 Biorefinery Process for Ethanol and Acetic Acid Production.....	4
Figure 1.2 Sketch Illustrating TEA	7
Figure 1.3 Sequence of Reaction Showing Stabilization of PAN by Thermo-oxidation	8
Figure 1.4 Intermolecular Cross-linking through Oxygen-Containing Groups of Stabilized PAN Fibers during the Carbonization Process	9
Figure 1.5 Dehydrogenation of Stabilized PAN Fibers during Carbonization Leading to Intermolecular Cross-linking.....	9
Figure 1.6 Cross-linking of Cyclized Sequences in PAN Fibers during the Carbonization Process.....	10
Figure 1.7 Processes for Producing Carbon Fiber from PAN and Pitch	13
Figure 1.8 Common Lignin Monomers	15
Figure 1.9 Major Linkages between Phenylpropane Units in Lignin	16
Figure 1.10 Proposed Model Structure of Softwood Lignin.....	17
Figure 1.11 Simplified Structure of Benzyl Ether Bonds between Lignin and Hemicelluloses	18
Figure 1.12 Simplified Structure of Benzyl Ester Bonds between Lignin and Hemicelluloses	19
Figure 1.13 Simplified Structure of Glycoside Bonds between Lignin and Hemicelluloses	19
Figure 1.14 Simplified Structure of Acetal Bonds between Lignin and Hemicelluloses	20
Figure 4.1 Wood Components	37
Figure 4.2 Laboratory Circulating Extraction Reactor	39

Figure 4.3 GL pH, Final pH and Wood Extracted of the Extracts.....	44
Figure 4.4 Temperatures during Green Liquor Extracting Experiment	45
Figure 4.5 Total Pressures during Green Liquor Extracting Experiment	47
Figure 4.6 4-O Methyl Glucuronic Acid	48
Figure 4.7 Lignin Concentration, Total Solids and Organics Content in the Extracts	51
Figure 4.8 Organics Content in the Total Solids.....	51
Figure 4.9 Xylan and Acetate Concentration in Extract.....	53
Figure 5.1 Protocol for Lignin Isolation Method Using Ethanol	57
Figure 5.2 Protocol for the Hydrolysis Lignin Isolation Method.....	59
Figure 5.3 Determination of Total Lignin Content	60
Figure 5.4 Protocol used in Analysis of Lignin Isolation Method	63
Figure 5.5 Properties of Isolated Lignin Samples	65
Figure 5.6 Ash Content in Lignin Samples.....	71
Figure 5.7 Lignin Content in Lignin Samples.....	72
Figure 5.8 Volatile Material Content in Lignin Samples Investigated.....	74
Figure 5.9 Particulate Material Content in Lignin Samples	75
Figure 5.10 Carbon Content in Coniferyl Alcohol, Sinapyl Alcohol and PAN.....	76
Figure 5.11 Carbon Content in Lignin Samples.....	77
Figure 6.1 Ideal Completely Crystalline Polymers Exhibits Only a T_m Value.....	81
Figure 6.2 Completely Amorphous Polymers Exhibits Only a T_g Value.....	81
Figure 6.3 Semi-crystalline Polymers Exhibits both T_m and T_g Values.....	81
Figure 6.4 Polyethylenedipate	83
Figure 6.5 Poly-ethyleneterephthalate	83

Figure 6.6 Polypropylene and Polyvinylchloride	84
Figure 6.7 Polypropylene and Polystyrene	84
Figure 6.8 Poly-methyl-methacrylate and Poly-butyl-methacrylate	85
Figure 6.9 Cross-linking Polymers.....	85
Figure 6.10 Simplified Diagram of a DSC Apparatus.....	86
Figure 6.11 Typical Molecular Weight Distribution and Average Molecular Weights of a Polymer	88
Figure 6.12 Simplified Diagram of a GPC Apparatus.....	90
Figure 6.13 Photograph of the Atlas Laboratory Mixing Extruder.....	92
Figure 6.14 Photograph of the LME Take-up System for Extruder.....	92
Figure 6.15 Typical Thermogram of Polystyrene	94
Figure 6.16 Typical Thermogram for Alcell Lignin	96
Figure 6.17 Linear Low-density Polyethylene Fiber Spinning.....	102
Figure 6.18 Fiber Spinning Using Lignin from 0% GL Extraction Experiment	103
Figure 6.19 Fiber Spinning Using Lignin from 6% GL Experiment	103
Figure 6.20 Fiber Spinning Using Alcell Lignin.....	104
Figure 6.21 Fiber Prepared from Alcell Lignin	105
Figure 7.1 Photograph of the Lindberg/Blue M Tube Furnace.....	108
Figure 7.2 Apparatus for Thermo-stabilization and Carbonization Experiments	109
Figure 7.3 Time verse Temperature Sequence for Thermo-stabilization Process	111
Figure 7.4 Time verse Temperature Sequence for Carbonization Process.....	112
Figure 7.5 Carbon Fibers from Alcell Lignin	114
Figure 7.6 Carbon Fibers from 0% GL Lignin	114

Figure 7.7 Carbon Fibers from 6% GL Lignin	115
Figure 7.8 Lignin Fibers before and after Thermo-stabilization.....	116
Figure 7.9 Lignin Based Carbon Fiber Process Flow Diagram	123
Figure 7.10 Thermo-stabilized Alcell Fiber.....	126
Figure 7.11 Carbon Fiber from Alcell	126
Figure 7.12 Thermo-stabilized Lignin Fiber Using 0% GL Sample	127
Figure 7.13 Carbon Fiber from 0% GL Lignin Fiber	127
Figure 7.14 Thermo-stabilized Lignin Fiber Using 6% GL Sample	128
Figure 7.15 Carbon Fiber from 6% GL Lignin Sample.....	128
Figure 7.16 Carbon Fiber from PAN	129
Figure 7.17 Carbon Fiber from PAN	129
Figure 7.18 Carbon Fiber from Pitch.....	130
Figure 7.19 Cross Section of Carbon Fiber from Pitch	130
Figure 7.20 TEA Curves of Carbon Fibers	134
Figure A.1 Principal Structure of Glucuronoxylan	151
Figure A.2 Material Balance Used in Extraction Experimental	153
Figure B.1 Initial Protocol for the Isolation of Lignin from Hemicelluloses Extracts....	156
Figure B.2 Separation of Lignin Precipitated on Different pH Values	157
Figure B.3 Separation of Centrifuged Lignin Precipitated on Different pH Values	157
Figure B.4 Effect of pH on the Lignin Concentrations from 6% GL Extracts	159

CHAPTER 1

BACKGROUND INFORMATION

1.1 Rationale for Study

The high price of petroleum is not new, but today it is receiving unprecedented attention from the government and public. Considerable funds have been invested by agencies such as the Department of Energy (DOE), the National Science Foundation (NSF), the Department of Agriculture (USDA) and the Environmental Protection Agency (EPA) in alternative energy research. Replacing gasoline with ethanol has been proven to be one solution for supplementing fuel supplies. Converting the hemicelluloses in wood to ethanol as a pulp mill bio-product has been extensively investigated by Mao and others (2007).

A parallel approach would be to improve the fuel efficiency of vehicles. This can be accomplished by reducing the weight of vehicles. A lighter structural material is required to achieve a goal of 80-miles-per-gallon for automotive vehicles. One method of achieving this goal would be the use of carbon fiber in composite materials used in the construction of automobiles (ORNL, 2008).

Unfortunately, high quality carbon fiber produced from polyacrylonitrile (PAN) is currently too expensive for large-scale use in transportation except in military aircraft. The cost of carbon fiber is about 20 times greater than the cost of carbon steel (http://www.ornl.gov/info/ornlreview/v33_3_00/carbon.htm). Carbon fiber in composite materials is a logical choice. However, the automobile industry is not interested in using carbon fiber until the cost is decreased to between \$3 and \$5 per pound (ORNL, 2008).

The high cost of carbon from PAN results from the high cost of the precursor materials and the many stages in the manufacturing process.

Lignin is one possible precursor material derived from renewable resources derived from biomass. Previous literature supports lignin as a potential precursor material for producing carbon fiber (Schmidl, 1992; Sudo, 1992; Kadla, 2002; Griffith, 2004; Kubo, 2005).

1.2 Hemicelluloses Pre-extraction Process

Traditionally chemical pulping is based on recovering cellulose and a portion of the hemicelluloses in wood as pulp which is then used in the papermaking process. Most hemicelluloses and almost all of the lignin are considered waste materials and are removed and burned to recover their fuel value. Many new products, such as ethanol, acetic acid, furfural, diesel fuel, and polymers are possible uses for these waste materials (van Heiningen, 2006).

A process has been developed by Dr. Adriaan van Heiningen to extract the hemicelluloses in the wood prior to the pulping process. The extracted materials can be converted into ethanol and acetic acid while using the residual wood to produce market Kraft pulp. However, even in this advanced process the extracted lignin is underutilized. Currently, lignin is separated and returned to the main black liquor stream to be burned for energy recovery. The hemicelluloses extraction process presents an opportunity to obtain a clean pure lignin feedstock suitable for the manufacture of carbon fiber. Most literature supports lignin as a precursor for producing carbon fiber, but the difficulty in recovering clean-pure lignin is recognized. Therefore, the production of carbon fiber from black liquor lignin has not been done commercially.

The “near neutral hemicelluloses extraction process” involves extracting hemicelluloses prior to pulping and uses the extract for the production of ethanol and acetic acid (see Figure 1.1). This process is currently being evaluated at the Old Town Fuel and Fiber Company in Old Town, Maine. In the process, the extracted liquor undergoes concentration by evaporation, hydrolysis, lignin separation, liquid/liquid extraction, fermentation and distillation for the production of acetic acid and ethanol. In the current study, the author wishes to investigate utilization of the lignin extract as a precursor material for carbon fiber.

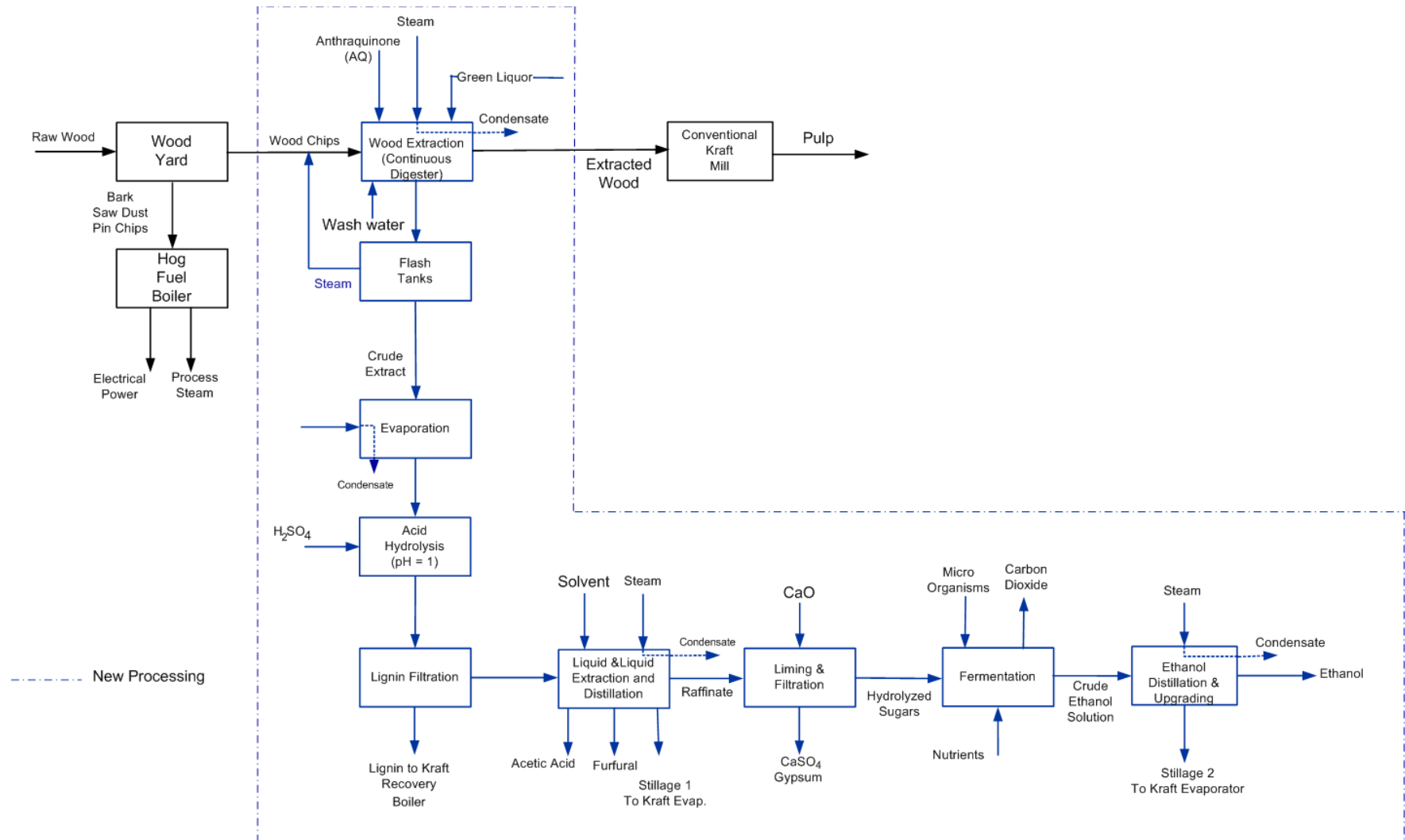


Figure 1.1 Biorefinery Process for Ethanol and Acetic Acid Production (Mao et al., 2007)

1.3 Carbon Fiber

Carbon fiber is an important engineering material used in the manufacture of advanced composite materials. Its significance results because carbon fiber possesses a unique combination of properties. Carbon fiber is lightweight, has high strength, flexibility and fatigue-resistance. These properties result from the orientation of carbon atoms along the fiber axis during the production process. Carbon fiber is manufactured by thermally treating a precursor fiber in a process termed “carbonization”. Formation of the precursor fiber can be done either by melt spinning or wet spinning. In the melt spinning process, the precursor raw material is simply melted and extruded through an orifice to form the fiber. In the wet spinning process, the precursor material is dissolved in a suitable solvent and then extruded through the orifice to form the fiber. Prior to carbonization, the precursor fiber is often subjected to a process termed “thermo-stabilization”. The thermo-stabilization process causes cross-linking of the polymer on the fiber surfaces; thus preventing shrinking, melting, and fusing.

Based on its mechanical properties, carbon fiber is classified into two groups; general purpose (GP) or high performance (HP). The precursor materials used to produce carbon fiber are extremely important in determining the final properties and its classification. Pitch, derived from petroleum or coal, and polyacrylonitrile (PAN) are the most important types of precursor materials used to produce carbon fiber commercially. Almost 80% of commercial carbon fiber is predicated on using PAN as the starting raw material because of its superior properties compared to those of pitch based carbon fiber. Carbon fiber produced from PAN is expensive; and thus has limited application to high-performance structural materials. There is a need for a low cost precursor material that

can produce carbon fiber with properties superior to those of pitch and approaching those of PAN.

Properties of Importance. The carbon content in commercial carbon fiber must be at least 92% carbon by weight. Carbon fiber comes in a variety of types. They can be short or continuous; their structure can be crystalline, amorphous, or partly crystalline (Chung, 1994). Chung further states that carbon fiber has a high modulus of elasticity that results from the fact that the carbon layers tend to be parallel to the fiber axis. Fiber “texture” is a term applied to this preferred orientation the crystal structure. The modulus of elasticity of carbon fiber is higher parallel to the fiber axis than perpendicular to the axis. The stronger the “fiber texture”, the greater the degree of alignment of the carbon layer parallel to the fiber axis. Carbon fiber with high fiber texture has high strength and high tensile energy absorption (TEA). The tensile energy absorption (TEA) refers to energy stored in the fiber when the fiber is under tension with force (F) and undergoes all extension or changes in length ($\Delta L_{\max}$) (see Equation 1.1 and Figure 1.2).

$$\text{TEA (Joules)} = \int_0^{L_{\max}} \mathbf{F} \times d\mathbf{L} \quad \text{Eq. 1.1}$$

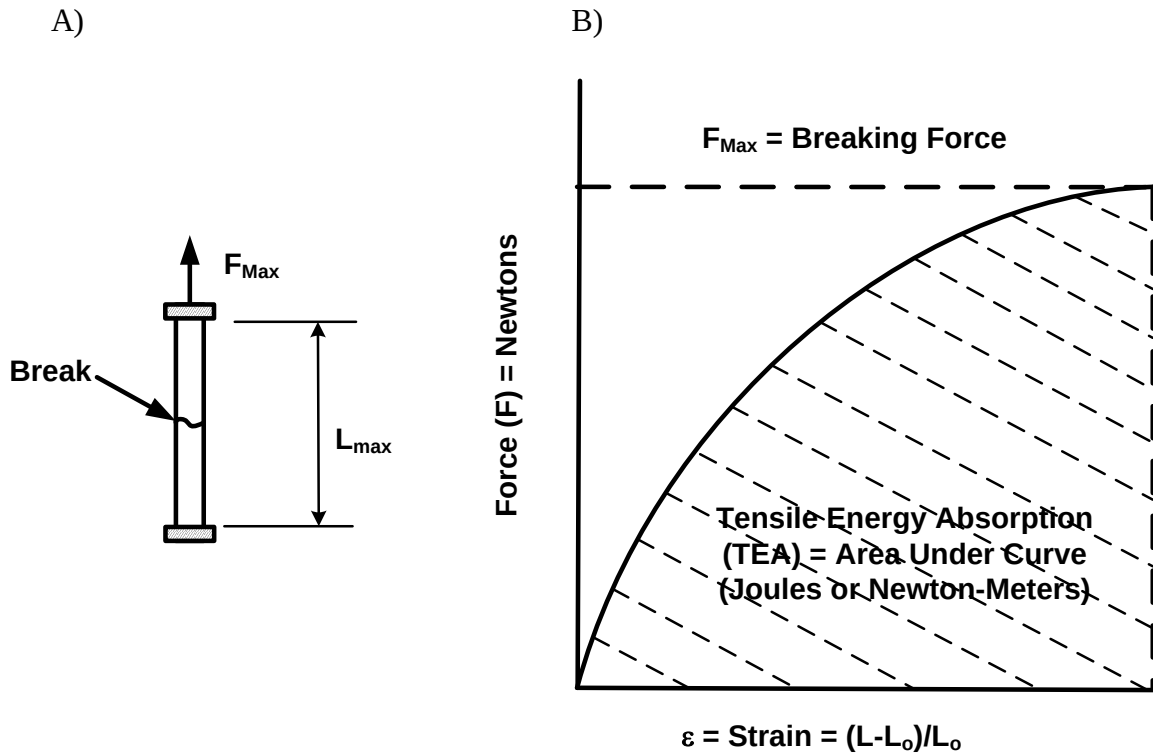


Figure 1.2 Sketch Illustrating TEA
A) Sample in Tensile Tester B) Stress Strain Curve

Formation of Carbon Fibers from PAN. In the production of PAN based carbon fiber, polyacrylonitrile forms a cyclic structure in a thermo-stabilization process. During the thermo-stabilization process “cyclization” and “dehydrogenation” of the polyacrylonitrile occurs (Figure 1.3).

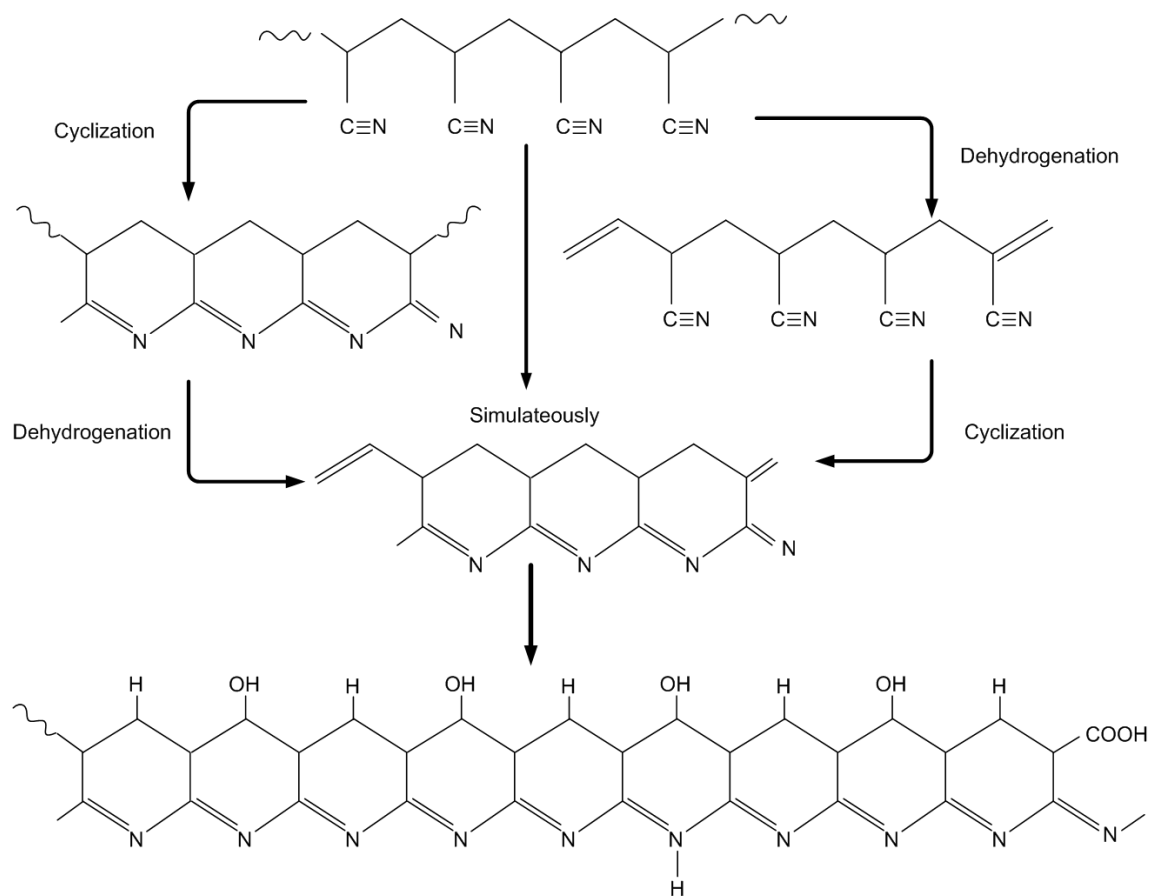


Figure 1.3 Sequence of Reaction Showing Stabilization of PAN by Thermo-oxidation (Chung, 1994)

During the carbonization process, intermolecular cross linking takes place with the release of water vapour, dehydrogenation and release of hydrogen cyanide to form a multitude of rings (Figure 1.4 and Figure 1.5). The final structure occurs by cross-linking of the cyclised sequences in the PAN during the carbonization process (Figure 1.6). The final carbon fiber forms a “graphite-like” structure in the lateral or x-direction in Figure 1.6.

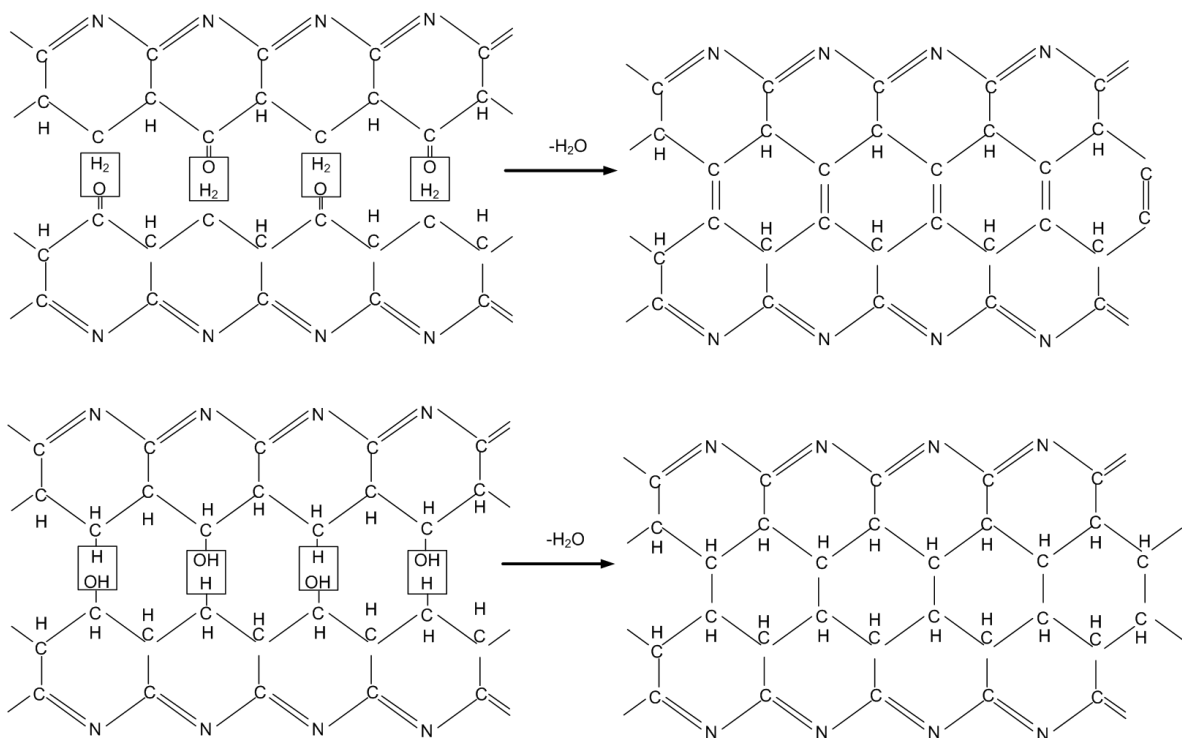


Figure 1.4 Intermolecular Cross-linking through Oxygen-Containing Groups of Stabilized PAN Fibers during the Carbonization Process (Chung, 1994)

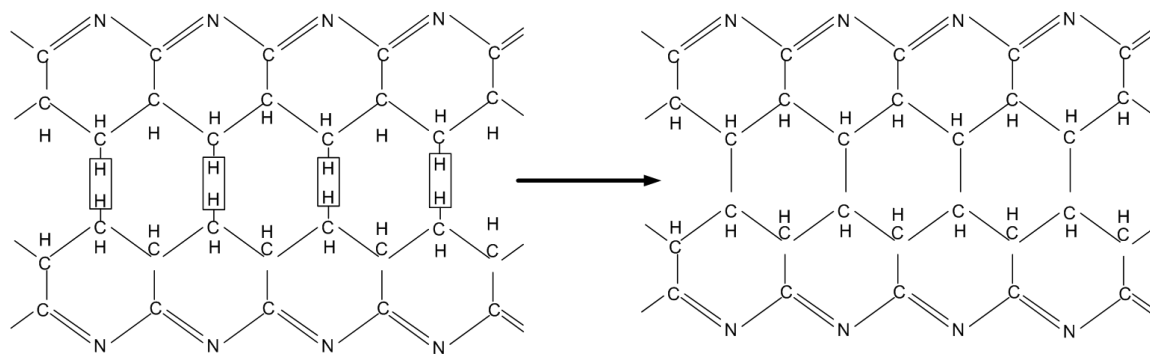


Figure 1.5 Dehydrogenation of Stabilized PAN Fibers during Carbonization Leading to Intermolecular Cross-linking (Chung, 1994)

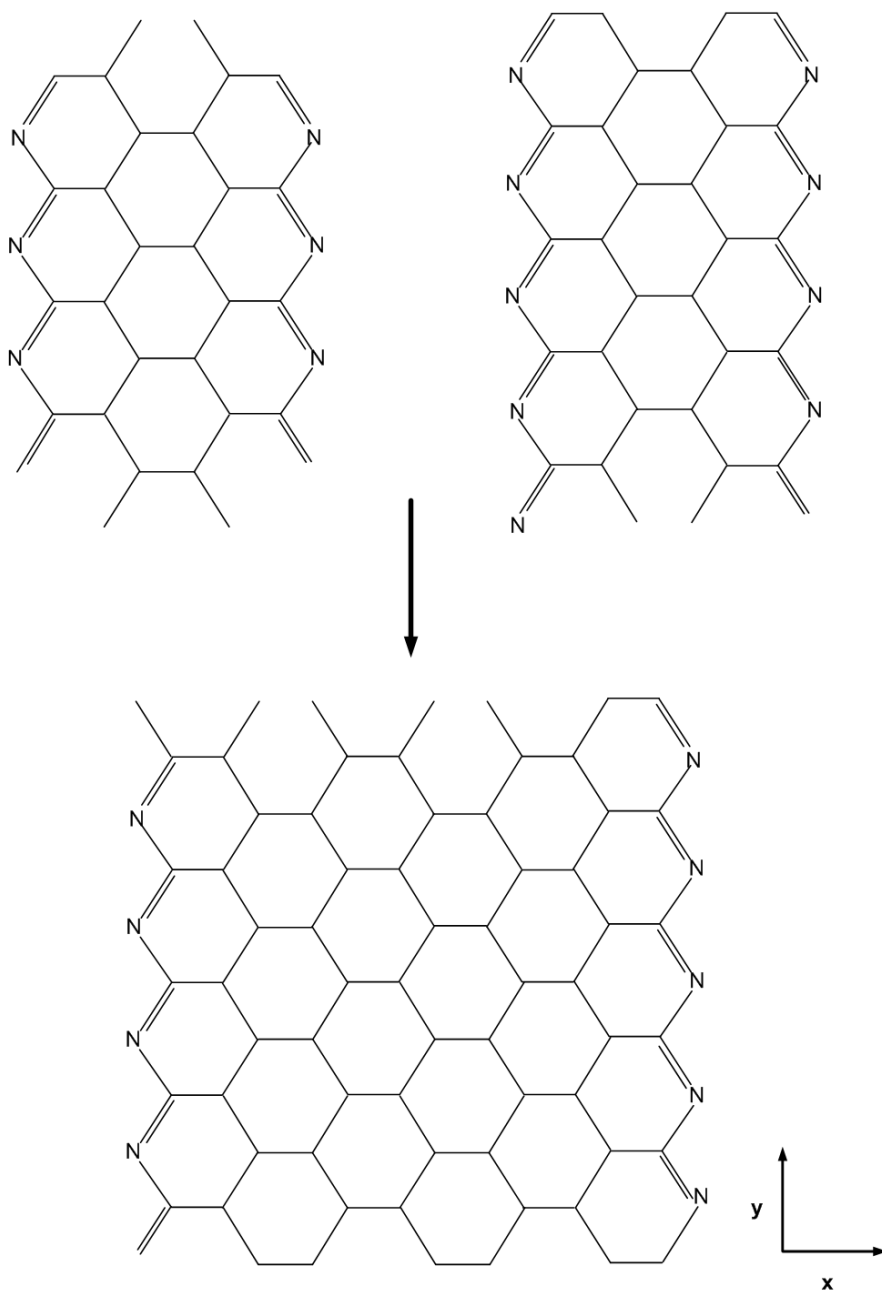


Figure 1.6 “Cross-linking of Cyclized Sequences in PAN Fibers during the Carbonization Process” (Chung, 1994)

1.3.1 Properties of Carbon Fibers

The properties of carbon fiber vary widely depending on the structural orientation of the fiber axis (Riggs, 1985). Positive properties of carbon fiber enumerated by Chung (1994) include: (1) low density, (2) high tensile modulus and strength, (3) low thermal expansion coefficient, (4) thermal stability in the absence of oxygen over 3000°C, (5) excellent creep resistance, (6) chemical stability, particularly in strong acid (7) biocompatibility, (8) high thermal conductivity and (9) low electrical resistivity.

Chung (1994) delineates several disadvantages of carbon fiber. Among the most noteworthy are: (1) high cost (currently), (2) anisotropy (in the axial versus transverse direction), (3) compressive strength is low compared to tensile strength and (4) oxidation of carbon fiber is catalyzed by an alkaline environment.

1.3.2 Applications of Carbon Fiber

Carbon fiber is used as a reinforcing material in composite products. Industrial use of carbon fiber began in the 1950s in the production of aircraft and aerospace materials because of its unique properties especially the low density, high modulus and fatigue resistance (Kadla et al., 2002). Because of its excellent properties, today carbon fiber is widely used in diverse applications such as tennis rackets, bicycles, fishing poles, boats and high performance jet aircraft to name a few. In the modern automobile industry, a priority of automobile manufacturers is to develop energy-saving vehicles. Carbon fiber composites could replace traditional steel components and greatly decrease the weight of vehicles resulting in substantial increase in fuel efficiency. With economic development, the superior performance of carbon fiber composite can be applied to many

more products. However, to make this a reality the price of carbon fibers must be reduced substantially by reducing the cost of the raw materials and simplification of the manufacturing process.

1.3.3 Commercial Precursor Materials for Carbon Fiber

High quality carbon fiber is currently manufactured from PAN and is derived from propylene and ammonia, which come from crude oil, nitrogen and natural gas. PAN has been extensively researched and is in commercial production (Kadla, 2002). Lower quality material is produced from petroleum pitch and coal tar.

1.3.4 Production Process for Carbon Fiber

Like all man-made fibers manufactured from polymeric precursors, carbon fiber is manufactured in several common steps starting with the raw polymer. The processing involves (1) spinning or extrusion of the polymer, (2) stabilization or-conversion of the spun fiber into a stable chemical form, (3) carbonization or conversion of the chemical structure into carbon and (4) graphitization or conversion of the carbon into graphite which has a distinct structure. Starting with pitch as the precursor, a process very similar to that used for PAN is employed except that melt spinning is used in place of wet spinning. The processes for using PAN or pitch as precursors to produce carbon fiber are shown in Figure 1.7 (Chung, 1994).

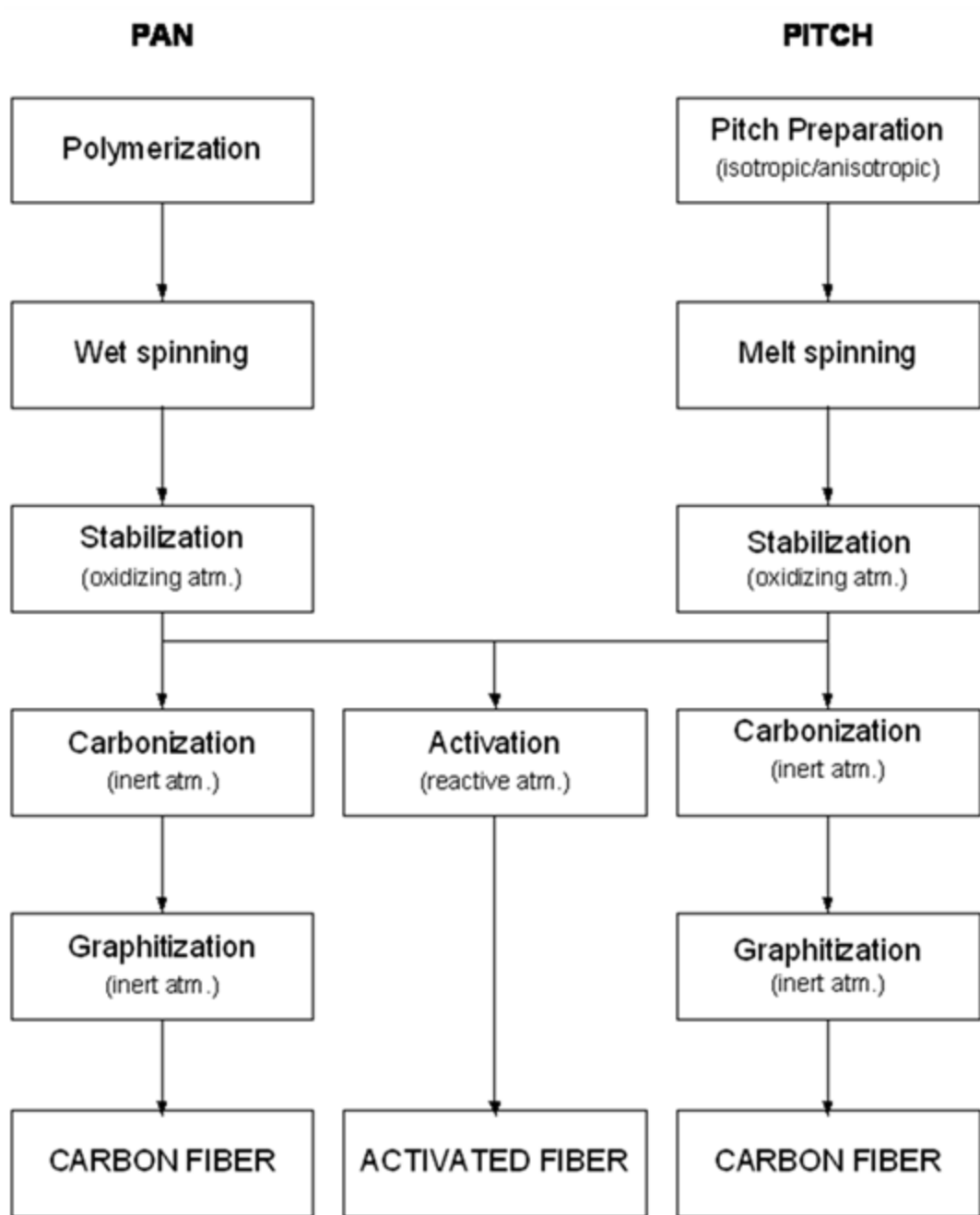


Figure 1.7 Processes for Producing Carbon Fiber from PAN and Pitch (Chung, 1994)

1.4 Lignin

Lignin is second only to cellulose as the most abundant renewable resource (Rouhi et al., 2001). Knowledge of lignin has evolved over one hundred years and the importance of lignin has been widely recognized since the early 1900s (Glasser et al, 2000). Our understanding of lignin is limited because of its complex structure. In recent years, through the application of modern methods of chemical analysis the lignin field has developed dramatically. This has lead to the knowledge of the structure of lignin and also to the applications of lignin.

1.4.1 Structure of Lignin

After more than one hundred years of research, many chemical aspects of lignin still remain unclear, but the principal structural elements of lignin have been clarified. Lignin is a complex, amorphous, cyclic, random polymer. Phenylpropane units constitute the main backbone of lignin which is randomly cross-linked by a variety of different chemical bonds. Lignin has the following characteristics: (1) basic phenylpropane units, (2) no repeating structure, (3) amorphous, random polymer, and (4) covalently bonded to the carbohydrates (Sjöström, 1993).

P-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are the three most common lignin precursors. Their chemical structures are showed in Figure 1.8. Three phenylpropane monomers, differing only in the number of methoxyl substituents, polymerize to form lignin. P-coumaryl alcohol is found predominately in lignin from grasses, while coniferyl alcohol is found in softwood lignin. Sinapyl alcohol is the structure found in lignin from hardwoods. (Sjöström, 1993)

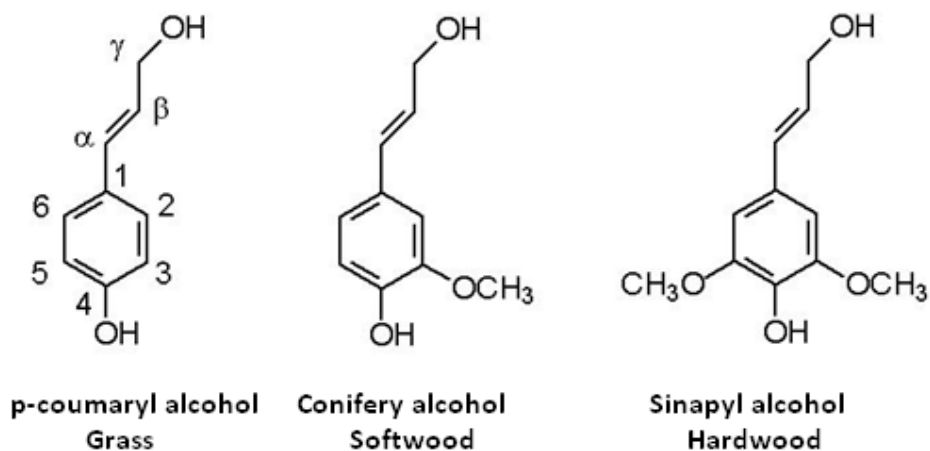


Figure 1.8 Common Lignin Monomers (Sjöström, 1993)

Figure 1.9 shows the major types of linkages between phenylpropane units observed in lignin (Sjöström, 1993). Although numerous structures are found in lignin, the predominant linkage is the β -O-4 linkage. Condensed lignin linkages are the 5-5, β -5, β -1, and β - β linkages.

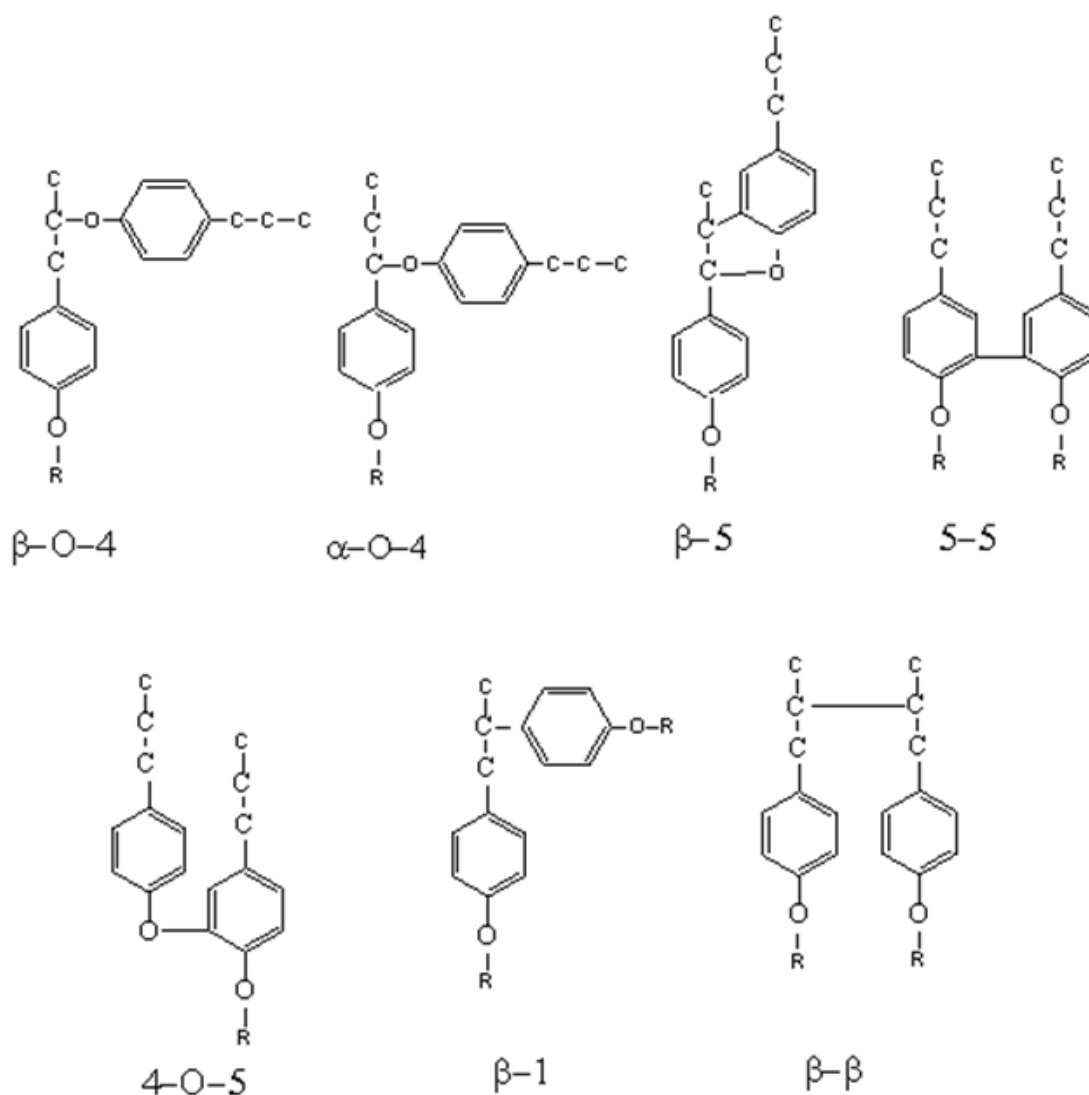


Figure 1.9 Major Linkages between Phenylpropane Units in Lignin (Sjöström, 1993)

The further polymerization of lignin involves monolignols with phenolic end groups or radicals, forming a large 3-dimensional branched polymer. Figure 1.10 shows the designed structural scheme of model softwood lignin (Brunow, G. 1998).

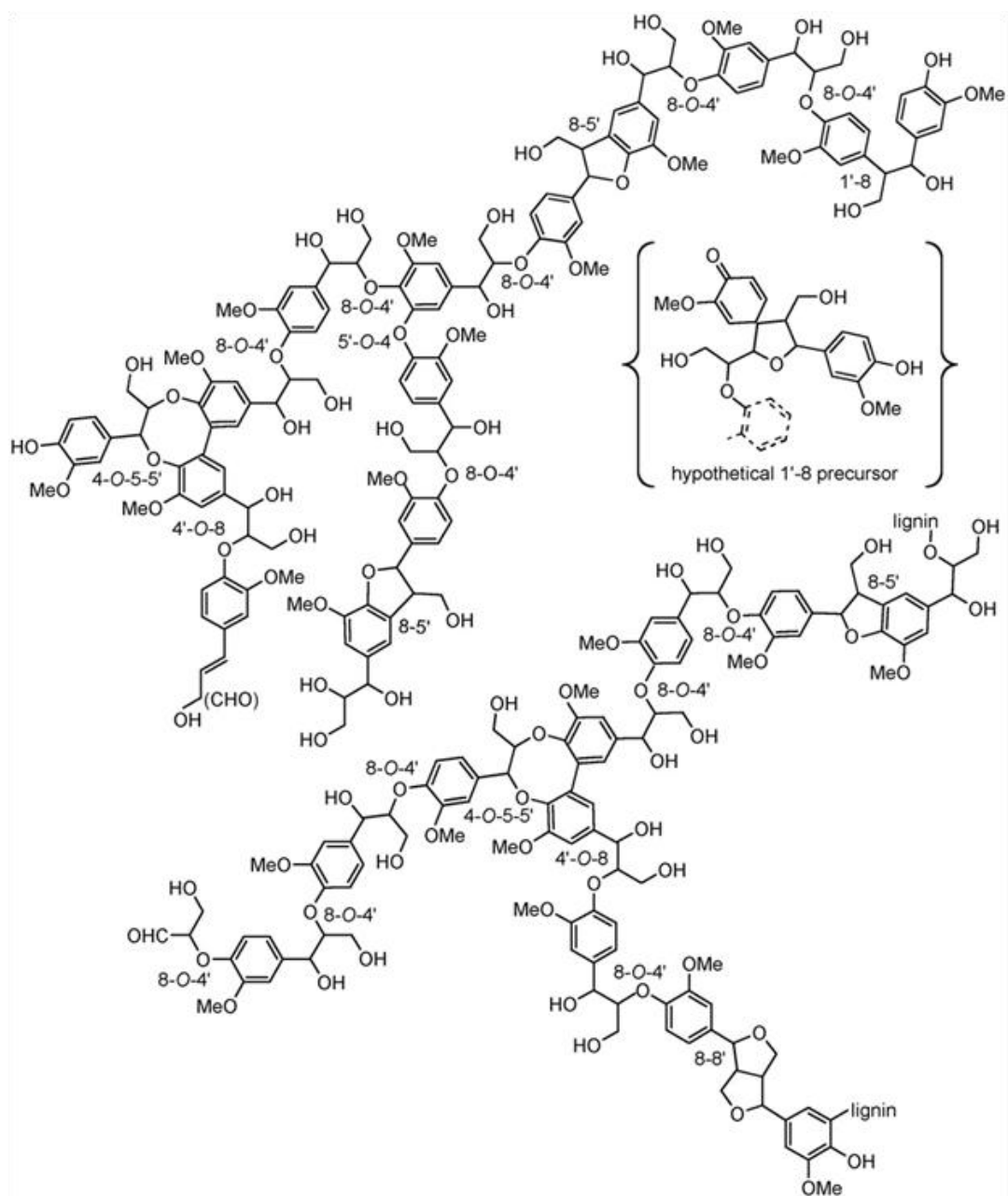


Figure 1.10 Proposed Model Structure of Softwood Lignin (Brunow, G. 1998)

1.4.2 Lignin-Carbohydrate Complex (LCC)

There is ample evidence supporting the concept that lignin is chemically bonded to carbohydrates (Salmén, et al. 1998). Separation and analysis of lignin-carbohydrate complexes have led to the conclusion that hemicellulose components (mainly xylan and

galactoglucomannan in softwood) are bonded with lignin. Fengel (1985) suggested that the main types of covalent linkages between lignin and carbohydrates are (1) benzyl ester linkage (Figure 1.11), (2) benzyl ether linkage (Figure 1.12), (3) phenyl glycoside linkage (Figure 1.13) and (4) acetal linkages (Figure 1.14). Figures 1.11 through 1.14 give simplified structures of the frequently suggested lignin-carbohydrates linkages (Koshijima et al., 2003).

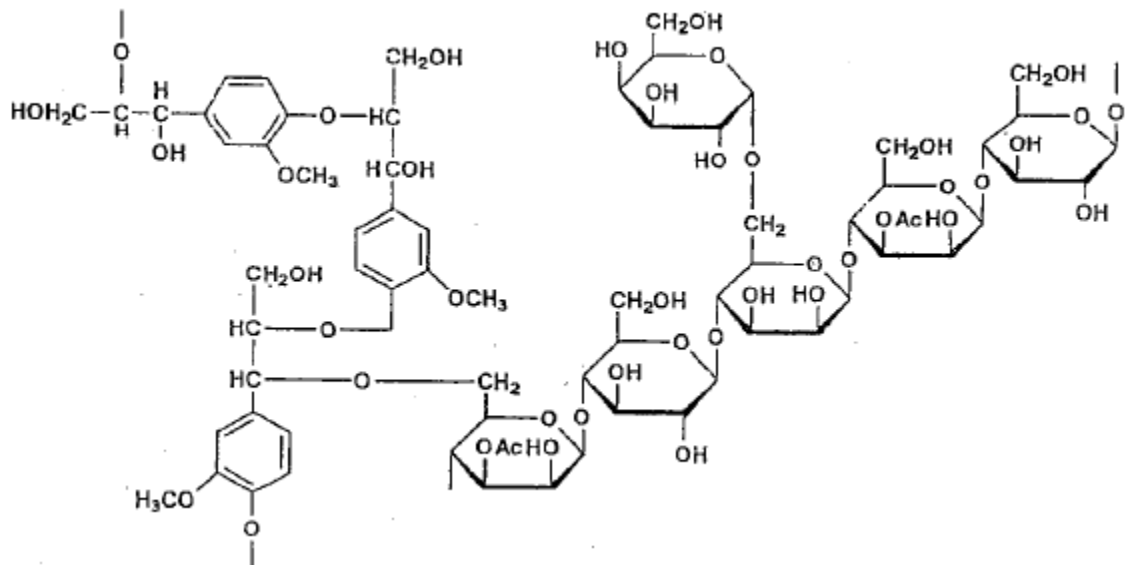


Figure 1.11 Simplified Structure of Benzyl Ether Bonds between Lignin and Hemicelluloses (Koshijima et al., 2003)

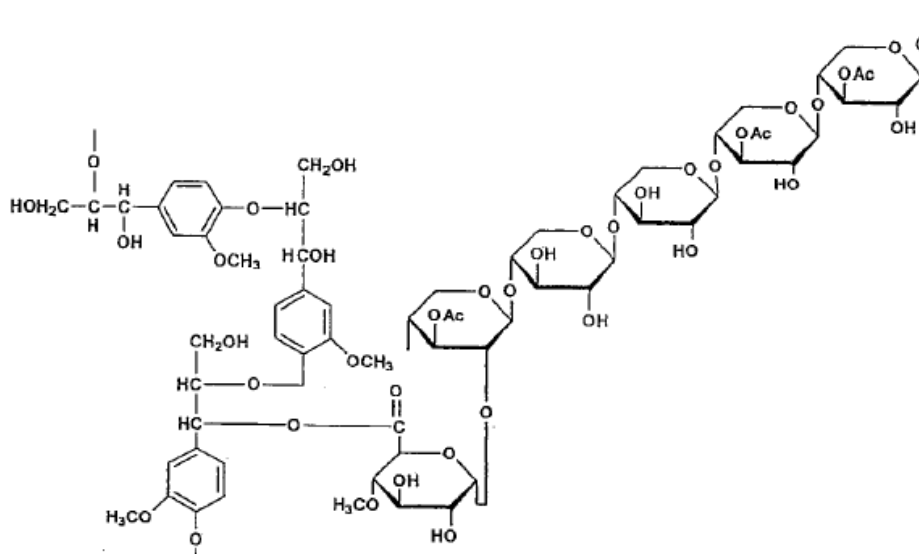


Figure 1.12 Simplified Structure of Benzyl Ester Bonds between Lignin and Hemicelluloses (Koshijima et al., 2003)

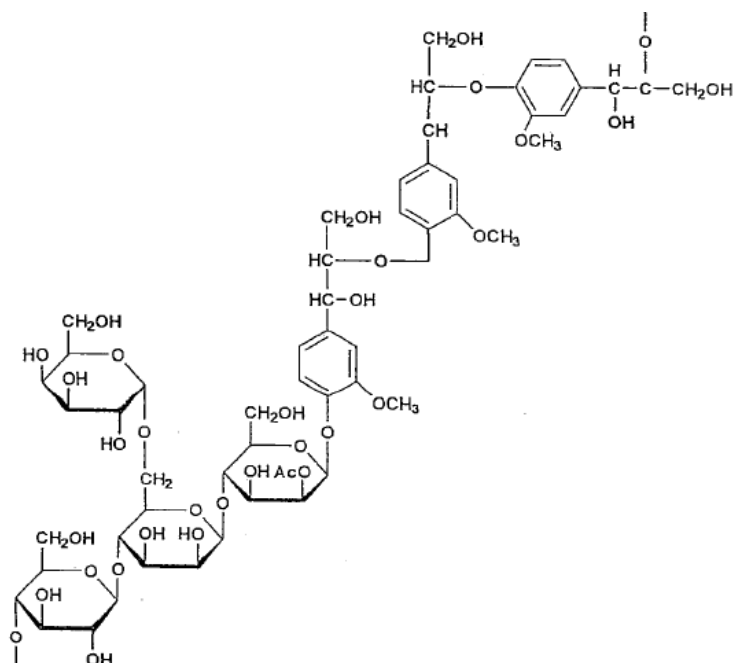


Figure 1.13 Simplified Structure of Glycoside Bonds between Lignin and Hemicelluloses (Koshijima et al., 2003)

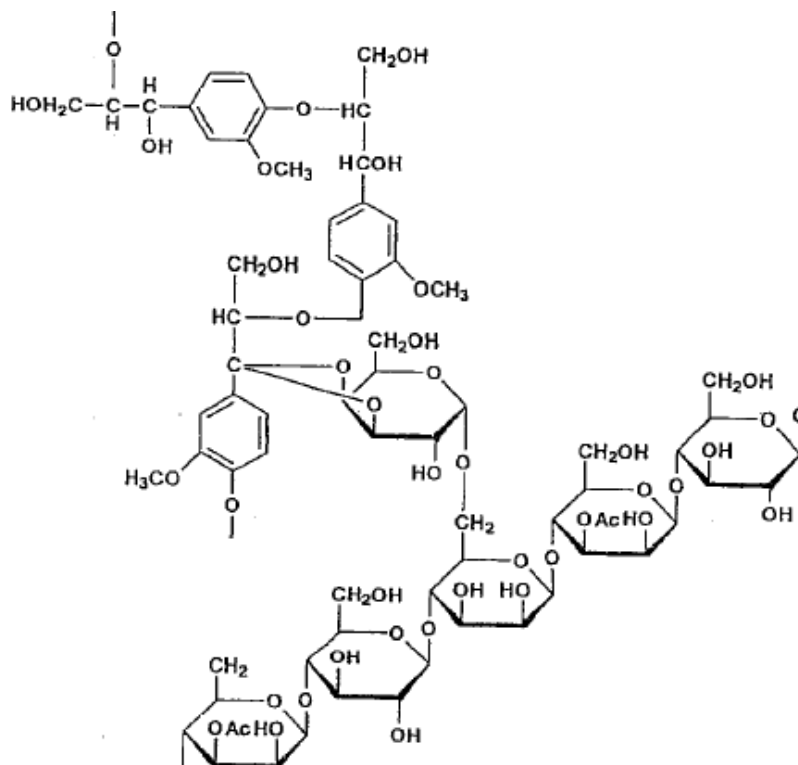


Figure 1.14 Simplified Structure of Acetal Bonds between Lignin and Hemicelluloses (Koshijima et al., 2003)

1.4.3 Applications of Lignin

Available industrial lignins are by-products of commercial pulping operations. Normally, lignins extracted from wood during pulping operations are used in the generation of steam and electrical power to satisfy the energy demand of the pulp mill. However, lignin may be used in the manufacture of a variety of higher value products; provided of course that the value of the derived by-product exceeds the cost of manufacture and the value of its energy content. Possible products from lignin suggested by van Dam (2004) are (1) wood adhesive, (2) UV stabilizer and color agent, (3) polymer additive, (4) surfactant, (5) durability enhancement, and (6) carbon fiber.

CHAPTER 2

REVIEW OF PREVIOUS LITERATURE ON LIGNIN BASED CARBON FIBER

Lignin is potentially a new precursor material for the production of carbon fiber. Lignin presents several advantages over PAN and pitch for the production of commercial carbon fiber. Lignin is readily available, relatively inexpensive and structurally rich in phenyl propane group with high carbon content (60%). Lignin, however, possesses several disadvantages, the most notable of which is the difficulty in recovery in a clean-pure form. A significant source of lignin in the form of black liquor results from pulping both wood and non-woody materials by the Kraft process. Currently black liquor is burned for its fuel value and has never been used commercially to produce carbon fiber.

The “near neutral hemicelluloses extraction process” is currently being developed to convert hemicelluloses into ethanol and acetic acid, but the extracted lignin is underutilized. This process presents an opportunity to obtain a clean lignin feedback suitable for the manufacture of carbon fiber. The economic viability of the “near neutral hemicelluloses extraction process” could possibly be improved provided lignin could be recovered as a by-product. It also presents an opportunity for the traditional pulping industry to generate an additional source of revenue.

2.1 Carbon Fiber from Lignin for Transportation

Lignin as a precursor for carbon fiber production has been studied for more than 40 years. Schmidl (1992) reported that the first lignin-based carbon fiber was produced in Japan in 1964 using thiolignin, alkali lignin and lignosulfonates. The first commercial lignin-based carbon fiber was manufactured in a small pilot plant-operated by Nippon Chemical Co. in 1970s. The poor mechanical properties of the carbon fiber product forced this project to be abandoned.

Recently considerable research has been done on the manufacture of carbon fiber from lignin at the Oak Ridge National Laboratory. Notable among this work is that of Baker and co-workers (2005) who developed specifications for lignin for use as a carbon precursor, and the work of Griffith et al. (2005) who describe the freedom car program.

Work at ORNL. The objective of the Freedom Car Program developed under the auspices Department of Energy is to apply carbon fiber composite technology to the automobile sector in transportation. The goal is to lower vehicle weight in an effort to decrease domestic fuel consumption. Warren (2009) reports data for the manufacturing cost of commercial polyacrylonitrile (PAN) based carbon fiber. The various components comprising the manufacturing cost are summarized in Table 2.1. Clearly, the cost of the PAN precursor represents more than 50% of the overall manufacturing cost. However, for use in the manufacture of automobiles, the cost of carbon fibers will need to be reduced to \$3-\$5/lb and the production will need to be increased by a factor of least forty. Alternate precursors to pitch and polyacrylonitrile (PAN) are being investigated as possible carbon fiber feed stock to achieve the objectives of the Freedom Car Program.

Table 2.1 Cost of Commercial PAN Based Carbon Fiber (Warren 2009)

Item	Precursor (PAN)	Stabilization & Oxidation	Carbonization/ Graphitization	Surface Treatment	Spooling Packaging	Overall
Cost (\$/lb)	5.04	1.54	2.32	0.37	0.61	9.88
Percent (%)	51	16	23	4	6	100

ORNL investigated lignin blends as a low-cost, high-production volume feedstock for carbon fiber. A critical factor in their investigation was the ability of the lignin to be melt-spun into lignin fiber. Lignin-based fiber has several attractive features. ORNL concludes that carbon fiber can be produced in high yields and can readily be stabilized, carbonized and graphitized. The physical structure and mechanical properties of lignin carbon fibers, although still below those desired by the automobile industry, indicate the feasibility of using lignin in transportation as a reinforcing agent for composite materials. Contamination is a major problem that must be overcome if commercially produced lignin is to be used as a precursor material. This requires the development of low-cost technology suitable for the removal of contaminants, such as sand, salts and other chemicals used in the pulping processes which extract the crude lignin, water, and entrained carbohydrates. A review of available technology and literature data is presented for filtration, precipitation and drying technology. A variety of other techniques related to fiber processing are described, notable among them is pre-treatment to remove volatile material, desalting, addition of plasticizers and high shear spinning dies. These authors also discuss methods for surface treatment of carbon fiber to increase compatibility of lignin with resins in blends.

2.2 Modified Lignin for Use in Carbon Fiber Production

Hydrogenated Lignin Precursor. Sudo (1992) describes a “new” process for the production of carbon fiber from hardwood lignin in which steam-explosion technology was used to isolate lignin from birch wood. Hydrogenation was used to modify the lignin to improve melt spinning. Chloroform and carbon disulfide were used to dissolve and separate the insoluble lignin fraction. The purified lignin was heated between 300-350 °C under vacuum for 30 min. This gave a molten viscous lignin which had a softening point of 110 °C and melted completely at 145 °C. This material was suitable for the preparation of fine filaments. Infusible lignin fibers were formed by thermo-stabilization the filaments at 210 °C. The filaments were carbonized by heating from room temperature to 1000 °C at a heating rate of 5 °C/min in a stream of nitrogen. Properties of the lignin based carbon fiber produced using Sudo’s procedure are summarized in Table 2.2. Sudo compared the chemical structure of the precursor to the crude lignin and concluded that there was a significant elimination of aliphatic functional groups relative to the original starting material.

Table 2.2 Summary of Physical Properties of Carbon Fibers from Lignin Literature Sources

Lignin Sources	Fiber Diameter (μm)	Elongation (%)	Tensile Strength (MPa)	Modulus of Elasticity (GPa)	Reference
Hydrogenated HW Lignin	7.6 ± 2.7	1.63 ± 0.29	660 ± 230	40.7 ± 6.3	Sudo (1992)
Phenolated HW Lignin	NA	1.4	455	32.5	Sudo (1993)
HW Lignin from HAc Pulping	14 ± 1.0	0.98 ± 0.25	355 ± 53	39.1 ± 13.3	Uraki (1995)
S. W Lignin HAc Pulping	84 ± 15	0.71 ± 0.14	26.4 ± 3.1	3.59 ± 0.43	Kubo (1998)
HW Alcell Lignin	31 ± 3	1.00 ± 0.23	388 ± 123	40.0 ± 14	Kadla (2002)

Phenolated Lignin Precursor. Sudo (1993) in a continuation of previous work investigated using phenolated lignin as a carbon fiber precursor. This work was done as an alternative to using hydrogenated lignin because of the high manufacturing cost associated with producing hydrogen. Similar to the hydrogenation process, steam-exploded lignin was the crude feedstock used in the phenolysis process. The phenolysis reaction was conducted by treating equal weights of phenol and crude lignin under vacuum at 180 to 300 °C for 2 to 5 hours. Para-toluene-sulfuric acid was used as the catalyst in the reaction. The resulting lignin-pitch was readily spun into fine filaments. The fine filaments were converted into carbon fiber after thermo-stabilization and carbonization. The overall yield for the process was 43.7% based upon the phenolated lignin. Properties of the carbon fiber from phenolated lignin are summarized in Table 2.2. The tensile strength of the carbon fiber was approximately 455 MPa, but was not as high as that of the hydrogenated lignin.

Acetylated Lignin Precursor. Researchers at Weyerhaeuser (Eckert, 2008) developed a method for acetylating softwood Kraft lignin for use in melt spinning lignin fiber. The acetylation process was conducted by using acetyl chloride, acetic anhydride and acetic acid as reagents. The acetylation reaction was conducted between the temperatures of 70 and 100 °C without the use of a catalyst. The acetylation reaction could also be conducted with a catalyst at lower temperature. The preferred catalysts embodied in the patent for obtaining lignin acetate that could be readily melted during spinning were organic amines, in particular tertiary amines such as tri-ethyl amine, tri-methyl amine and pyridine. The temperature for the reaction was approximately 50 °C. The acetylation technique permitted softwood Kraft lignin fiber to be spun at diameter between 5 and 100 µm. Unfortunately no

data are presented for the physical properties and the overall process yield for the carbon fiber product.

2.3 Organosolv Lignin as Precursor

Organosolv lignin has been used to prepare carbon fiber. The preferred solvents in the pulping processes used to liberate the crude lignin are acetic acid and ethanol.

Hardwood Lignin from Acetic Acid Pulping. Crude lignin was obtained by acetic acid pulping of birch wood and used as a precursor for producing carbon fiber (Uraki, 1995). The organosolv lignin obtained by aqueous acetic acid pulping was used without chemical modification outside of that done in the pulping process. The polydispersity of the resulting lignin ($M_w/M_n=2.3$) and partial acetylation of hydroxyl groups during the pulping process was thought to be responsible for the ability of the crude lignin to be readily spun into lignin fiber. Table 2.2 contains data on the physical properties of carbon fiber produced from crude lignin obtained by acetic acid pulping of hardwood.

Softwood Lignin from Acetic Acid Pulping. Kubo (1998) replicated Uraki's 1995 work but used softwood. Lignin was recovered by atmospheric pressure acetic acid pulping and used in the production of carbon fiber. A major difference existed between Uraki's original work and that done by Kubo. Uraki used the crude hardwood lignin obtained directly from the acetic acid pulping process in the production of carbon fibers. Kubo, by contrast, had to remove the high molecular mass infusible fraction of the crude softwood lignin to permit melt spinning. The high molecular weight infusible lignin was removed by filtering the crude lignin obtained from the acetic acid pulping process and then re-dissolved the low molecular weight fractions in acetic acid at a lower

concentration than used in the pulping process. This technique preferentially dissolved the lower molecular weight fractions of the crude lignin, which then re-precipitated. By using the above technique, carbon fiber could be prepared by direct carbonization thus avoiding the thermo-stabilization process. The physical properties of carbon fiber prepared by this technique are summarized in Table 2.2.

Hardwood Lignin Prepared by the Alcell Process. In the Alcell process, a 50 weight % ethanol/water mixture was used to produce hardwood organosolv pulp, lignin and sugars. (<http://www.p2pays.org/ref/10/09315.htm>) The Alcell pulping process was operated at temperatures between 190 and 200 °C, with corresponding operational pressure of 400-500 psig. The high operational pressure resulted from the high vapor pressure of ethanol. Lignin and sugar were recovered from displaced pulping liquor. Process water was used to precipitate the dissolved lignin which is recovered from the first-stage of spent liquor. The solid lignin was further purified by centrifugation, washed, dried and sold as a dried product. The product lignin can amount to approximately 18% by weight of the dry wood charge in the process. Alcell lignin is highly hydrophobic, low in ash and contains no sulfur and thus is distinctly different from either liginosulfonates obtained from the sulfite process or Kraft thiolignin. Properties of Alcell lignin, important to the production of carbon fiber, are its low contamination, low number-average molecular weight (1000 Daltons), low softening point (145 °C), low glass transition temperature (100 °C) and small median particle size (20-40µm) (<http://www.p2pays.org/ref/10/09315.htm>).

Kadla (2002) compared Alcell lignin to lignin obtained from hardwood Kraft lignin and Indulin AT (softwood Kraft lignin). The Alcell lignin used by Kadla was

obtained from Repap Enterprises in Newcastle, New Brunswick. Kadla reported that the Indulin AT could not be spun into lignin fiber because of charring before melting. Both the Alcell and hardwood Kraft lignin could be melt spun into lignin fiber, but the Alcell lignin had a considerably lower spinning temperature; about 140 °C for Alcell lignin compared to 200 °C for hardwood Kraft lignin. Infusible lignin fiber could be formed during the thermo-stabilization process using Alcell lignin fiber provided the heating rate was maintained below 12 °C/hour. The physical properties of carbon fiber produced from Alcell lignin are summarized in Table 2.2.

2.4 Carbon Fibers from Lignin – Synthetic Polymeric Blends

Work of Kadla (2002). Kadla investigated the applicability of lignin-poly ethylene oxide (PEO) blends as precursors for the production of carbon fiber. What is unique about Kadla's (2002) work is that commercially available Kraft hardwood lignin was used without chemical modification to produce carbon fibers by thermal spinning followed by carbonization. Fiber spinning was facilitated by the addition of the PEO to the commercial hardwood lignin. The lignin-PEO blends could readily be converted into fiber by the addition of 3 to 5% PEO. Above 5% PEO addition, fiber fusing occurred during thermal stabilization. The physical properties of carbon fiber from lignin-PEO blends are summarized in Table 2.3. Although the addition of PEO into the blend improved fiber spinning, the physical properties of the carbon fiber were not improved.

Table 2.3 Physical Properties of Carbon Fibers from Lignin-PEO Blends (Kadla, 2002)

Source	Fiber Diameter (μm)	Elongation (%)	Tensile Strength (MPa)	Modulus of Elasticity (GPa)
HardWood Lignin	46 $\pm$ 8	1.12 $\pm$ 0.22	422 $\pm$ 80	40 $\pm$ 11
Lignin-PEO (97-3)	34 $\pm$ 4	0.92 $\pm$ 0.21	448 $\pm$ 70	51 $\pm$ 13
Lignin-PEO (95-5)	46 $\pm$ 3	1.06 $\pm$ 0.14	396 $\pm$ 47	38 $\pm$ 5

Work of Kubo (2005). Kubo discusses the applications of a variety of lignin – synthetic polymer blends as precursors materials for the production of carbon fiber. Fiber spun from both unmodified hardwood Kraft and organosolv lignin proved to be brittle and difficult to handle. Kubo overcame this problem by using blends of lignin and synthetic polymers of poly (ethylene terephthalate) (PET), polyethylene oxide (PEO) and polypropylene (PP) to reduce the brittleness and improve the physical properties of the spun fiber properties. Blends were prepared that incorporated up to 25% of the synthetic polymer.

The physical properties of the lignin-based polymers were found to be dependent upon three factors; (1) the source and properties of the lignin, (2) the amount and physical properties of the synthetic polymer being incorporated, and (3) chemical interactions between the components. Incorporating synthetic polymers into the precursor blends enhance the ability of the lignin-polymer blend to be spun into fiber, reduced the brittleness of the spun fiber, and improved its flexibility. The physical properties of some lignin-polymer blends are summarized in Table 2.4. Adding poly (ethylene

terephthalate) to lignin to form a precursor blend (Table 2.4) raised both the modulus of elasticity and the tensile strength of the final carbon fiber product. Adding polypropylene to lignin-polymer blend precursor did not improve the physical properties. Kubo implies that adding polyethylene oxide to lignin is a desirable blend as a precursor for producing lignin fibers, although the properties of the final carbon fibers were not cited in the paper.

Table 2.4 Physical Properties of Carbon Fibers from Lignin Blends (Kubo, 2005)

Source	Fiber Diameter (μm)	Elongation (%)	Tensile Strength (MPa)	Modulus of Elasticity (GPa)
Lignin	NA	1.07	422	39.6
Lignin-PET (75-25)	NA	0.77	511	66.3
Lignin-PP (75-25)	NA	0.50	113	22.8

CHAPTER 3

OBJECTIVE AND SCOPE

The objective of this work was to produce a raw material suitable for the production of carbon fiber predicated on lignin from hardwood. It is desired that the lignin source be of sufficient quality that it can be used in the production of carbon fiber for use in automobiles and other transportation vehicles to improve mileage standards. Specifically the study concentrated on recovering lignin as a by-product from the “near-neutral hemicelluloses extraction process” as a method of improving the economics of the process. The scope of this study involved several tasks.

Task 1. Lignin Extraction. Lignin was extracted from mixed northeast hardwood chips using green liquor and water as the extraction solvents. Following extraction, dissolved lignin existed in a complex mixture with a variety of hemicellulose fragments, sodium acetate, acetic acid and lignin-carbohydrate complexes (LCC).

Task 2. Lignin Recovery. The objective of Task 2 was to obtain lignin in a purified form suitable for drawing into lignin fiber. The final procedure developed by the author involved acidification, double hydrolysis to cleave lignin-carbohydrate complexes, filtration to remove lignin and lastly removal of soluble impurities by washing with water.

Task 3. Lignin Characterization. The objective of this task was to characterize the recovered lignin samples as a precursor for use in producing lignin fiber with subsequent conversion to carbon fiber.

Subtask 3A. Analysis of Carbon Content. Solid samples were sent to the Analytical Laboratory operated by the Department of Plants, Soils & Environmental

Sciences at the University of Maine for analysis of their carbon content. The carbon content was determined for samples used in the preparation of lignin fiber and also for samples following conversion into carbon fiber product.

Subtask 3B. Estimation of Lignin Purity and Ash Level in Recovered Samples. The recovered lignin samples were analyzed to determine the total lignin content and residual ash for comparison with target values proposed by ORNL (Baker et al., 2002).

Subtask 3C. Volatile Material Content in Lignin. Low molecular weight lignin fragments can potentially cause defects in the structure of the carbon fiber during lignin carbonization if the heating rate is rapid and evaporation occurs. Consequently the volatility of the powdered lignin samples was estimated by measuring the change in mass of the sample before and after heating the samples in an oven held at 250 °C.

Subtask 3D. Analysis of Particulate Matter. Extraneous particulate matter in the recovered powdered lignin can cause imperfections in the final carbon fiber product. Consequently, particulate matter in the recovered lignin samples was estimated by dissolving the solid lignin samples in warm sodium hydroxide (NaOH), filtering the sample through a glass filter and measuring the residual particulates mass of the sample after filtration.

Subtask 3E. Glass Transition Temperature (T_g). The recovered lignin fractions were characterized for glass transition temperature (T_g) using differential scanning calorimetry (DSC). This work was performed at the University of Maine by using a Mettler Toledo DSC822 instrument in Professor Robert Rice's laboratory. The

purpose of these experiments was to determine conditions required in melt spinning the recovered lignin into lignin fibers.

Subtask 3F. Molecular Weight. The average molecular weight of selected lignin samples was determined by using Gel Permeation Chromatography (GPC) at the University of Maine. The purpose of this task was to estimate the molecular weight and distribution of the lignin fractions that produced the highest quality lignin fibers.

Task 4. Preparation of Lignin Fibers and Carbonization. Carbon fiber was prepared with the following tasks.

Subtask 4A. Melt Spinning Lignin Fibers. Lignin fibers were prepared from the recovered powdered lignin by melt spinning using an ATLAS Maxwell Laboratory Mixing Extruder.

Subtask 4B. Thermal Stabilization of Lignin Fibers. The lignin fibers were stabilized by slow heating the extruded fibers in an air stream at a heating rate 0.25 °C per minute to 200 °C; and then maintaining the lignin fiber samples for 24 hours at 200 °C in the Lindberg/Blue M Tube Furnace.

Subtask 4C. Carbonization of Lignin Fibers. The thermally stabilized lignin fibers were then carbonized under an argon atmosphere at a heating rate 5 °C per minute to 1000 °C; and then maintaining the lignin fiber samples for 20 minutes at 1000 °C in the Lindberg/Blue M Tube Furnace.

Task 5. SEM Photographs of Lignin and Carbonized Fiber. The surface character of the stabilized lignin fibers and their carbonized counterparts were observed by using a Scanning Electron Microscopy (SEM). This work was performed in the Laboratory for Surface Science and Technology (LASST) at the University of Maine.

CHAPTER 4

HEMICELLULOSE PRE-EXTRACTION EXPERIMENTS

Laboratory experiments were conducted to obtain lignin samples for use in the preparation of carbon fiber. In these laboratory experiments, hemicelluloses were extracted from Northeastern hardwood chips by using mixtures of sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S) similar to what is found in the green liquor stream in the recovery process of a Kraft mill. Approximately 0.05% by weight anthraquinone (AQ) was added as a pulping catalyst. The AQ is added to the extraction liquor to maintain the pulp yield and physical properties of the final pulp following Kraft pulping of the partially macerated chips.

Several hemicellulose extraction liquors were produced by changing the green liquor to wood application ratio. The objective of this chapter is to illustrate the chemical components of the wood that are extracted by application of green liquor to northeast hardwood chips. It is desired to delineate the optimum green liquor application rate to produce extracted lignin that is suitable for use as a precursor of carbon fiber.

4.1 Wood Components

The major polymeric constituents in wood are cellulose, hemicelluloses and lignins (see Figure 4.1). Cellulose makes up approximately 40-45% of the total mass of both hardwoods and softwoods (Sjöström, 1993). As such it is the most abundant polymer on earth (Kim et al., 2007). Cellulose is a linear polysaccharide comprised of 1,4 β -D-glucose units lined together by ether (-O-) linkages at the number 1 and 4 positions on the glucose molecule. The number average molecular weight of cellulose (M_n) is

related to the degree of polymerization (DP) and the molecular weight of one anhydro-glucose unit (M_G). The average molecular weight of cellulose is estimated from equation 4.1. From sugar analyses, the degree of polymerization of cellulose is thought to be approximately 10,000 units (Sjöström, 1993).

$$M_n = DP \times M_G \quad (\text{Eq. 4.1})$$

Hemicelluloses are linear and branched polysaccharide polymers composed primarily of five sugars: glucose, mannose, galactose, xylose, and arabinose. Some hemicelluloses also contain acetate and glucuronic acid groups. The average degree of polymerization (DP) of the hemicelluloses is 100-200 units. Hardwoods usually have slightly more than 30% hemicelluloses, while softwoods normally contain a little less than 30% hemicelluloses (Sjöström, 1993). Hardwood hemicelluloses often have higher DP (200 units) compared to softwood hemicelluloses (100 units) (Sjöström, 1993).

Lignin is a three dimensional macromolecular polymer made up of modified phenylpropane units (see Chapter 1). To date, no specific repeating unit has been determined, but this is a very controversial area. Hardwoods contain about 18-22% lignin, while softwoods are a bit higher with 22-30% lignin.

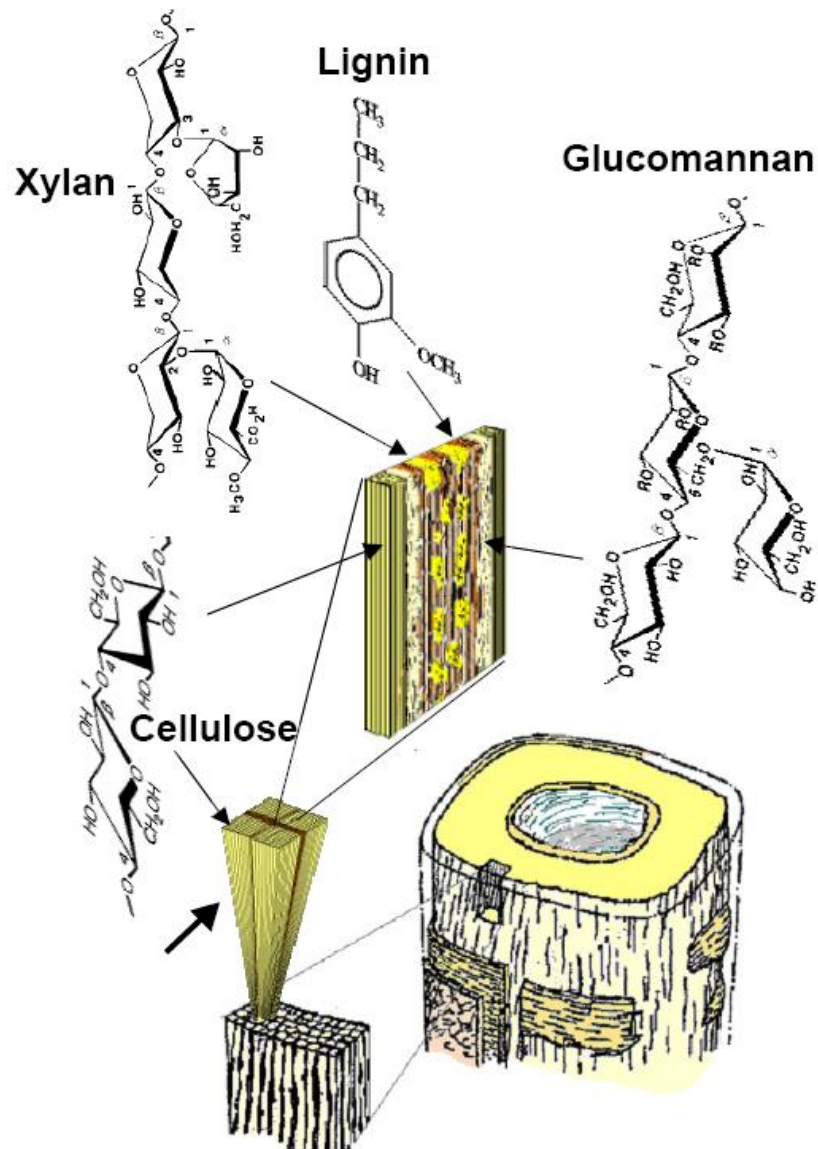


Figure 4.1 Wood Components (Akerholm et al., 2003)

4.2 Chemicals and Materials

Mixed northeast hardwood chips were obtained from a local pulp mills and were composed of birch, beech, maple, poplar and trace amounts of softwoods. The exact composition was unknown. Chemical reagents used in this study were sodium sulfide, sodium carbonate, sodium hydroxide, sulfuric acid and AQ. All reagents were purchased commercially and were industrial grade; except for sugar standards used in High Performance Anion Exchange Chromatography (HPAEC). Reagent grade chemicals were purchased for fucose, xylose, glucose, arabinose, mannose, galactose and acetic acid and were used as standards in the HPAEC analysis of the extracted carbohydrates.

4.3 Hemicelluloses Pre-extraction Experiments

The extracts were obtained by using the laboratory extractor in the Process Development Laboratory of the University of Maine. Green liquor extraction experiments were conducted with green liquor application rates of 0, 2, 4 and 6% based upon the mass of oven-dry wood. The 0% green liquor extraction experiment was conducted using pure water. The extraction experiments were performed at a liquor to wood ratio (L/W) of 4 to 1 using northeastern hardwood chips. The extraction experiments were conducted for 110 minutes at 160 °C in an indirectly-heated, seven-liter circulating digester (Figure 4.2). The contents of the extraction vessel were heated to the extraction temperature over a 55 minutes period of time using a linear temperature ramp. The time-temperature heating schedule was measured using the H-factor variable applicable to lignin removal for Kraft pulping. Samples of the wood extract were drained

from the extraction vessel following the heating period and were cooled and refrigerated. The methods used in the analysis of the extract samples are summarized in Appendix A.

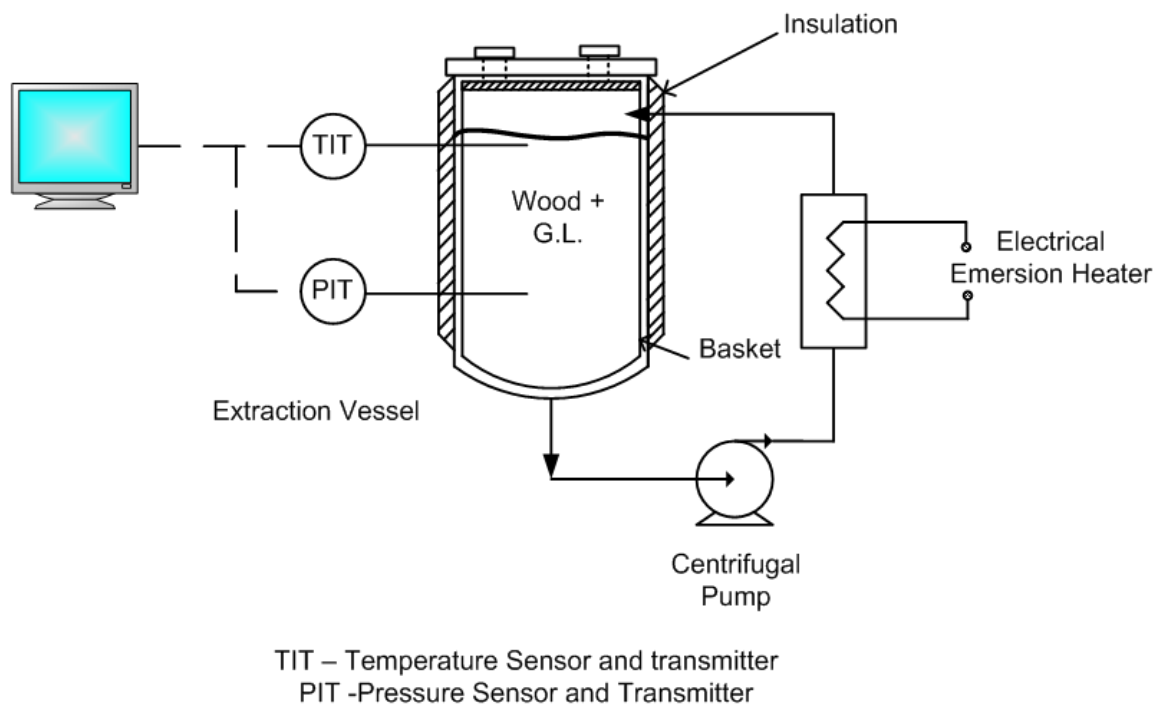


Figure 4.2 Laboratory Circulating Extraction Reactor

4.4 Results and Discussion

The data from the 0% (pure water), 2%, 4% and 6% green liquor extraction experiments are summarized in Table 4.1. The experiments were performed by following the same experimental method except for the different green liquor application rates. The final pH of the extracted liquor ranged between 3.3 and 8.9 depending upon the amount of green liquor applied (see Figure 4.3). The lowest final pH value was obtained by extracting the chips with 0% green liquor; that is, pure water. The mass of wood dissolved during the extraction process varied from 9.08 % for extraction with 2 % green liquor to 13.83 % extraction with pure water (see Figure 4.3). The data for the wood

yield or wood remaining after extraction is shown in Table 4.1. The total wood solids recovery was the sum of the mass of wood solids extracted and the mass of partially macerated wood. As the green liquor application rate increased from 0% to 6%, the wood recovery increased from 92.33% to 99.18%. The lack of closure of the material balance was thought to be related to the release of carbon dioxide, especially from carbohydrates containing uronic acids as the final pH of the extract decreases.

The final pressure in the extraction vessel was 75 psig greater than the saturated water vapor pressure at 160°C. This over pressure is thought to be caused by release of carbon dioxide (CO₂). Table 4.2 summaries the components in the original mixed northeast hardwood sample. The total lignin content was 26.48%. The cellulose content was 41.41% and the hemicelluloses content was 31.60%. The acetyl group content was 3.65% and the uronic acid group content in the original oven dried wood (x_{UA%}) was 2.79%.

Confidence Limits on Data. The confidence limits on the extraction data shown in Table 4.1 were estimated by performing the 6% green liquor experiment six times in exactly the same manner. The t-distribution is used when the sample size is small; namely fewer than 30 observations, which is the case with a sample size of six. The method outlined in Stephen (1977) was used to estimate the 95% confidence limits on the data (Equation 4.2). This was done using the measured mean value ($\bar{X}$), the standard deviation (s), the number of data points (n) and the t-statistic for a sample size of 6 [$t_{w/2}(5)=2.571$]. A two tail t-test was assumed in estimating the t-statistic ($t_{w/2}(n-1)$).

$$\bar{X} - t_{w/2}(n-1) \times \frac{s}{\sqrt{n}} < \mu < \bar{X} + t_{w/2}(n-1) \times \frac{s}{\sqrt{n}} \quad (\text{Eq. 4.2})$$

In the $t_{\alpha/2}$ -statistic, the total error or α value is 5% but represent a two-tail test with 2.5% error on each side of the distribution. The data for the confidence limits for the six percent green liquor extraction data are summarized Table 4.1.

The error bars for the other extraction experiments, 0%, 2%, and 4% green liquor extraction experiments were estimated from the error bars determined for the 6% green liquor extraction experiments. This was done by using equations Equation 4.3 and 4.4. In this method, the coefficient of variation (COV) or the percent error was estimated for the 6% green liquor data.

$$\mathbf{COV}_{6\%} = \left(\frac{\mathbf{S}}{\bar{\mathbf{X}}} \right)_{6\%} = \mathbf{COV}_{\mathbf{Other_Extraction}} \quad (\text{Eq. 4.3})$$

It was then assumed that the percent error or coefficient of variation in the other extraction experiments would be approximately the same as that observed in the 6% green liquor experiments as given in Equation 4.4. This assumption permitted an estimate of the standard deviations in the other extraction experiments.

$$\mathbf{S}_{\mathbf{Estimated}} = (\bar{\mathbf{X}} \times \mathbf{COV}_{6\%}) \quad (\text{Eq. 4.4})$$

Using this value of the estimated standard deviation, the 95% confidence limits for the other experiments was calculated by Equation 4.5.

$$\bar{\mathbf{X}} - t_{\alpha/2}(\mathbf{n} - 1) \times \frac{\mathbf{S}_{\mathbf{Estimated}}}{\sqrt{\mathbf{n}}} < \mu_{\mathbf{Estimated}} < \bar{\mathbf{X}} + t_{\alpha/2}(\mathbf{n} - 1) \times \frac{\mathbf{S}_{\mathbf{Estimated}}}{\sqrt{\mathbf{n}}} \quad (\text{Eq. 4.5})$$

Table 4.1 Summary of Green Liquor Pre-Extraction Data

Green Liquor (% TTA on wood)	Initial GL pH	Final pH	Final Pressure (psig)	Wood Extracted (%) (A)	Total Solid Content in Extract (%)	Organic Solids in Extract (%)	Lignin Concentration in Extract (g/L)	Wood Yield ^a (%) (B)	Total Wood Recovery (%) (A+B)
0 (water)	4.82 ±0.03	3.34 ±0.09	120	13.83 ±0.38	4.16 ±0.17	4.11 ±0.39	7.56 ±0.91	78.50 ±1.19	92.33 ±0.36
2	12.23 ±0.06	4.77 ±0.13	130	9.08 ±0.25	3.15 ±0.13	2.69 ±0.25	6.98 ±0.84	85.85 ±1.30	94.93 ±0.37
4	12.60 ±0.07	5.64 ±0.16	160	10.95 ±0.30	3.92 ±0.16	3.23 ±0.30	8.69 ±1.04	85.41 ±1.30	96.36 ±0.37
6	12.82 ±0.07	8.91 ±0.25	136	12.46 ±0.34	4.70 ±0.19	3.59 ±0.34	9.01 ±1.08	87.31 ±1.33	99.18 ±0.38
a Obtained by weighing the dried extracted wood mass									

Table 4.2 Chemical Analysis of the Raw Wood ---Data Estimated by Dr. Haixuan Zoua (2009)

Wood Yield (%)	Ash (%)	Extractives ^b (%)	Lignin (%)	UA (%)	Acetyl groups (%)	Arabinan (%)	Galactan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Cellulose (%)	HemiCell (%)
100	0.51	0.61	26.48	2.79	3.65	0.56	1.22	42.73	22.80	2.23	41.41	31.60
a Zou, H., University of Maine, Personal Communication (2009)												
b Extractives determined by following Tappi Standard T249 and T264 using dichloromethane (DCM) as the solvent												

4.4.1 Extract pH

Figure 4.3 illustrates the initial and final pH of the extract in liquor and the loss of wood solids following the extraction process. The initial pH of the extraction liquor was approximately 12.5 except pure water 4.82. The final pH of the extract liquor varied between approximately 3.34 for extraction with pure water to 8.91 in the extraction conducted using 6% green liquor. The manner in which the pH of the extract varies with time will influence the amount of CO₂ decomposed as well as the composition of the extraction liquor.

4.4.2 Wood Extracted

The amount of wood extracted during the process varied between 9.08 % and 13.83% depending on the green liquor application rate. A minimum value in the wood extraction curve occurred at an application rate of 2% GL. At low pH more xylan would be expected to be extracted while at high pH more acetyl groups would be cleaved from the xylan hemicelluloses and form sodium acetate. In addition, greater amounts of lignin are removed at high pH because of lignin hydrolysis. These two competing effects are thought to give rise to the observed minimum in the data shown in Figure 4.3 for the wood extracted. Acetyl groups cleaved at low pH would be expected to form acetic acid. Thus depending upon the final pH the cleaved acetyl groups would be present as both acetic acid and sodium acetate.

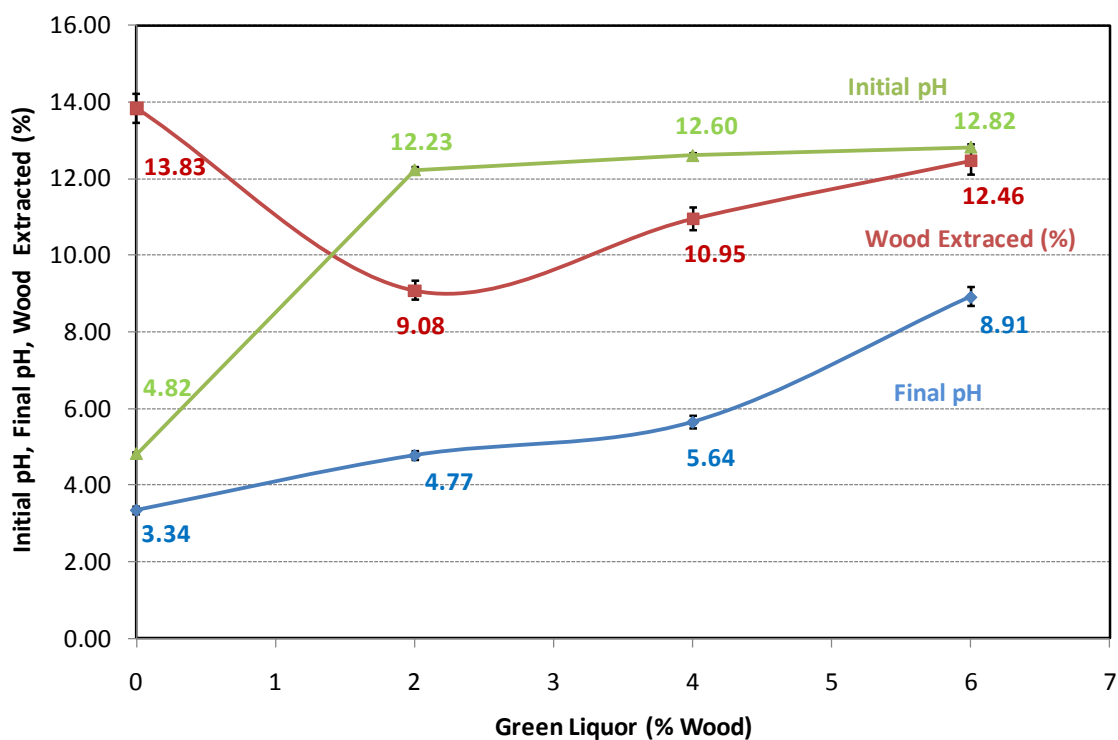


Figure 4.3 GL pH, Final pH and Wood Extracted (%) of the Extracts

4.4.3 Pressure and Temperature

Extraction Temperature. Figure 4.4 illustrates the temperature in the extractor as a function of time for the 0%, 2%, 4% and 6% green liquor extraction experiments respectively. The flow rate was thought to vary with the inlet pressure. Consequently, the temperature ramp varied somewhat because of the performance of the pump. The temperature ramp was not linear. However the maximum temperature was steady once the extractor reached the desired temperature.

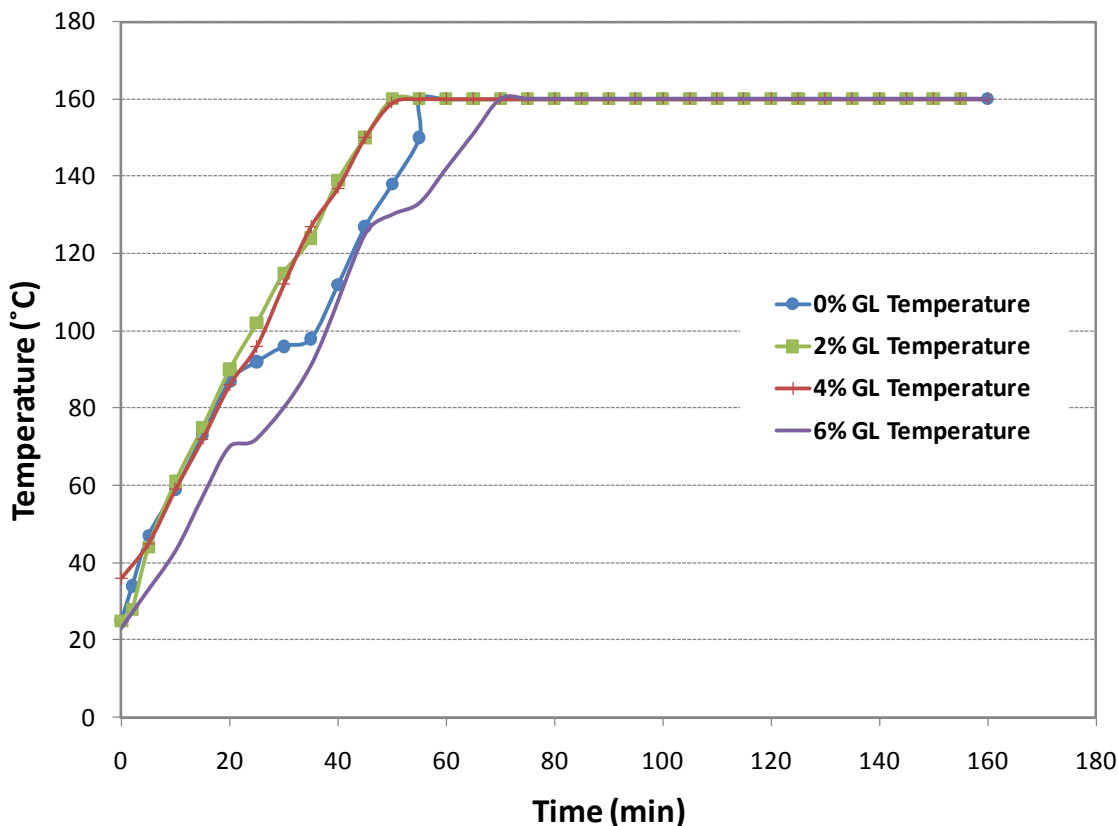
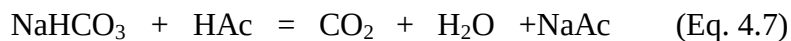


Figure 4.4 Temperatures during Green Liquor Extracting Experiment

Extraction Pressure. Figure 4.5 illustrates the total pressure in the extraction vessel as a function of time for the 0%, 2%, 4% and 6% green liquor extraction experiments. No pre-steaming was done during the experiment, but the digester was vented after about 25 minutes as seen in Figure 4.5. In a normal Kraft pulping experiment, in which non-volatile salts (Na^+ , S^- , HS^- etc) are present and the air is excluded from the vessel, the pressure in the digester is very close to the vapor pressure of water. In the extraction experiments using green liquor, which is predominantly sodium carbonate (Na_2CO_3) the pressure in the extractor after 50 minutes exceeded the vapor pressure of water by a considerable amount. This over pressure was attributed to decomposition of carbonate ion by the presence of acetic acid (HAc) formed from

cleavage of acetyl groups from the xylan polymer. The products of the decomposition are thought to be sodium acetate (NaAc) and carbon dioxide (Equation 4.6 and 4.7).



The vapor pressure of water is plotted in Figure 4.5 and may be compared directly to the pressure in the extraction vessel as a function of time. For example for 4% green liquor, the over pressure in the extractor reached as much 85 psig compared to the 75 psig contributed by the vapor pressure of saturated water (Figure 4.5). As the extraction proceeds at maximum temperature, the pressure continued to rise and reaches a maximum value depending upon the initial amount of green liquor added to the extraction vessel and the pH of the extraction liquor. The maximum pressure reached after 110 minutes at 160 °C was 120 psig in the 0% GL case (pure water). Similar data were 130 psig for 2% GL, 160 psig for 4% GL and 136 psig for 6% GL. The maximum overpressure occurred at the end of the 4% GL extraction experiment, in which the over pressure corresponded to about 85 psig in the 7-liter digester.

Extraction with Water and Decarboxylation of Uronic Acids. In the 0% GL extraction experiment pure water was used and the rise of pressure at elevated temperature was the lowest among all GL extractions but still significant. An attempt was made to explain the rise in pressure observed during the 0% green liquor extraction experiments since sodium carbonate was not present. Two hypotheses were put forward. The first dealt with the increase in vapor pressure because of the release of acetic acid from the wood. This hypothesis was dismissed since the saturated vapor pressure of 3.7 g/L acetic acid solution is almost the same as saturated vapor pressure of pure water

(Figure 4.5). The second hypothesis postulated that the pressure rise was due to carbon dioxide (CO₂) being released by decarboxylation of uronic acid. Leschinsky et al. (2009) hypothesizes that decarboxylation takes place under acidic conditions and that the molar amount of carbon dioxide (CO₂) corresponded to the molar amount of uronic acids degraded. However, the Leschinsky hypothesis has not been proved. Figure 4.6 illustrates the structure of 4-O-methyl glucuronic acid (C₇H₁₁O₇) and is only one of several uronic acids as explained by Sjöström (1993).

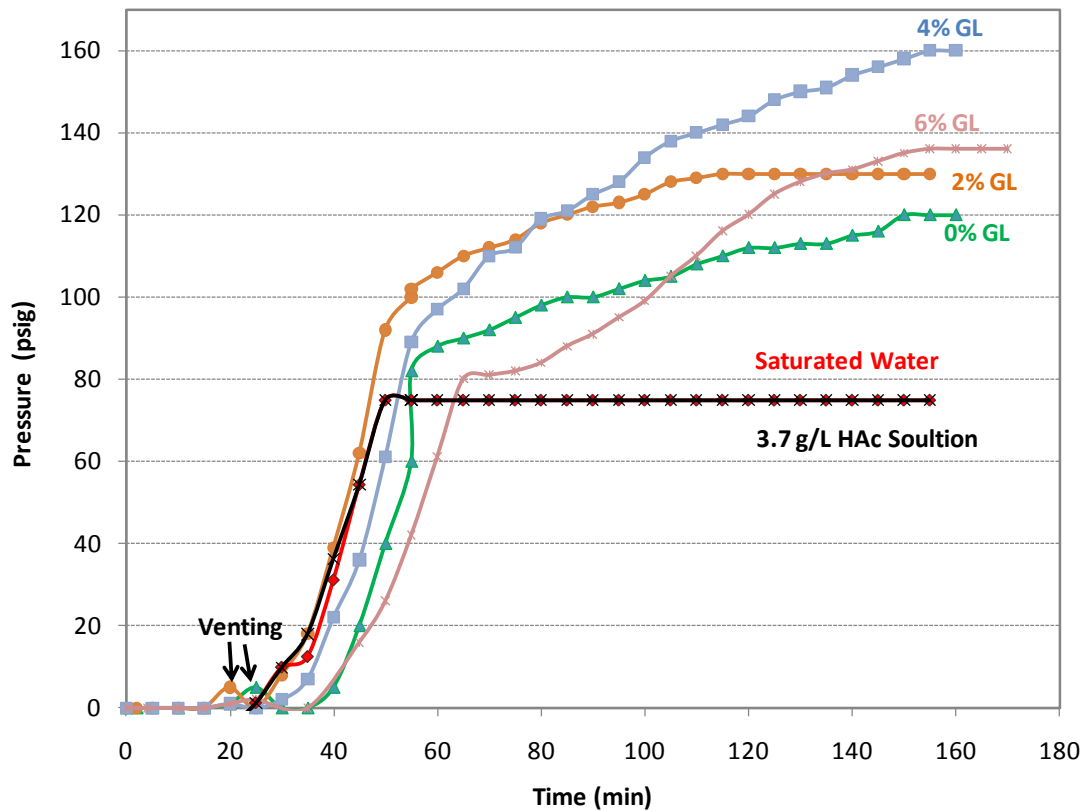


Figure 4.5 Total Pressures during Green Liquor Extracting Experiment

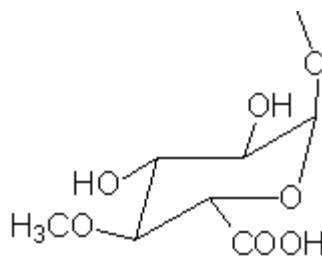


Figure 4.6 4-O Methyl Glucuronic Acid (Sjöström, 1993)

In an effort to prove this hypothesis, a simple calculation was made. First, the free volume of the laboratory extraction vessel (V_{free}) was estimated to be 1.99 liter by using Equation 4. 8. The inside diameter (ID_{digester}) and the unfilled height (free-board) of the digester (H_{free}) were measured as 6.125 inches and 4.125 inches respectively.

$$V_{\text{free}} = \pi \times \left(\frac{ID}{2} \right)^2 \times H_{\text{free}} = \mathbf{1.99 \text{ liters}} \quad (\text{Eq. 4.8})$$

Secondly, the partial pressure attributed to carbon dioxide (P_{CO_2}) released during the decarboxylation reaction was estimated by Equation 4.9 to be about 45 psig.

$$P_{\text{CO}_2} = P_{\text{total}} - P_{\text{water}} = \mathbf{120 \text{ psig} - 75 \text{ psig} = 45 \text{ psig}} \quad (\text{Eq. 4.9})$$

The estimate for the partial pressure of CO_2 (P_{CO_2}) was made by assuming Dalton's law. Thus the partial pressure of CO_2 (P_{CO_2}) is the difference between the observed total pressure (P_{total}) during the 0% green liquor extraction experiment which was 120 psig at 160 °C and the vapor pressure of saturated water (P_{water}) at the same temperature (75 psig).

Thirdly, the moles (n_{CO_2}) of the carbon dioxide in vapor phase were estimated to be about 0.17 moles by applying the ideal gas law to the free space in the extraction vessel (Equation 4.10).

$$n_{\text{CO}_2} = \frac{P_{\text{CO}_2} \times V_{\text{free}}}{R \times T} = \mathbf{0.17 \text{ moles}} \quad (\text{Eq. 4.10})$$

In equation 4.10, R is the universal gas constant [8.314 J/(mole×K)] and T is the experiment temperature (433.15 K or 160 °C).

In the green liquor extraction experiment, 944.1 grams (o.d. basis) of mixed Northeastern hardwood wood chips was used. The total mass of uronic acid (m_{UA}) in the wood was estimated to be 26.3 grams and was calculated from the total mass of wood (m_{wood}) and the uronic acid content in the wood (x_{UA}) from Equation 4.11. The uronic acid content was given in Table 4.2

$$m_{\text{UA}} = x_{\text{UA}} \% \times m_{\text{wood}} = \mathbf{2.79\% \times 944.1\text{gm} = 26.3 \text{ grams}} \quad (\text{Eq. 4.11})$$

The moles of uronic acid present in the wood was estimated to be 0.13 moles and was calculated from Equation 4.12 using the molecular weight (M_{UA}) of uronic acid ($\text{C}_7\text{H}_{11}\text{O}_7$) which was taken to be equal to 207 grams/mole.

$$n_{\text{UA}} = \frac{m_{\text{UA}}}{M_{\text{UA}}} = \frac{\mathbf{26.3\text{grams}}}{\mathbf{207\text{gram/mole}}} = \mathbf{0.13 \text{ moles}} \quad (\text{Eq. 4.12})$$

If one mole of CO_2 is released by decarboxylation of one mole of uronic acid, then the agreement between the estimated carbon dioxide content measured from the partial pressure (0.17 moles) agrees with the carbon dioxide content from the wood analysis (0.13 moles). Thus, it is plausible to conclude that decarboxylation may be taking place as postulated by Leschunsky et al. (2009). This decarboxylation could possibly take place in the extraction experiment conducted using pure water where the final pH is about 3.34 but also in the green liquor experiments where the final pH is less acidic. Lastly, it is interesting to note that the total pressure in the 6% green liquor experiment is less than that in the 4% green liquor extraction experiment.

4.4.4 Lignin Content in Extract

The concentration of lignin in the extract is illustrated in Figures 4.7. The lignin concentration varied between approximately 6.98 g/L for extraction with 2% green liquor to 9.01 in the experiment conducted using 6% green liquor. Unfortunately the error limits on the lignin analysis are high. For the 6% green liquor application rate, six separate extraction experiments were performed over several months. After each extraction experiment the lignin content was estimated by using duplicate determinations. The duplicate analyses agreed quite well but the total amount of lignin extracted in the separate experiments varied over time and gave rise to the high error limits. Since the duplicate experiments were performed over a several month period, it is thought that the wood sample may have been changing or the sampling was not precise.

4.4.5 Total Solids and Organics Solids in Extract

Depending upon the green liquor application rate, the total solids varied between 3.15% (2% GL) and 4.70% (6% GL) while the organic solids, defined from a combustion test (see Appendix A), varied between 2.69% (2% GL) and 4.11% (0% GL). As the green liquor application rate increased, a smaller fraction of the total solids content were organic solids (see Figure 4.8). In Figure 4.7, the total solids curve and the organic solids curve begin to diverge as the green liquor application rate increased. For the pure water experiment (0% GL), approximately 98.7% of the total solids were organic solids. By contrast for the 6% GL extraction experiments, only 76% of the total solids were organic solids (see Figure 4.8).

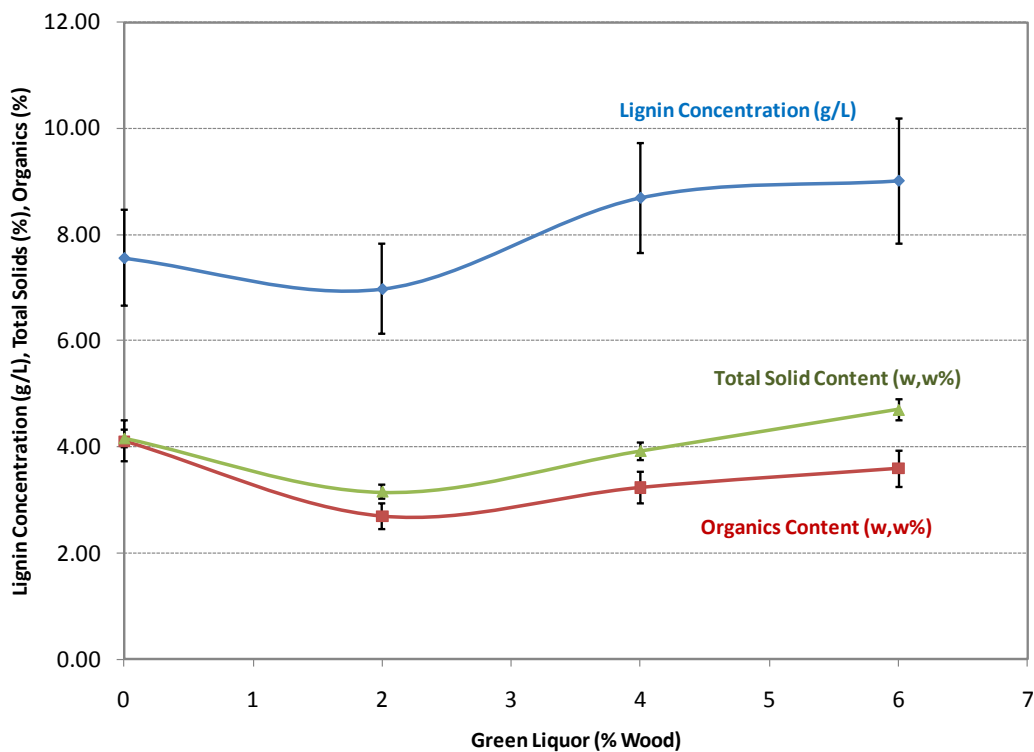


Figure 4.7 Lignin Concentration, Total Solids and Organics Content in the Extracts

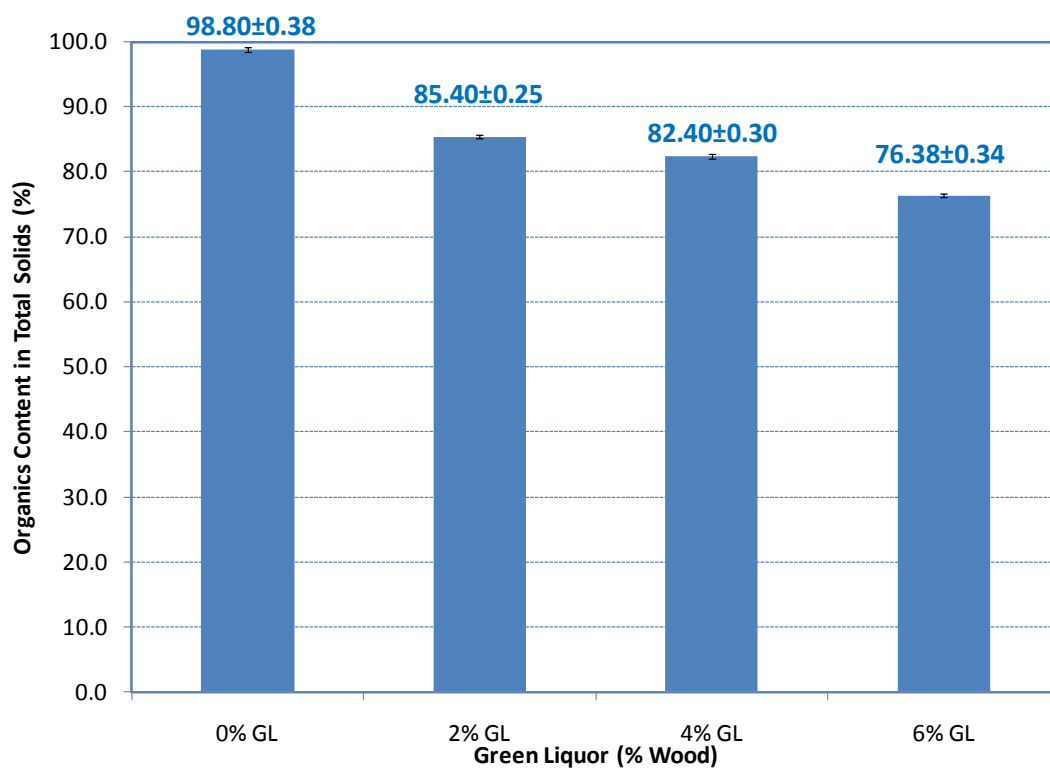


Figure 4.8 Organics Content in the Total Solids

4.4.6 Xylan and Acetate Concentrations in Extract

Figure 4.9 illustrates the variation in the xylan and acetate contents with increasing green liquor charge for extraction liquors performed under conditions similar to those used in this study (Mao et.al, 2008). The acetate curve shown in Figure 4.9 represents both the acetic acid and sodium acetate contents of the extraction liquor reported as acetate ion. Both the xylan and acetate concentrations are expressed as grams per liter in the extracted liquor. No error bars are reported in the study by Mao (2008).

As the green liquor application rate increases, the acetate content in the extraction liquor increased to about 11.8 gm/L at a green liquor application rate of approximately 6%. This is considerably greater than that obtained with water which was approximately 4 gm/L. By contrast the concentration of xylan in the extract decreased in the extract from about 22 g/L for the water extraction to less than 2.36 gm/L at the 6% liquor application rate. This decrease in xylan was thought to occur partially because of the decomposition of the xylan by peeling reactions which occur as the pH of the extract increases Sjöström (1993).

Similarly the ratio of the measured xylan to acetic acid or sodium acetate content in the extract varied from about 6 for the water extraction to approximately 0.2 for the case of the 6% application rate. Clearly, for mixed Northeastern hardwood, extraction with water greatly favors extraction and preservation of xylan while extraction with green liquor favored extraction of acetyl groups.

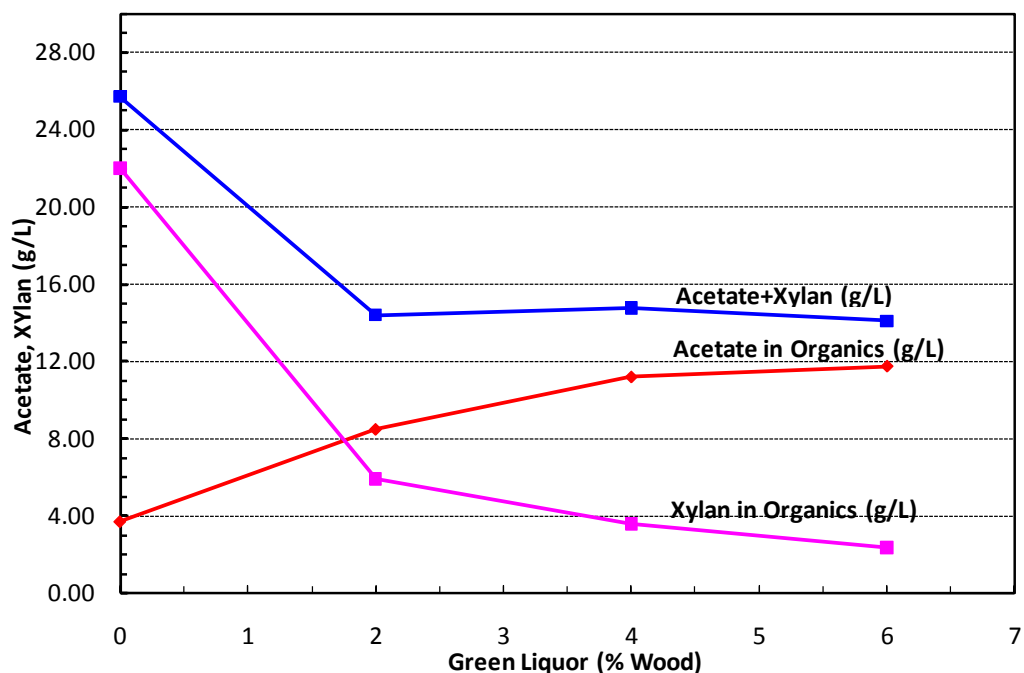


Figure 4.9 Xylan and Acetate Concentration in Extract (Mao, et al., 2008)

4.5 Conclusions

Extraction experiments were performed using green liquor as the extraction solvent. Application rates varied between 0% green liquor (pure water) and 6% GL. 0.05% AQ was added to the green liquor to simulate the near neutral hemicellulose extraction process. As the green liquor application rates increased in the experiments reported here, the pH of the extract increased. The higher green liquor application rate experiments resulted in greater amounts of lignin and sodium acetate being extracted but resulted in a decrease in the xylan extracted. The total pressure in the extraction experiments was thought to result from the partial pressures of both water and carbon dioxide. The carbon dioxide resulted during the extraction experiments from the decomposition of sodium carbonate and uronic acids.

Lignin extracted in the 0% green liquor and the 6% green liquor experiments were selected for purification and use as a precursor material for conversion into carbon fibers. The 6% GL experiments had the highest concentration of lignin while the 0% or pure water extraction had the highest xylan content. Thus these two extremes bracketed the types of lignin that would be removed in the near neutral hemicellulose extraction process.

CHAPTER 5

LIGNIN ISOLATION AND CHARACTERIZATION

This chapter describes the methods used to precipitate lignin from the extraction liquors described previously in Chapter 4. Extracted liquor sample obtained under the 6% green liquor extraction conditions were used in initial or scoping experiments that were designed to investigate lignin isolation and characterization techniques.

Appendix B summarizes preliminary work designed to investigate precipitation of lignin. Specifically it was designed to select an appropriate pH for lignin precipitation. Initially, a comparison was made between two methods of isolating lignin. Sun (1999) describes a method in which lignin is separated from carbohydrates by neutralization with phosphoric acid followed by precipitation with ethanol followed by phosphoric acid. A second method, developed by the author, involved simultaneously precipitating and cleaving lignin carbohydrate bonds by hydrolysis with sulphuric acid. This method was termed the “hydrolysis method” by the author. Samples of lignin isolated by the two methods were then characterized for their physical properties. The properties of the two isolation techniques were compared by using the two sample t-test.

5.1 ORNL Specifications for Lignin as a Carbon Fiber Precursor Material

Baker, Griffith and Compere (2005) at the Oak Ridge National Laboratory (ORNL) developed lignin specifications applicable for manufacturing carbon fibers (see Table 5.1). Specifications include the content of lignin, ash, volatile, and particulate matter. The specifications for volatile material and non-melting particulate matter are imbedded in the requirements for high-temperature textile melt-spinning at 250 °C. The

specifications for ash and particulate matter are based upon data for pitch fiber to minimize inclusions and defects which weaken carbon fiber (Baker et al. 2005).

Table 5.1 Lignin Specifications as a Precursor Material for the Production of Carbon Fiber (Baker et al. 2005)

Specification	Value
Lignin Content (w %)	99%
Ash Content (w %)	< 0.1%
Volatile Material (w %)	< 5% (at 250 °C)
Particulate Matter (w %)	100% Removal of particulate matter > 1µm in diameter

5.2 Lignin Separation Methods

Two (2) methods were compared for separating lignin from the carbohydrates in the raw hemicelluloses extract samples. These methods were predicated upon the preliminary lignin isolation techniques described in Appendix B. This isolation work was done to meet the lignin specifications summarized in Table 5.1. Both of these methods were predicated upon lowering the pH of the extract to precipitate lignin fractions.

5.2.1 Method of Sun (1999)

Figure 5.1 illustrates a novel two-step method developed by Sun and co-workers (1999) for separating lignin from carbohydrates. In this method, cooled extraction liquor

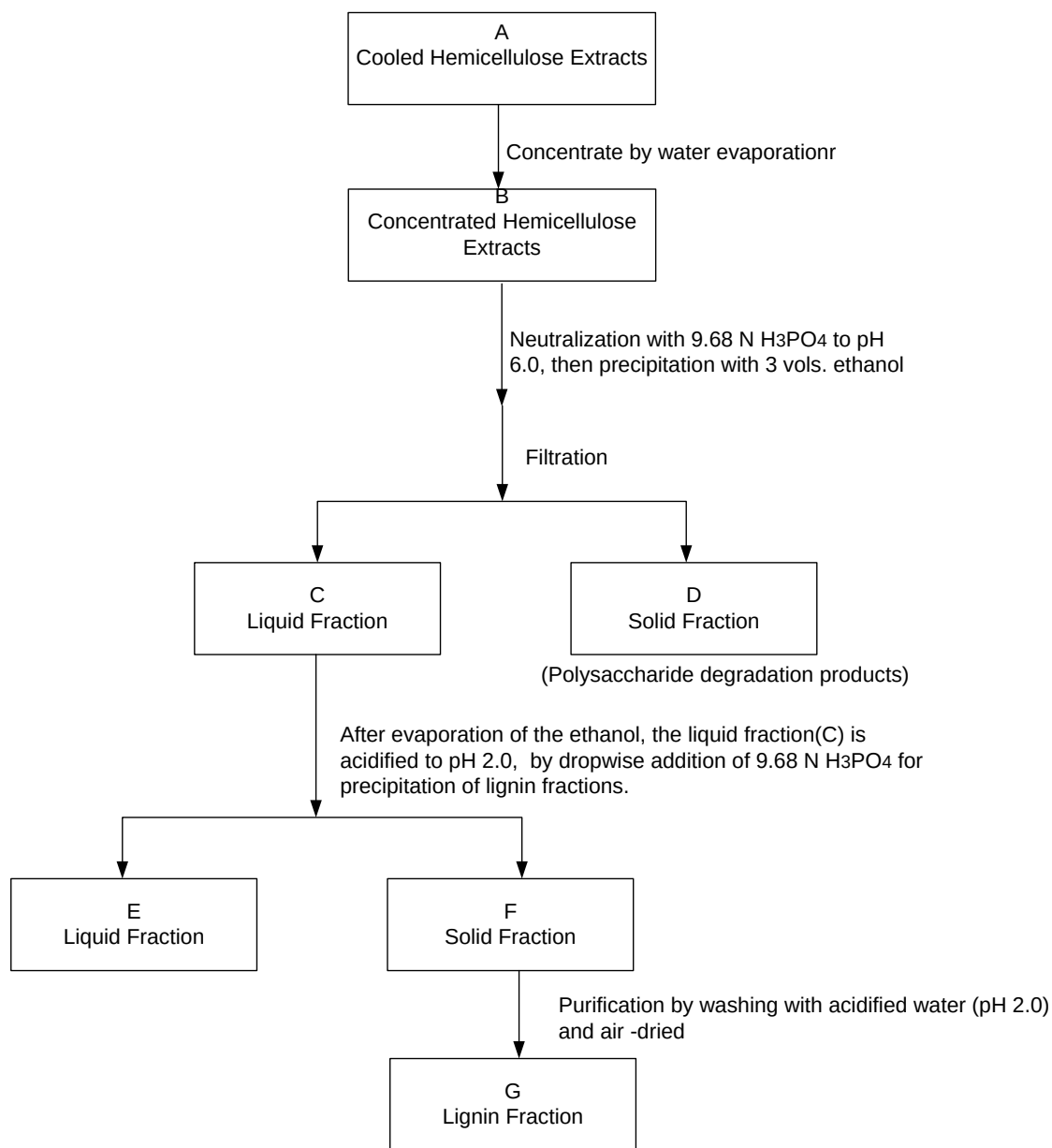


Figure 5.1 Protocol for Lignin Isolation Method Using Ethanol (Sun et al., 1999)

(A) was first concentrated by evaporation of water. The pH of the concentrated extraction liquor (B) was lowered to pH 6.0 by addition of 9.68 N H_3PO_4 . The polysaccharide degradation products (D) were then separated by precipitation from concentrated liquor (B) by extraction with three (3) volumes of ethanol. The ethanol was then evaporated from the liquid fraction (C) and the solid lignin fraction (F) precipitated by reducing the pH of the liquid fraction (C) to 2.0, again by addition of 9.68 N H_3PO_4 . The purified lignin fraction (G) was obtained by washing the solid fraction (F) with acidified water (pH 2.0). Lastly the recovered lignin fraction (G) was air dried.

5.2.2 Hydrolysis Method

A lignin isolation method developed by the author is shown in Figure 5.2. This method is based upon the hydrolysis of the lignin to cleave lignin-carbohydrate bonds. In this method, the cooled extraction liquor (A) was treated with 72% sulfuric acid to lower the pH to 1.0 and the sample stored at room temperature overnight. The sample was then was hydrolyzed at 121 °C for 2 hours to obtain a mixture of solids and liquids, designated (B). The solids fraction (D) was separated from the mixture (B) by filtration. The solids (D) were then washed with deionized water and air dried to obtain the purified lignin sample (E).

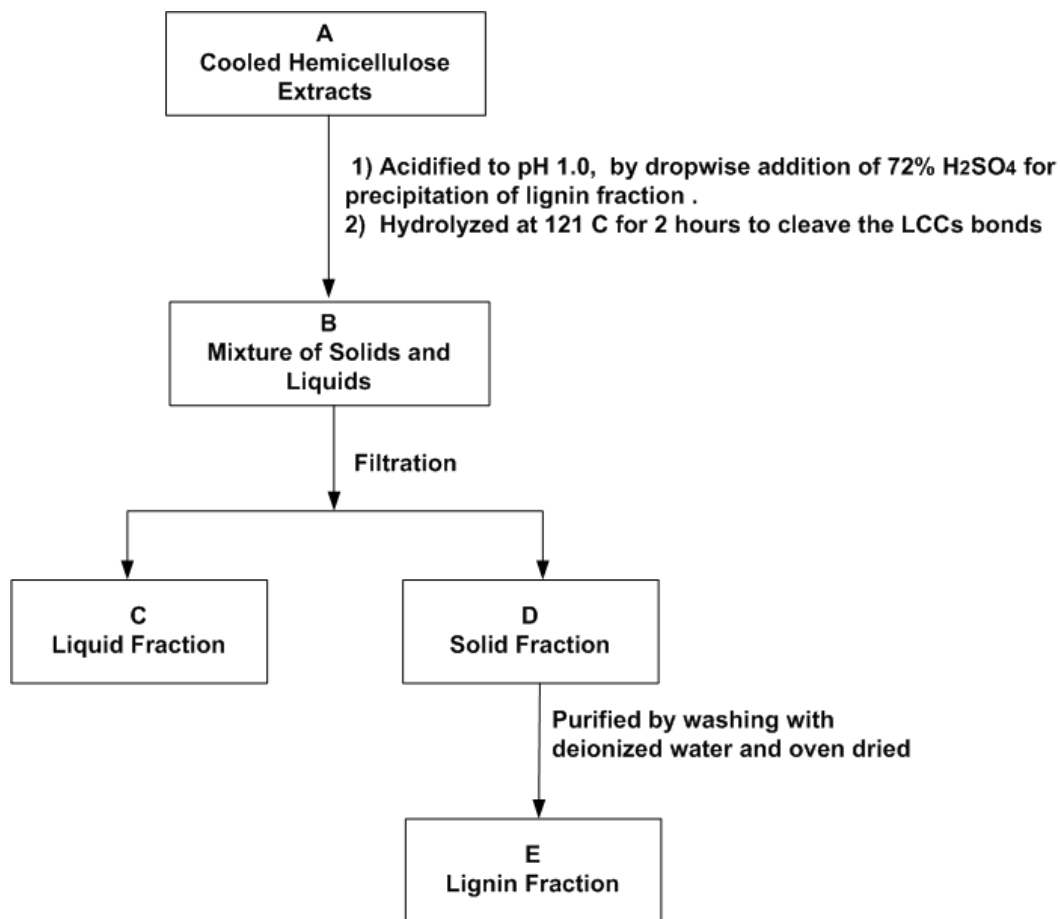


Figure 5.2 Protocol for the Hydrolysis Lignin Isolation Method

5.3 Analysis of Recovered Lignin

5.3.1 Lignin Content

The lignin content was estimated by measuring the amount of insoluble (Klason) and soluble lignin in the isolated lignin sample. The basic procedure is described in Figure 5.3.

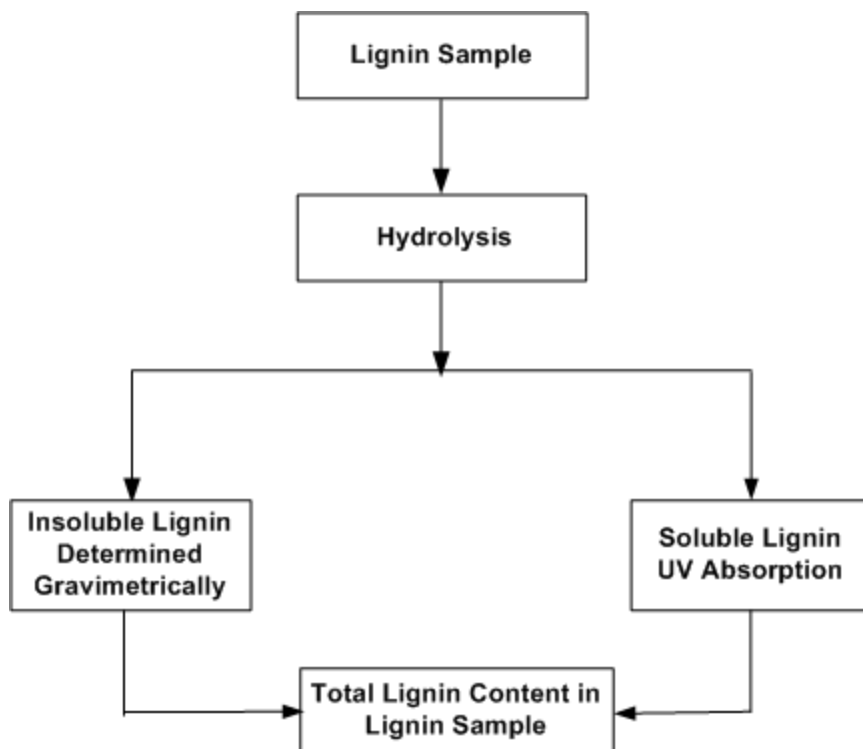


Figure 5.3 Determination of Total Lignin Content

Usually, the soluble lignin has a maximum absorption at a wavelength (λ) of 280 nm. However, the acid hydrolysis of the lignin sample gives rise to carbohydrate degradation products such as furfural and hydroxyl-methyl-furfural which absorb UV light strongly at 280 nm (Lin et al., 1992). Consequently, the UV absorption of the acid soluble lignin was measured at a wavelength (λ) of 205 nm. The acid-soluble lignin concentration (C_s) was calculated from Equation 5.1 given by Young (1981).

$$C_s = \frac{A}{E \times b} \quad (\text{Eq. 5.1})$$

The value of A is the absorption value, E (110 L/g cm) is the extinction coefficient and b (1 m) is the path length (TAPPI Useful Method T-249, 1984).

5.3.2 Ash Content at 900 °C

The ash content was determined by following TAPPI Test Method T-413. In this method a moisture-free sample of the recovered lignin was ignited in a muffle furnace at 900 °C. The weight fraction of residual ash was measured relative to the weight of the original sample.

5.3.3 Volatile Material Content at 250 °C

The volatile material content of the recovered lignin samples was measured in accordance with the ORNL standard (Table 5.1). This was done by heating the lignin sample in a muffle furnace for six (6) hours at 250 °C. The volatile material was estimated from the loss of mass of the sample and reported as a percentage weight loss.

5.3.4 Particulate Matter Content

The content of particulate matter was estimated by following the Mead-Westvaco Standard Method 017.04. In this method, a moisture-free sample of recovered lignin was completely dissolving in 5% NaOH solution. The liquid sample was then filtered through Whatman #41 filter paper to remove any insoluble particulate matter. The percentage of insoluble matter was estimated from the mass of solids filtered and the mass of the original sample.

5.3.5 Carbon Content

The carbon content of the recovered lignin samples was determined by sending samples to the Analytical Laboratory of the Department of Plant, Soils and Environmental Science at the University of Maine. In the carbon determination method the samples of

lignin were combusted in an induction furnace operated at 1,050 to 1,350 °C in an oxygen atmosphere. The carbon dioxide (CO₂) released in the combustion process is carried by helium gas through a packed bed of steel wool to remove residual oxygen. An aliquot of the CO₂ helium mixture is then sent to an infra-red detector where the concentration of CO₂ is determined.

5.3.6 Statistical Experimental Analysis

The results obtained from the two methods were compared by performing a two sample t-test assuming the t-distribution was applicable for small sample sizes. The objective of the statistical analysis was to determine which of the two lignin isolation procedures was more appropriate. In this method, six extraction experiments were carried out using 6% GL. The six samples were then split into two sub-sets of 3-samples each; that is three extractions for each method. The lignin in each of the 3-sample sub-sets was then isolated by the method of Sun (1999) and also by the hydrolysis method developed by the author. Samples of the lignin recovered by the two isolation techniques were then analyzed in duplicate for lignin purity, ash content, volatile material content, particulate matter and carbon content. For each property the mean value ($\bar{X}_A$ and $\bar{X}_B$) and standard deviations (s_A and s_B) were determined from the experimental measurements. The two sample t-test was then performed for each property to determine if there were differences in the mean values between the two methods (see Figure 5.4).

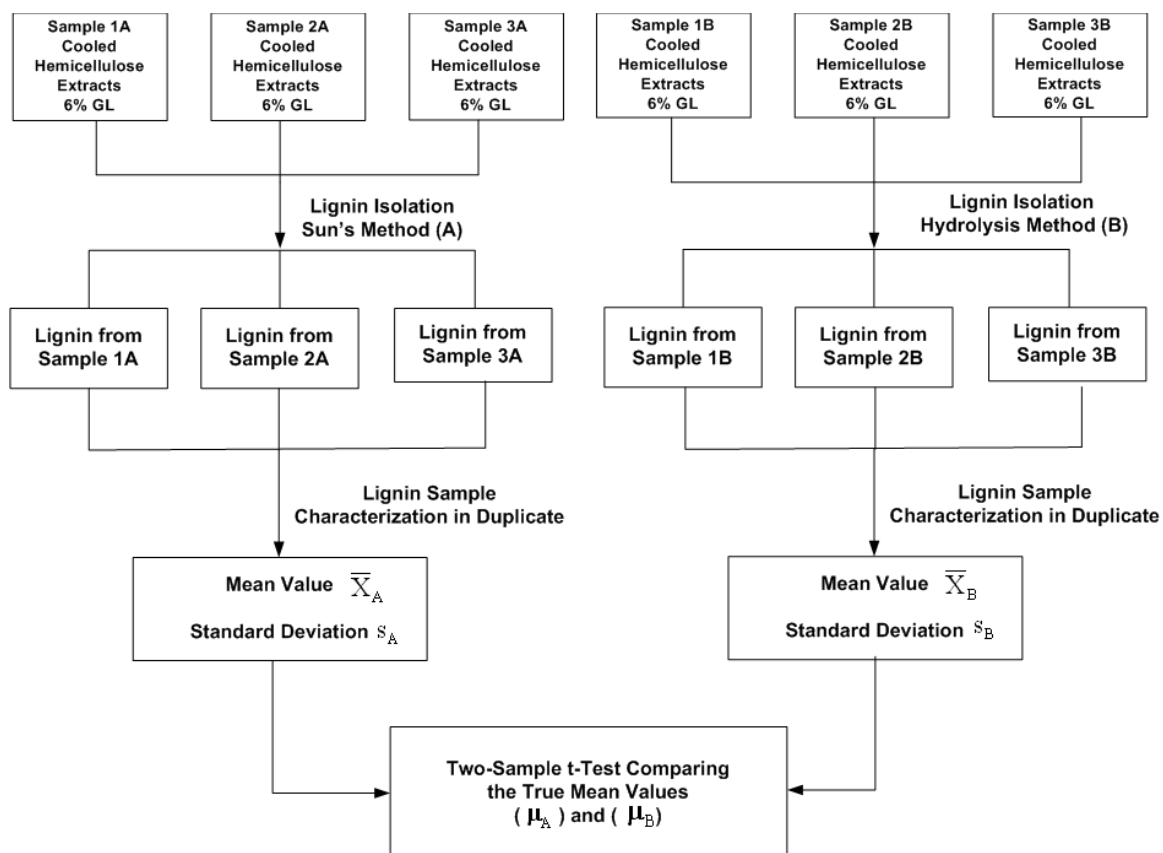


Figure 5.4 Protocol used in Analysis of Lignin Isolation Method

5.4 Results and Discussion

Table 5.2 summarizes the results for the property evaluation by the two methods.

The results are shown graphically in Figure 5.5

Table 5.2 Summary of the t-test Applied to the Properties of Lignin Isolated by the Two Methods

Method	Sample ID	Ash (%)	Klason Lignin (%)	Acid-soluble Lignin (%)	Total Lignin (%)	Volatile Matter (%)	Particulate Matter (%)	Carbon (%)
Sun Method (A)	1A	0.018	76.48	13.53	90.01	21.24	0.04	61.2
	2A	0.065	78.93	12.11	91.01	17.95	0.03	59.2
	3A	0.056	77.85	14.29	92.14	21.63	0.03	62.2
	$\bar{X}_A \pm \text{Error}$	0.05 ± 0.05	77.75 ± 3.04	13.31 ± 2.75	91.05 ± 2.64	20.27 ± 5.01	0.03 ± 0.01	60.9 ± 3.8
Hydrolysis Method (B)	1B	0.04	89.31	9.27	98.59	9.26	0.03	63.4
	2B	0.05	93.43	4.71	98.14	12.13	0.01	58.7
	3B	0.05	88.71	9.95	98.65	10.17	0.01	62.6
	$\bar{X}_B \pm \text{Error}$	0.04 ± 0.02	90.48 ± 6.38	7.97 ± 7.08	98.46 ± 0.70	10.52 ± 3.64	0.02 ± 0.02	61.6 ± 6.2
t-Statistic (Eq.5.3)	$t_{0.025}(4)=2.776$	0.39	7.75	3.03	11.69	6.76	1.90	0.41
Significance (Yes or No)		No	Yes	Yes	Yes	Yes	No	No

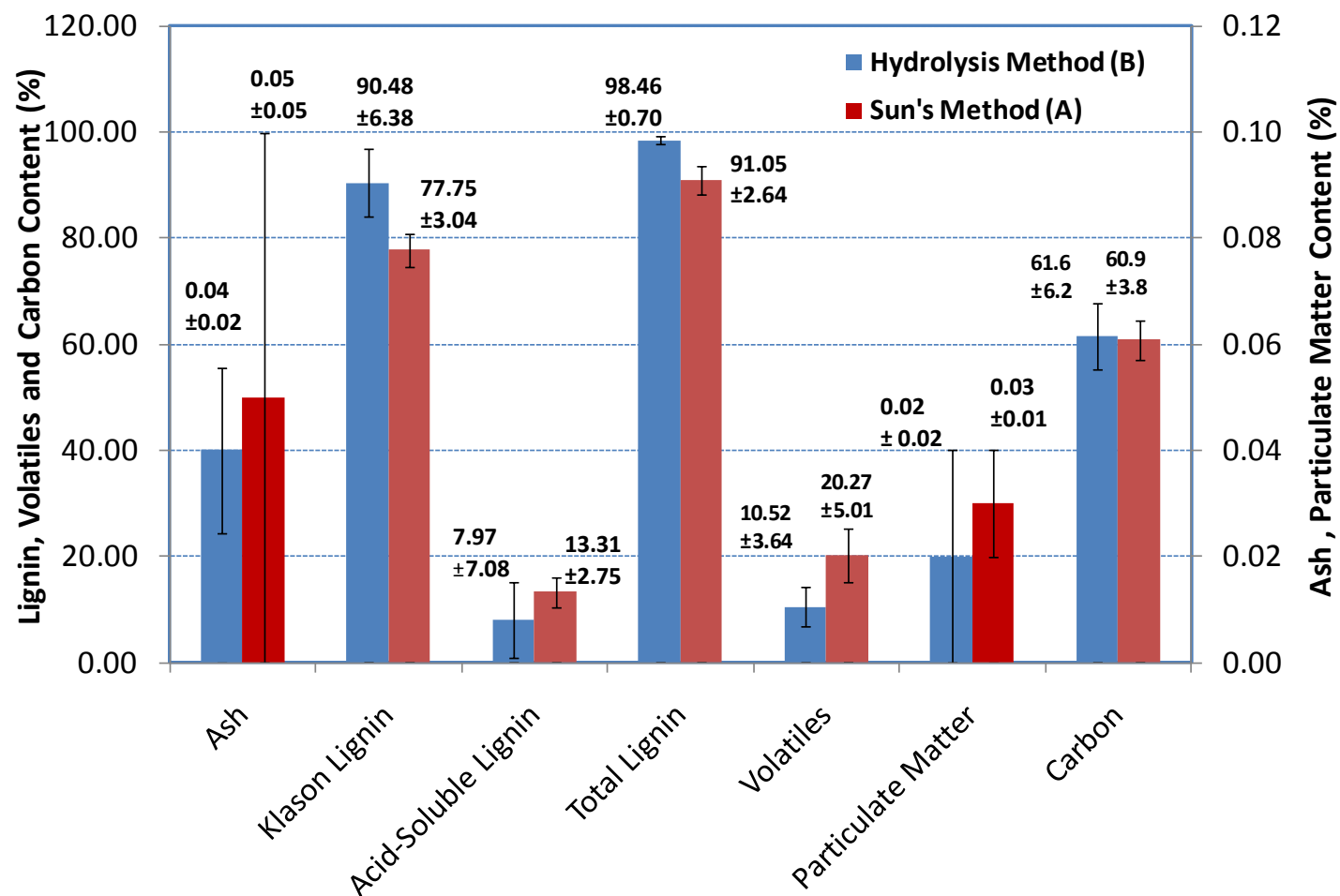


Figure 5.5 Properties of Isolated Lignin Samples

5.4.1 Two-Sample t-Test Used to Compare the Lignin Isolation Techniques

A two-small-sample t-test was used to compare the lignin isolation techniques developed by Sun (1999) and the author. In the two-sample t-test, a comparison is made between the mean values of the properties for the lignin samples recovered by Sun's method (A) and the hydrolysis method developed by the author (B). The two-sample t-test compares the hypothesis (H) that the true mean values of the two methods are the same versus the alternative (A) hypothesis that the mean values for the two populations (μ_A and μ_B) are different (Stephen, 1977).

Hypothesis (H): $\mu_A = \mu_B$ (There is no difference in the two separation techniques)

Alternative (A): $\mu_A \neq \mu_B$ (The two separation techniques are different)

The degrees of freedom (df) appropriate to the two-sample t-test relates to the number of experimental observations (n_A and n_B) for each property of interest (Equation 5.2).

$$df = (n_A + n_B - 2) \quad (\text{Eq. 5.2})$$

In the t-test, the hypothesis (H) is rejected in favor of the alternative (A) when the t-statistic result (Equation 5.3)

$$t = \frac{\bar{X}_A - \bar{X}_B}{\sqrt{\frac{\sum(X_A - \bar{X}_A)^2 + \sum(X_B - \bar{X}_B)^2}{n_A + n_B} \times \left(\frac{1}{n_A} + \frac{1}{n_B}\right)}} \quad (\text{Eq. 5.3})$$

is greater than $t_{\alpha/2}(n_A + n_B - 2)$ obtained from the t-distribution (see Equation 5.4).

$$t > t_{\alpha/2}(n_A + n_B - 2) \quad (\text{Eq. 5.4})$$

The $t_{\alpha/2}(n_A + n_B - 2)$ statistic is equal to 2.776 at a 95% confidence level when using a two tail significance level ($\alpha=0.05$) if the degrees of freedom are equal to 4; that is

[$t_{0.025}(4)=2.776$]. The results of the two-sample t-test are summarized in Table 5.2 for the lignin properties obtained using the two isolation techniques.

There is a significant difference in the calculated t-statistic between the two methods for the Klason lignin (7.75), acid-soluble lignin (3.03), total lignin (11.69) and volatile material (6.76). In these cases the t-statistic was greater than 2.78 (Table 5.2). There was no significant difference in the t-test for the carbon content, ash content and particulate matter content.

As seen in Figure 5.5, lignin isolated by the hydrolysis method is higher in Klason lignin and lower in soluble lignin when compared to lignin isolated by Sun's method. Also the total lignin content in the isolated lignin samples is greater with the hydrolysis method. The volatile material content is greater in Sun's method. High volatility can potentially cause difficulty during fiber spinning and lead to imperfections in the carbon fiber product. Based on this analysis the hydrolysis method was thought to be more effective than Sun's method. Consequently the hydrolysis was selected for isolating lignin samples for the production of lignin fibers.

5.4.2 Lignin Isolated by the Hydrolysis Method

Samples. Crude extract was obtained by extracting wood using the “near neutral hemicelluloses process” with 0%, 2% 4% and 6% green liquor. A sample of crude extract was also obtained from the Old Town Fuel and Fiber Company. This sample was prepared in a full-scale mill trial using 4% green liquor as the extraction solvent with commercial wood chips. Lignin was then isolated by using the hydrolysis method on each crude extract and the properties determined.

For comparison purposes, two samples of commercial lignin, Alcell and Indulin AT lignin were also obtained and their properties determined. Alcell lignin was supplied by Repap Technologies Limited (RTL). The sample of Alcell lignin was obtained by ethanol pulping of northeastern hardwood in a pilot plant facility and the lignin isolated by precipitation. The sample of Indulin AT was supplied by Mead-Westvaco Corporation and is commercial lignin that is isolated from Kraft black liquor obtained by pulping southern pine.

The results for the properties of the lignin samples are presented in Table 5.3. The first row in the table contains the lignin specifications defined by ORNL (Baker et al., 2005) as a precursor material.

Table 5.3 Comparing the Lignin Samples Isolated by Different Methods

Lignin Source	900C Ash (%)	800C Ash (%)	Klason Lignin (%)	Acid-soluble Lignin (%)	Total Lignin (%)	Volatiles Matter (%)	Particulate Matter (%)	Carbon (%)
Lignin Specification (ORNL)	<0.1	/	/	/	≥99	<5	100 removal ^b	/
0% GL	0.00 ±0.00	/	95.71 ±0.66	3.78 ±0.25	99.48 ±0.41	11.38 ±0.13	0.01 ±0.01	64.7
2% GL	0.00 ±0.00	/	90.78 ±1.40	7.19 ±0.97	97.97 ±0.43	10.50 ±0.92	0.01 ±0.00	64.6
4% GL	0.03 ±0.01	/	90.26 ±0.47	8.54 ±0.48	98.80 ±0.95	8.77 ±0.96	0.01 ±0.01	64.3
6% GL	0.04 ±0.02	/	90.48 ±6.38	7.97 ±7.08	98.46 ±0.70	10.52 ±3.64	0.02 ±0.02	61.6 ±6.2
Alcell (Organosol Process)	0.08 ±0.01	/	90.76 ±0.41	3.46 ±0.60	94.22 ±0.86	15.42 ±3.45	0.01 ±0.01	64.4
4% Old Town (6/26/09)	0.16 ±0.11	/	92.27 ±0.38	6.33 ±1.35	98.60 ±0.97	17.70 ±0.79	0.01 ±0.01	62.2
Indulin AT from Softwood Using Kraft Process	1.61 ±0.07	2.15 ±0.06	86.80 ±0.42	3.10 ±0.17	89.90 ±0.55	9.83 ±0.99	0.05 ±0.01	66.0
Properties of Indulin AT (MeadWestvaco) ^a	NA	3	NA	NA	97 (100-Ash)	8.5 260C	0.05	NA

a Properties of Indulin AT were obtained from the Mead-Westvaco data sheet.
b Particulate matter greater than 1 micron.

Ash Content. Figure 5.6 illustrates the values for the ash content of the different lignin samples. The Indulin AT had the highest ash (900 °C) content at $1.61\% \pm 0.07\%$. The ash content in the lignin extracted in the Old Town Fuel and Fiber Company sample was $0.16\% \pm 0.11\%$. This value was considerably higher than the lignin extracted in the University of Maine Laboratory. This difference was thought to occur because in the mill trials 70% of the extract liquor was recycled back to the extraction vessel to maintain a liquor to wood ratio of 2.2. This differed considerably from the laboratory experiments in which no liquor was recycled and the experiments were conducted in a batch mode using synthetic green liquor. The samples generated by the double hydrolysis method had an ash content less than 0.1% and met the lignin specification given in Table 5.1. The ash values were very low in the recovered lignin samples from the 0% and 2% green liquor extraction experiments. These low values for the inorganic matter in the recovered lignin are thought to result because the initial amount of sodium carbonate and other sodium salts was very low. The ash content measured at 800 °C by the author for the Indulin AT sample was $2.15\% \pm 0.06\%$. This value was however lower than the reported ash value of 3% specified by Mead-Westvaco Corporation in their published data sheet.

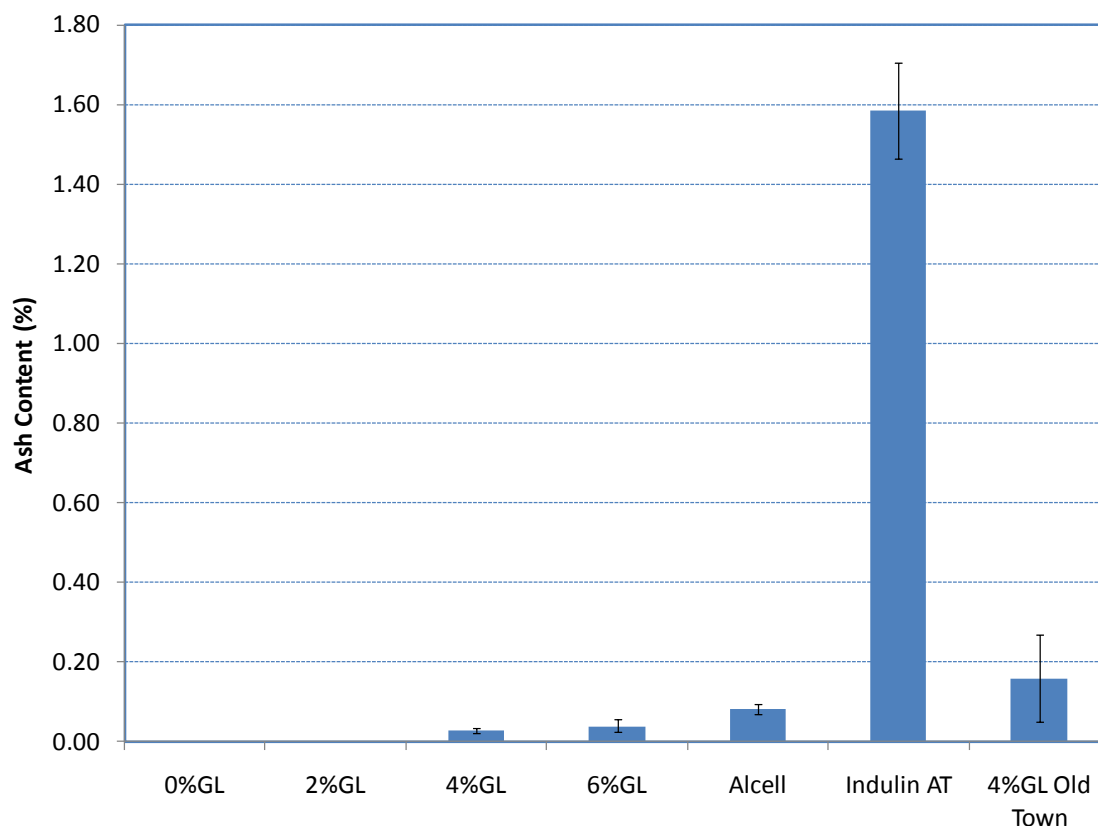


Figure 5.6 Ash Content in Lignin Samples

Lignin Content. Figure 5.7 illustrates the lignin content of the samples evaluated. The total lignin content is thought to be the most important parameter given by ORNL in their specification sheet. The range on the lignin contents varied between $89.90\% \pm 0.55\%$ and $99.48\% \pm 0.41\%$. The lignin content in all of the samples obtained by the near neutral hemicellulose extraction process and isolated using the hydrolysis method exceeded 98%, including that recovered from the sample obtained in the mill trial by Old Town Fuel and Fiber. The lignin separated from the 0% green liquor (pure water) experiment had the highest total lignin content of any of the samples ($99.48\% \pm 0.41\%$). The lignin content in the Alcell sample was $94.22\% \pm 0.86\%$ and was lower than lignin isolated using the hydrolysis method from the green liquor extraction process. The lowest lignin content ($89.90\% \pm 0.55\%$) was obtained for Indulin AT. There was a large

discrepancy between the measured lignin content and that reported by the Mead-Westvaco Corporation.

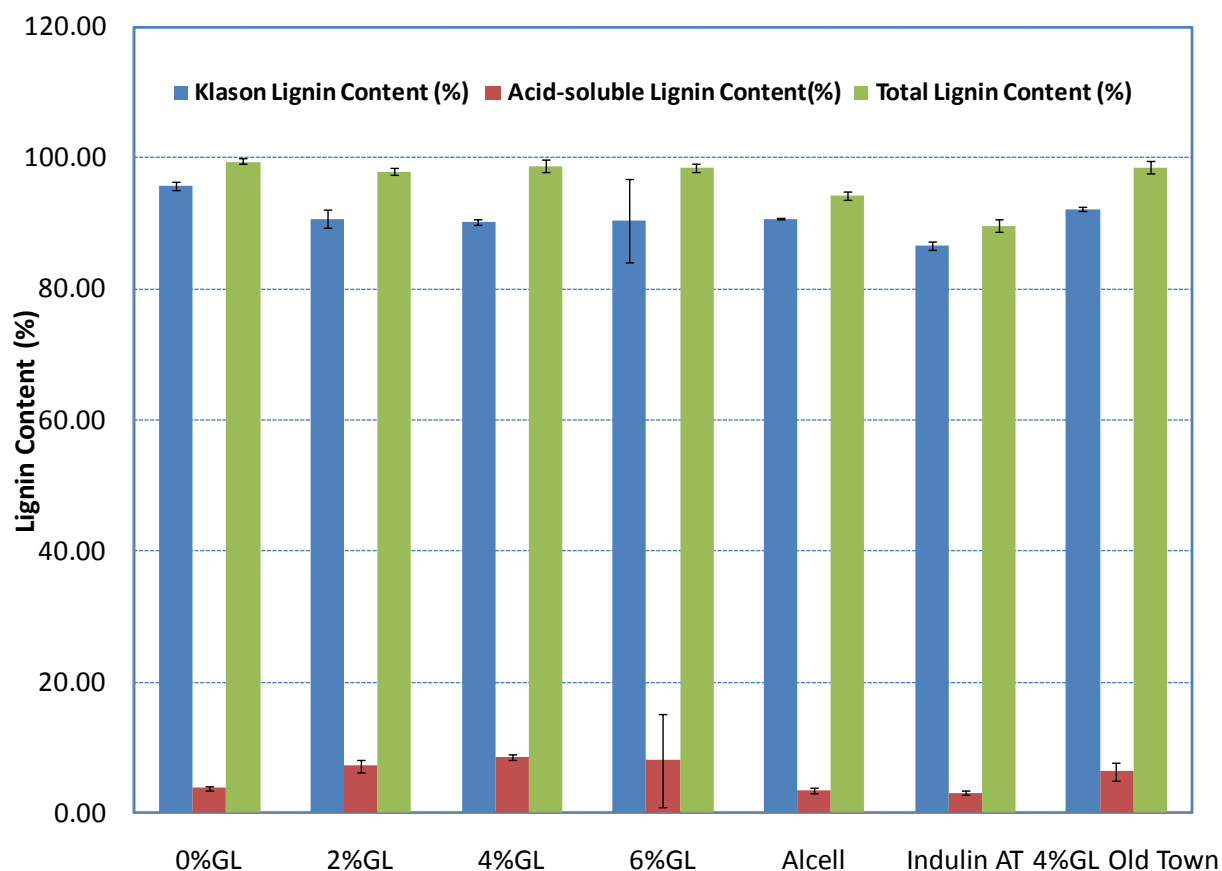


Figure 5.7 Lignin Content in Lignin Samples

Volatile Material Content. Figure 5.8 illustrates the volatile material content of the different lignin samples. The volatile material content varied between $8.77\% \pm 0.96\%$ for lignin sample recovered from the 4% green liquor extraction experiment conducted in the laboratory; and $17.70\% \pm 0.79\%$ for the lignin recovered from the sample obtained in the mill trial with 4% Green Liquor extraction. There are major difference between the processing in the mill trail and that done in the laboratory. But it is clear that the processing of the extract affects the volatile material content of the recovered lignin.

The volatile material content in the Alcell sample was $15.42\% \pm 3.45\%$. The high volatile material content present in the Alcell lignin was thought to be caused by the conditions used in the ethanol pulping process for hardwood; 50% ethanol in water at 190 to 200 °C and an operating pressure of 400 to 500 psig. It is thought that low molecular weight lignin would be removed in the ethanol pulping process especially since the lignin used in the by-product recovery process is obtained by precipitation with water. Also, Alcell lignin is not cross-linked to the extent one would expect lignin to be cross-linked by using the hydrolysis method for recovery and purification.

The ORNL specification for lignin (Table 5.1) requires that precursor material for use in the manufacture of carbon fiber has a volatile material content less than 5%. It is clear from the volatile material data shown in Figure 5.8 that none of the lignin samples investigated are qualified to meet the ORNL specification. The high volatile material content for the samples shown in Table 5.3 is thought to occur because some of the lignin is decomposing at 250 °C rather than low molecular weight lignin in the sample vaporizing.

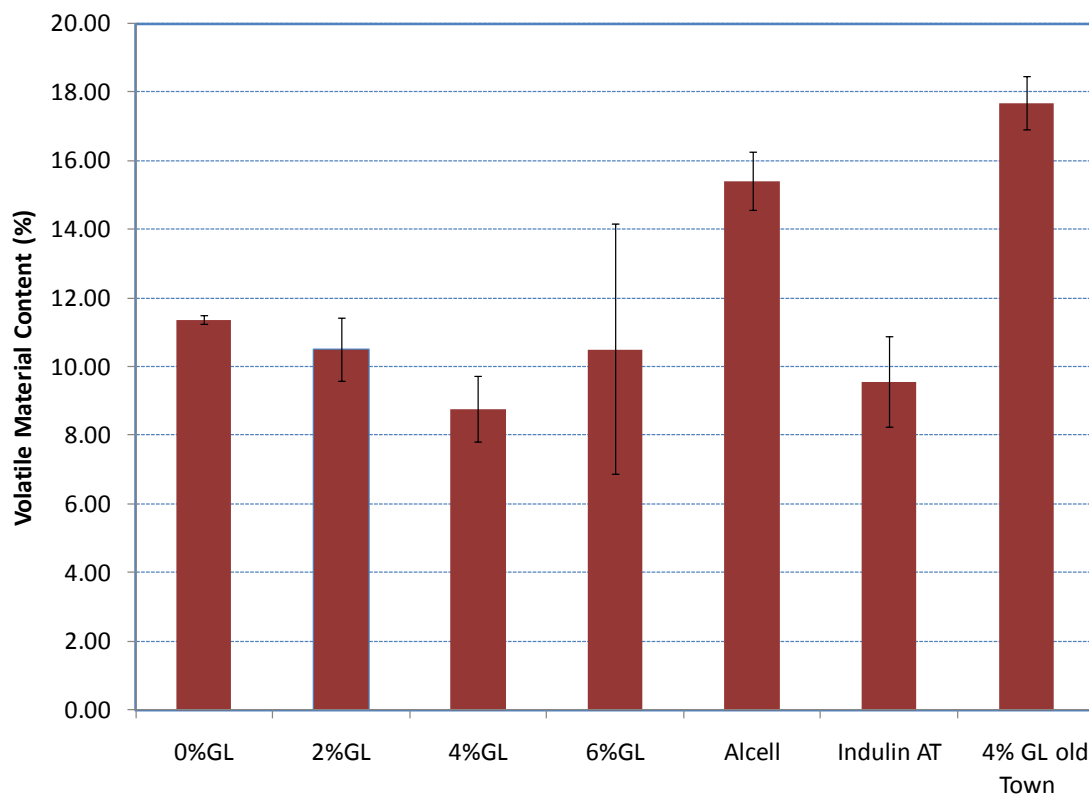


Figure 5.8 Volatile Material Content in Lignin Samples Investigated

Particulate Matter Content. Figure 5.9 illustrates the particulate matter content in the different lignin samples. All of the samples evaluated had particulate matter that is less than about 0.05%; which is thought to be low. However the variability in the measurement was high. The high variability in the results was thought to be due to the method of analysis and the fact that the particulate matter in the samples was low.

Lignin specification in Table 5.1 required 100% removal of particulate matter greater than 1 micron in the sample. The Wachtman filter paper used in the analysis had a distribution of pore sizes thought to be greater than 1 micron. The Indulin AT sample had the highest particulate matter content at $0.05\% \pm 0.01\%$ which was measured by the author. This value was in close agreement with the reported particulate matter content value of 0.05% specified by Mead-Westvaco Corporation in their data sheet.

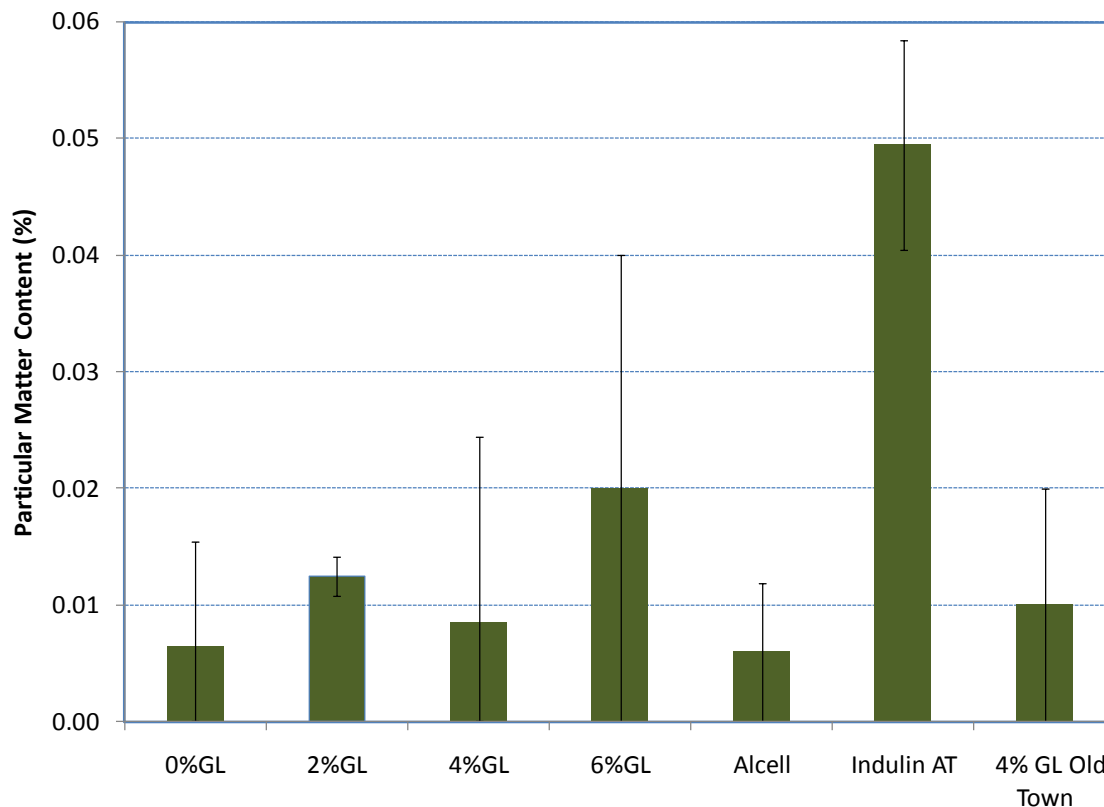


Figure 5.9 Particulate Material Content in Lignin Samples

Carbon Content. The carbon content for some common lignin monomers is illustrated in Figure 5.10. The structure for polyacrylonitrile (PAN) and its carbon content are also included for comparison. Coniferyl alcohol which is a common lignin monomer found in softwood has a carbon content of about 72%. By contrast, sinapyl alcohol, a common lignin monomer found in hardwood has 63% carbon; while PAN which is the premiere precursor material used in the manufacture of commercial carbon fiber has a carbon content of 68% respectively (Figure 5.10).

Figure 5.11 illustrates the carbon content of the different lignin samples measured in the current study. The carbon content of lignin isolated from the 6% green liquor extraction experiment by the hydrolysis method of purification was $61.6\% \pm 6.2\%$, which is closed to the theoretical value for sinapyl alcohol (63%). The carbon content of lignin

samples isolated from the 0%, 2% and 4% green liquor extraction experiment by the hydrolysis method was 64.7%, 64.6% and 64.3% respectively. The carbon content of Alcell lignin was 64.4%. The carbon content of Indulin AT had the highest carbon content and was estimated to be 66%. However, this value is lower than the theoretical value for coniferyl alcohol (72%). The lignin content of Indulin AT was only 89.69% (Table 5.3). Thus the low carbon content in the Indulin AT samples results from the presence of impurities, thought most likely to be primarily carbohydrates.

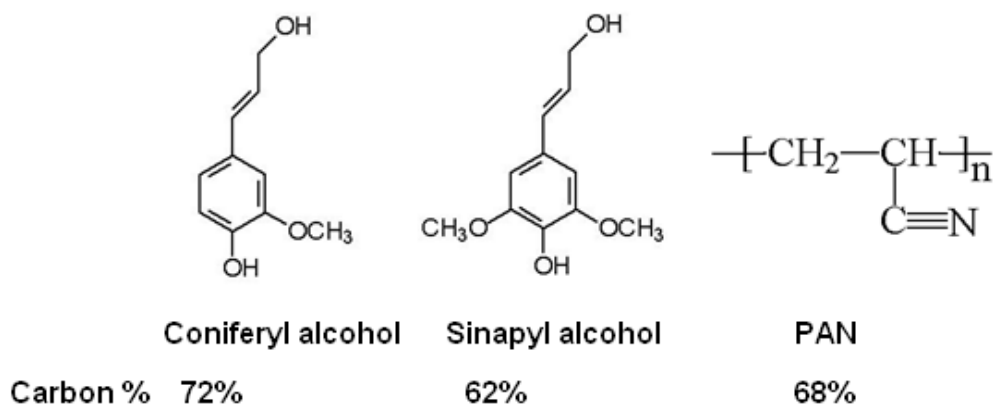


Figure 5.10 Carbon Content in Coniferyl Alcohol, Sinapyl Alcohol and PAN

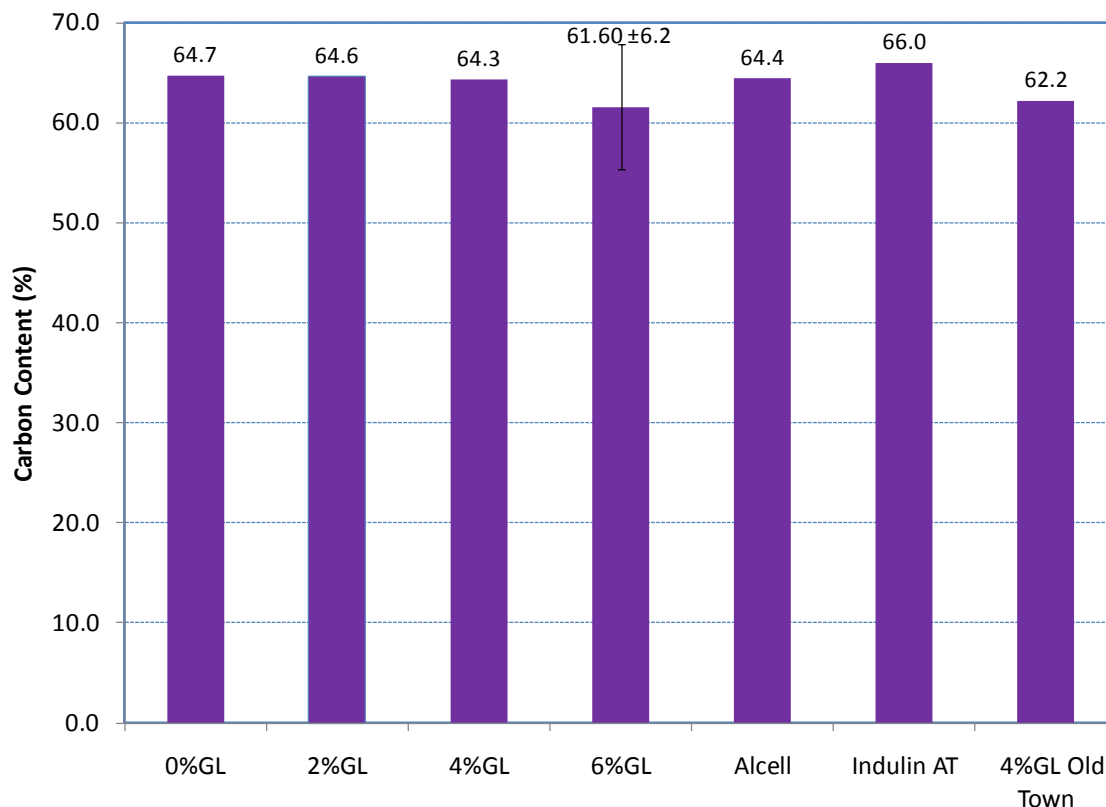


Figure 5.11 Carbon Content in Lignin Samples

5.5 Conclusions

Comparison of Methods of Lignin Isolation. Two methods were evaluated for the recovery and isolation of precursor lignin. The two-sample t-test applied to the experimental results indicated that there was a significant difference between the hydrolysis method developed by the author and Sun's method for isolating lignin that is based on ethanol precipitation (see Figure 5.5 and Table 5.3). This was true for the measured values for the Klason lignin, acid-soluble lignin, total lignin content and volatile material content. The hydrolysis method of purification was found to be simpler to use and more effective than Sun's method. A distinct advantage of the hydrolysis method of isolation is that it produces high purity lignin. A disadvantage of the method

however is that hydrolysis is known to cross-link the lignin; which possibly could negatively affect the production of lignin fibers. During hydrolysis used to cleave lignin carbohydrate complex bonds, the lignin was cross-linked and thus raised the molecular weight. The glass transition temperature (T_g) is however to increase with molecular weight and could make the melt spinning more difficult.

Applicability of ORNL Lignin Precursor Specification. It has been shown that lignin obtained by the hemicellulose pre-extraction process and isolated by the hydrolysis method can meet all of the specification stipulated by ORNL except for the specification related to volatile material at 250 °C. In this case it is felt that the high volatile material content originates from the decomposition of lignin rather than from low molecular weight lignin that is vaporizing.

Carbon Content in Isolated Lignin Samples. The most important precursor material for the production of commercial carbon fiber is polyacrylonitrile (PAN). The carbon content of PAN is 68% (see Figure 5.10). Unfortunately PAN is produced from petroleum and natural gas and is a high cost precursor material that is partially reflected in the final cost of the carbon fiber product. The carbon content in PAN is 6% higher than of lignin from hardwood (sinapyl alcohol). This obviously is a disadvantage for precursor lignin. However, lignin as a precursor material could potentially reduce the price of carbon fiber. Also, lignin has a ring structure which potentially could form the main backbone found in carbon fiber. Having a carbon ring structure is an advantage that may increase the physical property of carbon fiber produced from lignin.

Lignin Isolated from 6% Green Liquor. The error limits estimated from the t-statistic here high for the properties measured for the lignin samples isolated from 6%

green liquor. This was thought to result from the fact that only three extraction experiments were performed for the 6% green liquor extraction experiment and one of the samples (2B) could be considered an outlier compared to samples 1B and 3B. The cause of sample 2B being significantly different than 1B and 3B was thought to be related to the quality and uniformity of the wood chips (see Figure 5.4 and Table 5.2).

Samples Selected for Further Study. Based upon the work present above, a variety of lignin samples were selected as precursor materials for preparation of lignin fiber by melt spinning. The lignin samples obtained from the 0% and 6% green liquor extraction experiments were selected for further study. The basis for this decision was that these samples represent lignins obtained by water extraction (0%) and also the maximum amount of alkali (6%) though possible as a solvent in the hemicellulose extraction process. As such they represent the limits on lignin obtainable by the process. For comparison purposes, both the Alcell lignin and Indulin AT were selected for use as lignin standards for comparison to the 0% and 6% samples. The Indulin AT sample was selected for study because it represents the purist form of commercially available lignin. The Alcell lignin was selected because it represented lignin obtained by extraction using a more hydrophobic solvent compared to green liquor. Lastly the lignin isolated from the mill sample was selected because it represented lignin from the most advanced biorefinery extraction process currently available.

CHAPTER 6

LIGNIN FIBER SPINNING

This chapter investigates the glass transition temperature (T_g) and the weight-average molecular weight (M_w) of the lignin sample recovered from the “near neutral hemicelluloses extraction process” and isolated by using the hydrolysis method. The glass transition temperature and the average molecular weight are critical properties required for the production of lignin fiber by the melt spinning process. One objective of this research is to develop the melt spinning process for the production of lignin fiber that is suitable for conversion to carbon fiber.

6.1 Lignin Glass Transition Temperature

The glass transition temperature (T_g) of lignin determines the conditions required in the melt spinning process for its conversion into lignin fiber. The glass transition temperature (T_g) is one of the most important properties of lignin because it sets the softening temperature of the lignin and thus the temperature of the extruder.

The crystalline melting temperature (T_m) and the glass transition temperature (T_g) are two parameters that define polymer materials. The crystalline melting temperature, (T_m) is the temperature at which a crystalline polymer melts or changes phase. The glass transition temperature (T_g) is the temperature at which a polymer becomes brittle on cooling, or softens on heating. Whether a polymer exhibits two thermal transitions or only one transition depends on its morphology. Ideally, a completely crystalline polymer (Figure 6.1) exhibits only a melting temperature (T_m). A completely amorphous polymer (Figure 6.2) exhibits only a glass transition temperature (T_g). A semi-crystalline polymer

(Figure 6.3) exhibits both a glass transition temperature (T_g) and a melting temperature (T_m) as discussed by Odian (2004). Lignin is an amorphous polymer and thus exhibits a glass transition temperature (T_g).

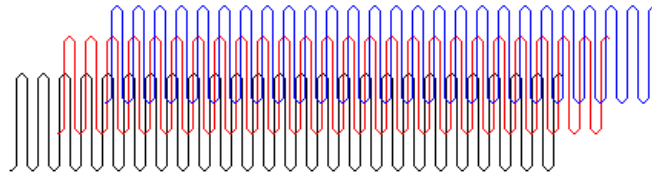


Figure 6.1 Ideal Completely Crystalline Polymers Exhibits Only a T_m Value
(<http://faculty.uscupstate.edu/llever/Polymer%20Resources>)



Figure 6.2 Completely Amorphous Polymers Exhibits Only a T_g Value
(<http://faculty.uscupstate.edu/llever/Polymer%20Resources>)

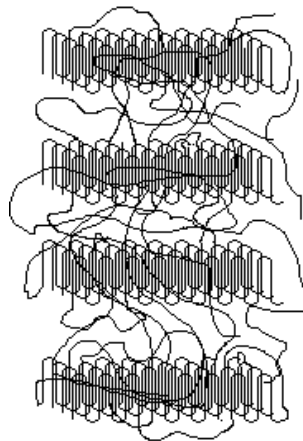


Figure 6.3 Semi-crystalline Polymers Exhibits both T_m and T_g Values
(<http://faculty.uscupstate.edu/llever/Polymer%20Resources>)

There is a dramatic change in properties of any polymer at the glass transition temperature. For example, there is a sharp increase in stiffness of an amorphous polymer when its temperature is reduced below the glass transition (T_g) temperature (Young, 1981). Theoretically at a temperature below the glass transition temperature (T_g), amorphous polymer materials are in the glassy state. In this state, the molecules are frozen in place. They may be able to vibrate slightly, but do not have any segmental motion. At a temperature above the glass transition temperature (T_g) value, segmental chain motion is evident for a polymer. The glass transition does not happen at a specific point but occurs over a temperature range, because of a variety of reasons, one of which is that polymers are polydispersed. The glass transition temperature (T_g) is then defined as some intermediate temperature within this range (Schmidl, 1992).

Another view of the glass transition is that it represents a state of “isofree” volume as described by Fried (1995). The isofree volume (V_f) is defined as the difference between the actual volume (V_{act}) at a given temperature and the volume (V_0) at absolute zero temperature (0 K) as illustrated in Equation 6.1.

$$V_f = V_{act} - V_0 \quad \text{Eq. 6.1}$$

The isofree volume influences other polymer properties such as its viscoelastic behaviour, melting viscosity and permeability (Fried, 1995). A description of these polymeric properties is beyond the scope of this thesis.

6.1.1 Factors Influencing the T_g Value

The glass transition temperature (T_g) can vary widely for different polymers. Since the glass transition temperature (T_g) value depends on the amount of thermal

energy required to keep the polymer chains moving, a number of factors will influence the T_g value of polymeric materials. Those factors include: (1) chain stiffness, (2) intermolecular forces, (3) pendant groups and (4) cross-linking.

(<http://faculty.uscupstate.edu/llever/Polymer%20Resources/FactorsTg.htm>)

Chain Stiffness. Stiffening groups in the polymer chain will reduce the flexibility of the chain and raise value of the glass transition temperature (T_g). For example, poly-ethylene-adipate with the adipate group in the backbone (Figure 6.4) has a T_g value of only -70°C . By contrast, poly-ethylene-terephthalate has a monomeric group (benzene ring) in the back bone (Figure 6.5) and the T_g value is $+69^\circ\text{C}$. For lignin, phenyl groups are stiffening groups and they will increase the T_g value of lignin, while flexible groups such as methoxy groups will decrease the T_g value of lignin.

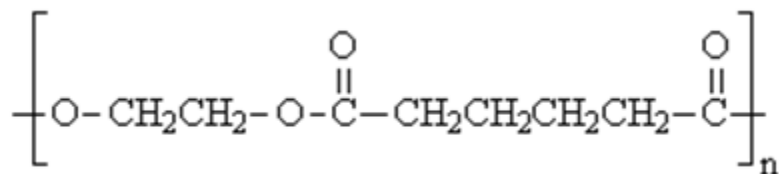


Figure 6.4 Polyethyleneadipate ($T_g = -70^\circ\text{C}$)

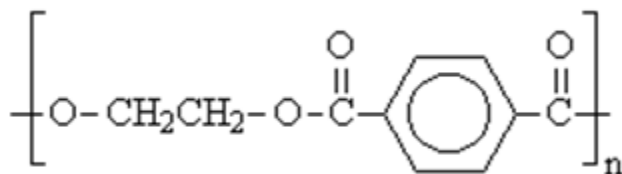


Figure 6.5 Poly-ethyleneterephthalate ($T_g = 69^\circ\text{C}$)

Intermolecular Forces. Strong intermolecular forces in a polymer will lead to a higher value for the glass transition temperature (T_g). For example, polyvinylchloride (Figure 6.6) has stronger intermolecular forces than polypropylene (Figure 6.6) because

of the dipole-dipole forces from the C-Cl bond. The T_g values are considerably different between polypropylene ($-20\text{ }^{\circ}\text{C}$) and polyvinylchloride ($+81\text{ }^{\circ}\text{C}$).



Figure 6.6 Polypropylene ($T_g = -20^{\circ}\text{C}$) and Polyvinylchloride ($T_g = 81^{\circ}\text{C}$)

Pendant Groups. The influence of pendant groups on the glass transition temperature depends upon the chemical properties of the pendant groups. In general there are two types of pendant groups: bulky pendant groups that cause steric hindrance and flexible pendant groups that permit rotation. Bulky pendant groups, such as a benzene ring, can catch on neighboring chains, much like a "fish hook" and restrict rotational freedom. This increases the value for the glass transition temperature (T_g). For Example, polypropylene has a T_g value of $-20\text{ }^{\circ}\text{C}$, while polystyrene has a higher T_g value of 100°C (Figure 6.7), which is considerably higher. Flexible pendant groups, such as aliphatic chains, tend to limit how close chains can pack. This increases the rotational motion and lowers the T_g value. For examples, poly (methyl methacrylate) has a T_g value of $105\text{ }^{\circ}\text{C}$, while poly (butyl methacrylate) has a T_g value of 20°C (Figure 6.8), which is considerably lower.



Figure 6.7 Polypropylene ($T_g = -20\text{ }^{\circ}\text{C}$) and Polystyrene ($T_g = 100\text{ }^{\circ}\text{C}$)

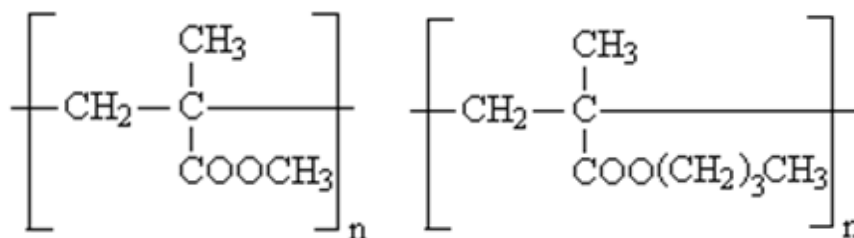


Figure 6.8 Poly (Methyl Methacrylate) ($T_g=105\text{ }^\circ\text{C}$) and Poly (Butyl Methacrylate) ($T_g= 20\text{ }^\circ\text{C}$)

Cross-Linking. Some polymers have cross-links between polymer chains creating three-dimensional networks (Figure 6.9). A high density of cross-linking restricts the motion of the chains and leads to a rigid material and raises the T_g value. The high degree of cross-linking in lignin results in high values for T_g .



Figure 6 9 Cross-linking Polymers

Plasticizer. Adding external plasticizer to an amorphous polymer will lower its T_g value. Water is a kind of plasticizer and even a small amount of moisture in a lignin sample will decrease its glass transition temperature (T_g).

6.1.2 Glass Transition Temperature Determination

The glass transition temperatures for the isolated lignin sample were determined by using a Differential Scanning Calorimetry (DSC). Generally, the DSC instrument includes two heating discs which are in thermal contact with one another. The two discs are isolated from the environment as shown in Figure 6.10. A metal pan is placed on each disc. One is a sample pan, and the other is an empty reference pan. Theoretically, by heating both pans at a controlled known rate and measuring the heat flow between them the DSC is able to measure the T_g of the material in the sample pan.

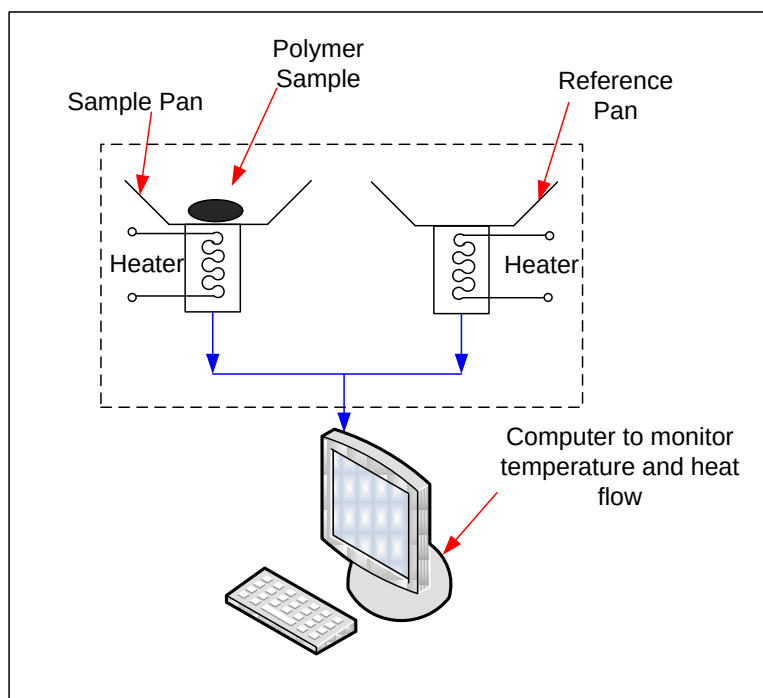


Figure 6.10 Simplified Diagram of a DSC Apparatus
(<http://pslc.ws/macrog/dsc.htm>)

6.2 Lignin Molecular Weight

Generally, a polymer having a high molecular weight will exhibit a high glass transition temperature. Therefore the molecular weight of lignin, as it relates to the glass transition temperature and the temperature of extrusion, is an important property affecting the production of carbon fiber.

The molecular weight of a polymer determines many of its physical properties. Unlike monomers, the molecular weight of a polymer however is not a unique value but rather an average value. This is a consequence of the fact that polymeric substances are composed of molecules having a distribution of individual molecular weights. In material science, there are four molecular weight averages in common use (Sjöström, 1993). The number-average molecular weight (M_n) is often obtained from osmometry experiments. The equation for calculating the number-average molecular weight is given in Equation 6.2. The weight-average molecular weight (M_w) can be obtained from light scattering experiments and gel permeation chromatography (GPC), which can also give the number-average molecular weight (M_n). The weight-average molecular weight is given by Equation 6.3 and gives its relationship to the number average molecular weight. The so-called z-average molecular weight (M_z) is obtained from sedimentation equilibrium experiments obtained using an ultra-centrifuge. The z-average molecular weight is illustrated by Equation 6.4. Lastly, the viscosity-average molecular weight (M_v) is obtained from viscosity measurements and is given by Equation 6.5. The four molecular weight averages are defined below in terms of the numbers of molecules, N_i having molecular weights M_i and w_i , the weight of species with molecular weights M_i (Tobolsky et al. 1971).

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i w_i}{\sum_i (w_i / M_i)} \quad (\text{Eq. 6.2})$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i w_i M_i}{\sum_i w_i} \quad (\text{Eq. 6.3})$$

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i w_i M_i^2}{\sum_i w_i M_i} \quad (\text{Eq. 6.4})$$

$$M_v = \left(\frac{\sum_i w_i M_i^{1+\alpha}}{\sum_i w_i M_i} \right)^{1/\alpha} \quad (\text{Eq. 6.5})$$

The quantity “ α ” in Equation 6.5 is an empirical constant that depends on the solvent used to dissolve the polymer and its temperature. The relationship of the four molecular weight values is illustrated in Figure 6.11 (Sjöström, 1993).

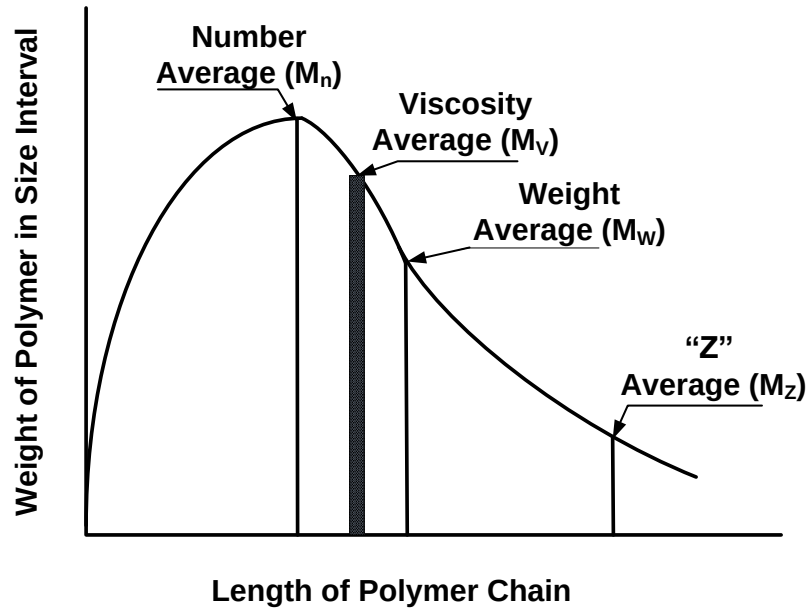


Figure 6.11 Typical Molecular Weight Distribution and Average Molecular Weights of a Polymer (Sjöström, 1993)

6.2.1Molecular Weight Determination

Analytical techniques for measuring molecular weight of polymers are divided into two general classes: (1) absolute methods such vapor pressure osmometry (VPO) and low angle laser light scattering (LALLS), and (2) relative methods such as gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) or gel filtration chromatography (Schemidl, 1992).

In this study the molecular weight of the lignin sample was determined by using GPC. A simplified diagram of a GPC apparatus is shown in Figure 6.12. Generally, a sample of a dilute polymer solution is introduced into a solvent stream flowing through the column. Polymer molecules can diffuse into the internal pore structure of the gel when the dissolved polymers flow past the porous beads. A larger fraction of the interior of the gel is penetrated by smaller polymer molecules. Therefore, the larger molecule the sooner it flows through the column and the less time it spends inside the gel. The different substances in the mixture are eluted from the column in order of their molecular size as distinguished from their molecular weight. This is illustrated in the chromatogram shown in Figure 6.12.

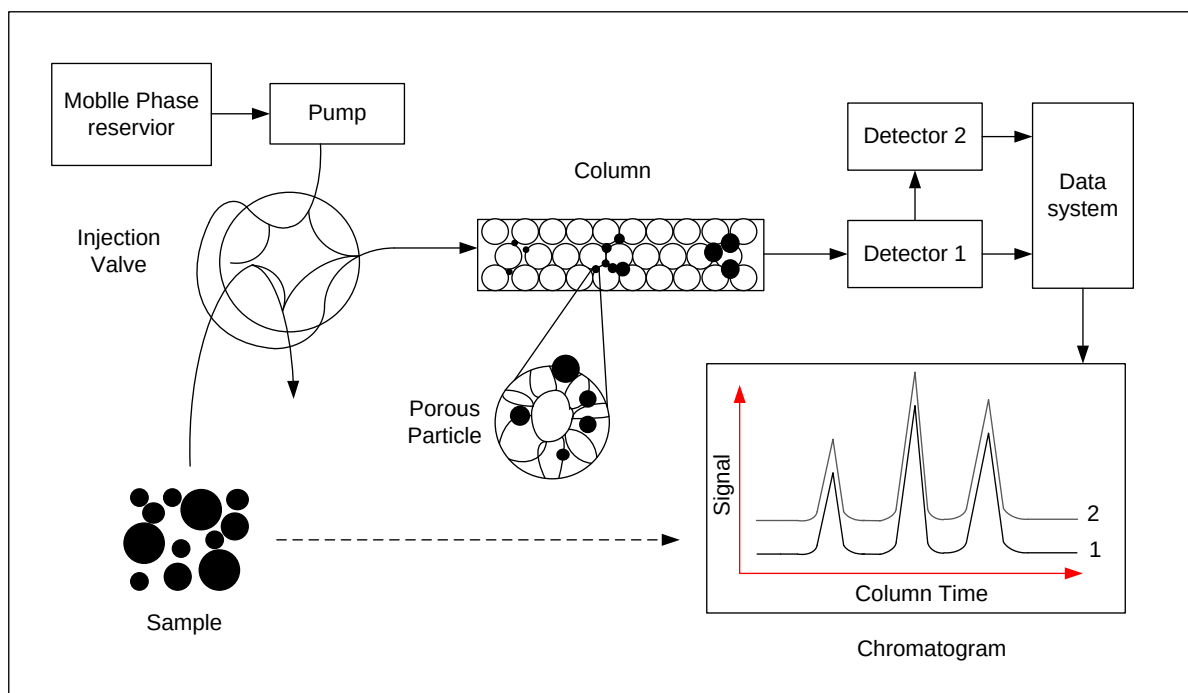


Figure 6.12 Simplified Diagram of a GPC Apparatus
<http://www.chemlatech.edu/~hji/polymer/11oct02.htm>

6.3 Lignin Fiber Spinning

6.3.1 Polymer Fiber Spinning

Thermoplastic polymer can be fabricated into polymeric fiber or small cylindrical elements of various lengths. Depending upon the physical properties of the polymer, polymeric fiber can be formed by the following methods: 1) melt spinning, 2) melt assisted spinning, 3) dry spinning, 4) wet spinning and 5) dry-jet wet spinning (Chung, 1994).

Commercial carbon fiber is produced using polyacrylonitrile (PAN) or pitch. Precursor fiber is fabricated by the different spinning methods. Pitch fiber is formed by simple melt spinning in which the pitch is heated above its softening point and the liquid extruded through a small orifice. Because PAN decomposes below its melting

temperature, melt spinning is not possible. Consequently, PAN fiber is formed by a wet spinning process in which the PAN is dissolved using an organic solvent. The PAN solution is then extruded through the orifice to form the fiber. In the fiber formation process the solvent is evaporated and recovered. Upon evaporation of the organic solvent, the PAN precipitates and is drawn out as a solid fiber. The diameter of the fiber is controlled by the draw ratio, which is the ratio of the velocity at which the fiber is pulled divided by the velocity of the PAN solution flowing out of the orifice.

6.3.2 Lignin Fiber Spinning

Melt spinning is the most rapid, convenient and commonly used method of forming polymeric fiber. Lignin is a thermoplastic polymer; it melts and flows upon heating. Therefore, the melt spinning technique is applicable to forming lignin fiber. In the experimental work reported here an Atlas Laboratory Mixing Extruder (LME) was used to form lignin fiber by melt spinning.

A picture of the Atlas Laboratory Mixing Extruder (LME) used in this study is shown in Figure 6.13. A major advantage of using an Atlas Laboratory Mixing Extruder is that a sample size as small as one (1) gram of material can be used in the extrusion process. Other advantages of the LME apparatus are short residence time, variable speed control, extrusion temperatures up to 400 °C and fiber diameter as low as 30 microns can be drawn. In the apparatus a heated rotor is used to melt the polymer which is then pumped to a spin pack. The molten polymer samples exits the spin pack through a spinneret nozzle. The cylindrical fiber that is formed in the extrusion process is wound onto a spinning spool in a Take-up System (Figure 6.14). The nozzles come in a variety of sizes (0.8 to 3.2 mm) depending upon the desired fiber diameter. A draw ratio of

about 100 to 1 is required to spin a 30 μm diameter fiber assuming a flow velocity out the nozzle of 3 m/s and a nozzle diameter of 0.8 mm.



Figure 6.13 Photograph of the Atlas Laboratory Mixing Extruder



Figure 6.14 Photograph of the LME Take-up System for Extruder

6.4 Results and Discussion

6.4.1 Lignin Glass Transition Temperature

The glass transition temperature (T_g) of lignin determines the extrusion temperature required in melt spinning the recovered lignin into fiber. The recovered lignin samples were characterized for T_g using differential scanning calorimetry (DSC). This work was performed at the University of Maine by using a Mettler Toledo DSC822 in Professor Robert Rice's laboratory. The analyses for the glass transition temperatures were carried out over the temperature range 0°C to 210 °C for the lignin samples and 0°C to 280 °C for the thermo-stabilized lignin sample. The sample was submerged in a nitrogen environment and heated at a rate of 10 °C/min. In the DSC experiments, polystyrene was used as a standard that was supplied by Polymer Standard Service (PSS), USA Inc.

Table 6.1 summarizes the properties of the standard polystyrene used in this study. The polystyrene has a weight-average molecular weight of 5,610 Daltons. It was selected as the standard because its weight-average molecular weight was closed to that of the extracted lignin. For each sample, the DSC experiment was performed three times in exactly the same manner. This permitted an estimate of the mean value and error limits for the glass transition temperature (T_g) for the polystyrene. The measured T_g value was determined to be 93.5 ± 0.2 °C. Okubo (1995) reports the T_g value of standard polystyrene as 82.4 °C. The difference in the T_g values measured in the present study and that of Okubo is thought to be related to differences in the molecular weight of the standard polystyrene. A typical thermogram obtained for polystyrene is illustrated in Figure 6.15. The glass transition for the polystyrene standard involves an endothermic process. The glass transition temperature (T_g)

for the standard polystyrene occurred at approximately temperature 93.4 °C (see Figure 6.15).

The T_g value was taken at the midpoint in the glass transition curve.

Table 6.1 Properties of Standard Polystyrene

Standard	M_w (Dalton)	M_n (Dalton)	Polydispersity (M_w/M_n)	T_g (°C)
Polystyrene Sample A	5,610 ^a	5,270 ^a	1.06 ^a	93.5 ± 0.2
Polystyrene Sample B	5,480 ^b	5,200 ^b	1.04 ^b	82.4 ^b
a Certification of Analysis of PSS-ps5.6k				
b Okubo, N. 1995				

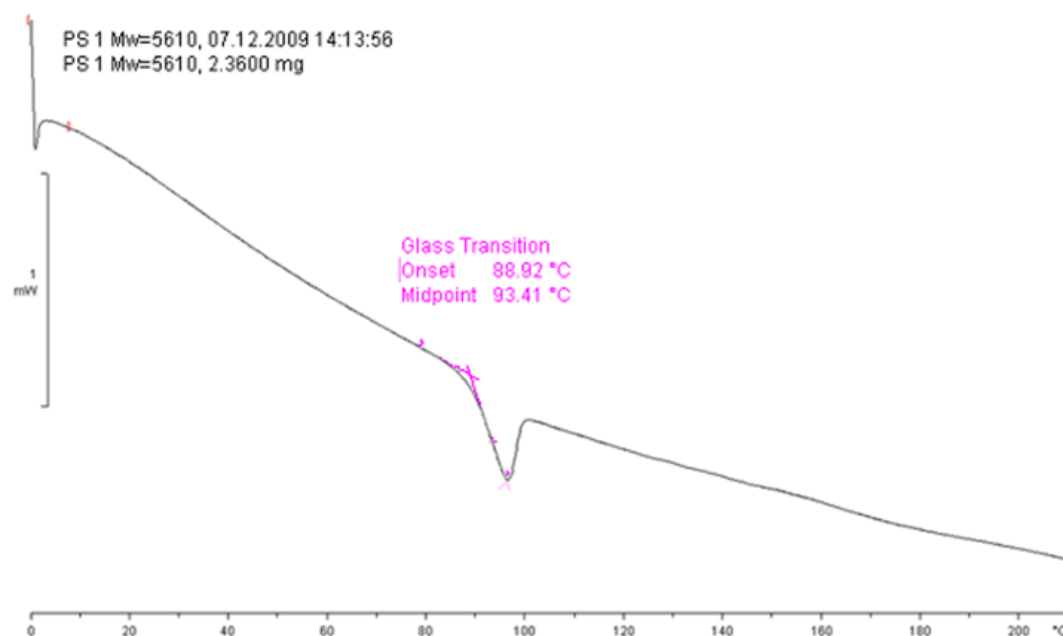


Figure 6.15 Typical Thermogram of Polystyrene (93.4 °C)

Table 6.2 summaries the T_g values of commercial Indulin AT, Alcell and the lignin samples recovered from the green liquor extraction experiments that were isolated using the hydrolysis method. The T_g values for the thermo-stabilized lignin sample are

also listed in Table 6.2. The error bars on the T_g values for Alcell lignin were estimated by performing the DSC experiment three times in exactly the same manner. Figure 6.16 illustrates the thermogram for a typical Alcell lignin sample. The glass transition of the Alcell lignin is an endothermic process and the glass transition of the Alcell lignin occurred at approximately 108.8 °C, which was taken at the midpoint in the glass transition curve. The lignin isolated from the 0% GL extraction experiment had the highest measured T_g value and was about 167 °C. The T_g value of Indulin AT was about 154 °C. The thermo-stabilization process normally increases the T_g value of lignin (Kadla et al., 2002). This was found to be true for thermal stabilization for both the Alcell lignin and the lignin isolated from the 6% GL extraction experiment. In both cases the thermal transition was endothermic. However for the lignin recovered in the 0% GL extraction experiment, the T_g value decreased from 167 °C to 160 °C.

Table 6.2 Glass Transition Temperatures T_g for Different Lignin Samples

Lignin	T_g (°C)	Thermo-stabilized Lignin T_g (°C)	Species
0% GL (Hemicellulose Extraction)	167	160	Mixed Northeastern Hardwood
2% GL (Hemicellulose Extraction)	129	NA	Mixed Northeastern Hardwood
4% GL (Hemicellulose Extraction)	125	NA	Mixed Northeastern Hardwood
6% GL (Hemicellulose Extraction)	109	156	Mixed Northeastern Hardwood
Indulin AT ^a (Kraft Pulping)	154	NA	Pine
Alcell ^b (Ethanol Pulping)	108.6 ± 0.6	155	Mixed Northeastern Hardwood



Figure 6.16 Typical Thermogram for Alcell Lignin (108.8°C)

Table 6.3 lists the T_g values for a series of lignin samples reported by Schmidl (1992). There is a wide range of the glass transition temperatures for the lignin samples reported by Schmidl. The glass transition temperature (T_g) for the lignin samples varied between 97 °C and 171 °C. The considerable difference in the T_g value for the various lignin sample was thought to reflect the lignin source, the pulping process and molecular weight differences between the samples. Schmidl reports that the organsolv lignin had the lowest T_g value (97 °C), while Indulin AT had the highest T_g value (171 °C). This disparity in the values is thought to be related to high poly-dispersity levels (M_w/M_n) and the breadth of the lignin molecular weight distributions.

Table 6.3 Lignin Glass Transition Temperatures Reported by Schmidl (1992)

Lignin	T _g (°C)	T _g Range (°C)	Species
IndulinAT Kraft Pulping (MeadWestvaco)	171	138-206	Loblolly Pine
Mixed Southern Hardwood Kraft Pulping (Charleston S. C)	161	137-196	Oak, Sweet Gum
Northeastern Hardwood Kraft Pulping (Maine Paper Mill)	132	121-165	Paper Birch
Organosolv Aspen	97	NA	NA
Japanese Cypress	124	109-157	NA

6.4.2 Lignin Molecular Weight

The isolated lignin samples were characterized for weight-average molecular weight (M_w) by using Gel Permeation Chromatography (GPC). The recovered lignin sample was completely dissolved in 0.8 gm/L of lithium chloride/dimethylacetamide (LiCl/DMAc) solution and the GPC column operated at 80 °C. Pullulan was selected as the molecular weight standard to permit comparison with data obtained from Mead-Westvaco Corporation for the molecular weight of Indulin AT. Table 6.4 summaries the weight-average molecular weight (M_w) values in grams per mole (Daltons). Data are reported for Indulin AT, Alcell and the isolated lignin samples recovered from the different green liquor extraction experiments.

The weight-average molecular weight of Alcell lignin was approximately 4,600 Daltons and was close to the value of 3,900 Daltons reported by Baumberger et al. (2007). The weight-average molecular weight of Indulin AT was approximately 4,600 Daltons and was close to the results of 4,800-5,800 Daltons reported by Mead-Westvaco to the author. There is a small difference in the weight-average molecular weight

measured for the Alcell lignin sample (4,600 Daltons) and the lignin recovered from the 0% GL extraction experiment (5,200 Daltons). This difference was thought to result because the lignin recovered in the 0% GL extraction experiment was more condensed due to the low final pH of the extraction process.

The lowest weight-average molecular weights occurred in the lignin samples recovered from the 4% and 6% green liquor extraction experiments. This was thought to result from the higher pH values that occurred during these experiments (Table 6.4). Increasing the GL application rate exposes the wood to a higher alkali concentration for a longer period of time before neutralization occurs. Thus, it was thought that greater lignin and carbohydrate degradation and dissolution occurred under the higher pH conditions.

Table 6.4 Lignin Molecular Weights by GPC

Lignin	M_w (Daltons)	Extraction Final pH	Species
0% GL (Hemicellulose Extraction)	5,200	3.34	Mixed Northeastern Hardwood
2% GL (Hemicellulose Extraction)	4,000	4.77	Mixed Northeastern Hardwood
4% GL (Hemicellulose Extraction)	3,200	5.64	Mixed Northeastern Hardwood
6% GL (Hemicellulose Extraction)	3,400	8.91	Mixed Northeastern Hardwood
Indulin AT ^a (Kraft Pulping)	4,600	NA	Pine
Alcell ^b (Ethanol Pulping)	4,600	NA	Mixed Northeastern Hardwood
a The M _w of Indulin AT reported by the Mead Westvaco is between 4,800 and 5,800 Daltons.			
b The M _w of Alcell reported by Baumberger et al., (2007) was 3,900 Daltons.			

Table 6.5 lists molecular weight and polydispersity (M_w/M_n) values for a series of lignin samples reported by Schmidl (1992). The weight-average molecular weight (M_w) values were obtained by dissolving the lignin samples in 0.1 M LiBr/DMSO (lithium bromide/ dimethyl sulfoxide) and conducting GPC measurements at 85°C. The number-average molecular weight values originate from vapor pressure osmometry measurements (VPO). The weight-average molecular weight (M_w) varied between 2,403 and 6,058 for the samples. The lignin source and pulping process were thought to be responsible for the considerable difference in the weight-average molecular weight (M_w) values observed by Schmidl (1992). The organosolv lignin had the lowest M_w value (2,403 Daltons) while Indulin AT had the highest M_w value (6,058 Daltons). A similar pattern was observed for the number-average molecular weight (M_n). The high polydispersity (M_w/M_n) values indicated that the lignin molecular weight value had a broad distribution. Low polydispersity values generally reflect a narrow molecular weight distribution. Birch Kraft lignin had the lowest polydispersity (2.725) value observed with Schmidl's lignin samples.

Table 6.5 Lignin Molecular Weight Measurements Reported by Schmidl (1992)

Lignin	M_n (Daltons)	M_w (Daltons)	M_w/M_n
IndulinAT Kraft Pulping (Mead-Westvaco)	1,582	6,058	3.829
Mixed Southern Hardwood Kraft Pulping (Charleston ,S. C)	997	3,357	3.360
Birch (Northeastern Hardwood) Kraft Pulping (Maine Paper Mill)	1,148	3,128	2.725
Organosolv Aspen	809	2,403	2.970

6.4.3 Dependence of T_g upon Molecular Weight

It is well known that the glass transition temperature of a polymer substance is affected by its physical properties such as molecular weight, branching and degree of cross-linking. The value of the glass transition temperature (T_g) increases as the molecular weight (M) of the polymeric material increased. The value of the glass transition temperature (T_g) can be correlated by an equation of the form given by Equation 6.6.

$$T_g = T_g^{\infty} + \frac{K}{M} \quad \text{Eq. 6.6}$$

The value of T_g^{∞} is the glass transition temperature of the polymer with a very large or infinite molecular weight and K is a constant (Young, 1981). As the molecular weight increases, the glass transition temperature of the polymer approaches the value at infinite molecular weight (T_g^{∞}).

6.4.4 Lignin Fiber Spinning

Fiber spinning experiments were conducted in the Atlas Laboratory Mixing Extruder using linear low-density polyethylene (LLDPE) as a standard and various recovered lignin samples. A summary of the spinning experiments including the thermal conditions in the extruder and the appearance of the fiber are summarized in Table 6.6.

Table 6.6 Summary of Fiber Spinning Experiment

Sample		Spinning Temperature (°C)		Fiber Appearance
		Rotor	Nozzle	
LLDPE	Linear Low-density Polyethylene	140-160	150-180	Fine Fiber
Indulin AT	Kraft Pine Lignin (MeadWestvaco)	140-240	240-250	Charring
4% GL Lignin	Mixed Hardwood Lignin from 4% GL (Old Town 6/26/09) Extracts	180-195	200-210	Fiber
0% GL Lignin	Mixed Hardwood Lignin from 0% GL	165-170	180-190	Fine Fiber
6% GL Lignin	Mixed Hardwood Lignin from 6% GL (Luo, Jie 6/05/09) Extracts	185-190	202-208	Fine Fiber
Alcell	Repap Tech. Inc. Organosolv Lignin	145-150	160-170	Fine Fiber

LLDPE Fiber Spinning Experiments. Initially, linear low-density polyethylene (LLDPE) samples were first tested in the Atlas Laboratory Mixing Extruder (see Figure 6.17). The LLDPE was easily processed into flexible-uniform-fine fiber. The spinning temperatures required in these experiments varied between 140 °C and 180 °C. Based on the results of these experiments it was concluded that the extrusion apparatus was working properly.



Figure 6.17 Linear Low-density Polyethylene (LLDPE) Fiber Spinning

Indulin AT Fiber Spinning Experiments. Spinning experiments were then performed by using Indulin AT, a commercial Kraft pine lignin. Spinning temperatures between 140 °C and 250 °C were investigated. However, after many attempts the Indulin AT could not be spun into acceptable lignin fiber. Extrusion experiments performed at the lower temperatures did not soften the lignin sufficiently to form a solid fiber. Experiments performed at high temperature lead to charring of the Indulin AT before melting occurred and here again lignin fiber could not be formed. To utilize Indulin AT as a precursor either solvent spinning would have to be done, or alternatively the glass transition temperatures would have to be lowered by changing the structure of the lignin.

Lignin Fiber Spinning from GL Samples. Lignin spinning experiments were conducted using samples recovered from the hydrolysis method applied to the 0% GL and 6% GL extraction experiments. Continuous spinning was readily achieved with the lignin from the green liquor samples (see Figure 6.18 and Figure 6.19). The lignin fiber, although readily obtained, was extremely brittle and could not be wound on the drum in the take-up system. The spinning temperature required for lignin recovered from the 6% GL experiment varied between 185 °C and 208 °C. By contrast, the spinning temperature required for lignin that was recovered from the 0% GL experiment varied between

165 °C and 190 °C; and was approximately 20 °C lower than the temperatures required for spinning the 6% GL lignin. The lignin precursor obtained from the mill trial using 4% GL was also tested. The mill lignin could be readily spun into fiber. But again, the fiber was brittle and resembled the lignin fiber obtained with the laboratory samples. In the experiments conducted using the lignin from the mill trials, the spinning temperature varied between 180 °C and 210 °C. The spinning temperature for the mill sample was similar to the lignin extracted from 6% GL.



Figure 6.18 Fiber Spinning Using Lignin from 0% GL Extraction Experiment

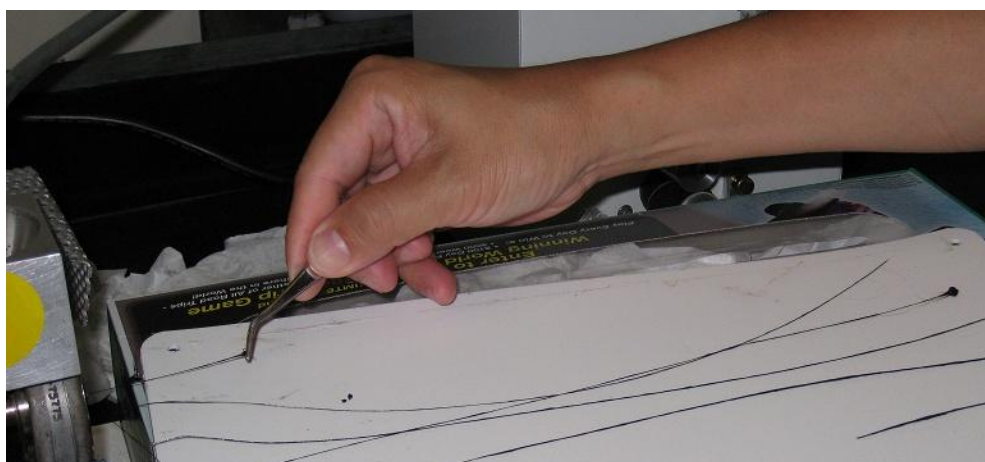


Figure 6.19 Fiber Spinning Using Lignin from 6% GL Experiment

Alcell Fiber Spinning Experiments. Lastly, lignin spinning experiments were conducted using Alcell lignin. Similar to the recovered GL lignin, the Alcell lignin could be readily spun into fiber (see Figure 6.20 and Figure 6.21). By contrast however, fiber spun from the Alcell lignin was considerably more flexible than fiber spun from lignin isolated from green liquor extraction. Even with this improvement however, the Alcell lignin fiber was still brittle. This greater flexibility permitted Alcell lignin fibers to be spun with considerably smaller diameter (Figure 6.21). The spinning temperature required in the Alcell lignin spinning experiments varied between 145 °C and 170 °C and was considerably lower than the spinning temperature required for the GL lignin. This lower spinning temperature was thought to result from differences in the structure and molecular weight of the Alcell lignin, which was thought to be less cross-linked. This observation was thought to be very important and key to obtaining lignin that can be spun into high quality lignin fiber.



Figure 6.20 Fiber Spinning Using Alcell Lignin



Figure 6.21 Fiber Prepared from Alcell Lignin

6.5 Conclusions

The properties of the recovered lignin should be characterized by the glass transition temperature (T_g) and the weight-average molecular weight (M_w). The glass transition temperature (T_g) dictates whether the recovered lignin can be spun using melt spinning. The molecular weight and its distribution, given by the polydispersity will influence the glass transition temperature (T_g) and the brittleness of the recovered fiber. The results of the spinning experiments show that the lignin fibers produced using Alcell lignin were the least brittle of all of the samples. These results suggest a relationship between the glass transition temperature (T_g) and the brittleness of the recovered lignin. The Alcell lignin had the lowest measured glass transition temperature ($T_g = 108.6\text{ }^{\circ}\text{C}$). This conclusion is borne out by the work of Sudo (1992) who showed that flexible lignin fiber could be produced by hydrogenating birch hardwood lignin prior to melt spinning.

The large increase in flexibility was attributed by Sudo to the lower glass transition temperature (T_g) values brought about by changes in lignin structure.

It should be pointed out that the ORNL specifications fail to give parameters for the very important properties of glass transition temperature and molecular weight.

In summary, Alcell lignin and lignin isolated following GL extraction of hardwood could readily be formed into continuous-fine fiber using the Atlas Laboratory Mixing Extruder. This was thought to occur because of their low glass transition temperatures indicative of a favourable lignin structure. By contrast, softwood lignin could not be processed into lignin fiber by melt spinning. The poor performance of the Indulin AT was presumed to be the result of its high glass transition temperature and its unfavourable structure. The lignin fibers formed from the 0% GL lignin, 6% GL lignin and Alcell lignin were selected and used as precursor materials for conversion into carbon fibers.

CHAPTER 7

LIGNIN FIBER STABILIZATION AND CARBONIZATION

The process used to produce carbon fiber in this study consisted of two steps. In the first step the spun lignin fiber was thermally stabilized by heating the fiber in an air atmosphere to a temperature of approximately 200 °C. The second step in the carbon fiber production process involved carbonizing the stabilized fiber in an inert atmosphere at 1000 °C. During both heating processes the samples were unrestrained and free to shrink and change shape. The objective of this chapter is to discuss the details of the thermo-stabilization and carbonization processes. Lastly, the microstructure of the lignin based carbon fiber was studied using scanning electron microscope (SEM).

7.1 Lignin Fiber Thermal-stabilization

In order to convert lignin fiber into carbon fiber a thermo-stabilization stage is necessary. This step prevents the lignin fiber from softening which will result in fiber deformation. Thermo-stabilization involves oxidation of the lignin. The resulting reactions raise the lignin softening temperature (Chung, 1994). The thermoplastic character of lignin is changed during the thermosetting process, enabling the lignin fiber to maintain a fiber form during the subsequent carbonization (Chung, 1994). Heating during thermo-stabilization was performed in air at 200 °C by using a Lindberg/Blue M Tube Furnace that is shown in Figure 7.1.



Figure 7.1 Photograph of the Lindberg/Blue M Tube Furnace

7.2 Lignin Fiber Carbonization

After the thermo-stabilization process, the lignin fiber was carbonized by heating the samples to 1000 °C. The purpose of carbonization is to eliminate all elements except carbon in order to produce a graphite-like structure with high carbon content. To accomplish this goal oxygen must be excluded during the carbonization process to prevent combustion of the lignin and subsequent carbon fiber. Consequently, the carbonization process was performed using argon at 1,000 °C in the Lindberg/Blue M Tube Furnace.

7.3 Lindberg/Blue M Tube Furnace

The Lindberg/Blue M Tube furnace has a built-in 16-segment digital microprocessor temperature controller with an advanced self-tuning feature. Self-tuning automatically sets the best parameter values to control the furnace operation. The Lindberg/Blue M Tube furnace can be used to maintain a constant temperature in the

range between room temperature and 1100 °C. Figure 7.2 is a schematic diagram illustrating the thermo-stabilization and carbonization experiments. A ceramic boat was used to house the samples during the stabilization and carbonization processes. The ceramic boat was contained in a quartz tube equipped with rubber stoppers to preclude air from entering the quartz tube. Ceramic wool was used to isolate the ceramic boat and served as insulation to prevent the rubber stoppers from melting.

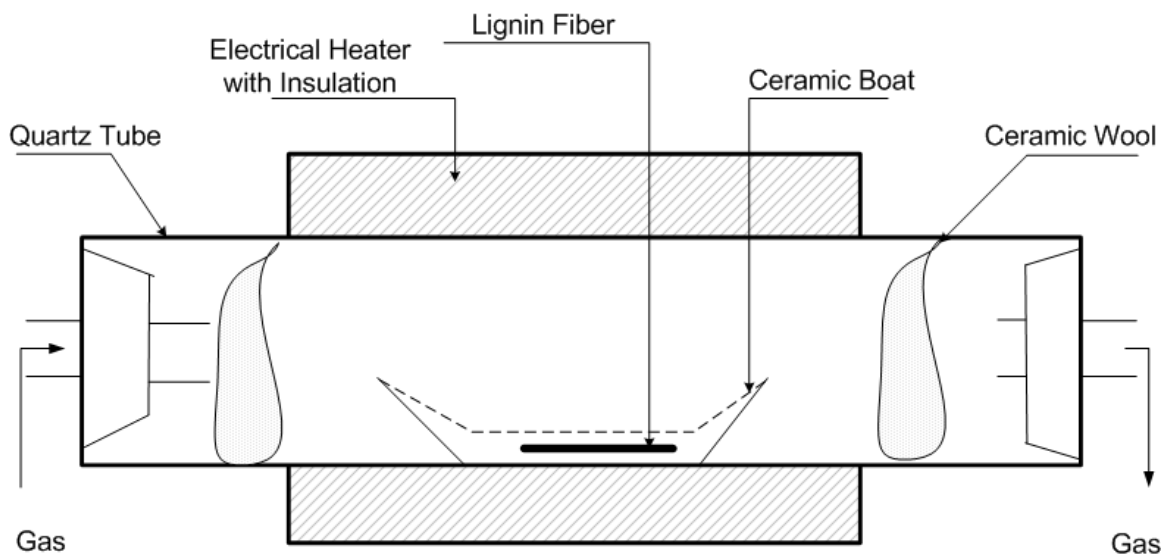


Figure 7.2 Apparatus for Thermo-stabilization and Carbonization Experiments

7.4 Carbon Fiber Surface Microstructure

A scanning electron microscope (SEM) was used to observe the surface microstructure of the carbon fiber. This work was done using the SEM located in the Laboratory for Surface Science and Technology (LASST) at the University of Maine. The scanning electron microscope images an object by scanning the surface with a high-energy beam of electrons focused in a back-and-forth scan pattern. The beam of electrons interacts with the atoms in the sample and produces photons representative of the surface topography, composition and other properties such as electrical conductivity.

The photons are captured on a cathode ray tube and produce an image much like a light photograph. A computer file is then created that is representative of the image on the screen.

7.5 Samples

Carbon fibers were obtained by using the Alcell lignin and the lignin samples recovered by extraction with 0% and 6% green liquor and isolated by the hydrolysis method.

For comparison purposes, SEM images were also made for commercial PAN- and pitch-based carbon fibers. The PAN based carbon fiber sample (PANEX35) was supplied by Zoltek Corporation; while the pitch based carbon fiber sample (P25) was supplied by Cytec Industries Inc.

7.6 Results and Discussion

7.6.1 Lignin Fiber Thermo-stabilization and Carbonization

Before carbonization, the lignin fiber was stabilized to convert the lignin fiber into an infusible substance in air to prevent melting during the carbonization process. The thermo-stabilization process was carried out in two heating stages. First, the lignin fiber was heated from room temperature to 105 °C at a rate of 1 °C/min. The lignin fiber was then held at 105 °C for 1 hour to remove moisture in the sample. Second, the lignin fiber was then heated from 105 °C to 200 °C at a rate of 0.25 °C/min. In the last step the lignin fiber sample was held at 200°C for 24 hours to oxidize the lignin and raise the glass

transition temperature (T_g) value thus reducing vaporization of low molecular weight material during carbonization (Sudo et al. 1992).

After the thermo-stabilization process, the stabilized lignin fibers were carbonized by following the method suggested by Sudo et al. (1992). The samples were heated from room temperature to 1,000 °C at a rate of 5°C/min in a stream of argon. Once the sample reached the maximum temperature of 1,000°C, the sample was maintained at temperature for 20 minutes. Following the carbonization step, the furnace temperature was reduced and the sample allowed to cool down for eight hours. The time-temperature sequence for the thermo-stabilization and carbonization process is illustrated in Figure 7.3 and 7.4. The thermo-stabilization and carbonization procedures are summarized in Table 7.1.

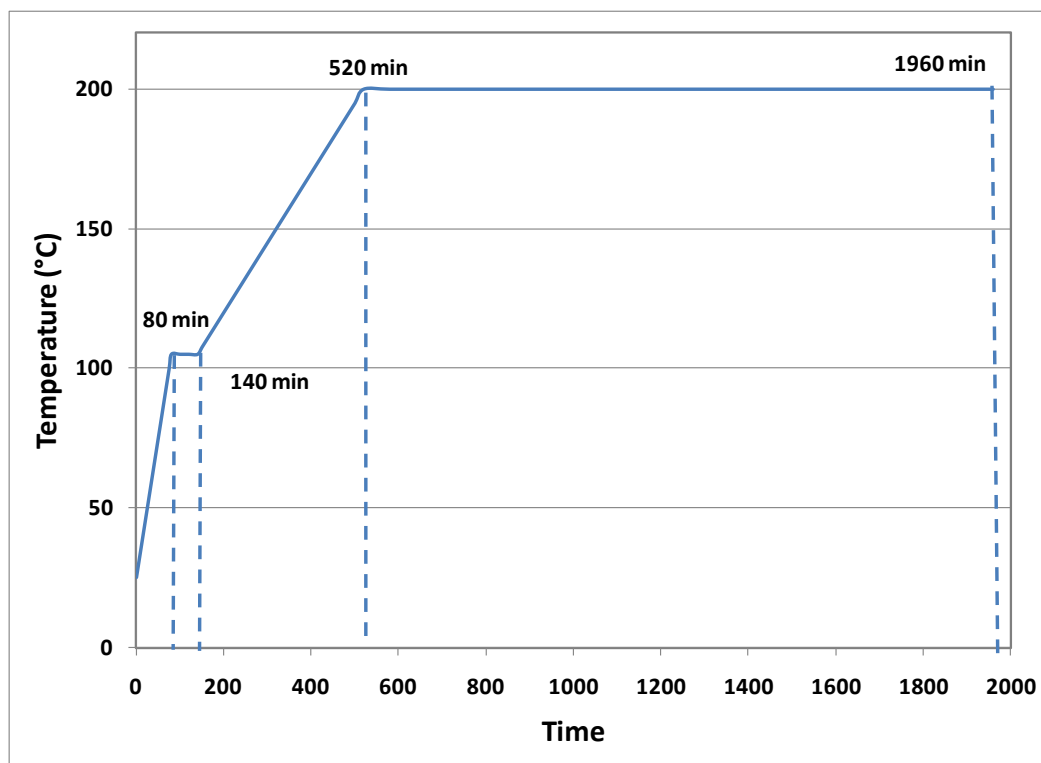


Figure 7.3 Time verse Temperature Sequence for Thermo-stabilization Process

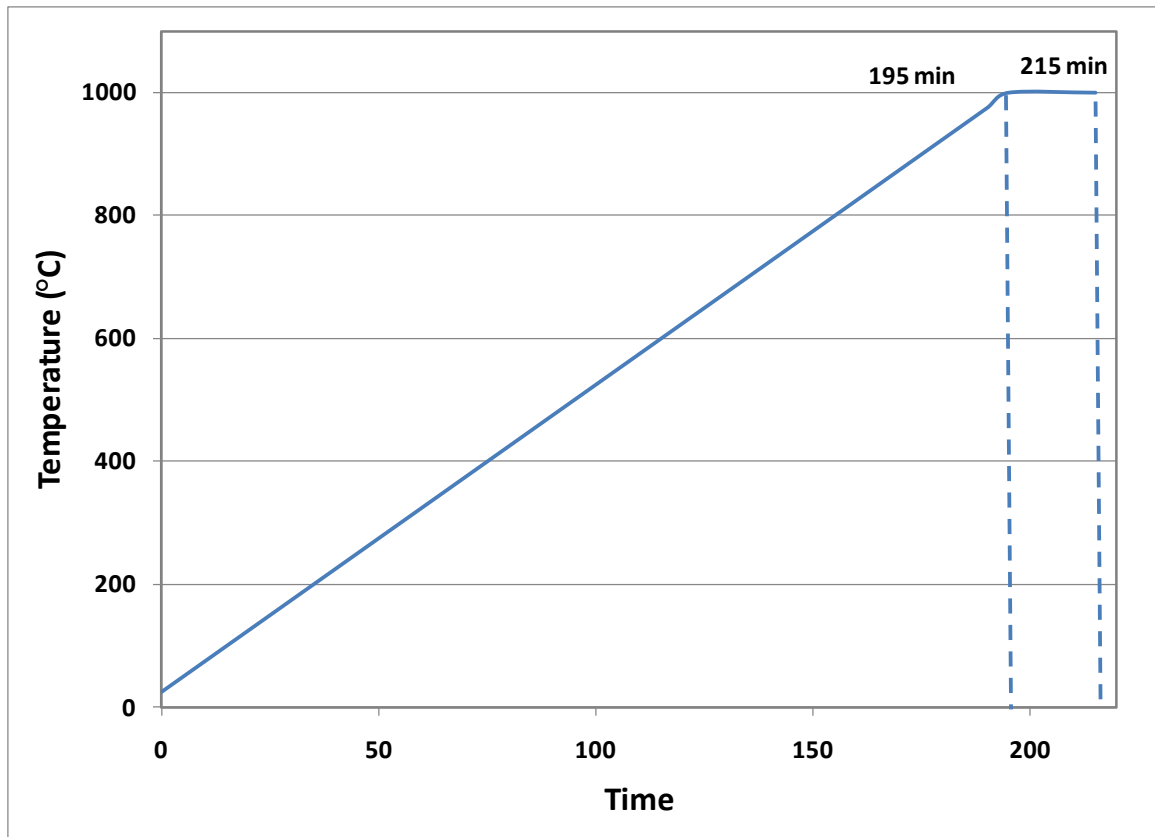


Figure 7.4 Time verse Temperature Sequence for Carbonization Process

Table 7.1 Summary of Lignin Fiber Thermo-stabilization and Carbonization Process

Process	Stage	Temperature (°C) from to		Heating Rate (°C/min)	Time at Temperature (hr)	Gas	Purpose of Processing Step
Thermo-stabilization	I	25	105	1	1	Air	Bake out the moisture
	II	105	200	0.25	24	Air	Form infusible fiber
Carbonization	I	25	1,000	5	0.33	Argon	Form carbon fiber

The carbonization process was carried out using three lignin fiber samples; (1) Alcell, (2) lignin recovered using 0% green liquor (pure water), and (3) lignin recovered from the 6% green liquor extraction experiment. Photographs of the lignin fiber samples taken in the various stages of processing are illustrated in Figure 7.5 (Alcell), Figure 7.6 (0% GL) and, Figure 7.7 (6% GL).



Figure 7.5 Carbon Fibers from Alcell Lignin

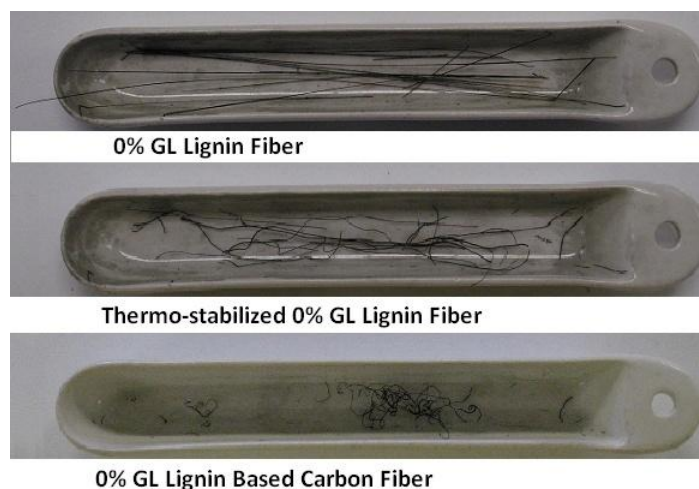


Figure 7.6 Carbon Fibers from 0% GL Lignin

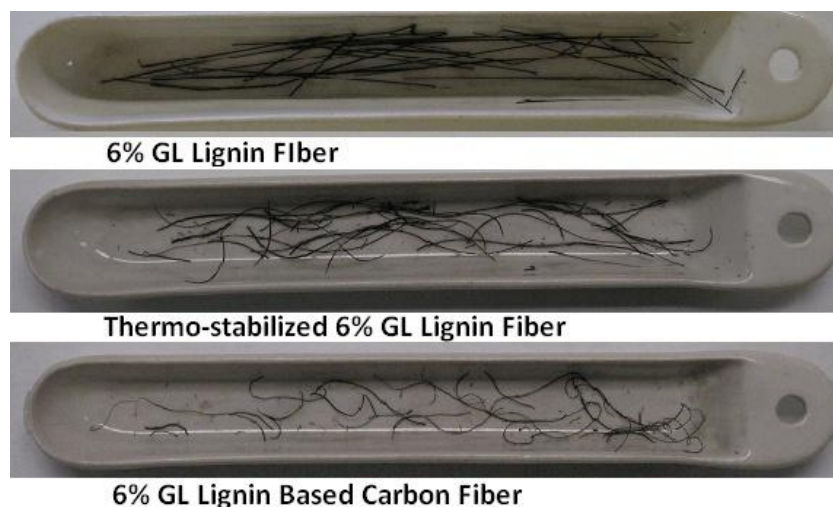


Figure 7.7 Carbon Fibers from 6% GL Lignin

7.6.2 Effects of Thermo-stabilization on Lignin Glass Transition Temperature

A variety of physical changes took place during the thermo-stabilization process (Figure 7.8). There was a distinct change in (A) the color of the lignin fiber, from dark brown to shiny black; (B) a loss in weight or mass of the fiber; (C) a considerable shrinkage or change in the length of the fiber, and (D) the formation of kinks and curls in the carbon fiber. Unfortunately the change in color does not show up clearly in the photographs. The lignin fibers shrink considerably during the thermo-stabilization process. Fiber shrinkage was completed at 200 °C. Chung (1994) attributes the shrinkage of the lignin fibers during thermo-stabilization to a realignment of the lignin molecules that were previously aligned and stretched during the fiber spinning process. The shrinkage during thermo-stabilization is the result of a relaxation process. Also, during the stabilization process the lignin fibers had a tendency to curl (Figure 7.8). The tendency to curl was attributed to the fact that there was no way to restrain the fibers during the heating process in the present apparatus.

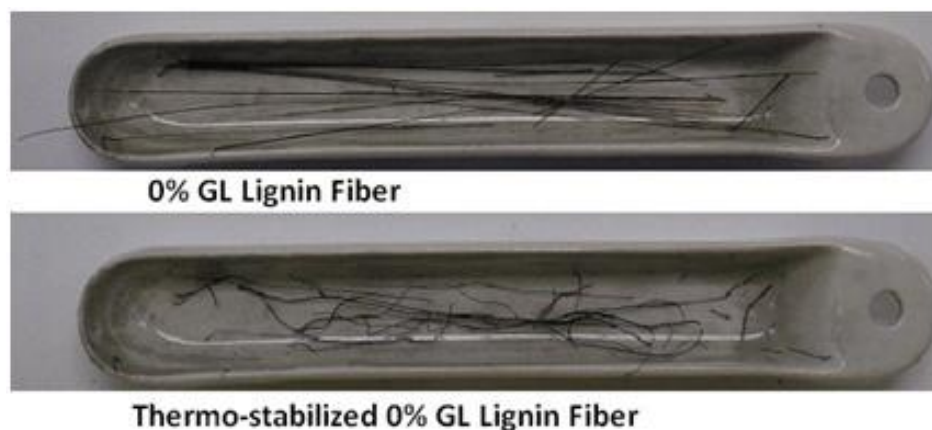


Figure 7.8 Lignin Fibers before and after Thermo-stabilization

During the thermo-stabilization process, lignin oxidation reactions occur that increase the glass transition temperature (T_g) of the lignin fiber, even at slow heating rates such as 0.25 °C/min. The glass transition temperature (T_g) can increase faster than the furnace temperature at the slow heating rate. After the thermo-stabilization process, the lignin fiber was in a glassy non-tacky state and forms an infusible fiber (Kadla, 2002). Table 7.2 summaries the glass transition temperature of lignin samples before and after the thermo-stabilization process. The decrease in glass transition temperature for the lignin obtained using water extraction (0% GL) suggests the lignin structure is changing, most likely due to thermal decomposition.

Table 7.2 Lignin Glass Transition Temperature before and after Thermo-stabilization

Lignin	Before Thermo-stabilization T_g (°C)	After Thermo-stabilization T_g (°C)
0% GL	167	160
6% GL	109	156
Alcell	108.6±0.6	155

7.6.3 Carbonization of Lignin Fiber

Weight Loss During Carbonization. For pitch, during carbonization at a heating rate (5°C/min) in an inert atmosphere, reactions occur that reorganize its structure (Chung, 1994). Similar reactions are also thought to occur with lignin. Intermolecular cross-linking is thought to occur through the lignin structure. During carbonization of PAN, water vapor, ammonia, hydrogen cyanide (HCN), carbon monoxide, carbon dioxide, nitrogen and possibly methane are given off (Chung, 1994). Similar to PAN and pitch, the weight loss in the present experiments is related to the loss of low molecular weight molecules. With lignin as the precursor material, since only carbon (C), hydrogen (H) and oxygen (O) are present, during the carbonization process the likely degradation products are water vapor, carbon monoxide, carbon dioxide, and possibly hydrogen and methane. Argon gas was used to dilute the toxic waste gas, as well as to prevent ingress of atmospheric air and combustion of the lignin fiber.

Lignin Carbon Content. The carbon content of the lignin samples before and after carbonization are summarized in Table 7.3. Table 7.3 also includes the data for the carbon content of commercial carbon fibers from PAN and pitch. The carbon content of the commercial PAN based carbon fiber was reported to be 95%, while the carbon content of the commercial pitch based carbon fiber was 97+%. Comparing PAN- and pitch-based carbon fiber, the carbon content of the various carbonized lignin fibers produced at the University of Maine were over 95%. These results were encouraging and suggest additional research to improve lignin as a precursor.

Table 7.3 Carbon Content in Lignin before and after Carbonization

Lignin	Before Carbonization Carbon Content (%)	After Carbonization Carbon Content (%)
0% GL	64.7	98.1
6% GL	63.4	95.3
Alcell	64.4	98.0
PANEX35 ^a	NA	95
P25 ^b	NA	97+
a. Zoltek, PANEX35 typical properties data sheet. b. Cytec P25 typical properties data sheet.		

7.6.4 Yield of the Thermo-stabilization and Carbonization Processes

The transformation of the raw precursor materials into finished products is an important economic aspect in the production of carbon fiber. Low carbon fiber yield results in a high production cost. The conversion of the lignin fiber into carbon fiber during the thermal stabilization and carbonization processes was measured in terms of the process yields. The yield fraction (Y_{TS}) in the thermo-stabilization process is defined as the ratio of the mass of lignin fiber (m_{TS}) present following thermo-stabilization to the amount of lignin fiber present at the beginning of the process (m_{TS}^0) (Equation 7.1). A similar definition holds for the yield fraction (Y_C) during the carbonization process (Equation 7.2). The yield fraction (Y_{Total}) for the carbonization process is written in terms of the mass of carbon fiber (m_{CF}) produced to the mass of stabilized lignin fiber (m_{TS}) as feed to the carbonization process (Equation 7.3). The overall process yield is defined as

the product of the thermo-stabilization yield (Y_{TS}) and the carbonization yield (Y_C) (Equation 7.3).

$$Y_{TS} = \left(\frac{m_{TS}}{m_{TS}^0} \right) \quad (\text{Eq. 7.1})$$

$$Y_C = \left(\frac{m_{CF}}{m_{TS}} \right) \quad (\text{Eq. 7.2})$$

$$Y_{\text{Total}} = Y_C * Y_{TS} = \left(\frac{m_{CF}}{m_{TS}} \right) * \left(\frac{m_{TS}}{m_{TS}^0} \right) = \left(\frac{m_{CF}}{m_{TS}^0} \right) \quad (\text{Eq. 7.3})$$

Table 7.4 summarizes yield data for conversion of the spun lignin fiber samples into carbon fibers following the thermo-stabilization and carbonization processes. Also included in Table 7.4 are data for the overall process yield. The yield of carbon fiber varies depending upon the precursor lignin and the carbon fiber manufacture process. For comparison purposes Table 7.4 also includes data for the thermo-stabilization, carbonization and overall process yields for several precursor materials including pitch, Alcell lignin, hardwood Kraft lignin and lignin recovered by acetic acid pulping obtained from the literature.

Table 7.4 Yields Values for Each Step in the Production of Carbon Fibers

Carbon Fiber Sample	Thermo-Stabilization (Y _{TS} %) Yield ^a	Carbonization (Y _C %) Yield ^b	Overall Process (Y _{Total} %)Yield ^c
Alcell Lignin Based Carbon Fiber	82.4	42.7	35.2
0% GL Lignin Based Carbon Fiber	80.2	39.9	32.0
6% GL Lignin Based Carbon Fiber	82.0	40.2	32.9
Alcell Lignin Based Carbon Fiber ^d (Kadla et al.,2002)	97.0	46.2	40.0
Kraft Lignin Base Carbon Fiber ^d (Kadla et al.,2002)	94.4	51.6	45.7
Acetic Acid Lignin Based Carbon Fiber ^d (Uraki et al.,1995)	88.0	40.1	32.7
Tar Pitch Based Carbon Fiber ^d (Uraki et al.,1995)	110.0	80.0	33.4
a Based on the lignin fiber b Based on the thermo-stabilized lignin fiber c Based on the lignin fiber d Based on pretreated precursors (thermal pretreatment of lignin at 145 °C under vacuum for 1 hour).			

Thermal Stabilization Yield. The yield values were approximately 80% for the various thermo-stabilized lignin fiber produced at the University of Maine. This may be compared to the yields of thermo-stabilized lignin fiber reported in the literatures that is approximately 90%. It was felt that the yield of thermo-stabilized lignin fiber produced in our laboratory agreed well with those reported in the literature. However Uraki and co-workers (1995) report the yield of thermo-stabilized tar-pitch fiber to be approximately 110%. Uraki's data implies a weight gain during the thermo-stabilization process, most likely resulting from the addition of oxygen into the chemical structure of tar pitch. Under all circumstance no weight gain was observed in the lignin samples evaluated in the current study. The significant difference in the yield of the thermo-stabilization process between lignin fiber and tar-pitch fiber reported by Uraki (1995) was attributed to differences in the chemical structures between tar pitch and lignin.

Carbonization Yield. There is a significant difference in yield between the thermo-stabilization and the carbonization processes (Table 7.4). By contrast to the 80% yield observed in the carbon-stabilization process, the yield during the carbonization process varied between 40% and 50% depending upon the precursor material. Low carbonization yields are expected because the carbon fiber samples were heated to 1,000 °C and large quantizes of low molecular weight materials (H_2O , CO , CO_2 , O_2 , H_2 and possibly CH_4) are released from the lignin fiber. Good agreement was obtained between the yield data for carbonization reported in this study for hardwood lignin obtained with the 0% and 6% GL extraction samples and that reported by Kalda (2002) and Uraki (1995). Similarly, good agreement was obtained for the carbonization yield for the Alcell lignin found in this study and that reported by Kalda (2002). Here again

Uraki (1995) reported a carbonization yield of 80% for tar pitch fibers that is approximately twice the value reported in this study and by Kadla (2002) for both hardwood Kraft lignin (51.6%) and Alcell lignin (46.2%). Uraki attributes the high carbonization yield to its high carbon content that is reported by Chung (1994) to be greater than 90% compared to hardwood lignin that is approximately 62%.

Overall Yield. In the final analysis the overall yield for the carbon fiber product was about 30% to 40% for the two step thermo-stabilization and carbonization process. The overall yield is controlled by the yield of the carbonization process since it has a considerably lower yield than yield in the thermo-stabilization step. It is interesting to note that Usaki reports the overall yield of tar pitch to carbon fiber to be only 33% (Table 7.4). This value is similar to that for lignin measured in the current study. This is surprising in light of the high carbon content in tar pitch; reported to be about 90% (Chung, 1994). A simple process flow diagram for the manufacture of carbon fiber from lignin is illustrated in Figure 7.9. It is assumed that the lignin content in the hardwood is 25% going to the extraction process. Following the extraction process 3% of the wood is extracted in the form of lignin. In the hydrolysis isolation process wood solids are lost and approximately 1.2% of the wood remains as lignin precursor. In the spinning processes the losses of wood solids should be minor. There are however additional losses in the thermal stabilization and carbonization processes. Of the 1.2% wood solids recovered as lignin following the hydrolysis process, approximately 0.96% based on wood would be present following thermal stabilization and 0.38% wood solids as lignin would be converted into carbon fiber. Thus the overall yield based on wood is estimated to be approximately 0.38 %.

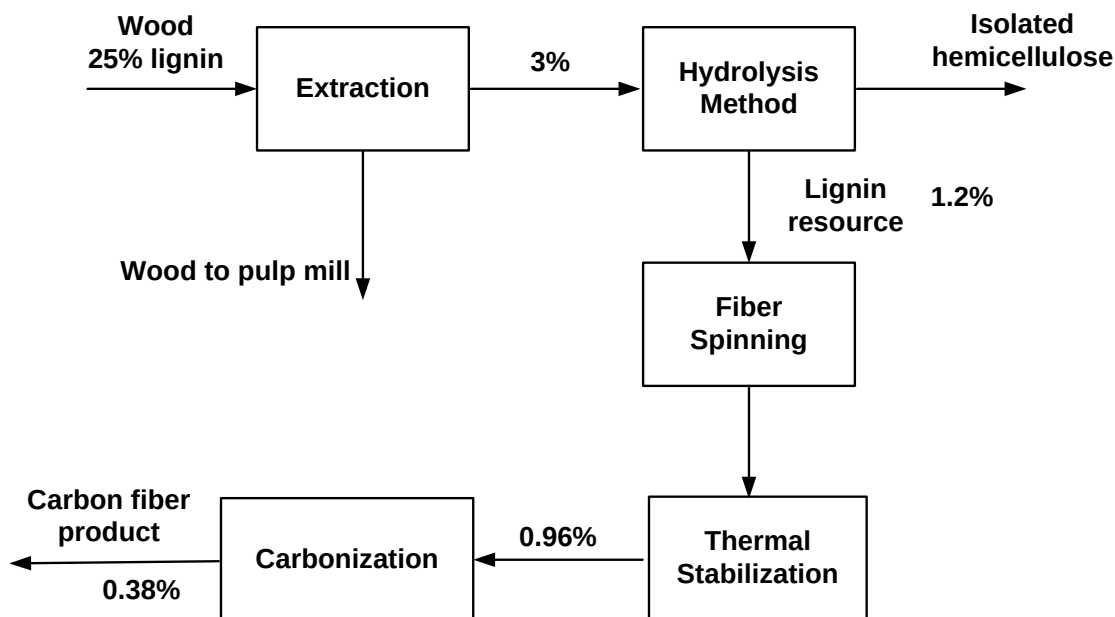


Figure 7.9 Lignin Based Carbon Fiber Process Flow Diagram

7.6.5 Surface Microstructure of Carbon Fiber

SEM micrographs for the carbon fibers produced in the current study are illustrated in Figures 7.10 through 7.19. The micrographs were taken of thermally stabilized fiber and the final carbon fiber product and illustrate clearly the morphology and micro-structure of the sample. Micrographs are presented for a variety of precursors, including the experimental samples from Alcell lignin, 0% GL, 6% GL lignin and commercial samples produced from PAN and pitch.

Imperfections in Laboratory Samples. Figures 7.10 through 7.15 relate to the carbon fiber samples prepared in the laboratory. These micrographs illustrate that the carbonization process used in the laboratory significantly alters the surface of the carbon fiber. The surface feature of the carbonized fiber samples prepared in the laboratory display numerous imperfections and flaws. The major cause of these flaws is thought to result from the release of volatile materials. Two other lesser possibilities are impurities

in the lignin precursor material and also possibly of contamination of the lignin by dust in the laboratory. Figure 7.13 shows carbon fiber produced using lignin isolated from the 0% GL and represents a cross section of the fiber. This figure shows imperfections deep within the structure of the fiber and gives credence to the thought that the major cause of the imperfections results from too high a content of volatile material (see Table 5.3).

Release of Volatile Material. The release of volatile material was thought to cause the numerous pores or surface irregularities observed in the carbon fiber samples in the present study. Problems associated with the release of volatile materials may be solved by lowering the heating rate during the thermo-stabilization or carbonization process. In the laboratory study the heating rate select was 5 °C per minute based upon the work of Sudo (1992). This rate could possibly be too high. Another likely reason for the surface imperfections was that the content of volatile material was too high. In the experiments reported here, the ORNL specification for volatile material was exceeded. In the experimental samples, the volatile material content invariably exceeded 10% (see Table 5.3) compared to a specification of “less than 5%”. A potential solution to this problem would be to add a pre-heating step to the carbonization process with the goal of driving off additional volatile material.

Ash and Particulate Matter in the Lignin Precursor Materials. Although impurities in the lignin precursor materials are possible, this was not thought to be a major contributor leading to the imperfections observed in the carbon fiber samples. The lignin precursor used in the experiments met the ORNL imperfection specifications for ash and particulate matter as shown in Tables 5.1 and 5.3. The ORNL specification for ash was less than 0.1% (Table 5.1) while the samples used to prepare the lignin fiber had

ash contents that were 0.08% or less (Table 5.6). It is possible, although considered unlikely, that the impurity specification must be lowered.

Laboratory Dust. Under the current laboratory condition, dust contamination of the lignin precursor fibers during preparation spinning, and handling is essentially unavoidable. If laboratory dust is producing the imperfections, then the experiments would have to perform in a specially designed clean room much like what is done in the manufacture of computer chips.

Commercial Samples. The photomicrographs of commercial samples of carbon fiber are shown in Figures 7.16 through 7.19. Carbon fibers produced from PAN (PANEX35) are illustrated in Figure 7.16 and Figure 7.17. The fiber diameter is $8.4\mu\text{m}$. There are no holes on the surface of PAN based carbon fiber, but some lines. The lines on the surface were thought to be caused by ridges in the orifice used to extrude the PAN fiber. Also, some flaws are contained on the fiber. The cross-section displayed in Figure 7.17 illustrates that the PAN based carbon fiber is a solid fiber. Figure 7.18 and Figure 7.19 show the surface structure of carbon fiber from pitch (P25). The fiber diameter for the carbon fiber produced from pitch was approximately $11.6\mu\text{m}$. The cross-section displayed in Figure 7.19 illustrates that the pitch-based carbon fiber is thought to be solid but more porous than carbon fiber produces from PAN (see Figure 7.17).

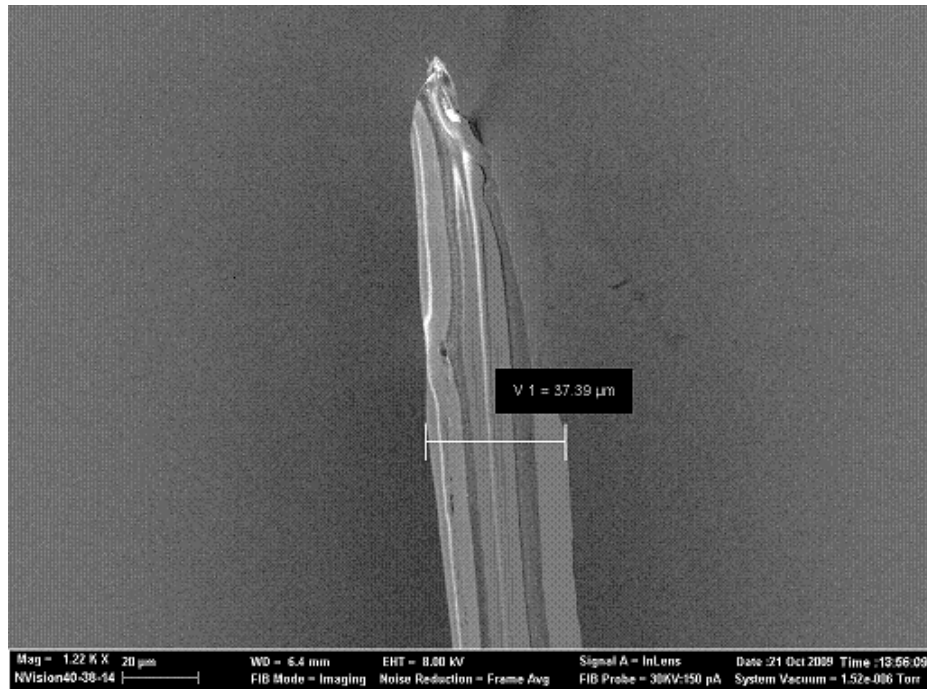


Figure 7.10 Thermo-stabilized Alcell Fiber ($D=37.4 \mu\text{m}$)

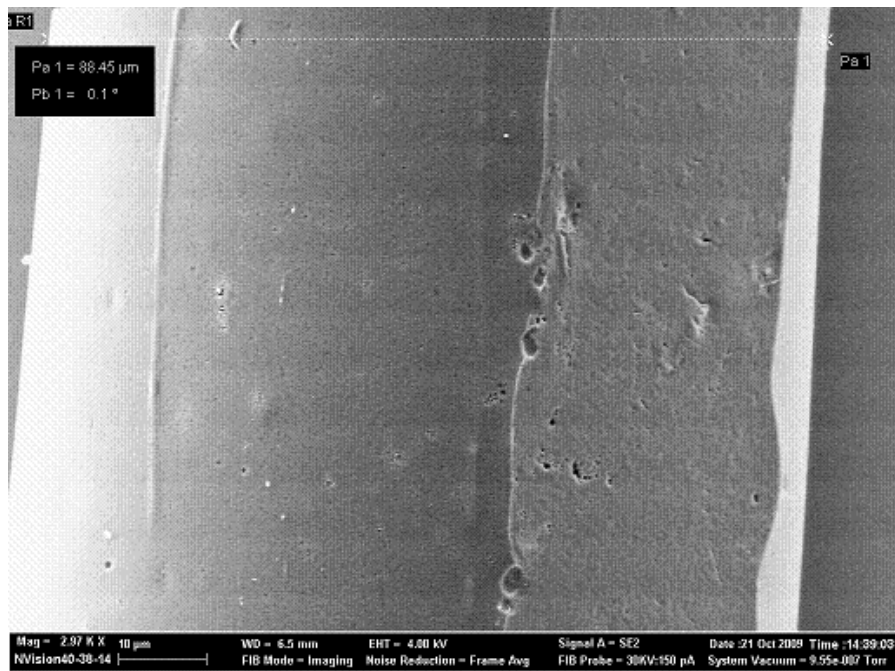


Figure 7.11 Carbon Fiber from Alcell ($D=88.4 \mu\text{m}$)

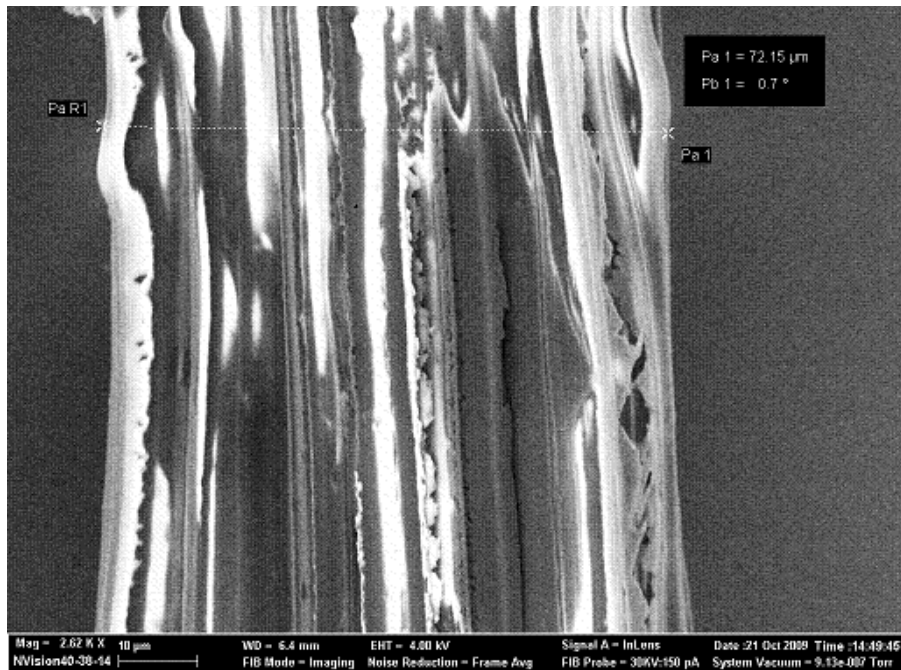


Figure 7.12 Thermo-stabilized Lignin Fiber Using 0% GL Sample ($D=72.1 \mu\text{m}$)

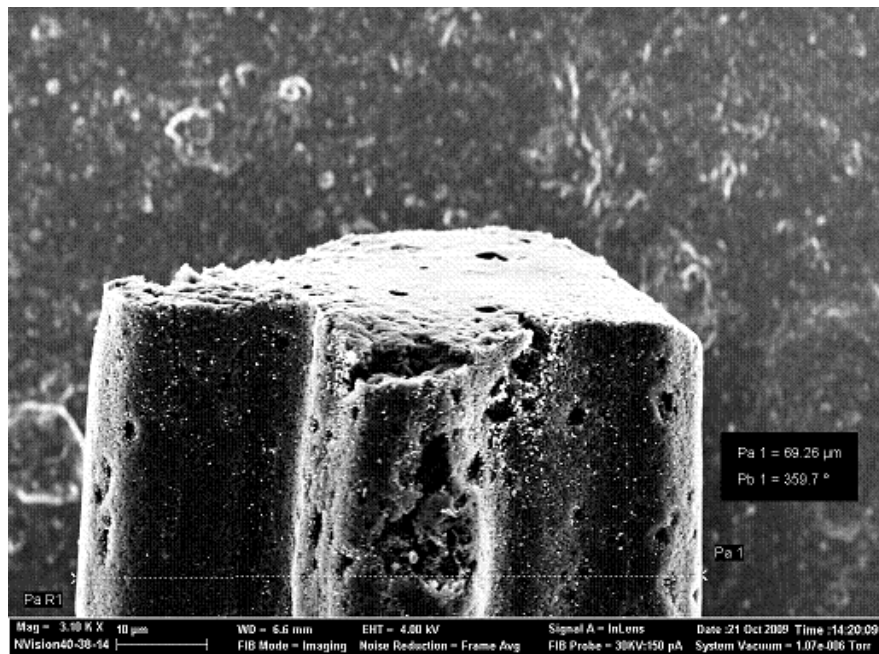


Figure 7.13 Carbon Fiber from 0% GL Lignin Fiber ($D=69.3 \mu\text{m}$)

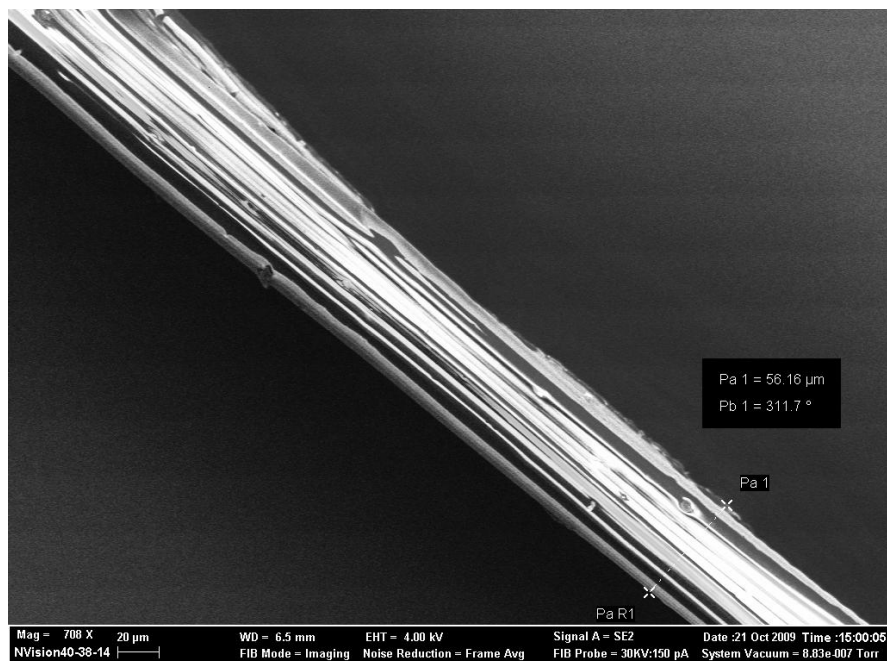


Figure 7.14 Thermo-stabilized Lignin Fiber Using 6% GL Sample ($D=56.1 \mu\text{m}$)

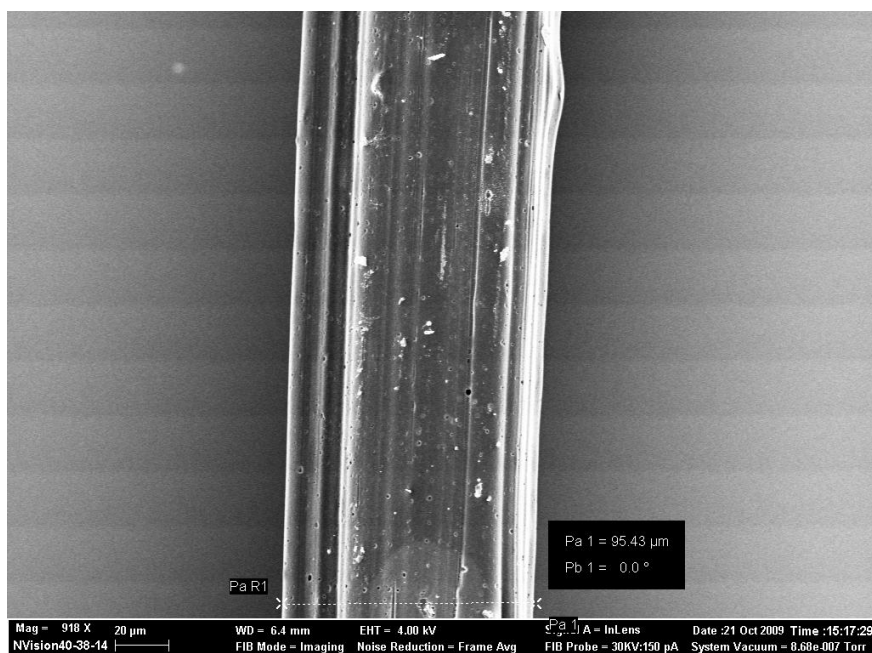


Figure 7.15 Carbon Fiber from 6% GL Lignin Sample ($D=95.4 \mu\text{m}$)

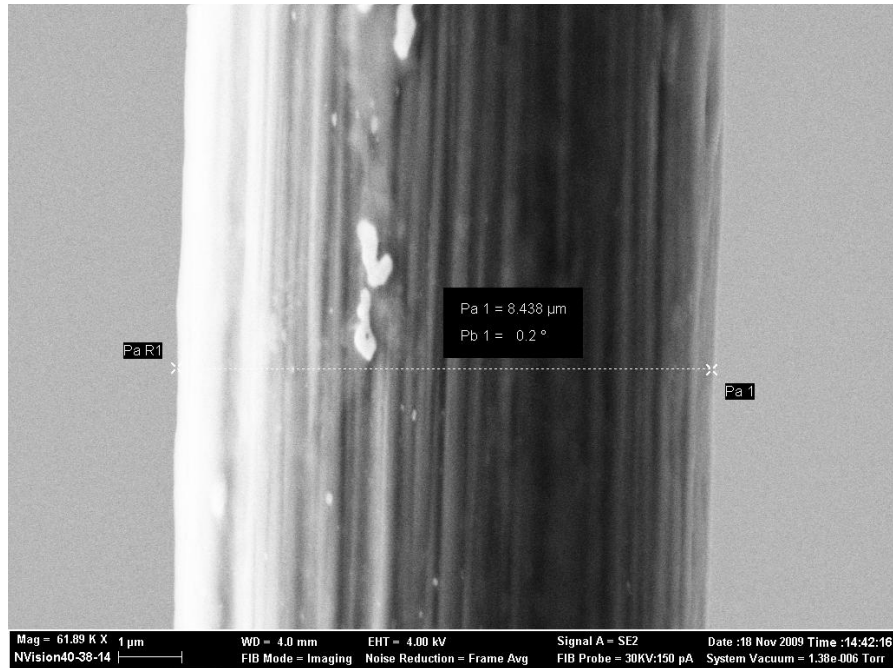


Figure 7.16 Carbon Fiber from PAN (PANEX35) ($D=8.4\ \mu m$)

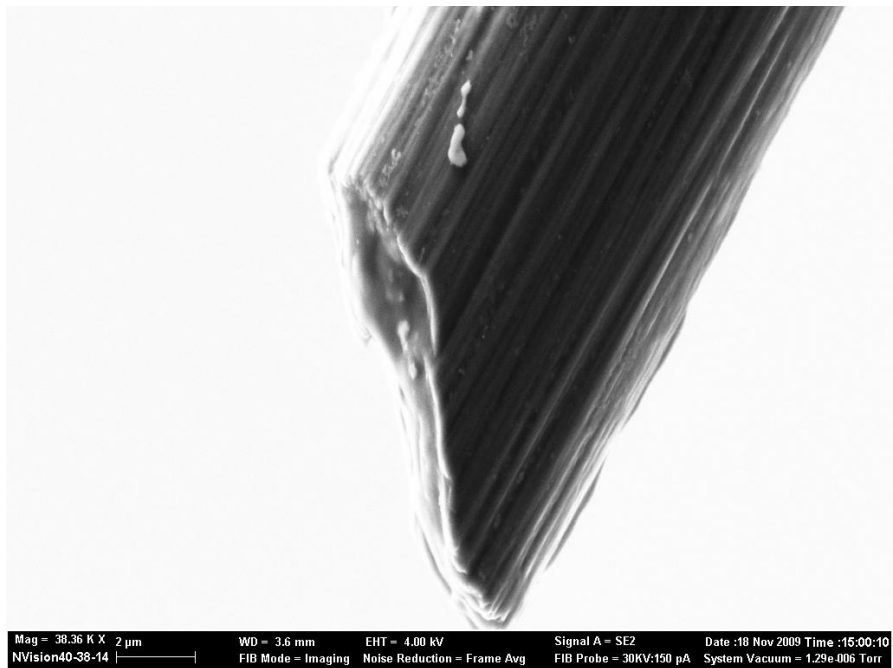


Figure 7.17 Carbon Fiber from PAN

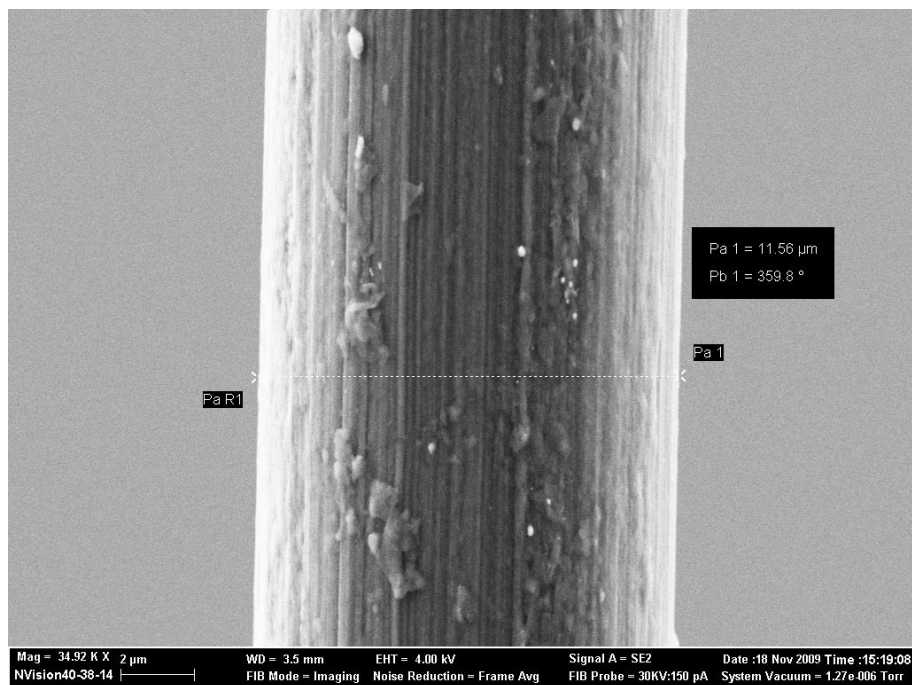


Figure 7.18 Carbon Fiber from Pitch (P25) (D=11.6 μm)

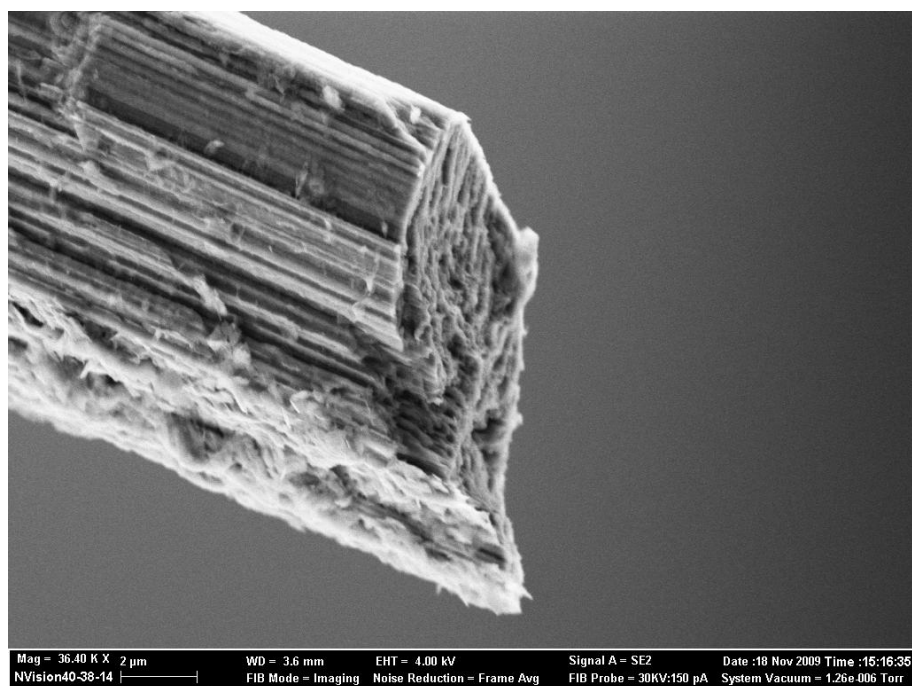


Figure 7.19 Cross Section of Carbon Fiber from Pitch

7.6.6 Properties of Carbon Fiber

Precursor Sources. The carbon fiber manufactured at the University of Maine from lignin precursors was extremely brittle. This brittleness problem precluded measurement of the physical properties, which would be very low. Several other investigators also report brittle carbon fiber from recovered lignin; see for example the work of Schmidl (1992), Sudo (1992) and Kadla (2002). Rather it is the objective of this study to report literature values for commercial carbon fiber and to suggest possible approaches to overcome the brittleness problem predicated upon work reported in the literature. Table 7.5 lists the properties of commercial carbon fiber manufactured from PAN (PANEX35) and pitch (P25).

Table 7.5 Properties of Carbon Fiber

Precursor Materials	PAN ^a	Pitch ^b	Plasticized Indulin AT	Hardwood Lignin	Hydrogenated Lignin
Manufacturer	Zoltek (2009)	Cytec (2009)	Schmidl (1992)	Kadla (2002)	Sudo (1992)
Fiber Diameter (μm)	7.2	11	103±3.5	46±8	7.6±2.7
Elongation (%)	1.71	0.91	0.32±0.11	1.12±0.22	1.63±0.19
Tensile Strength (MPa)	4,137	1,560	150±20	422±80	660±230
Tensile Modulus (GPa)	242	172	49.1±14.4	40±11	40.7±6.3
Density (gm/cm ³)	1.81	1.90	NA	NA	NA
Carbon Content (%)	95	97+	91	NA	NA
Price (\$/lb)	10~80	45	NA	NA	NA
a Zoltek, PANEX35 typical properties data sheet.					
b Cytec P25 typical properties data sheet.					

Fiber Diameter. The diameter of the carbon fiber produced in this study varied between 35 and 95 μm . These large diameters resulted because the lignin fibers could not be wound on the take-up drum because of their brittleness. The lignin flowed easily and small diameters could be produced if they were pulled fast enough. But the intrinsic problem was that the draw ratio could not be controlled because the lignin fiber could not be wound on the take-up drum. Schmidl (1992) produced carbon fiber of approximately 103 μm from Indulin AT but also had difficulty with brittleness. Kadla (2002) reported carbon fiber with diameters of approximately 46 μm from hardwood lignin but does not discuss brittleness. Rather Kadla states that “if the hardwood-based carbon fibers had diameters less than 10 μm , the mechanical strength would be the same as that of isotropic pitch and suitable for the general performance grades”. The diameters for all of the commercial carbon fibers were extremely small and varied from about 7 to 11 μm . The diameter of commercial PANEX35 from PAN for example is reported to be 7.2 μm while that of P25 manufactured from pitch is 11 μm . The diameter of carbon fiber produced from hydrogenated lignin was reported by Sudo (1992) to be approximately 7.6 μm and compares favorably with commercial carbon fiber produced from PAN.

Tensile Strength. The tensile strength of the carbon fiber produced by Schmidl was very low (only 150 MPa) and was thought to be similar to the carbon fiber produced in the current study. However, Kadla (2002) and Sudo (1992) produced carbon fiber from lignin that was considerably stronger than those produced by Schmidl (see Table 7.5) and had values of 422 and 660 MPa respectively. The PAN based carbon fiber has the highest tensile strength (4,137 MPa) while carbon fibers from petroleum pitch is less than

half this value (1,560 MPa). For comparison purposes the tensile strength of commercial carbon steel is 324 MPa.

(<http://www.matweb.com/search/datasheet.aspx?matguid=e81073a6992a45bc977f18aae2789d07&ckck=1>).

Modulus of Elasticity and Elongation. The modulus of elasticity for commercial carbon fiber varied between about 172 to 242 GPa depending upon the precursor material. The modulus of elasticity for the experimental carbon fiber reported in the literature was about 40 to 50 GPa. The experimental samples of carbon fiber from lignin are considerably lower than the commercial materials. The elongation values for the commercial carbon fibers varied from about 0.91% for pitch to 1.71% for PAN. The elongation of carbon fiber from hydrogenated lignin reported by Sudo (1992) was about 1.63% and is close to the carbon fiber from PAN 1.71%. Similar results are reported by Kadla (2002) for carbon fibers from hardwood lignin (1.12%). Lastly the elongation reported by Shmidl (1992) was quite low; only about 0.32%.

Tensile Energy Absorption (TEA). Carbon fiber with high fiber texture has high strength and high tensile energy absorption (TEA). Figure 7.20 illustrates the TEA values for carbon fiber produced from different precursors. Clearly, PAN based carbon fiber has the highest strength and tensile energy absorption values. By contrast, Indulin AT based carbon fiber has the lowest strength and tensile energy absorption of any precursor. Table 7.6 summarizes the TEA values relative to PAN. In Table 7.6 the relative TEA value of PAN based carbon fiber was assumed to be 100%. The relative TEA value for the commercial pitch based carbon fiber was 20.1% relative to that of PAN. For lignin based carbon fiber all of the TEA values fall on the same straight line; with the highest TEA

being for the hydrogenated lignin. However, the hydrogenated lignin sample reported by Sudo was only 15.2% of that for PAN. The carbon fiber produced from hardwood lignin by Kadla was only 6.7% of that for PAN. The relative TEA value for the carbon fiber from Indulin AT reported by Schimdl was very low, only about 0.7% of that of PAN.

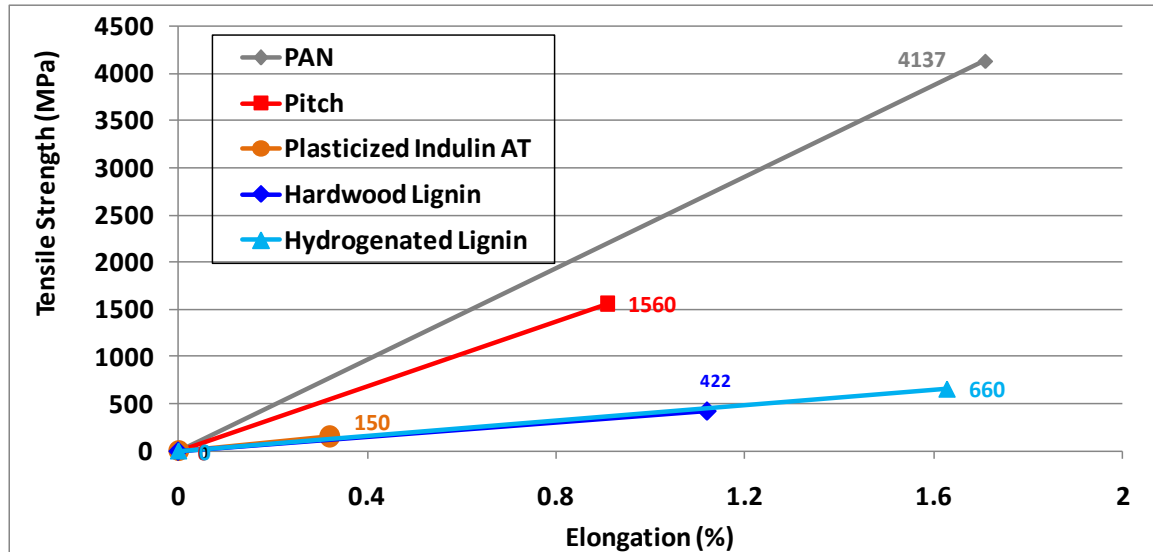


Figure 7.20 TEA Curves of Carbon Fibers

Table 7.6 Relative TEA Values of Carbon fibers

Precursor Materials	PAN ^a	Pitch ^b	Plasticized Indulin AT	Hardwood Lignin	Hydrogenated Lignin
Manufacturer	Zoltek (2009)	Cytec (2009)	Schmidl (1992)	Kadla (2002)	Sudo (1992)
Relative TEA Value (%)	100	20.1	0.7	6.7	15.2
Relative to PAN based carbon fiber					

Density of Carbon Fibers. The density of carbon fibers is an important parameter. In conjunction with the fiber diameter, the density sets the mass of the fibers for a given length. The density of commercial carbon fiber is reported to be approximately 1.81 gm/cm^3 for PAN precursor and 1.90 gm/cm^3 for pitch. Both of these values are much lower than the density of steel which is around 7.8 gm/cm^3 . Unfortunately no data are reported for the density of carbon fiber from lignin in the literature.

7.7 Conclusions

The spun lignin fibers could be readily stabilized thermally and then converted into carbon fibers using the laboratory techniques employed in the current study. There were noticeable changes in color and shape in the lignin fibers on thermal stabilization. Numerous curls formed in the lignin fiber during the thermal stabilization process. The curl in the lignin fiber was thought to result from the lignin fibers undergoing free shrinkage during the thermo-stabilization process. A potential solution to this process is to restrain the lignin fibers during stabilization. However, the lignin fibers need to be strong enough to resist the shrinkage forces that will occur during stabilization if the fibers are restrained. The yield of the starting material during the thermo-stabilization process was about 80% (Equation 7.1) and on carbonization about 40% (Equation 7.2). Thus, the overall process yield for the stabilization and carbonization processes was about 32% (Equation 7.3).

The work reported here shows that hardwood lignin fibers and the subsequent carbon fibers produced from purified lignin are brittle. This brittleness is thought to be due to the high glass transition temperature and cross-linking of the lignin molecules.

The photomicrographs of the carbon fiber produced from hardwood lignin in the current study show many surface and sub-surface imperfections. These imperfections are thought to result from the high volatile material content in the precursor lignin and the high heating rate used in the laboratory production technique. These imperfections could potentially be reduced by lowering the heating rate and/or by pre-treatment of the precursor lignin at high temperature.

The brittleness in the lignin fibers resulted in poor physical properties for the carbon fiber. Specifically the tensile strength, modulus of elasticity and elongation are all extremely low. One method for potentially correcting the problem is to hydrogenate the lignin to reduce its glass transition temperature (T_g) and reduce cross linking to form a more linear structure. Commercial PAN based carbon fiber has high physical properties and low density but is very expensive. The carbon fibers from pitch has much lower physical properties when compared to the PAN. Kadla (2002) hypothesizes that carbon fibers from hardwood lignin could be competitive with carbon fiber from pitch provided that the lignin fibers can be produced with a diameter less than 10 μm .

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The following conclusions can be drawn based upon the experimental results and the literature work reported here.

Carbon Fiber from PAN. PAN is the primary precursor material used in the commercial manufacture of carbon fiber. Its high performance is attributed to the high degree of alignment of the carbon layers parallel to the fiber axis (Chung, 1994). Currently the use of PAN based carbon fiber in composite materials is limited by the high cost of manufacture. There is a need for a low cost precursor that can be used to manufacture carbon fiber with physical properties approaching those of PAN based carbon fiber. Lignin is one possible material because of its high carbon content, ring structure, abundance in nature and low cost.

Lignin Precursors Described in the Literature. Several lignin precursors have been previously evaluated. These include hardwood and softwood lignin obtained from the Kraft process, lignin isolated by organosolv pulping, modified lignins, and lignin polymer blends. Organosolv lignin includes that isolated from the Alcell and acetic acid pulping processes. Modified lignins include acetylated softwood lignin, hydrogenated hardwood lignin and phenolated hardwood lignin. Lignin-polymer blends include mixtures of hardwood lignin from the Kraft process with PET, PP, and PEO. No literature citations could be found that evaluate lignin isolated from green liquor extract.

“Near Neutral Hemicellulose Extraction Process”. Laboratory experiments were performed using the green liquor as the solvent. The final pH value of the extract increased as the green liquor application rate increases. High green liquor application rates resulted in increased amounts of lignin and sodium acetate being extracted but resulted in a decreased in the xylan extraction rate. The 6% GL experiments had the highest concentration of lignin while pure water extraction had the highest xylan content.

Lignin Isolation Methods. Two methods of lignin isolation were evaluated in the current study; the method of Sun (1999) which involved precipitation of lignin using ethanol, and the hydrolysis method developed by the author. The two-sample t-test was used to compare the two methods of isolating lignin. The results of the two-sample t-test indicated that there was a significant difference between the two lignin isolation methods. The hydrolysis method developed in this work was found to be simpler to use and more effective than Sun’s method. A distinct advantage of the hydrolysis method is that it produces high purity lignin. However, a disadvantage of the method is that the lignin is thought to be significantly cross-linked which possibly could negatively affect the production of lignin fibers because it raises the glass transition temperature of the lignin.

Lignin Precursor Specification Recommended by ORNL. The Oak Ridge National Laboratory recommends specifications for lignin as a precursor for carbon fiber. These involve specifications for ash content, volatile matter, particulate matter and lignin purity. However, the ORNL specifications fail to set target values for the very important parameters of glass transition temperature and molecular weight. The glass transition temperature (T_g) is critical to determining whether the recovered lignin can be spun using

melt spinning. The molecular weight (M_w) will influence the glass transition temperature (T_g) value and the brittleness of the recovered fiber.

Lignin Glass Transition Temperature and Molecular Weight. The weight-average molecular weight (M_w) of the isolated lignin decreased with increasing green liquor application rate. A small difference was observed between the weight-average molecular weight (M_w) for the Alcell lignin (4,600 Daltons) and lignin recovered from the pure water (0% GL) extraction experiment (5,200 Daltons). By contrast there was a significant difference in the measured values for the glass transition temperature (T_g) between the Alcell lignin sample (108.6 °C) and the lignin recovered in the pure water (0% GL) extraction experiment (167 °C). Cowie and Arrighi (2007) point out that several other factors such as the degree of cross-linking, chain flexibility, molecular structure and branching are known to affect the glass transition temperature (T_g).

Lignin Precursor's Evaluated. Several lignin precursors were evaluated in the present study. These include Indulin AT, Alcell lignin, lignin isolated from laboratory extraction experiments and mill trials conducted by Old Town Fuel and Fiber Inc. that were used to evaluate the “near neutral hemicellulose extraction process”. All laboratory and mill extract samples were isolated by using the author’s hydrolysis method.

Properties of Lignin Precursor. Lignin obtained by the hemicellulose pre-extraction process and isolated by the hydrolysis method met all of the specification stipulated by ORNL except for the specification related to the volatile material content at 250°C. The ORNL standard requires that the volatile matter in the lignin precursor be less than 5% of the mass of the precursor when heated to 250 °C. The samples used in the

current study had volatile matter contents in excess of ten (10) weight percent (%) and thus exceeded the ORNL standard.

Lignin Fiber. The Indulin AT (softwood lignin) could not be processed into lignin fiber because of lignin charring before melting. The hardwood lignin recovered by extraction with GL and lignin extracted using ethanol in the Alcell process could readily be formed into continuous fibers with diameter values of approximately 35 to 40 μm using the Atlas Laboratory Mixing Extruder. However, the lignin fiber produced were extremely brittle. Of all of the samples evaluated, the Alcell lignin fiber was thought to be the least brittle. This decrease in brittleness in the Alcell lignin fiber was thought to be due to its lower glass transition temperature (T_g) value.

Imperfections in Lignin-Based Carbon Fiber. Preliminary lignin fiber thermo-stabilization and carbonization studies were carried out in this thesis. SEM micrographs were taken of the carbon based fiber obtained from the green liquor and Alcell processes and compared to micrographs taken of commercial materials. A large number of flaws were seen in micrographs taken of the laboratory samples following carbonization relative to the commercial materials. These flaws existed both in the interior structure and also at the surface of the laboratory prepared carbon fiber. The imperfections in the laboratory samples of carbon fiber were thought to be caused by the high volatile material content of the lignin precursor and also by the heating rate that was too high during the carbonization process.

Hydrogenated Lignin Precursor. Sudo and co-worker (1992) report preparing carbon fiber from hydrogenated lignin that had physical properties comparable to those of

carbon fiber prepared from pitch; but were only approximately 25% of the value of carbon fiber from PAN.

8.2 Recommendations

The previous work has shown that hardwood lignin and carbon fiber produced from purified lignin were brittle. This brittleness is thought to be due to the high glass transition temperature and cross-linking of the lignin molecules. Recommendations for future work have been identified and include the following:

Reduce Volatile Material Content. A preheating process prior to fiber spinning is recommended to reduce the high volatile material content exhibited by the lignin precursors evaluated in the current study.

Reduction in Surface Flaws During Carbonization. It is recommended that the heating rate applied during the carbonization process be lowered in an effort to reduce the surface flaws of the carbon fiber product.

Lignin Hydrogenation Studies. It is recommended that the structure of the lignin recovered using the hydrolysis method be modified by using the catalytic hydrogenation technique describe by Sudo and co-worker (1992). According to Sudo and co-worker (1992), hydrogenation modifies the lignin structure, lower its glass transition temperature and reduce the tendency for cross-linking and brittleness. The recommended process would entail extracting lignin from hardwood chips using sodium carbonate, acid hydrolysis to break carbohydrate-lignin bonds and reduce the carbohydrate content, lignin precipitation and washing followed by catalytic hydrogenation.

Lignin Acetylation Studies. Lignin from softwood could not be formed into fibers by the melting spinning method because charring of softwood lignin takes place prior to melting. Eckert and co-workers (2008) developed a method to convert softwood Kraft lignin into fine filaments using the melt spinning method. This was accomplished by modifying the lignin by acetylation. The acetylation technique reduces cross-linkages in softwood lignin and lowers its glass transition temperature. Acetylation modification also can be applied to the hardwood lignin recovered from the “near neutral hemicelluloses extraction process”.

Lignin Depolymerization Studies. Srebotnik and co-workers (2000) reported that lignin could be depolymerized by *Trametes villosa* laccase in the presence of a radical mediator. Srebotnik used 1-hydroxybenzotriazole (HOBt) as the radical mediator to cleave both phenolic and nonphenolic linkages, such as β -O-4-linkage which is one of the predominate linkages in lignin. After depolymerization, the number-average molecular weight of *Trametes villosa* laccase/HOBt treated lignin was decreased by approximately 25%. Besides lowering the molecular weight by depolymerization, the *Trametes villosa* laccase/HOBt system should also lower the glass transition temperature of the lignin.

TGA Studies. It is recommended that Thermal Gravimetric Analysis (TGA) studies be conducted to determine the amount of volatile material that is released during the thermo-stabilization process. The value of the volatile material released can be identified if the TGA apparatus is coupled with an IR detector.

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APPENDIX A

ANALYSIS OF RAW EXTRACTS

Solids and Organic Contents

The total solids content of the extract was estimated by following TAPPI standard T-650. In this method, an aliquot of the sample was taken and its mass measured (m_T). The aliquot was then evaporated to dryness over a hotplate at 105 °C and the remaining “solids” measured (m_S). The solids content (x_S) was estimated from Equation A.1.

$$x_S (\%) = \left(\frac{m_S}{m_T} \right) * 100 \quad (\text{Eq. A.1})$$

The ash content (x_{Ash}) in the residual solids was estimated by following TAPPI Standard T211. In this method the total residual solids in the sample (m_S) were combusted at 525 °C overnight in a muffle furnace to determine the mass of the ash material in the sample (m_{Ash}). The ash content (x_{Ash}) was estimated from Equation A.2.

$$x_{\text{Ash}} (\%) = \left(\frac{m_{\text{Ash}}}{m_S} \right) * 100 \quad (\text{Eq. 4.3})$$

It was assumed that all of the inorganic material in the sample was sodium. The temperature of 525 °C was selected to avoid decomposition of sodium carbonate. The measured ash contents was assumed to be sodium carbonate and corrected to only sodium. The organics content (x_O) of the extract was taken to be the difference in mass of the residual solids (m_S) after correcting for the molecular weights of sodium (M_{Na}) and sodium carbonate ($M_{\text{Na}_2\text{CO}_3}$) as shown in Equation A.3.

$$x_o (\%) = \left[1 - x_{\text{Ash}} * \left(\frac{2 * M_{\text{Na}}}{M_{\text{Na}_2\text{CO}_3}} \right) \right] * 100 \quad (\text{Eq. A.3})$$

Lignin Content

The lignin content was estimated by measuring both the amount of acid-soluble and acid-insoluble (Klason) lignin (Equation A.4). The Klason lignin content was determined by following the gravimetric method proposed by Effland (1977) which is a modification of TAPPI Standard T-222. Carbohydrates were removed from the samples by primary and secondary hydrolysis concentrated sulfuric acid. The acid soluble lignin was determined by following TAPPI Useful Method U250. Acid soluble lignin was determined spectro-photometrically by measuring the transmittance of undiluted hydrolyzate at 205 nanometers. The total lignin content (L_{total}) was estimated from the Klason (L_{Klason}) and soluble (L_{Soluble}) lignin contents.

$$L_{\text{Total}} = L_{\text{Klason}} + L_{\text{Soluble}} \quad (\text{Eq. A.4})$$

Acetyl Group Content

During the extraction process acetyl groups (CH_3CO) bonded to the O-acetyl-4-O-methylglucurono- β -D xylan (Figure A.1) were cleaved by hydrolysis reactions (Sjostrom, 1993). The acetyl groups appear in the extract as both the acetate ion (CH_3COO^-) and as acetic acid (CH_3COOH) depending upon the pH of the extract. The total content of extracted acetyl group was analyzed by High Performance Liquid Chromatography (HPLC) at the University of Maine.

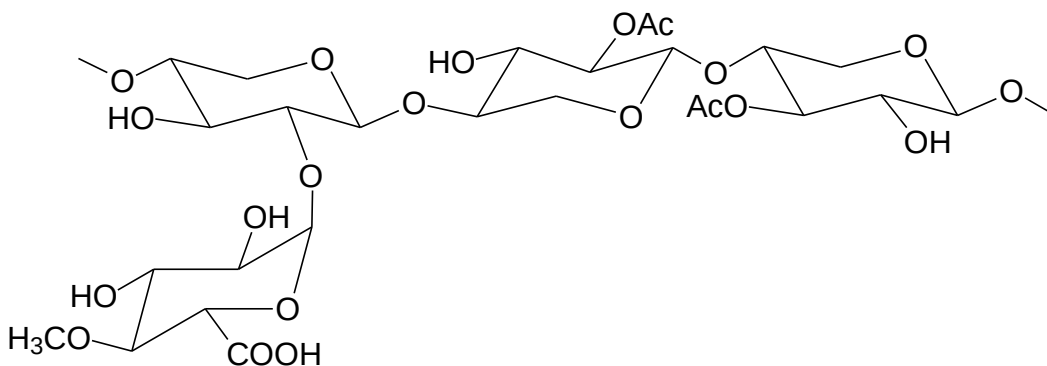


Figure A.1 Principal Structure of Glucuronoxylan

Uronic Anhydride Content

The uronic anhydride content in the hemicelluloses extraction was determined by using the chromophoric group analysis following a two-step acid hydrolysis treatment developed by Scott (1979). In this method dimethylphenol is used as a standard and the content of uronic anhydride is calculated from the difference in UV absorption measurements made at wave lengths of 400 and 450 nm.

Sugar Content

The component sugars composition the hemicellulose polymer in the extract were measuring using High Performance Anion Exchange Chromatography with Pulse Amperometric Detection (HPAEC-PAD) instrument by following the method developed by Tunc (2008). The sugars were determined following after standard hydrolysis with 4% sulfuric acid. Fucose was used as an internal standard to calibrate the hydrolyzed sugar content. A standard pulp obtained from the Pulp and Paper Research Institute of Canada

(PAPRICAN) with known sugar content was also analyzed at the end of each analysis sequence to validate the accuracy of the HPAEC instrument.

Material Balance on Wood

Partially Macerated Wood. Following the extraction process, the partially macerated wood was removed from the digester, dried completely and its mass (m_{Ext}) determined. A sample of the partially macerated wood was then ground and the ash content ($x_{\text{wood_ash}}$) estimated by combustion in a muffle furnace at 900 °C. The ash-free yield of macerated wood following extraction (Y_{Ext}) was then estimated by comparing the mass of oven dry wood before (m_o) and after (m_{Ext}) hemicelluloses extraction by using Equation A.5 and correcting for the sodium adsorbed in the wood during the extraction process.

$$Y_{\text{Ext}} (\%) = \left(\frac{m_{\text{Ext}} * (1 - x_{\text{wood_ash}}) (\text{o.d.}) (\text{g})}{m_o (\text{o.d.}) (\text{g})} \right) * 100 \quad (\text{Eq. A.5})$$

Extracted Wood Solids. The mass of extracted wood solids was estimated from material balance calculations as shown in Figure A.2.

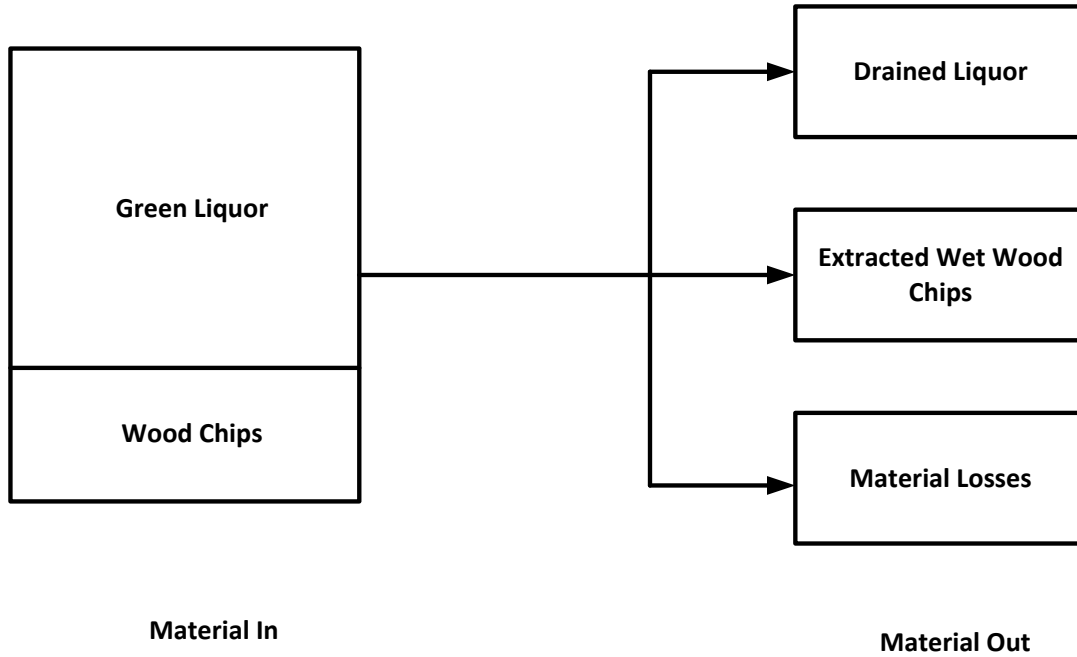


Figure A.2 Material Balance Used in Extraction Experimental

The total mass in the digester prior to the extraction ($m_{\text{In_digester}}$) was taken to be the mass of dry wood (m_o) plus the mass of green liquor added to the digester (m_{GL}) (Equation A.6). In addition the mass of water in the wood (m_{water}) was taken into account when performing the material balance. This gave a liquor to wood ratio of 4 to 1.

$$m_{\text{In_digester}} = m_o + m_{\text{GL}} + m_{\text{water}} \quad (\text{Eq. A.6})$$

The recovered mass following the extraction ($m_{\text{Recovered}}$) was taken to be the mass of drained liquor (m_{DL}) plus the mass of extracted wet wood ($m_{\text{Ext_Wet_Wood}}$) which included the dissolved solids in the liquor remaining in the partially macerated wood (Equation A.7).

$$m_{\text{Recovered}} = m_{\text{DL}} + m_{\text{Ext_Wet_Wood}} \quad (\text{Eq. A.7})$$

The recovered mass following extraction ($m_{\text{Recovered}}$) does not include losses that occur in the piping system and a small amount of water that was lost as steam when the

extraction vessel was opened. These losses were designated as a process residual (R_{Loss}) and were estimated as the difference between the initial mass in the digester ($m_{In_digester}$) and the total mass recovered ($m_{Recovered}$) (Equation A.8).

$$R_{Loss} = (m_{In_digester} - m_{Recovered}) = (m_o + m_{GL} + m_{water}) - (m_{DL} + m_{Ext_Wet_Wood}) \quad (\text{Eq. A.8})$$

The difference between the mass of wet wood ($m_{Ext_wet_wood}$) following extraction and the dry mass of extracted salt free wood ($m_{Ext_Dry_Wood}$) represents the mass of liquor remaining in the extracted wood chips (m_{Liquor_Chips}) (Equation A.9).

$$m_{Liquor_chips} = (m_{Ext_Wet_Wood} - m_{Ext_Dry_Wood}) \quad (\text{Eq. A.9})$$

The mass of extracted wood was taken to be the organic content in the mass of drained liquor (m_{DL}) plus the organic content in the mass of liquor in the extracted chips ($m_{Ext_wet_wood} - m_{Ext_Dry_Wood}$) plus the organic content in the mass in the residual liquor (R_{Loss}) (Equation A.10).

$$\% \text{ Extracted Wood} = \left[\frac{(m_{DL} + m_{Liquor_chips} + R_{Loss}) \times x_o}{m_o} \right] \quad (\text{Eq. A.10})$$

In the estimation of the amount of extracted wood, it was assumed that the organic content in the drained liquor (x_o) equaled that in the chips and in the lost liquor in the piping.

APPENDIX B

PRELIMINARY EXPERIMENTS

Initial Lignin Separation Method

A two-step lignin isolation method was employed to isolate lignin fractions from the hemicelluloses pre-extraction process (Figure B.1). A 200 gram sample of hemicelluloses extract (A) obtained in the 6% GL experiment was treated with differing amounts of two (2) molar sulfuric acid. The solutions of acidified extract had final pH values from approximately 7.11 to 1.0. After acidification, the temperature of the sample increased significantly because of the heat of solution. After cooling, the liquor samples were refrigerated and maintained at 4°C for 24 hours. This reduction in pH and temperature causes lignin to precipitate from the solution. At lower pH values, a greater mass of precipitate was recovered. Following the acidification and cooling steps, the precipitated lignin (B) was separated from the mixture by centrifugation at 8,000 rpm for 60 minutes. The precipitated solids (B) were then separated and washed with deionised water, centrifuged again at 8,000 rpm for 60 minutes, and lastly subjected to freeze drying to remove the water from the purified sample (C). The liquid sample, originating from the first centrifugation (D), was stored for future analysis that involved measuring the final pH and the total lignin concentration. The solid lignin fraction (C) was characterized according to the pH of the supernatant liquid (D), the total lignin, and the carbohydrate and carbon content in the solids samples.

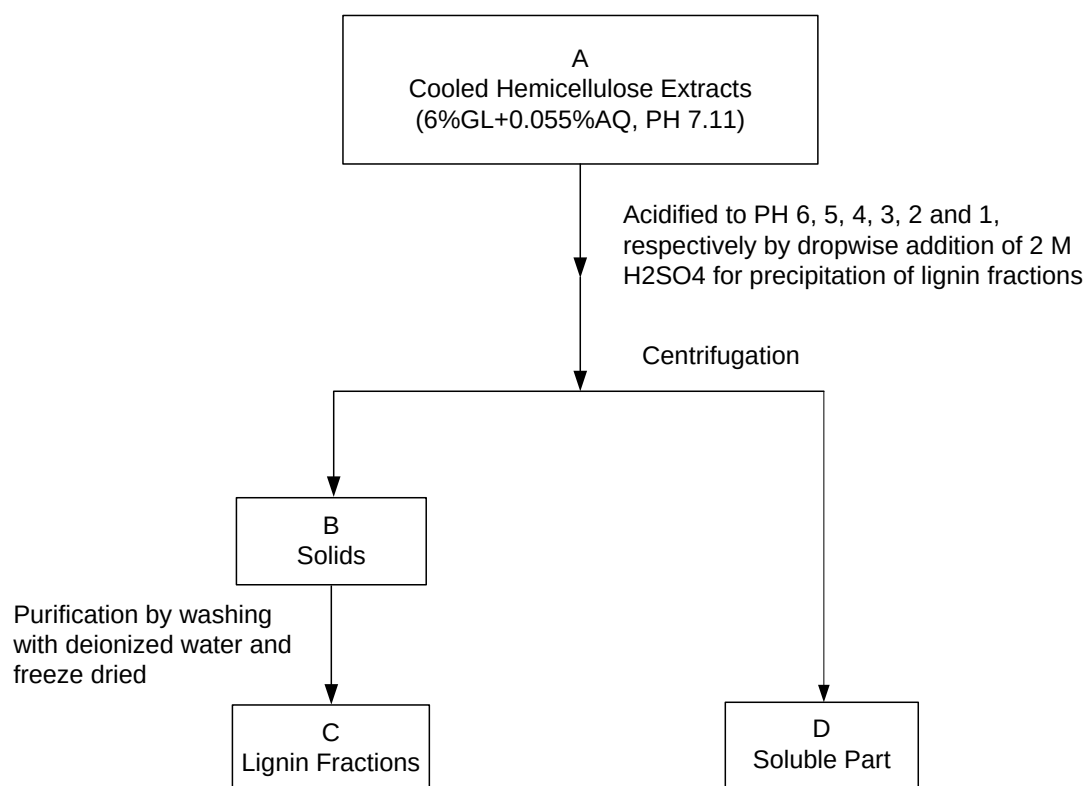


Figure B.1 Initial Protocol for the Isolation of Lignin from Hemicelluloses Extracts

Effect of pH on Separation of Lignin

Photographs of the various samples following acidification are shown in Figure B.2 for the initial lignin isolation experiments. The color of the samples became lighter at the lower pH values. Figure B.3 samples following acidification, storage at 4 °C and centrifugation at 8000 rpm for 60 minutes. The solids removed by this procedure are clearly visible in the centrifugation tubes (Figure B.3).

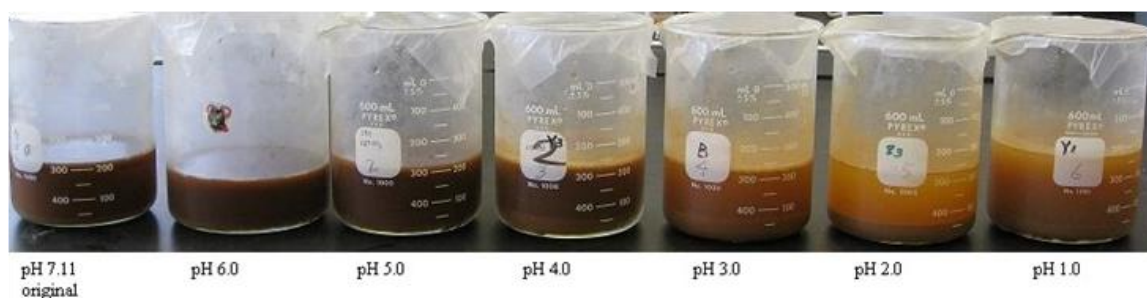


Figure B.2 Separation of Lignin Precipitated on Different pH Values (6% GL)



Figure B.3 Separation of Centrifuged Lignin Precipitated on Different pH Values (6% GL)

Table B.1 summarizes the lignin concentration and total solids for the solid (C) and liquid (D) fractions obtained using the isolation method illustrated in Figure B.1. The total lignin concentrations (C+D) of the 6% green liquor extracts were varied but less than 9.24 g/L. It was thought that some of the lignin was lost during the isolation process.

Table B.1 Summary of Lignin Separation from the 6% Green Liquor Extracts
(Normalized to 1 Liter of Extract)

pH of Acidified Samples	Liquid Phase (D) Soluble Lignin Concentration (gm/L)	Solid Phase (C) Total Lignin Concentration (gm/L)	Total Lignin (C)+(D) Concentration (gm/L)	Total Solid Concentration (gm/L)
7.11 (Raw Sample)	NA	NA	9.24	52.28
7.11(Raw Sample after Centrifugation)	6.76	0.81	7.56	1.04
6.0	6.72	0.70	7.43	1.21
5.0	6.26	1.51	7.78	2.41
4.0	5.12	1.92	7.04	3.14
3.0	4.57	3.15	7.72	4.99
2.0	4.33	3.16	7.49	4.71
1.0	5.25	2.97	8.22	4.77

The total lignin concentration in the solid phase (C) and the total soluble lignin concentration in the liquid phase (D) are shown as a function of the pH in Figure B.4. The total lignin concentration in the solid phase varied from 0.81 gm/L of extracts at pH 7.11 to 3.16 gm/L of extracts at pH 2.0. The total soluble lignin concentration in the liquid phase varied from 6.75 gm/L of extracts at pH 7.11 to 4.33 gm/L of extracts at pH 2.0. As the pH of the 6% green liquor extracts was decreased from 7.11 to 1.0, Figure B.4 clearly shows that the highest incremental amount of precipitated lignin occurred in the pH range between 4.0 and 3.0. For pH values lower than 2.0 the amount of precipitated lignin decreased, but not significantly. The sum of the lignin in the solid phase and the liquid phase was nearly constant, but lower than the total lignin contained in the original 6% green liquor extracts (9.24 gm/L). One explanation was that during the lignin separation process, some lignin was

lost during the washing that was not controlled. Also, the data show that more lignin existed as soluble lignin (D) than as precipitated lignin.

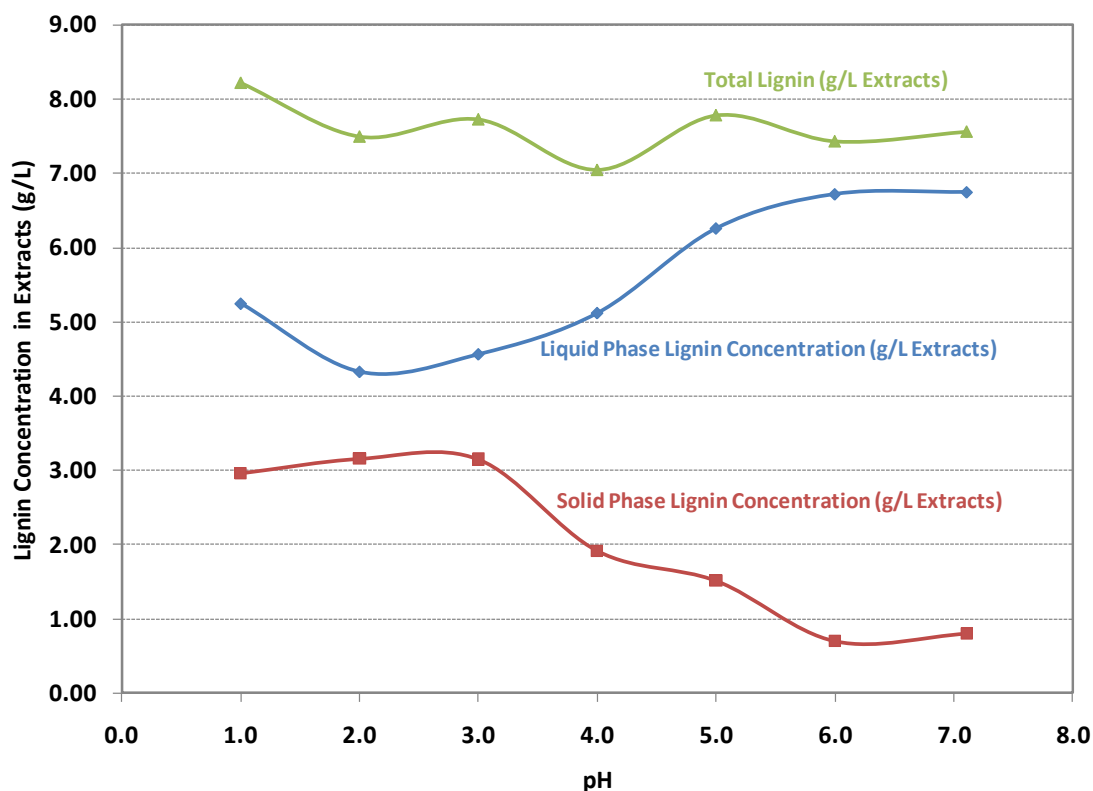


Figure B.4 Effect of pH on the Lignin Concentrations from 6% GL Extracts

The total lignin, carbohydrate, uronic anhydride and carbon contents were used to characterize the lignin purity at the various pH values (Table B.2). The lignin content in the solids was low and ranged between 58% and 77%. By contrast the carbohydrates content in the solids is very high and varied between 8.2% and 25.1%. The carbon content was estimated to be about 58%. This is lower than the carbon content of sinapyl alcohol, the primary hardwood lignin monomer, which is 63%. The carbohydrates in the solids lead to a lower total carbon content in the samples. Clearly, this lignin isolation method could not completely cleave the lignin-carbohydrates bond and is not suitable for recovery of lignin for use in the preparation of carbon fiber.

Table B.2 Summary of Composition Data for the Recovered Solid Samples

Sample	Lignin (%)	Carbon (%)	UA ^a (%)	Arabinan (%)	Galactan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Cellulose (%)	HemiCell (%)	Carbohydrates (%)	Material Recovery (%)
pH7.11 ^b	77.4	56.9	1.0	0.1	0.3	1.4	15.0	0.0	1.4	16.5	17.8	95.2
pH 6.0	58.0	56.1	1.3	0.1	0.2	1.2	22.1	0.0	1.2	23.8	25.1	83.1
pH 5.0	62.7	54.0	0.3	0.04	0.1	0.3	7.4	0.0	0.3	7.8	8.2	70.9
pH 4.0	61.1	52.6	1.9	0.3	0.4	0.5	18.5	0.0	0.5	21.2	21.8	82.9
pH 3.0	63.2	57.9	1.5	0.3	0.4	0.5	17.1	0.0	0.5	19.5	20.0	83.2
pH 2.0	67.2	58.3	1.7	0.3	0.5	0.5	18.4	0.0	0.5	21.0	21.5	88.6
pH 1.0	62.2	58.2	1.8	0.3	0.5	0.4	18.7	0.1	0.4	21.7	22.0	84.2
Paprican ^c	4.4	/	0.1	0.6	0.5	74.2	8.1	0.2	72.7	17.9	90.6	95.4

All components content are based upon the solid.
a UA Uronic anhydride
b Original sample after centrifuge
c Paprican Standard pulp (Ash 0.5%)

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Jie Luo was born in Zhengzhou, China on Oct. 18, 1979. She graduated from the No. 11 high school in 1998. She enrolled in Nanjing University of Science and Technology where she received her Bachelor of Science Degree in Chemical Engineering in 2002. Jie continued her studies at Nanjing University of Science and Technology and obtained a Master of Science Degree in Material Science and Engineering in 2004. Jie is currently studying at the University of Maine under the supervision of Professor Joseph M. Genco. Jie Luo is a candidate for the Master of Science degree in Chemical Engineering from the University of Maine in May, 2010.