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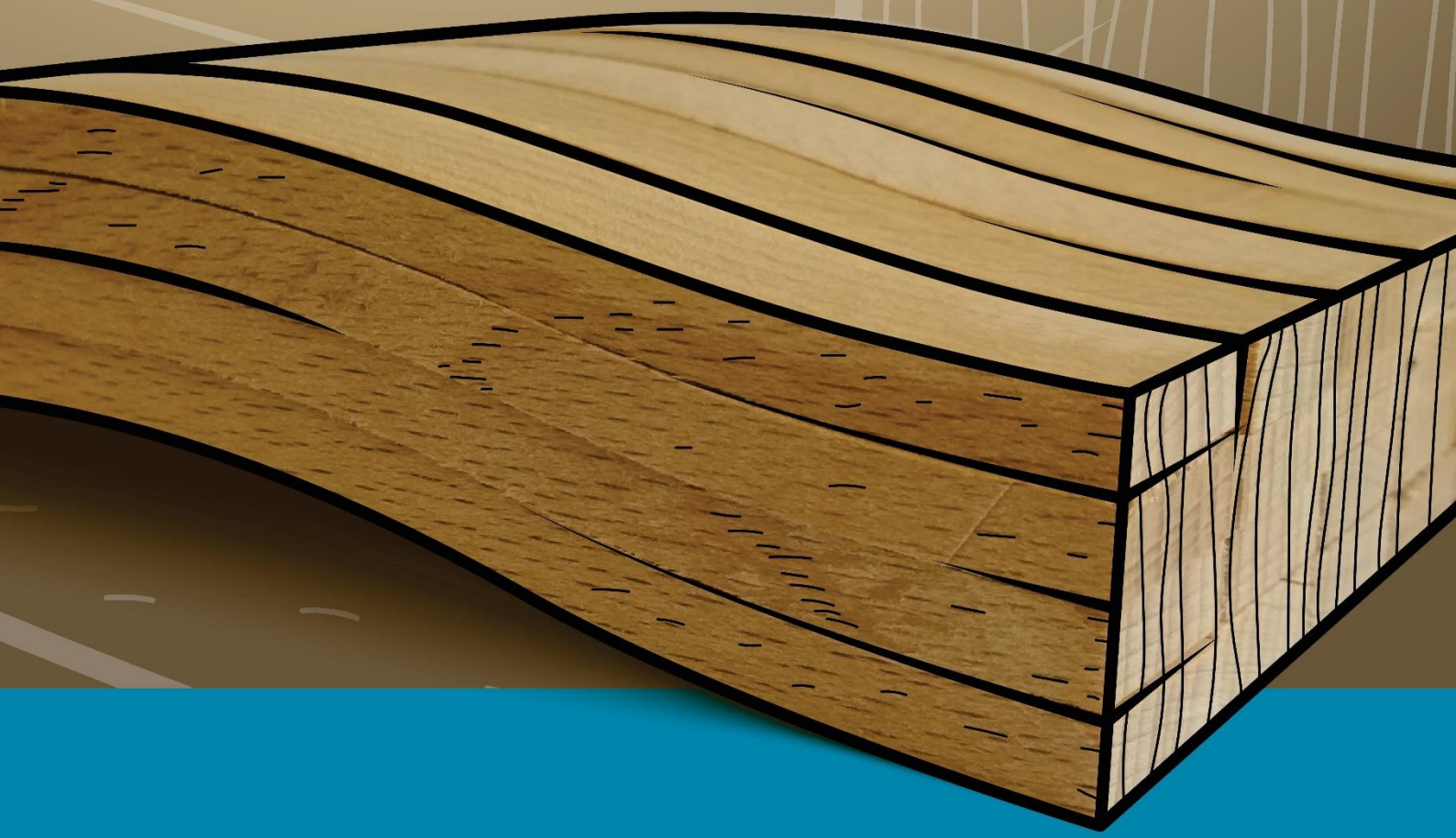

WOOD KPLUS

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10TH HARDWOOD CONFERENCE PROCEEDINGS

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Delignification experiments for the production of transparent wood

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ABSTRACT

Transparent wood is a composite which has a number of favourable properties. Its production is divided into 2 main stages. The first is the delignification stage; the second is the polymer infiltration stage. This paper deals with the first stage, aiming at the analysis of the H_2O_2 steam process and the definition of the further research direction. The experiments were carried out at different temperatures. In some cases, the samples were pre-treated with NaOH. The delignification of balsa, poplar, beech, oak and ash veneers was successfully completed. The delignification time showed a large variation between different treatments and within different treatments. Favourable results have been achieved with hot and pre-treated processes. The lignin content of the poplar samples was 0.79%, which is the lowest result obtained so far for the hydrogen peroxide steam delignification procedure. The results obtained in this research are well suited for future use. The success of delignification in hydrogen peroxide steam requires further experiments.

INTRODUCTION

Transparent wood-based composites, or simply transparent wood, was put to the foreground again in the last 5-6 years. Research to date has shown that transparent wood can be a very versatile composite for a wide range of applications, from construction to solar cell manufacturing (Li 2019a, Zhu 2016). Wood is an orthogonally anisotropic cellular material composed of cellulose, hemicellulose and lignin, which accumulates by-products (extractives) during its life cycle. This system has high light absorption and reflectance (Molnár 1999, Tolvaj 2013). Therefore, the wood is not transparent. Transparent wood production has two main stages. In the first stage, the parts containing chromophore groups, i.e. lignin and extractives, are removed, while retaining the cellular structure. This is the lignin removal or delignification stage. In a second stage, the resulting cellulose template is impregnated by a polymer with matching refractive index (n) to eliminate the high refractive index difference between the cellulose template ($n\approx1.53$) and air ($n\approx1$) within the template (Li et al. 2016). For this purpose, polymers of fossil origin (PMMA, epoxy resin) are most commonly used. The best results so far were reported by Li et.al. (2018), where, even for a 3 mm balsa wood, a light transmission of 89% and a haze of 53% were measured.

Of the two stages, the first stage is the most important and time-consuming. Several methods for delignification have been used so far (Li 2016, Gan 2017, Zhu 2016, Frey 2018, Jia 2017, Fu 2017, Li 2019). Most studies have performed the treatment in sodium chlorite ($NaClO_2$) solution, achieving a residual lignin content of 2-5% with a delignification time of 3-12 h (Li 2016, Li 2018, Yaddanapudi 2017, Gan 2017). It is important to note that when treating in solution, the samples may fall apart during the process (Li 2017). The best results obtained so far were obtained with the hydrogen peroxide steam method. For a 210 x 190 x 0.8 mm (L x T x R) basswood, a lignin content of 1.06 % was achieved in 4 h (Li 2019a). An additional advantage of H_2O_2 steam process is that no harmful by-product is generated during the process, as H_2O_2 decomposes into water and oxygen (Li 2019a). In this study, we focus on the H_2O_2 steam process using different parameters.

EXPERIMENTAL METHODS

Materials:

In this study balsa (*Ochroma pyramidale*), poplar (*Popolus* sp.), beech (*Fagus sylvatica*), oak (*Quercus* sp.) and ash (*Fraxinus* sp.) was used. The chemicals used in removing lignin from the wood were hydrogen peroxide (30% solution) and potassium hydroxide (NaOH, flake). The solvents used were ethanol alcohol and DI water.

Hydrogen peroxide steam delignification.

Reduced temperature process. Delignification of dried samples (103±2 °C, 24 h) was performed at 90 °C, above H_2O_2 solution. After treatment, the samples were washed several times in DI water.

Hot procedure. Delignification of the dried samples was performed over boiling (120°C) H_2O_2 solution. (Li 2019a). Delignification was carried out until complete bleaching of the samples. In some cases, samples were pre-treated with 10 wt% NaOH solution. The pre-treatment was carried out at 80°C for 4 h. The pre-treated samples were washed in DI water. This was followed by steam treatment. The delignified samples were washed several times in DI water. The samples were then dehydrated in ethanol. The samples were stored in ethanol until further use.

Lignin content determination.

The residual lignin content of the delignified samples was determined indirectly. The method was used to determine the holocellulose content. Delignified samples were dried to constant weight. 0,5 g sample was spiked into 100 ml Erlenmeyer flasks. The lignin removal solution contained 16 ml DI water, 0,2 g $NaClO_2$ and 0,1 ml acetic acid. The solution was heated in a water bath at 70°C for 4 hours. 0,2g $NaClO_2$ and 0,1 ml acetic acid were added to the flasks every hour. After the 12-hour exploration phase, the solutions were cooled. The samples were filtered through a G1 glass filter and dried to constant weight at 103±2°C. The residual lignin content was calculated according to Eq. 1 (Rowell 2005):

$$Lignin\% = \frac{m_b - m_{hc}}{m_b} * 100 \text{Lignin}\% = \frac{\mathrm{m_b\text{-}m_{hc}}}{\mathrm{m_b}} * 100 \quad (1)$$

where, m_b [g] is the weight of the sample taken, m_{hc} [g] is the weight of the holocellulose

RESULTS AND DISCUSSION

Reduced temperature process

Using this method, the samples did not bleach after 12 hours, but their original colour was faded. Probably, at the temperature of 90°C, H_2O_2 did not decompose properly and could not oxidize the lignin sufficiently. In the water-saturated state, a slight transmittance was already observed (Fig. 1 B). Due to the very long process, this method is not economical.

Hot process with pre-treatment.

The sodium hydroxide pre-treatment resulted in browning of the samples and reduced size (Fig. 1 C). The NaOH pre-treatment did not accelerate the time of the hydrogen peroxide steam treatment. This is probably the result of the wash-through, as the NaOH could not exert its catalytic effect. The samples were degraded by the refluxing condensate and fell apart after treatment (Fig. 1 D).

Hot process.

Using only H_2O_2 steam proved to be an effective procedure for both thin (0.6 mm) and thick (2 mm) samples (Fig. 1 E). Samples delignification in hydrogen peroxide steam do not present the same risk of disintegration as delignification in solution, but back-injection of condensate also destroyed the samples in this case (Fig. 1 E). This method is also well suited for oak, ash and beech (Fig. 1 F-G), but for these species a prolonged delignification time (8-12 h) is expected, based on the present experiments.

The residual lignin content was determined for balsa (thickness 1 mm) and poplar (thickness 0.6 mm) samples delignified in hydrogen peroxide steam. The values obtained are of the same order of magnitude as those reported in the literature. The lignin content of the balsa samples was 2.52%. For the poplar

samples, a lignin content was 0.79%, which is the lowest result of the hydrogen peroxide steam delignification procedure for tangential section samples to date (Li 2019a).

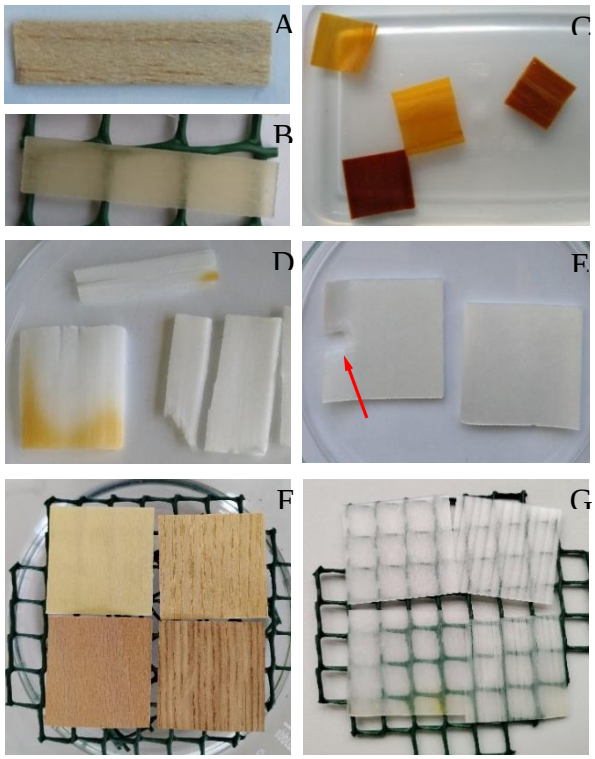

Figure 1: Natural balsa wood (A) and balsa wood after reduced temperature treatment (B). Samples after NaOH pre-treatment (C) and delignification (D). 2 mm poplar samples after hot treatment (E) and condensate-induced deterioration (red arrow). Poplar beech, ash, oak samples before delignification (F) and after hot treatment (G)

CONCLUSIONS

In summary, in this study we have examined the first stage of transparent wood production. To study the delignification stage, the hydrogen peroxide steam process was used with different parameters. The delignification time was greatly increased with the reduced temperature process. Thus, this method is not economical. The hot method has already produced more favourable results. In this case the samples were bleached in 8-12 h. It can be concluded that this method is well suited for poplar, beech, oak and ash. The NaOH pre-treatment used did not significantly accelerate the delignification process. Further experiments with the pre-treatment will be carried out. Overall, the hot process is well suited, but further research is needed to accelerate the process.

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