SEVEN publicações acadêmicas
EM PARCERIA COM: IEMS UNIASSELVI

Exploration of chemical and physical transformations in natural and heat-cured eucalyptus wood

Ricardo Marques Barreiros[1], Felipe Dutra Lisboa[2], Cantídio Fernando Gouvea[3], Alessandra Maria Ferreira Reis[4], Emmanuel Zullo Godinho[5], Kelly Bossardi Dias[6].

ABSTRACT
In 2018, global industrial production of roundwood experienced remarkable growth of 5%, reaching a record 2.03 billion cubic meters. In this scenario, Brazil stands out as one of the main players, ranking fifth in both production and consumption of roundwood, with an annual average of 150 million cubic meters.

Keywords: Industrial production, Reforestation, Eucalyptus.

INTRODUCTION

In 2018, global industrial production of roundwood experienced a remarkable 5% growth, reaching a record 2.03 billion cubic meters. In this scenario, Brazil stands out as one of the main players, ranking fifth in both production and consumption of roundwood, with an annual average of 150 million cubic meters (FAO, 2018).

Brazil's significant contribution to this production comes largely from the cultivation of species such as *Eucalyptus* and *Pinus*. Of these, around 70% are eucalyptus species. This raw material plays a crucial role in supplying strategic sectors such as energy and pulp, as well as being widely used in structural applications and in the furniture industry.

The success of eucalyptus in Brazil is due to several factors. Its easy adaptation to a variety of national biomes, its rectilinear characteristic, the rapid increase in volume and the high level of technology associated with its cultivation (IBÁ, 2016) are all elements that contribute to the preference for this species.

This expansion and efficiency in the production of roundwood in Brazil reflects not only the country's ability to meet growing demand, but also the adoption of sustainable practices and advanced technologies in forest management and the timber industry.

[1] Paulista State University, Faculty of Agronomic Sciences, Botucatu Campus – São Paulo
[2] Paulista State University, Institute of Science and Engineering, Itapeva Campus – São Paulo
[3] Federal University of Sergipe, São Cristóvão Campus – Sergipe
[4] Federal University of Sergipe, São Cristóvão Campus – Sergipe
[5] University of São Paulo, Pirassununga Campus – São Paulo
[6] Paulista State University, Institute of Science and Engineering, Itapeva Campus – São Paulo

The use of reforestation species, especially eucalyptus, plays a fundamental role in reducing the pressure on native species. The latter are often exploited in a predatory manner, especially in construction and furniture production, due to their high final value. Fast-growing species, such as eucalyptus, are emerging as viable alternatives to replace traditional species that grow more slowly.

The advantage in growing these species not only offers a solution to growing demand, but also allows for genetic improvement, resulting in products that are better adapted to specific uses. However, despite these advantages, the full adoption of these species faces challenges, such as pest attacks, poor dimensional stability and other problems pointed out by the industry.

These obstacles are often pointed out as limitations to the widespread acceptance of these species by end consumers. Consequently, the research and implementation of treatment techniques, applicable on an industrial scale, become essential to improve the quality of these products. These techniques not only aim to overcome the aforementioned challenges, but also to ensure that fast-growing species such as eucalyptus meet the quality standards required for a variety of applications, thus promoting their wider acceptance on the market.

Wood modification processes can be classified into four distinct types: chemical, surface, impregnation and thermal. Among these, the thermal process has experienced a remarkable evolution in commercial terms, predominantly due to its low cost (MODES et al., 2017).

Thermorectification, which is a form of thermal rectification of wood, gives wood colors similar to those of more economically valuable tropical species. It also improves dimensional stability and resistance to fungi, making it a process that adds considerable value to the material (MOURA; BRITO; BORTOLETTO JÚNIOR, 2012). This technique can not only boost the supply of wood from reforestation in various regions, but also help to reduce the pressure on endangered native species (BRITO; GARCIA; BORTOLETTO JÚNIOR, 2006).

According to Majano-Majano, Hughes and Cabo (2012), the main wood species subjected to heat treatment were, to some extent, from the *Pinus* genus. Only more recently has there been growing interest in these heat-treated woods for structural applications. This progress indicates an expansion in the scope of application of these woods, paving the way for their use in previously unexplored structural contexts.

The heat treatment technique involves the intense and controlled application of heat, often combined with pressure in specific cases, with the aim of improving the final product. This process is carried out at temperatures lower than those of carbonization, usually up to 280°C, causing changes in the structure of the wood due to the action of the heat (BORGES; QUIRINO, 2004).

The improvements provided by this treatment are associated with the reorganization of the wood's chemical and anatomical constituents. Although the main focus is furniture production, heat treatment can also be applied to structural elements or the manufacture of panels. This was evidenced by Ferreira et al.

(2018), who compared heat-treated pine panels with those subjected to traditional treatments, obtaining similar results in both approaches.

Thus, heat treatment not only provides advantages in terms of the structural reorganization of wood, but also diversifies its applications, standing out not only in furniture production, but also as a viable alternative for structural elements and the manufacture of panels. This versatility highlights the potential of this method for optimizing various wood-based products.

In the context of heat treatment, the choice of temperature range is a critical variable, since very low temperatures may not cause significant changes, while extreme temperatures can result in material degradation. According to Pessoa, Filho and Brito (2006), for *Eucalyptus grandis*, higher temperatures provide more effective results, mainly due to greater resistance to termite attacks. Although not providing total resistance to xylophagous agents, materials subjected to these temperatures showed less damage and greater termite mortality. This trend towards higher temperatures was also corroborated by Fontoura et al. (2015) in mechanical characterization tests on *Hovenia dulcis* wood.

According to Windeisen, Strobel and Wegener (2007), the changes in wood characteristics resulting from heat treatments are influenced by the species, moisture content, prevailing atmosphere, application method, temperature and exposure time. In addition, temperature has a more significant impact than time on the heat treatment process, and chemical and physical changes above 150 °C are considered permanent.

These considerations highlight the importance of carefully selecting the heat treatment temperature in order to optimize the desired results and minimize unwanted effects on the treated wood.

Among the various heat treatment processes, it is common for them to share the characteristic of exposing the wood to high temperatures for a prolonged period (ROUSSET; PERRÉ; GIRARD, 2004). However, in some species, exposure time may not be a crucial variable, as demonstrated by Fontoura et al. (2015), who found that, for *Hovenia dulcis*, treatment for two or four hours did not generate significant changes in the modulus of elasticity (MOE) and modulus of rupture (MOR) of the wood.

In laboratory experiments, thermo-rectification is generally carried out using forced air circulation at temperatures ranging from 100 to 200°C, with exposure times ranging from two hours to a whole day. This process aims to promote the degradation of part of the hemicelluloses and the condensation of other components (BRITO; GARCIA; BORTOLETTO, 2006). It is therefore essential to carry out studies on thermo-rectification in various species of reforested wood, as the unique anatomical properties of each species can give the final product unique characteristics. In addition, research into trees destined for sectors other than the furniture industry could reveal valuable potential uses for some forests, resulting in products with greater added value and equivalent technological potential.

The literature highlights the importance of improving our understanding of the heat treatment process in order to obtain the benefits of heat treatment with minimal losses in relation to the wood's original properties. In this context, the species in question is widely used in forest plantations in Brazil, and the clones selected for this study are considered essential for the timber industries in the southwestern region of São Paulo.

Specific research into the heat treatment of these clones plays a crucial role, not only to maximize the benefits of this process, but also to adapt the techniques to the unique characteristics of the wood of this species. By optimizing heat treatment, it is possible to exploit the full potential of this raw material, ensuring its efficient and sustainable use in local industries. This type of study contributes to the development of more effective practices in the application of heat treatment, resulting in treated wood products that meet both the needs of industries and environmental requirements.

This comprehensive approach aims to provide a complete understanding of the changes that occur in wood subjected to different heat treatment conditions, allowing a comprehensive assessment of the impact of these variations on the material's physical and chemical properties. This detailed analysis is essential to inform more effective and sustainable heat treatment practices, as well as to maximize the potential for using the wood from these hybrid clones in various industrial applications.

OBJECTIVE

The main objective of this study was to evaluate the physical and chemical performance of the wood from two hybrid *Eucalyptus urograndis* clones. Specifically, the basic density, volumetric swelling and various chemical parameters were analyzed, such as ash, total extractives, holocellulose and lignin. The analyses were carried out on both *raw* wood samples and samples subjected to heat treatment at different temperatures: 140, 160, 180, 200 and 220°C. The treatments were carried out under normal oxygen conditions inside a heat treatment chamber.

METHODOLOGY

OBTAINING THE MATERIAL FOR THE STUDY

The wood used in this study came from 12 randomly selected trees from two *Eucalyptus urograndis* hybrid clones, referred to here as L and H, 6 trees from each clone. These trees were grown in plantations spaced 3.00 m x 2.00 m, located in similar soil and climate conditions in the region of Buri, São Paulo, Brazil, and sampled at 8.5 years of age. It is important to note that this material was initially planted for pulp production; however, due to the trees' large size, there was an interest in analyzing their potential under various variables.

MATERIAL PREPARATION AND HEAT TREATMENT

For the thermorectification process, the basal logs of these trees were split at a sawmill, resulting in planks centered on the pith, all 2.54 cm thick and varying in width according to the different log diameters to enable the physical and chemical properties of the wood to be determined.

The total number of specimens was 156, 26 from each treatment. This comprehensive sampling approach allowed for a robust analysis of the changes in wood properties resulting from the different heat treatments applied.

PHYSICAL CHARACTERIZATION OF WOOD

The physical characterization of eucalyptus wood was carried out by determining the basic density and assessing dimensional instability by swelling the wood, both *in natura* (control) and thermally treated.

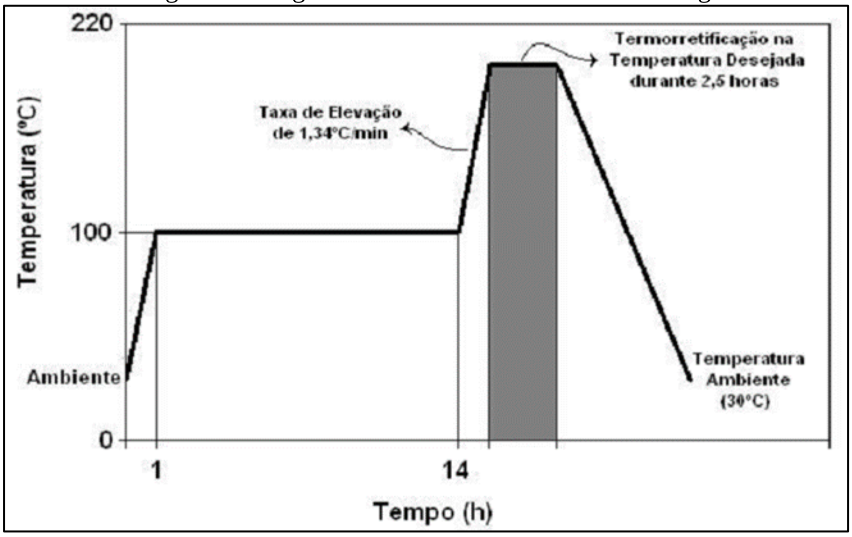
For this purpose, specimens free of defects such as knots and cracks were used, in accordance with the specifications of ABNT NBR 7190 (1997). These specimens had dimensions of 2.0 cm x 3.0 cm x 5.0 cm, with the longest edge oriented in the longitudinal direction, while the longest edge was oriented in the longitudinal direction.

Afterwards, the ends of the boards were removed due to cracks and cut into 70 cm long pieces. These pieces were duly identified and their tops sealed with silicone paste suitable for high temperatures. With the exception of the control sample (witness), all the pieces were subjected to thermo-melting in an electric chamber at temperatures of 140, 160, 180, 200 and 220 ºC.

For each heat-setting temperature, two pieces of each board and each clone were separated and stacked in a grid with boards inside the electric oven. This material was heated to 100 °C for two hours and then subjected to a temperature rise of 1.34 °C/min until the final temperatures for each treatment were reached (CALONEGO et al., 2014). The control sample had its temperature raised to 100 °C until it reached constant mass.

Each treatment was kept on for 2.5 hours, taking into account the statement by Bhuiyan, Hirai and Sobue (2001) that cellulose crystallizes after the first hour. After each heat treatment, the oven was turned off and the pieces of wood were left inside to cool naturally until they reached room temperature.

Figure 1 - Program followed for wood thermo-curing



Source: Calonego et al. (2014).

SPECIMEN PREPARATION

From each piece resulting from all the treatments, two slats were removed and positioned between the pith and the periphery, one on each side of the pith. These slats were then cut into specimens measuring 5 cm x 3 cm x 2 cm, oriented in the longitudinal, radial and tangential planes, respectively smaller in the tangential direction.

For each treatment, 13 specimens were selected and saturated to determine basic density and swelling. All the specimens were duly identified and subjected to tests in accordance with the normative specifications of ABNT NBR 7190 (1997). This rigorous methodology provides a consistent assessment of the physical properties of wood under different heat treatment conditions.

CHEMICAL CHARACTERIZATION OF WOOD

The chemical characterization of eucalyptus wood was carried out by determining the content of high molecular mass chemical substances (holocellulose and lignin) and low molecular mass chemical substances (extractives and ash) in the *raw* (control) and heat-treated wood.

Thirteen specimens from each treatment were used in composite samples. These samples were prepared in accordance with TAPPI standard T 264 cm-97 (1999), in which each composite sample was reduced to chips and then sawdust in a Willey-type macromill. The resulting sawdust was sorted using sieves to obtain the fraction between 40 and 60 *mesh*. Subsequently, the absolute dry content of the sawdust from each treatment was determined in accordance with TAPPI standard T 201 om-93 (1999).

The holocellulose content (alpha-cellulose + hemicelluloses) was determined using the buffered sodium chlorite method.

The total extractive content was obtained according to TAPPI standard T 264 cm-97 (1999).

The ash content (inorganic material) was determined according to the TAPPI T 211 OM-02 standard (1999).

The lignin content was calculated using Equation 1.

All the chemical analyses were carried out in triplicate, ensuring the reliability of the results.

$$L = 100 - Et - H \quad (1)$$

Where: L = Lignin content, in %; Et = Total extractives content, in %; H = Holocellulose content, in %.

STATISTICAL ANALYSIS

Statistical analyses were carried out using the R program, version 3.6.2, on the *64-bit Windows* platform. Linear regression analysis tests were applied to factorial treatments, considering two variables as factors: temperature and clone.

- **Temperature:** this is a continuous variable used for linear regression. The control condition was a temperature of 100 °C, chosen for mathematical modeling reasons.
- **Clone:** this is a qualitative factor, generating two different curves in the factorial system.

Analyses were carried out separately for each of the curves, assessing the effect of temperature within each clone. In addition, comparisons were made between the curves to assess the similarity of the treatment effect in both clones.

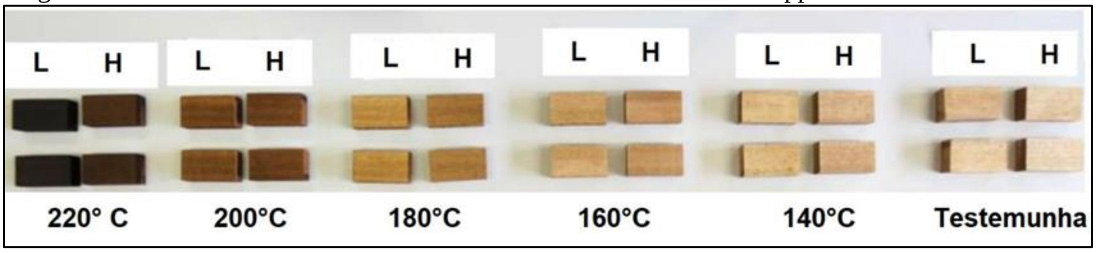
All the tests were carried out at a 5% significance level, guaranteeing the statistical reliability of the results obtained. The use of factorial analysis provides a more in-depth understanding of the impact of temperature and clone on wood properties.

DEVELOPMENT

STAINING THE WOOD PIECES

During the visual analysis of the wood pieces, both before and after the heat treatments, significant changes in coloration were observed in response to the different temperatures applied (Figure 2).

Figure 2 - Wood color behavior of clones L and H after and before the application of heat treatment



This change in color is the result of various chemical alterations during heat treatment. The visual perception of color can play a crucial role in the acceptance or rejection of the product on the market. If, for example, pieces with a darker color are less accepted by consumers, this will have important implications.

In order to obtain pieces with a color closer to that of the wood *in its natural state*, lower temperatures can be considered during the thermorectification processes. At lower temperatures, the change in color is less noticeable, which can be advantageous for maintaining the wood's original appearance.

BASIC DENSITY AND VOLUMETRIC SWELLING

The physical tests were carried out on both the *raw* wood and the thermally rectified wood of clones L and H. The behavior of basic density is shown in Figure 3, while volumetric swelling is illustrated in Figure 4.

Figure 3 - Behavior of the basic density of wood from clones L and H in relation to the heat treatments applied

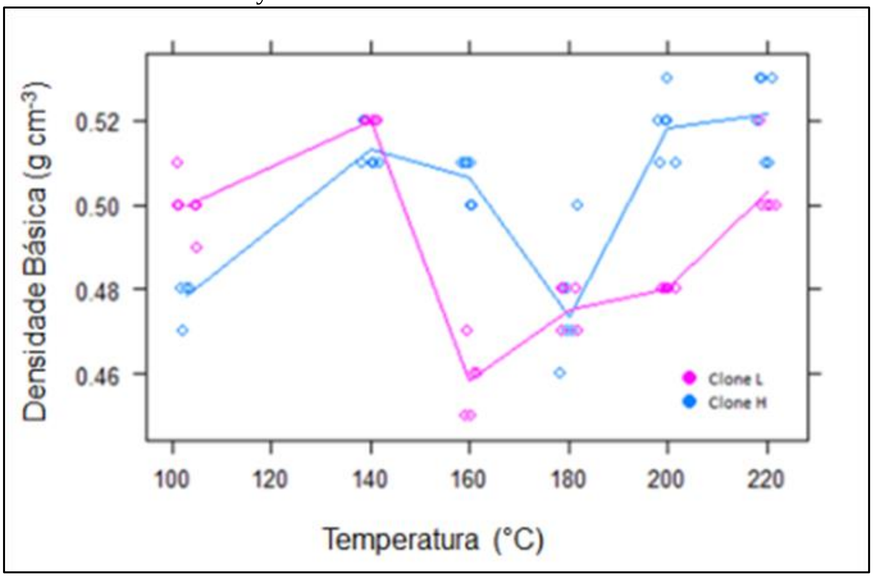
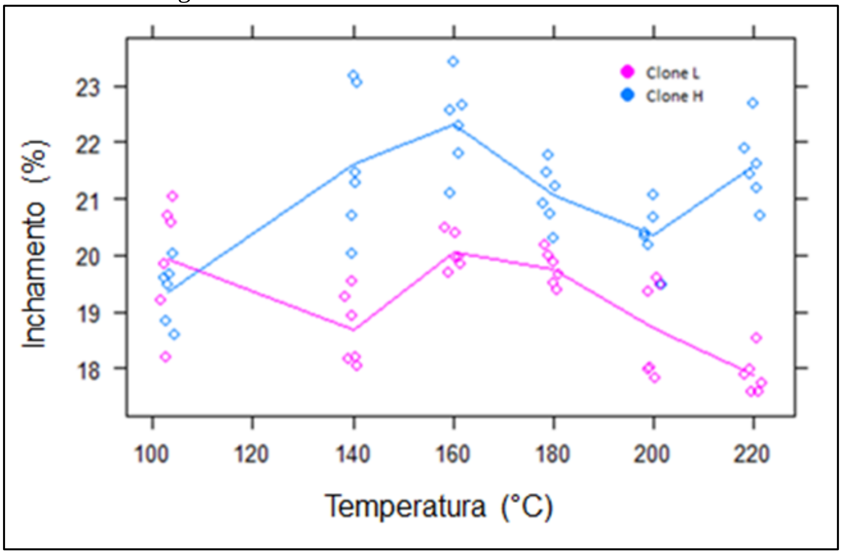


Figure 4 - Wood swelling behavior of clones L and H in relation to the heat treatments applied



These figures provide a clear visualization of how basic density and volumetric swelling varied in response to the different heat treatments applied to the L and H clones. Analysis of these results contributes to a deeper understanding of the impact of heat treatments on the physical properties of wood.

The appearance of cracks from the heat treatments presented significant challenges in obtaining specimens without this defect. This difficulty contributed to noise in the statistical analyses, especially in relation to swelling.

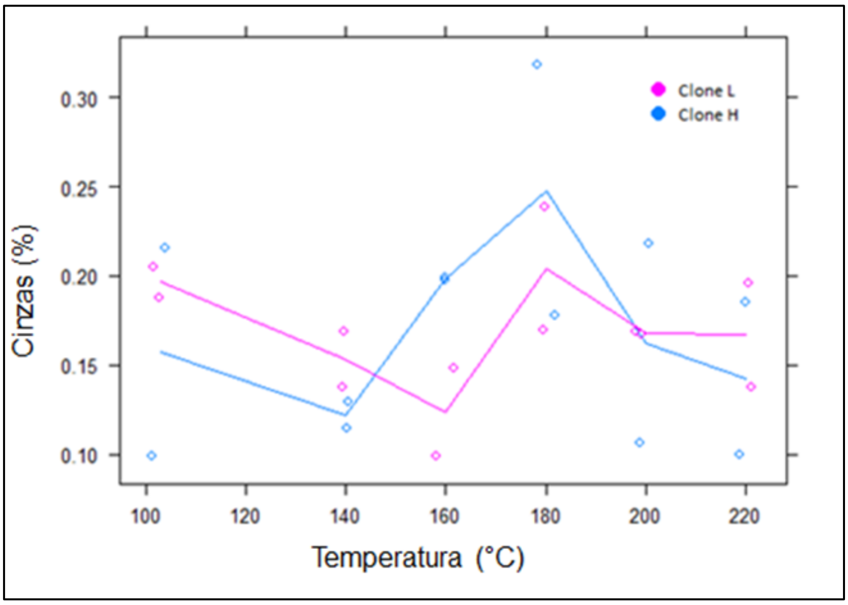
The appearance of cracks made it difficult to obtain completely homogeneous specimens, i.e. without defects, making measurements more complex and generating behavior without known statistical patterns. A material with less accelerated growth, which accumulates fewer growth stresses, would be more desirable. This could result in fewer cracks during the thermo-melting process, making it easier to obtain more consistent and reliable data.

This challenge highlights the importance not only of statistical analysis, but also of the initial physical condition of the wood, which directly influences the quality and reliability of the results obtained in the tests.

CHEMICAL COMPOSITION

The chemical composition of the wood from clones L and H was assessed, including the determination of ash, total extractives, holocellulose and lignin content. Figure 5 shows the behavior of the ash content in response to the heat treatments applied.

Figure 5 - Behavior of the ash content of wood from clones L and H in relation to the heat treatments applied

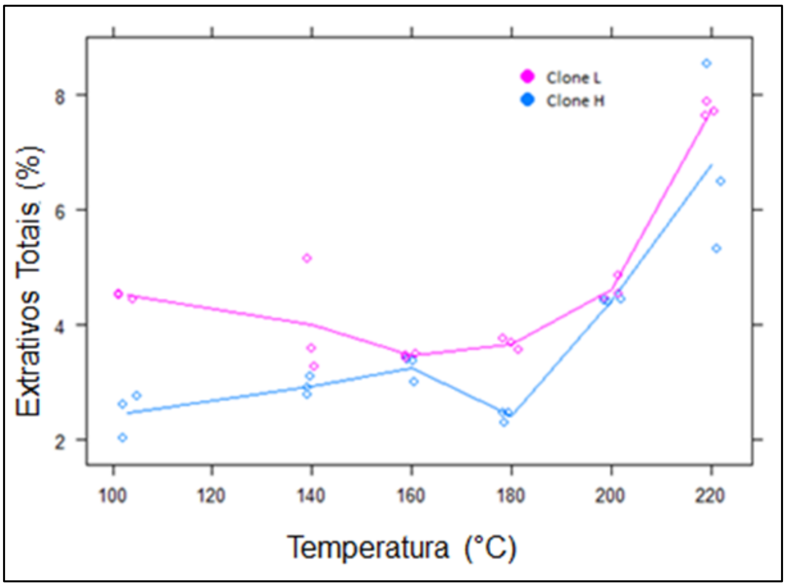


Although a decrease in ash content was observed at lower temperatures and an increase at higher temperatures, no significant interference of heat treatments on ash content was identified, considering a significance level of 5%. This analysis provides valuable information on the stability of the wood's chemical composition in response to different heat treatments.

For the total extractive content (Figure 6), there was a decrease at lower temperatures and an increase at higher temperatures. This phenomenon can be attributed to the degradation of part of the wood constituents, especially the volatile extractives, at lower temperatures. At higher temperatures, this degradation became more significant, mainly due to the degradation of holocellulose.

It is important to note that, despite the differences in temperature, the behavior between the clones did not differ significantly at a significance level of 5%. This suggests that the variation in temperature was the main determining factor in the changes observed in total extractive content.

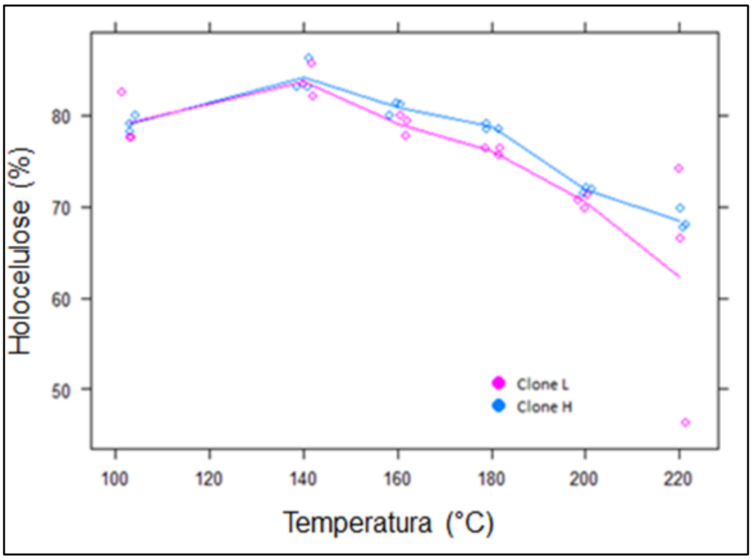
Figure 6 - Behavior of the total extractive content of the wood of clones L and H in relation to the heat treatments applied



With regard to holocellulose (Figure 7), there was a reduction in its content as the temperature increased, a similar behavior for both clones. This pattern was confirmed by statistical tests with a significance level of 5%. The degradation of holocellulose can be attributed to the fact that hemicelluloses have smaller polymer chains than cellulose (alpha-cellulose), making them more susceptible to thermal degradation.

It is interesting to note that this behavior is in line with similar findings in studies of the thermal degradation of wood from various eucalyptus clones, as reported by Pereira et al. (2013).

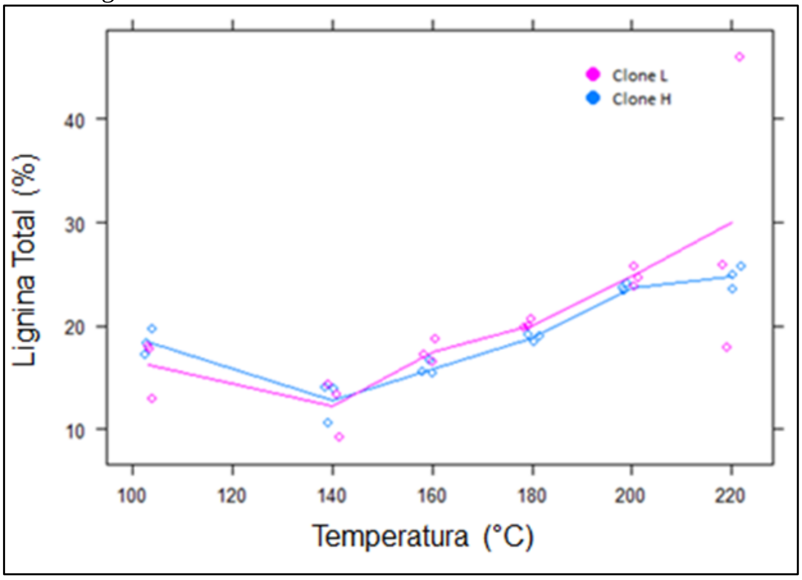
Figure 7 - Behavior of the holocellulose content of the wood of clones L and H in relation to the heat treatments applied



With regard to the lignin content (Figure 8), there was a significant difference in its average content in relation to the treatments applied, with a significance level of 5%. In the 140 °C treatment, its content decreased and then increased continuously for both clones.

This perceived increase can be attributed to a decrease in holocellulose. This behavior suggests that thermo-rectification caused the lignin and hemicellulose chains (smaller chains) to loosen, facilitating their degradation. This effect was corroborated by the determination of holocellulose.

Figure 8 - Behavior of the lignin content in the wood of clones L and H in relation to the heat treatments applied



With regard to the chemical properties analyzed, there was no interference from the clone factor. This can be seen from the similarity of the curves generated for each of the treatments carried out and the statistical tests carried out during the study, all with a significance level of 5%. These results indicate that, for both hybrids, heat treatment acted in a similar way in terms of the chemical composition of the wood.

This uniformity in chemical responses suggests that clones L and H showed comparable chemical behavior under different heat treatment conditions, which is relevant information for practical considerations in future applications of these heat-treated materials.

This consistency between the clones could also simplify future practical applications, as it indicates that the genetic variations between these clones may not have a significant impact on the chemical changes induced by thermo-rectification.

FINAL CONSIDERATIONS

This work has provided valuable *insights*, including:

Temperatures suitable for heat treatment**:** the most suitable treatments for heat treatment in both clones were those carried out up to 180 °C. This is based on the fact that the coloration is little changed compared to natural wood, and the likely lower energy consumption compared to treatments at higher temperatures.

Physical properties: it was not possible to obtain conclusive results for the physical properties due to collapses and cracks in the pieces. These defects may have occurred because these clones were not intended for splitting in sawmills, but for pulp production. When aggressive treatment was applied to the wood, it reacted by forming these defects.

Chemical properties: heat treatment at higher temperatures (200 and 220°C) degraded most of the wood's chemical constituents in both clones. This result raises concerns about the possible reduction in the wood's mechanical resistance if used for structural purposes.

These considerations highlight the importance of considering not only aesthetic changes, but also the impact on physical and chemical properties when applying heat treatments to wood. The balance between achieving the desired effects and maintaining essential properties is crucial when using heat treatment as a wood modification technique.

REFERENCES

Brazilian Association of Technical Standards (ABNT). (1997). Actions on structures, properties of wood and design of serviceability limit states - NBR 7190: 1997. ABNT. Rio de Janeiro.

Bhuiyan, T. R., Hirai, N., & Sobue, N. (2001). Effect of intermittent heat treatment on crystallinity in wood cellulose. Journal of Wood Science, 47(5), 336-341.

Borges, L. M., & Quirino, W. F. (2004). Hygroscopicity of heat-treated Pinus caribaea var. hondurensis wood. Revista Biomassa & Energia, 1(2), 173-182.

Brito, J. O., Garcia, J. N., & Bortoletto Júnior, G. (2006). Basic density and shrinkage of Eucalyptus grandis wood subjected to different thermorectification temperatures. Revista Cerne, 12(2), 182-188.

Calonego, F. W., Severo, E. T. D., & Latorraca, J. V. F. (2014). Effect of thermal modification on the physical properties of juvenile and mature woods of Eucalyptus grandis. Floresta e Ambiente, 21, 108-113.

Ferreira, B. S., Campos, C. I., & Rangel, E. C. (2018). Effect of heat treatment on the gluing quality of wood veneers for plywood production. Ciência Florestal (Online), 28, 274-282.

Fontoura, M. R., et al. (2015). Mechanical and chemical properties of thermally treated Hovenia dulcis Thunberg wood. Ciência da Madeira (Braz. J. Wood Science), 6(3), 166-175.

Food and Agriculture Organization (FAO). (2018). Global Forest Products. http://www.fao.org/3/ca7415en/ca7415en.pdf

Brazilian Tree Industry (IBÁ). (2016). Annual Report. http://www.iba.org/images/shared/Biblioteca/IBA_RelatorioAnual2016_pdf

Majano-Majano, A., Hughes, M., & Cabo, J. L. F. (2012). The fracture toughness and properties of thermally modified beech and ash at different moisture contents. Wood Science and Technology, 46(1), 5-21.

Modes, K. S., Santini, E. J., Vivian, M. A., & Haselein, C. R. (2017). Effect of heat treatment on the mechanical properties of Pinus taeda and Eucalyptus grandis wood. Ciência Florestal, 27, 291-302.

Moura, L. F. de, Brito, J. O., & Bortoletto Jr, G. (2012). Effects of heat treatment on mass loss and mechanical properties of Eucalyptus grandis and Pinus caribaea var. hondurensis. Floresta, 42(2), 305-314.

Pereira, B. L. C., et al. (2013). Study of the thermal degradation of Eucalyptus wood using thermogravimetry and calorimetry. Revista Árvore, 37(3), 567-576.

Pessoa, A. M. C., Filho, E. B., & Brito, J. O. (2006). Evaluation of thermally treated Eucalyptus grandis wood submitted to attack by the drywood termite Cryptotermes brevis. Scientia Forestalis, 1(72), 11-16.

Rousset, P., Perré, P., & Girard, P. (2004). Modification of mass transfer properties in poplar wood (P. robusta) by thermal treatment at high temperature. Holz als Roh- und Werkstoff, 62(2), 113-119.

Technical Association of the Pulp and Paper Industry (TAPPI). (1999). Test methods (compact disc): 1998-1999. TAPPI (CD-ROM). Atlanta.

Windeisen, E., Strobel, C., & Wegener, C. (2007). Chemical changes during the production of thermo-treated beech wood. Wood Science and Technology, 41(6), 523-536.