

# Increased H monomers in lignin change molecular weight, linkages, structure and recalcitrance

## Background

- Higher coumaryl alcohol (H monomer) content in alfalfa lignin correlated with lower molecular weight and was preferentially extracted during base pretreatment, indicating the H monomer reduced biomass recalcitrance. Theoretical calculations predict that **incorporation of H monomers could reduce recalcitrance of the lignin in biomass** by lowering molecular weight and also form H-based homopolymers. Studies on the structural influence of H monomers on lignin at varying compositions is needed to understand its role in the recalcitrant properties of lignin.

## Approach

- Lignin dehydrogenation polymers **were synthesized incorporating alternate amounts of sinapyl (S), coniferyl (G) and H monomers**. The polymers structures and molecular weight were then characterized using liquid and solid state NMR, gel permeation chromatography, thioacidolysis and pyrolysis-MBMS.

## Outcome

- Low amounts of H (5 mol%) on G-based polymers formed more  **$\beta$ -5 linkages that lead to lower molecular weight polymers**.
- Solid state NMR shows the high-H (20 mol%) polymers resulted in the formation of separate homopolymers, a G or S/G-based and a **separate H-based homopolymer**.
- An increase was seen in labile  $\beta$ -O-4 linkages** based on thioacidolysis recovery and NMR analysis in the S/G=1 polymer structure with high H content, which could result in a decrease in recalcitrant properties of the lignin.

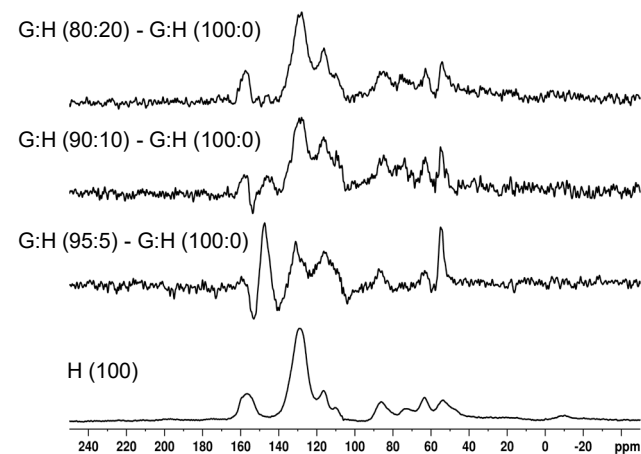
## Significance

- The decrease in molecular weight, increase in  $\beta$ -O-4 linkages and the formation of separate H-based homopolymers in DHPs suggests H monomers can play a role in the reduction of recalcitrant properties of lignin in biomass and also support previous findings in alfalfa studies and theoretical calculations.

Effect of monomer ratios on synthesized lignin molecular weight (Mw) and linkages

DHP	S:G:H (50:50:0)	S:G:H (40:40:20)	G:H (100:0)	G:H (95:5)
Mw (g/mol)	4800	7800	7700	2100
thio recovery ( $\mu$ mol/g)	225	938	404	525

Solid-state NMR subtraction spectra at different G:H ratios.



Harman-Ware, et al., The effect of coumaryl alcohol incorporation on the structure and composition of lignin dehydrogenation polymers

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