

Controlled lignin oxidation and hemicellulose deacetylation inside beech wood

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Context and objective

The acetyl groups in hemicellulose such as xylan and aromatic lignin in the 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. Recently, holocellulose preparation by peracetic acid (PAA) has been proposed to yield pulps with higher molecular weight. PAA is known to selectively react with phenolic groups, and this has been 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.

Materials and methods

Beech wood with an apparent density of 0.53 g/cm³ and 8% of moisture content was used in this study. A sliding microtome was used to prepare wood slices with to 30-200 μm in thickness. 50×10×4 mm³ (L×R×T) wood pieces were sawn.

Peracetic acid was prepared by mixing glacial acetic and 30% hydrogen peroxide at room temperature in volume ratio 2:1 (acetic acid:H₂O₂). 1.5% (v/v) of 96% H₂SO₄ was added as catalyst (Zhao et al. 2007). The produced PAA was analyzed by oxidant-reductive titration using ceric sulfate and sodium thiosulfate (Greenspan and Mackellar 1948). Then glacial acetic and distilled water were used to dilute the produced PAA. Peracetic acid synthesis is controlled by oxidant-reductive titration (Greenspan and Mackellar 1948). The mixing of glacial acetic acid and 30% hydrogen peroxide in volume ratio (2:1) and 1.5% H₂SO₄ gave a mixture of 42% PAA and 3.53% H₂O₂.

Lignin oxidation: Wood samples were put in excess of PAA and put under reduced pressure to evacuate the air trapped in the lumen to fill the pores with PAA. Then, the excess reactant was removed and kept at 70°C. To stop the reaction, they were washed with hot water, 1% NaOH solution and distilled water in the same way by filling and emptying the pores to extract the soluble fraction. They were dried at 105°C overnight to assess the weight loss.

Oxidized lignin recovery: The washing solution after the PAA reaction was recovered and the oxidized lignin was precipitated with 2.2N HCl. The precipitate was recovered by centrifugation and dried in desiccator.

Hemicellulose deacetylation: For the hemicellulose deacetylation, samples followed a similar process with that of the oxidation: the pore filling with NaOH solutions (0.5, 1, 2, 3.5 and 5 wt%) followed by removal of reactant excess and reaction at room temperature. They were washed with distilled water using a repetitive process of filling and emptying the wood pores.

Results and discussion

Oxidation and lignin recovery: After 1 h of treatment with 42% PAA at 70°C and the washing. In ¹³C CP/MAS solid-state NMR spectrum, the peaks of aromatic group between

125-155 ppm and methoxy group at 55 ppm totally disappeared for the treated wood and all other peaks remain intact (Fig. 1). In IR spectrum, peaks at 1593 cm^{-1} and 1505 cm^{-1} are disappeared and the absorbance of peak at 1462 cm^{-1} decreased (Fig. 2). This confirmed the complete oxidation of lignin and showed the specific attack on PAA on phenolic groups leaving untouched the holocellulose. The 4 mm beech wood was cut in half to assess the reaction homogeneity. The IR results recorded on the surface and the core of this cut sample are the same showing the homogeneity of the reaction through the entire bulk piece.

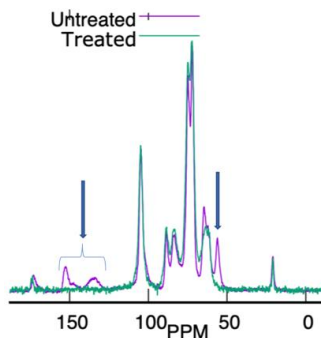


Fig. 1: ^{13}C CP/MAS spectra of oxidized (green) and untreated (purple) thin wood slices

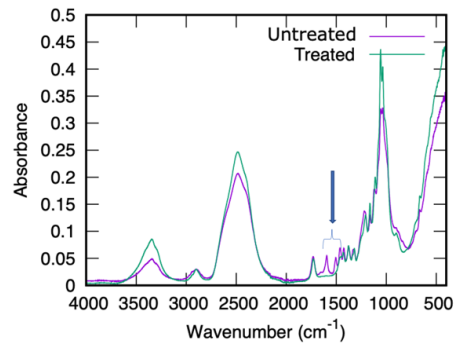


Fig. 2: FT-IR spectra of oxidized (green) and untreated (purple) thin wood slices

When the sample was treated with 42% PAA for 4 h, the solution still contained active PAA of 12%. This means equivalent of 30%PAA was consumed to completely oxidize the lignin aromatic group. Thus, we considered that 30% of PAA should be enough to oxidize the whole lignin in the wood cell wall. However, when treated with 30% PAA, peaks at 1593 cm^{-1} and 1505 cm^{-1} in the IR spectra did not completely disappear in the spectra (Fig. 3) and peaks between 125-155 ppm on ^{13}C CP/MAS solid-state NMR indicating the presence of residual lignin after 4 h when treated with 30%PAA (Fig. 4). The PAA was, on the other hand, The presence of residual lignin is also confirmed in (Tab. 1). Treatment with 42% PAA allowed after washing to remove all the oxidized lignin. In contrary, 30% PAA eliminated less than one third of expected lignin amount.

Judging from the resonance intensity of ^{13}C CP/MAS solid-state NMR in the 155-125 region, 30% of PAA within 2 hours have oxidized half of lignin (Fig. 4).

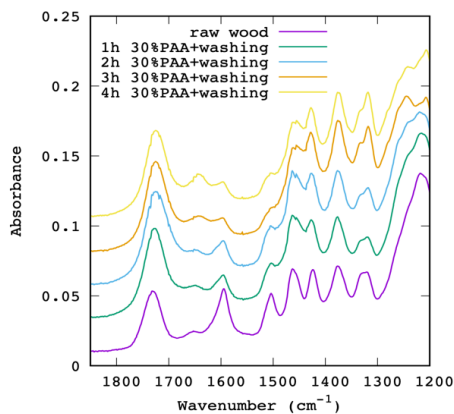


Fig. 3: FT-IR spectra of wood samples treated with 30 % PAA for different reaction time

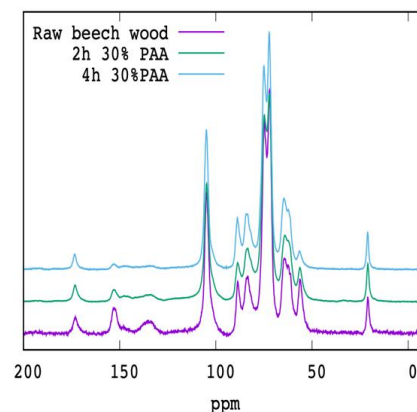


Fig. 4: ^{13}C CP/MAS NMR spectra of wood samples treated with 30 % PAA for different reaction time.

Tab.1: Weight loss by PAA treatment

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

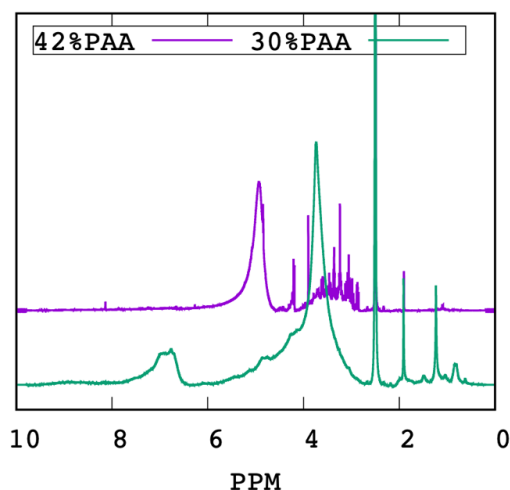


Fig. 5: ^1H NMR spectra of substance from the extracts after 30% (green) and 42% (purple) PAA treatment recovered by precipitation with HCl.

The presence of residual lignin is also confirmed in weight loss summarized in Tab. 1. Treatment with 42% PAA and subsequent washing allowed to remove all the oxidized lignin. In contrast, 30% PAA eliminated less than one third of expected lignin amount.

Judging from the resonance intensity of ^{13}C CP/MAS solid-state NMR in the 125-155 region, 30% of PAA within 2 hours have oxidized half of lignin (Fig. 4).

The ^1H NMR (in DMSO) spectra of oxidized lignin recovered by precipitating the washing solution with HCl are shown in Fig. 5. The peak at around 7 ppm corresponding to aromatic ring is absent when treated with 42% PAA. On the other hand, with 30% of PAA, there is a peak at 7 ppm which confirms the recovery of degraded lignin. As the consumption of oxidants were the same in the two cases, the origin of the difference between the two cases is not clear for the moment.

Deacetylation : The absorbance of peak at 1733 cm^{-1} assigned to carbonyl of acetyl group is normalized to the absorbance at 1045 cm^{-1} of cellulose backbone. The deacetylation reaction was complete after 30 minutes using 1% NaOH solution at room temperature on wood slices (Fig 6). On the other hand, when the surface and at the middle of a 4 mm-thick block are compared, the surface was more deacetylated than the core at the low NaOH concentration, and 1% was not enough to deacetylate the core even if the pores were filled by the solution. When high NaOH concentration (5%) was used the surface and the core were completely deacetylated (Fig. 7). The sodium ions are probably retained on the surface due to the high affinity with the polysaccharide (Schwarzkopf 1932), leading to ion exchange allowing only water to penetrate. At high concentration the ion fixing sites might be saturated, leaving enough hydroxide to penetrate for the complete deacetylation reaction.

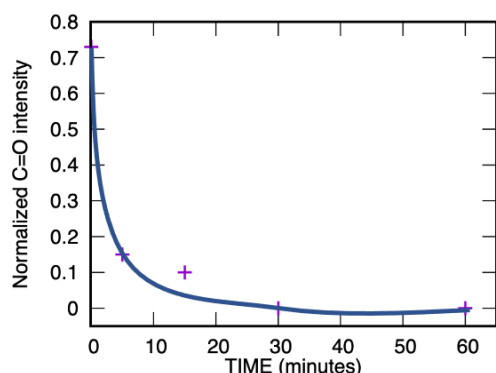


Fig. 6: Normalized FT-IR intensity of C=O band at 1733 cm^{-1} of wood slice treated in 1% NaOH solution for different reaction time

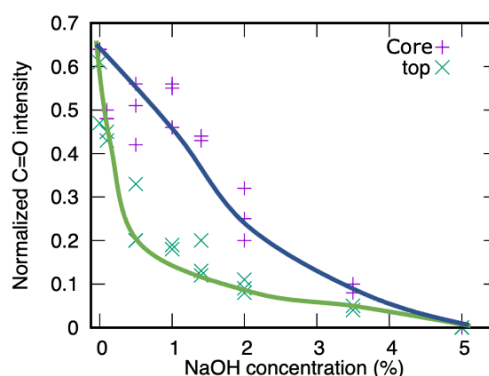


Fig. 7: Normalized FT-IR intensity of C=O band at 1733 cm^{-1} of wood block treated in NaOH solution of different concentrations.

Conclusion and perspectives

Having control on the modification of the wood cell wall can expand the property range and open new utilizations of the bulk wood. Lignin can be extensively oxidized with 30% of peracetic acid within 4 hours at $70\text{ }^{\circ}\text{C}$ by just filling the wood pores with the solution. Partially oxidized lignin can be recovered after the washing when low peracetic acid concentration is used. The hemicellulose deacetylation can be done with small amount of NaOH, but the impregnation of NaOH is impeded by the ion-exchange property of the cell wall creating a gradient of NaOH concentration inside bulk wood leading to heterogeneous deacetylation distribution under conditions where deacetylation is not complete.

Beech wood treated with 30% of PAA within 2h and washed can be compressed up to 60% without damaging the cell wall. The mechanical properties of this densified wood are being studied.

Acknowledgement

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