# Upgrading biorefinery lignins through green and cost-efficient reactive extraction

Davide Rigo and Mikhail Balakshin

FinnCERES Materials Cluster

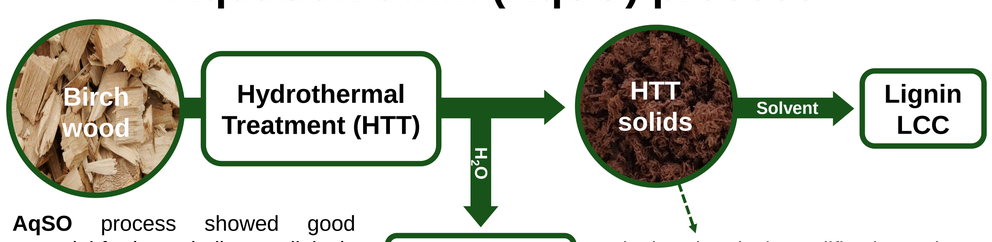
Aalto University

## Abstract

We here report a **benign-by-design** simple process that simultaneously functionalizes and extracts lignin from biorefinery residues (**Reactive Extraction, REx**) at a proof-of-concept level. The reactive extraction of lignin from crude biorefinery residues was performed with aqueous ethanol under mild conditions in the presence of catalytic amounts of a strong acid ($H_2SO_4$). Comprehensive analysis on the reactive extracted lignins was performed by means of wet chemistry methods (*i.e.* methoxy/ethoxy groups evaluation), and 2D NMR techniques. By tuning the reaction conditions (time, EtOH concentration, etc.) we were able to tune the **lignins structure** and **degree of ethoxylation**.

## Introduction

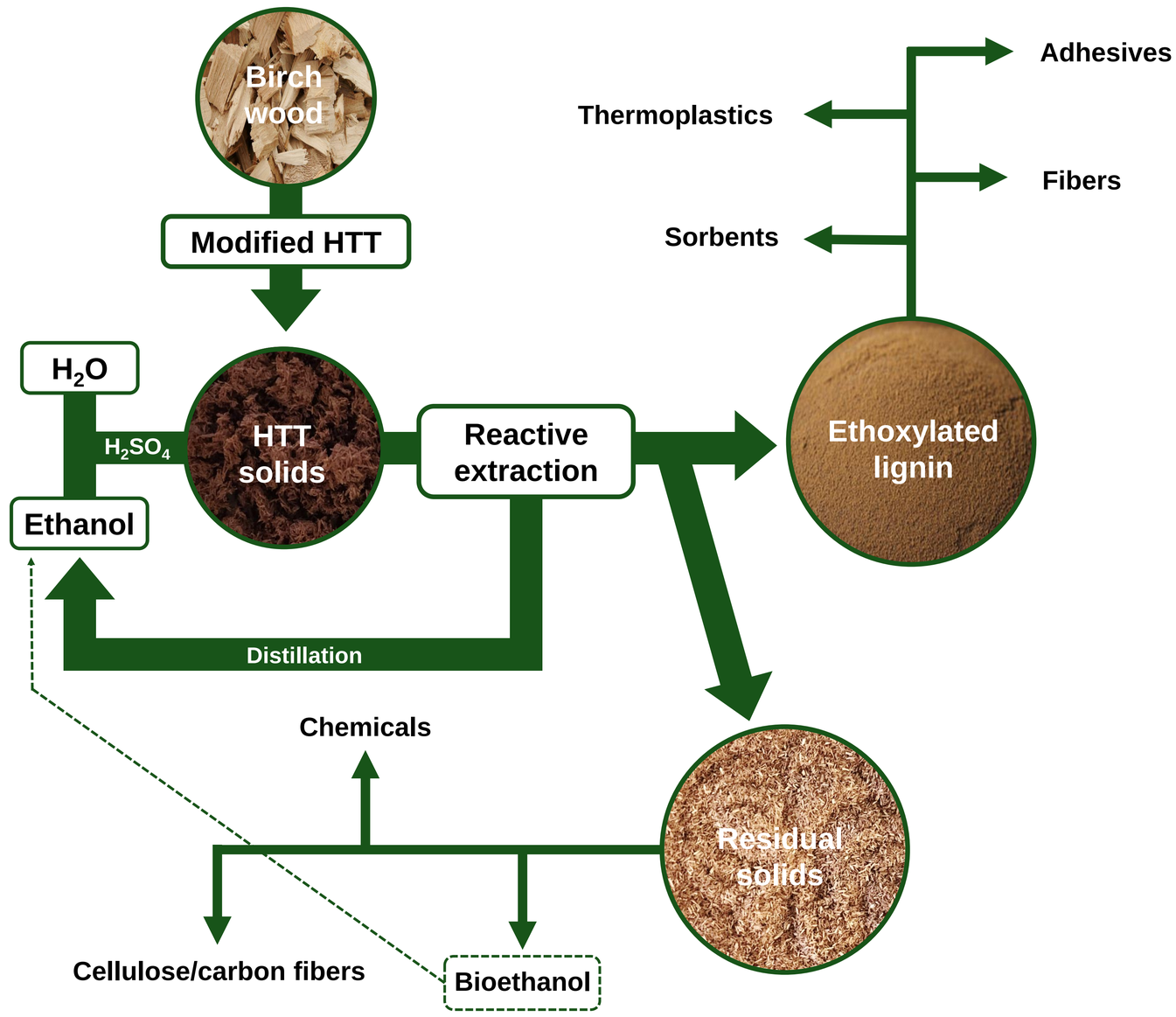
### AquaSolvOmni (AqSO) process



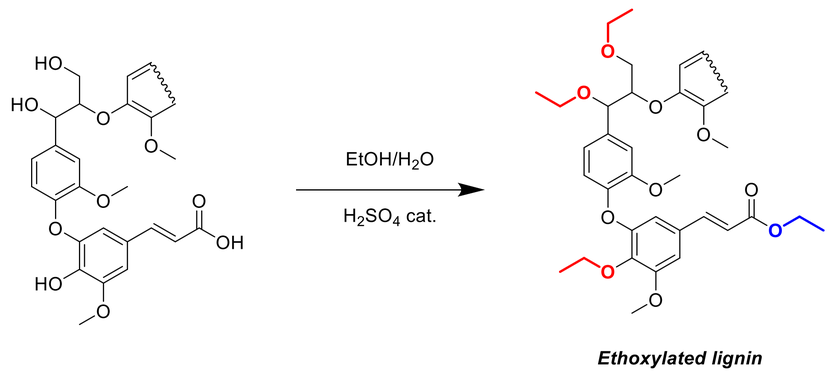

**AqSO** process showed good potential for its main ligno-cellulosic products to be used in high value applications, such as adhesives, thermoplastics, manmade fibers, and sorbents, in addition to the traditional biorefinery products (e.g., sugars monomers, pulps). [1]

Lignin chemical modifications, i.e., **alkylation**, are widely considered to efficiently upgrade lignin towards important applications. [2]
A valuable opportunity is the upgrading of HTT solids throughout ***Reactive Extraction (REx).***

[1] Tarasov, D., Schlee, P., Pranovich, A., Moreno, A., Rigo, D., Wang, L., Sipponen, M., Xu, C., Balakshin, M. Towards a new generation of biorefinery: AqSO process to streamline the development of high-value sustainable products from all lignocellulosic biomass components. Submitted to GreenChem
[2] M. Y. Balakshin, E. A. Capanema, I. Sulaeva, P. Schlee, Z. Huang, M. Feng, M. Borghei, O. J. Rojas, A. Potthast and T. Rosenau, *ChemSusChem*, **2021**, *14*, 1016–1036.

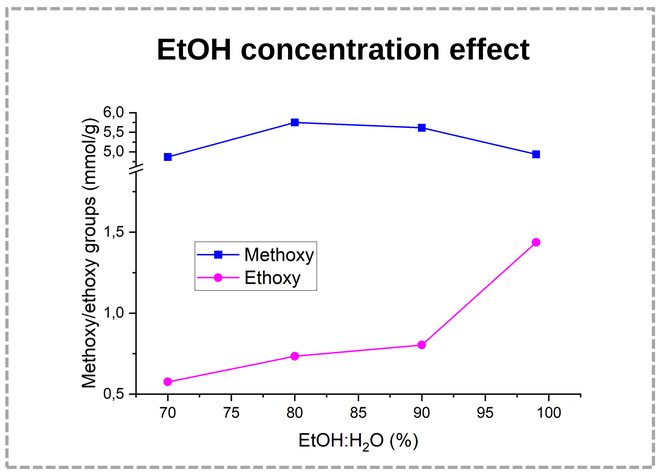


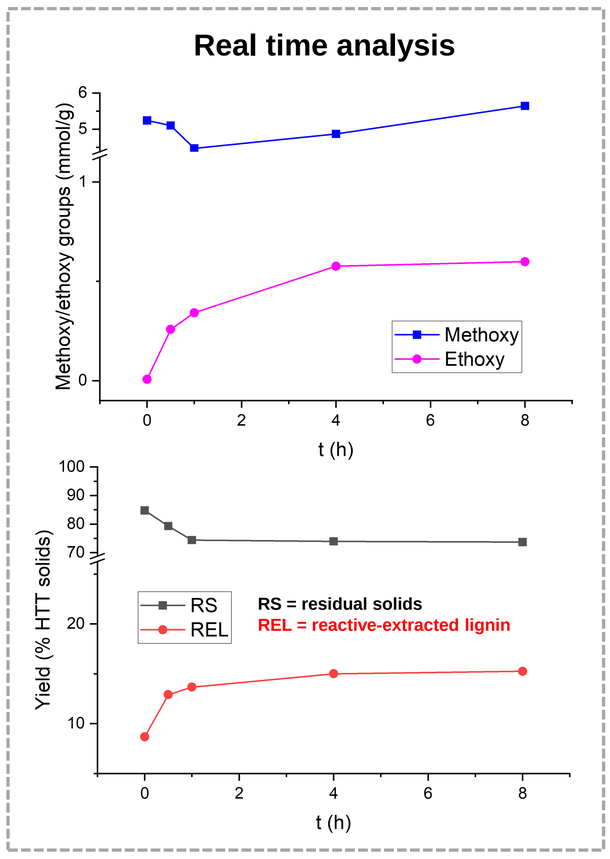

## Results and discussion




By reacting HTT solids for different time-frames and/or by varying the EtOH concentration it is possible to tune the **degree of ethoxylation** of the reactive-extracted lignins (REL).

The desired degree of ethoxylation depends on the **application** the lignin is intended for.

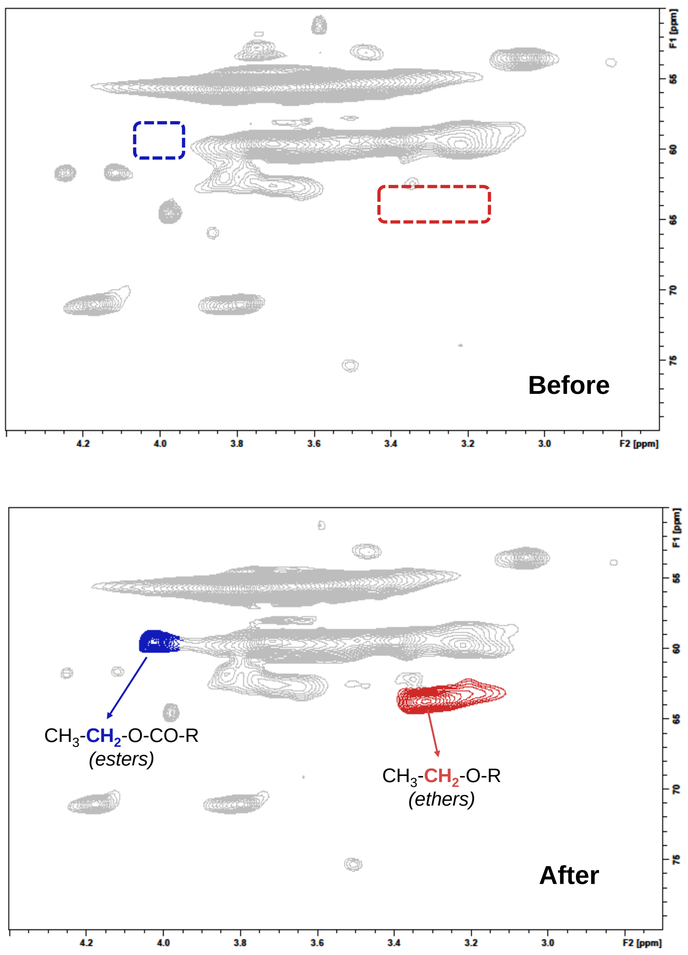



**Maximized yield** of REL is achieved from 4h on.

**EtOH concentration** is the most **crucial parameter** to improve the degree of ethoxylation.

Both **esterification** of –COOH and **ethoxylation** of –OH simultaneously occur during **reactive extraction (REx).**




## Conclusions

### Reactive extraction (Rex) concept

- ✓ One pot lignin functionalization-extraction
- ✓ Tunable lignin properties
- ✓ Tunable degree of ethoxylation
- ✓ Benign-by-design procedure
- ✓ Cost-efficient
- ✓ Easily scalable

## Materials and methods