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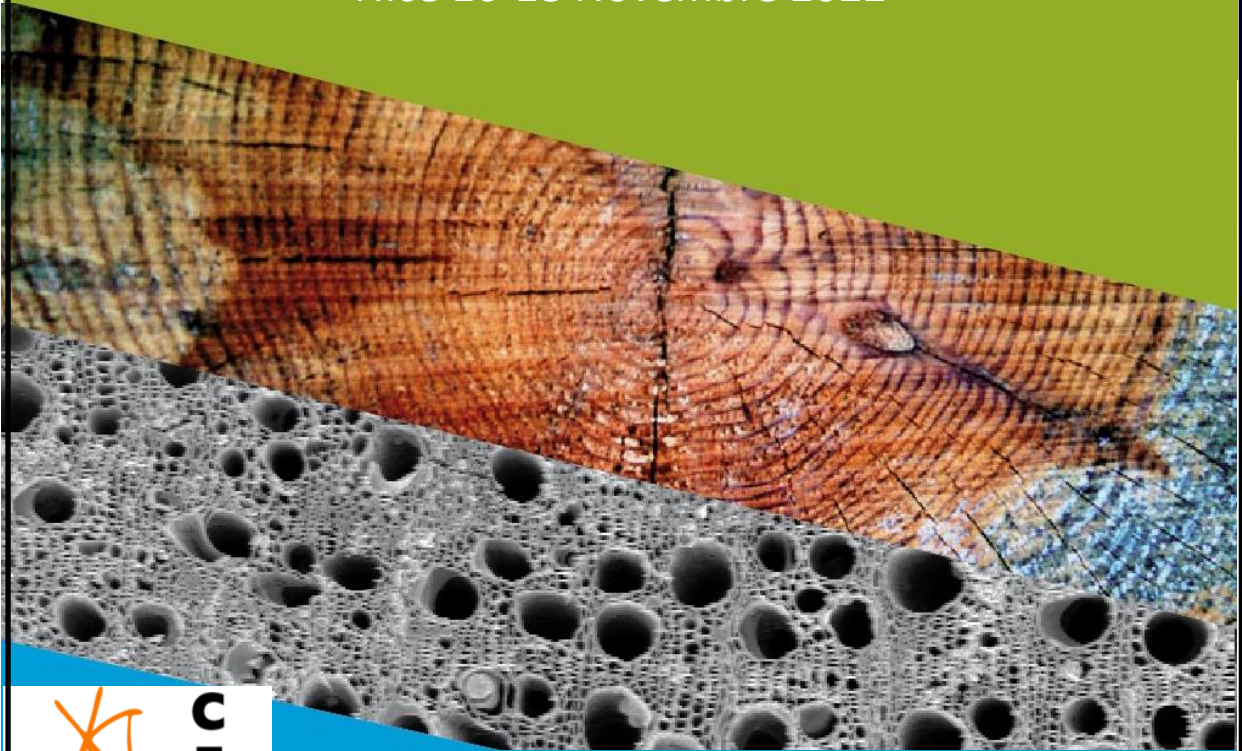
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# 11èmes Journées Scientifiques du GDR3544 Sciences du bois

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**GDR** Groupement  
de recherche  
**Sciences du bois**

## Actes

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## Reduction of wood thermal conductivity by delignification

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### Context and objectives

Wood is a material commonly used in construction. The carbon dioxide absorbed during its life cycle is stored in the material as carbon. The thermal insulation industry has been using petroleum-based materials like polystyrene and polyurethane foams as efficient thermal insulants, but not eco-friendly. Wood as a bio-sourced material has a lower thermal conductivity than conventional building materials like concrete and metal. It can potentially undergo modifications through nanotechnology to further reduce its thermal conductivity. The objective of the work is to use wood as a bio-sourced alternative thermal insulation material.

In this work, various French species of wood were delignified chemically with the methods cited in the literature, i.e. the alkaline kraft method and the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) bleaching method. After delignification, nanopores are created in addition to the macropores initially available. The mesoporous structure increases the total porosity of the wood, which reduces its density as well as its thermal conductivity across the grain. Delignified wood presents great interest as future insulation material, with the benefit of superior mechanical strength when compared to traditional insulating materials. France is the top producer and exporter of poplar in Europe, so poplar exhibits the highest potential to be transformed into a thermal insulant by delignification because of its fast growth rate, low density and low thermal conductivity.

### Materials and methods

#### *Delignification of wood*

The wood specimens of solid woods and wood veneers were acquired from Institut Pascal and LaBoMaP research centers. The solid wood were sawn into dimensions of 100 mm x 100 mm with a thickness of 10mm, while the wood veneers of thickness range from 1 mm to 3 mm were cut into dimensions of 100 mm x 100 mm. The wood specimens include both hardwoods (oak, beech, poplar) and softwoods (silver fir, douglas fir). The alkaline kraft treatment was carried out with sodium hydroxide (NaOH) and sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) supplied by Sigma Aldrich. 35% Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) used in bleaching was also supplied by Sigma Aldrich.

The woods were soaked in a mixture of 2.5M sodium hydroxide (NaOH) and 0.4M sodium sulfite (Na<sub>2</sub>SO<sub>3</sub>) at boiling temperature for 8 hours, followed by 8 hours of immersion in boiling hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) diluted to 7.5%. The woods were then washed with deionized water and air-dried for one day before freeze-drying or oven-drying at 70°C (Zhu *et al.*, 2016).

### *Degree of delignification*

The delignification efficiency was measured through dry mass loss ratio and color evaluation. The wood specimens were weighed before and after treatment. Their water content was also determined with the oven-dry method.

### *CIELAB color space measurement*

The values of color space  $L^*a^*b^*$  were measured with a colorimeter PCE-XXM 30. To quantify the whitening effect of delignification, the values were compared with white color ( $L^* = 100$ ;  $a^* = 0$ ;  $b^* = 0$ ). The color difference  $\Delta E$  is calculated using Eq.1. A smaller  $\Delta E$  implies that the colors are close to white.

$$\Delta E = \sqrt{(L^* - 100)^2 + (a^* - 0)^2 + (b^* - 0)^2} \quad (\text{Eq.1})$$

### *Dimensional variation of wood*

The dimensions of the wood were measured with a digital caliper before and after treatment to determine the variation of volume and density.

### *Thermal conductivity measurement*

Thermal conductivity was determined using a FP2C conductivity meter hot wire device, based on the semi-infinite domain hypothesis and assumption of radial heat transfer. By placing the hot wire probe between two wood samples, constant heat flux is generated by the hot wire that locally heats the material. The temperature evolution is recorded by the thermocouple welded in the middle of the wire. The thermal conductivity  $k$  is then determined from the linear part of the time-temperature curve. This hot wire probe can measure thermal conductivities from 0.02 to 5 W/m.K, with an accuracy of 5%. By orientating the hot wire across or along the fiber direction, longitudinal and transversal thermal conductivity can be obtained, as shown in Fig. 1 and Fig. 2 (Jannot *et al.*, 2011). Three measurements were taken for each case after conditioning in a climate chamber at 25°C and relative humidity of 20% for 24 hours.



Fig. 1 : Probe orientation to measure the transversal thermal conductivity



Fig. 2 : Probe orientation to measure the longitudinal thermal conductivity

## **Results and discussion**

### *Delignification efficiency*

Alkaline kraft method using sodium hydroxide (NaOH) and sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) firstly swelled the fibers with its high pH, then dissolved the wood extractives and broke the intermolecular ester bonds crosslinking hemicellulose and lignin, causing the wood color to darken, due to the formation of new chromophore structures, as shown in Fig.3(b). The sulphonation enhanced the dissolution of lignin as well (Sun and Cheng, 2002; Li *et al.*, 2012). The hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was used to bleach the wood through lignin-degrading oxidation and to remove unreacted chemicals. The degradation of lignin, hemicellulose and extractives was represented by the mass loss ratio at anhydrous condition. For the same duration of delignification treatment, the thinner wood veneers showed a higher mass loss ratio than the thicker solid woods, due to the more efficient chemical reaction.

After drying, shrinkage in the transverse direction of wood fibers was observed in all cases, especially wood veneers, as shown in Fig. 3(d), while the longitudinal lengths of wood fibers remained unchanged. During the evaporation of the liquid present in the pores, capillary pressure was generated and caused lumen collapse, due to the drying tension, as shown in Fig. 3(f). The lumen closures increase the density and limit the reduction of thermal conductivity.

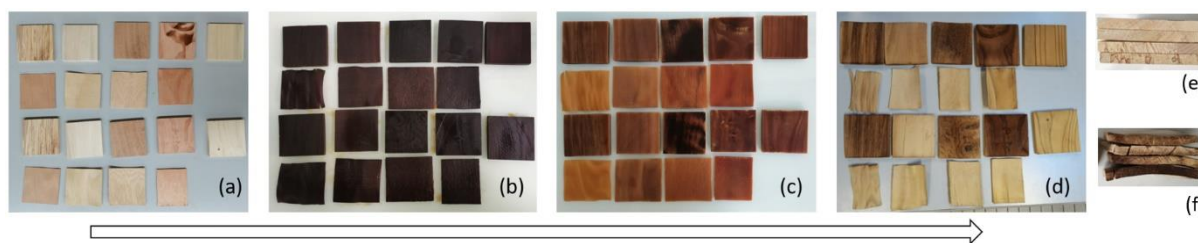


Fig. 3: Color and dimensional variations of woods at different stages of delignification. Wood species from 1<sup>st</sup> column to 5<sup>th</sup> column: beech, poplar, douglas fir, oak, fir. 1<sup>st</sup> and 3<sup>rd</sup> row: solid woods. 2<sup>nd</sup> and 4<sup>th</sup> row: wood veneers. a) Before treatment. b) After 8h bath in a boiling mixture of NaOH and Na<sub>2</sub>SO<sub>3</sub>. c) After 8h bleaching in H<sub>2</sub>O<sub>2</sub>. d) After one-day air drying e) Side view of solid woods before delignification. f) Side view of deformed delignified solid woods due to collapse when drying.

#### *Factors affecting the thermal conductivity*

After delignification, both transversal and longitudinal thermal conductivities decrease, except for silver fir, which is believed to gain lignin or extractives from other wood species. The samples of silver fir were not only darkened due to contamination but also exhibited the lowest dry mass loss ratio. The wood species with a higher dry mass loss ratio, indicating more efficient removal of lignin, hemicellulose and extractives, showed a higher reduction of thermal conductivity in both directions (Fig. 4). Among the samples, poplar is the wood species with the lowest density and also the lowest thermal conductivity both before and after delignification. Poplar is commonly known as a fast-growing species with low-density wood cells, compared to other species.

Wood exhibits brownish color due to the phenolic character and the chromophore groups of lignin with strong light-absorbing capability (Shi *et al.*, 2018). Lignin is dark brown, while cellulose is white, so the color indicates the amount of lignin present in the wood (Wachter *et al.*, 2019). The removal of lignin was confirmed by the mass loss ratio, but the whitening effect of wood did not turn out as expected. After delignification, all wood species became darker in color due to the creation of new chromophore groups after the chemical reaction and/or contamination by the extracted matrix. Nevertheless, the wood species with a whiter surface, i.e. poplar, has lower thermal conductivity in all cases (Fig.5). It is believed that the thermal conductivity can be further reduced if the wood becomes completely white when a total delignification is achieved.

#### **Conclusion and perspectives**

The removal of lignin from wood reduces its mass but the collapse associated to drying shrinkage may increase its density. Thus, the porosity may not be entirely conserved. The reduction of thermal conductivity is observed despite the presence of collapse and darkening in the color of delignified wood. It is believed that the thermal conductivity can be further reduced if the collapse does not occur and the treatment exhibits a higher delignification efficiency. More samples and trials are required to determine the lowest thermal conductivity that a delignified wood can achieve. To prevent collapse, there are solutions such as the replacement of water with liquid of low surface tension, or drying below the collapse threshold temperature. Reconditioning of deformed delignified wood by steaming or rewetting is possible only if the

lignin is not strongly depleted (Segmehl, 2017). To reach a higher delignification degree, a more intensive whitening effect can be achieved by using a higher concentration of H<sub>2</sub>O<sub>2</sub> or by replacing the darken H<sub>2</sub>O<sub>2</sub> bleaching solution throughout the treatment. Fabrication of delignified wood to be used as a bio-sourced thermal insulant requires a thermal conductivity below 0.042 W/m.K. Among the locally available wood species, poplar can potentially achieve the lowest transversal thermal conductivity after effective delignification.

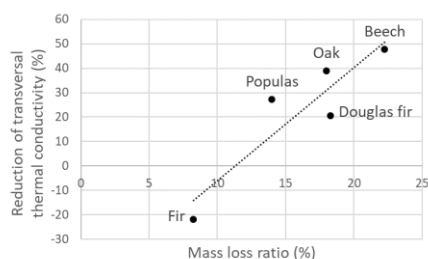


Fig. 4 : Reduction of transversal thermal conductivity in various wood species

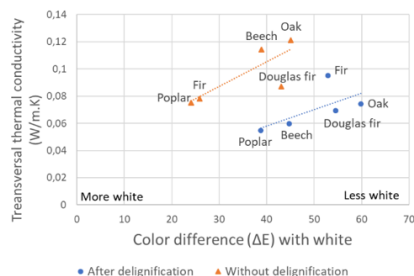


Fig. 5 : Transversal thermal conductivity in various wood species

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## References

- Jannot Y., Degiovanni A., Félix V., Bal H. (2011) Measurement of the thermal conductivity of thin insulating anisotropic material with a stationary hot strip method. *Measurement Sci. and Technol.*, 22(3), 035705. <https://doi.org/10.1088/0957-0233/22/3/035705>
- Li Q., Gao Y., Wang H., Li B., Liu, C., Yu, G., & Mu, X. (2012). Comparison of different alkali-based pretreatments of corn stover for improving enzymatic saccharification. *Bioresource Technol.*, 125, 193–199. <https://doi.org/10.1016/j.biortech.2012.08.095>
- Segmehl, J. S. (2017). Wood and wood-derived cellulose scaffolds for the preparation of multi-functional materials (190 p.) [ETH Zurich; Application/pdf]. <https://doi.org/10.3929/ETHZ-B-000230544>
- Shi, J., Lu, Y., Zhang, Y., Cai, L., & Shi, S. Q. (2018). Effect of thermal treatment with water, H<sub>2</sub>SO<sub>4</sub> and NaOH aqueous solution on color, cell wall and chemical structure of poplar wood. *Scientific Reports*, 8(1), 17735. <https://doi.org/10.1038/s41598-018-36086-9>
- Sun, Y., & Cheng, J. (2002). Hydrolysis of lignocellulosic materials for ethanol production: A review. *Bioresource Technol.*, 83(1), 1-11. [https://doi.org/10.1016/S0960-8524\(01\)00212-7](https://doi.org/10.1016/S0960-8524(01)00212-7)
- Wachter, I., Tomas, S., & Rolinec, M. (2019). Optimization of Two-Step Alkali Process of Lignin Removal from Basswood. *Research Papers Faculty of Materials Science and Technology Slovak University of Technology*, 27, 153–161. <https://doi.org/10.2478/rput-2019-0016>
- Zhu, M., Song, J., Li, T., Gong, A., Wang, Y., Dai, J., Yao, Y., Luo, W., Henderson, D., & Hu, L. (2016). Highly Anisotropic, Highly Transparent Wood Composites. *Advanced Materials*, 28(26), 5181–5187. <https://doi.org/10.1002/adma.201600427>