Organosolv lignins isolation from different biomasses and their characterisation

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Introduction

The development of new strategies for lignocellulose valorisation goes in line with the demand of implementing circular economy principles by large industries, such as the timber industry (Salem *et al*, 2021). Lignin, which for a long time has been considered as a is a waste residue of pulp and paper industry, is generally burned or landfilled in substantial quantities (Garlapati *et al*, 2020). While contributing to environmental pollution, such handling of lignin is also an ineffective usage of a potentially high-valued polymer.

Lignin is a heterogenic phenylpropanoid biopolymer found in most terrestrial plants, which gives the plant its mechanical strength. It is the most abundant natural aromatic polymer, accounting for roughly 30% of organic carbon in the biosphere, and acts as a cellular glue material to interconnect cellulose and hemicellulose (Figueiredo *et al*, 2018). The lignin polymer consists of three different cross-linked monolignol units: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. The *p*-hydroxyphenyl unit (H), guaiacyl unit (G), and syringyl unit (S) are the building blocks based on these monolignols when integrated into the lignin macromolecule, there is a difference in the distribution of monolignol units depending on the type of plant biomass (Schoenherr *et al*, 2018).

One of the main barriers for lignin valorisation stems from its complicated and heterogenic structure Wang *et al*, 2019). A number of methods for lignin extraction and characterisation have been developed over the course of decades. Using the Organosolv method, it is possible to preserve lignin's structure close to its native form as it exists in the plant cell wall through the extraction with organic solvents (Zhang *et al*, 2016). Size-exclusion chromatography (SEC) is presently the most effective and optimal method for lignins molecular weight distribution determination (Andrianova *et al*, 2018). Fourier transform infrared spectroscopy (FTIR) is a technique that is useful for the determination of functional groups and structural units (monolignols) present in lignin (Khan *et al*, 2018).

The purpose of this study was to optimize and implement analytical procedures for lignin analysis by size-exclusion chromatography and Fourier transform infrared spectroscopy, as well as investigate the effect of the different solvent usage in Organosolv extraction method on lignin properties and structure. A study was conducted on lignin extracted from three different biomass types: hardwood (aspen wood), softwood (pine wood), and grassy biomas (barley straw). From each biomass, the lignin was extracted with usage of ethanol and 1,4-dioxane as the solvent.

Results and discussion

The usage of different solvents in the extraction showed variability in the yield and of the color of the lignin. Dioxane extraction resulted in 2-3 times higher yield and darker color of lignin. Lignins extracted with ethanol were of lighter color, where pine wood lignin had a pinkish hue. In the case of pine wood, an formation of ethoxylated compounds was observed during extraction with ethanol.

The results from size-exclusion chromatography showed, that lignin extracted with ethanol has slightly higher molecular weight (avg. $M_n \approx 2300$ g/mol, $M_w \approx 3400$ g/mol), compared to lignin extracted from the same biomass using dioxane as the extraction solvent (avg. $M_n \approx 1900$ g/mol, $M_w \approx 2800$ g/mol). The highest and lowest molecular weights belonged to the aspen ethanol lignin and barley straw dioxane lignin, respectively. The polydispersity indices ranged from 1.37 to 1.76. No correlation was observed between the polydispersity index and the biomass/extraction solvent used. The method showed high repeatability results (<1.2%). Overlayed chromatograms of analysed lignins can be found on Figure 1.

The FTIR results showed that aspen wood lignin is rich in S and G units (~2:1 with ethanol and ~1:1 with dioxane extraction). The presence of S and G units in pine wood did not show significant difference for ethanol and dioxane extracted lignin, the ratio was ~1:2. The barley straw lignins monolignol ratio was not affected by extraction solvent, where the S and G unit ratio was ~1:2. Overlayed spectas of analysed lignins can be found on Figure 2.

Based on current work, it can be concluded that the choice of the biomass feedstock and extraction solvent influence molecular weight distribution of lignins, as well as on the content of monolignols. For further implementation and valorisation of lignin, the optimal biomass and extraction procedure can be selected based on this study.

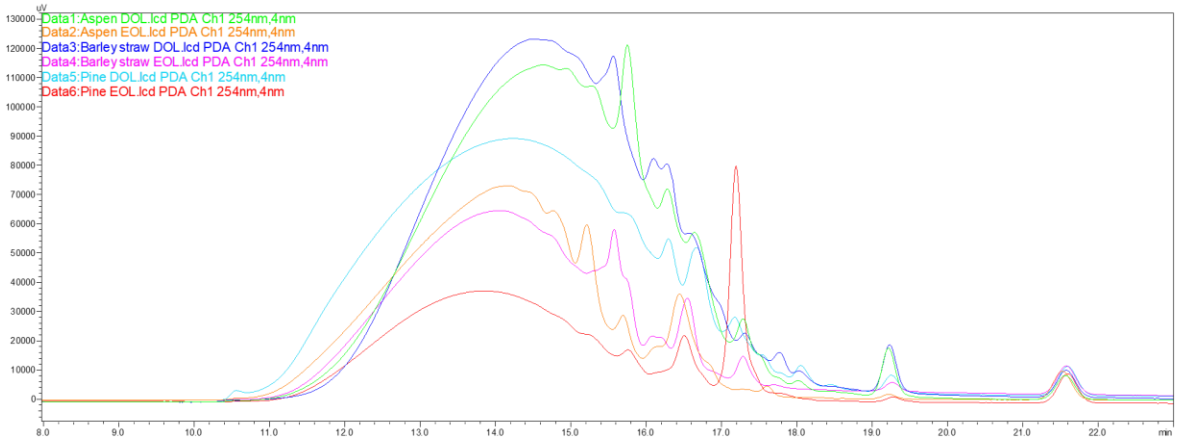

*Figure 1. Investigated lignins SEC chromatograms overlay, the main wide peak comes from the main lignin polymer, following signals are denaturation products and monolignols, * – systematic peaks. EOL – Ethanol Organosolv Lignin; DOL – Dioxane Organosolv Lignin.*

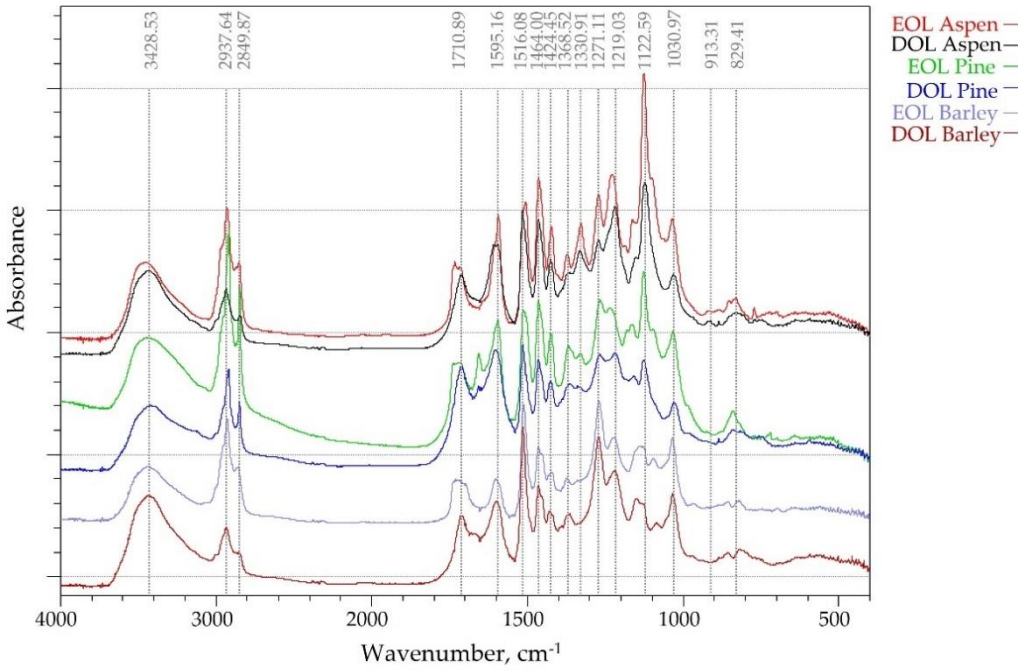

Figure 2. Analysed lignins FTIR spectra overlay. Syringyl unit specific bands: 1331 cm⁻¹ and 1123 cm⁻¹, Guaiacyl specific bands: 1271 cm⁻¹, 1219 cm⁻¹, and 1031 cm⁻¹. EOL – Ethanol Organosolv Lignin; DOL – Dioxane Organosolv Lignin.