Scaling Up Reductive Lignin Depolymerization: A Sustainable

Pathway towards Biomaterials and Green Chemicals

Balaji Sridharan^a, Paul Jusner^a, Brent Daelemans^a, Marc Comí Bonachí^a, Elias Feghali^{a,b}, Kelly Servaes^a, Karolien

Vanbroekhoven^a

^aFlemish Institute for Technological Research (VITO), Unit Separation and Conversion Technology, Boeretang 200, 2400, Mol, Belgium

^bChemical Engineering Program, Notre Dame University-Louaize, Zouk Mosbeh 1211, Lebanon

The emergence of lignin-first biorefineries highlights the potential of lignin's aromatic-rich structure for producing high-value green chemicals and additives. A crucial step in lignin valorization is depolymerization, where the complex lignin biopolymer is broken down into monomers, dimers, and oligomers, with their functionality dictated by the catalyst and process conditions. Reductive depolymerization, in particular, has seen significant progress, though primarily on a small (g to mg) semi-continuous scale and with wood as the starting material [1], [2], [3]. To meet the immediate demand for lignin-derived chemicals, integrating reductive depolymerization with existing biorefineries (e.g., kraft, hydrolysis, organosolv) is essential.

To facilitate the upscaling of lignin valorization, this study demonstrates the long-term continuous reductive depolymerization of various lignins sourced from commercial biorefineries.

Depolymerization was conducted in a packed bed reactor containing 15 - 30 g of a noble metal catalyst such as Pd/Al₂O₃ or Ru/Al₂O₃. The influence of process parameters—including temperature (200–250°C), lignin concentration (5–7 wt.% in methanol), feed rate (25–100 mL/h), and catalyst selection—was systematically studied. The quality of the resulting depolymerized lignin oil (DLO) was extensively characterized using GC-MS/FID, NMR (¹³C, ³¹P and 2D HSQC), GPC, and CHN analysis.

Within the tested process conditions, continuous reductive depolymerization of hydrolysis and organosolv lignins was successfully demonstrated for over 100 hours of time-on-stream (TOS) at 235°C using Pd/Al_2O_3 and methanol as the solvent [4]. A significant reduction in lignin molecular weight was observed, particularly at higher temperatures. Optimized conditions yielded an overall carbon efficiency exceeding 90%, indicating minimal carbon loss to coke formation or permanent gases. These observations are in line with observations from a previous study [4].

Results from this study were successfully scaled up to pilot scale at the LignoValue plant at VITO. Additionally, depolymerized lignin was used as a precursor for synthesizing various biopolymers, such as polyurethane foams and epoxy resins, with scale-up efforts ongoing within the EU-funded COUNTLESS project. Furthermore, DLO serves as a valuable source of monomeric alkylphenols, including propanol guaiacol (PG) and dihydrosinapyl alcohol (DSA), enhancing the process's overall techno-economic viability. Finally, an extensive techno-economic analysis was conducted to identify key cost drivers and guide future improvements to the technology.

References:

- [1] E. Kuatsjah et al., "Lignin Utilization," Proc Natl Acad Sci U S A, vol. 120, no. 4, Nov. 2022, doi: 10.1073/PNAS.2212246120.
- [2] X. Huang, O. M. Morales Gonzalez, J. Zhu, T. I. Korányi, M. D. Boot, and E. J. M. Hensen, "Reductive fractionation of woody biomass into lignin monomers and cellulose by tandem metal triflate and Pd/C catalysis," *Green Chemistry*, vol. 19, no. 1, pp. 175–187, 2017, doi: 10.1039/C6GC02962K.
- [3] E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, G. T. Beckham, and Y. Román-Leshkov, "Flowthrough Reductive Catalytic Fractionation of Biomass," *Joule*, vol. 1, no. 3, pp. 613–622, Nov. 2017, doi: 10.1016/j.joule.2017.10.004.
- [4] P. Jusner *et al.,* "Assessing the potential for upscaling the continuous production of lignin oils through reductive catalytic depolymerization," *Chemical Engineering Journal*, vol. 499, p. 156474, Nov. 2024, doi: 10.1016/J.CEJ.2024.156474.

COUNTLESS project is supported by the Circular Bio-based Europe Joint Undertaking and its members. Grant agreement ID: 101112453.







