



## Research paper

# Repolymerization of pyrolytic lignin for producing carbon fiber with improved properties



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## ABSTRACT

Lignin is a promising precursor of low-cost carbon fibers. However, the mechanical properties of carbon fibers produced from melt-spinning of raw lignin are poor, restricted by the randomly cross-linked polymer structures of lignin. In the present study, carbon fibers were produced from lignin-derived phenolic oil. Pyrolytic lignin was isolated from pyrolysis oil of red oak and washed with toluene to remove volatile impurities. Upon repolymerizing with 0.5% of sulfuric acid, the toluene-washed pyrolytic lignin became solid with the glass transition temperature ( $T_g$ ) of 101 °C and the average molecular weight of 1267 Da. The repolymerized pyrolytic lignin was further processed into carbon fibers through melt-spinning, oxidative stabilization and carbonization at 1000 °C. The average tensile strength and modulus of the fibers were 855 MPa and 85 GPa, while the highest values of individual fibers were 1014 MPa and 122 GPa, respectively. The present study suggests that the quality of the carbon fiber produced from pyrolytic lignin could be further improved by process optimization.

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## 1. Introduction

Carbon fiber is a light weight material with superior mechanical properties and corrosion resistance. Thus, carbon fiber can be used as reinforced composites in automobile and aerospace industries, construction, sports equipment and more [1–3]. Despite great potential, the application of carbon fibers is currently limited, mainly due to the high cost of the precursor. Currently, a large portion of carbon fibers in the market are produced from polyacrylonitrile (PAN), and the precursor alone costs as much as 51% of the production cost of the carbon fiber [2]. PAN is derived from petroleum and releases toxic gas during carbon fiber processing, raising various environmental concerns [4,5]. Low-cost carbon fibers made from non-petroleum precursors could enable the application of carbon fibers in large scale. The Department of Energy suggested that the alternative carbon fibers with a tensile strength of 1720 MPa and modulus of 172 GPa, and with cost below 11–15.40 \$ kg<sup>-1</sup>, could be widely used in the automobile industry to reduce vehicle weight and improve fuel economy [6,7]. Lignin derived from lignocellulosic biomass has been of particular interest as an alternative precursor since it naturally contains a six-membered-

ring aromatic structure and is abundantly available at low cost [8,9].

Lignin-based carbon fibers have been studied for nearly 50 years. The historical background of the development and recent advances have been thoroughly reviewed by Baker [7]. In the previous studies, carbon fibers were produced from lignin either by thermal processing, chemical modification or mixing lignin with other polymers. Although various types of lignin have been tested and the fiber manufacturing process was also carefully optimized, the quality of lignin-based carbon fibers is still too low to be considered for structural applications [8,10–12]. To date, the lignin-derived carbon fiber with the highest quality was reported by Oak Ridge National Lab [13] with tensile strength and modulus of 1070 MPa and 83 GPa, respectively. The fibers were made by melt-spinning an organic-solvent purified, Kraft hardwood lignin with a low glass transition temperature ( $T_g = 86$  °C) after thermal treatment. In general, lignin-based carbon fibers have tensile strength lower than 500 MPa.

The quality of lignin-based carbon fibers is low, attributed to the intrinsic nature of lignin structure. Lignin structure is also affected by its biomass origin and isolation method [14,15]. Lignin is a phenyl propane-based macropolymer and is linked with carbohydrates through covalent bonds in biomass. To separate lignin from the rest of biomass, chemical treatments involving salts, acids, and/or organic solvents are commonly employed. Technical lignin produced either from paper, pulping or cellulosic biorefineries usually

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contain considerable amounts of organic and inorganic impurities derived from the biomass plant, the extraction process, as well as, lignin handling and storage. These impurities have to be removed from the lignin prior to carbon fiber production through acid washing, which otherwise cause various defects within the fibers. A melt-spinning method is generally used to process lignin due to its low cost. When lignin is melt-spun at elevated temperatures, the cleavage of weak ether and ester bonds in the lignin polymer release volatile products and create void spaces within the fibers [4] ultimately reducing the mechanical strength of the fibers. More importantly, lignin is a three-dimensional polymer formed by random cross linking of its three precursor monomers. Due to the lack of molecular orientation and linearity within the polymer, the resulting fibers have amorphous structures, corresponding to low mechanical strength of the fibers.

While technical lignin is polymeric material isolated from biomass by the removal of carbohydrates through chemical or biochemical process, pyrolytic lignin is depolymerized lignin produced by heat. When lignocellulosic biomass is rapidly heated to 450 °C–600 °C in an inert environment and the pyrolysis vapor is quenched, up to 75% of biomass can be recovered as bio-oil. Due to its robust process and low capital cost, pyrolysis is one of the major liquefaction technologies of biomass. During pyrolysis, phenolic monomers and oligomers produced from lignin (i.e., pyrolytic lignin) are condensed and form a complex mixture along with carbohydrate-derived sugars, furans, acids, ketones and aldehydes in bio-oil. Although accounting for 20%–30% of bio-oil [16], pyrolytic lignin is usually referred to as the less-preferred product because it increases the viscosity of bio-oil during storage and could even cause phase separation [17]. This is because pyrolytic lignin is unstable and has a tendency for polymerization. On the other hand, pyrolytic lignin can be extracted from bio-oil by simple water-washing and upgraded independently for other value-added applications. Potential applications of pyrolytic lignin include bio-adhesive [18], resin [19], bioasphalt [20], solid fuel [21], as well as, carbon fiber [22]. For example, Sahaf et al. [23] studied rheological and tunable thermoplastic properties of pyrolytic lignin and reported that pyrolytic lignin could be considered for hot melt adhesive applications. On the other hand, pyrolytic lignin as the precursor of carbon fiber can potentially provide several advantages over lignin. While it has some structural similarities with lignin [24], pyrolytic lignin is made of smaller phenolic units with reactive functional groups, such as phenolic hydroxyl groups, carbonyl groups and vinyl groups [16]. Thus, pyrolytic lignin has the potential to be re-polymerized [25] into more desirable structures versus lignin. Compared to as-received technical lignin, pyrolytic lignin may contain fewer impurities because the majority of impurities in biomass remain in biochar instead of bio-oil when biomass is pyrolyzed.

In the present study, carbon fibers were produced from pyrolytic lignin derived from the fast pyrolysis of red oak. Pyrolytic lignin isolated from the heavy fraction of bio-oil was repolymerized with acid catalyst prior to spinning into fibers. Both the precursor and carbon fibers were characterized in this work.

## 2. Experimental

### 2.1. Preparation of pyrolytic lignin

Red oak (*Quercus Rubra*) was purchased from Wood Residues Solutions (Montello, WI). It was first ground by a mill cut, and then pyrolyzed in a pilot-scale, fluidized bed reactor at Iowa State University's BioCentury Research Farm. Pyrolysis temperature was 500 °C and bio-oil was collected in a five-stage bio-oil condensation system. Detailed reactor configuration and the composition of bio-

oil collected in each condenser was previously reported elsewhere [26]. Bio-oil collected in the first condenser consisted of pyrolytic sugars and phenols. It was water-washed three times to remove sugars. The remaining water-insoluble fraction was designated as pyrolytic lignin and used in this study.

### 2.2. Pretreatment of pyrolytic lignin

Pyrolytic lignin was subsequently washed with toluene in a mass ratio of 1:1 three times for 15 min and then centrifuged for 20 min to remove any residual water and toluene. The toluene-washed pyrolytic lignin was further heated at 90 °C for 15 min to remove any volatiles. Each time, 10 g–15 g of toluene-washed pyrolytic lignin was placed in a 200 ml beaker and set on a heating plate. A funnel with its cone-side downward was placed right above the beaker. The neck-side of the funnel was connected to a vacuum tube to facilitate the removal of volatiles. For thermal treatment, the pyrolytic lignin was heated in an oil bath at 105 °C for 2 h with a magnetic stirring bar. A 0.5% of sulfuric acid (SA) was added dropwise into the pyrolytic lignin to catalyze polymerization reaction [27,28]. The produced precursor was designated as SA treated precursor in this study.

### 2.3. Characterization of pyrolytic lignin

Dionex Ultimate 3000 series high performance liquid chromatography (HPLC) together with a Shodex Refractive Index (RI) and Diode Array Detectors (DAD) was used to conduct gel permeation chromatography (GPC) analyses for relative molecular weight distribution. Two GPC columns (3  $\mu\text{m}$ , 100  $\text{\AA}$ , 300  $\times$  7.5 mm; PLgel, Agilent, p/n PL1110-6320) were calibrated with six monodispersed polystyrene standards ranging from 162 g mol<sup>-1</sup> to 38640 g mol<sup>-1</sup>. Tetrahydrofuran was used as the solvent for samples and the eluent in the columns.

An Agilent 7890B gas chromatography (GC) with Agilent 5977A mass-selective-detector (MSD) and flame ionization detector (FID) system was used to identify the chemical composition in the pyrolytic lignin and precursors. The capillary column used in the GC was a ZB-1701 (60 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ). The injection temperature was 250 °C and the oven temperature was kept at 40 °C for 3 min, and then ramped to 280 °C with 3 °C min<sup>-1</sup>.

A Thermo Scientific Nicolet iS10 (Thermo Fisher Scientific Inc., Waltham, MA) equipped with a Smart iTR accessory was used to conduct Fourier Transform Infrared (FTIR) analysis to determine the functional groups in the pyrolytic lignin and precursors. With wave numbers ranging from 750 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, each sample was scanned 32 times at a resolution of 4 cm<sup>-1</sup> and interval of 1 cm<sup>-1</sup>.

Thermogravimetric analysis (TGA) was conducted using a Mettler Toledo TGA/DSC instrument. The samples were heated at a rate of 10 °C min<sup>-1</sup> from 25 °C to 1000 °C under nitrogen with a flow rate of 100 ml min<sup>-1</sup>. The experiment was duplicated for reproducibility.

Glass transition temperature ( $T_g$ ) was determined by using a differential scanning calorimeter (DSC, Q20, TA instruments). Each sample was heated to 125 °C with a heating rate of 10 °C min<sup>-1</sup>. Nitrogen was used as the purge gas with a flow rate of 50 ml min<sup>-1</sup>. The midpoint  $T_g$  of precursor was determined by using a TA software.

The CHNS elemental analysis of the pyrolytic lignin and precursor were conducted using Elementar (vario MICRO cube) elemental analyzer.

### 2.4. Production of carbon fiber

About 6 g of pyrolytic lignin was fed into a twin-screw

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