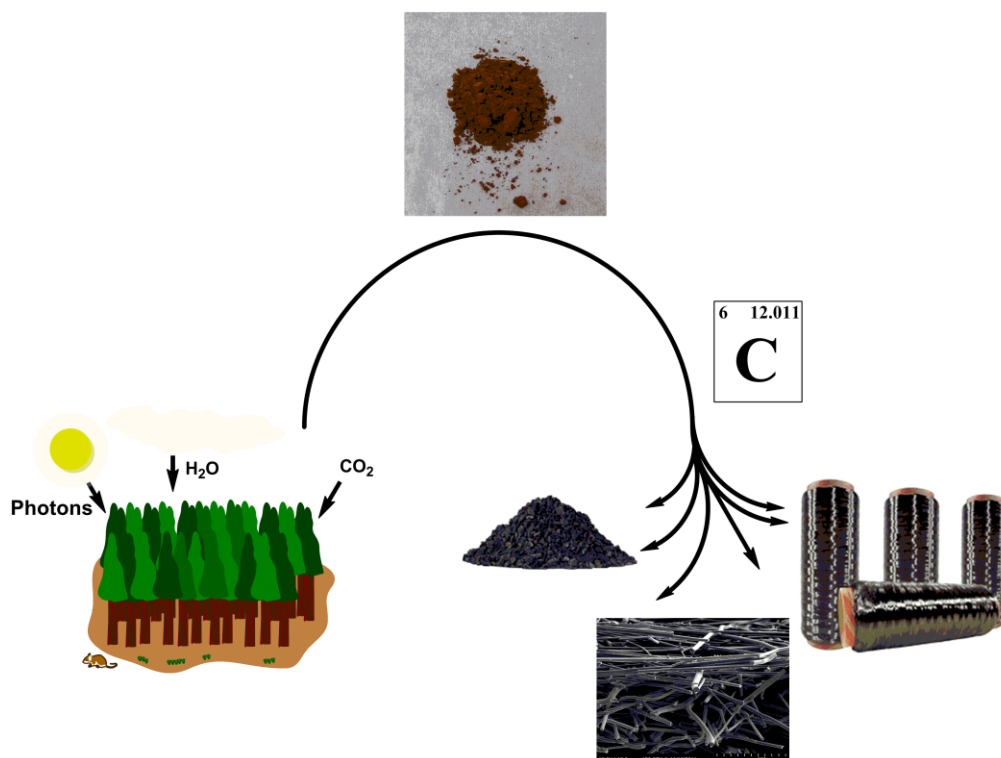


Lignin-Derived Carbon Materials

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Dedication ((optional))

Lignin is a highly abundant source of renewable carbon that can be considered as a valuable sustainable source of biobased materials. By application specific pretreatments and manufacturing method, lignin can be converted to a variety of value added carbon materials. However, the physical and chemical heterogenities in lignin complicate its use as a feedstock. In this review, lignin manufacturing process, effects of pretreatments and manufacturing methods on the properties of lignin, properties and applications of various lignin derived carbon materials such as carbon fibers, carbon mats, activated carbons, carbon films; are discussed.

1. Introduction

Lignin, the largest biomass source with aromatic property and a carbon content above 60%, can be considered as the most attractive sustainable precursor for carbonaceous materials.¹⁻⁷ The use of lignin for the production of bio-based commodity has minimum environmental effects. Additionally, this energy feedstock does not belong to the human food chain. Lignin constitutes of the major component of cell walls of vascular plants, which gives plants neutral resistance against chemical or microbial attack and protects plants from other environmental stresses.⁴ The amount of lignin differs among plant types. Generally, in woody plants, the amount of lignin is 15-40% of the plant weight, whereas in herbs, the amount of lignin is less than 15%.¹ The estimated natural production of lignin on earth is in the range of 5-36 X 10⁸ tons annually.⁵⁸ The annual production of commercial lignin is more than 70 million tons.⁹ Most commercial lignins are produced as side products in paper and pulping industries and in biorefineries.^{7, 9}

In recent years, a great deal of research has focused on the development of lignin derived carbon fibers, activated carbons, and many other carbonaceous materials.^{3, 9-14} Lignin is also used in commercial applications such as concrete additives, thermoplastic materials.^{5, 15} However, the use of lignin in different products other than as inexpensive fuel is still very limited due to lignin's heterogeneous molecular weight, functionality and thermal properties that vary with source and isolation process of lignin.^{1-2, 16-19}

In this review, synthesis, properties and applications of variety of lignin derived carbon materials such as carbon fibers, carbon mats, activated carbons, carbon films, etc. are discussed. In addition, lignin manufacturing process, effects of pretreatments and manufacturing methods on the properties of lignin materials are also discussed. There are several review papers on lignin composite materials.^{1, 20-21} A few reviews also present that are themed on a carbon materials derived from lignin.²²⁻²⁴ However, only a very limited literature (mostly book chapters) on lignin derived carbon materials are available that cover variety of lignin based carbon materials.²⁵ This review is designed to cover most of lignin based carbon materials and provide design guides for future carbonaceous materials from lignin.

2. Chemical compositions and physical properties of lignin

Lignin is an amorphous complex biopolymer with heterogeneous aromatic structure, derived mainly from *p*-coumaryl, coniferyl and sinapyl alcohols.^{2, 4} These alcohols or monolignols form lignin monomeric units *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) respectively (Figure 1).^{2-3, 16} In lignin macromolecule, these monomeric units are linked by variety of carbon-oxygen and carbon-carbon bonds such as β -O-4, 5-5, 4-O-5, β - β and so on where the β -O-4 is the most common one (Figure 2).^{1, 4, 26}

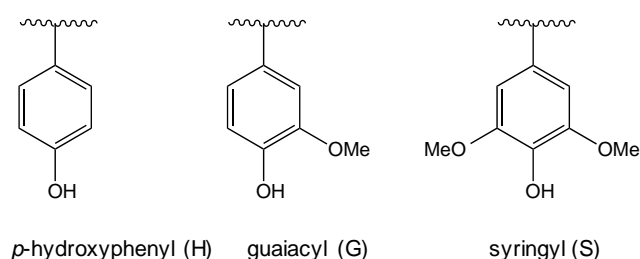


Figure 1. Structural units of lignin

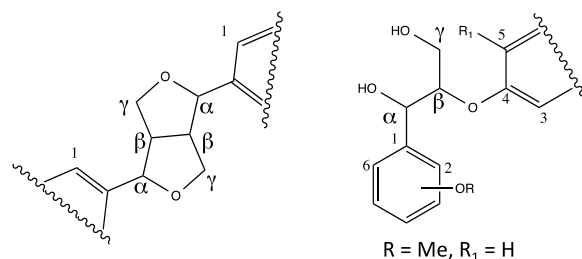


Figure 2. Common chemical bonds in lignin

The molecular weight and composition of any particular lignin type largely depend on the plant source and environmental and developmental factors. Properties of lignin also highly depend on the extraction procedure. Plant lignins can be divided mainly in three classes, commonly called softwood, hardwood and grass lignins.⁴ Softwood contains higher amount of lignin than hardwood, while grasses contain the least amount of lignin. The typical S/G ratios in hardwood and softwood lignins are 2:1 and 1:2-1:3, respectively.²⁷ Lignins from grasses have S/G ratio about 1:1-1:2.²⁷ Lignins from softwoods and grasses contain large amount of *p*-hydroxyphenyl (H) unit. The additional methoxy groups on the aromatic ring of syringyl (S) unit prevent formation of 5-5 or dibenzodioxocin linkages. For this reason, the formation of linear structures in softwood lignin is less favorable than hardwood lignin, where syringyl (S) unit is present in excess.^{1, 4, 26, 28}

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The majority of lignin is an amorphous thermoplastic polymer and has a glass transition temperature (T_g) in the melt-processible temperature range at 50-150 °C. Several other lignins possess T_g higher than 150 °C and a few reported cases even indicates higher value of T_g than the degradation temperature depending on the lignin isolation and processing method.^{5, 29} For example, one study reports that the T_g of native hardwood lignin is between 65 and 85 °C while that of softwood lignin is between 90 and 105 °C.¹⁸ In another example from our own previous study, solvent-extracted hardwood lignin showed T_g 108 °C⁵ while T_g of softwood Kraft lignin was 153 °C.²⁸

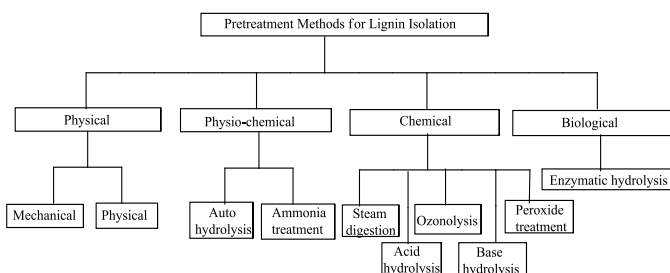
3. Lignin extraction from various sources

Extraction of pure lignin from plant sources has several challenges.² The challenges in isolating lignin from plants are primarily associated with the complex structure of the cell wall and the interactions of its components.¹⁹ In addition, lignin condensation and oxidation reactions occur during various isolation procedures, which makes the process complicated. Due to the highly linked structures of lignin and carbohydrates in plant materials, it is impossible to isolate pure lignin without any chemical mediated cleavages.²⁰ Isolation of lignin from plants can generally be pursued in two ways.²¹ In the first case, carbohydrate is hydrolyzed using enzymes and dissolved away from lignin, which is obtained as an insoluble material. In the second case, chemicals are used to dissolve lignin to separate from the cellulose fiber and the process produces the spent liquor known as the black liquor containing lignin. The second method is more often implemented commercially.

The first method typically involves a pre-treatment of the feedstock because enzymatic hydrolysis cannot be directly applied to woody biomass. Pretreatments are used to break the bonds between lignin and carbohydrates in the biomass. A variety of pretreatment methods such as ball milling, mechanical, acid treatments, alkali treatments, hydrogen peroxide treatment, or enzymatic hydrolysis are used to separate carbohydrates and lignin (Scheme 1).^{4, 16, 25} All pretreatments decrease the size of biomass and disassemble its physical structure to be amenable to its post treatments. In most cases, these pretreatments also alter the chemical structure of lignin. Lignin carbohydrate bonds are more stable than various bonds in lignin. Therefore, for example, the use of acid treatment to obtain lignin results not only in extensive cleavage of lignin carbohydrate bonds, but also cleavage of certain amounts of lignin-lignin ether bonds. In the case of acid pretreatments, lignin undergoes depolymerization through the cleavage of β -O-4 and other bonds. At the same time, electrophilic attacks of side chain carbonium ions to aromatic rings occur, which form a new set of carbon-carbon bonds. This bond formation reverses the depolymerizations of lignin and generates new condensed phases in the lignin matrix. On the other hand, a decrease in the acidity of the solvent to avoid degradation of lignin structures results in lignin with a high amount of carbohydrates. Mechanical pretreatments also alter lignin's chemical structure by increasing the amount of carbonyl and phenolic-OH groups and cleaving the β -O-4 linkages.^{4, 16, 25} After pretreatment, the resulting biomass is treated with

enzymes, which hydrolyze cellulose and produce lignin. The produced lignin is then further purified.

The second method of lignin isolation uses chemical reagents to isolate lignin from carbohydrates. Based on the reagents used, lignins generated in this process can be broadly divided into two types, 1) sulfur containing lignins such as kraft lignin and, 2) non-sulfur containing lignins such as soda lignin and organosolv lignins.²⁸ It should be noted that sulfur-containing lignins are more commercially available worldwide than the non-sulfur lignins. Some chemical pulping processes are briefly described in the following section.



Scheme 1. Different Pretreatment methods used in lignin isolation

3.1. Acid sulfite process

In this process, salts of sulfurous acid are used as reagents which add sulfonic acid groups to the lignin backbone. This process makes the lignin water-soluble. The degraded lignin is dissolved out from carbohydrates and forms a dark pulp.

3.2. Alkaline kraft process

In kraft process, lignin is treated with a solution of sodium hydroxide and sodium sulfide at relatively high temperature (170°C). During the treatments, ether linkages are cleaved, which consequently increases the number of phenolic hydroxyl groups. This treatment also breaks lignin and decreases its molecular weight. Further, thiol groups are incorporated into lignin in this process. Due to the presence of alkaline medium in the treatment, the phenolic groups on lignin get ionized which in turn dissolves the lignin in water and forms a dark pulp.

3.3. Organosolv process

In case of organosolv process, pulping feedstock in organic solvents with acidic or basic catalysts produces lignin. This process is more environmentally friendly than kraft or sulfite process because in this case, solvents can be recovered and reused. This method efficiently fractionates biomass into lignin, cellulosic fibers, and hemicellulosic sugars.

3.4. Soda pulping

A soda pulping is mainly used for non-wood fibers such as grass, straw, sugarcane bagasse, etc. that have relatively open and more accessible structures with low lignin content. The feedstock is digested at around 160 °C with an aqueous solution of sodium hydroxide. In this case, lignin depolymerization occurs by the cleavage of β -O-4 bonds, which first starts in phenolic units and then continues in non-

phenolic units at a later phase of lignin degradation. These reactions generate free phenolic groups, which under alkaline conditions ionize and facilitate dissolution of lignins in the alkaline solvent.

In later steps, different methods such as extraction and precipitation with different solvents are used to collect lignin from the lignin solution. Lignin is also collected using acid or enzymatic hydrolysis. This hydrolysis method works better and gives high yield of lignin in the case of softwood kraft pulp.^{4, 16, 25}

It should be noted that, most of these methods were initially developed with a goal to achieve high quality cellulose with great yields and thus less attention has been given to the production of pure lignin with native structure. Almost all extraction processes change the structure of the isolated lignin, making it difficult to produce homogeneous pure lignins for industrial applications.

4. Effects of manufacturing processes on properties of lignin

Lignin's molecular weight, physical and chemical properties largely depend on the source and the isolation methods of the lignin. The combined impact of the pretreatment method and the extraction procedure on the properties of lignin is dominant over the effect of the lignin source. Different researchers reported the effect of extraction procedure on lignin's molecular weight. Wörmeyer et al. studied an effect of different pretreatment methods on the properties of rye straw lignin.³⁰ They studied straw and Alcell organosolv lignin, soda pulp lignin, and three Aquasolv lignins (obtained by a combination of thermal hydrolysis and enzymatic hydrolysis procedures) such as Aquasolv liquid (AL), Aquasolv solid (AS) and dioxane extracted Aquasolv solid (DAS) along with liquid hot water processed (LHW) (obtained by hydrothermal process) lignins. They found the LHW and the DAS lignin contained the highest amount of acid insoluble lignin or solid lignin followed in descending order by the soda, the organosolv, the AL and the AS lignins (Figure 3). Carbohydrate content was high in both straw organosolv (7% w/w) and AS (13.2%) lignins that makes the AS lignin less suitable for various material applications. When molecular weights of all lignins using Size Exclusion Chromatography (SEC) were compared, straw organosolv lignin was found to have the highest weight-average molecular weights (M_w) followed by the soda lignin, DAS and AL lignins (Table 1).

The thermal stability of these lignins by thermogravimetric analysis (TGA) showed comparable degradation with increase of temperature (Figure 4a), however, T_{mdS} (Temperature of maximum decomposition) of these lignins are varied. Interestingly, the AS lignin, DAS lignin and LHW lignin's solid residue based samples have higher T_{mdS} (Figure 4b) than corresponding liquid fraction based products. Also, solid residue based lignin samples showed different weight loss trend than the liquid fraction based samples. LHW lignin was found to lose less weight than other straw based lignin and degraded only at high temperature. In a comparison study, T_{mdS} of S lignin, DAS lignin and LHW lignin were found to surpass the T_{md} of novolac resin. These studies clearly showed that the pretreatment affects on the thermal stability of the produced lignin.

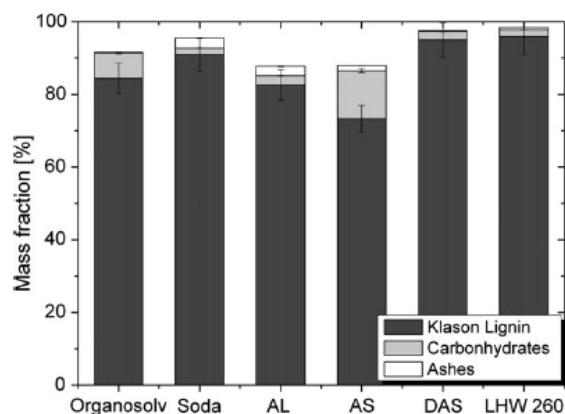


Figure 3. Composition of the produced straw lignin products³⁰

Table 1. Molecular weight of lignin products obtained using SEC.³⁰

Lignin type	M_w (g/mol)	M_w/M_n
Alcell Organosolv lignin	2390	2.9
Straw Organosolv lignin	8680	5.1
Soda lignin	8000	4.8
Aquasolv lignin	2600	3.1
Dioxane extracted Aquasolv solid lignin	7080	4.0

Sun et al. studied the effect of extraction procedures on the molecular weight of wheat straw lignin.³¹ In this study, alkali lignins, ball-milled lignins, enzyme lignins and organosolve lignins were prepared and molecular weights of these lignins were studied by SEC. The result showed the alkali lignin, milled lignin, enzyme lignin and organosolv lignin were composed of lower molecular weight lignin fragments. The M_w of enzymatic lignin, ball-milled lignin, organosolv lignin and alkali lignin were 2020, 1890, 1640 and 1400 g/mol, respectively, which corresponded to the reducing contents of associated polysaccharides in the isolated lignin fractions.

In another study, Toledano et al. explored the influence of extraction treatment on the olive tree pruning lignin structure.³² In this case, organosolv treatment, alkali treatment and autohydrolysis treatment were performed to isolate lignin. Different processes produced lignin with varying concentration (g/L) such as organosolv lignin (55.5), autohydrolysis lignin (0.59), alkali treated lignin (31.8) with purity of 65.8%, 26.9% and 4.5% respectively. Autohydrolysis lignin was found to have the lowest M_w , while Organosolv lignin had the highest molecular weight (Table 2). Additionally, autohydrolysis lignin and organosolv lignin were found to have higher contents of hydroxyl groups. Alkali treated lignin contained lower hydroxyl group content but high carboxyl group indicating alkali treatment promoted oxidation reactions. High carboxyl content can be related to more degradation in lignin structure. Organosolv lignin was found to have the lowest carboxyl group content.

In a recent work, Saito et al. prepared the high molecular weight lignin fraction via formaldehyde crosslinking,^{5, 29} while as-received lignin contained a significant amount of low molecular weight fraction. The crosslinked high molecular weight fraction of lignin showed a much higher T_g than that of as-received lignin.

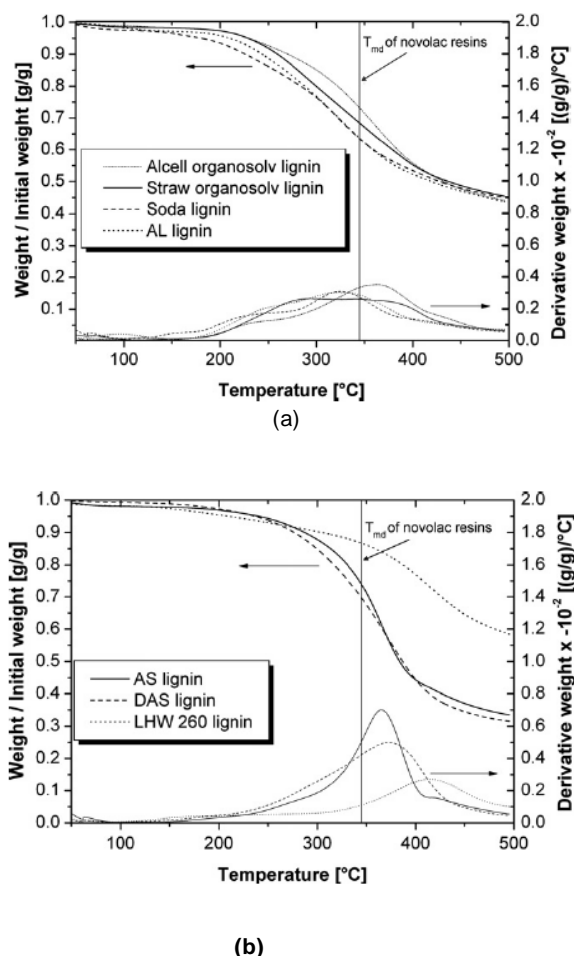


Figure 4. (a) TGA of Alcell organosolv lignin, straw organosolv lignin, soda lignin and aquasolv liquid lignin.³⁰ (b) TGA of aquasolv solid lignin, dioxane extracted aquasolv solid lignin and liquid hot water processed lignin.³⁰

Table 2. Functional group contents and M_w , M_n and polydispersity (M_w/M_n) of alkali lignin (AL), hydrolysis lignin (HL) and organosolv lignin (OL).³²

Functional Groups	Alkali treated lignin	Hydrolysis lignin	Organosolv lignin
Hydroxyl	2.62 ± 0.05	10.12 ± 0.18	9.81 ± 0.04
Carbonyl	0.12 ± 0.01	0.53 ± 0.01	0.24 ± 0.01
Carboxyl	6.57 ± 0.07	7.15 ± 0.12	4.03 ± 0.08
Molecular Weight (g/mol)			
M_w	10,900	3660	12,900
M_n	4930	2120	2250
M_w/M_n	2.21	1.73	5.74

The key for the successful synthesis of lignin-based thermoplastic copolymers in these studies was the utilization of the high molecular weight lignin fraction to produce an efficient connection between the hard segment (i.e. lignin) and the soft segment. The initial study⁵ not only showed effectiveness of the formaldehyde crosslinking but also the increase of lignin molecular weight and T_g by methanol (MeOH) fractionation. The effect of methanol fractionation was further investigated in the most recent article.²³

Solvent fractionation to increase molecular weight and T_g is a more facile approach than performing a formaldehyde crosslinking reaction; however, the initial study on MeOH fractionation of hardwood-based solvent extracted lignin showed very small isolated yield of MeOH insoluble lignin (17%).^{5,33} Switching to the lignin source from a hardwood-

based solvent extracted lignin to a softwood kraft lignin, the yield of MeOH insoluble lignin increased to 50%²³ due to the increased amount of high molecular weight and MeOH insoluble fraction in the softwood Kraft lignin.

In the study of methanol fractionation of softwood Kraft lignin,²³ the MeOH insoluble lignin showed much higher T_g (211 °C) than as-received lignin (153 °C) due to the removal of a low molecular weight (LMW) fraction, which appeared at higher retention time in DMF SEC without LiBr (Figure 5a), while MeOH soluble lignin showed an increased LMW fraction and a lower T_g (117 °C) compared to the as-received lignin (Table 3). The difference of T_g over the range of roughly 100 °C from the same batch of the sample is quite significant and no other conventional polymers possess this kind of characteristic. More importantly, the trend of these T_g values agreed very well with the Fox equation using the LMW area from RI peaks in SEC (Figure 5a) converting to the weight fraction (Figure 5b), which indicates that the LMW lignin oligomer fraction contributes to lowering its T_g , and the estimated T_g of LMW fraction from the Fox equation was -89 °C. The Fox-equation-derived T_g value of oligomeric lignin was so low that it justified the plasticization effect by the LMW lignin fraction. The capability to tailor the T_g of lignin is extremely important for its processing in applications such as carbon fiber precursors because it directly correlates to the melt-processing temperature or the stabilization conditions prior to carbonization.

The amount of LMW fraction also correlated well with the char yield through a linear regression (Figure 5b), i.e. an increase in the LMW fraction decreased its char yield (Table 3). High char yield of MeOH insoluble lignin is advantageous for using lignin as a carbon precursor. Although the lignin peak from SEC data from neat DMF most likely represents both single lignin molecules and lignin aggregates in DMF, the data correlated very well with other physical properties and the resulting significantly high PDI rather represents heterogeneities existing in lignin sample. Single, monomodal peaks of these lignin samples obtained in the case of DMF SEC with LiBr (Table 3) indicates that the size of lignin corresponds to a single distribution, but combined results of DMF SEC both with and without LiBr suggested that the chemical structure and compositions among as-received, MeOH insoluble, and MeOH soluble lignins are significantly altered. It should be noted that researchers tend to report low lignin molecular weight with single monomodal distribution, similar to the data from RI detector in DMF SEC with LiBr in this study, however, absolute molecular weight from light scattering detector was significantly higher and conventionally reported narrower PDI does not reflect property of lignin.

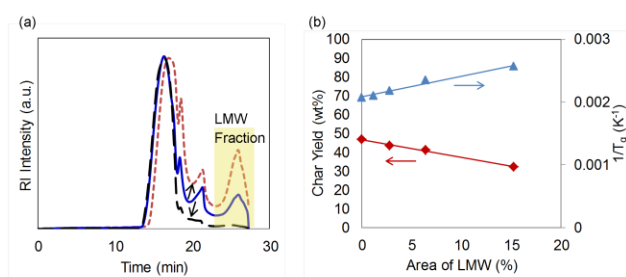


Figure 5. (a) SEC curves of As-received Lignin (—), MeOH Insoluble Lignin (---), and MeOH Soluble Lignin (·····), (b) The linear regression of char yield and $1/T_g$ as a function of LMW fraction from the SEC curve.²³

Table 3. T_g obtained from DSC, thermal degradation properties obtained from TGA, and molecular weight of lignin via MeOH fractionation²³

	T_g [°C]	Residual wt % at 1000 °C	$M_n^{[a]}$ [g/mol]	PDI ^[a]	$M_n^{[b1]}$ [g/mol]	PDI ^[b1]	$M_w^{[b2]}$ [g/mol]
As-received lignin	153	41	10,000	110	2,360	3.05	96,100
MeOH insoluble lignin	211	47	443,000	3.5	6,520	2.28	188,000
MeOH soluble lignin	117	32	3,800	129	1,590	1.90	86,600

[a] DMF SEC without LiBr, Determined from refractive index detector

[b1] DMF SEC with LiBr, Determined from refractive index detector

[b2] DMF SEC with LiBr, Determined from light scattering detector

These molecular weight analyses in conjunction with T_g and char yield data raise a good question to the research field about what properties researchers measure for lignin samples in SEC analysis, e.g., monomodal distribution might not mean much due to the heterogeneity of lignin samples. This study also investigated the chemical composition and LMW-containing MeOH soluble lignin revealed higher contents of aliphatic carbon and guaiacyl groups and a lower content of aliphatic hydroxyl groups, which corresponded to lowering its T_g and char yield.

5. Lignin production: from tree to carbon material precursor

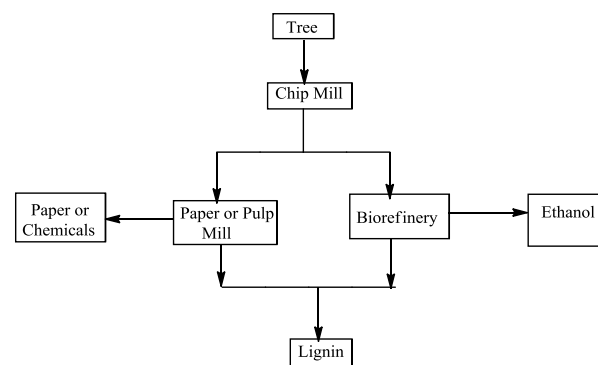
Lignin is a good precursor for graphitic structures because of its highly aromatic structural contents. Based on the precursor type, carbon materials can be divided broadly in three types, graphite type, diamond type, and amorphous type. Lignin-derived carbon can be considered as an amorphous carbon with domains of microcrystalline graphite, which are randomly stacked with a turbostratic structure.³⁴⁻³⁵

Lignin-derived carbon material manufacturing processes typically involve several steps (Scheme 2).³⁶ At first, trees (or other plants) are harvested in different fields depending on the types. At one point of tree's lifecycle, it is collected and transported to a chip mill for conversion to wood chip to use as a feedstock by either a bio-refinery or pulp or paper mill. At the bio-refinery, lignin is dissolved away from cellulose into black liquor and ethanol is produced from the cellulose present in the wood chips. At the pulp mill, lignin is also dissolved away from cellulose into black liquor and the cellulose is used for the productions of paper and chemicals. Finally, in both cases, the lignin is collected from the black liquor by precipitation. The obtained lignin is then washed and dried. The dried lignin is packed either in powder or pellet forms which are then used in variety of applications.

6. Lignin-derived carbon materials

6.1. Structural carbon fibers

Carbon fibers are high performance materials with salient properties of high stiffness, great tensile strengths, elevated temperature tolerance, low thermal expansion, lightweight, high flexibility, and high fatigue resistance.^{3, 10-12, 14-15, 22, 37-40} These properties make carbon fibers important component in advanced composites for a variety of industries, including aerospace, civil engineering, automotive and wind power applications. Many of these enhanced material properties can be correlated to the orientation of graphite layers, which are mostly aligned parallel to the long axis of the fiber. The properties of carbon fibers largely depend on the precursor materials. Currently, carbon fibers are mainly manufactured from polyacrylonitrile (PAN) precursor and to a small extent from mesophase pitches, which make carbon fibers expensive due to the high volatile price of the petroleum based feedstock and corresponding processing expenses.^{22, 39} Thus, there is a huge demand for a low cost carbon fiber precursor material, which can be converted to decent quality carbon fiber.



Scheme 2. Flow chart for the commercial production of lignin.

Lignin is a non-petroleum-based alternative carbon fiber precursor, which is renewable and abundant. Lignin as a precursor for carbon fiber production has been studied for more than 50 years. A detailed history of past and current research on lignin based carbon fiber are discussed in a 2013 review paper.²² Thus, this article will mention only a few research milestones of lignin carbon fiber research.

Otani et al. reported methods of making lignin based carbon fibers by melt spinning and dry spinning of lignins in 1966.⁴¹ He also patented a process to manufacture carbon fibers from lignin in 1969. Lignin based carbon fibers were first made commercially by Nippon Kayaku Co.^{22, 39} The process involved carbonization of dried fibers made from lignin dissolved in an alkali solution with polyvinyl alcohol which was added as a plasticizer. Sudo and co-workers showed that lignin could be converted into a molten viscous material with suitable properties for thermal spinning by hydrocracking, phenolation, or hydrogenolysis followed by heat treatment on vacuum.^{13, 42} They described a process for the production of carbon fiber from hardwood lignin in which steam explosion technology was used to isolate lignin from birch wood. In this process, the steam-exploded lignin was hydrogenated using a Raney Nickel catalyst to lower its softening point to 110 °C and modify the lignin to improve melt spinnability. Comparing the chemical structure of the precursor to the crude lignin, it was found that precursor contained significantly less amount of aliphatic functional groups than the original starting material. Lignin carbon fibers made in this process was found to have diameter approximately 7.6 μm with tensile strength of 0.660 GPa. The

fibers had modest mechanical properties with moderate tensile strength. Uraki et al. worked on the production of carbon fibers from birchwood derived organosolv lignin obtained by aqueous acetic acid pulping.⁴³ The fiber was made by melt-spinning the clean and dried lignin. The produced carbon fibers with a $14 \pm 1 \mu\text{m}$ diameter showed tensile strength of about 0.035 GPa and modulus of about 39.1 GPa.

Kadla et al. reported preparation of carbon fibers from various lignins.^{12, 14, 44} In their study, when Alcell lignin, hardwood kraft lignin and softwood kraft lignin were compared as lignin fiber precursor, it was found that the softwood kraft lignin could not be spun into lignin fiber, charring occurred before melting. On the other hand, both Alcell and hardwood kraft lignin were found to be melt-spinnable to make lignin fiber. Alcell lignin showed lower spinning temperature than the hardwood kraft lignin (Table 4.). Kadla investigated the applicability of lignin-polyethylene oxide (PEO) blends as precursors for the production of carbon fibers. In this work, a blend of commercially available unmodified kraft hardwood lignin and polyethylene oxide (PEO) was used to make moderate strength carbon fibers by thermal spinning followed by carbonization (Table 5). Use of PEO facilitated the fiber spinnability but did not significantly alter the properties of the fiber. In another work, this group made carbon fibers from bio-oil derived pyrolytic lignin by thermal spinning followed by carbonization. Pyrolytic lignin showed melt spinnability at a lower temperature than other technical lignins (Table 6). Fibers generated in this process were found to have hollow structures and these fibers were prone to fiber-fiber fusion during thermal stabilization probably due to low softening temperature.

Table 4. Spinning temperatures of lignin/polyethylene oxide (PEO fiber) blends¹⁴

Lignin/ PEO blend	Hardwood kraft lignin (°C)	Alcell lignin (°C)
100/ 0	195-228	138-165
95/ 5	189-198	153-172
87.5/ 12.5	191-200	138-172
75/ 25	150-182	120-157

Table 5. Mechanical Properties of carbon fibers from hardwood kraft lignin, hardwood kraft and PEO blend and Alcell lignin¹⁴

Lignin	Diameter (μm)	Tensile-strength (MPa)	Modulus (GPa)
Hardwood Kraft	46±8	422±80	40±11
Hardwood kraft/ PEO (100K) 95/5	46±3	396±47	38±5
Hardwood kraft/ PEO (600K) 95/5	63±7	339±53	33±53
Alcell	31±3	388±123	40±14

Table 6. Spinning temperature and T_g of pyrolytic, Alcell and kraft lignins⁴⁴

Lignin	Spinning temperature (°C)		T_g (°C)	M_w (PDI)
	Zone 1	Zone 2		
Kraft	170	202	131	1256 (2.2)
Alcell	130	158	77	790 (2.5)
Pyrolytic	105	125	70	702 (2.3)

Kubo reported the application of a variety of lignin-synthetic polymer blends as precursor material for the production of carbon fiber. Fibers made from unmodified hardwood kraft and organosolv lignin were found to be brittle. The use of blends of lignin and synthetic polymers such as poly (ethylene terephthalate) (PET), PEO and polypropylene (PP) was found to reduce the brittleness and showed improved tenacity (Table 7).

Table 7. Mechanical Properties of hardwood kraft lignin, hardwood kraft and PEO blend and Alcell lignin¹⁴

Lignin	Diameter (μm)	Tensile-strength (MPa)	Modulus (GPa)
Hardwood Kraft	46±8	605	41
Hardwood kraft/ polypropylene 95/5	47±5	332	57
Hardwood kraft/ polyethylene terephthalate 95/5	31±5	669	84

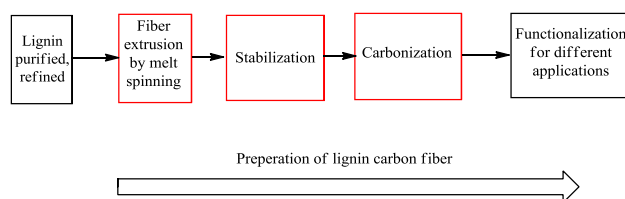
In recent years, considerable research effort has contributed to the production of carbon fiber from lignin at the Oak Ridge National Laboratory (ORNL). Baker et al. at ORNL investigated lignin and its blends as low-cost, high-production volume feedstock for carbon fiber. They found difficulties in the melt spinning of as-received hardwood kraft lignin, where the melt spinning of organic-solvent-washed hardwood kraft lignin was easily performed.²² The carbon fibers obtained in this process showed tensile strength of 0.517 GPa and also the yield of carbon fibers from starting lignin was only moderate. Baker also worked with Alcell lignin. They found that the increase of T_g and softening temperature (T_s) of Alcell lignin by use of a thermal pretreatment could enhance the tensile strength and yield of Alcell lignin derived carbon fiber. The tensile strength and obtained yield of thermally pretreated lignin carbon fiber were 0.710 GPa and 41%, respectively, whereas the original untreated lignin carbon fiber had tensile strength and yield of 0.338 GPa and 31%, respectively.

At present, lignin carbon fibers with average tensile strength as high as 1.07 GPa with moduli of 82.7 GPa can be prepared from modified lignin.^{22, 45} Synthesis of such higher performance lignin carbon fibers requires highly pure lignin with tuned properties. Especially, contamination had a major effect on the properties of carbon fibers. Based on their research, the ORNL team described a general specification of lignin for the production of carbon fiber (Table 8).

Table 8. ORNL specification for lignin feedstock to be used as carbon fiber precursor.^{10, 37}

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

Based on the precursor materials, two types of lignin carbon fibers are made, 1) carbon fibers from unmodified lignin where no additive is used, 2) carbon fibers from a blend of lignin and additive, which are coextruded. In this review, the manufacturing process from unmodified lignin derived carbon fiber will be discussed as an example. The process to produce carbon fiber from purified lignin can be divided into three steps (Scheme 3); i) carbon fiber precursor spinning, ii) thermal stabilization, and iii) carbonization. The process requires highly pure lignin to produce good quality carbon fiber. Also, the lignin should have a narrow molecular weight distribution,²² which more likely mean requiring less heterogeneous batch of lignin than actually narrow PDI as discussed in above section. This property facilitates an even increase in molecular weight of the entire fiber during the thermal stabilization that results in a more uniformly structured carbon fiber during carbonization. In some cases, lignin is washed and dried under vacuum prior to spinning and thermally pretreated under vacuum for about 1h to remove any volatile.

**Scheme 3.** Preparation of carbon fibers from lignin.

6.1.1. Melt-spinning

The majority of lignin melts and flows upon heating if T_g is low enough.¹⁰ The spinning temperature is related to its T_g , T_s , and molten viscosity of the lignin sample. For a material having low melting viscosity, a low spinning temperature is required. The thermal spinning temperature of lignin should be well below its decomposition or cross-linking temperature.^{10, 12, 22, 38} Thus, the spinning temperatures of different lignins vary with the lignin's property. For example, the spinning temperature of Alcell lignin is 138-165 °C whereas; hardwood kraft lignin required a temperature range of 195-228 °C.¹⁰ In both cases, these temperatures are lower than their corresponding thermal decomposition temperatures, 170 and 268 °C, respectively.

6.1.2. Thermo-stabilization

In the manufacturing of carbon fiber from lignin fiber, a thermo-stabilization is used to make lignin fibers stable towards high temperature, which prevents the fiber fusion during the carbonization step.^{10, 12, 14-15} During thermo-stabilization, lignin is cross-linked to raise lignin softening temperature. Reactions occurring during thermo-stabilization step increase the T_g , changing the thermoplastic property of lignin to thermosetting. This transformation of thermoplasticity to thermosetting properties is necessary for lignin fibers to maintain a fiber form and prevents from softening and deformation during the carbonization step.

The rate of heating of lignin fibers during thermo-stabilization has a profound effect on fiber stability and fusion

susceptibility. Thus, in general, thermo-stabilization is performed in different stages with different heating rate. An example of such heating profile is first heating the lignin from room temperature to about 105 °C at a rate of 1 °C/min.¹⁰ The lignin fiber is then held at 105 °C for 1 h to remove moisture in the sample. Next, the lignin fiber is heated from 105 °C to 200 °C at a rate of 0.25 °C/min. In the last step, the lignin fiber sample is held at 200 °C for 24 h to further oxidize and cross-link the lignin and raise T_g value. During thermo-stabilization, the oxygen content of the various lignins increases to a maximum and then decreased with increasing temperature.^{12, 15} The slower heating rate favors reactions that increase oxygen content at low temperatures and decrease oxygen at higher temperature. At temperature below 250°C with a slower heating rate, oxidation of lignin dominates. Due to the presence of oxygen in this stage, reactions such as autooxidation, variety of rearrangements and radical coupling reactions occur in lignin, which generates functional groups such as carbonyl groups on lignin. At this stage, breaking of aliphatic side chains, methoxy groups, and β -O-4 bonds occur. Thus, the relative amount of aryl ether structures in lignin significantly decreases after thermo stabilization. At temperature above 250°C, dehydration reaction, condensation, cross-linking and elimination reactions dominate, where water, CO and CO₂ are released from lignin through the formation of keto, ester and anhydride linkages.¹²

It should be noted, the chemistries of thermo stabilization of lignin and pitch based carbon fibers are quite different.^{12, 15} In the lignin-based systems, slight weight loss occurs during thermal spinning and stabilization. These yield losses are accompanied by an increase in molecular weight, which is the result of condensations and dehydrations in the lignin macromolecule. In contrary, in case of pitch based fiber, increase of weight occurs during oxidative stabilization. During the thermo stabilization, alkyl components of pitch are oxidized before dehydrogenation and cyclization reaction, which increases the weight. Lignin due to the presence of oxidized side-chain, during thermo stabilization, undergoes condensation reaction and releases water and consequently loses weight.

6.1.3. Carbonization

After the thermo-stabilization process, the lignin fiber is carbonized by heating the samples to 1000 °C or higher. The purpose of carbonization is to eliminate all elements except carbon and graphitize the structure. Thus, in this step, the majority of weight loss occurs. With the increase of carbonization temperature, the extent of oxygen-containing functional groups such as carbonyl, carboxyl, methoxy groups decreases and a significant increase of aryl and condensed acyl carbons occurs.¹⁰ These changes make the carbon fiber more hydrophobic. To prevent lignin combustion or any carbon fiber precursor combustion, this process requires oxygen free atmosphere. Thus, carbonization process is generally carried out in Argon or Nitrogen atmosphere where a heating rate of 3-5 °C/min is used in a batch mode and multiple processes at different temperature in a continuous mode. Similarly to the thermo-stabilization, the heating rate in carbonization has a major effect on the structure of the carbon fiber. In some cases, it was found that slow heating rates resulted in highly brittle and porous carbon fiber, while rapid heating rate produced carbon fiber with less brittleness and more stable fiber structure. Carbonization process changes the surface and porosity of carbon fibers to a large extent by releasing volatile components which in turn generates imperfections and defects on the surface of the fiber. SEM images of lignin based carbon fibers at different stages of preparation are shown in the Figure 6.¹¹

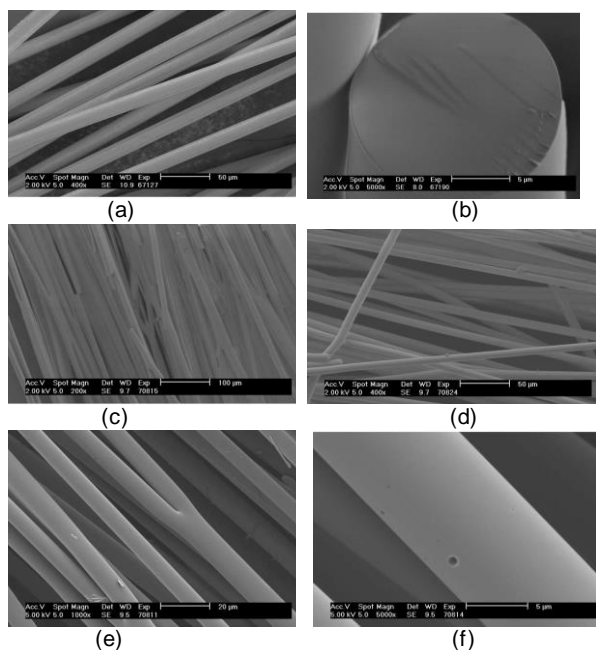


Figure 6. SEM images of a,b) lignin fibers extruded from organic solvent extracted kraft hardwood lignin; c,d) oxidized lignin fiber at a heating rate of (c) 0.05 °C/min and (d) 0.025 °C/min showing different degrees of fusion; e,f) carbon fiber, carbonized to 1000 °C at 2 °C/min after stabilization at a heating rate of 0.05 °C/min.¹¹

6.2. Carbon fiber mats

Lignin can be utilized as a sustainable precursor for fabricating free-standing carbon fiber mats. One of the attractive applications of the carbon fiber mats is utilization as high performance electrode materials for lithium ion batteries. Current carbon materials like battery-grade graphites have high production costs and they provide limited storage capacities. Lignin-based carbon fiber mats could be used as an alternative to the battery-grade graphite. Microstructures of these carbons can be controlled by incorporating different functional groups in lignins.^{3,6} Use of carbon fiber mats as electrode materials has several advantages: 1) lignin-based carbon can form highly porous free-standing fibrous mats that can be directly used as electrode materials without adding any binder or current collector agent, which not only reduces the complexity and processing time of a battery but also reduces the cost. 2) Anodes made from battery-grade graphite are highly sensitive to electrolyte solutions, which can promote exfoliation and formation of an unstable solid electrolyte interface (SEI) resulting in loss of capacity and failure.⁴⁶ Due to highly porous structures, lignin fiber mats are more stable towards electrolytes than battery grade graphite and 3) the electrochemical performance of the carbon fiber mats can be further tuned by chemical or physical modifications such as doping.

Recently Tenhaeff et al. reported a use of such lignin-derived stable free-standing porous carbon fiber mats as anodic materials.³⁵ In this work, fibrous three dimensional lignin-derived carbon mats are produced from solvent extracted lignin using a combination of forced air driven melt processing and thermal conversion methods (Figure 7). The conversion of lignin mat produced by melt processing to an electrically connected monolithic mat is conducted by thermal stabilization and carbonization. In this process, controlling the temperature is crucial as that influences the extent of fiber-fiber fusion and mat density. The fused fiber mat structure is essential for eliminating the binder and current collector components from the electrode materials. The resulting free-

standing lignin-derived carbon fiber mat based electrodes exhibited comparable electrochemical performance to commercial carbon-based anodes at a fraction of the materials and processing costs. The tentative estimated costs of lignin carbon fibers are \$3/lb for monolithic, electrically interconnected, self-supporting mats. This value is significantly lower than the price of battery grade graphite powder (\$12/lb for unprocessed battery grade graphite). The compositional and electrochemical characterization showed that carbonized lignin had a disordered nanocrystalline microstructure. The carbonized mats cycle reversibly in conventional aprotic organic electrolytes with Coulombic efficiencies over 99.9%. Moreover, lignin carbon fibers carbonized at 2000 °C can cycle reversibly in 1M LiPF₆ in propylene carbonate, while irreversible lithium insertion and extraction was observed in more disordered LCFs, carbonized at 1000 °C with the smallest nanoscale graphitic domains.

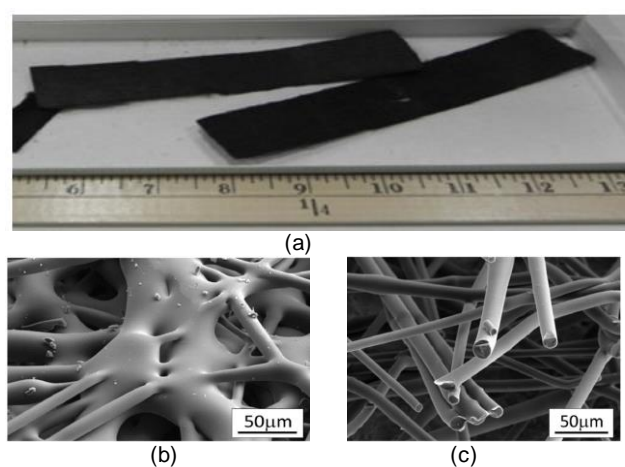


Figure 7. a) Fused lignin carbon fiber mats after carbonization.; b,c) SEM images of lignin carbon fibers mats with different degrees of fusion and density.³⁵

Chatterjee et al. reported the synthesis of organosolv lignin based microstructured carbon materials with a unique carbon mesostructure and graphite-like electrical properties.³ These materials showed similar performance to conventional anode materials in Li-ion or Na-ion batteries. In this work, lignin based fibrous materials were synthesized using a combination of chemical modifications and carbon fiber processing techniques. Lignin was modified by incorporating different ester groups, which resulted in highly compatible with melt processing and conversion into active battery electrodes. Modified lignins were subsequently converted to microstructured carbons using the carbon fiber processing technique consisting melt-extrusions, stabilizations, and low temperature carbonization in a nitrogen atmosphere. The applied chemical modification and subsequent thermo-mechanical conversion methods were effective in preserving the heterogeneous structure present in the lignin, which are nanoscale crystalline domains that were linked to the enhanced electrochemical performance. SEM analysis of carbon materials showed fibers had a hollow center and a microporous surface morphology (Figure 8). BET surface area measurements of these fibers showed the most of the fibers had surface areas similar to commercial graphitic carbon (Table 9). Thus, combined with a fused carbon fiber-based anode architecture, these materials could promote short diffusion paths for lithium ions, while mitigating aging processes, which would result in charge loss or irreversible capacity. When the conductivities of carbon fiber samples were assessed by resistivity measurements, this carbon

material showed resistivity comparable to the typical values for graphite.

In a recent work, Wang et al. reported the use of lignin-derived fused electro-spun carbon fibrous mats as high performance anode materials for lithium ion batteries.⁶ In this work, a nitrogen-doped free-standing fused lignin fiber mat was made from organosolv lignin-polyethylene oxide (90:10) blend by electro-spinning followed by carbonization and thermal annealing in the presence of urea. The fused carbon fibers without nitrogen doping exhibited high specific capacity up to 445 mAh/g at a current density of 30 mA/g and good cyclic stability at different current rates. After thermal annealing in the presence of urea, the charge capacity was further improved to as high as 576 mAh/g and still maintained a good capacity of about 200 mAh/g even at a high current rate of 2000 mA/g.

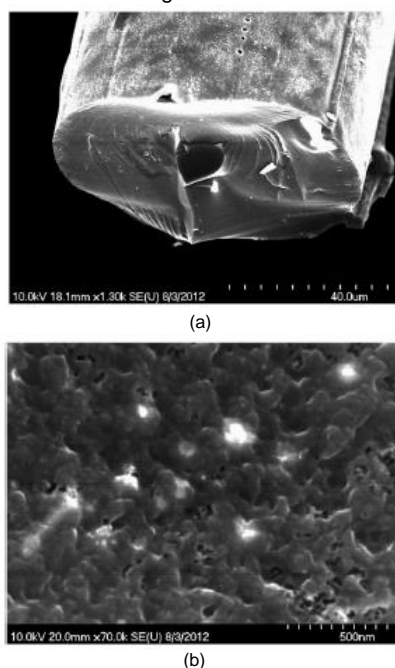


Figure 8. SEM images of a) carbon fiber made from phthalic anhydride modified lignin and b) microscale porosity of phthalic anhydride modified lignin.³

Table 9. BET surface areas and pore volumes of unmodified and modified lignins after oxidation and carbonization.^a

Carbon type	BET Surface area (m ² /g)	Adsorbed pore volume (cm ³ /g)
Phthalic Anhydride modified	32.7230 (1.5566)	0.0133 (0.0009)
Acetic anhydride modified	37.4293 (1.2133)	0.0151 (0.0006)
Succinic anhydride modified	15.3236 (1.8268)	0.0077 (0.0008)
Maleic Anhydride modified	6.3865 (1.2363)	0.0018 (0.0007)
Unmodified	8.1976 (0.7089)	0.0042 (0.003)

^aStandard deviations in each case is specified inside parentheses³

6.3. Activated carbons

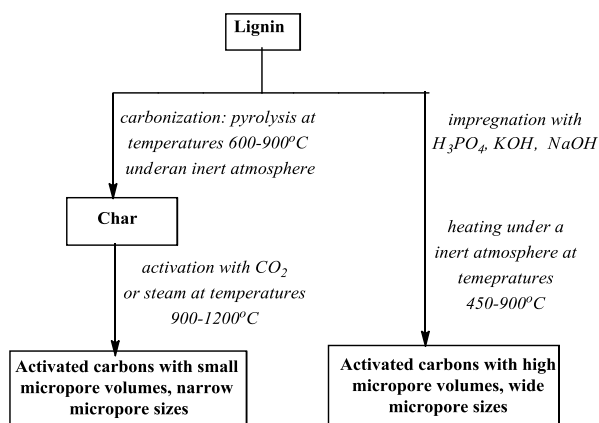
Activated carbons are highly porous materials with large internal surface area. They can be effectively used as adsorbents in a wide range of applications such as gas separation, catalyst support, filtration systems, and others.^{23-25, 47} Due to lignin's high carbon content and functionalized phenolic structure, it can be considered as one of ideal precursors for activated carbons. Properties of activated carbons largely depend on quantity and nature of pores present in it. Pores can be divided into micropores (pore diameter below 2 nm), mesopores (pore diameter between 2-50 nm), and macropores (pore diameter larger than 50 nm).⁴⁸ Porosity of activated carbon depends on the types of surface functional groups present on the precursor and method of activation. Lignin content of the feedstock controls the yield of the char and corresponding activated carbon yield. The microstructure of char and activated carbons also depends on the lignin and cellulose contents of the biomass source. According to the study of Gergova et al., lignin-derived char had more total pore volume and higher BET surface area compared to cellulose-based char.⁴⁹ On the other hand, lignin chars had low reactivity than cellulosic chars and thus, it was easier to activate chars with high cellulosic contents. It was also found that, activation of lignin produces mostly micropores, while activation of cellulose produces a mixture of pore size.

Traditionally, activated carbons can be divided into two types: powdered activated carbon (PAC) and granular activated carbon (GAC).⁴⁷ Powdered activated carbon (PAC) contains fine particles with less than 0.2 mm diameter and thus, presents a large external surface area and relatively small diffusional resistance. These properties of PAC result in a very high adsorption capacity. On the other hand, granular activated carbon (GAC) has larger particle size of about 5 mm in diameter, with smaller external surface area and adsorption capacity relative to PAC. However, GAC is more stable towards continuous contact processes.

Activated carbons are mainly prepared by physical and chemical activations (Scheme 4).^{23, 25} In both cases, the yields of the char depends on the lignin content of the starting material. In the physical activation, starting material is carbonized and then the resulting char is activated using carbon dioxide or steam. An application of a long activation time produced carbons with relatively high microporosity and wide micropore size distribution. In one case, when the starting material was activated at 850 °C for 20 h in CO₂, the process produced activated carbons with surface area 1853 m²/g with a micropore volume of 0.57 cm³/g. On the other hand, the increase in the carbonization temperature only generated moderate changes in the BET surface area and micropore volume of the carbon.

In the chemical activation, lignin is first activated by impregnating different chemical reagents such as zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄) and then lignin is carbonized. During activation, the release of different substances from lignin generates pores on the surface and results in high surface area and porosity in the produced carbon. In chemical activation, the ratio of lignin to impregnating reagent and the activation temperature are two most important parameters. Hayashi et al. studied the effect of different parameters of the chemical activation on the properties of the activated carbon. They reported that use of ZnCl₂ as activating agents produced activated carbons with surface area about 1000 m²/g. The surface area was found to be maximum when an impregnation ratio of lignin to ZnCl₂

of 1:2.3, was used. At a low temperature (generally <500 °C), the surface area and microporosity of the activated carbons increased with the increase in temperature. However, at a higher temperature (>600°C), the surface area and microporosity of this material decreased. At a high temperature, the carbon structure shrank and that in turn decreased the surface area and pore volume of the material. Interestingly, when alkali metal compounds were used as activating agents, activated carbons were found to have low surface area when the carbonization temperature was below 500 °C. These compounds were found most effective above 800 °C in generating high surface area mostly due to the pore enlargement. Authors noted that above 800 °C, the excess enlargement caused merging of pores, resulting in an increase in mesopores and a decrease of micropore volume, and of surface area. Fierro et al. showed that when H₃PO₄ was used as the activating agent, low impregnation ratios promoted the creation of micropores.⁵⁰ The acid/lignin ratios equal to or higher than 1.0 slightly affected the pore size distribution. Increasing impregnation times reduced the BET surface area and the total pore volume. Moreover, impregnation times also affected the pore size distribution of the activated carbons.

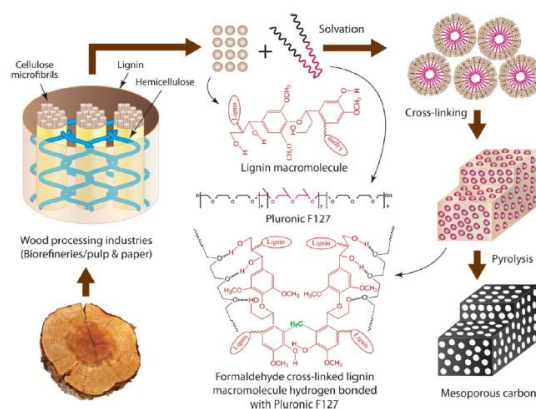


Scheme 4. Preparations of activated carbons²⁵

Gonzalez-Serrano et al. reported that all activated carbons produced in the range 350–600 °C showed fairly high values of micropore volume and its variation was the same as that of surface area.⁵¹ However, the same behavior was also observed for the mesopore volume. It was suggested that increasing the activation temperature and impregnation ratio leads to widening of the pore size distribution with a higher relative contribution of mesoporosity.

In recent years, the use of activated carbons in various applications such as energy storage systems is receiving significant attentions. However, use of porous carbon in these systems requires precise control over the type of porosity. Narrow distributions of pores are favored due to the increases in surface area of regular pore distributions vs. broad distributions of pores. However, activated carbon produced from lignin does not exhibit controlled mesoporosity; usually microporosity (pore width <2 nm) dominates in such products. Controlling pore sizes during carbon synthesis is extremely difficult, primarily because as the mass shrinks during pyrolysis, the pores collapse. Thus, in one such work, Saha et al. developed mesoporous carbon from lignin using a surfactant-templated approach (Scheme 5).⁵²⁻⁵³ The work was performed using methanol soluble fraction of kraft-processed hardwood lignin and an acid catalyzed pre-cross-linked derivative of the hardwood lignin.

The use of solvent extracted lower molecular weight lignin fraction facilitated the controlling of the template synthesis of carbon. In this process, mesoporous carbon was synthesized by i) cross-linking lignin with formaldehyde using an acid or a base catalyst in the presence of a surfactant (Pluronic F127) and ii) treating precross-linked lignin with (Pluronic F127) under acidic conditions. The portion of the surfactant reacted with the hydroxyl groups of lignin and formed a miscible part while the other portion did not interact and formed a miscible domain at the core of the resin. The product was subsequently pyrolysed, which removed the surfactant and carbonized the material simultaneously. When no activation was used, mesoporous carbons made in this process were found to have BET surface areas in the range of 205-418 m²/g.⁵² (Table 10) The synthesized carbons also exhibited characteristic mesopores at a volume 2-6 times than that of micropores. Further, Saha et al. showed the surface areas of these materials could be further increased by incorporating an activation step.⁵³ Thus, when surfactant template lignin derived mesoporous carbon was physically and chemically activated with CO₂ and KOH, both surface area and total pore volume of the mesoporous carbon increased.



Scheme 5. Synthesis of mesoporous carbon from lignin.⁵²

Another important type of lignin activated carbon is activated carbon fibers. This can be considered as the fiber form of activated carbon.⁵⁴⁻⁵⁵ Compared to powdered activated carbons, the activated carbon fiber has higher specific surface area and porosity. Due to a fibrous structure, the activated carbon fiber facilitates its use in variety of applications. This highly porous material is made by activating lignin carbon fibers. Shen et al. described that the synthesis of activated carbon fibers with controllable pore size were fabricated from alkali lignin.⁵⁵ The material was made by melt-spinning of a synthesized lignin-phenol-formaldehyde resin followed by thermo-stabilization and carbonization. In this case, no separate activation step was used. During the carbonization step, small molecules such as water, formaldehydes released from the material generate macropores.

Hu et al. reported the synthesis of sub-micrometer sized activated lignin carbon fibers from alkali lignin where alkali metal hydroxides were used as activating agents.⁵⁴ In this case, an aqueous solution of alkali lignin and alkali metal hydroxide (<50% of lignin's weight) was blended with poly(ethylene oxide) and electro-spun to form a fiber mat, which was then simultaneously activated and carbonized by heating upto 850 °C. The activated carbon fibers made in this process were found to have specific surface areas and pore volumes up to 1400 m²/g and 0.91 cm³/g. When NaOH activation was used, resulting carbon fiber materials showed both mesoporosity and microporosity with a maximum

surface area of 1440 m²/g. When KOH was used, carbon materials were found to have mainly microporosity with a maximum surface area of 1407 m²/g.

Table 10. Pore textural characteristics of lignin derived carbons^a

Entry	Preparation (Surfactant content w.t. %)	BET specific surface area (m ² /g)	Mesopore volume (cm ³ /g)	Total pore volume (cm ³ /g)
LMC-1	HCHO/acid (105)	418	0.34	0.50
LMC-2	HCHO/acid (210)	205	0.13	0.20
LMC-3	HCHO/base (160)	222	0.15	0.22
LMC-4	HCHO/base (160)	214	0.17	0.19
LMC-5	Precrossed lignin/THF (116)	208	0.24	0.28
LMC-6	Precrossed lignin/DMF (116)	276	0.11	0.22

^a LMC = Lignin mesoporous carbon, Here only a part of the original table is shown⁵²

6.4. Lignin Film

Lignin is used to make thin films using the vacuum thermal evaporation technique (PVD, physical vapor deposition) in recent report.⁵⁶ These films have possible applications in surface coatings, composites and transducer in sensing devices. The properties of these thin films such as crystallinity, thickness, molecular arrangement influenced the performance of the related devices. In the PVD technique, the organic materials are first vaporized from solid sources. This vapor is then transported under vacuum. When this vapor comes in contact with the substrate, the vapor solidifies and forms a thin film on the surface of the substrate without causing defects. The thickness of the film typically varies from nano to micrometers.

Volpati et al. produced thin carbon films of 20-120 nm thickness from lignin using PVD method. The lignin used here was extracted from sugar cane bagasse using a modified organosolv process. The reported M_w, M_n and PDI of lignins were 1970 g/mol, 1190 g/mol and 1.66, respectively. While the lignin PVD films with 120 nm thickness was deposited onto Au interdigitated electrode (IDE) for dc and ac electrical characterization. A conductivity of 3.6 X 10⁻¹⁰ S/m was determined from the current versus voltage dc measurement. A dielectric constant of 8.0, Tan δ of 3.9 X 10⁻³, and conductivity of 1.75 X 10⁻⁹ S/m were determined using impedance spectroscopy, at 1 KHz. Interestingly, these thin lignin films were found to react with vapors of aniline. When the Au IDE coated with 120 nm lignin PVD film was used as a sensing unit by exposing to aniline vapor, both DC and AC

electrical measurements revealed the sensitivity of lignin towards aniline. AFM analysis showed a decrease in the film surface roughness after exposure to aniline.

7. Outlook

Lignin is the major constituent of biomass. The U.S. Renewable Fuels Standard (RFS) mandated to produce 16 billion gallons of lignocellulosic biofuels (primarily EtOH) by 2022.⁵⁷ This decision inevitably generate enormous amount of lignin as a co-product of biofuel manufacture. This remarkable level of lignin production and availability is a rather exciting opportunity to develop valuable use of lignin in various applications. An application of lignin based carbon materials that fulfill consumer needs and maximize the environmental sustainability is rapidly developing. All the potential use of lignin-derived carbon materials described here show a promising development and some of the novel materials might be on a consumer market in near future. However, it should also be noted that further intensive research is needed to foster understanding the basic chemistry and processing technology of lignin more efficiently to provide improved properties, value, service life and utility, which can offer better renewable carbon based products. The fostered knowledge for manufacturing lignin-based carbon materials should also contribute to many other valued-added applications of lignin. Good usage of lignin will help to achieve a clean and sustainable society.

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+Keywords: lignin • carbon materials • carbon fiber • activated carbon • carbon film

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