Carbon fibers derived from liquefied and fractionated poplar lignins: The effect of molecular weight

Highlights
- Hot aqueous ethanol can fractionate lignin via liquid-liquid equilibrium
- Fractionated lignin was spun into fibers using the same aqueous ethanol solvent
- Impurities and molecular weight (MW) are key metrics for lignin-based carbon fibers
- Increased MW HP lignin fractions have elevated Tg and can be stabilized faster

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Carbon fibers derived from liquefied and fractionated poplar lignins: The effect of molecular weight

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SUMMARY
Lignin recovered from poplar, a key woody biomass resource proposed for lignocellulosic refineries, was investigated for conversion into carbon fibers. Aqueous solutions of ethanol at selected temperatures and compositions, where the requisite solvent and liquefied-lignin phases form, were used to purify and fractionate hybrid poplar (HP) lignin using the Aqueous Lignin Purification with Hot Agents (ALPHA) process. Sugars (<0.1%) and ash (0.01 ± 0.01%) content of the highest molecular weight fraction (Mw = 52 kDa) approached the limits of detection. This 52 kDa fraction could be dry spun with excellent stability and was subsequently converted into carbon fibers having strength (1.1 ± 0.2 GPa) and modulus (78 ± 8 GPa) essentially double those previously achieved with neat poplar and other hardwood lignins. Of equal importance, stabilization times were decreased by a factor of five. Such stabilization and strength/modulus improvements are essential for reducing the overall manufacturing cost of carbon fibers being proposed for cost-sensitive applications.

INTRODUCTION
As noted in DOE’s most recent national assessment of biomass energy resources,1 by 2040, the USA will be able to generate 1 billion tons of non-food biomass annually without negatively impacting either food production or the environment. As we collectively push for a more sustainable and resilient energy economy, especially amid rising uncertainty in petrochemical supplies, nurturing the nascent biomass industry becomes an increasingly attractive proposition. Cellulose is a prime candidate for bioethanol, and vegetable oils/fats are appropriate for biodiesel, but prospects for lignin, the second-most abundant biopolymer on the planet, remain uncertain. Although the complex structure and recalcitrant nature of lignin present challenges, its aromatic functionality (unique among biomasses) and abundance (comprising up to 30% of dry woody biomass) make lignin attractive for a broad range of potential applications. Furthermore, techno-economic analysis of the lignocellulosic bioethanol refinery2,3 indicates that the lignin should be converted into value-added co-products, thereby reducing ethanol fuel costs, if the overall facility is to be economically viable. Unfortunately, today’s industrial lignin is only modestly valued, with 99% still being used just to fuel steam boilers.

One of the most attractive potential uses for lignin from biomass is as a precursor for carbon fiber. With their high strength and low density, carbon fibers are well known for their use in aircraft and aerospace applications. Unfortunately, ultrahigh-performance carbon fibers (e.g., T800 or IM7 fibers, with strengths of over 5.4 GPa) are also extremely expensive (about $100/kg in 2021). For cost-sensitive applications, such as automotive and sporting goods, carbon fibers equivalent to T300 can be used, which at about half the strength provide moderately high performance at a significantly lower cost.4–7

To produce carbon fibers, carbon-rich, processable polymers are typically used as the starting precursors for carbon fiber (because carbon does not melt). The dominant (95% market share) precursor is petroleum-derived polycrylonitrile (PAN), used to produce the commercial fibers discussed above. The precursor is spun into fibers, which are then stabilized (typically via oxidation) and carbonized to produce the final, carbon fiber product.

On the spectrum of performance/cost ratio, a grade of carbon fibers has been proposed by ORNL5,8,9 that would be suitable for automotive applications, whose performance (i.e., a strength of 1.7 GPa) would be
somewhat lower than the T300 grade. However, to be viable, these carbon fibers would need to cost no more than $11–15/kg. With close to 50% of the fiber cost coming from the precursor, low-cost (and sustainable) precursors are thus of significant current interest.4,10–12

Lignin is uniquely attractive among biopolymers because of its high carbon content (~50%), aromaticity (which facilitates carbon-layer formation), and abundance. Furthermore, a base-case techno-economic analysis, incorporating both an NREL study13 and our results for a fractionated and purified lignin,14 indicates that total expenses for producing the carbon fibers would be <$12/kg, in-line with the cost objectives stated above. With a market price of $22/kg, this would be a highly profitable co-product for biomass energy crops.15,16

Unfortunately, because of the impurities inherent in lignin (primarily polysaccharides and metal salts), along with the wide range of functionalities and molecular weights in the lignin species, numerous problems can arise from substituting unpurified and unfractionated lignin directly into a process or formulation designed for well-defined, modern petrochemical feedstocks. Thus, as for crude oil, fractionation is a path to realizing the potential of lignin as a natural resource. However, today it is imperative that lignin-refining strategies also include sustainability as a core principle.

Thies and co-workers17–19 have discovered that renewable organic solvents that form homogeneous, one-phase solutions with water, including lower molecular weight (MW) alcohols and acetic acid, can be used to simultaneously fractionate and purify lignin, using either batch or continuous processing. With this so-called ALPHA (Aqueous Lignin Purification using Hot Agents) process, lignin is contacted with a hot, one-phase aqueous solvent, such as acetic acid or ethanol in solution with water. Two liquid phases then form due to (lignin) polymer–solvent interactions14,20: a lignin-rich phase, containing approximately 50 wt % lignin, and a solvent-rich phase containing approximately 10 wt % lignin. The higher MW lignin molecules preferentially concentrate in the lignin-rich phase, while the solvent-rich phase is typically enriched in both lower MW molecules and impurities (primarily salts). Based on the properties of the starting lignin, the solvent-to-lignin ratio, the solvent composition, and the temperature, manipulation of the lignin yield, the extent of fractionation, and the lignin molecular weight become possible.21 Application of the ALPHA process to as-recovered lignins has demonstrated significant improvements in final-product performance.22

Since our discovery, other researchers have also used greener solvents, such as aqueous acetone23,24 and aqueous ethanol24–26 to fractionate lignin. However, in none of those cases did the lignin liquefy in the presence of the solvent; instead, only solid–liquid equilibrium was established. Furthermore, purification of the lignin was not addressed.

With respect to what would be an appropriate biomass resource for the lignin precursor, DOE’s assessment1 predicts that a key woody biomass resource in 10–20 years will be poplar. Thus, hybrid poplar (HP), which on average comprises 20%–29% lignin with an S:G ratio of 1.5–1.75, 13%–17% xylan, and also contains 0.6%–2.0% ash,27 was selected as the biomass for this investigation. Most previous work on poplar lignin as a precursor for carbon fibers was carried out at the Center for Renewable Carbon.28,29 In brief, they used Organosolv fractionation followed by a sequence of isolation and washing steps to recovery a purified lignin. This lignin was then melt spun into carbon fibers, with tensile strengths up to 0.544 GPa and moduli to 36.5 GPa being obtained for fibers having diameters of 17 ± 2 µm. The typically low stabilization rates (0.05°C/min) of hardwood lignins were increased by blending in 15%–25% of switchgrass-derived lignin (which rapidly stabilizes) with the HP lignin; however, no significant improvement in strength or modulus was obtained.

Poplar and other hardwood lignins are generally processed into fibers by melt spinning, as they have relatively low softening points.15,29 However, our team’s first study on lignin-based carbon fibers30 was with softwood lignins recovered from the Kraft process, which are not readily melt spinnable.6 Thus, spinning a lignin-rich solution of Kraft lignin dissolved in a solvent (called dry spinning) was required. In that work, the lignin had to be partially acetylated to render it soluble in the spinning solvent, but with the advent of our ALPHA process, such chemical modification of the lignin has become unnecessary. (From a sustainability standpoint, minimal chemical modification of the lignin is of course preferred.) Thus, in a subsequent study,31 ALPHA-fractionated lignin was dry spun using the same solvents for spinning as for fractionation. The highest MW lignin fractions produced the strongest carbon fibers to date from chemically unmodified lignin (strength of 1.39 GPa and modulus of 98 GPa).
Herein, we have investigated the use of lignin derived from a key energy crop, hybrid poplar, for conversion into carbon fibers. The strong chemical and impurity differences between Kraft and HP lignin made the requisite ALPHA processing and dry spinning of the lignin notably different. Tindall et al.19 had recently demonstrated that ultraclean lignins (i.e., with sugars \( \leq 0.1 \) wt % and ash \( \leq 0.05 \) wt %) of controlled molecular weight could be generated from HP lignin via ALPHA. Here, the focus was on determining the ability of the ALPHA process to produce precursors (in the form of lignin-rich phases from ALPHA) suitable for dry spinning and conversion into quality carbon fibers. Additionally, we present the first case of using bio-ethanol for both lignin fractionation and purification—and for dry spinning.

RESULTS AND DISCUSSION

Lignin fractionation and analysis

Compared to Kraft lignins, lignins derived from lignocellulosic biorefineries (e.g., from hybrid poplar and corn stover) present their own set of challenges with respect to fractionation and purification via ALPHA. In particular, polysaccharide impurities, which are typically present at several percent in as-recovered HP lignins (2.65\% in this work), are a significant concern for fiber spinning. Although our NREL-based carbohydrates analysis procedure19 hydrolyzes the polysaccharides to simple sugars and thus cannot be used to assess the degree of polymerization, the frequent clogging and visual observation of insoluble material when dry spinning the starting bulk lignin suggested that long-chain, insoluble carbohydrates were present in the feed. As a spinnable precursor is necessary to produce carbon fibers, fractionation efforts were thus first focused on separating this insoluble material from the as-recovered lignin.

Previous work with Kraft lignin32 had shown that 80/20 EtOH/water mixtures yielded the maximum solubility of lignin in the solvent-rich phase (SR), and preliminary measurements herein had shown that HP lignin (from this study) has a higher solubility in EtOH/water solutions than Kraft lignin. Thus, for the generation of HP11K, we chose to use a weaker solution (60/40 EtOH/water) for the first ALPHA stage, see Figure 1A. For the second ALPHA stage, the dried, purified lignin from the SR filtrate phase was contacted with a 30/70 EtOH/water solution, resulting in precipitation of lignin fraction HP11K as a lignin-rich (LR) phase. Although the yield of HP11K was relatively high at 40\% of the as-recovered feed lignin (see Table 1), its M\text{w} was somewhat low at 11k, although still significantly higher than the feed (M\text{w} = 7.6k). TGA results revealed relatively high ash levels for this fraction, well below those of the feed lignin, but almost double those obtained for our carbon fiber work with softwood Kraft lignins.31

Figure 1. Block flow diagram of ALPHA fractionation processes

Block flow diagrams showing the fractionation scheme for (A) HP11K, (B) HP24K, and (C) HP52K. Note that LR has been used as an abbreviation for lignin-rich phase and SR for solvent-rich phase.
Based on the above MWs and purities, we concluded that subsequent ALPHA fractionations should use 80/20 EtOH/water solutions for the first ALPHA stage of lignin dissolution plus vacuum filtration. Additionally, the S/L ratio for Stage 1 was reduced from 6:1 to 3:1, as previous work\(^3^2\) with Kraft lignins had indicated that lignin dissolution could be equally effective at the lower S/L ratio. Additionally, a halving of solvent usage would also improve the TEA/LCA for the process.

The purpose of subsequent ALPHA stages, then, was to induce precipitation of the lignin from the SR filtrate phase of Stage 1. Previous work\(^1^9\) had shown that lignin MW can be controlled by simple water addition, with incremental additions of water being used to precipitate out a series of LR liquid phases. However, in practice, controlling lignin MW solely by water addition, as was the case for HP24K (Figure 1B), resulted in low yields (8% of the starting bulk lignin) of the desired, higher MW lignin fraction. In contrast, for the HP52k fraction (Figure 1C), intermediate and higher MW lignins comprising 42% of the starting lignin were simultaneously precipitated out as an LR phase in Stage 2 via water addition. However, for Stage 3, not water but a stronger, 60/40 EtOH/water ALPHA solvent was added to the LR phase. As shown in Table 1, the result was both a 50% increase in the yield of higher MW lignin and a doubling of its molecular weight to 52k. Furthermore, although HP24k had remarkably low levels of ash and sugars (<0.1 wt %) approaching the limits of detection, HP52k was even purer, containing essentially undetectable levels of ash (with ash results duplicated to verify).

In summary, we see that Stage 1 conditions are critical for removing the impurities, Stage 2 conditions are more flexible (those used for HP24k and HP52k could have been exchanged with minimal impact on final lignin properties) and can be adjusted based on downstream needs or TEA/LCA findings, but selection of conditions for the third and final ALPHA stage is critical for attaining the highest MW fractions. Finally, although the conditions for isolating HP 24k and HP52k were both successful in producing fractions of elevated MW and high purity, we would not refer to any of the stages as being optimized at this point. Instead, the range of viable conditions employed demonstrates the flexibility of aqueous ethanol, both hot and at ambient temperatures, as a solvent for lignin fractionation. In conjuction with TEA, future experiments could better map out the cost–performance landscape of ALPHA processing.

### Dry spinning of ALPHA lignins

The process of dry spinning consists of extruding a solvated, polymer-rich solution (known as a spinning dope) through a spinneret into ambient air, allowing the solvent to evaporate during drawdown, and then taking up the dry lignin filaments on a roll continuously, see Figure 2A.

The various dope compositions that were found to lead to successful fiber spinning are given in Table 1. Note that only about 30% ethanol (with the balance being water) was required to spin the starting lignin, but 60% ethanol was needed to spin HP52K. That is, the higher the molecular weight of the lignin, the stronger the solvent (i.e., more ethanol) that was required to achieve a low-enough viscosity for fiber spinning. The optimal solids (i.e., lignin) content in the dope ranged from 60 to 70 wt %. Although a low-viscosity solution can be extruded through a spinneret more easily, a dilute solution is harder to draw down into thin filaments.

As an aside, it is interesting to compare the above compositions with those of the LR phases generated via ALPHA, which were the source of lignin fractions HP11, 24, and 52K (see Figures 1A–1C, respectively).

### Table 1. Characterization for each of the lignin fractions generated in this study, including the yield, sugars and ash content, glass-transition temperature (Tg), weight-average molecular weight (Mw), and approximate minimum composition of ethanol needed in the spinning solvent for successful processing

| Sample label | Yield of Feed Lignin (wt %) | Sugars (wt %) | Ash (wt %) | Tg (°C) | Lignin Fraction Mw (kDa) | EtOH Req’d For Spinning (wt %) |
|--------------|----------------------------|---------------|------------|---------|--------------------------|--------------------------------|
| HP7.6K       | 100                        | 2.7           | 1.22       | 102     | 7.6                      | 30                             |
| HP11K        | 40                         | <0.1          | 0.13       | 110     | 11                       | 40                             |
| HP24K        | 8                          | <0.1          | 0.04       | 135     | 24                       | 50                             |
| HP52K        | 12                         | <0.1          | 0.02       | 147     | 52                       | 60                             |

Based on the above MWs and purities, we concluded that subsequent ALPHA fractionations should use 80/20 EtOH/water solutions for the first ALPHA stage of lignin dissolution plus vacuum filtration. Additionally, the S/L ratio for Stage 1 was reduced from 6:1 to 3:1, as previous work\(^3^2\) with Kraft lignins had indicated that lignin dissolution could be equally effective at the lower S/L ratio. Additionally, a halving of solvent usage would also improve the TEA/LCA for the process.

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As an aside, it is interesting to compare the above compositions with those of the LR phases generated via ALPHA, which were the source of lignin fractions HP11, 24, and 52K (see Figures 1A–1C, respectively).
These LR phases all originally had lignin solids contents of ~50 wt %, which means that for a commercial process they would need to be only partially dried to obtain the desired solids content for spinning. Furthermore, the liquid–liquid equilibrium solvent compositions of the LR phases for HP11, 24, and 52K (30, 55, and 60% EtOH, respectively) are in surprisingly good agreement with the EtOH spinning compositions presented in Table 1, which were determined independently through dry spinning experiments.

Dry spinning the as-recovered, feed lignin (HP7.6K) did not lead to stable fiber-spinning, as frequent fiber breakage was experienced. This would be highly undesirable for commercial scale-up, where process interruptions are expensive. Also, it was hard to draw down the filaments, which was likely caused by the presence of low-MW lignin moieties in the unfractionated lignin. Additionally, the presence of impurities, such as insoluble sugars and metals salts that did not dissolve in the ALPHA solvent used for dry spinning, could have caused flow disturbances, resulting in poor fiber drawdown.

In contrast, lignin fractions HP11, 24, and 52K were not only fractionated but were also purified via ALPHA, yielding a stable spinning process with steady extrusion pressure and significant fiber drawdown. Stable spinning was achieved at temperatures between 50°C and 70°C. Due to solvent out-diffusion during fiber drawdown, an extended surface area is created that leads to fibers with non-circular cross-section and surface crenulations, as observed in Figure 2B. As shown in our prior dry spinning studies, although increased surface area is desirable in ultimate composite applications, sharp notches and defects created by rapid solvent out-diffusion can be detrimental to fiber strength. In this study, however, crenulations on the fiber surface were mild and did not generate any undesired sharp crevices. Thus, crenulations on the fiber surface were not expected to affect the fiber strength in any significant manner but could slightly enhance the fiber-matrix interfacial area in composite applications. With the combination of low viscosity (apparent viscosities always less than 100 Pa s, see supplemental information), the use of fine-spinneret capillaries (~100 μm), and appropriate solution compositions, fiber drawdowns as high as 8.6 were achieved with as-spun fiber diameters as fine as 17.0 ± 1.4 μm.

Finally, it is important to note that in all previously reported work on carbon fibers derived from hardwood lignins, the lignin precursors were not dry spun but instead were melt spun (i.e., neat lignin with no added solvent). Successfully melt-spun lignins all had glass-transition temperatures (Tg’s) < 130°C, but the higher Tg lignins degraded during spinning. Such degradation not only disrupts the spinning process but also produces inferior quality, as-spun fibers. Contrast this situation with dry spinning, where the presence of the solvent obviates such concerns. As discussed above, the dry-spun 52K lignin fraction (Tg = 147°C, see Table 1) exhibited excellent spinnability and generated fine fiber filaments.

**Stabilization**

Before lignin fibers can be converted into carbon, they must undergo stabilization. The objective of stabilization is to cross-link the lignin within each fiber, but not let the lignin fibers fuse with each other during the heating process. Thus, the cross-linking/oxidative reaction temperature at any point in the stabilization process must be below the Tg at that same point. Thus, this step in processing is limited by the material, as

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**Figure 2. Fiber-spinning roll and as-spun fiber micrograph**

(A) Dry-spun lignin fibers taken up continuously on drawdown roll and (B) SEM micrograph of representative, as-spun lignin fibers.
higher temperatures yield higher rates of reaction; however, if the temperature crosses the Tg threshold, fibers may begin to undesirably fuse.

Unfortunately, all prior studies with poplar and other hardwood lignins indicate that due to the low initial Tg of the starting lignin, the oxidative stabilization of neat, hardwood-lignin-based fibers requires a very slow heating rate of 0.05°C/min for cross-linking to occur without fiber fusion, a process that takes several days to complete.

Therefore, DSC measurements were performed on our three HP lignin fractions to determine Tg’s. Results (See Table 1) indicate that an increase in molecular weight consistently leads to an increase in Tg. Previous work has reported differences in Tg for poplar lignins, but those differences were primarily due to large changes in the S/G ratio among various poplar genotypes. Here, however, we are increasing the Tg of the lignin solely through ALPHA fractionation of a conventional HP lignin currently being grown as an energy crop.

Figure 3 displays an SEM micrograph of stabilized lignin fibers produced from the unfractionated, starting bulk lignin (HP7.6k). Even at the slow heating rate of 0.05°C/min, the lignin fibers fused with neighboring fibers during stabilization. This is consistent with the literature cited above, where some unfractionated hardwood lignins could not be stabilized even at this very slow heating rate. SEM micrographs of stabilized HP11K lignin fibers (Figure 4) indicate that successful stabilization without fiber fusion was achieved at 0.05°C/min, but higher heating rates produced fiber fusion. Finally, Figure 5 displays SEM micrographs of HP52K lignin fibers stabilized at a relatively high heating rate of 0.25°C/min. Interestingly, no fusion was seen even at a heating rate five times what has been previously reported in the literature. Based on these results, we conclude that oxidative stabilization times for poplar lignins can be reduced from the 80 + h reported in prior studies to only 16 h. Such a dramatic reduction in stabilization times is a significant step in our efforts to produce low-cost carbon fibers by reducing processing costs.

Carbonization

Figure 6 displays SEM micrographs of carbon fibers produced using different molecular weight fractions; note that the final carbon fibers have crenulations on the fiber surface that are retained from the as-spun state. The SEMs also confirm that there are no major defects in the cross section or lateral section of the fiber, confirming that stabilization was successful and that lignin was adequately cross-linked.

The optimum carbonization temperature for high-strength carbon fibers is dependent on the molecular and chemical composition of the precursor. For example, the range is 1300°C–1500°C for PAN and is close to 2000°C for mesophase pitch. Based on our prior studies with softwood Kraft lignin, 1000°C was our selection for the carbonization temperature. However, as a check, a limited quantity of HP52K-based lignin fibers was also carbonized at 750°C and 1500°C. At all temperatures, the carbon fibers retained the overall non-circular and crenulated shape of the as-spun fibers, and no significant change in microtexture was observed in the fiber cross section. However, defects in the form of pores started to

Figure 3. SEM image of stabilized fiber produced with lignin fraction HP7.6K using a 0.05°C/min heating rate. Fiber fusion is indicated with blue arrows.
appear for a carbonization temperature of 1500°C, indicating that 1000°C was the appropriate carbonization temperature.

**Carbon fiber microstructure and properties**

Raman spectra were obtained for carbon fibers (CF) produced from both the unfractionated, as-recovered lignin and from the lignin fractions generated via ALPHA. In addition to obtaining spectra at 1000°C for all four lignins, we measured the spectra for the HP52K fraction at 750°C and 1500°C (see Figure 7). Graphitic development in carbon fibers is associated with the G-peak at 1580 cm⁻¹, whereas disordered carbon produces the D-peak at 1310 cm⁻¹. The ratio of these peaks, I_D/I_G, is a relative measure of graphitic development and was determined to be 4.8 ± 0.9 for the unfractionated sample as well as for all ALPHA fractions, with no statistically significant difference among the samples within a 95% confidence interval. This indicates that the molecular weight of a given HP lignin fraction did not significantly affect graphitic development in the final CFs. In previous work with a softwood Kraft lignin fractionated and purified via ALPHA,³¹ three fractions of increasing molecular weight were also generated, and similar I_D/I_G ratios were obtained for all but the highest MW fraction, for which a significantly smaller I_D/I_G of 3.6 ± 0.5 was obtained. In contrast, an I_D/I_G ratio of 1.47 has been reported for commercial T-300 high-performance carbon fiber and 1.64 for a laboratory PAN fiber stabilized at 1000°C.⁴³ For CFs produced from the 52 kDa fraction, I_D/I_G ratios were measured at 5.2 ± 0.96, 5.1 ± 0.52, and 3.76 ± 0.07 for carbonization at 750°C, 1000°C, and 1500°C, respectively (see Figure 7A). Thus, an increase in carbonization temperature led to a small increase in the graphitic order of the highest MW softwood Kraft lignin fraction isolated via ALPHA by our team (Jin et al., 2018). Thus, Raman analysis shows that a small but detectable degree of graphitic development can be developed in HP lignins with an increase in carbonization temperature. However, for the HP lignin fractions generated in this work, graphitic order was not enhanced by increases in lignin molecular weight for any given mol wt.

Figure 7B shows the 2-θ profile of X-ray scans of HP52K-based CFs carbonized at different temperatures. Very broad (002) peaks are centered around 22.9°, 23.0°, and 23.9° for CFs carbonized at 750°C, 1000°C, and 1500°C, respectively (see Figure 7A). In contrast, PAN-based T650 carbon fiber shows (002) peak at 25.1° and highly
graphitic K1100 carbon fibers show a peak at 26.4°. It is interesting to note that highly graphitic CFs such as K1100 and those from our prior studies display (002) peak at a significantly higher 2θ angle of 26.0°–26.4°. Even “turbostratic graphite” such as that in T300 PAN-based CFs displays (002) peak at about 25°. In sharp contrast, these peaks in current lignin-derived CFs heat-treated to 1000°C and 1500°C appear at less than 24°, showing distant stacking and poor formation of (002) layer planes. Interplanar d002 spacing from these 2θ peak locations (Braggs law) were calculated at approximately 0.39 ± 0.02, 0.38 ± 0.02, and 0.37 ± 0.02 nm for fibers carbonized at 750°C, 1000°C, and 1500°C, with Lc (Scherrer Equation) of about 1.4 ± 0.2 nm. In contrast, for PAN-based T650 fibers, d002 spacing is 0.35 nm and Lc is 2.2 nm. Again, due to very low graphitic contents, quantitative differences in graphitic crystallinity were difficult to detect for the two different heat treatment temperatures.

Tensile strengths for CFs derived from the three HP lignin fractions generated via ALPHA and carbonized at 1000°C are given in Table 2. Recall that fibers dry spun from the unfractionated starting lignin partially fused during stabilization, thus leading to CFs with average tensile strengths of only 0.27 ± 0.1 GPa. As these fibers could not be drawn down during spinning, they were also quite thick. Tensile strengths for CFs produced from the HP11K and HP24K lignin fractions were in-line with the best values reported for a poplar lignin (0.544 ± 0.1 GPa) as discussed in the introduction, and were essentially equal to tensile strengths reported for other hardwood-lignin-based CFs. However, CFs produced from our highest MW, HP52K lignin fraction had tensile strengths almost double those previously reported for any neat, hardwood-lignin-based CF.

Incidentally, the tensile strength of HP52K-based CFs carbonized at 750°C and 1500°C was 0.85 ± 0.2 and 0.33 ± 0.1 GPa, respectively. The small increase in strength as carbonization temperature increased from 750°C to 1000°C was likely caused by enhanced carbon-layer formation, and the subsequent decrease in strength from 1000°C to 1500°C by increased defects in the fibers, as discussed above. These results clearly indicate the importance of optimizing carbonization temperature for the type and grade of CF precursor being used.

The tensile modulus of carbon fibers can be obtained from the slope of stress-strain curves. However, typical strain measurements from single-filament tests are based on machine crosshead displacement, and so must be corrected for system compliance to obtain the true strain. In this study, this was done using three different gage lengths (10, 16, and 25 mm). The compliance-corrected modulus of HP52K-based CFs
carbonized at 750°C and 1000°C was 58 ± 11 GPa and 78.8 ± 8 GPa. CFs carbonized at 1500°C displayed very low stress and strain levels at failure. These low strain levels are below the resolution limits of our experimental protocol and incorrectly resulted in measured moduli of only about 50 GPa. The tensile modulus of HP52K carbonized at 1000°C is consistent with our prior results for softwood-Kraft-lignin-based CFs of 74 GPa,31 double that previously obtained with a poplar lignin by Hosseinaei et al.,29 and at par with the modulus (73 GPa) for E-glass fibers.47

Conclusions
In addition to producing ultraclean lignin fractions of increased molecular weight as a precursor for carbon fibers, the ALPHA process enables the facile integration of lignin fractionation/purification with downstream dry spinning. Particularly in the context of a lignocellulosic refinery, where the aqueous ethanol product serves as the working ALPHA solvent, this technology offers the possibility of an elegant co-product option. Key to a doubling of both the strength and modulus of a poplar-lignin-based CF was the isolation of a very clean lignin fraction with a Tg of 147°C, higher than what could be melt spun without degradation. This higher Tg resulted in a factor of 5 reduction in stabilization times versus previously investigated poplar and other hardwood lignins. Additionally, the carbon fibers reported in this work display the highest reported strength and modulus of neat poplar or other hardwood lignin-based carbon fibers (1.1 ± 0.2 GPa and 78 ± 8 GPa, respectively). Both the stabilization and strength/modulus improvements are essential for producing high-quality carbon fibers for cost-sensitive applications. Finally, this study confirms our previous work with softwood Kraft lignins, demonstrating once again that the isolation of

| Sample label | Mw (Da) | Equivalent diameter (μm) | Average tensile strength ± std dev (GPa) |
|--------------|---------|--------------------------|----------------------------------------|
| HP7.6K (unfractionated) | 7600 | 38 ± 9 | 0.27 ± 0.1 |
| HP11K | 11,100 | 9.8 ± 0.5 | 0.6 ± 0.13 |
| HP24K | 24,000 | 9.8 ± 0.8 | 0.53 ± 0.1 |
| HP52K | 52,000 | 6.8 ± 0.8 | 1.1 ± 0.23 |
highly pure, higher MW lignins leads to significant improvements in the bulk properties of the resultant carbon fibers.

Limitations of study
As with other pre-commercial bioproducts, the variability intrinsic to lignin is a potential limitation. While a large enough batch-size could provide enough lignin precursor for an entire study, thereby mitigating tree-to-tree lignin variation, that was not feasible for this study. Still, all reasonable precautions were taken to ensure that the lignin samples produced in separate extraction batches were as similar as possible. Much to the same point, lignin characterization is not a totally solved problem in modern-day lignin research. In fact, there is not yet a unified and fully established method for quantifying lignin molecular weight distribution or functionality. Thus, while we can clearly show that our fractionation has impacted the Tg, we cannot prove that it is solely molecular weight (opposed to functionality) that is driving this change. Lastly, also due to the pre-commercial nature of this lignin, batch processes had to be used instead of continuous processes. For fibers, the transient nature of batch fiber processing means that the fibers are inherently prone to slight variations in structure for reasons unrelated to the intentionally changing lignin precursor.

STAR METHODS
Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION
Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105449.

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AUTHOR CONTRIBUTIONS
Conceptualization, M.C.T. and A.A.O.; Methodology, G.W.T. and S.V.K.; Validation, S.V.K. and G.W.T.; Investigation, S.V.K. and G.W.T.; Writing – Original Draft S.V.K. and G.W.T.; Writing – Review and Editing M.C.T., G.W.T., S.V.K., and A.A.O.; Supervision A.A.O. and M.C.T.

DECLARATION OF INTERESTS
The authors would like to declare that Mark Thies (lead contact and one of the corresponding authors) holds stake in the patent: US10053482B2. This patent covers the ALPHA (aqueous lignin purification with hot agents) process used in this work to generate lignin fractions.
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STAR★METHODS

KEY RESOURCES TABLE

| REAGENT or RESOURCE | SOURCE | IDENTIFIER |
|---------------------|--------|------------|
| Software and algorithms | | |
| Raman Analysis Software | Renishaw | WiRE 3.4 |
| MALS Analysis Software | Wyatt Technologies | Astra 7.3 |
| Other | | |
| MALS DAWN, ambient, 785nm laser, filtered detectors | Wyatt Technology | DAWN |
| Differential Refractometer | Optilab | WREX-08 |
| Styragel HT5 GPC Column | Waters | WAT045955 |
| Polargel-L GPC Column | Agilent | PL1117-6830 |
| 0.22 µm PTFE Filter | VWR | 76479-010 |
| TGA Analyzer | TA Instruments | Q5000R |
| DSC Analyzer | TA Instruments | MDSC 2920 calorimeter |
| Sugar HPLC Column | Bio-rad | Aminex HPX-87H (300 × 7.8mm) |
| Refractive Index Detector | Waters | 2414 |
| HPLC System | Waters | 600 |
| Batch Fiber Spinning Unit | Alex James & Associates Inc. | Custom |
| Scanning Electron Microscope | Hitachi | SU5000 |
| Scanning Electron Microscope | Hitachi | Regulus8230 |
| Raman Microscope | Renishaw | inVia |
| Wide Angle X-ray Scattering Device | Rigaku | SmartLab |
| Tensile Testing Machine | MTI | Phoenix |

RESOURCE AVAILABILITY

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Mark Thies (mcths@clemson.edu).

Materials availability
This study did not generate unique reagents.

Data and code availability
- All data reported in this paper will be shared by the lead contact upon request.
- This study did not generate original code.
- Any additional information required to reanalyze the data reported in this work is available from the lead contact upon reasonable request.

METHOD DETAILS

Lignin isolation and fractionation
Hybrid poplar (HP) lignin was extracted from wood chips (Populus nigra var. charkowiensis × P. nigra var. caudina cv. NE19) by alkaline pulping. The starting HP wood chips contained 23–24% lignin with an S:G ratio of 1.77–1.90, 17–18% xylan, and 1% ash, consistent with the HP averages cited above. To isolate the lignin from the biomass, the chips were first loaded into a 20-L digester along with NaOH at 18 wt % loading on biomass and a liquor-to-wood ratio of 5:1 (wt:wt). The digester was heated via a steam jacket to 150°C and held at temperature for 3 h. Afterward, the vessel was allowed to cool below 100°C and subsequently
opened. The resulting alkaline liquor was separated from the pulped solids by decanting, followed by a pressing of the solids to remove any entrained liquor. This liquor was then acidified to a pH of 2.0 via the addition of 96.6 wt % sulfuric acid. Upon acidification, lignin precipitates from solution as a fine solid. These lignin solids were separated from the brine by centrifugation for 2 h at 8000 rpm. To ensure the removal of residual salt from the brine, the lignin was then washed twice (at a lignin-to-water ratio of 1:5 by mass) and then, finally, dried in a vacuum oven at 50°C for 24 h. This lignin had a weight-average molecular weight of 7.6 kDa and was used both for spinning and as the feed for subsequent lignin fractions.

Three lignin fractions, designated as HP11K, HP24K, and HP52K according to their weight-average molecular weights, were isolated for dry-spinning into fibers using variations of the ALPHA process. For all fractions, a custom-made, conical-bottom variant of a model 4541, 2-L Parr reactor vessel was used to generate the desired phase split between the solvent-rich and the lignin-rich phases via ALPHA. The vessel was externally heated via pulse width modulation (PWM)-controlled heating tapes, with the internal temperature measured via a thermocouple mounted through the conical bottom. For all three fractions, the first stage of ALPHA (i.e., the leftmost block in Figures 1A–1C) was to combine the raw feed HP lignin with an ethanol (EtOH)/water solution in the vessel, followed by stirring for 30 min at temperature. The two liquid phases that formed in the vessel were then vacuum-filtered simultaneously (Whatman Grade 4 filter paper, WHA1004125) at temperature to remove the solid sugars and salt impurities insoluble in either phase. As described below, the filtrate (i.e., solvent-rich (SR) phase) was then further processed via ALPHA, using the vessel setup described above, and the impurities-rich retentate (i.e., lignin-rich (LR) phase) was set aside.

To generate lignin fraction HP11K (see Figure 1A), the feed lignin was first dissolved in a solution of 60/40 EtOH/water (w/w) at a solvent-to-lignin (S/L) ratio of 6:1 (wt:wt) and a temperature of 60°C. After 30 min of mixing, liquid–liquid phase separation, and vacuum filtration (as described above), the resulting filtrate (i.e., the SR phase) of purified lignin was dried and ground into a powder (i.e., the “Drying” block in the figure), with the drying step being performed so that the next ALPHA stage would be carried out at precisely known composition. Next, the dried, purified lignin was subjected to a single ALPHA stage using 30/70 EtOH/water (w/w) at S/L = 6:1 and 45°C (i.e., the rightmost block in the figure), using the Parr reactor setup described above, again with 30 min stirring. At these conditions, the desired liquid–liquid phase split occurred, with the lower-MW lignins being soluble in the SR phase along with metal impurities, and the LR phase enriched in higher-MW chains and depleted of salts. This lignin-rich phase (HP11k in the figure) was dried instead of being directly spun, so that a spinning dope of accurately known composition could be formulated.

Lignin fraction HP24K was generated (see Figure 1B) by first combining the feed HP lignin with a solution of 80/20 EtOH/water (w/w) at an S/L of 3:1 (wt:wt) and a temperature of 60°C, followed by mixing, phase separation, and filtration as described above. Water was then added directly to the undried filtrate (solvent-rich phase) to reduce the EtOH composition from 80 to 57 wt % ethanol, precipitating out an intermediate-MW, lignin-rich liquid phase. This precipitate was set aside, and more water was added to decrease the EtOH composition from 57 to 55%, causing an additional, higher-MW fraction of the starting bulk lignin to precipitate. This lignin-rich liquid phase (HP24k in the figure) was then dried for reconstitution of a spinning dope of known composition.

Fraction HP52K (Figure 1C) was generated using the same EtOH/water solvent composition, S/L ratio, and temperature as HP24K through the filtration step. After filtration, water was added to the undried filtrate (solvent-rich phase) at 25°C to decrease the EtOH/water composition to 50/50. At these conditions, ~42% of the starting lignin precipitated. The collected, lignin-rich phase was then dried so that compositions for the next ALPHA stage would be accurately known. A single ALPHA stage using 60/40 EtOH/water at an S/L ratio of 6:1 and a temperature of 37°C was then applied to this dried, purified lignin and used to precipitate out the highest-MW, lignin-rich phase (HP52k in the figure), which then had to be dried so that the composition of the spinning dope would be accurately known, as was the case for HP11K and HP24K. As will be subsequently shown in the stabilization section, controlling lignin molecular weight via ALPHA can be a critical step in the generation of hardwood-lignin-based carbon fibers.

**Lignin characterization**

Molecular weight characterization of lignin samples was performed using gel permeation chromatography (GPC) for separation followed by multi-angle light scattering (MALS) (DAWN Ambient, with 785 nm laser
option and fluorescence-blocking filters) and differential refractometry (Optilab-WREX-08) for detection. For the mobile phase, dimethyl formamide (DMF) with 0.05 M LiBr was used; the stationary phase consisted of a Styragel HT5 (Waters) column followed by a Polargel-L (Agilent) column in series. The mobile phase was supplied at a flowrate of 0.6 mL/min. Samples were prepared by dissolution in the mobile-phase solvent at a concentration of 1.5 mg/mL. Samples were then sonicated and filtered through 0.22 μm PTFE filters (VWR 76479-010) before being loaded into the instrument. Use of the MALS device allows for the measurement of molecular weight distribution without the need for a calibration standard. This is especially helpful for a biopolymer like lignin, for which there is no representative standard readily available. Due to the nature of light scattering, \( M_w \) (weight-average molecular weight) is measured directly, whereas \( M_n \) (number-average molecular weight) follows based solely on the separation performance of the GPC columns. Therefore, in this study we chose to focus on \( M_w \).

Polysaccharide content of lignin samples was determined by an NREL-based method described elsewhere.\(^\text{19}\) Ash content was determined using Thermogravimetric Analyzer (TGA) Q5000IR (TA Instruments). Thermal transitions of various molecular weight fractions of HP lignin were measured by differential scanning calorimetry (DSC) using an MDSC 2920 calorimeter (TA instrument, New Castle, DE). Heating–cooling cycles were carried out under inert (helium) atmosphere.

**Dry-spinning, stabilization, and carbonization of ALPHA lignins**

Ethanol–water mixtures of appropriate composition and amount were added to lignin fractions HP11K, HP24K, and HP52K to reconstitute a lignin-rich liquid phase that now served as the spinning dope. After adequate mixing, this one-phase solution was transferred into a custom-designed barrel fitted with a spinneret. Dry-spinning of the dope was conducted using a batch-spinning unit (Alex James Associates Inc., Greenville, SC). As-spun fibers were stabilized under constant load in a forced-air convection oven (Memmert GmbH + Co, Schwabach, Germany). Stabilized fibers were carbonized under constant length constraint in an Astro 1000 furnace (Thermal Technology LLC).

**Microstructure of the resultant carbon fibers**

To analyze the cross-section and longitudinal surface of the carbon fibers, two high-resolution field-emission scanning electron microscopes (FE-SEM; Hitachi SU5000 and Regulus8230) were employed. To determine the relative graphitic content in carbon fibers obtained from various MW fractions, CF filaments were scanned under Renishaw inVia Raman microscope, using a laser wavelength of 785 nm and laser power of 25 mW. The laser was focused on the fiber surface using 50x magnification. Data were analyzed using WiRE Raman Software version 3.4. Wide-angle X-ray diffraction experiments were conducted on carbon fibers using a Rigaku SmartLab powder diffractometer, using Cu K\( \alpha \) radiation (1.5406 Å) and a Hypix3000 detector. Location of the 0-0 peaks was calibrated using NIST Silicon standard.

**Tensile testing**

Tensile testing of carbon fibers was based on standard test method ASTM D3379-75. Single fibers were mounted on a paper tab with a 10 mm gauge length and bonded to the tab using epoxy resin. After curing of the resin, paper tabs were mounted and pulled until failure in an MTI Phoenix testing machine. To accurately determine the cross-sectional area, tested fibers were imaged by SEM. Standard test method ASTM C1557-03 was followed to estimate the system compliance in order to calculate true modulus. Single filaments of 10, 16, and 25 mm gage lengths were used for system compliance correction.

**QUANTIFICATION AND STATISTICAL ANALYSIS**

Quantification and statistical analysis were performed using Microsoft Excel for both tensile testing and Raman spectroscopy data. In both cases, each data point was collected from a single fiber; at least 15 data points were collected for tensile testing and at least 3 data points were collected for Raman spectroscopy. Pairwise Student’s t-tests were used to quantify statistically significant difference between data sets.