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Effect of Citric Acid on the Properties of Sapwood of *Pinus sylvestris* Submitted to Thermomechanical Treatment

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Abstract: The present study aimed to evaluate the effect of citric acid on the properties of solid pine wood, which were submitted to thermomechanical treatment. A preliminary test was performed in a previous study to evaluate the influence of different temperatures of pressing and concentrations of citric acid on the physical properties of wood. After choosing the best treatments (170 °C and 5% and 10% of citric acid), the effect of these on the chemical properties (SEM, FTIR and pH); on the density profile using an X-ray microtomography and on the resistance to aging through an abrasion test were evaluated. The result of the chemical analysis showed an increase of the presence of ester functional groups, as well as better coverage and higher acidity of the surface. The density profile technique allowed us to observe the formation of peaks of density on the surface where the acid was applied. Lastly, it was also possible to verify an increase in the resistance to abrasions because of the application of citric acid.

Keywords: citric acid; thermomechanical modification; dimensional stability; solid timber

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1. Introduction

Citric acid ($C_6H_8O_7$) is an organic acid present in citric fruits (oranges and lemons), which can be found in an anhydrous form as a white, odorless crystalline powder [1].

According to [2], it is a substance that is already widely used in the food and pharmaceutical sectors. In wood, it has been applied as a crosslinking agent [3], as an adhesive in the manufacture of panels [4] and to improve the dimensional stability of wood composites [5].

In general, the main changes caused in wood by citric acid are attributed to the esterification reactions caused between the carboxyl groups (-COOH) of the acid and the hydroxyl groups (-OH) present in the wood structure [6]. However, studies focusing on the effect of this substance on the properties of wood are still very incipient.

On the other hand, wood modification has already been evaluated by many studies using the technique of Fourier-transform infrared spectroscopy (FTIR), with a focus on the identification of esterification reactions through the evaluation of the peaks of bands 1720–1750 cm^{-1} and 1200–1300 cm^{-1} [7,8], through the technique of scanning electron microscopy, which allows to evaluate the changes provoked on the surface of the material through the analysis of micrographs [9,10], and through the technique of pH, which allows to evaluate alterations to the hydrogen ionic activity in wood [11].

Another technique that has been widely applied in many studies to evaluate changes to wood in a nondestructive manner is X-ray densitometry [12,13], which allows to obtain a density profile in a rapid and automatized way to verify how the distribution of the substance applied occurs inside of the material.

Lastly, ref. [14] verified mixed results for the effect of thermal treatments for the resistance to abrasion, with an increase of the resistance in the radial plane and a reduction in the tangential plane.

In this context, the present study aimed to evaluate the effect of the application of citric acid on densified boards of *Pinus sylvestris*, which were measured through the evaluation of the chemical properties (SEM, FTIR and pH); the density profile and the resistance to abrasion.

2. Materials and Methods

2.1. Wood Samples

Timbers of sapwood of *Pinus sylvestris* with dimensions of 380 by 15 by 2.8 cm (length × width × thickness) and 0.57 g/cm^3 of dry density were obtained at the carpentry of the Faculty of Forest Sciences and Forest Ecology of the Georg August Universität Göttingen.

The timbers were sawn into sixteen boards of 15 by 45 by 2.5 cm, conditioned in a climatization room (20 °C; 65%) to achieve a constant weight. Figure 1 presents the cutting scheme of the samples and the test blocks for the technological characterization.

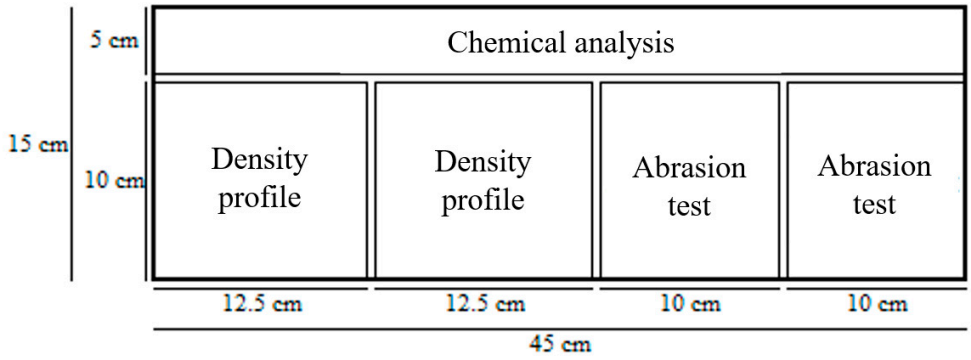

Figure 1. Cutting scheme of the samples of timber of *Pinus sylvestris* for the technological characterization.

2.2. Chemical Modification

The preparation of the solution (CA) was carried out by diluting CA in water at room temperature (+28 °C) in a 1:1 ratio, according to the methodology proposed by [4].

The application of CA was carried out using a paint roller to distribute the solution onto one of the surfaces and subsequent heating in an oven at 60 °C for 6 h, so that CA can react when adding functional chemical groups to the wood. The amount of CA applied was calculated by taking into account the mass surface volume of 450 by 150 mm (length × width) and 2.5 mm in depth. This resulted in average amounts of 0.0096 g/cm^2 and 0.0191 g/cm^2 for the concentrations of 5% and 10% of CA, respectively.

2.3. Thermomechanical Treatment

The application of the thermomechanical treatment on the samples of *Pinus sylvestris* was carried out in the carpentry of the Faculty of Forest Sciences and Forest Ecology, located in the Georg August Universität Göttingen, where it was possible to use a press with the following characteristics: pressing area of 60 by 60 cm; load capacity of 400 kN; electric resistance heating and a control panel for temperature, time and pressure adjustments. The maximum pressure applied was 50% of the estimated perpendicular compression strength of the wood: 2.6 MPa.

A steel platewith dimensions of 60 × 60 × 0.5 cm (length × width × thickness) was placed between the samples to isolate one of the surfaces of the material, allowing to apply the thermomechanical treatment on only one of the sides (Figure 2).

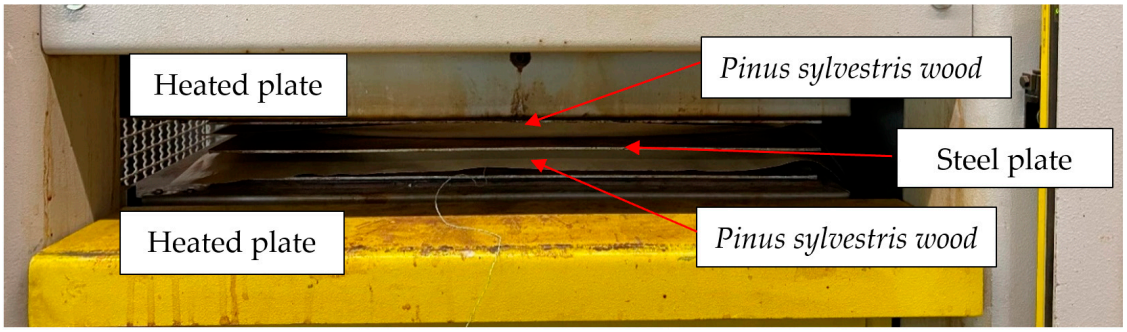

Figure 2. Application of the thermomechanical treatment on timber of *Pinus sylvestris*.

This way, the treatment (Figure 3) was divided into three steps:

I. Heating—initial temperature to treatment temperature (170 °C) and half of the full pressure (1.3 MPa);
II. Treatment—treatment temperature (170 °C) and full pressure (2.6 MPa) over a period of 10 min;
III. Posttreatment—treatment temperature (170 °C) and half-pressure release (1.30 MPa) over a period of 5 min and with all the pressure released over a period of 5 min.

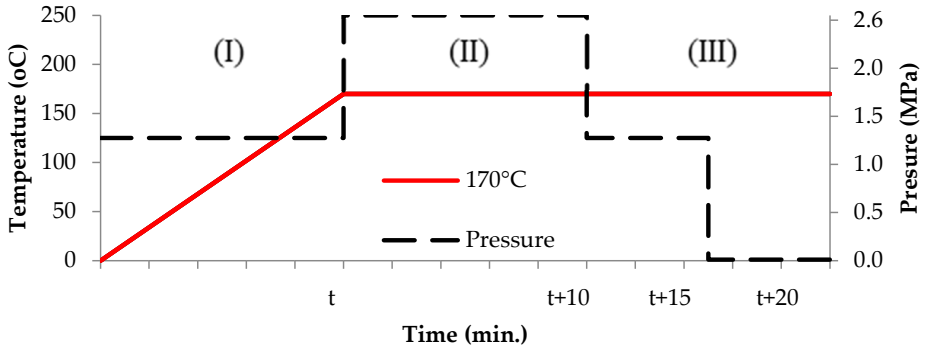

Figure 3. Schedule of the densification process.

The total time of the treatment was 29 min and 20 s.

2.4. Chemical Characterization

2.4.1. Fourier-Transform Infrared Spectroscopy

The spectroscopy test was performed using a BRUKER Alpha spectrophotometer and the mid-infrared range (MIR), which range covers waves from 4000 cm^{-1} to 300 cm^{-1} with a resolution of 1 cm^{-1}, with the aid of a diffuse reflectance accessory. To obtain the samples, it was necessary to obtain small veneers from the material, which were clamped in the spectrometer.

The measurements were carried out on 3 different points per sample for both the control and treated samples, generating spectra in the absorbance mode. This way, using OPUS 7.5 software, the spectra was generated with the average of ten measurements for each treatment. For comparison, the methodology proposed by [15] was used, which consists of the normalization of the average spectra in relation to a band height of 906 cm^{-1}, assigned by [16], to the wagging motion of the hydrogen atom on the C-1 position of the glucose ring in cellulose, which does not suffer alterations after heat application.

2.4.2. Scanning Electron Microscopy

The scanning electron microscopy test was realized using a PHENOMWORLD Phenom XL spectrometer, which allowed to obtain high-resolution images of all samples prior to and after applying the evaluated treatments. The images were obtained using a voltage

of 15 kV of tension, a scale of 200 µm and a magnification of 300×. For this, it was necessary to prepare 4 samples (1 × 1 × 1 cm^3) for each treatment, which were covered by a layer of gold and silver with vacuum impregnation, according to the methodology proposed by [17].

2.4.3. pH

The pH test was performed using an INOLAB 7110 pH meter, which allowed to verify changes to the acidity of the wood prior to and after applying the evaluated treatments. For this, it was necessary to prepare 3 samples (5 × 5 × width of the treatment in cm^3).

The pH was measured through the evaluation of the activity of the hydrogen ion, which was measured by placing an electrode on the surface of the sample, according to the following steps:

(I) Deposition of a drop of water over the wood surface;
(II) Placement of the electrode in the wet area;
(III) Measurement of the pH 2 min after the placement of the electrode to allow the stabilization of the parameter.

2.5. Density Profile

The density profile analysis was carried out through X-ray microcomputed tomography (XµCT) using a Grecon density profiler and the mid-infrared range (MIR), which range covers waves from 4000 cm^{-1} to 800 cm^{-1} with a resolution of 1 cm^{-1}, with the aid of a diffuse reflectance accessory.

For this, it was necessary to prepare samples (50 × 50 × width of the treatment in mm^3), which were inserted into the machine in a way that the X-ray ran longitudinally through the sample, and the density profile was obtained in the radial direction. The density profile was obtained using a resolution of 0.05 mm and a voltage of 33 kV.

2.6. Abrasion Test

The resistance to abrasion test was performed in accordance with [18] using a Taber Abraser. For this, 5 test blocks of 10 by 10 cm (length × width) for each treatment were exposed to a load of 1000 g, velocity of 60 rotations per minute (rWL) and 1000 cycles.

The wear rate (WR) was calculated in accordance to Equation (1).

$$WR = [(Mi - Mf)/N] \times 100, \quad (1)$$

where WR = wear rate (%), Mi = initial mass (g), Mf = final mass (g) and N = number of cycles.

The abrasion rate (Δt) was calculated in accordance with Equation (2).

$$\Delta t = [(ti - tf)/ti] \times 100, \quad (2)$$

where Δt = abrasion rate (%), ti = initial thickness (mm) and tf = final thickness (mm).

2.7. Data Analysis

The data were evaluated using IBM SPSS 21 (Statistical Package for Social Sciences) software.

The effect of the amount of citric acid on the specific mass and other physical properties in the preliminary test were evaluated using analysis of variance (ANOVA), with a subsequent comparison of the means performed by Tukey's test at the $\alpha = 0.05$ level of significance.

The same criteria were adopted to evaluate the influence of citric acid on wood aging (abrasion test), on the chemical analysis through Fourier-transform infrared reflectance spectroscopy (FTIR) and in the density profile through X-ray microcomputed tomography (XµCT).

3. Results

3.1. Thermomechanical Treatment

Table 1 presents the specific mass of *Pinus sylvestris* before and after the application of the treatments and the average values of the compression rate (CR), densification rate (DR) and mass loss (ML).

Table 1. Densification variables of the treatments tested.

Treatment	Properties				
	DR (%)	CR (%)	ML (%)	Initial Specific Mass (g/cm^3)	Final Specific Mass (g/cm^3)
170 °C $CA_{0\%}$	20.08 a	23.35 a	7.97 b	0.59 a	0.71 a
170 °C $CA_{5\%}$	23.57 ab	25.03 a	7.36 ab	0.56 a	0.70 a
170 °C $CA_{10\%}$	29.17 b	26.98 a	7.18 a	0.58 a	0.74 b

DR: densification rate, CR: compression rate and ML: mass loss. Values followed by the same letter in the same column are not statistically different, according to Tukey's test.

The application of citric acid led to a significant improvement of the DR, with an increase between 17.43% (CA5%) and 45.29% (CA10%) when compared to the samples densified without citric acid.

On the other hand, the CR presented a tendency to increase due to the application of citric acid, with an improvement of 7.21% and 15.70% for the amounts of 5% and 10% of the substance, respectively.

The ML presented a significant difference for all treatments evaluated, with a tendency to reduce between 7.65% and 9.91% as a consequence of the application of citric acid.

Lastly, the specific mass presented a significant difference for the samples treated with $CA_{10\%}$ when compared to the samples densified without citric acid and with $CA_{5\%}$. This improvement was a consequence of a higher reduction in the width of the sample represented by a higher CR (29.17%) and a lesser ML (7.18%) than the other treatments.

3.2. Chemical Analysis

3.2.1. Fourier-Transform Infrared Spectroscopy

Figure 4 shows the spectra for all the evaluated treatments, which were obtained using the Fourier-transform infrared spectroscopy technique. The analysis of these spectra aimed to identify evidence of esterification reactions, considering as a hypothesis a possible link between the hydroxyl groups of wood and carboxyl groups of citric acid.

By analyzing the spectra, it was possible to observe two different patterns by having the spectrum of the untreated sample as a reference. For the densified and 5% of citric acid treatments, a decrease in the height of the peaks was observed, maybe because the amount was not enough to promote a significant change.

On the other hand, it was possible to verify that, for the treatment of 10% of citric acid, the behavior was the opposite, with the spectra presenting higher heights in both spectra (1374 cm^{-1} and 1735 cm^{-1}) when compared to the untreated wood.

Focusing on the effect of citric acid, it was possible to observe that the higher concentration of citric acid (10%) resulted in a higher esterification rate. According to the heights of the peaks in both spectra (1374 cm^{-1} and 1735 cm^{-1}), it is possible to infer not only that there was a greater amount of esterification reactions but also that this higher amount of reactions was able to partially compensate the thermal degradation promoted by the thermomechanical treatment.

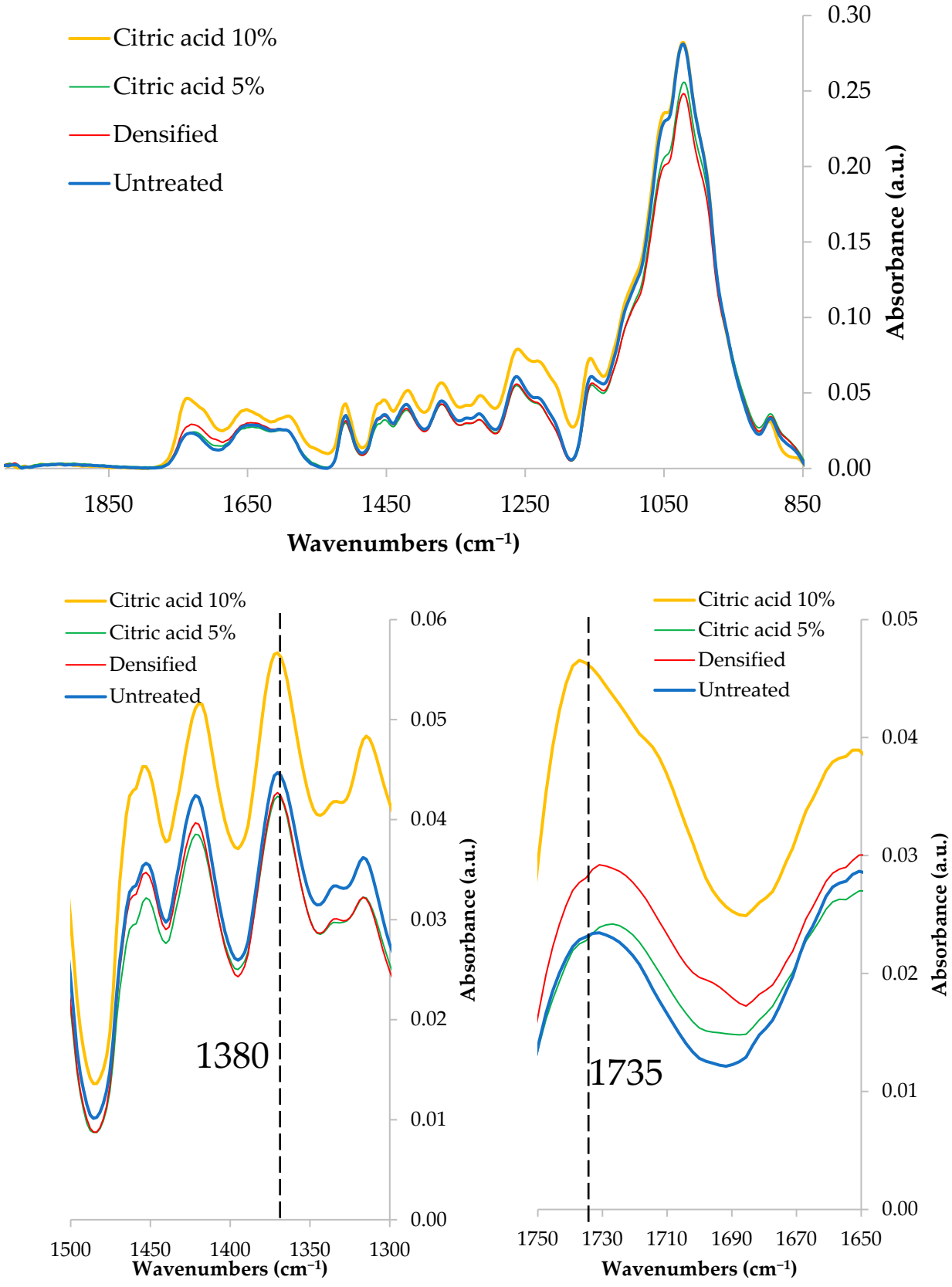

Figure 4. FTIR spectra of *Pinus sylvestris* sapwood for each treatment.

3.2.2. Scanning Electron Microscopy

Figure 5 presents the surface of *Pinus sylvestris* wood for each treatment evaluated, which were obtained using the scanning electron microscopy technique.

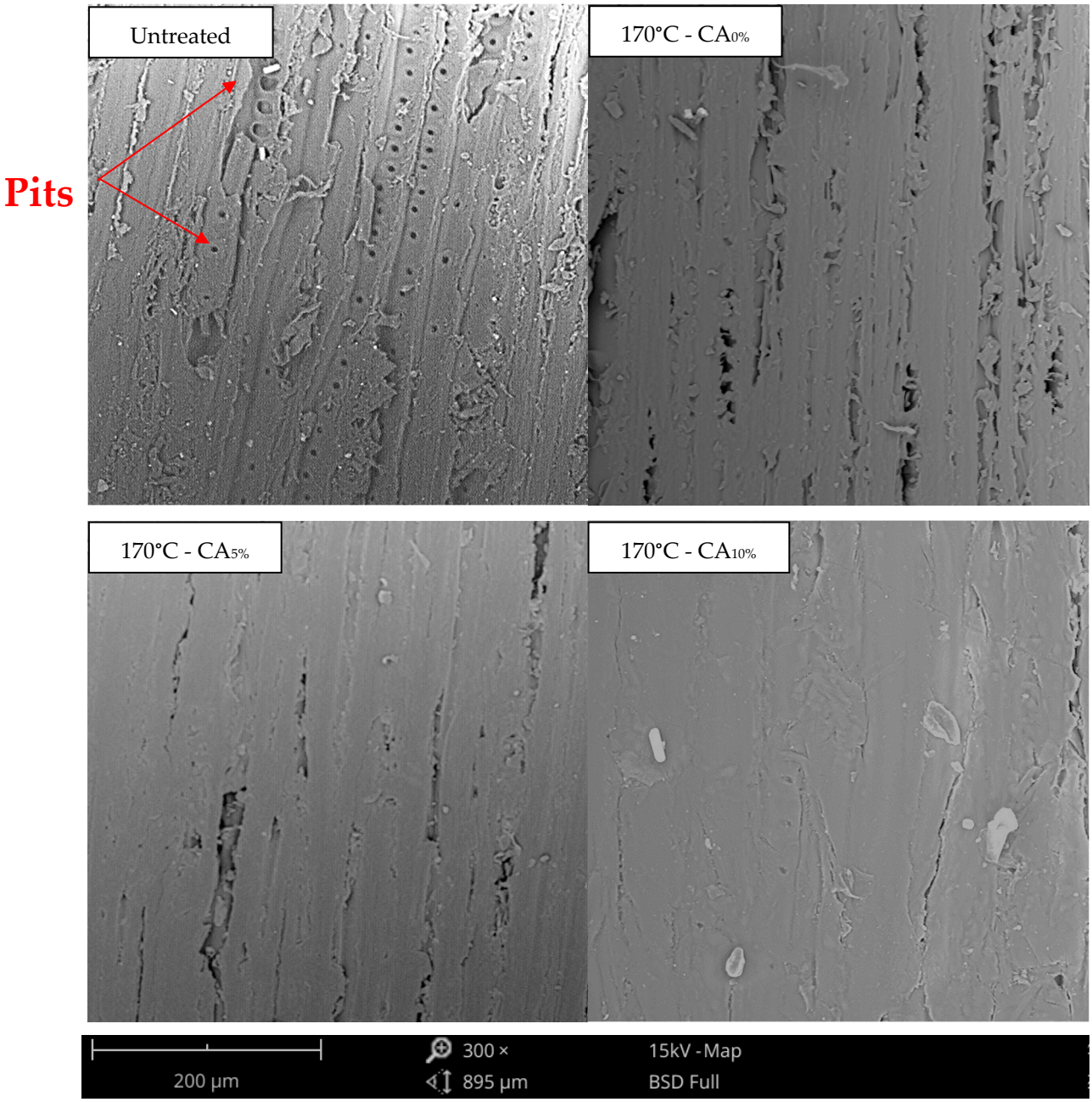

Figure 5. SEM analysis of *Pinus sylvestris* sapwood for each evaluated treatment.

From the pictures, it was possible to verify that the untreated *Pinus sylvestris* wood (control) presented a very irregular and porous surface, with many pits and valleys.

Evaluating the effect of the densification, it was possible to observe that the application of the thermomechanical treatment, as the main consequence, reduced the number of apparent pits.

Regarding the effect of citric acid, it was possible to observe that the substance acted as a film, revesting the surface and reducing considerably the number of valleys when compared to the densified wood without citric acid. Considering the amount of citric acid applied, it was possible to verify that the largest amount of citric acid (10%) presented

a better coating when compared to the lowest amount of the substance (5%), so that the valleys were almost completely covered.

3.2.3. pH

Figure 6 presents the average pH of *Pinus sylvestris* for each treatment evaluated.

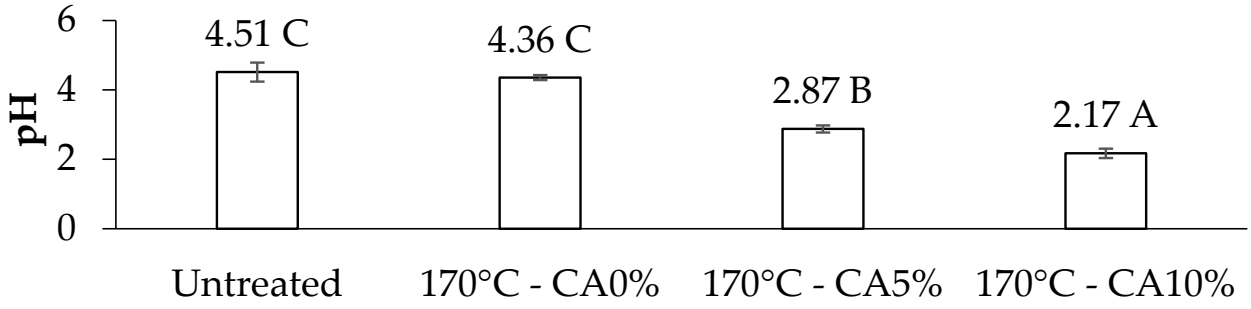

Figure 6. pH of *Pinus sylvestris* sapwood for each evaluated treatment. Values followed by the same letter are not statistically different, according to Tukey's test.

The pH showed a significant difference for all the evaluated treatments. When compared to the untreated wood (control), all the treatments applied promoted a reduction in pH and, consequently, an increase in acidity on the wood surface.

Evaluating the effect of the densification, it was possible to observe that the thermomechanical treatment caused a nonsignificant reduction of the pH (3.52%).

On the other hand, when evaluating the effect of citric acid, it was possible to observe that the combined treatment presented a significant reduction in the pH by 36.36% and 51.86% for the amounts of 5% and 10% of citric acid, respectively.

3.3. Density Profile

Figure 7 presents the density profile of *Pinus sylvestris* sapwood for each treatment evaluated.

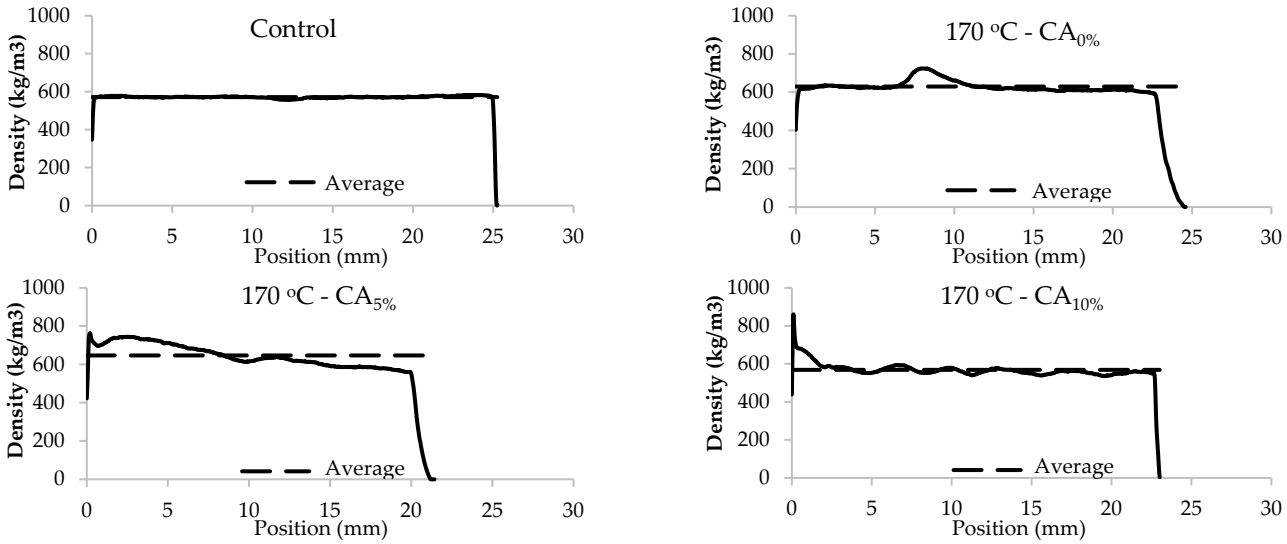

Figure 7. Density profiles of *Pinus sylvestris* sapwood for each treatment.

This way, it was possible to verify that the untreated wood presented a very homogeneous and close to the average line of 0.56 g/cm^3.

Evaluating the effect of the densification, it was possible to verify that the thermomechanical treatment provoked a peak of density (0.76 g/cm^3) close to the position 7.5 mm.

Making a visual analysis of the sample, it was possible to verify that the increase in density was a consequence of the change in the direction of the growth rings.

Lastly, for the treatments of modified citric acid, it was possible to verify a similar pattern for both concentrations (5% and 10%) where the peak of density did not occur in the middle of the sample but in the region where the substance was applied, reaching density peaks of 0.76 g/cm^3 ($CA_{5\%}$) and 0.86 g/cm^3 ($CA_{10\%}$).

3.4. Abrasion Test

Figure 8 presents the abrasion (Δt) and wear rate (WR) of *Pinus sylvestris* for each treatment.

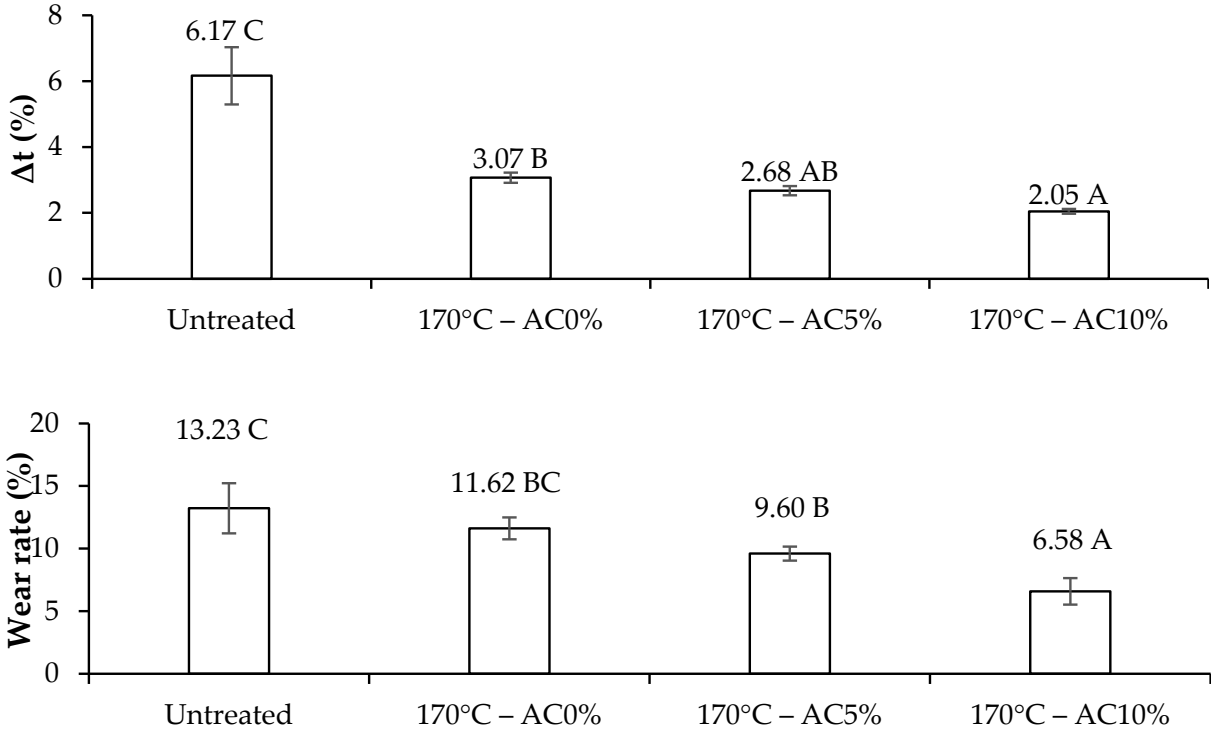

Figure 8. Abrasion and wear rate of *Pinus sylvestris* for each treatment. Values followed by the same letter are not statistically different, according to Tukey's test.

The samples of *Pinus sylvestris* without treatment presented the highest abrasion and wear rate between all the evaluated conditions.

Considering the effect of the thermomechanical treatment, the densified samples presented a significant difference in comparison with the untreated samples, with an average reduction of 50.21% for the Δt and 16.70% for the WR.

On the other hand, considering the effect of citric acid, it was possible to verify a significant increase in the performance of both properties when compared to the untreated and densified samples, with an average reduction of 61.65% for the Δt and 42.00% for the WR.

Additionally, it was possible to verify that the application of a higher amount of citric acid (10%) promoted a better performance of both properties, although significantly different only for the WR.

Lastly, when considering the visual aspect (Figure 9), it was possible to observe that the abrasion was noticeable in all the evaluated treatments. In this context, it was possible to verify that, although citric acid promoted a reduction in the abrasion through a smaller reduction in the thickness and mass loss, the technique applied was not enough efficient to penetrate the deeper layers of the wood.

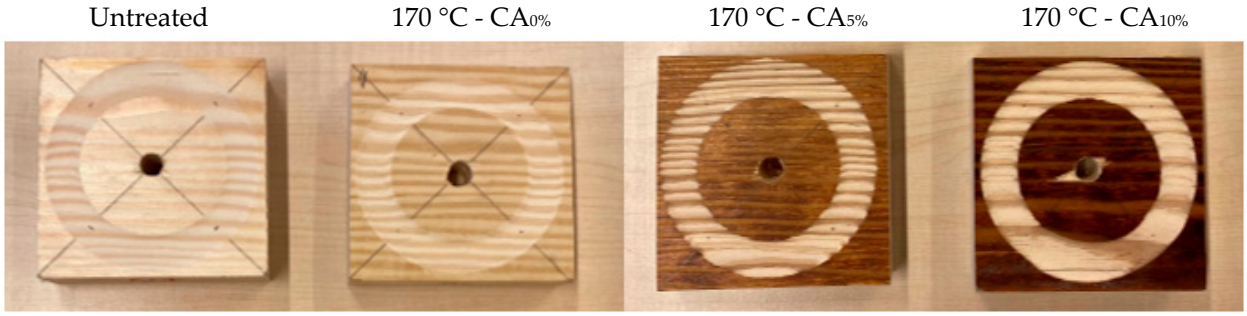

Figure 9. Visual aspect of *Pinus sylvestris* for each treatment after the abrasion test.

4. Discussion

4.1. Thermomechanical Treatment

When considering the effect of the thermomechanical treatment on the densification rate (DR), different results were found by [19,20], who applied thermomechanical treatments on boards of *Pinus sylvestris* and *Pinus elliotti* and verified a DR between 83% and 93%. In this context, ref. [21] stated that an increase in the specific mass of a wood after the application of a thermomechanical treatment may be associated withwith many factors, such as temperature, time and pressure applied.

Therefore, the divergence in the results may be associated withwith the pressure applied during the present study, since the samples were exposed to similar temperatures but with a pressure of 2.6 MPa, while the authors applied pressures of 6 MPa and 4.9 MPa, respectively.

For the effect of the thermomechanical treatment on the compression rate (CR), the results corroborated with [22], who applied a thermomechanical treatment on wood of *Pinus sylvestris* at a temperature of 150 °C for a period of 10 min. According to the same authors, the variation presented by the CR was mainly associated with the presence of internal tensions that were generated inside the cellular structure during the compression and the loss of humidity due to the exposure to high temperatures, both factors being responsible for the springback behavior of the wood after densification.

Lastly, the effect of citric acid on the mass loss matched the results obtained by [10], who verified that the application of citric acid promoted a reduction in the permeability of boards of *Pinus strobus*. Therefore, this behavior suggested that the application of the substance may have acted as a barrier, making it difficult for water to exit during the heating stage (first stage of the thermomechanical treatment), thus reducing the ML presented by the treatments.

4.2. Chemical Analysis

4.2.1. Fourier-Transform Infrared Spectroscopy

In this context, emphasis was given to two specific peaks: one between the 1725 cm^{-1} and 1740 cm^{-1} bands, related to the stretching of carbonyl groups (C=O) in the esters of wood polymers and citric acid [23], and the other one found in the 1374 cm^{-1} spectra, which, according to [24], is related to the polysaccharides (C-H bonds of CH3 groups) that are deformed in carbohydrates.

According to [25], who applied thermal treatments on wood of *Pinus pinaster*, the reduction in the peaks was associated with the thermal degradation of polysaccharides and weight loss presented in the wood as a consequence of the exposure of the material to high temperatures (170 °C).

This result corroborated with [25,26], who verified an increase in the esterification reactions after applying citric acid on wood panels of *Sorghum bicolor* L. Monech and *Vitis vinifera* L., respectively.

4.2.2. Scanning Electron Microscopy

The result of the untreated samples corroborated with [27], who evaluated the microstructure of *Pinus sylvestris* sapwood and observed that it is a species with a very porous and irregular surface, with many apparent pits, characteristics that are typical of low-density pinewood.

For the effect of the thermomechanical treatment, the results corroborated with [9], who evaluated the effect of densification on the microstructure of *Populus tomentosa* wood and verified a reduction in the number of pits per unity of area. A similar result was obtained by [28], who applied a thermomechanical treatment on *Pinus sylvestris* wood and verified a reduction in the wood porosity.

In this context, ref. [29] stated that the densification of wood through thermomechanical treatment led to the occurrence of morphological changes such as the reduction of pits and valleys, which were compressed by the pressure applied on the press.

Finally, for the effect of citric acid, the observed results corroborated with [10], who applied citric acid on *Pinus strobus* and *Pinus contorta* wood and verified a considerable reduction in the porosity of both species. According to [30], this behavior was a consequence of the capacity of citric acid to establish chemical bonds between the carboxyl groups (-COOH) available on its structure and the free hydroxyl groups (-OH) available on the wood structure, a process that is known as ester bonds.

4.2.3. pH

The *Pinus sylvestris* sapwood without treatment presented an average pH of 4.51, a result very close to that observed by [31], who verified a pH of 4.6 for untreated *Pinus roxburghii* wood.

The effect of the thermomechanical treatment differed from [11], who verified a significant reduction in the pH (3.5–4) of *Pinus radiata* wood after the application of thermal treatments due to the occurrence of reactions that led to the production of acetic and formic acids. In this context, the different results might have been associated with the temperature chosen (170 °C), which might have been insufficient to promote greater changes in the wood surface.

Lastly, the effect of citric acid corroborated with [32], who verified a reduction in the pH of *Fagus sylvatica* wood because of the application of citric acid. According to [33], such a reduction in pH observed in wood is the result of esterification reactions between the hydroxyls of the material and the carboxyls of citric acid, thus generating a new structure with a greater availability of protons.

4.3. Density Profile

Several studies with *Pinus sylvestris* have discovered that wood of this species can present foreign bodies such as knots [34] and resin bags [35], capable of significantly increasing the density of wood. Therefore, the obtained results suggest that the samples of *Pinus sylvestris* sapwood did not contain such bodies.

Additionally, it was not possible to verify any difference between earlywood and latewood in the obtained density profile, differing from the results obtained by [36], who were able to verify this difference in *Pinus sylvestris* wood using the X-ray tomography technique. However, this result might be associated with the resolution applied to the equipment, which might have not been sufficient to detect such differences.

For the effect of the thermomechanical treatment, it was possible to observe that the increase in density did not occur homogeneously throughout the sample but due to a peak in the density that was 20% higher than the average curve (0.63 g/cm^3). This result corroborated with [37], who applied a thermomechanical treatment on *Pinus sylvestris* and verified the formation of density peaks along the sample.

According to [38], who applied a thermomechanical treatment on boards of *Populus tomentosa*, the lower density in the surface of the sample might have been associated with

the loss of moisture that occurred when the wood was in contact with the hot plates of the press.

Lastly, the effect of citric acid corroborated with [13], who evaluated the effect of citric acid applied using an impregnation chamber on the density profile of sapwood of *Pinus sylvestris* and verified the formation of peaks next to the edge of the sample, suggesting a higher accumulation of the substance on the surface of the material.

In addition, these results suggest that the citric acid might have acted as a barrier, preventing the exit of moisture present in the innermost layers of the material and, consequently, increased the density of the most superficial layer. Such behavior corroborates a study carried out by [10], who verified a reduction in the permeability of *Pinus strobus* L wood through citric acid impregnation.

4.4. Abrasion Test

The results for the abrasion test on the untreated samples of *Pinus sylvestris* corroborated with [38], who verified an abrasion rate of 6.00% for the sapwood of *Pinus sylvestris* without any treatment.

For the effect of the thermomechanical treatment, a similar result was observed by [39], who registered an increase in the resistance to abrasions after applying a thermomechanical treatment on boards of *Paulownia* spp., with a reduction in weight loss between 40% and 75% due to the pressure applied.

According to [40], the resistance to abrasions might be associated with the specific mass of the material, so that higher-density materials also tend to present a greater resistance to abrasions.

Lastly, for the effect of citric acid, it was not possible to find any results in the literature evaluating the effect of this substance on the abrasion resistance of wood. However, when considering the effect of chemical modifications on wood, ref. [41] verified an increase in the abrasion resistance after promoting an acetylation reaction on boards of *Fagus sylvatica*, and [42] obtained similar results by promoting a furfurylation reaction on boards of *Pinus radiata*.

5. Conclusions

The combination between the thermomechanical treatment and citric acid presented significant improvements in the chemical and surface properties, in the density profile and in the resistance to abrasions of *Pinus sylvestris* sapwood.

The application of a higher concentration of citric acid (10%) might be justified by the better results presented in the chemical analysis, in the density profile and in the abrasion resistance of *Pinus sylvestris* sapwood.

Lastly, when considering the visual aspect, the application of citric acid provoked an intense darkening of the surface for the same temperature applied, changing its color from a light yellow to dark brown.

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