Study of lignin-water molecular interactions using NIR spectroscopy: the effect of the drying process of the hardwood kraft lignin

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Kraft lignin, a widely available aromatic compound generated as a residue by the pulp and paper industry, has revealed enormous potential to be valorized into a wide range of chemicals and biomaterials in the last two decades (Hodásová et al., 2015; Naseem et al., 2016).

However, the understanding of lignin chemistry remains challenging due to its chemical complexity. Lignin polymer is a hygroscopic material owing to the presence of many hydrophilic functional groups such as hydroxyl (phenolic and aliphatic), methoxyl, carbonyl and carboxyl in its complex chemical structure (Xiao et al., 2019). Such specific configuration of functional groups may greately affect performance of lignin-derived compounds in particular applications (Volkova et al., 2012).

The goal of this work was to investigate the effect of the drying temperature on the hygroscopic properties of hardwood kraft lignin isolated from industrial black liquor. Sorption isotherms were determined by dynamic vapor sorption (DVS) technique. In addition, molecular interactions occurring between water and isolated kraft lignins were studied through 2D spectral correlations of NIR spectra collected from samples at diverse moisture contents.

Based on visual analysis, an important effect of the drying temperature on the lignin color was observed. Moreover, sorption isotherms revealed that the drying process considerably influenced the hygroscopicity of the lignin polymer.

Dynamic NIR spectra collected as a function of relative humidity (0-95%) during sorption-desorption cycles evidenced chemical differences between lignins dried at room conditions (25 °C) and mild oven-dryed (50 ºC). It was noticed that spectra variations during the water sorption process of kraft lignin dried at 25 ºC were more intense than observed for the same lignin dried at 50 ºC. These observations were confirmed by 2D spectral correlation analyses. Finally, it was demonstrated that the drying process considerably affects the lignin chemistry and, consequently, moisture sorption mechanisms and kinetics.

**Keywords:** hardwood kraft lignin, hygroscopicity, DVS, NIR spectroscopy, 2DCOS

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