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Spectroscopic identification of most suited technical lignin for use in biocomposites

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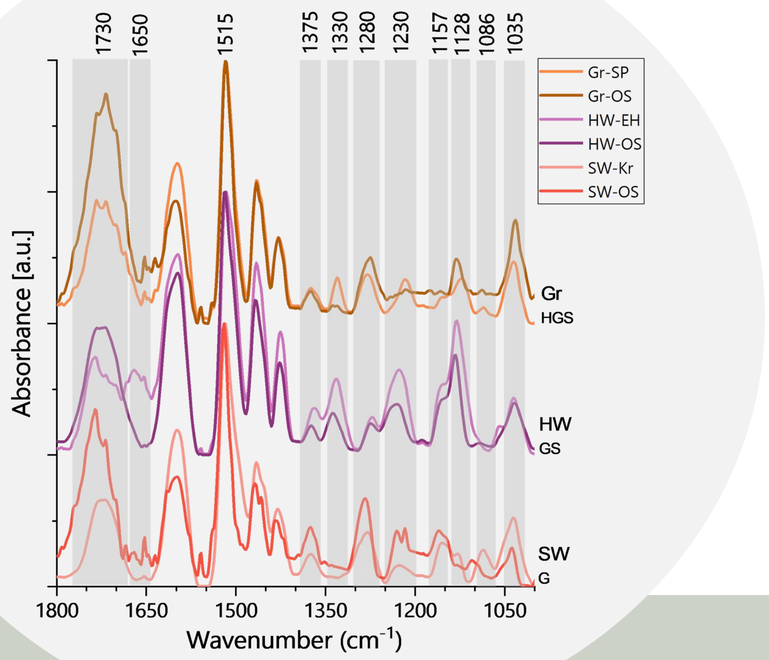
Softwood lignin has more aromatic uncondensed –OH and G units than hardwood's, meaning more C_5 free to recondense. Also, **SW-OS** has more *carboxylic acids*, *aliphatic –OH,* and *hydroxycinnamic acid monomer*s, which hints towards higher re-condensation potential as a binder for entirely wood-based biocomposites.

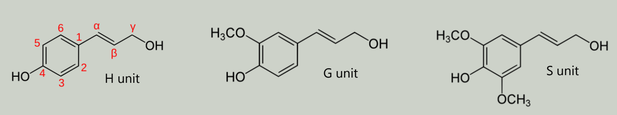
Motivation

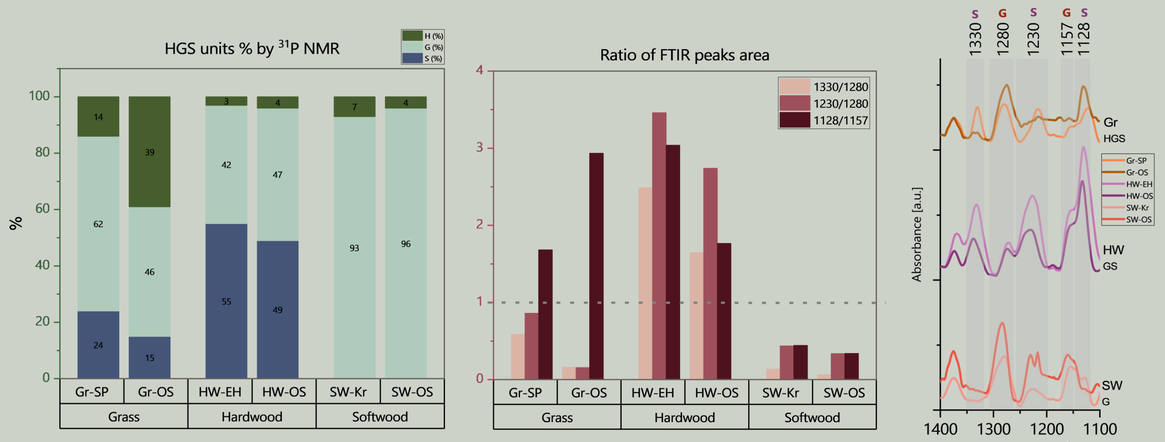
A significant portion of wood's potential (50%) is currently lost as by-products in sawmills. However, these by-products can be more effectively utilized by incorporating them into high-performance biocomposites. To identify an appropriate **lignin binder** for a hot-pressed construction material entirely derived from wood products, we conducted a comparison of six technical lignins from different origins and extraction processes. The results contribute to the advancement of sustainable building materials by enhancing our understanding of the chemical motifs of different lignins and their potential as a binder.

Source		Extraction Process	
Grass	Gr	Soda Pulping	SP
Grass	Gr	Organosolv	OS
Softwood	SW	Kraft	Kr
Softwood	SW	Organosolv	OS
Hardwood	HW	Enzymatic Hydrolysis	EH
Hardwood	HW	Organosolv	OS



HGS units

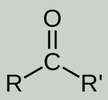


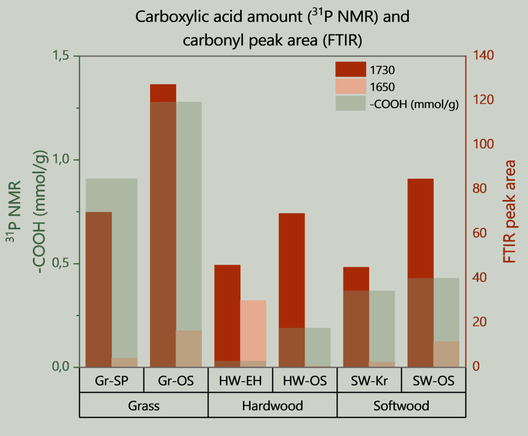


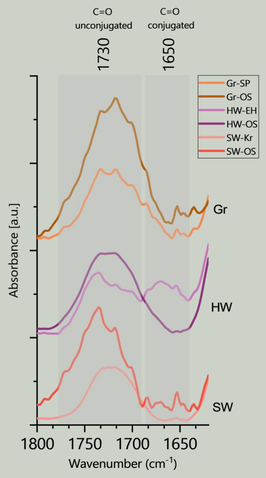
- Softwood lignin has more G units (^{31}P NMR) and therefore the most prominent bands in FTIR are the 1280 cm^{-1} and 1157 cm^{-1}
- Hardwood lignin has G and S units (^{31}P NMR) and therefore the most prominent bands in FTIR are 1330 cm^{-1}, 1230 cm^{-1} and 1128 cm^{-1}
- Grass lignin has G, S and H units (^{31}P NMR) and therefore the FTIR band 1280 cm^{-1} is just a bit more prominent than the 1330 cm^{-1} and 1230 cm^{-1}, and the 1128 cm^{-1} is more prominent than 1157 cm^{-1}
- HGS units % are what mostly defines lignin FTIR spectra shape

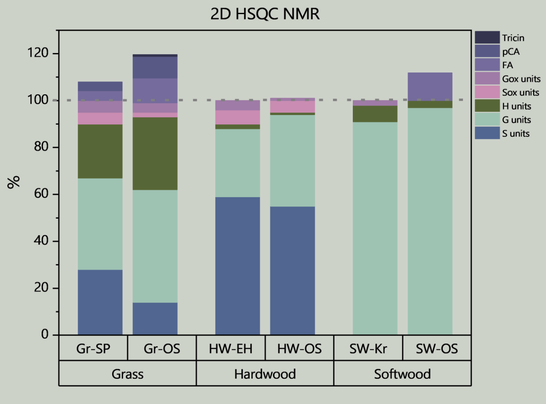
Lignin band (cm^{-1})	Vibration	Assignment[1]
1738-1709	ν (C=O)	C=O stretch in unconjugated ketone, carbonyl and in ester groups (frequently of carbohydrate origin); conjugated aldehydes and carboxylic acids absorb around and below 1700
1655-1675	ν (C=O)	C=O stretch; in conjugated p-subst, aryl ketones; strong electronegative substituents lower the wavenumber
1593-1605	ν (aromatic skeletal)	aromatic skeletal vibrations plus C=O stretch; S>G; G condensed > G etherified
1505-1515	ν (aromatic skeletal)	aromatic skeletal vibrations, G>S
1460-1470	δ (C-H)	C-H deformations, asymmetric in -CH2- and -CH3
1430-1422	ν (aromatic skeletal) + δ (C-H)	aromatic skeletal vibrations combined with C-H in-plane deformations
1365-1370	ν (C-H) + phen.-OH	aliphatic C-H stretch in CH3, not in OMe; phen. OH
1330-1325	ν (C-O)	C-O; S ring plus G ring condensed (G ring substituted in pos. 5)
1270-1266	ν (C-O) + ν (C=O)	G ring plus C=O stretch
1221-1230	ν (C-O) + ν (C=O)	C-C plus C-O plus C=O stretch; G condensed > G etherified
1166	ν (C-O) + ν (C=O)	typical for HSG lignins, C=O in ester groups (conj.)
1140	δ (C-H)	aromatic C-H in-plane deformation; typical for G units; whereby G condensed > etherified
1128-1125	δ (C-H) + ν (C=O)	aromatic C-H in-plane deformations (typical for S units); plus secondary alcohols plus C=O stretch
1086	δ (C-O)	C-O deformation in secondary alcohols and aliphatic ethers
1035-1030	δ (C-H) + δ (C-O) + ν (C=O)	aromatic C-H in plane deformations, G > S; plus C-O deform, in primary alcohols, plus C=O stretch (unconj.)

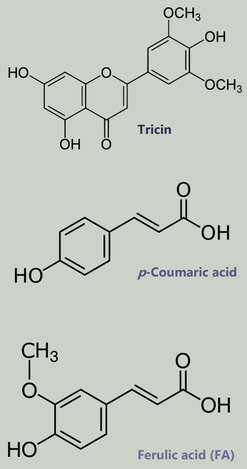
Carbonyl groups

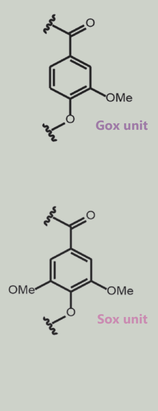






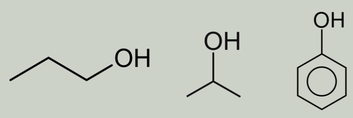


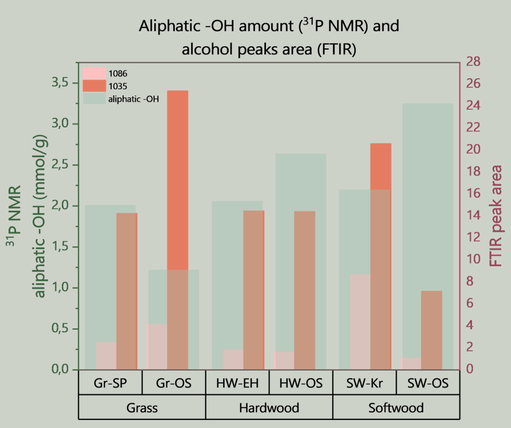


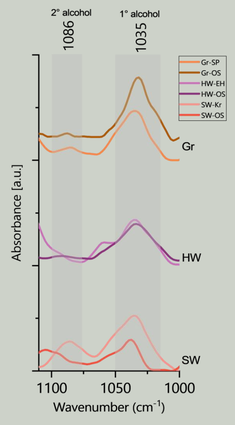


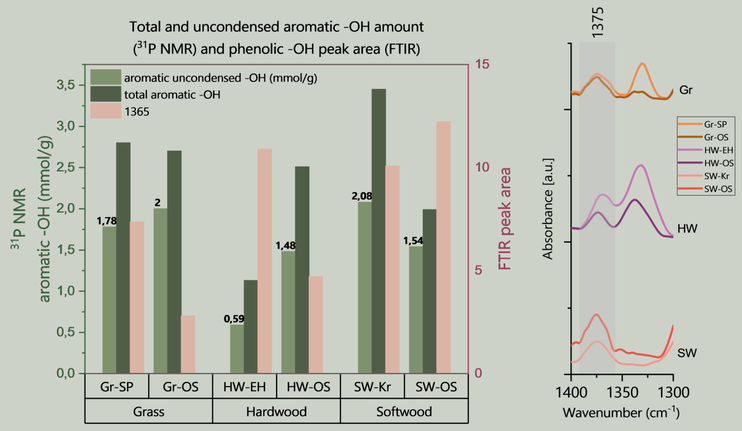
- For softwood and grasses, lignins with more carboxylic groups (^{31}P NMR) are the OS ones and have a more intense unconjugated carbonyl band (FTIR)
  - They also have more *p*CA and FA % in relation to HGS units (2D HSQC NMR)
- For hardwoods, the % of oxidized GS units is higher in **HW-EH**, which also have very few carboxylic acids, so the C=O band shifts to the right (conjugated carboxyl 1650 cm^{-1} peak more intense)
  - HW-OS carbonyl peak (FTIR) has more contributions of other structures (like ester) than carboxylic acids

Alcohol and phenolic groups









- Aliphatic –OH (^{31}P NMR) and 1° and 2° alcohol bands (FTIR) do **not** correlate
- Total aromatic –OH (^{31}P NMR) and phenolic –OH band 1375 cm^{-1} (FTIR) do **not** correlate
  - Phenolic vibrations are incorporated into the bands in the region 1260-1165 cm^{-1}
  - Aromatic uncondensed –OH (^{31}P NMR) also does not correlate
- Lignins with more aromatic uncondensed –OH have more reactive carbons (C_5) available

Conclusion

- Grass lignins do not come from wood and therefore are not fit for an entirely wood-based biocomposite.
- Softwood organosolv lignin chemical composition hints towards a more effective binder for wood-based biocomposites.

Reference
[1] Faix, O. "Classification of Lignins from Different Botanical Origins by FT-IR Spectroscopy" 45, no. s1 (1991): 21–28. https://doi.org/10.1515/hfsg.1991.45.s1.21.

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