KERALTA Assira
NISHIYAMA Yoshiharu
OGAWA Yu

Controlled lignin oxidation and hemicellulose deacetylation inside beech wood

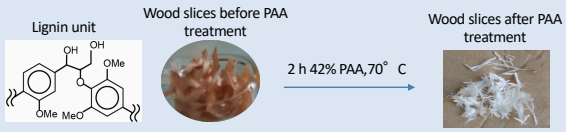
assira.keralta@cermav.cnrs.fr

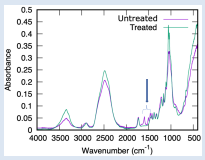
Context and objective

Acetyl groups in hemicellulose such as xylan and aromatic lignin in the wood cell wall confer hydrophobicity and rigidity to wood. Oxidizing lignin and deacetylating hemicellulose would lead to modification of hygroscopic and mechanical properties of the cell wall. Peracetic acid (PAA) is known to react selectively on phenolic groups. It was used in the single step pulping process (Westin et al. 2021). Our goal is to have control on lignin oxidation and hemicellulose deacetylation reactions on bulk wood by just filling the wood pores with chemical using PAA and an alkaline solution.

Lignin oxidation

Method: A) Wood slices were impregnated with 42% PAA for 2 h at 70 ° C, then washed at pH 10, dried in atmosphere and analysed (figures 1 and 3).
B) Lumen of 4 mm thick bulk wood was filled with 30% PAA and Kept at 70° C for 1, 2, 3 and 4 h and washed at pH 10, dried in atmosphere and analysed (figures 2 and 4).





Total removal of lignin
Specific attack on phenolic groups

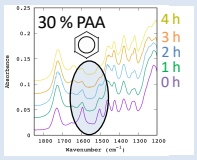
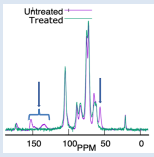


Figure 1: FT-IR spectra of oxidized (green) and untreated (purple) thin wood slices

Figure 2: FT-IR spectra of wood samples treated with 30% PAA for different reaction time



Filling lumen with 30% PAA allow lignin removal from the cell wall

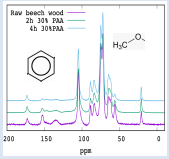


Figure 3: ^{13}C CP/MAS spectra of oxidized (green) and untreated (purple) thin wood slices

Figure 4: ^{13}C CP/MAS spectra of wood samples treated with 30% PAA for different reaction time

Recovery of oxidized lignin

Method: After the reaction, the oxidized substances were extracted at PH 10 Then precipitated at PH 5, Dried in desiccator

- No aromatic substances recovered after 42% PAA
- Presence of substances with aromatic after 30% PAA
- Lignin was oxidized to non-aromatic compounds such as muconic acid in 42 % PAA.

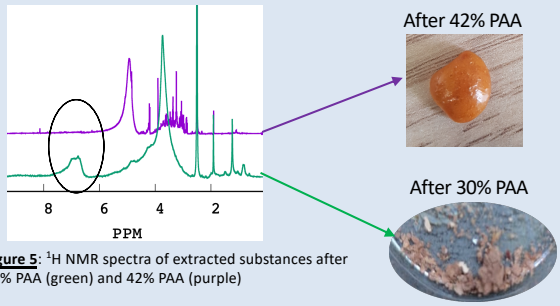


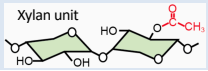
Figure 5: ^{1}H NMR spectra of extracted substances after 30% PAA (green) and 42% PAA (purple)

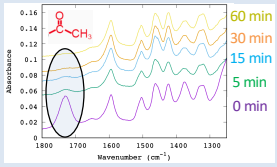
Table 1: Weight loss by PAA treatment

% Peracetic acid	Duration (h)	Weight loss (%)
42	4	30
30	4	8.4
30	2	4.8

Hemicellulose deacetylation

Method: wood slices were impregnated with 1% NaOH solution and left at room temperature for 1 h, washed with distilled water and dried in atmosphere.
Lumen of 4mm-thick wood was filled with NaOH solutions of different concentrations, left at room temperature for 1 h, washed, dried and divided in two parts for FT-IR analysis.





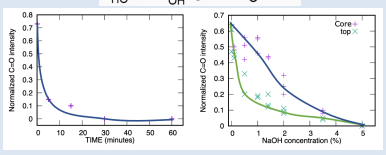


Figure 6: FT-IR spectra of wood slices treated with 1% NaOH.

Figure 7: Normalized FT-IR intensities of C=O band at 1733 cm^{-1} of wood slice treated with 1% NaOH solution for different reaction time (left) and of block wood treated in NaOH solutions of different concentration (right)

Thin wood slices can be totally deacetylated with 1% NaOH solution.
There is a gradient of NaOH concentration inside the bulk wood leading to a heterogeneous deacetylation when NaOH solution < 5% was used, probably due to the affinity between sodium ions and the cell wall (Schwarzkopf, 1932).

Perspectives

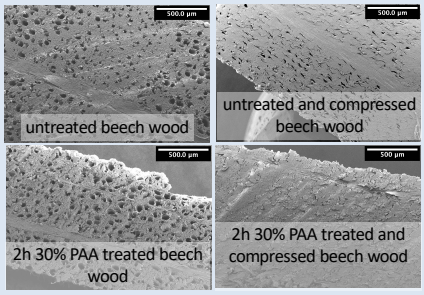


Figure 8: SEM images of untreated, treated and compressed beech wood

Treated wood can be compressed up to 60% without presenting cell damage

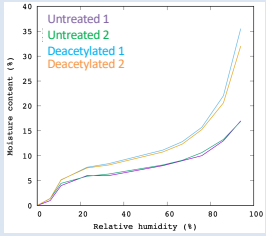


Figure 9: Adsorption isotherm of raw and deacetylated beech wood

Deacetylated wood adsorb two times more moisture than raw wood

References

Westin P.-O, Yang X., Svedberg A., Grundberg H., Berglund L.A. (2021). Single Step PAA Delignification of Wood Chips for High-Performance Holocellulose Fibers. Cellulose. 28, 1873–1880.
Schwarzkopf O (1932). Zur Kenntnis Der Alkalicellulose I. Ein Beispiel Für Die Bestimmung Der Verteilung Bei Gelreaktionen. Z. Für Elektrochem. Angew. Phys. Chem. 38 (6), 353–358.

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