

Lignin carbon fiber: The path for quality

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Lignin represents an abundant biopolymer and a major waste from lignocellulosic processing plants, yet the utilization of lignin for fungible products remains one of the most challenging technical barriers for pulp mills and the modern biorefinery industry [1]. In recent decades, lignin has been sought after as a precursor polymer for carbon fiber due to the high carbon content (up to 60%). Lignin carbon fiber is expected to be compatible with the market size of the pulp and paper industry and may have transformative impact on petroleum-based carbon fiber [1].

CHALLENGES IN FABRICATING LIGNIN

Current strategies for fabricating lignin carbon fiber include blending lignin with other polymers served as plasticizers [2], reinforcing lignin carbon fiber using functional materials like carbon nanotube [3] and cellulose nanofiber [4], and modifying lignin phenolic hydroxyl groups (Ar-OH) through esterification [5,6]. Nevertheless, the quality and mechanical performance of current lignin carbon fiber are still too low to compete with commercialized petroleum-based carbon fiber, making lignin carbon fiber impractical for industrial application.

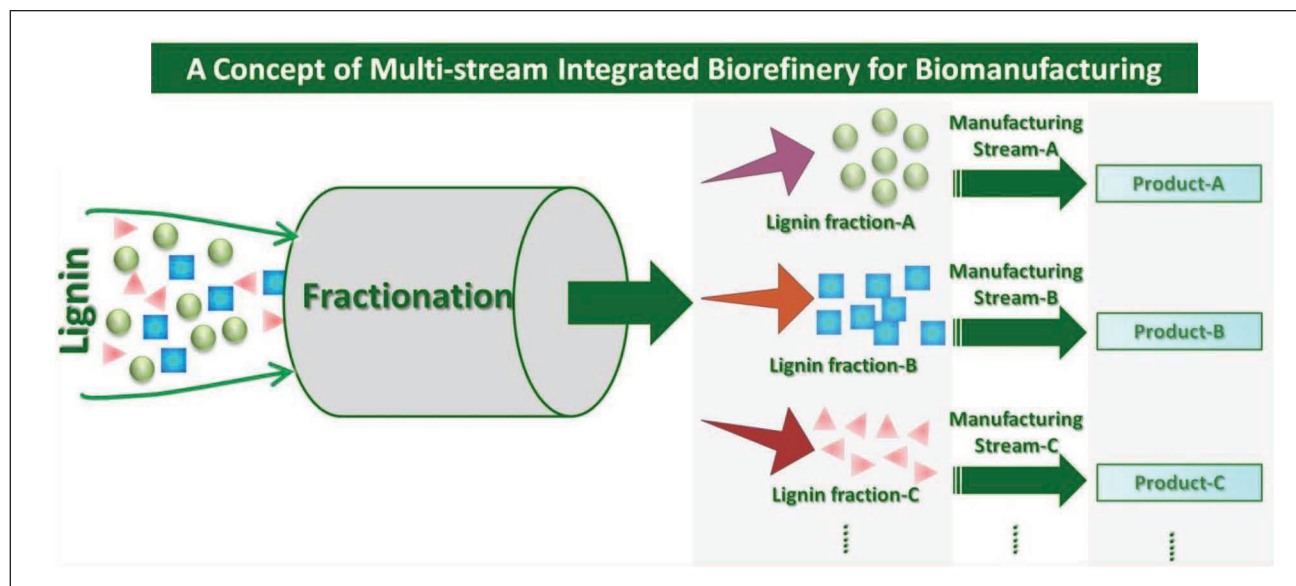
The real challenge of the poor quality lies in the heterogeneity of the lignin structure, which is caused by broad mole-

cule weights, various interunitary linkages, and diverse functional groups. These inherent molecular characteristics could hinder the crystallite turbostratic carbon structure formation during the carbonization and graphitization of lignin carbon fiber. Thereby, the modification of lignin molecules toward more uniform structure could be the path for producing quality lignin carbon fiber.

TOWARDS HIGHER QUALITY LIGNIN CARBON FIBER

Two recent works have shed light onto the path for quality lignin carbon fiber. In the first work, Sun et al. (2016) [7] have shown the potential of organosolv lignin as the precursor of quality lignin fiber. Organosolv lignin is derived from organic solvent-based extraction of biomass and is purer than most other types of lignin due to less polysaccharide content and modified condensed structures [7,8]. In fact, the most abundant industrial lignin is currently generated from the widely-used kraft pulping process, namely kraft lignin. Most types of lignin, including kraft lignin, need to be purified and further fractionated to improve their uniformity before manufacturing carbon fiber toward high quality.

Recently, Li et al. (2017) [9] have shown that biochemical fractionation using an enzyme-mediator system can derive lignin fractions to produce carbon fiber with certain mechan-



1. Lignin fractionation to enable multiple product streams for biomanufacturing.

SPECIAL FEATURE

ical performance similar to some commercial carbon fibers. The carbon fiber derived from fractionated lignin improved spinnability, fiber morphology, and crystallite structure, all of which might have led to the improved mechanical performance and quality. The underlying molecular mechanisms for improved spinnability and crystallite structure could be due to the more uniform molecular weights, interunitary linkages, and functional groups. The detailed mechanisms are yet to be revealed.

POTENTIAL OF A MULTI-STREAM INTEGRATED BIOREFINERY

Despite the need for further studies, the recent work unveiled the potential of a multi-stream integrated biorefinery for biomanufacturing enabled by lignin fractionation and utilization. As shown in **Fig. 1**, lignin fractionation could produce multiple lignin streams with different uniformity and chemical characteristics. The fractionated lignin streams could be used as starting materials for multiple biomanufacturing streams to make different final value-added products.

Basically, previous studies have demonstrated that low molecular weight lignin fraction is more suitable for bioconversion for lipid [10,11], bioplastics [12,13], and asphalt binder modifier [14], and high molecular weight lignin fraction could be better feedstock for carbon fiber, as demonstrated in the recent work [7,9]. The multiple lignin streams will inevitably enhance cost-effectiveness and sustainability for both the pulp and paper industry and lignocellulosic biorefineries. **TJ**

LITERATURE CITED

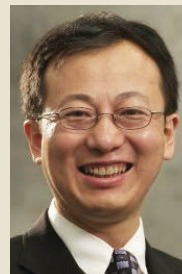
1. Ragauskas, A.J., Beckham, G.T., Biddy, M.J., et al., *Science* 344(6185): 709(2014).
2. Kadla, J.F. and Kubo, S., *Composites, Part A* 35(3): 395(2004).
3. Liu, H.C., Chien, A., and Newcomb, B.A., *ACS Sustainable Chem. Eng.* 3(9): 1943(2015).
4. Ago, M., Okajima, K., Jakes J.E., et al., *Biomacromolecules* 13(3): 918(2012).
5. Thunga, M., Chen, K., Grewell, D., et al., *Carbon* 68: 159(2014).
6. Ding, R., Wu, H., Thunga, M., et al., *Carbon* 100: 126(2016).
7. Sun, Q., Khunsupat, R., Akato, K., et al. *Green Chem.* 18(18): 5015(2016).
8. Sadeghifar, H., Wells, T., Khuu Le, R., et al., *ACS Sustainable Chem. Eng.* 5(1): 580(2017).
9. Li, Q., Xie, S., Serem, W.K., et al., *Green Chem.*, 2017, DOI: 10.1039/c6gc03555h.
10. Zhao, C., Xie, S., Pu, Y., et al., *Green Chem.* 18(5): 1306(2016).
11. Xie, S., Sun, Q., Pu, Y., et al., *ACS Sustainable Chem. Eng.* 5(3): 2215(2017).
12. Lin, L., Cheng, Y., Pu, Y., et al., *Green Chem.* 18(20): 5536(2016).
13. Shi, Y., Li, Q., Wang, X., et al., *Process Biochem.* 52: 238(2017).
14. Xie, S., Li, Q., Karki, P., et al. *ACS Sustainable Chem. Eng.*, 2017, DOI: 10.1021/acssuschemeng.6b03064.

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