TOWARDS SPECIFIC DESCRIPTION OF AUTOHYDROLYZED LIGNIN'S CHEMICAL STRUCTURES

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As the scientific community barrels forward with efforts to establish the lignocellulosic biorefinery process at an industrial scale, in-house underutilization of lignin continues to thwart process profitability. Due to this pestilence, the properties of lignin (as it would appear in a real process) have come under heavy investigation. We have thoroughly developed a biorefinery process for producing carbohydrates from raw biomass utilizing a mild-intensity sequence of autohydrolysis, mechanical refining, and finally, cellulolytic hydrolysis. It has been concluded that this process, depending on the starting material, is capable of recovering ~70-90 wt% of biomass' structural polysaccharides as monomers and hemicelluosic oligomers. Lignin is in greatest abundance in two locations within the process: 1) the liquid phase after autohydrolysis ("autohydrolyzate"), and 2) the solid phase after enzymatic hydrolysis. In order to effectively evaluate means of valorization for both aforementioned lignin streams, it is first imperative to exact specific characterizations upon each of them. For the insoluble lignins, an isolation protocol was employed to generate representative lignin isolates from both raw and autohydrolyzed + enzymatically-hydrolyzed solids. Two raw lignin isolates (MWL and CEL) and one pretreated lignin isolate (AHCEL) from six different biomasses were subjected to physical and spectral characterization to obtain molecular weights, the quantities of hydroxyl moieties, and finally, the quantities of specific inter-lignin chemical structures. For example, nonwoody AHCEL isolates, ranging in yields from 31-46 wt% of starting lignin, were found to have approximate molecular weights ranging from 9K – 11K g/mol. Furthermore, the β-O-4' ether content in nonwood AHCEL ranged from 18-23 #/100 Ar, surprisingly higher than what was quantified in hardwood AHCEL, 15-17 #/100 Ar. Concerning autohydrolyzate-soluble lignins, we have investigated a protocol for separating soluble lignins from autohydrolyzate solution. Liquid-liquid extraction of autohydrolyzate using ethyl acetate was found to produce a lower molecular weight lignin fraction (nonwood ~840 g/mol; hardwood ~860 g/mol) that did not represent the entirety of the solubilized lignin. Application of adsorptive resin to autohydrolyzate was then investigated to obtain the higher-molecular weight autohydrolyzate lignins (nonwood ~1440 g/mol; hardwood ~940 g/mol) that eluded capture by ethyl acetate. Both autohydrolyzate lignin isolates are to be subjected to the same analytical protocols as the insoluble lignin isolates. It is our hope that the wealth of lignin characterization data produced will propel valorization technologies for lignin in the context of a biorefinery process.