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# Exploring the solid wood modification with preserved hierarchical structure via non-cellulosic substances removal

CHIN Yi Hien<sup>1,2,3</sup>[0009-0008-6698-0984], BIWOLE Pascal<sup>1,4</sup>[0000-0001-6325-1390], GRIL Joseph<sup>1,5</sup>[0000-0003-1483-0294], VIAL Christophe<sup>1</sup>[0000-0002-9503-1605], MOUTOU PITTI Ros-tand<sup>1,6</sup>[0000-0002-4596-4693], OULDBOUKHITINE Salah-Eddine<sup>1</sup>[0000-0002-9300-6545], LABONNE Nicolas<sup>2</sup>, HORIKAWA Yoshiaki<sup>3</sup>[0000-0003-0204-0455]

<sup>1</sup>Université Clermont Auvergne, CNRS, SIGMA Clermont, Institut Pascal, France

<sup>2</sup>Dagard Company, 23600 Boussac, France

<sup>3</sup>Institute of Agriculture, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

<sup>4</sup>MINES Paris, PSL Research University, PERSEE - Center for Processes, Renewable Energies and Energy Systems, France

<sup>5</sup>Université Clermont Auvergne, INRAE, PIAF, 63000 Clermont Ferrand, France

<sup>6</sup>CENAREST, IRT, BP 14070, Libreville, Gabon

yi\_hien.chin@doctorant.uca.fr

**Abstract.** Wood is a bio-based material that has always been used for various purposes due to its excellent mechanical and thermal properties. Innovations have been made in wood modification technology to create new functionalities while improving its current advantages. Wood is composed of three main chemical elements: cellulose, hemicellulose, and lignin. This study focuses on the modification of wood by the removal of non-cellulosic substances to create a cellulose scaffold. The creation of pores after treatments contributes to lower density and therefore lower thermal conductivity. Besides, a new composite can be invented by impregnation of other materials between the cellulose fibers. The top-down modification approach increases the production scalability but the drying of the modified wood remains challenging for the industrial professionals. This work starts by reviewing the protocol of various wood delignification methods that preserve the natural hierarchical structure of solid wood. Then, it focuses on experimental trials on French poplar wood (*Populus spp.*) using soda pulping, alkaline sulfite pulping, organosolv pulping, hydrogen peroxide bleaching and sodium chlorite bleaching. To look for potential drying solutions, a comparative study was done on different drying techniques. It was found that dielectric heating has the highest drying rate across all moisture contents whereas convective blow drying exhibits the lowest sectional shrinkage. The findings encourage further exploration of delignified wood's properties leading to large-scale modified wood manufacturing in the future.

**Keywords:** Bio-based material; Delignification; Drying technologies; Nanotechnology; Poplar wood; Wood modification

## 1 Introduction

To reduce CO<sub>2</sub> emissions towards sustainable development, especially in the building industry, it is necessary to substitute non-renewable materials with low embodied energy and bio-based products. Delignified wood was reported to have low thermal conductivity, making it a potential biodegradable thermal insulator [1]. Despite numerous wood delignification methods that had been proposed for various functionalizations, there was not a thorough comparative analysis of these techniques, a single method was usually applied to each research study. French poplar wood (*Populus spp.*) had been identified as an abundant and fast-growing resource. The aims of this work are to study the degree of lignin removal by three delignification techniques and to suggest potential drying techniques for large-scale production. This work starts by reviewing the current state of knowledge in bulk wood delignification. Soda pulping, alkaline sulfite pulping and organosolv pulping were chosen to be combined with or without bleaching steps to modify poplar wood. The NaOH modified wood samples were subjected to ambient-air drying, convective blow drying, oven heating and dielectric heating. The information reported allows a better understanding of wood modification and drying mechanisms for the design of appropriate manufacturing procedures.

## 2 State-of-the-art

Wood tissue is a hierarchically composite material with complex organizations from macro to micro scales as presented in Fig. 1. Among the total mass of wood, cellulose makes up 40 to 50%, hemicelluloses 20 to 30 %, and lignin 20 to 30%. The cellulose microfibrils, which include both crystalline and amorphous cellulose, have nanometric lateral dimensions (a width of 3 nm and a length of 1  $\mu\text{m}$ ) [2]. They are attached by lignin to provide mechanical strength and rigidity to the structure of the wood. Hemicellulose is comprised of different sugar units, such as glucose, mannose, galactose, xylose, and arabinose. Lignin is a natural glue between the wood cells and the middle lamella. The opaque, brown appearance of wood is the result of the presence of chromophore groups and the phenolic character of lignin with strong light-capturing capability [3]. Cellulose and hemicellulose are hydrophilic, whereas lignin is less hydrophilic. The removal of non-cellulosic matrices from wood is a subtractive chemical treatment that is also known as delignification. This modification treatment not only changes the chemistry composition of the natural wood but also creates nanochannels in the empty inter-fiber spacing, along with the creation of nanopores in the cell wall and the micropores at the cell wall corner, thus increasing the specific surface area from around 1 to over 40 m<sup>2</sup>/g depending on the drying methods [4].

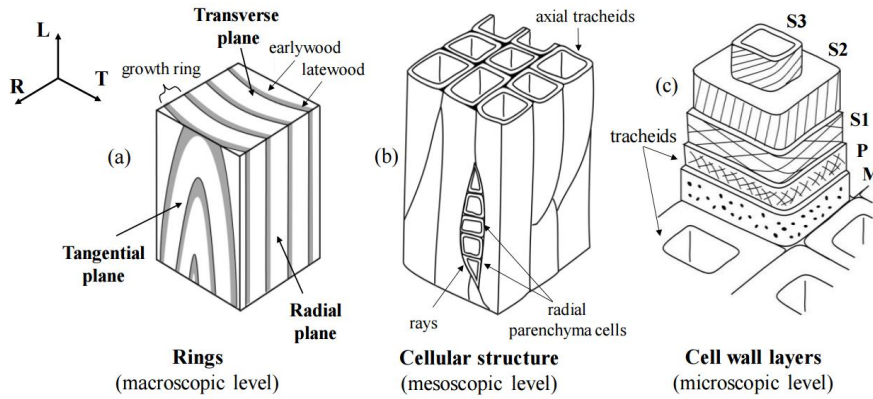


Fig. 1. Sketch of the hierarchical structure of wood [5]: (a) growth rings, layout, and main axes; (b) honeycomb-shaped cell tissue; (c) multi-layered cell wall defined by the variable orientation of cellulose microfibrils

The details of the delignification methods reported in the literature are summarized in Table 1. One of the common techniques in pulping, the high temperature and high pH soda process fragmentates the lignin structure by cleavage of lignin-carbohydrate bonds and  $\beta$ -O-4 linkage using sodium hydroxide (NaOH) [6]. Alkaline sulfite pulping uses a solution system of sodium hydroxide (NaOH) and sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) that contains active delignifying nucleophiles, such as sulfite ( $\text{SO}_3^{2-}$ ), bisulfite ( $\text{HSO}_3^-$ ), and hydroxide ( $\text{OH}^-$ ) anions. It is often followed by hydrogen peroxide bleaching to remove the unreacted chemicals and to decolorize the wood [1]. Another method identified was organosolv pulping (alcoholysis with ethylene glycol) which hydrolyses hemicellulose and removes lignin by ether linkage cleavage. It is followed by the sodium chlorite/acetic acid ( $\text{NaClO}_2/\text{AA}$ ) bleaching that produces chlorine dioxide to oxidize the aromatic rings from lignin via electrophilic attack [7].

Table 1. Experimental details of wood modification techniques involving soda pulping, alkaline sulfite pulping and organosolv pulping reported in the literature.

Delignifying methods	Wood species & dimensions [mm <sup>3</sup> ]	Delignification protocols	Additional bleaching step	Applications & Refs.
Soda pulping	Paulownia ( <i>Paulownia tomentosa</i> ) 600 x 45 x 12.5	5 wt% NaOH at high temperature for 1 h	No	Thermal insulator [8]
	Spruce ( <i>Picea abies</i> ) 5 x 5 x 5	10 wt% NaOH at 80°C for 8 h under constant stirring	No	Cellulose scaffold [6]
Alkaline sulfite pulping	Basswood ( <i>Tilia americana</i> )	NaOH + $\text{Na}_2\text{SO}_3$ at boiling temperature for 3 h	Treatment with $\text{H}_2\text{O}_2$ for 5 h	Thermal insulator [1]

	120 x 30 x 12 Beech ( <i>Fagus sylvatica</i> ) 40 x 50 x 5	2.5 mol.L <sup>-1</sup> NaOH + 0.4 mol.L <sup>-1</sup> Na <sub>2</sub> SO <sub>3</sub> at boiling temperature for 48 h	Boiling 30 wt% H <sub>2</sub> O <sub>2</sub> until white without stirring	Transparent wood [9]
Organosolv pulping	Japanese Cedar ( <i>Cryptomeria japonica</i> ) 10 x 10 x 10	Alcoholysis with Ethylene glycol + H <sub>2</sub> O + 97 % H <sub>2</sub> SO <sub>4</sub> at 150 °C for 1 h	Wise method using 150ml H <sub>2</sub> O + 1 g NaClO <sub>2</sub> + 0.2 ml acetic acid at 70 °C for 8 h, add the same amount of reac- tant every hour	Colorless wood [7]

### 3 Materials and methods

French poplar wood planks were purchased from Chagnon Carpentry, France. They were cut into a 100 mm by 10 mm section in the transversal plane and then longitudinally 100 mm along the grain (Fig. 2). Three samples from the batch were oven-dried at 103°C to determine the average initial moisture content.

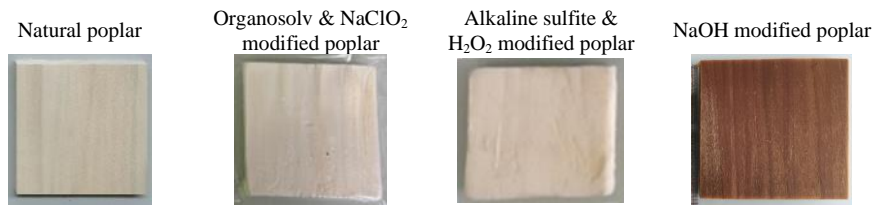


Fig. 2. Visual appearance comparison of poplar wood after different treatments.

A summary of experimental steps is shown in Fig. 3. Three kinds of wood modification techniques were used on the poplar wood samples. NaOH modified wood was prepared by soda pulping. Wood samples were treated in a stock solution of sodium hydroxide (10 wt%) at 100 °C for 8 hours. Alkaline sulfite & H<sub>2</sub>O<sub>2</sub> modified wood were prepared first by being introduced in a mixture of 2.5 mol.L<sup>-1</sup> NaOH and 0.4 mol.L<sup>-1</sup> M Na<sub>2</sub>SO<sub>3</sub> at 100 °C for 6 hours, followed by hydrogen peroxide (35 %) bleaching at 70°C for 4 hours. Organosolv & NaClO<sub>2</sub> modified wood were subjected to two-step delignification involving alcoholysis and sodium chlorite bleaching. The solvent employed for the alcoholysis reaction was composed of ethylene glycol, 97 wt% sulfuric acid, and water in a ratio of 99:0.5:0.5. The wood was heated in the solutions at 140 °C for 4 hours. After washing, they were bleached at 70 °C for 8 hours, 8 g of NaClO<sub>2</sub> and 1.6 ml of acetic acid were added into the 1200 ml bleaching solution every hour [7]. Upon completion of the wood modification processes, the samples were rinsed thoroughly to

remove the remaining chemical reagents and lignin fragments. Then, they were stored in ethanol for over a week to allow the exchange of solvent.

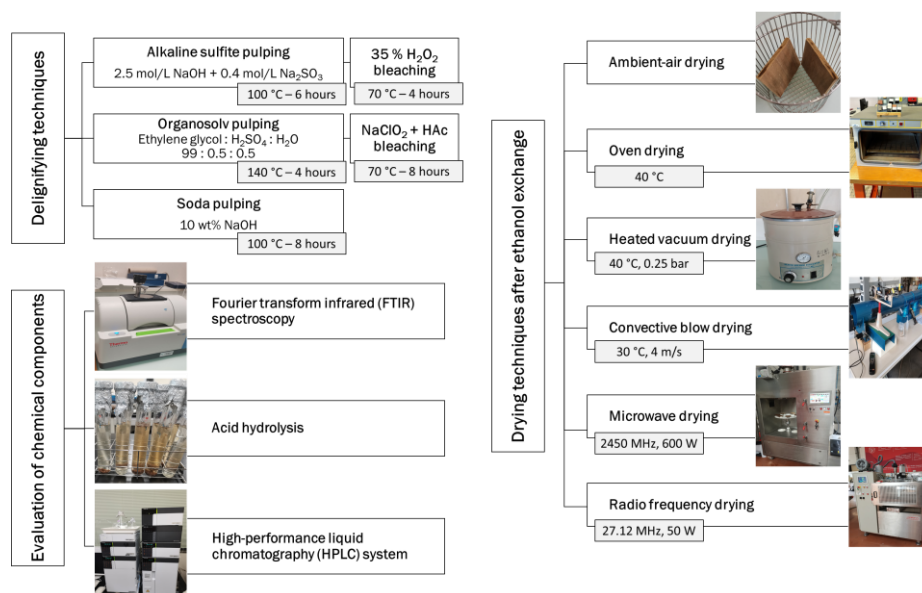


Fig. 3. Diagram summarizing each experimental step (delignifying techniques, evaluation of chemical components and drying techniques).

NaOH modified wood samples were used to study the drying kinetics of a few drying techniques. The heating was stopped when excessive shrinkage and deformation were observed. For ambient-air drying, the samples were simply left in an ambient environment. A laboratory oven (Firlabo, France) was used to oven-dry the samples at 40 °C. A heated vacuum desiccator (GCA/Precision Scientific, Chicago, USA) was connected to a vacuum pump to dry the modified wood samples at 40 °C and 0.25 bar. For convective blow drying, a tube blow dryer (Polytech Clermont, France) equipped with an air heater and a fan was used to blow air of 30 °C at a velocity of 4 m/s on a suspended sample. Dielectric drying through electromagnetic radiation was carried out using a multi-energy microwave oven Labotron MEO12 (Sairem, France) for microwave heating (2450 MHz at 600 W) and Labotron RF 3000 (Sairem, France) for radio frequency heating (27.12 MHz at 50 W).

A weighing balance (Sartorius, Germany) with a minimum sample weight of 0.1 g was used to weigh the wood samples and the size was determined with a digital caliper at a precision of +/- 0.01 mm. Fourier transform infrared (FTIR) spectroscopy (Spectrum Frontier, PerkinElmer, USA) equipped with an attenuated total reflection (ATR) accessory was used to acquire the spectra, which were then normalized with the absorbance of the band 1030 cm<sup>-1</sup>. To determine the acid-insoluble lignin content, two specimens for each treatment were treated by acid hydrolysis by first heating in 72 wt% sulfuric acid at 30 °C for 1 hr., then in 4 wt% sulfuric acid solution at 120 °C for 1 hr.

The solid residue was dried and weighed as acid-insoluble content. The monosaccharide contents were estimated by a high-performance liquid chromatography (HPLC) system (Shimadzu, Japan).

## 4 Results and discussions

### 4.1 Degree of lignin removal

Three kinds of chemical modification were performed on the poplar bulk wood sample, which resulted in NaOH modified wood, alkaline sulfite & H<sub>2</sub>O<sub>2</sub> modified wood and organosolv & NaClO<sub>2</sub> modified wood.

FTIR spectroscopy method was used to detect the change in the content of chemical components through the intensity change in each assigned band. When comparing the modified wood to the natural untreated wood, the overall change in peak patterns and intensities for modified wood indicates an alteration of the wood's chemical composition (Fig. 4). The decreasing intensity of the peaks at 1730 and 1240 cm<sup>-1</sup> assigned to acetyl functional groups was a result of effective hemicellulose removal [10]. Organosolv & NaClO<sub>2</sub> treatment led to the disappearance of the peaks at 1508, 1465, and 1264 cm<sup>-1</sup>, indicating the complete removal of lignin. In contrast, these peaks remain for the NaOH and alkaline sulfite & H<sub>2</sub>O<sub>2</sub> modified wood. This is further confirmed by the remaining acid-insoluble lignin content in Table 2. A higher treatment temperature, treatment duration or delignifying solution concentration may be required for NaOH and alkaline sulfite & H<sub>2</sub>O<sub>2</sub> modification method to increase the degree of lignin removal.

In the natural untreated poplar wood samples, the acid-insoluble lignin represents nearly 20% of its mass. Significant removal of substances, especially acid-insoluble lignin, was observed in organosolv & NaClO<sub>2</sub> modified wood. The high glucose content was maintained in all modified wood, suggesting that cellulose was not much affected by the treatments, so that only lignin and hemicellulose were preferentially altered. Organosolv & NaClO<sub>2</sub> modification, alkaline sulfite & H<sub>2</sub>O<sub>2</sub> modification and NaOH modification appear to be the most to the least lignin removal efficiency respectively, based on the remaining acid-insoluble content.

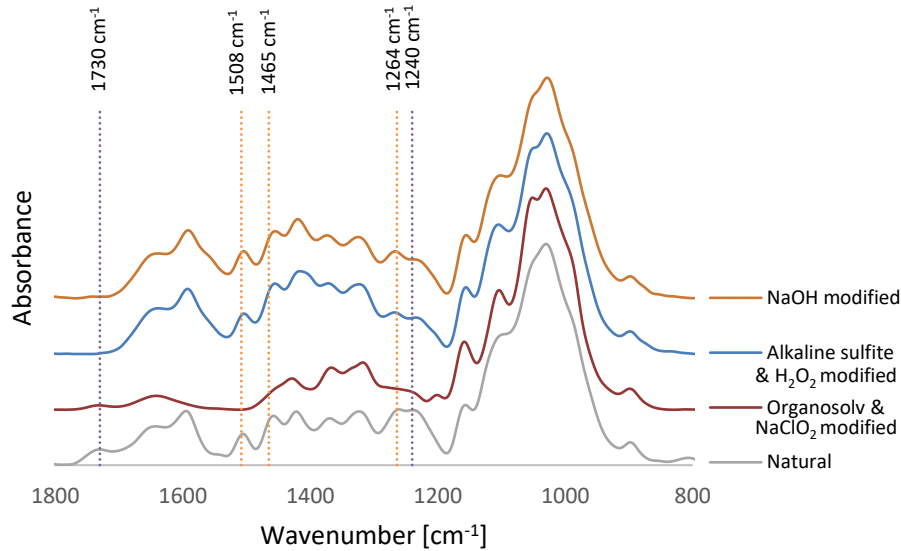


Fig. 4. FTIR spectra of poplar wood under different modification treatments.

Table 2. Percentage of chemical components in poplar wood before and after modification treatments.

Chemical components	Percentage of chemical components [%]			
	Natural poplar	Organosolv & NaClO <sub>2</sub> modified poplar	Alkaline sulfite & H <sub>2</sub> O <sub>2</sub> modified poplar	NaOH modified poplar
Acid-insoluble content	19.3	0.1	12.5	16.1
Fucose	2	0.8	1.2	1.4
Xylose	15	3	9.6	9.3
Arabinose	1.1	0.5	0.8	0.7
Mannose	5.5	2.3	2.9	3.4
Glucose	52.4	59.8	58.6	59.2
Galactose	4.6	2.9	4.1	4.1
Removed substances	0	30.6	10.2	5.9

## 4.2 Drying kinetics

Due to the creation of capillary pressure during liquid evaporation, the modified wood would shrink when directly oven-dried. In most of the experimental studies, delignified wood samples were freeze-dried to remove water without altering the microstructure. Herein, we examined alternative drying techniques using NaOH modified wood which



were solvent exchanged with ethanol, an organic solvent with a lower surface tension than water.

Ambient-air drying is the least efficient method due to its dependence on the temperature and relative humidity of the surroundings (Fig. 5). Blow drying has an initial rapid decline in moisture content because surface moisture evaporates quickly through convection, but less effective later when the liquid has to diffuse from the core to surface. Compared to oven drying, vacuum oven drying is more efficient as the lower pressure facilitates the evaporation of ethanol. Dielectric heating (microwave and radio frequency) is the fastest drying technique as it causes the moisture molecule of the whole piece of modified wood to vibrate and vaporize. For all drying methods, the drying rate decreases as the moisture content of samples reduces, as shown in Fig. 6. Only the drying rate of vacuum oven drying and dielectric heating exceeds 1%/min, other methods need longer drying duration even at high moisture content.

All samples were finally subjected to oven drying at 103 °C to determine the dry mass and the dimensional variation. The dimension along the fiber direction was slightly affected by the wood modification and drying treatments, whereas the significant shrinkage of the sectional surface reflects the collapse of cell lumens. This study suggests that for applications requiring rapid drying, microwave or radio frequency heating would be preferable, yet these methods result in great dimensional shrinkage and densifies the samples despite organic solvent exchange. Blow drying stands out as the most adequate method in preserving the wood's dimensions, which is crucial for manufacturing functional wood scaffolds.

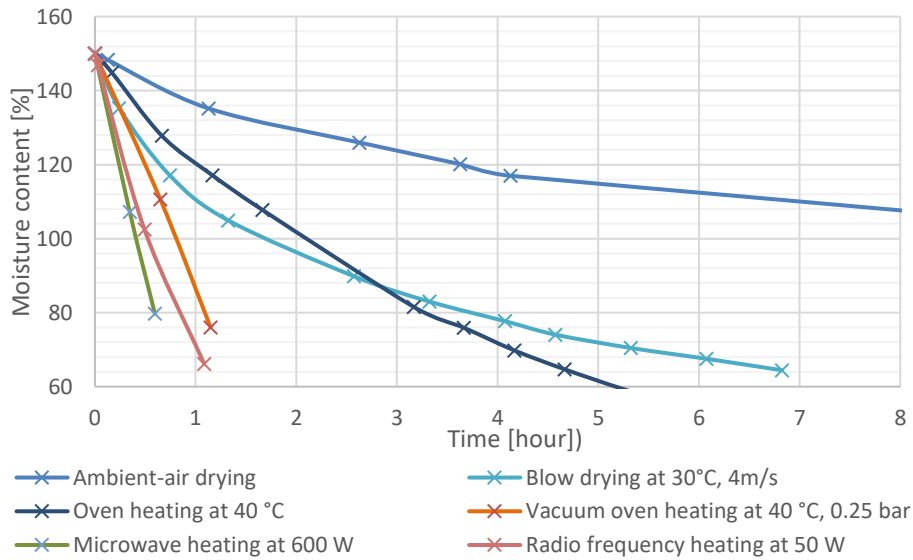


Fig. 5. Moisture content evolution of NaOH modified wood by different drying techniques.

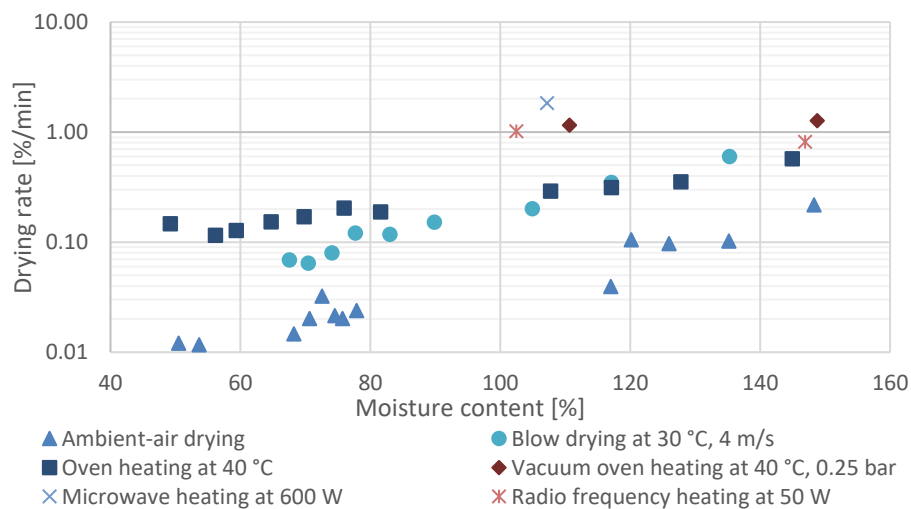


Fig. 6. Drying rate at logarithmic scale of different moisture contents for each drying technique.

## 5 Conclusion and perspectives

In this study, solid wood modifications and drying techniques were experimented on French poplar wood for the first time. The combination of organosolv pulping and sodium chlorite bleaching was proven to be the most effective in achieving complete removal of non-cellulosic substances towards the wood modification in producing cellulose scaffolds. Soda pulping and alkaline sulfite pulping followed by hydrogen peroxide bleaching showed their suitability in the poplar wood modification with intended lignin retention. Further optimization by employing a higher concentration of delignifying solutions, higher temperature or longer treatment duration may contribute to a more significant reduction of lignin content. Additionally, this work presented drying kinetics of possible drying techniques for upscaling applications as functionalized wood scaffolds or biobased thermal insulators. These findings empower industry professionals in decision-making about solutions best suited to their specific requirements. Future investigations should focus on the effects of delignification on the thermal, mechanical, and hygric properties of the French poplar wood.

## 6 Acknowledgments

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