Optimisation of alcoholysis treatment in Poplar wood delignification

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Context and objectives

In researching functionalization of wood, the removal of lignin is essential to produce bio-based material with high cellulose content. Various delignification methods exist, especially in the paper-making industry, where delignification takes place in the chemical pulping processes. In particular, colorless wood blocks can be produced by two-step delignification involving alcoholysis and sodium chlorite bleaching (Horikawa et al 2020). The alcoholysis procedure not only removes lignin by cleavage of the ether linkages, but also causes the hydrolysis of hemicellulose. The subsequent sodium chlorite bleaching decomposes the aromatic rings in lignin, providing the wood block with a colorless appearance (Hirano et al 2023). In this treatment, complete removal of lignin and chromophores can be achieved while preserving the hierarchical structure and the anatomic features of wood.

In this work, the optimal protocol for the alcoholysis treatment of Japanese cedar (150°C for 1 hour) was firstly applied on the French Poplar wood block. However, cracks and defibrillations were observed during the following sodium chlorite bleaching. Hence, the aim of this work was to suggest the optimal alcoholysis treatment condition for the French Poplar wood by reducing the temperature of alcoholysis treatment while lengthening the cooking duration. The wood samples which were subjected to a single step treatment (alcoholysis or sodium chlorite bleaching) were also studied for comparison purposes.

Materials and methods

Two-step delignification involving alcoholysis and sodium chlorite bleaching

Cubic wood blocks of 10 mm side length were prepared from Poplar wood with faces in the transverse, radial and tangential planes accordingly (Fig. 1a). Reagents were purchased from Wako (Japan) and Sigma-Aldrich (France). The wood blocks were impregnated in solvent consisting of ethylene glycol, water and 97 % H_2SO_4 at a mass ratio 99:0.5:0.5 under vacuum for 30 minutes before being heated in a portable reactor (TVS-N2 Type, Taiatsu Techno Corp, Japan) using oil bath. After washing, the samples were bleached according to the Wise method using a sodium chlorite solution at 70°C water bath for 8 hours. Every hour, 1 g of $NaClO_2$ and

0.2 ml acetic acid were added into the solution. The colorless wood samples were then washed thoroughly and freeze-dried.

Fourier transform infrared (FTIR) spectroscopy

A PerkinElmer Frontier system (Waltham, MA, USA) with an Attenuated Total Reflection (ATR) accessory was used to obtain the FTIR spectra of the core of wood samples within the 4000-500 cm^{-1} range at 4 cm^{-1} resolution. The spectral pretreatments were done by the ATR correction functions and normalized by the top band of the fingerprint region at ~ 1000 cm^{-1}.

Estimation of lignin and polysaccharide contents

The natural and colorless wood samples were first subjected to acid hydrolysis in a two-stage treatment (72 % sulfuric acid at 30°C for 1 hour followed by 4 % sulfuric acid at 121°C for 1 hour). The acid-insoluble residue, mainly represented by Klason lignin, was dried and weighed as the lignin content. The monosaccharide concentration was measured by high-performance liquid chromatography (HPLC) equipped with a separation column (Asahipak NH2P-50 4E, Showa Denko K.K., Tokyo, Japan), a differential refractive index detector and an autosampler (Prominence, Shimadzu, Kyoto, Japan). The polysaccharide content was calculated from the corresponding monosaccharide concentration with the anhydrous correction factors of 0.90 for glucose, mannose and galactose, 0.88 for xylose and arabinose.

X-ray diffraction analysis

X-ray diffractograms were obtained in the reflection mode using an automated multipurpose X-ray diffractometer (SmartLab, Rigaku, Tokyo, Japan) at 40 kV and 30 mA. The relative crystallinity index (RCI) and full width at half maximum (FWHM) at a peak of (200) were calculated from the diffractogram by Pseudo-Voigt function fitting.

Pore volume fraction

The pore volume fraction, V_p was estimated with the dry wood sample density, ρ_{sample} and the density of dry cell wall, $\rho_{cell\ wall}$ which is about 1.5 g/cm^3, with the following equation:

$$\text{Pore volume fraction (\%)} = \left(1 - \frac{\rho_{sample}}{\rho_{cell\ wall}}\right) \times 100\%$$

Results and discussion

Influence of lignin and hemicellulose removal

After the two-step delignification involving alcoholysis and sodium chlorite bleaching, the Poplar wood block decolorized and became free from lignin and hemicellulose. Both steps were essential to remove the non-cellulosic components, as shown in Fig. 1b and Fig. 1c, the brownish color retained due to the remaining light-absorbing chromophore structures in lignin. In the case of alcoholysis at 150°C for 1 hour followed by sodium chlorite bleaching, cracks appeared after the final washing step along the radial direction where the ray cells located (Fig. 1f). For the samples subjected to alcoholysis at 100°C and 120°C for 1 hour, no cracks were observed (Fig. 1d and Fig. 1e). In all cases, the 3-dimensional wooden architecture was preserved. It was also observed that the sample swells more in the tangential direction after alcoholysis treatment compared to the radial direction. After the 2-step treatment and freeze-drying, the dimension variation in tangential direction was also more significant than that in longitudinal and radial directions.

After the two-step treatment, the spectral bands at 1508 cm^{-1} flattened, indicating the absence of lignin in the cores of wood blocks. As for the band at 1730 cm^{-1} assigned to acetylated

hemicellulose, only alcoholysis at 150°C successfully removed hemicellulose in 1 hour (Fig. 2). The chemical components analysis carried out showed that the colorless Poplar wood block (treated with alcoholysis at 150°C for 1 hour followed by sodium chlorite bleaching) has nearly all of the acid-insoluble content removed and is mainly composed of cellulose (Fig. 3).

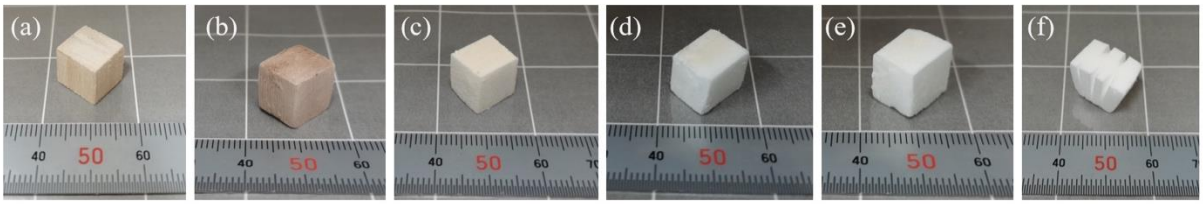

Fig. 1: Poplar wood blocks: (a) without treatment; (b) after alcoholysis at 150°C for 1 hour; (c) after $NaClO_2$ bleaching; (d) after alcoholysis at 100°C for 1 hour and $NaClO_2$ bleaching; (e) after alcoholysis at 120°C for 1 hour and $NaClO_2$ bleaching; (f) after alcoholysis at 150°C for 1 hour and $NaClO_2$ bleaching

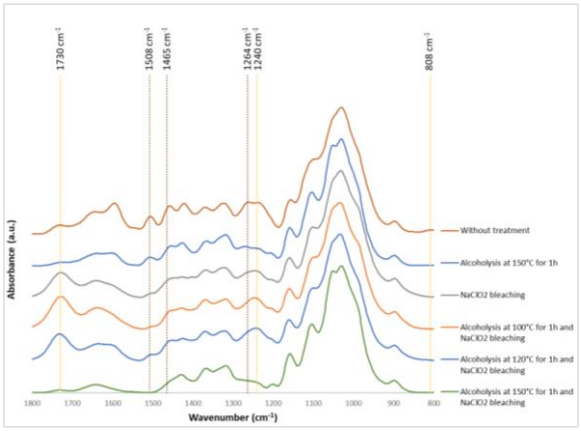

Fig. 2: FTIR spectra for the cores of Poplar wood blocks under different treatment conditions

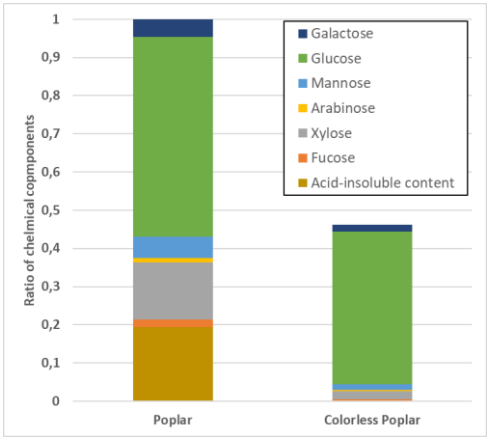

Fig. 3 : Ratio of chemical components in Poplar wood before and after treatment

Similar patterns were observed in the wide-angle X-ray diffractograms, indicating that the natural cellulose crystalline structure was maintained. The higher crystalline index and lower full width at half maximum of (200) of colorless Poplar calculated (Tab.1) reflects the higher relative crystallinity due to the improvement of cellulose microfibril orientation after treatment (Horikawa et al. 2020).

Tab. 1 : Crystalline index and full width at half maximum of untreated and colorless Poplar

	Crystalline index	Full width at half maximum of (200)(°)
Untreated Poplar	0.759	2.98
Colorless Poplar	0.829	2.49

Influence of alcoholysis temperature and duration

According to Fig. 4, an alcoholysis treatment at higher temperature or longer duration causes higher mass loss due to more substance removal. Consequently, the density reduces and the pore volume fraction increases (Fig. 5 and Fig. 6). It seemed that alcoholysis treatment at 120°C for more than 3 hours is required before sodium chlorite bleaching to achieve sufficient delignification efficiency, while an alcoholysis treatment of more than 5 hours is needed at 100°C. However, cracks were observed for most samples under these conditions, except for the samples treated for more than 5 hours at 120°C for which, surprisingly, no cracks were present.

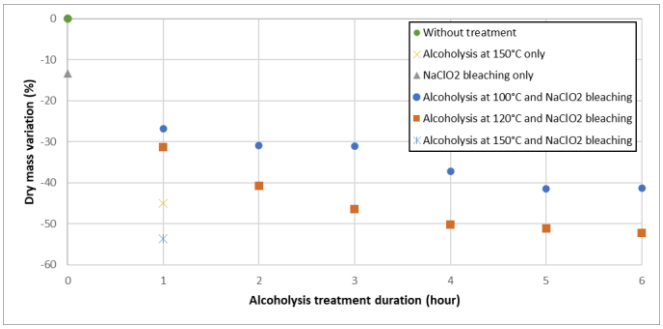

Fig. 4: Dry mass variation of poplar wood under different treatment conditions

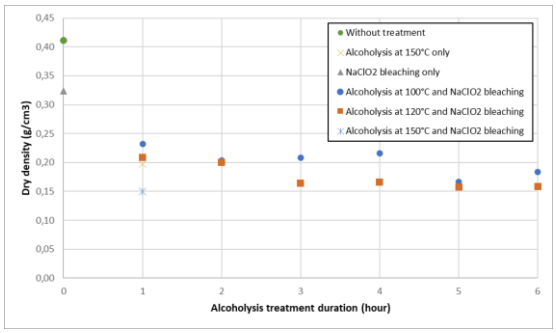

Fig. 5 : Dry density of Poplar wood under different treatment conditions

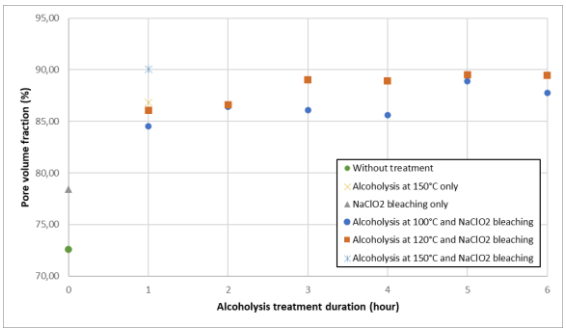

Fig. 6 : Pore volume fraction of Poplar wood under different treatment conditions

Conclusion and perspectives

The removal of lignin and hemicelluloses from Poplar wood reduces its density close to that of balsa wood. Such low density represents low thermal conductivity and shows potential for utilization as bio-based insulation material. However, the mechanical properties still need to be tested against higher density requirements, depending on the usage, which may be attained by reducing the level of delignification. In addition, the surface of all samples after the two-step treatment decolorized, indicating the importance of solvent accessibility and the possibility to delignify wood veneers of a few millimeters homogeneously by alcoholysis at 100°C for 1 hour, followed by sodium chlorite bleaching. For scale-up production, alternative drying methods and environmentally friendly bleaching reagents must be investigated.

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