Lignins-First Flexible Biorefinery: Valorization Process Design for Sustainable Construction Material

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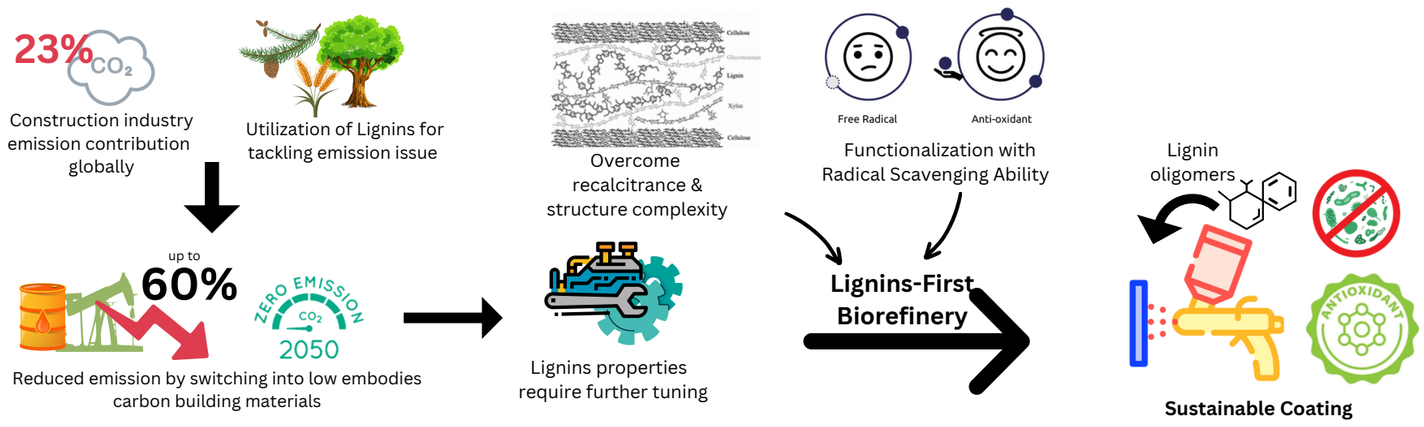
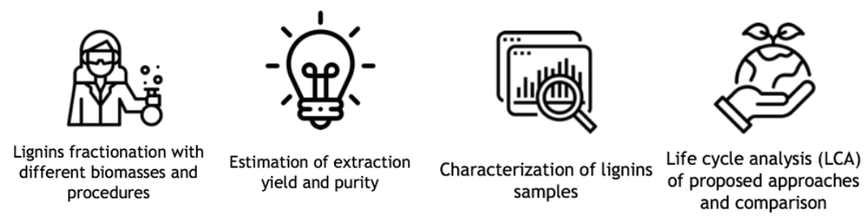
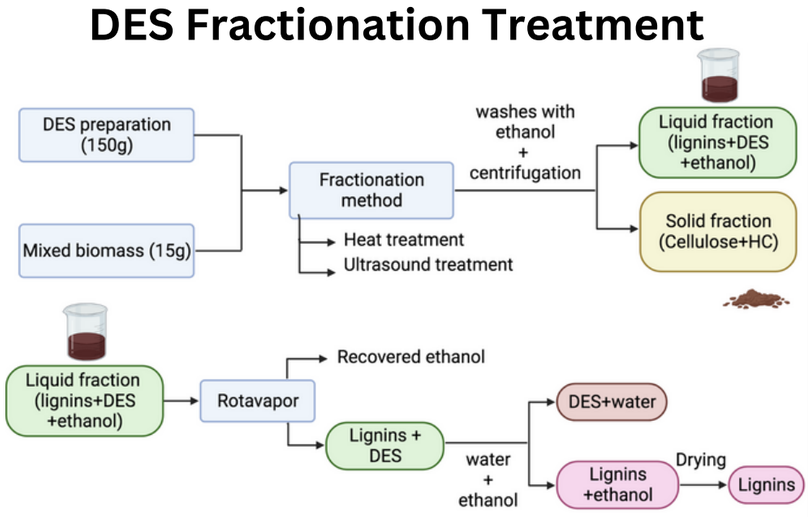
Introduction



Objectives and Experimental Plan



DES Fractionation Treatment

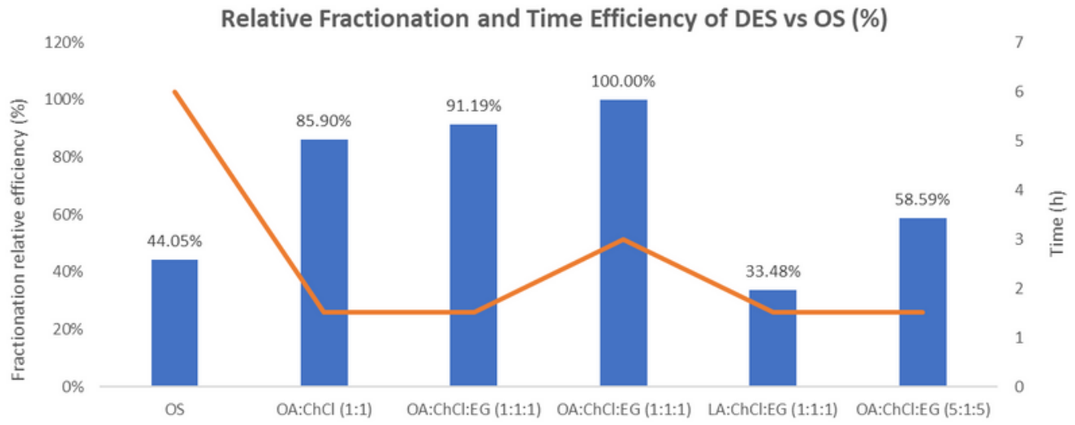


Results Analysis

Flexibility through the integrated approach

- Fractionation similar rates for mixed biomass and individual biomasses (95.44%)
- Lower Mw obtained through an integrated approach
- Wider range of available products with mixed biomass fractionation

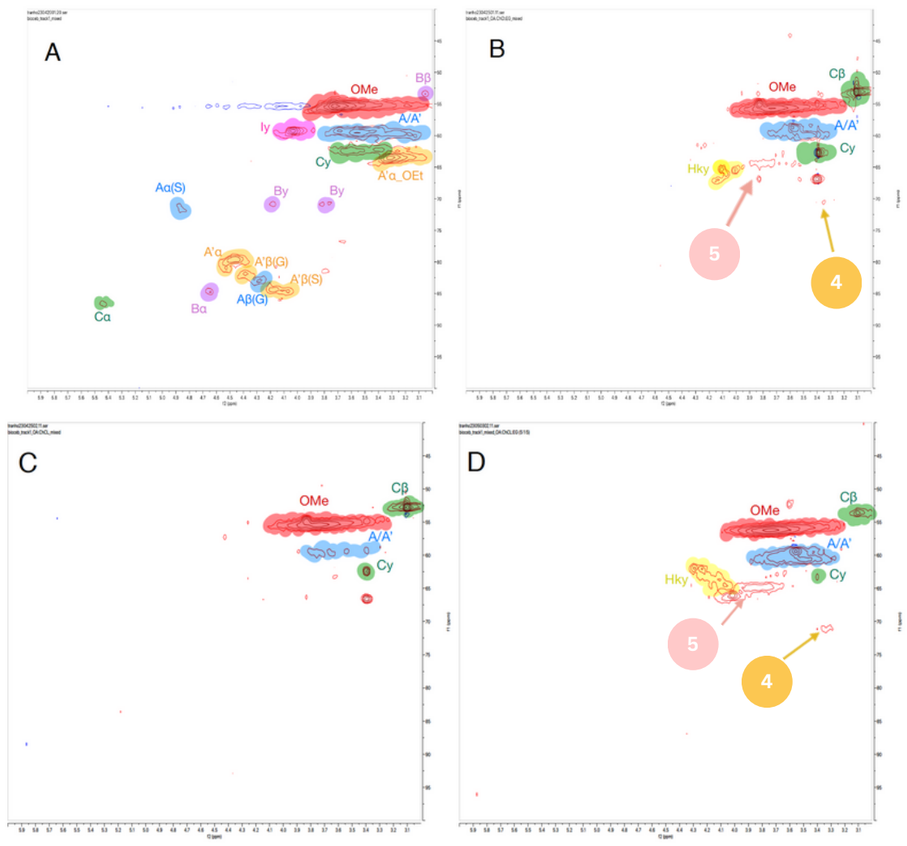
Relative performance of DES fractionation of the biomass



- The considerable drop in duration period and increase in the relative fractionation efficiency set DES as the preferred treatment for lignins isolation.
- While DES lignins present "thinner" grains" and darker colors, OS lignins were found much"rougher" and lighter colors. This can be doomed in the former case's acidity conferred by the employed solvent.
- Different fractionation treatments presented distinct textures and colors when comparing OS and DES-isolated lignins.

Isolated lignins by DES treatment in the left (OA:ChCl and OA:ChCl:EG correspondingly) and OS treatment in the right

DES effect on Isolated Lignins



2D HSQC-NMR spectra of aliphatic side chain region of A. OS B. OA:ChCl:EG (1:1:1) C. OA:ChCl (1:1) D. OA:ChCl:EG (5:1:5)

ATR FTIR spectrums of isolated lignins from OS treatment (black) and OA:ChCl:EG (1:1:1) (red)

ß-5 conserved

1. Little reduction in C-H bond availability in DES-treated lignins. It shows the **ß-5 bond is less likely to be cleaved** in DES treatment

ß-O-4 Selective Cleavage

2. A significant drop is observed n C-O-C aliphatic region. It emphasized that the **ß-O-4 bond is selectively cleaved** to prevent C-C bond cleavages (ß-5, ß-ß, or 5-5") leading to less condensation.

Molecular Uniformity & Weight Distribution

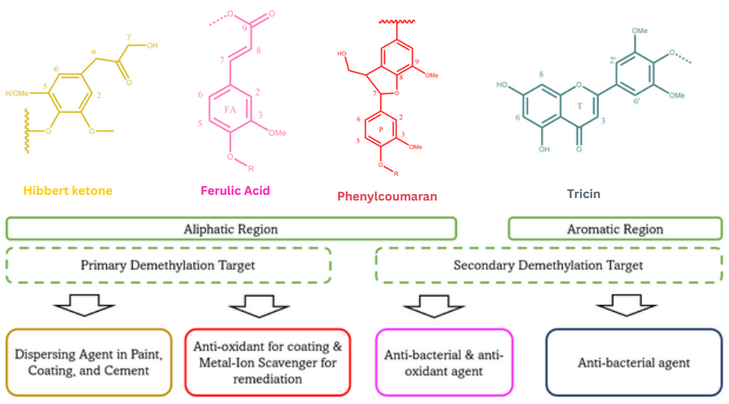
3. The Mn of lignins from DES treatment is comparatively lower than OS due to smaller oligomers possibly found with a lower polydispersity index. It indicates that **DES oligomers or monomers are more consistent** in terms of molecular size and weight. Additionally, **lower Mw are identified for the DES** isolation of lignins.

Stabilizer Signal

4. Comparing to current research's result, there is small signals on *70.20/3.32* (A'' –EG/A'' –GLY) in OA:ChCl:EG 1:1:1 and *70.64/3.34* for OA:ChCl:EG 5:1:5 2D NMR results which are believed as EG traces.

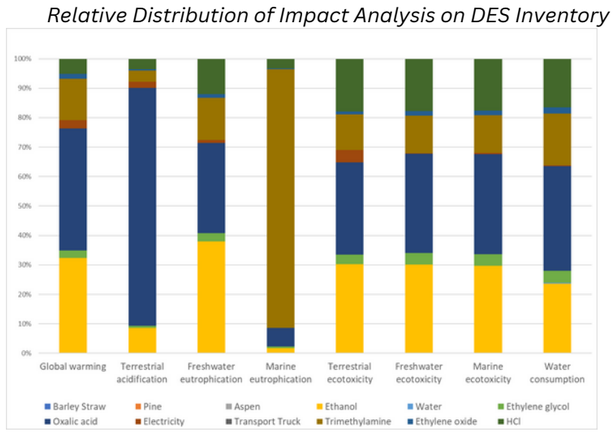
Novel Chemical Bonds Formed by EG Stabilization

5. These keeper signals were attributed to polyol-incorporated β–O–4 structures. During the fractionation, the acidic DES forms carbocation intermediates via dehydration at the Cα position of lignin. Then, the carbocation intermediate was trapped by the EG to generate polyol-alkoxylated lignins.

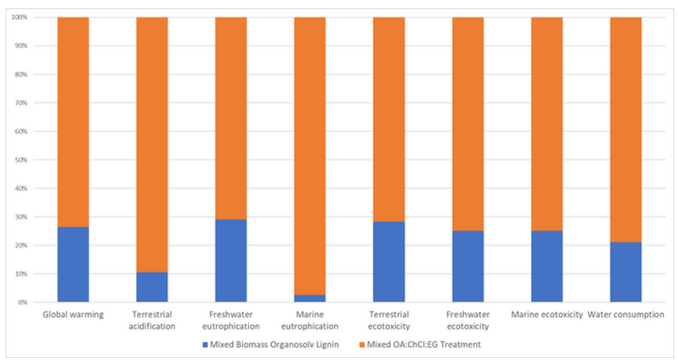


Life Cycle Assessment

Relative Distribution of Impact Analysis on DES Inventory



Comparison on LCIA Relative Distribution



- The DES treatment yields a noticeable LCIA criteria compared to OS. This result can be traced from the inventory analysis, where oxalic acid emits significant carbon emissions from the oxidation of sucrose using vanadium pentoxide.
- In addition, choline chloride production involves the dehydration of Trimethylamine and Ethylene Oxide with HCl, which contributes to major water discharge into the environment.

Main Footprints from Respective Treatments

	OS	DES
	24.6 kg CO_2 eq	68.53 kg CO_2 eq
	224 L	840 L

1 kg of lignins

Future Perspectives

- Depolymerization of isolated lignins through microbial approaches.
- Estimation of the further effect of functionalization on abundancy of hydroxyl group on lignins product

Conclusions

- **Flexibility** approach through implementation of the **integrated approach;** not only access to wider amount of interest molecules, but also fractionation of lower MW lignins
- **Lignins-first** through **DES fractionation** approach: performance with higher fractionation and time efficiency rates when compared to OS results
- **Simultaneous fractionation and functionalization** through ternary DES with EG

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