WoodComp3D

Modified Lignin as a Binder in Hot-Pressed Biocomposites: Fractionation and Maleation

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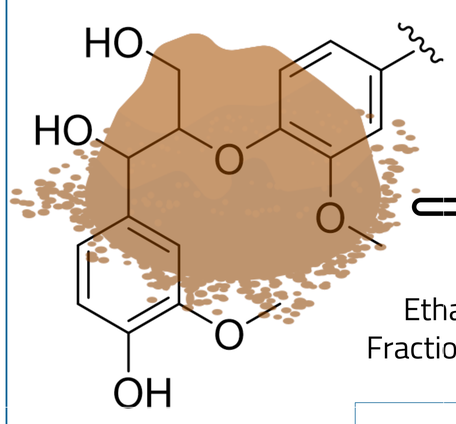
Introduction

Tons of biomass are being underutilized as part of the wood production chain, burned as pellets where carbon is released into the atmosphere [1,2]. In the WoodComp3D project, we produce hot-pressed lignocellulosic biocomposites with high mechanical strength, where lignin, as in the natural wood, plays the role of a binder [3], however, its full potential remains untapped.

One of the primary obstacles is its heterogeneity. To address this, fractionation of lignin presents an opportunity for a more comprehensive valorization of lignin, which is not commonly achieved when only specific, often soluble lignin fractions are utilized. Furthermore, separated lignin fractions can be modified to improve their binding properties. The great interest lies in modifications by compounds of biobased origin, such as furfural and 5-HMF, which can be used to produce maleic anhydride. The reaction with hydroxyl groups of lignin leads to the ring opening of maleic anhydride and further esterification of the installed carboxyl groups, resulting in cross-linking [4]. However, different lignin fractions will react differently with maleic anhydride due to their respective molecular weights and the respective availability of hydroxyl groups for maleation.

This study not only enriches our understanding of lignin's binding capabilities but also advances complete biomass valorization where waste streams are turned into value-added products.



Softwood Kraft Lignin
MW: 2.1 kDa, PD 2.34

Ethanol Fractionation

Soluble Fraction
- Yield: 55%,
- MW: 1.5 kDa, PD 1.52

Insoluble Fraction
- Yield: 45%
- MW: 3.1 kDa*, PD 3.07

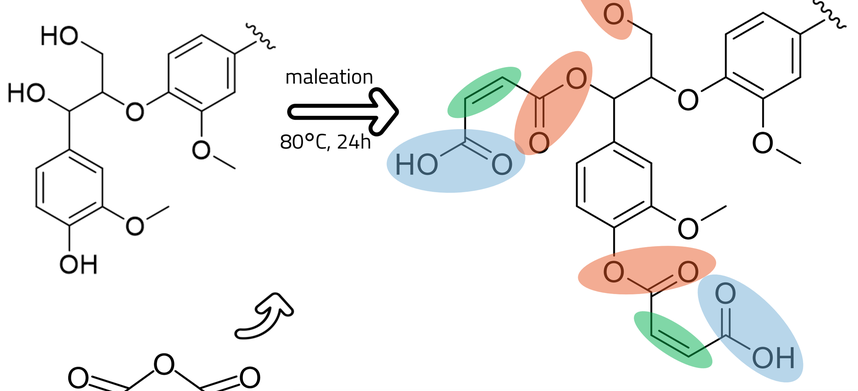
Fractionation:
Lignin (100 g/L) stirred (600 rpm) in 96% EtOH for 1 hour and centrifuged

*GPC eluent used was 1o mM NaOH

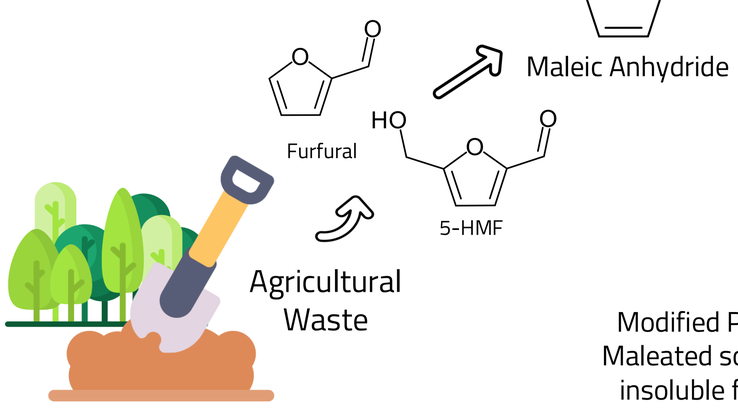
Understanding Lignin's binding capability

Fractions modified and studied separately

Maleation:
- Solvent free
- Mechanical stirring
- 80°C, 24h
- MA 95%wt (~1.5 equiv relative to the total number of OH groups of lignin)

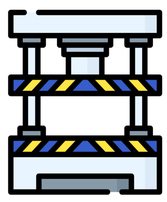


Maleation:
- Ring-opening of MA by hydroxyl groups of lignin.
- Esterification of the installed carboxyl groups, leading to crosslinking.



Modified Products: Maleated soluble and insoluble fractions

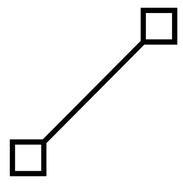
Workflow
- Delignification of woodchips with peroxyacetic acid
- Fibers swelling
- Reintroduction of chemically modified lignin
- Hot-pressing
- Mechanical strength testing



Hot Press
45 MPa, 190°C

3D Composite

Mechanical Strength of the Composite

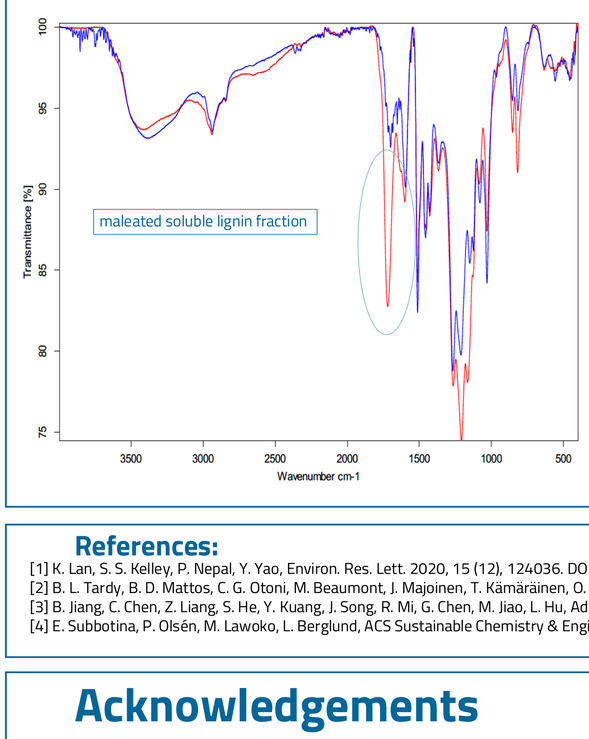


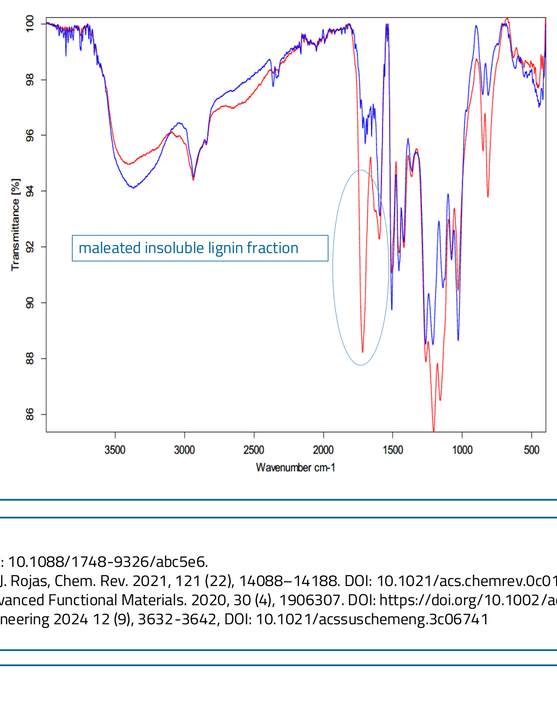
Correlation

Lignin Properties: Functional Groups Content (-OH, -COOH, etc.), Molecular Weight, Glass Transition Temperature

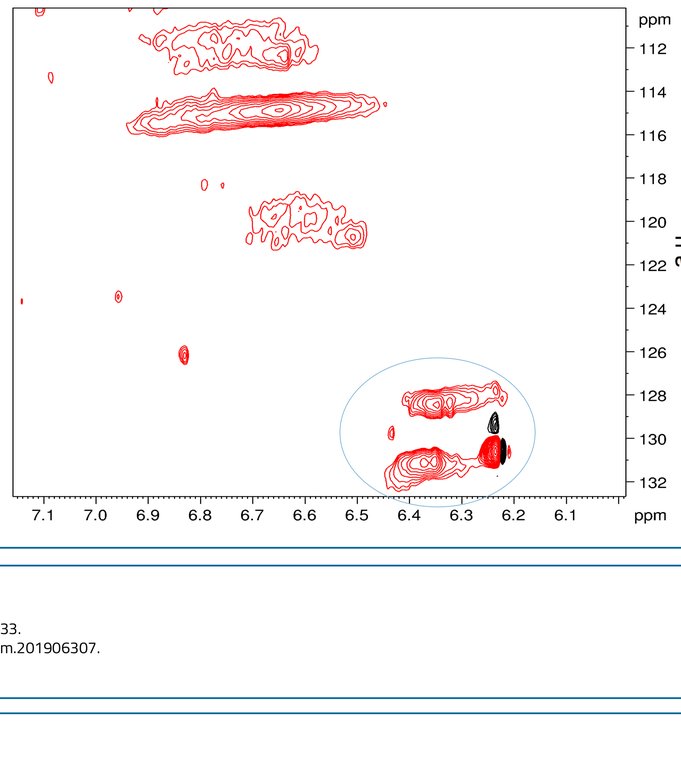
Analytics

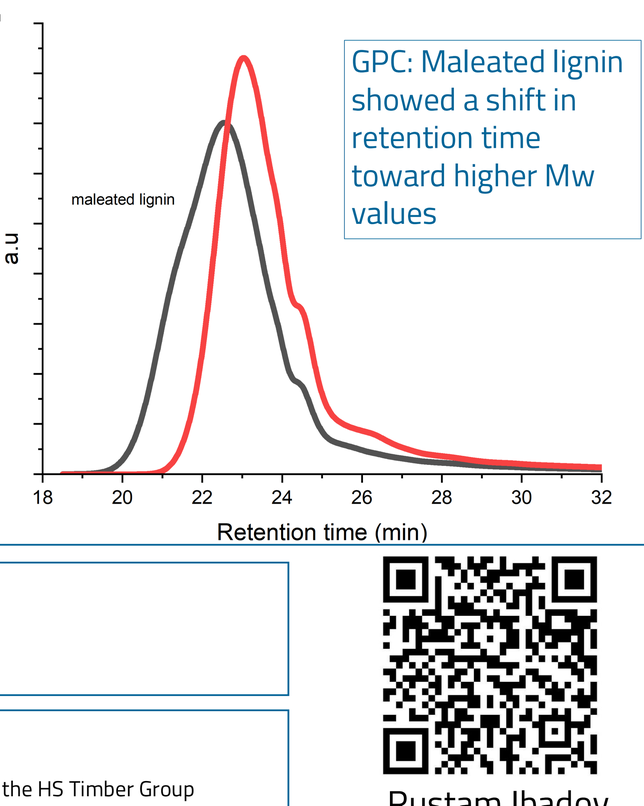
FTIR: both soluble and insoluble fractions show a significant increase of C=O groups content (~1700–1750 cm^{-1})





HSQC NMR: signals corresponding to maleic acid half esters as an evidence of successful maleation





GPC: Maleated lignin showed a shift in retention time toward higher Mw values

References:
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