

FIRE PERFORMANCE OF *Pinus taeda* WOOD TREATED WITH ZINC BORATE BEFORE AND AFTER LEACHING

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ABSTRACT

Owing to its physico-mechanical properties, wood is widely used in housing for both outdoor structures and indoors in floors, ceilings and others. However, its vulnerability to fire makes protection necessary for occupant safety and damage prevention. In this study, the fire performance of *Pinus taeda* (loblolly pine) wood from northeastern Uruguay treated with zinc borate synthesized in our laboratory is tested. The effect of leaching on zinc borate fire retardant properties was also evaluated. The following parameters associated with the thermal degradation process of wood were analyzed: flame spread, carbonized area, carbonization index and mass loss. The wood was radially and tangentially exposed to the flame in a Vandersall tunnel under controlled conditions for three exposure times: 30, 60, and 80 seconds. The micromorphology of the surfaces exposed to the flame at each exposure time was analyzed with a scanning electron microscope in order to evaluate fiber damage, zinc borate distribution within the wood, and the effects of leaching on fire performance. A clear improvement in the fire resistance of the zinc borate -treated wood could be verified for all exposure times; leaching did not affect its fire retardant properties despite the harsh conditions of the test, making the product potentially suitable for outdoor use.

Keywords: Fire retardant, leaching effect, *Pinus taeda*, scanning electron microscope, Vandersall tunnel, thermal degradation, physical wood properties.

INTRODUCTION

As the industry increasingly gravitates toward the use of sustainable materials, wood makes for a desirable alternative in construction; it is suitable for structural use, as well as in floors, ceilings, and outdoors. Its mechanical and physical properties are therefore of utmost importance; it must have high bending strength and adequate elasticity (Ballarin and Palma 2003, Moya *et al.* 2013, Senalik and Farber 2021, Walley and Rogers 2022), adequate thermal expansion, diffusivity, electrical conductivity (Skaar 1988, Mohammed *et al.* 2017, Goli *et al.* 2019), and capacity to transfer heat.

However, its main disadvantages are its hygroscopicity (Almeida *et al.* 2018) and its high degree of flammability. Fire performance depends on the thermophysical properties (specific heat, conductivity, diffusivity, and thermal inertia) and on how the heat is transferred to the underlying layers (Aseeva *et al.* 2014).

The thermal degradation of wood is a complex thermochemical process that involves many simultaneous reactions, and depends on the chemical composition of the wood (Poletto *et al.* 2012). Its polymeric components degrade at different temperatures: cellulose between 270 °C to 350 °C; hemicellulose between 180 °C and 300 °C and lignin between 250 °C and 500 °C. Due to its cross-linked structure and its high molecular weight, lignin has high thermal stability, making it the component that contributes the most to coal formation

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(Ali *et al.* 2019, Lowden and Hull 2013).

The burning process occurs in a series of stages, progressing as the temperature increases. The first stage pyrolysis begins as the wood heats up, generating volatile gases, coal and tar (liquid residue), which then, in the presence of an ignition source, react with oxygen combustion releasing carbon monoxide, carbon dioxide and water. This exothermic reaction keeps pyrolysis going and generates more volatiles, and continues until the wood is fully converted to coal and no volatiles remain (Ali *et al.* 2019, Lowden and Hull 2013, Mensah *et al.* 2023).

Fire retardant treatments applied either by deep impregnation or superficially manage to reduce the degree of flammability of the wood (Vakhitova 2019). These treatments hinder or inhibit some of the stages of the burning process through different mechanisms, which can be either physical (cooling, formation of a coating, dilution) or chemical (reactions in the gas or solid phases). Fire retardants are commonly based on ammonium phosphates, carbonates, resins, organic compounds and borates (Vakhitova 2019, Jiang *et al.* 2010).

Borate-based compounds have great potential. They are effective fungicides, bactericides and insecticides (Hosseini Hashemi *et al.* 2010, Mohareb *et al.* 2010, Lloyd *et al.* 2020), while being less toxic than most commercial products (Bolt *et al.* 2017, Uluisik *et al.* 2018, Bolt *et al.* 2020). As flame retardants, boron compounds intervene in the gas and condensation phases of thermal degradation (Garba 1999).

However, boron species are leachable, and have high solubility and ion mobility in aqueous solvents, making it difficult to retain them inside the wood (Caldeira 2010). Vakhitova (2019) showed that boric acid or borax treated wood when subjected to certain humidity conditions for over a year is no longer fire resistant. Many strategies have been tested to reduce leaching, such as combining borate-based compounds with metallic species by forming different precipitates (Obanda *et al.* 2008).

Among borate-based compounds, zinc borate (ZnB) is applied to wood composite and particleboard, as well as to other materials such as PVC (Polyvinyl chloride) for fire protection (Stark *et al.* 2010, Fang *et al.* 2013). However, in the case of solid wood, ZnB is valued as a fungicide rather than a fire protector. Commercial ZnB products usually nanometric-sized are impregnated by the Bethell method or by double vacuum (Tascioglu *et al.* 2014, Mantanis *et al.* 2014, Lykidis *et al.* 2016).

As stated by Yang *et al.* (1999) ZnB works as a fire retardant in three different ways. When endothermically dehydrated, it vaporizes hydration water, absorbing heat and diluting the oxygen and flammable gas mixture. At a high enough temperature, it can melt and form an insulating glassy layer over the flammable surface. ZnB also changes the decomposition path of some flammable substances, preventing the formation of flammable gases.

In this work, ZnB synthesized in our laboratory was applied in depth to solid wood and tested as a fire protector loblolly pine (*Pinus taeda*). The impact leaching had on its effectiveness was evaluated. Morphology studies were carried out throughout.

MATERIALS AND METHODS

Wood samples and impregnation

A total of 290 sapwood samples from a 24-year-old loblolly pine (*Pinus taeda* L.) of dimensions $(25 \times 9 \times 1) \pm 0,02 \text{ cm}^3$ were used. Half the samples were cut radially and the other half tangentially in order to expose both anatomical planes of the wood to the flame (Figure 1). After oven drying at 103 °C for 24 hours, the samples were weighed and then conditioned at 22 °C and 65 % RH for 15 days in a humidity chamber.

A 5 % (w/v) ZnB suspension was synthesized in our laboratory from boric acid and zinc oxide in an ammonia medium, with a molar ratio of 4:1, B: Zn (Camargo and Ibañez 2018). 115 samples of each plane (230 in total) were impregnated with the suspension according to a modified EN-113-1 (2020) standard. The remaining 60 samples, 30 of each plane, were left untreated and used as control. The method used was a double vacuum (0,5 h initial vacuum at 20,6 bar, 0,5 h second vacuum at 20,6 bar 0,5 h immersed in the suspension) in a laboratory reactor.

Samples were weighed again after treatment to determine net solid retention Equation 1.

$$R\left(\frac{\text{kg}}{\text{m}^3}\right) = (w_2 - w_1)\left(\frac{C}{v}\right) \quad (1)$$

Where: R is ZnB retention (kg/m^3); w_1 : initial anhydrous mass (kg); w_2 treated mass (kg); C: ZnB concentration (%); v: sample volume (m^3).

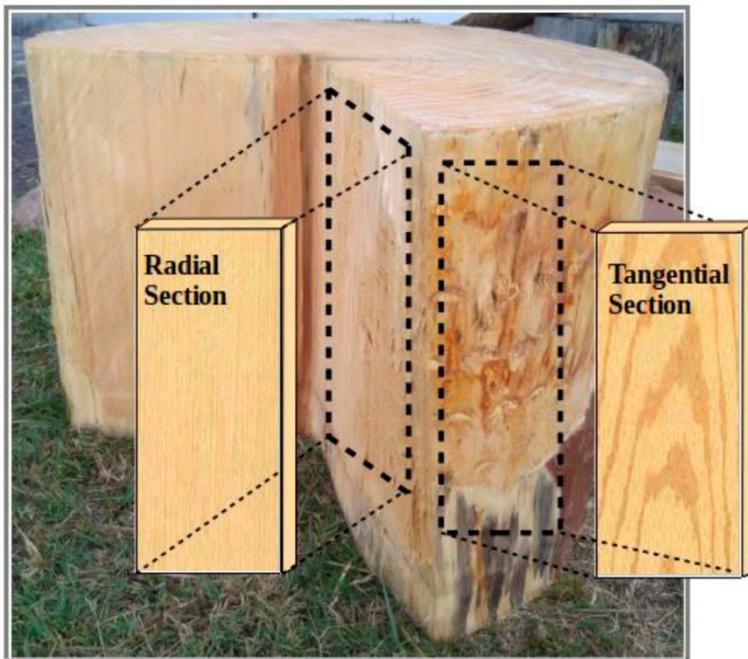


Figure 1: Diagram of tangentially and radially oriented samples.

A total of 130 samples (65 of each plane) with retention values that did not differ by more than 15 % from the mean were chosen for the subsequent tests.

Digestion method

5 of the chosen samples of each plane (a total of 10) were milled in a Marconi mill (Sao Paulo, Brasil) and sieved through a N° 30 mesh (Hu and Qi 2010). Sample digestion was carried out according to Ramanathan and Ting (2015) and the adapted AWP A07-04 standard (2005). 0,25 g of loblolly pine (*Pinus taeda* L.) milled were digested with 20 ml of concentrated HCl + HNO₃ (1:1) at 80 °C for 120 minutes; HNO₃ (69 % w/w), and HCl (37 % w/w), were both purchased from Merck Pte., Ltd. The mixture was allowed to rest for 20 minutes at room temperature and filtered through a 0,45 mm sieve. Distilled water was added, until reaching 100 ml. The solution was set aside for boron quantification (2.4).

Leaching

The leaching tests were based on a modified UNE EN 84 (2020) standard. 30 of the previously selected samples of each plane orientation (a total of 60) were immersed in distilled water in a 1: 6 (wood sample: water) volume ratio without stirring, at a controlled temperature of 20°C. Through the 14-day test, the leaching water was changed for fresh distilled water nine times: first at 24 hours, and then in 24-72 hour intervals. Boron concentration on the resulting nine leaching waters was measured (see 2.4) (Donmez Cavdar *et al.* 2015).

Quantification of boron in the digested samples and leaching water by potentiometric titration

Boron was quantified through the formation of an acidifying complex between mannitol and boric acid or borates present in the sample or the leaching water (Dawson *et al.* 1990). The solution and the leaching water were titrated with a diluted alkaline solution of NaOH. The amount of boron was calculated as the equivalent amount of NaOH required to reach the original pH (Wilson 1958).

Study of fire performance: Flame spread, carbonization area, carbonization index and mass loss

Vandersall tunnel

A Vandersall tunnel, shown in Figure 2, was built for the fire exposure tests (Leon and Carmona 2008).

The samples are placed in the chamber at a 45 ° angle to the horizontal. The lower end of one of their faces is exposed to a blue stabilized flame from a Bunsen burner of 1 cm in diameter, premixed mode, using butane-propane (30 - 70 % v/v); the visible portion of the flame is 5 cm. The gas flow is regulable so that the inner cone of the flame stays in a fixed position, keeping the gas combustion rate and the temperature of the flame constant (Mazela *et al.* 2014, Hilado 1967).

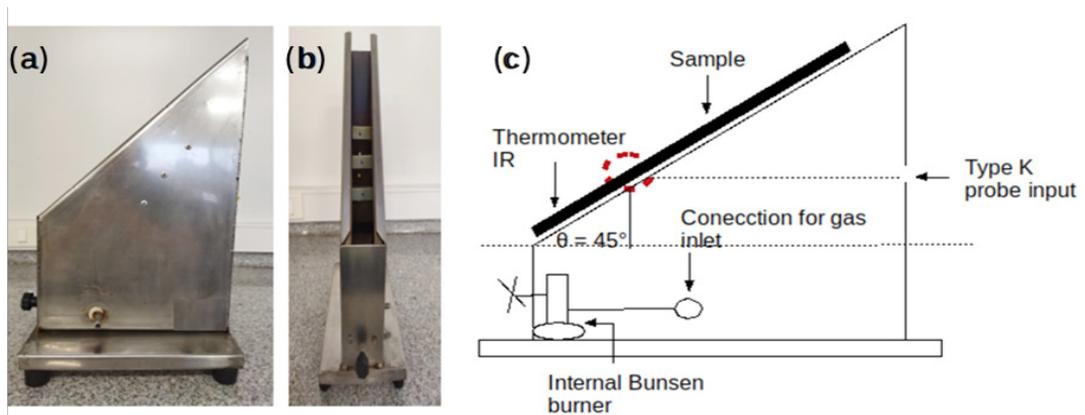


Figure 2: Diagram and photo of the Vandersall tunnel. (a) front view; (b) side view; (c) scheme.

Setup

For the setup of the Vandersall tunnel, 30 wood samples identical in size to those later used in the test were exposed to the flame. The position of the flame was set so that the sample would be 2 cm away. The exposure times for the study were determined ($t_1 = 30$ sec, $t_2 = 60$ sec, and $t_3 = 80$ sec) so that carbonized areas were reproducible and did not reach the upper edge of the sample.

The temperature of the wood inside the Vandersall tunnel was measured at two points (Figure 2): 1) on the external surface (opposite to the one exposed to the flame) 1 cm away from the edge, using a HI 99550-00 infrared thermometer (Hanna Inst. Mexico City, Mx) (range -10 / 300 °C); 2) on the internal surface (exposed to flame) 10 cm away from the flame-wood interface, with a HI 935005 thermometer (Hanna Inst. Mexico City, Mexico) for thermocouple type K (range were used. -50 / 1350 °C).

Fire performance test

The procedure was repeated with the test samples; 30 control samples, 60 treated samples (30 per plane) and 60 treated and leached samples (30 per plane) were exposed to the flame. After each exposure time, samples were removed from the tunnel and the following parameters were determined:

1. Flame spread (F_s) - progress of carbonization per unit of time ($\text{cm}\cdot\text{s}^{-1}$)
2. Carbonization area (C_a) on the internal surface (cm^2)

3. Mass loss (M_i)- the difference in anhydrous mass (g) before and after exposure
4. Carbonization index (C_i) - carbonized to non-carbonized volume ratio, Equation 2.

$$C_i(\%) = \frac{(L_{max} a_{max} e_{max})}{V_i} \quad (2)$$

Where:

L_{max} carbonization length

a_{max} carbonization width

e_{max} carbonization thickness

V_i total anhydrous volume of each sample before exposure to the flame

The area, length, width and thickness of carbonization were measured using Fiji image analysis and processing software (Schneider *et al.* 2012). The software receives optical images as input and through a color segmentation complement identifies the charred area allowing it to be measured (Camargo and Ibáñez 2018, García Enríquez *et al.* 2009). The optical images were taken with a Nikon D5600 24 megapixel camera, placed 20 cm away from the samples.

60 samples treated with a commercial fire retardant (RC) of known effectiveness were used as positive control. RC is composed of ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), urea CH_4N_2O , sodium octaborate $Na_2B_8O_{13} \cdot 4H_2O$, 96% ethyl alcohol and benzalkonium chloride. Following the manufacturer's instructions the product was applied with a brush in three stages, leaving the sample to dry for 24 hours between each application.

Once dry, the samples were subjected to the same procedures as the samples treated with ZnB (except for the leaching) and then exposed to the flame for a single exposure time of 80 seconds. No in-depth fire protection products were found in the market.

Microscopic analysis by scanning electron microscopy (SEM)

The morphological characterization of the carbonized wood was performed with a JCM 6000 Plus scanning electron microscopy (JEOL Ltd, Tokyo., JP) under high vacuum conditions operating at 10 kV in SED mode (Secondary Electron Detector).

Statistical analysis

A one-way analysis of the variance model (ANOVA, oneway) was run on the results. Means were compared with the Tukey test at a confidence level of $\alpha = 0,05$ using Statistical Analysis Software (SAS 2014).

RESULTS AND DISCUSSION

Sample impregnation and boron quantification

Table 1 shows anhydrous density, mean retention values, boron content in treated samples before leaching and boron content in the leaching water. Retention values were as expected, though higher than those reported by Terzi *et al.* (2009), who impregnated wood with a 2 % ZnB solution, and higher than the average retention values for protection against biotic agents. This would make the treatment more costly.

Samples cut in the tangential plane showed higher boron retention but also higher leaching than samples

cut in the radial plane. Among other factors, wood density and porosity index influence retention. Since density did not differ significantly between planes, the difference in retention values could be explained by the fact that radial permeability (observed in the tangential plane) is greater than tangential permeability (radial plane) (Milota *et al.* 1995, Hansman *et al.* 2002).

According to Siau (1984), the rays of the tangential plane are more effective in promoting flow in the radial direction than the abundance of pits of the radial plane are in promoting tangential flow; in short, the rays promote the penetration and distribution of ZnB inside the wood.

Leached boron does not exceed 1 % of the initial boron in the wood, hence it is expected that leaching will have almost no effect on fire retardant properties.

Compared to rose gum (*Eucalyptus grandis*) treated with the same product, loblolly pine (*Pinus taeda*) retains more boron and is less susceptible to leaching (Camargo and Ibañez 2018). This could be explained by the difference in permeability between conifers and hardwoods. This was attributed to a greater complexity in hardwoods anatomical structure that interferes with the diffusion transport mechanism, and to the misalignment of the longitudinal cells in rose gum (*Eucalyptus grandis*) due to the presence of vessels.

Table 1: Density, retention and boron concentration values of loblolly pine (*Pinus taeda*) samples in the tangential and radial planes.

Plane	Tangential	Radial
Density (kg/m ³)	456,6 ± 10,1	445,1 ± 5,2
Retention (kg/m ³)	33,4 ± 0,60	20,6 ± 0,4
Initial Boron (kg/m ³)	18,76 ± 0,17	9,71 ± 0,14
Leached boron (kg/m ³)	0,0064 ± 0,0001	0,0043 ± 0,0001

Initial boron: boron retained in the sample as determined after digestion.

Leached boron: boron in leaching water

Fire performance

Temperature

Table 2 shows the average temperatures of the external and internal faces of the samples at each of the three exposure times. Measuring both faces suggests how the heat flows through the wood. Temperatures of the samples treated with ZnB were lower than those of the untreated samples. It is likely that ZnB dehydrates generating water steam, which cools down the flame and hinders heat transfer.

According to Garba (1999), the lower temperatures could also be attributed to boron residues reacting with cellulose hydroxyl groups, which generates water and forms inorganic coal which as an insulating material, slows down polymer degradation.

Table 2: Average temperature of loblolly pine (*Pinus taeda*) samples treated with ZnB and control samples during flame exposure tests.

Plane Treatment	Tangential		Radial	
	no ZnB	ZnB	no ZnB	ZnB
	30 s of exposure to the flame			
External Temp (°C)	29,17 a	25,33 b	26,50 a	25 b
Internal Temp (°C)	94,16 a	70,40 b	110,75 a	104 b
	60 s of exposure to the flame			
External Temp (°C)	48,66 a	34 b	41,22 a	34,50 b
Internal Temp (°C)	184,30 a	83,90 b	183,90 a	174,30 a
	80 s of exposure to the flame			
External Temp (°C)	65,75 a	41,25 b	57,66 a	43b
Internal Temp (°C)	213 a	89 b	181 a	127,40 b

The same letters indicated that there was no statistical difference among temperatures for $\alpha=0,05$.

Flame spread, carbonization area

Figure 3 shows a diagram of flame spread versus carbonization area. The points that make up the curves correspond to the three exposure times (30, 60 and 80 seconds).

As defined by Diemberger and Hasburgh (2016) flame spread is the sliding movement of the flame away from the ignition point over the surface of the wood. Flame spread rate depends on the response of the wood to the distribution of heat flow until the surface reaches volatilization temperature. As wood is exposed to the flame, it forms a layer of coal that provides thermal insulation, slowing down thermal degradation.

Carbonization is the transformation of the surface and ultrastructure of wood in response to temperature (Ali *et al.* 2019). It can be measured through carbonization area (Ca)(cm²) and carbonization index (Ci)(%).

Flame spread slows down as exposure time and carbonization area increase (Figure 3). Samples treated with ZnB perform better than untreated samples at a significance level of 0,05, regardless of anatomical plane or exposure time, showing ZnB decreases flame spread. With the exception of the tangential plane at 30 s, the Ca of untreated samples was larger than the Ca of treated samples ($\alpha = 0,05$).

Despite having a higher melting point than commonly used borates (Popescu and Pfriem 2020), ZnB is able to reduce superficial combustion by insulating the surface of the wood. In the case of untreated samples, there were no significant differences in Ca between the radial and tangential planes either (for $\alpha = 0,05$). Leaching did not result in any significant difference in Ca for $\alpha = 0,05$.

When comparing flame spread on loblolly pine (*Pinus taeda*) to rose gum (*Eucalyptus grandis*) under identical conditions, no clear trend can be observed, regardless of plane or exposure time (Camargo and Ibáñez 2018). It was expected that flame spread would be faster on porous softwood (Garba 1999) since the difference in anatomy and density between species affects the pyrolysis/combustion ratio and therefore flame spread.

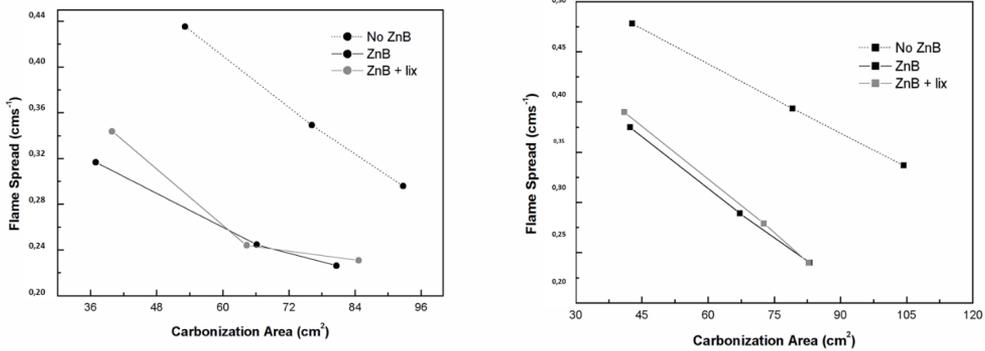


Figure 3: Diagrams of flame spread versus carbonization area, for untreated, ZnB treated and ZnB treated and leached wood, for (a) tangential and (b) radial planes.

Carbonization index and mass loss

Figure 4 shows a diagram of carbonization index versus mass loss. The points that make up the curves correspond to the three exposure times (30, 60 and 80 seconds).

C_i (Figure 4) follows the same trend as C_a . There were no significant differences between the leached and non-leached samples, regardless of plane or exposure time. This indicates that leaching did not affect the fire-retardant properties of ZnB.

It could also be observed that for the same exposure time, mass losses were higher for treated wood than for untreated wood, despite presenting a lower carbonization index. rose gum (*Eucalyptus grandis* W. Hill ex Maiden) wood tested in identical conditions had a similar behavior to that of loblolly pine (*Pinus taeda*) (Camargo and Ibañez 2018). loblolly pine (*Pinus taeda*) presented higher C_i in the tangential plane at 60 and 80 s, and lower in the radial plane at all exposure times.

Carbonization is affected by different factors such as the density of wood, thermal properties (affected by anatomy), permeability and chemical composition (Dietenberger and Hasburgh 2016), which explains loblolly pine (*Pinus taeda*) tendency to present smaller carbonized areas.

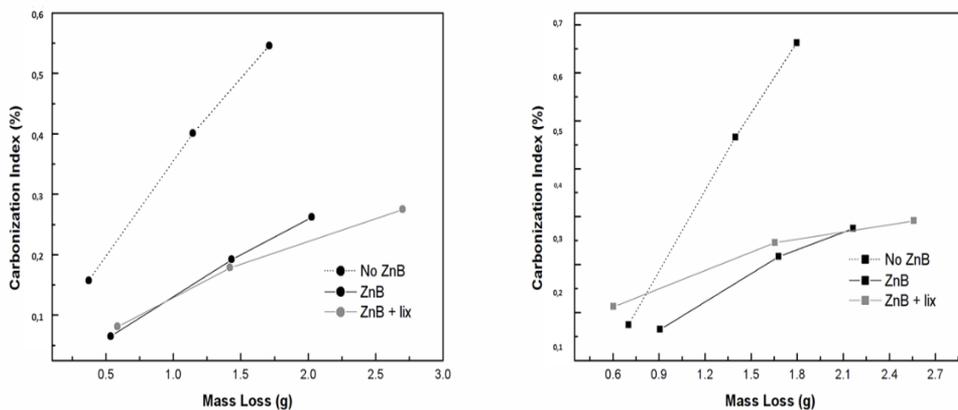


Figure 4: Diagrams of carbonization index versus mass loss, for untreated, ZnB treated and ZnB treated and leached wood, for (a) tangential and (b) radial planes.

In Table 3 the results of the RC are compared to those of ZnB. The treatments show similar behavior, with the exception of mass loss for which RC yields better results.

Table 3: Comparison between RC and ZnB applied to loblolly pine (*Pinus taeda*) samples through the following parameters: flame spread, carbonized area, carbonization index and mass loss.

Parameters	Section	
	Tangential	Radial
Flame spread (cms ⁻¹)	0,2401b (ZnB) / 0,2846c (RC)	0,2264b (ZnB)/ 0,2757a (RC)
Carbonized area (cm ²)	82,99b (ZnB)/ 89,75b (RC)	80,62b (ZnB)/ 84,32b (RC)
Carbonization index (IC %)	0,2759b (ZnB)/ 0,6091a (RC)	0,2625b (ZnB)/ 0,5135a (RC)
Mass loss (g)	2,165a (ZnB)/1,339c (RC)	2,025a (ZnB) /1,525c (RC)

SEM analysis

SEM analysis is used to study the micromorphology, surface topology and ultrastructure surface of the wood (Ali *et al.* 2019).

Figure 5 shows SEM images of the tangential and radial planes of samples exposed to the flame for 80 s. The initial state of the wood (without any treatment) is shown in row 1. In the tangential plane, the fibers initially are parallel to each other and homogeneously distributed (Figure 5 a1); after exposure to fire, the wood cracks and the fibers lose their structure, changing their distribution along the surface and leaving spaces through which the flame spreads further and oxygen enters (Figure 5 a2).

In the radial plane the same changes are observed, as hollow spaces give the surface a striped pattern (Figure 5 b2). However, the deformation of the fibers is not so noticeable.

Wood anisotropy explains why the effects of fire damage differ depending on whether the flame faces the tangential or radial surface. For the tangential plane, volatilized gases, oxygen and even the flame itself tend to move more easily in the radial direction, the same way that gases would diffuse inside the wood (Milota *et al.* 1995).

Rose gum (*Eucalyptus grandis*) wood was observed to behave similarly: thermal degradation makes the fibers expand and holes appear on the surface (Branca and Di Blasi 2007).

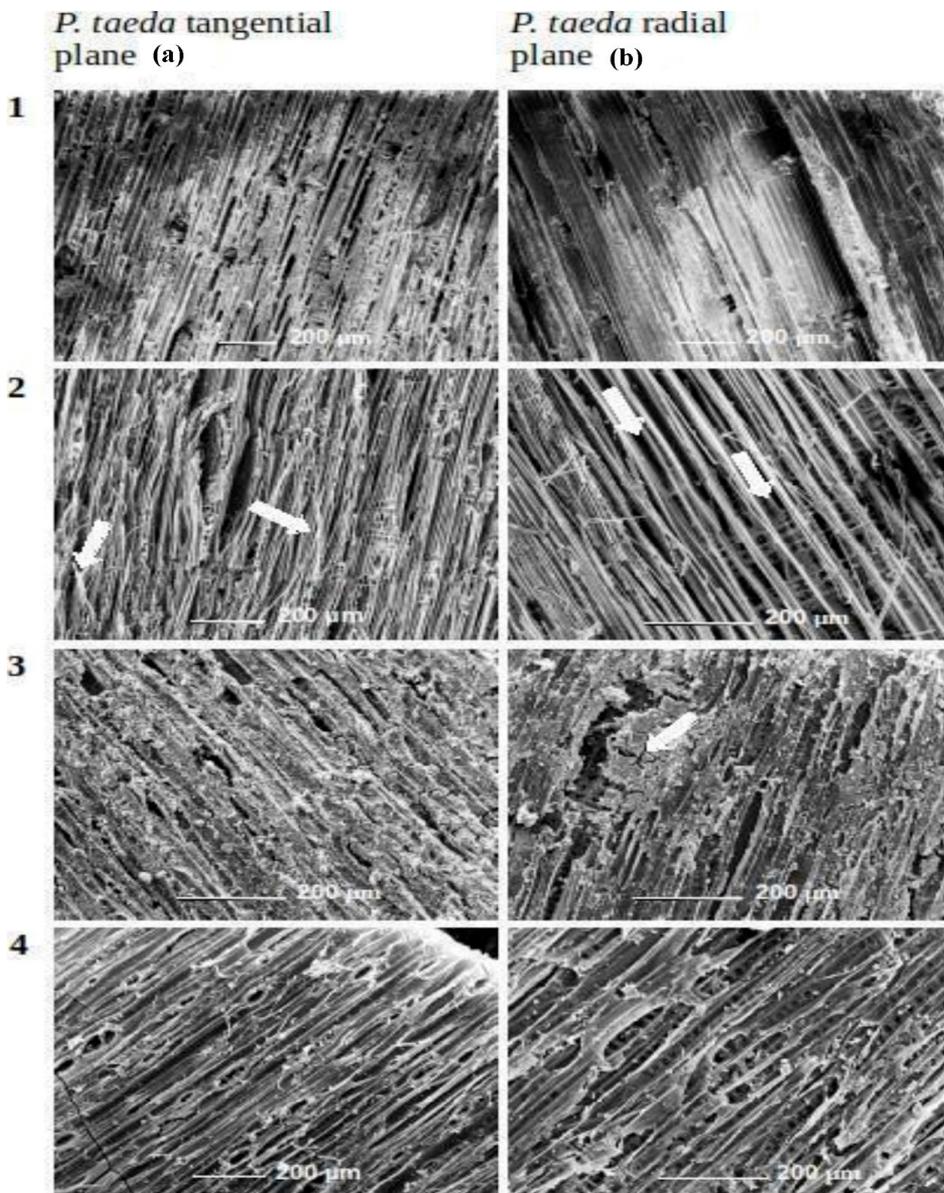


Figure 5: SEM Image of loblolly pine (*Pinus taeda*): Column (a) tangential plane. Column (b) radial plane. Row 1: no treatment, no exposure to fire; Row 2: no treatment, 80s of exposure to fire; Row 3: treated, 80s of exposure to fire; Row 4: treated, leached, 80s of exposure to fire.

The surface of ZnB treated loblolly pine (*Pinus taeda*) after fire exposure does not indicate structural damage; the fibers are still like they were before fire exposure (Figure 5 row 3 and 1). It can be observed that the internal surfaces of wood are completely covered by a dense ZnB coating of rough texture (Figure 5 row 3), which would indicate that ZnB is able to act as a barrier between wood and the flame, retarding flame spread and carbonization by blocking heat transfer and oxygen diffusion to the underlying layers (Jiang *et al.* 2010).

The leached samples do not present any more structural damage than the non-leached samples; the fibers preserve their structure and orientation without exception. The ZnB coating on the surface of leached samples is slightly thinner than that of the non-leached samples. This thinning is associated with solvation and dissolution; these reactions occur when ZnB interacts with water molecules during leaching, as diffusion moves the water into the sample. Some of the ZnB solubilizes and becomes part of the aqueous phase of the leaching system.

However, the links between the ZnB that remains solid and wood components seem to be more stable than those formed between the solubilized ZnB and water. This explains why ZnB is still an effective fire retardant even after leaching.

Ramos *et al* (2006) identified adsorption as the preferential mechanism by which borates and the components of the cell wall of the wood link together. Since it is physical rather than chemical adsorption, it leaches easily. However, as stated before, leaching does not cause significant ZnB loss, and it does not have any significant negative effect on fire resistance properties.

The results are a promising starting point for ZnB treated wood use in class 2 or even class 3 applications, in which the humidity would not affect the fire-retardant properties of the product. It must be researched further given the limitations of these results. For example, the samples burned in the Vandersall tunnel are 25 cm long and are placed in a specific thermic environment; using longer samples would shed light into the incidence of the heat flux along the wood piece, particularly regarding flame spread. Given ZnB treated wood is to be used in construction, a parameter that must be addressed is smoke and its characteristics.

CONCLUSIONS

Measurement of fire performance parameters showed ZnB synthesized in our laboratory can be used as a fire retardant on solid wood, slowing down flame spread and reducing mass loss and carbonization index. ZnB treated wood preserved its fiber structure after fire exposure in all exposure times, had an improved resistance to fire, and behaved similarly to the commercial retardant used as positive control. The rigorous leaching conditions did not negatively affect the fire retardant properties of ZnB.

AUTHORSHIP CONTRIBUTIONS

AC: Data curation, formal analysis, methodology, software, validation, visualization, writing - original draft. MI: Conceptualization, data curation, funding acquisition, methodology, validation, visualization, writing - review & editing.

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