Pentafluoropyridine with ^{19}F NMR offers a safe and cost-effective alternative to quantify phenolic groups in lignin and lignin-derived products

Background

- Phenolic groups are important for both reactivity and material properties in lignin and lignin-derived products. A widely implemented method for quantifying phenolic groups in lignin is phosphitylation followed by ^{31}P NMR spectroscopy. This straightforward method suffers from important drawbacks such as an expensive hazardous derivatization agent and degradation of the reagent and derivatized samples.

Approach

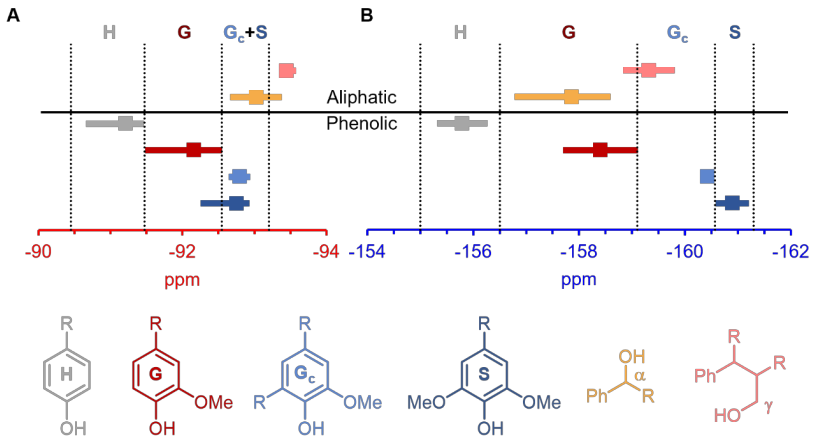
- We hypothesized that derivatizing lignins with pentafluoropyridine (PFP) followed by ^{19}F NMR could offer a safer and cheaper method to quantify phenolics ($6/g for PFP vs. $217/g for the phosphitylation reagent). We screened approximately 30 lignin model compounds for their reactivity with PFP. From these results, we compared ^{19}F NMR method to the ^{31}P method for three lignins: poplar RCF oil, softwood kraft lignin, and corn stover milled wood lignin.

Results

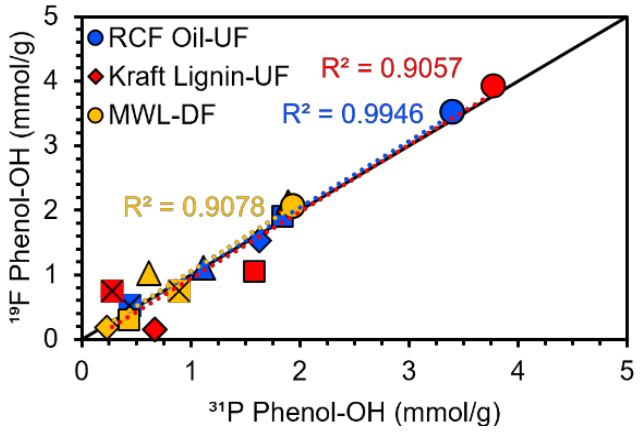
- Using a 40% H_2O/DMSO solvent allowed for complete and selective reaction with most model compounds studied. Although aliphatic hydroxyl groups may react with PFP, high selectivity to the phenolic reaction is obtained by using a short (5 min) reaction time. The chemical shift of the products allowed for differentiation of 5-substituted, S, G, and H moieties. Good agreement with ^{31}P results for total phenol quantification was obtained for all three lignins studied. There were some differences for specific moieties: for softwood, the ^{19}F method measured a lower amount of S units while for RCF oil, the S, G, and 5-substituted moieties were indistinguishable.

Significance

- A comparable analytical method avoids the use of a dangerous reagent and improves safety – especially for less experienced chemists. The method supplements the tools available to characterize lignin hydroxyl groups. Furthermore, the higher derivatized sample stability in DMSO allows for future higher-throughput applications.



^{19}F NMR chemical shift of phenolic moieties in 40% H_2O/DMSO.



Parity plot of ^{31}P results versus ^{19}F for poplar RCF oil, softwood kraft lignin, and corn stover milled wood lignin.

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