Catalytic depolymerization of isolated lignin to low molecular weight aromatics

Karina Hablich, [a] Alfonso Cornejo, [a] Víctor Martínez-Merino, [a] Fernando Bimbela, [a] Luis M. Gandía. [a]

a) Institute for Advanced Materials (INAMAT) - Dpt. of Sciences, Campus de Arrosadía, Universidad Pública de Navarra, E31006 Pamplona, Spain

karina.hablich@unavarra.es

Lignin isolated from lignocellulosic residues is a promising candidate to be catalytically converted into low molecular weight phenolic compounds, thus being a source of renewable phenolic compounds. These may be an alternative to petroleum-based compounds. To realize its full potential, it is necessary to characterize lignin in detail in order to gain further insight on its actual structure and to determine how it behaves in various potential applications.[1]

Besides structural features, such as β-O-4 content or the functional group content in both the lignin and in the depolymerization products, the molecular weight will determine not only the depolymerization degree but also its further application. In consequence, determination of the molecular weight of lignin and depolymerization products is crucial. In this sense, Size Exclusion Chromatography, SEC, is by far the most widely used technique for determining the molecular weight and size distribution[2]. However, Diffusion Ordered Spectroscopy in Nuclear Magnetic Resonance, DOSY-NMR, correlates the molecular weight with the functionality of the molecular fragment, thus allowing the selective estimation of the molecular weight.

In this work, industrial lignocellulosic residues (poplar sawdust) were subjected to different delignification treatments (organosolv and alkaline), and depolymerized by reductive methods like hydrodeoxygenation and hydrogenolysis, the latter being a promising route to valorize lignin into low molecular weight and value added products. [3] Catalytic lignin depolymerization was conducted in a pressurized batch stirred tank reactor at different temperatures (200-270 ^{o}C) and pressures ranging 3-10 MPa, using a 5 wt.% CuNi/MgAl catalyst. The catalyst was prepared by incipient wetness impregnation of a hydrotalcite-like commercial Mg-Al support. Lignin and depolymerized product samples were evaluated by several analytical techniques, including DOSY Spectroscopy, which was systematically used in the determination of the molecular weight of the resulting products and compared with the data provided by SEC.

[1] El Mansouri, N.; Salvado, J. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. *Industrial Crops and Products,* **2006**, 24, 8-16. https://doi.org/10.1016/j.indcrop.2005.10.002

[2] Rinaldi, R.; Jastrzebsky, R.; Clough, M.; Ralph, J.; Kennema, M.; Bruijnincx, P.; Weckhuysen, B. Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew. Chem. Int. Ed.*, **2016**, 55, 8164-8215. https://doi.org/10.1002/anie.201510351.

[3] Wang, S.; Gao, W.; Xiao, L.; Shi, J.; Sun, R.; Song, G. Hidrogenolysis of biorefinery corncob lignin into aromatic phenols over activated carbon-supported nickel. *Sustainable Energy Fuels.* , **2019**, 3, 401-408. https://doi.org/10.1039/c8se00359a.