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Proceeding Paper

A Study of the Best Conditions for the Acetylation of *P. taeda* from Uruguay †

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Abstract: Chemical modification is an environmentally friendly option for wood preservation. It can improve the performance and dimensional stability of wood, increase its resistance to deterioration and ensure safe disposal once out of service. Wood acetylation is the esterification of accessible hydroxyl groups in the cell wall with acetic anhydride, which reduces the hygroscopicity of wood. Acetic acid is obtained as a byproduct of the reaction. The aim of this work is to determine the best reaction conditions for the acetylation of *Pinus taeda* wood with acetic anhydride. The experimental design used was a 2^2 factorial design with three repetitions in the midpoints. Reaction temperature and reaction time were taken as independent variables, each at two levels. The weight gain percentage of wood (WPG) and its chemical changes were used as response variables. The durability of the wood acetylated under the best treatment conditions as determined before was tested against decay fungi (*Gloeophyllum separium* and *Trametes versicolor*). The results show that temperature was the most impactful variable on the WPG results. Higher WPGs were obtained at temperatures above 100 °C. The acetylated wood was highly resistant to fungal attack, with very low mass losses.

Keywords: wood modification; wood; mechanical properties; durability

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1. Introduction

Wood is widely used for its physical and mechanical properties; however, it is very vulnerable to certain natural conditions which affect resistance and durability [1]. Weathering and deterioration result from the combination of abiotic (i.e., humidity, sunlight, high or low temperatures, chemicals, abrasion by wind-dragged materials) and biotic agents (i.e., fungi and moulds, bacteria, insects and marine boring animals) [1,2].

In order to protect wood and increase its resistance to deterioration, several preservation methods have been developed, tested and used. The most well-known methods include the application of chemicals, humidity control, the removal of certain compounds from wood and the modification of its chemical structure [2].

There is a growing interest in non-biocidal wood protection methods. This is due to the restrictions on the use of toxic preservatives and the significant growth in the use of non-renewable materials, which have been replacing timber in the market [1,2].

Chemical modification, a non-biocidal wood protection method, consists of a set of techniques that can modify the chemistry of wood [3], which can improve its performance and dimensional stability, increase its resistance to deterioration and ensure safe disposal once out of service. It is the reaction between a chemical reagent and the hydroxyl groups of wood polymers, resulting in a single covalent bond. Acetylation is a widely developed process that has been studied for more than 60 years and commercially produced for 30 [1,4], and it has been used to achieve a product that is commercialized in Europe and Japan.

Acetic anhydride (AA), an electrophilic reagent, is forced to move through wood pits, resulting in the esterification of accessible nucleophilic hydroxyl groups in the cell wall (Figure 1). Acetic acid, a byproduct of the reaction, has to be removed [5–7]. When some hydroxyl groups of cell wall polymers are replaced with acetyl groups, the hygroscopicity, water uptake and wettability of the wood are reduced [8].

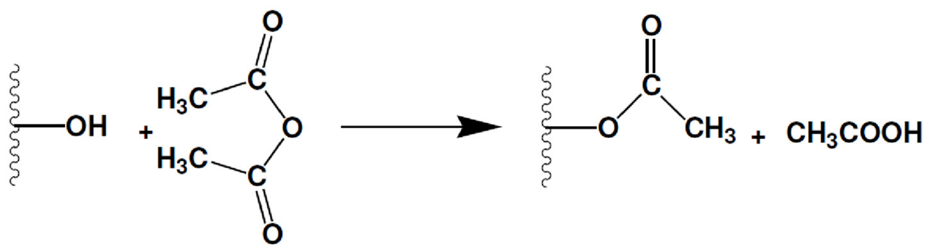

Figure 1. Acetylation reaction.

This work studies the best reaction conditions for the acetylation of *Pinus taeda* wood, commercially used in Uruguay, with acetic anhydride (AA) in liquid phase. There are very few previous studies on the acetylation process of solid *Pinus taeda* wood.

2. Materials and Methods

2.1. Samples

The *Pinus taeda* used was obtained from five trees from a contemporaneous and monospecific stand located in Cerro Largo, Uruguay (32°33′95.59″ S, 54°44′22.01″ O elevation 159 m). Sapwood samples were prepared in 500 blocks of dimensions (1.0 ± 0.3) mm × (1.0 ± 0.3) mm × (1.0 ± 0.3) mm, which were later extracted with ethanol for 24 h in Soxhlet.

2.2. Acetylation Reaction

Acetylation tests were based on Jebrane et al. [9]. Extractive-free wood was placed in a stainless steel reactor of 1 L of capacity, with temperature (type K thermocouple) and pressure (vacuomanometer) control. The acetylation process started with an initial 30 min vacuum; after which, the reaction mixture—K_2CO_3 (1.1 mmol/g of dry wood), N,N-dimetilformamida (DMF) and AA (97:3 *v*/*v*) [9]—was added and then heated through electrical resistance for 2 and 6 h.

At the end of the reaction, the samples were immersed in water at 70 °C, and then the excess reagents—solvent, catalyst and byproducts—were removed in Soxhlet equipment using Hexane/ethanol/Acetone (4:1:1 *v*/*v*/*v*) for 8 h [9]. Samples were dried at 90 °C until constant weight was obtained.

The experimental design used to identify the best reaction conditions was a 2^2 factorial design considering 3 repetitions in the midpoints. In this design, the independent variables were the reaction temperature at two levels (60 °C and 100 °C) and the reaction time, also at two levels (2 and 6 h). The weight gain percentage of wood, WPG = (Weight after acetylation (g) − Weight before acetylation(g)) × 100/Weight before acetylation (g), and its chemical changes observed in FTIR were used as response variables.

2.3. FTIR Analysis

Fourier-transform infrared spectroscopy (FTIR) was performed with an IR Prestige-21 Shimadzu spectrometer (Kyoto, Japan), working at a 5 cm^{-1} resolution and running 32 scans per sample.

2.4. Durability Test

The samples acetylated under the best reaction conditions were tested against decay according to the EN 113-1 standard [10]. Two fungi were used: white rot fungus *Trametes versicolor* and brown rot fungus *Gloeophylum separium.* Both fungi were sourced from Laboratorio Forestal, Sede Tacuarembó, Universidad de la República. They were kept in Petri dishes with MEA, malt extract (20 g/L) − agar (18 g/L) from Oxoid Ltd. (Basingstoke, UK), at 25 °C and 85% RH.

The fungi were inoculated in 12 flasks containing MEA. The flasks were previously sterilized at 121° for 15 min. Modified wood samples and control samples were sterilized with flowing steam, in 15 min intervals on the first day and 10 min on the second day. They were then conditioned in a climate chamber at 22 °C and 75% relative humidity (RH) for 10 days. Once the fungi covered the bottom of the flasks, three samples were placed in each flask (two modified and one control). The five flasks (total samples: 15) were incubated for 16 weeks at 22 °C and 75% RH.

After the incubation period, the mycelium was carefully removed from the surface of the wood. Samples were then dried at 103 ± 2 °C until constant weight was obtained. The fungicidal effectiveness of the chemical modification was determined as the average % weight loss (initial dry mass − final dry mass/initial dry mass) of the treated sample.

2.5. Statistical Analysis

Data analysis was performed using R programming language 4.3.2 (R Core Team 2013). Tukey tests were performed to analyze significance of differences between wood mass losses.

3. Results and Discussion

The WPG results are shown in Table 1. It can be observed that mass gains were low, which indicates that there are more bonded acetyls in layer S2 than in the middle lamella [11].

Table 1. Weight percentage gain (WPG) of acetylated wood samples.

Run	Temp (°C)	Time (h)	WPG (%)	Std. Dev
1	60	2.0	2.64	0.00
2	60	6.0	4.79	0.00
3	80	4.0	5.85	0.52
4	100	2.0	5.50	0.00
5	100	6.0	5.89	0.00

Most references in the literature acetylate *Pinus taeda* particles and obtain values between 8% and 20% depending on the reaction conditions [12,13]. The same is the case for solid samples of other pine species like *Pinus radiata* (23% [14] to 23.94% [14]) and *Pinus nigra* (5.7% to 23.4% [15]).

The highest mass gains were obtained under the most extreme conditions tested (highest temperature and longest time). No changes in the appearance of wood were observed in any of the reactions.

A statistical analysis of the design shows a larger influence of the temperature variable on the WPG results, which were not as affected by time.

The graphic in Figure 2 shows that higher WPGs were obtained when the reaction temperature was over 100 °C. Figure 3 shows an FTIR graph.

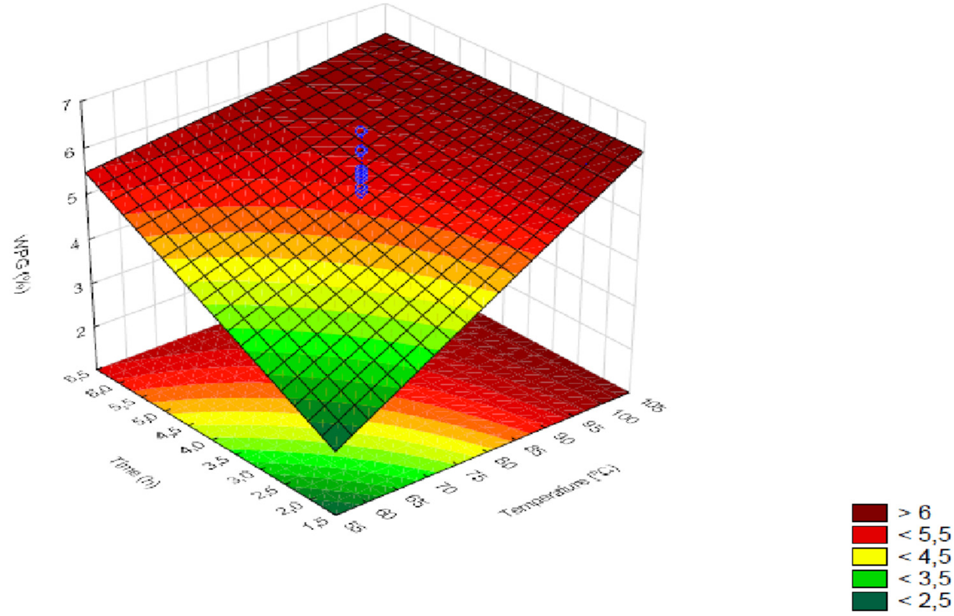

Figure 2. The 2^2 experimental design; MS Residual = 0.470 DV: WPG (%). Tje blue circles represent the best conditions for wood acetilation.

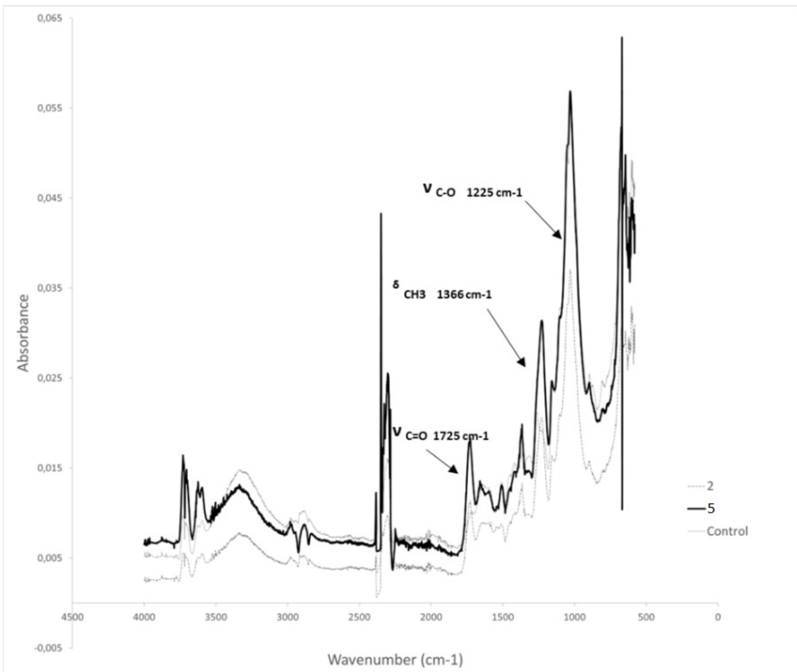

Figure 3. FTIR graph comparing curves of wood acetylated under best (run 5) and worst (run 2) conditions.

The FTIR spectrum analysis is in line with the literature [3,16,17], indicating that the number of acetyl groups increases in comparison to non-acetylated wood (controls) as observed in the following wavenumbers: 1745 cm^{-1} (C=O vibration), 1374 cm^{-1} (C-H strain vibrations in CH3) and 1265 cm^{-1} (C-C plus C-O stretching plus aromatic strain vibrations =C-H in plane from lignin, superimposed with C-O valence vibration, 1031 cm^{-1} and the asymmetric CO stretching vibration of the grafted ester group C-O-C=O, 1242 cm^{-1}). The observable differences in these peaks show that a temperature above 100 °C and a reaction time of 6 h are the best conditions for the acetylation of *P. taeda* under the tested conditions.

The durability of the samples acetylated under the best conditions was tested against basidiomycetes. Table 2 shows the results.

Table 2. Weight losses against wood rot fungi, mean values with their cv.

	Control	Acetylated Samples
T. versicolor	22.08 (0.33)	2.03 (0.27)
G. separium	20.12 (0.23)	2.29 (0.42)

The mass losses of the control samples were above 20% for both fungi, validating the test. The mass losses of the acetylated samples were below 3%, meaning that they are protected against rot fungi according to EN 113-1. This is most likely because of the low humidity absorption, which is below the 28% necessary for fungi to grow. There was an improvement in the durability of wood. Further work will optimize the acetylation process to increase WPG and improve the permeability and uniform distribution of reactives inside wood.

4. Conclusions

Pinus taeda wood grown in Uruguay is suitable for acetylation. The more extreme acetylation conditions produced, the better the WPG results.

Although WPGs were low, acetylated wood performed significantly better than controls against rot fungi.

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