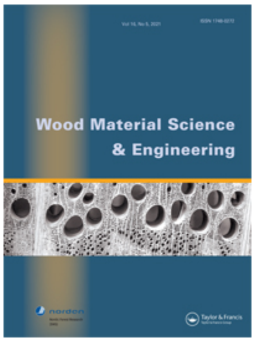


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ORIGINAL ARTICLE



# Furfurylation of tropical wood species with and without silver nanoparticles: Part II: Evaluation of wood properties

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**ABSTRACT**
The purpose of the work was to assess the combined effect of furfurylation, along with the addition of silver nanoparticles (NPsAg), on the thermal stability, density, water absorption, hardness and biological durability of juvenile tropical woods originating from Costa Rican forest plantations. It was demonstrated that the weight percentage gain (WPG) of wood treated with furfuryl alcohol (FA) varied from 14.44% to 44.26%, and from 12.92% to 44.52% after the addition of NPsAg. Additionally, for species with WPG over 25%, thermal stability as well as durability was greater, while water absorption was lower, compared to species with lower WPGs. Improvement of hardness was only achieved with WPG values over 35%; therefore, only species of high permeability (*V. ferruginea, V. guatemalensis, C. odorata, S. saman* and *E. cyclocarpum*) showed improvement regarding this property. The addition of NPsAg induced the same behaviour as when using plain FA treatment, however, regarding wood durability, the addition of NPsAg was effective only for species with WPG under 20%.

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**KEYWORDS**
Wood modification; furfurylation; tropical species; silver nanoparticles; wood durability

## 1. Introduction

Furfurylation is a wood modification treatment which can be implemented for the purposes of addressing essential wood material drawbacks such as its hygroscopicity and susceptibility to biodegradation (Hill 2006, Rowell 2012, Militz 2020). Some of the recent works regarding furfurylation focused on the improvement of wood properties (Venås and Rinnan 2008) demonstrating reduction of its hygroscopicity (Baysal *et al.* 2004, Esteves *et al.* 2011), as well as improvement of its mechanical properties (Lande *et al.* 2004b, Xie *et al.* 2013) and durability against fungi, termites, bacteria and weathering (Temiz *et al.* 2007, Gascón-Garrido *et al.* 2013, Dong *et al.* 2014, Li *et al.* 2015, Mantanis 2017, Sejati *et al.* 2017, Kong *et al.* 2018).

Furfuryl alcohol (FA) can be formed through the hydrogenation of pentosans that are present in agricultural by-products and has been successfully utilised for the chemical modification of wood (Schneider 1995, Westin 1996, Westin *et al.* 1998, Lande *et al.* 2004a, Nordstierna *et al.* 2008, Lande *et al.* 2008a, 2008b). The FA polymer reacts with itself and possibly reacts with cell wall lignin (Lande *et al.* 2004a, 2008a, Nordstierna *et al.* 2008, Gérardin 2016, Li *et al.* 2016). Barsberg and Thygesen (2017) found that furfurylated wood cell walls can be described as a poly(FA)-wood hybrid material (copolymer) in which covalent bonds are formed between poly(FA) and lignin. The formation of covalent bonds prevents FA leaching and acts as a kinetic barrier for moisture access to wood hydroxyl groups even at high water vapour pressures. However, others suppose that FA does not form chemical bonds with the polymeric constituents of wood (Hill 2006, Rowell 2012). While for many softwoods and hardwoods, research results regarding furfurylation are numerous, current research on the furfurylation of tropical species is quite limited (Hadi *et al.* 2020, Hadi *et al.* 2021).

Tropical hardwoods are characterised by a lignin content, type and distribution different than those of softwood species (Saka 2000, Simon *et al.* 2018). While softwood lignin is mainly composed of the guaiacyl type (Zhou *et al.* 2016), in the case of tropical species guaiacyl lignin is mainly present in the vessels, whereas syringyl-guaiacyl lignin is located in the secondary walls of rays and fibres (Saka 2000). As a result, the content and chemical type of lignin in hardwood species vary among species and genera (Saka 2000, Bose *et al.* 2009). In the meantime, in Central America, Costa Rica has implemented reforestation programs through the plantation of fast-growing hardwood species for lumber production (Moya *et al.* 2015). In these programs, early-age tree harvesting yields juvenile wood (Adebawo *et al.* 2016), which is characterised by reduced dimensional stability and decay resistance (Adebawo *et al.* 2016, Moya *et al.* 2019) and require the implementation of technologies towards enhancement of its properties (Gaitán-Alvarez *et al.* 2020, Moya *et al.* 2020).

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Several furfurylation studies have focused on the effect of various additives on the effectiveness of FA on softwood species (Venås and Rinnan 2008). This potential has been further enhanced by the significant development of nanotechnology in wood protection applications (Papadopoulos *et al.* 2019). For example, nanosilver effectively increased durability against decay of tropical wood, when used in concentrations of 50 ppm (Moya *et al.* 2014, 2017a). It was also demonstrated that nano Ag improved the durability of heat-treated wood as well as particleboards against white rot (Moradi Malek *et al.* 2013, Taghiyari *et al.* 2014). Furfurylation, along with impregnation with nanosilver (FA-NPsAg), seems attractive since it provides an opportunity to improve dimensional stability, decay resistance, fire retardancy and other wood properties of tropical hardwood species (Berrocal *et al.* 2017, Moya *et al.* 2017a, Gaitán-Alvarez *et al.* 2020). In fact, previous research of nine FA-treated tropical species with confocal laser scanning microscopy demonstrated, fluorescence in the 600 nm band in FA treated fibres and WPG of over 25%, while in radial and axial parenchyma furfurylation was limited (Gaitán-Alvarez *et al.* 2021). Furthermore, FTIR spectroscopy revealed changes of lignin after treatment of wood with FA and FA-NPsAg compared to untreated wood. However, no significant difference was found between FA and NPsAg treatment, probably because the NPsAg concentration was insufficient to induce perceptible change in the bonds (Gaitán-Alvarez *et al.* 2021). However, there is still margin for enrichment of current knowledge regarding other tropical hardwood properties (Hadi *et al.* 2020, Hadi *et al.* 2021) and possible room for new applications regarding tropical species in general.

In this regard, the objective of this work was to study the effect of furfurylation along with nanosilver addition on thermal stability, colour, density, water absorption, hardness and biological durability against decay of nine hardwood species, commonly used in commercial reforestations in Costa Rica.

## 2. Methodology

### 2.1. Materials

Sapwood samples of nine fast-growing tropical species, originating from plantations in Costa Rica, were used in this work, namely Spanish cedar *(Cedrela odorata)*, Spanish elm *(Cordia alliodora)*, guanacaste *(Enterolobium cyclocarpum)*, gmelina (*Gmelina arborea*), pilón *(Hieronyma alchorneoides)*, rain tree *(Samanea saman)*, teak *(Tectona grandis)*, chancho colorado *(Vochysia ferruginea)* and chanco blanco *(Vochysia guatemalensis)*. These species appear to be sufficiently permeable and present satisfactory behaviour in wood modification (Moya *et al.* 2017b, 2020, Gaitán-Alvarez *et al.* 2020). Forty-five sapwood specimens measuring 50 mm × 50 mm × 20 mm (tangential × radial × longitudinal) were prepared for each species after conditioning to a moisture content of 12%.

The chemical reagents used in this work were: 98% furfuryl alcohol solution (Sigma Aldrich, Belgium), sodium borate decahydrate (J.T. Baker, Madrid), citric acid (Central Drug House, New Delhi), and oxalic acid dehydrate (Oxford Lab Fine Chem, Maharastra, India). Three components were employed for the synthesis of silver nanoparticles (NPsAg), namely, silver nitrate ($AgNO_3$) as a source of reduced metal (MERCK, pureness 99.9%), ethylene glycol ($C_2H_6O_2$) as a reducing agent (J.T. Baker, pureness 99.9%), and polyvinyl pyrrolidone as a stabilising agent (Magnacol Ltd., UK). The synthesis procedure used has been described elsewhere (Moya *et al.* 2014, 2017b).

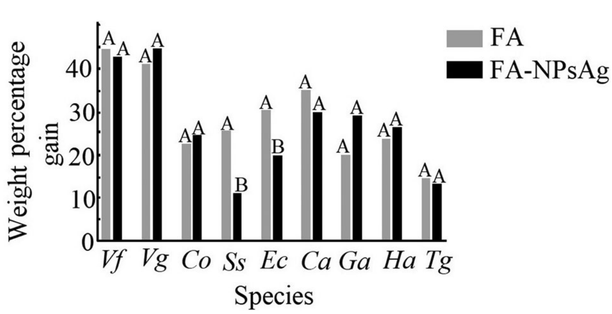


**Figure 1.** Weight percentage gain of wood from nine tropical species of Costa Rica, treated with furfuryl alcohol (FA) and furfuryl alcohol with silver nanoparticles (FA-NPsAg).

Notes: Different characters between FA and FA-NPsAg treatments indicate statistically significant differences at 95%.

### 2.2. Treatments

Two treatments were carried out for the furfurylation of wood specimens: (i) FA treatment, which included a furfuryl alcohol solution, composed of FA (50%), distilled water (46.2%), sodium borate as buffer agent (2%) and a mixture of oxalic acid and citric acid (1.75% in total) as a catalyst, and (ii) FA-NPsAg treatment, which included FA solution with the addition of silver nanoparticles at a proportion of 50 ppm. Details about the synthesis and preparation of the silver nanoparticles can be found in Moya *et al.* (2014, 2017a).

The details of the furfurylation process are presented in Gaitán-Alvarez *et al.* (2021). Fifteen specimens were oven dried (OD) and then introduced in a reactor and vacuum treated for 45 min at −70 kPa (gauge). Afterwards, impregnation solution (FA or FA-NPsAg) was transferred in the reactor and a 690 kPa pressure was applied for 2 h. After pressure treatment, excess solution was removed from each specimen surface. The specimens were then heated inside the reactor at 40°C for 4 h and then vacuum treated at −70 kPa (gauge) for 20 min. Then, the specimens were removed from the reactor, wrapped in aluminium foil, and placed in an oven for 16 h at 103°C to induce the reaction. After this interval, they were dried for another 24 h at 103°C to reach the oven-dry state. Another fifteen samples were left untreated for comparison purposes. Weight percentage gain of wood (WPG) was calculated according to Equation 1.

$$(\mathrm{WPG}) = \frac{\text{OD Weight}_{\text{after furfurylation}}(\mathrm{g})\text{-OD Weight}_{\text{before furfurylation}}(\mathrm{g})}{\text{OD Weight}_{\text{before furfurylation}}(\mathrm{g})} \quad (1)$$

According to previously published results (Gaitán-Alvarez *et al.* 2021), the weight percentage gain (WPG) of furfurylated wood varied from 14.44 to 44.26% after FA and from 12.92%

to 44.52% after FA-NPsAg treatment. The WPG differences among the used species are presented in Figure 1.

### 2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to monitor the thermal decomposition kinetics and acquire information about physical transitions as well as chemical reactions of each species/treatment combination. TGA was carried out under atmospheric pressure in an inert nitrogen ambient. For each species/treatment combination, 5 mg specimens, composed of previously dried sawdust, were used. Specimens were heated from 50°C to 600°C in an ultra-high purity nitrogen atmosphere flowing at 100 ml min$^{-1}$ with a heating rate of 20°C/min. Analyses were carried out in a SDT Q600 thermogravimetric analyser (TA Instruments, New Castle, DE, USA). The TGA returned values for the weight loss against temperature from which the derivative thermogravimetry was obtained (DTG) allowing to determine the position and temperature at which specimen degradation took place. The TGA data and their derivatives (DTG) were analysed in TA Instruments Universal Analysis 2000 software (New Castle, DE, USA). Furthermore, 3 TGA profile parameters were also determined: temperature corresponding to 10% weight, temperature corresponding to maximum rate of weight loss, and residual mass at 600°C.

### 2.4. Physical properties and hardness

Wood density and water absorption were determined. Density was determined using 15 specimens for each treatment/species combination. The volume (length × width × thickness) and the weight of the specimens were determined. Then, the density was calculated (weight/volume). Water absorption was determined after immersion in water for 24 h and again weighed, according to ASTM D4446-13 (1985). Janka hardness was determined for 20 specimens per variable according to ASTM D143-21 (2016).

### 2.5. Decay resistance

For the determination of durability against accelerated decay, the methodology described in ASTM D2017-05 was applied (2005) using 15 cubic specimens with a side of 2 cm for each species/treatment/fungi combination. Two fungal species were used, namely *Trametes versicolor* and *Lenzites acuta*, corresponding to white rot and brown rot, respectively.

### 2.6. Statistical analysis

Testing for normality and homogeneity of data, as well as for the elimination of atypical data or outliers was carried out for the assessed variables. A descriptive analysis was then carried out, with determination of the mean, standard deviation, and coefficient of variation for each variable studied. Analysis of variance (ANOVA) with a statistical significance value of $p < 0.05$ was applied to determine the effect of furfurylation treatments (independent variable) on the determined properties (response variables). Tukey's test was used to determine the statistical significance of the difference among means. Analysis was performed using SAS 9.4 software (SAS Institute Inc., Cary, N.C.).

## 3. Results and discussion

### 3.1. Thermogravimetric analysis (TGA)

The acquired TGA and DTG profiles are shown in Figure 2, while relevant data is summarised in Table 1. For specimens of all three treatments, TGA and DTG revealed a small degradation near 200°C (first stage of thermal decomposition of wood), mainly caused by evaporation of water (Tenorio and Moya, 2013, Moya *et al.* 2017b, Dong *et al.* 2020). These points are indicated with a white arrow in Figure 2. Although loss of water was more or less evident both for untreated and furfurylated wood, greater mass loss at temperatures up to 200°C was observed in untreated wood, indicating that furfurylated wood contains lower moisture content than untreated wood.

The fact that, even though all specimens were conditioned in the same ambient conditions after furfurylation, equilibrium moisture content of furfurylated wood was lower than that of untreated wood, was also reported in other studies (Epmeier *et al.* 2007, Gérardin 2016). This can be attributed to the interaction of FA with the OH- groups of the cell-wall polymers, thus preventing wood from absorbing moisture (Baysal *et al.* 2004) and therefore yielding lower weight loss when heated to 200°C. It is worth mentioning that, in species which showed higher WPG values such as *V. ferruginea* and *V. grandis* (Figure 2a,b), the difference between the untreated and FA-treated wood curves was greater than the respective difference among species which showed low WPG (e.g. *H. alchornoides* and *T. grandis*, Figure 2h,i). In these cases, moisture absorption decreased with increasing WPG (Epmeier *et al.* 2007, Gérardin, 2016).

The second stage of degradation of these tropical species occurred between 200°C and 400°C, with a decomposition peak located in the range of 343–362°C (Table 1). During this stage, two distinct parts of the degradation process occurred: (i) over 250°C where hemicellulose degradation was initiated and (ii) around 300°C in which the degradation of cellulose, simultaneously with maximum decomposition, took place (Browne 1958, Demirbas 2004, Poletto *et al.* 2010, Moya *et al.* 2018). Degradation of lignin, which takes place over 250°C as well, was slower and was thus dimmed by hemicellulose degradation, therefore it appeared as a small shoulder between 300°C and 325°C in the TGA (Tenorio and Moya 2013, Gaitán-Álvarez *et al.* 2018, Dong *et al.* 2020) as well as in the DTG curve (Demirbas 2004, Poletto *et al.* 2010). The temperature at which 10% of the mass was lost was assessed in the above temperature range (Table 1). Results showed that the species that showed the highest WPG values after treatment with FA and FA-NPsAg (Table 1) namely *V. ferruginea, V. grandis, C. odorata, S. saman* and *G. arborea*, were the most thermally stable since they lost 10% of their weight at higher temperatures than untreated specimens did. For the other species with

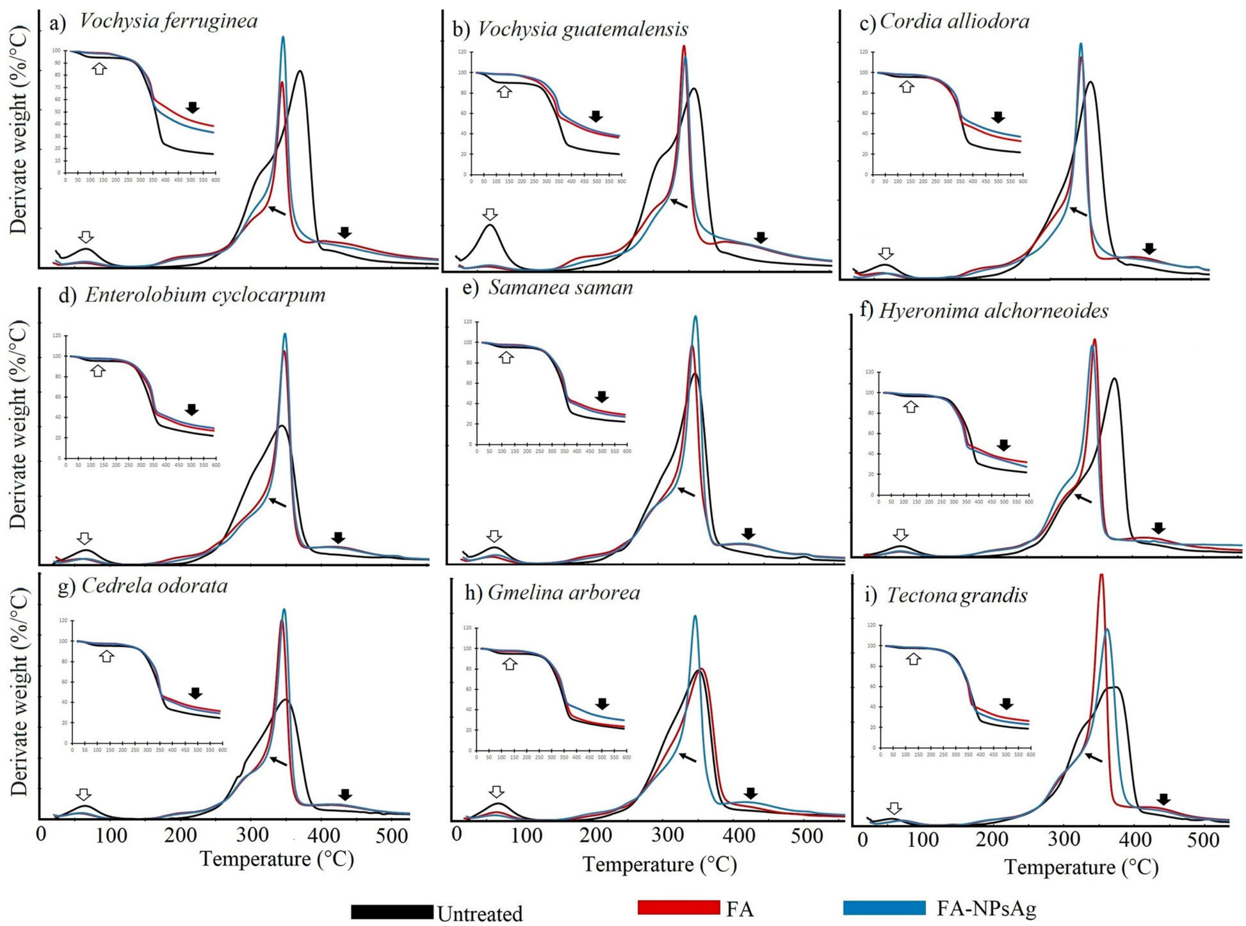


**Figure 2.** DTG analysis of wood from nine fast-growth tropical species of Costa Rica, after different furfurylation treatments.
Note: white arrow indicates water loss, thin arrow indicates shoulder between 300°C and 325°C, black arrow indicates lignin degradation.

showed lower WPG values (*E. cyclocarpum, C. alliodora, H. alchornoides* and *T. grandis*) the corresponding temperature for FA treated specimens was similar to that of untreated ones, while FA-NPsAg-treated wood showed higher temperature (Table 1). In addition, the DTG profiles indicated that, in species with a high WPG value, the shoulder between 300°C and 325°C tended to flatten, as happened in *V. ferruginea*, *V. grandis*, *C. odorata*, *S. saman* and *E. cyclocarpum* (Figure 2a–e), whereas in species with lower WPG (*C. alliodora*, *G. arborea*, *H. alchornoides* and *T. grandis*) the shoulder (300°C and 325°C) presented a shape similar to that of the untreated wood (Figure 2f–i). On the other hand, the temperature where the highest rate of weight loss was recorded varied among all species, from 339°C to 371°C (Table 1). For untreated specimens, this temperature was greater than for treated ones (FA and FA-NPsAg), with an exception for *S. saman* and *E. cyclocarpum*, where temperature of the untreated specimens was higher than that of treated ones (Table 1).

Regarding the third stage of thermal degradation, which corresponds to lignin degradation above 380°C (Demirbas, 2004, Poletto *et al.* 2010), the DTG profile revealed stronger degradation of untreated wood compared to wood treated with FA and FA-NPsAg, which was marked by black arrows in Figure 2. The species with greater WPG namely *V. ferruginea*, *V. grandis*, *C. odorata*, *S. saman* and *E. cyclocarpum* (Figure 2a–e) presented greater differences in the TGA profile than species with lower WPG, such as *C. alliodora*, *G. arborea*, *H. alchornoides* and *T. grandis* (Figure 2f–i). Regarding the assessment of the residue at 600°C, untreated specimens presented lower residual mass than treated ones (both FA and FA-NPsAg) and greater differences appeared for species with the highest WPG values (Table 1). Notably, regarding the effect of NPsAg on the residue, *V. ferruginea*, *S. saman*, *H. alchornoides*, *C. odorata* and *T. grandis* FA-treated samples showed more residual mass than the FA-NPsAg-treated samples, whereas for the rest of the species the effect was the opposite with greater residual mass for FA-NPsAg-treated specimens than for FA-treated ones.

It is well known that the three major wood constituents (cellulose, hemicelluloses, and lignin) have different thermostabilities (Lande *et al.* 2010). The thermal degradation of hemicellulose and lignin is initiated above 250°C (Tenorio and Moya, 2013, Gaitán-Álvarez *et al.* 2018, Dong *et al.* 2020), cellulose degradation as well as maximum mass loss rate occurs at around 300°C while lignin is completely degraded at temperatures over 400°C (Demirbas, 2004, Poletto *et al.* 2010, Tenorio and Moya, 2013). Considering this information, furfurylation increased thermal stability at the onset of hemicellulose and lignin degradation, as an increase in temperature to consume 10% of the mass was observed (Table 1) and the shoulder between 300°C and

**Table 1.** Thermogravimetric data of wood from nine fast-growth tropical species in Costa Rica, with different furfurylation treatments.

| | | TGA analysis | | |
|---|---|---|---|---|
| Species | Treatment | $T_{10\%}$[a] (°C) | $T_{max}$[b] (°C) | Residue at 600°C (%) |
| *Vochysiaferruginea* | Untreated | 270 | 371 | 15 |
| | FA | 273 | 346 | 38 |
| | FA-NPsAg | 277 | 340 | 33 |
| *Vochysiaguatemalensis* | Untreated | 271 | 350 | 20 |
| | FA | 269 | 343 | 36 |
| | FA-NPsAg | 282 | 346 | 38 |
| *Cordia alliodora* | Untreated | 276 | 360 | 21 |
| | FA | 267 | 346 | 33 |
| | FA-NPsAg | 277 | 344 | 37 |
| *Enterolobium cyclocarpum* | Untreated | 266 | 339 | 22 |
| | FA | 264 | 349 | 27 |
| | FA-NPs Ag | 274 | 351 | 29 |
| *Samaneasaman* | Untreated | 268 | 345 | 22 |
| | FA | 269 | 354 | 29 |
| | FA-NPsAg | 272 | 347 | 27 |
| *Hieronyma alchorneoides* | Untreated | 289 | 376 | 22 |
| | FA | 280 | 347 | 32 |
| | FA-NPsAg | 280 | 344 | 27 |
| *Cedrela odorata* | Untreated | 271 | 351 | 25 |
| | FA | 273 | 348 | 31 |
| | FA-NPsAg | 273 | 344 | 29 |
| *Gmelina arborea* | Untreated | 268 | 352 | 21 |
| | FA | 273 | 352 | 24 |
| | FA-NPsAg | 271 | 347 | 30 |
| *Tectona grandis* | Untreated | 284 | 371 | 19 |
| | FA | 281 | 362 | 26 |
| | FA-NPsAg | 281 | 354 | 23 |

[a]Temperature corresponding to 10% weight loss.
[b]Temperature corresponding to the maximum rate of weight loss.

325°C tended to fuse with degradation of cellulose and FA itself (Figure 2), yielding an apparent decrease in maximum degradation temperature. At the end of degradation, the greater amount of residue was likely caused by the formation of coal (Kong *et al.* 2018) and the improved thermal stability of furfurylated wood (Dong *et al.* 2020). Thermal stability increased upon increase of WPG, hence the non-uniform effect of furfurylation among the tested tropical species, which was greater for species that allow higher FA penetration. Furthermore, the effect of FA- NPsAg treatment on the tested species was irregular; in some species it resulted to increased thermal stability, as did the FA treatment, but this was not observed for all species. Remarkably, the use of NPsAg did not present a particular effect for any one of the species, nor did it increase thermal stability in any of them, compared to the plain FA treatment.

**Table 2.** Physical properties of furfurylated wood from nine fast-growing tropical species in Costa Rica, with and without the addition of silver nanoparticles.

| Species | Treatment | Density (kg/m$^3$) | Water absorption (%) | Janka Hardness (N) |
|---|---|---|---|---|
| *Vochysia ferruginea* | Untreated | $364.0^{A}$ | $41.7^{A}$ | $167.4^{A}$ |
| | FA | $662.0^{B}$ | $16.2^{B}$ | $177.5^{B}$ |
| | FA-NPs Ag | $527.9^{C}$ | $10.4^{C}$ | $193.0^{B}$ |
| *Vochysia guatemalensis* | Untreated | $359.0^{A}$ | $46.5^{A}$ | $143.8^{A}$ |
| | FA | $610.7^{B}$ | $17.6^{B}$ | $200.7^{B}$ |
| | FA-NPs Ag | $589.3^{B}$ | $14.2^{B}$ | $160.2^{C}$ |
| *Cordia alliodora* | Untreated | $364.7^{A}$ | $35.4^{A}$ | $179.6^{A}$ |
| | FA | $539.5^{B}$ | $28.4^{B}$ | $197.1^{B}$ |
| | FA-NPs Ag | $539.2^{B}$ | $17.2^{C}$ | $221.0^{B}$ |
| *Enterolobium cyclocarpum* | Untreated | $517.8^{A}$ | $30.9^{A}$ | $279.8^{A}$ |
| | FA | $591.8^{B}$ | $26.9^{A}$ | $264.0^{A}$ |
| | FA-NPs Ag | $557.2^{AB}$ | $16.7^{B}$ | $319.3^{B}$ |
| *Samanea saman* | Untreated | $604.1^{A}$ | $28.0^{A}$ | $413.9^{A}$ |
| | FA | $695.2^{B}$ | $24.7^{A}$ | $381.6^{A}$ |
| | FA-NPs Ag | $693.1^{B}$ | $10.5^{B}$ | $575.5^{B}$ |
| *Hieronyma alchorneoides* | Untreated | $643.9^{A}$ | $19.3^{A}$ | $416.8^{A}$ |
| | FA | $848.9^{B}$ | $8.5^{B}$ | $561.8^{B}$ |
| | FA-NPs Ag | $848.9^{B}$ | $8.7^{B}$ | $404.9^{A}$ |
| *Cedrella odorata* | Untreated | $335.6^{A}$ | $34.7^{A}$ | $133.3^{A}$ |
| | FA | $412.1^{B}$ | $28.9^{B}$ | $122.9^{A}$ |
| | FA-NPs Ag | $371.9^{AB}$ | $25.9^{B}$ | $111.2^{A}$ |
| *Gmelina arborea* | Untreated | $486.9^{A}$ | $12.1^{A}$ | $278.1^{A}$ |
| | FA | $490.4^{A}$ | $23.2^{B}$ | $247.2^{A}$ |
| | FA-NPs Ag | $576.6^{B}$ | $22.1^{B}$ | $212.2^{A}$ |
| *Tectona grandis* | Untreated | $568.2^{A}$ | $23.9^{A}$ | $367.3^{A}$ |
| | FA | $659.9^{B}$ | $15.9^{B}$ | $381.8^{A}$ |
| | FA-NPs Ag | $652.8^{B}$ | $11.9^{B}$ | $362.2^{A}$ |

Notes: Different characters indicate statistically significant differences among treatments (untreated, FA and FA-NPsAg) (99%).

### *3.2. Hardness and physical properties*

Density tests showed that the value of all species with different treatments varied between 335.65 and 848.91 kg/m$^3$, with the lowest value for *V. ferruginea* and the highest value for *H. alchornoides* (Table 2). For most of the species, density showed significant increase after FA and FA-NPsAg treatments, except for FA-treated *G. arborea*, and FA-NPsAg-treated *C. odorata* and *H. alchornoides* wood, for which no statistical difference compared to untreated wood was observed (Table 2). The lack diffrences in these three species can be attributed to that WPG values (Figure 1) were lower and that weight gain was not suffecient for to increase wood density (Lande *et al.* 2004a, 2008a, Xie *et al.* 2013).

Regarding water absorption, the lowest value was presented by *H. alchornoides* (8.51%) and the highest from *V. grandis* (46.59%). A significantly lower water absorption value was expressed by furfurylated specimens compared to untreated ones for all species except *S. saman* and *E. cyclocarpum*. A tendency towards lower water absorption of wood was observed after FA-NPsAg treatment compared to FA treated wood, however it was only statistically significant for *V. ferruginea* and *C. alliodora* (Table 2). The reduced water absorption can be attributed to the reduction of water flow inside wood (Lande *et al.* 2008a) because of FA treatment but also to the fact that furfurylation neutralises OH groups, thus reducing hygroscopicity of wood (Baysal *et al.* 2004, Lande *et al.* 2008b, Sandberg *et al.* 2017). Additionally, Xie *et al.* (2013) indicated that water absorption occurs at certain WPG levels, without reporting more details. In the present work these changes occurred at WPG higher than 25%. For WPG values lower than 20% (e.g. for *G. arborea* and *T. grandis*), no effects were observed regarding water absorption values. Also, when NPsAg was present in the FA solution, no effects on water absorption were detected, likely because either these particles had no direct effect on the OH groups of wood, or their effect was superimposed by the presence of FA (Can *et al.* 2018, 2019).

Janka hardness values varied between 1089.60 and 5505.61 N, in *C. odorata* and *H. alchornoides* respectively (Table 2). For most species, hardness was significantly increased after furfurylation treatments (FA and FA-NPsAg), as is the case in *V. ferruginea*, *V. grandis* and *C. alliodora* (Table 2), whose WPG values were high (Figure 1). However,

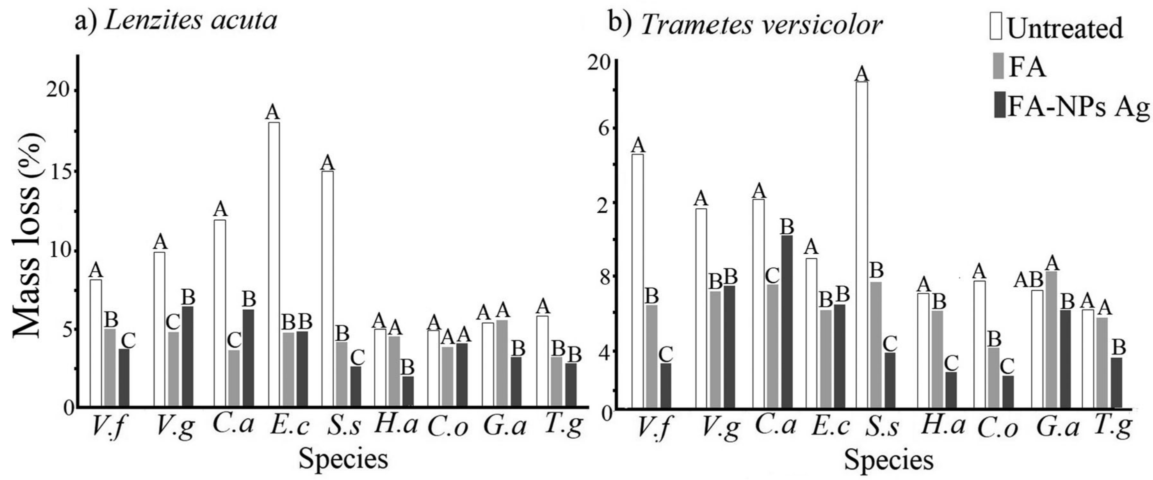


**Figure 3.** Mass loss due to the decay by *Lenzitus acuta* (a) and *Trametes versicolor* (b) in wood from nine fast-growing tropical species of Costa Rica, after two different furfurylation treatments.

Notes: different letters between treatments (untreated, FA and FA-NPsAg) indicate statistical differences at 99%.

statistical analysis showed that only *S. saman* and *H. alchornoides* presented statistically significant improvement (Table 2). It was found that for *S. saman* and *E. cyclocarpum* specimens no difference between hardness of FA-treated and untreated wood was detected, while hardness was statistically greater for FA-NPsAg-treated specimens, compared to FA treated and untreated ones. For *H. alchornoides* plain FA treatment resulted to significant increase of hardness and FA-NPsAg treatment did not induce significant change of the property. For *C. odorata*, *G. arborea* and *T. grandis,* both tested treatments did not induce significant effects on wood hardness.

The results of the present work agree with Xie *et al.* (2013) who reported significant increase of mechanical properties of wood when FA WPG exceeds 35%. Moreover, Xie *et al.* (2013) reported that, unless FA fully penetrates through the specimen thickness, no significant improvement in the properties of furfurylated wood can be expected, hence explaining why low-WPG species did not present extensive difference between FA treated and untreated wood.

### 3.3. Durability against decay

The tested treatments resulted in almost all cases to an increase of durability against the used fungi. Durability against decay by *Lenzites acuta* varied from 3.98% to 18.06% (Figure 3a). For species with WPG values over 25%, the differences between FA-treated and untreated wood regarding mass loss by *L. acuta* were greater compared to the respective differences presented by species with lower WPG values. For species with WPG under 20%, no difference in mass loss appeared between untreated and FA-treated wood, while FA-NPsAg treated specimens showed lower mass loss than those of the other two groups (Figure 3a). Regarding species' durability against *Trametes versicolor*, mass loss values varied between 3.14% and 15.06%, revealing variable durability among species like that against *L. acuta*. Species with high WPG values (*V. ferruginea*, *V. grandis*, *C. alliodora*, *E. cyclocarpum*, *S. saman*) presented the largest differences compared to untreated wood, while species with lower WPG showed differences mainly between the FA-treated and untreated wood (Figure 3b). Noticeably, mass loss was statistically lower in FA-NPsAg treated specimens, except for *V. grandis* and *E. cyclocarpum* (Figure 3b).

According to Lande *et al.* (2004a), to attain sufficient durability of wood, a WPG value of over 35% is recommended. However, in the present study it was found that species with WPG values of over 25% obtained significant results regarding decay resistance. This difference could be attributed to the great variability of natural durability among wood of the tested tropical species against decay. However, despite mass loss results in low-durability species (*V. ferruginea*, *V. grandis*, *C. alliodora*, *E. cyclocarpum* and *S. saman)* FA treatments, accompanied by high WPG values, induced high decay resistance of wood. Furthermore, in naturally durable species associated with WPG below 20% (as in *H. alchornoides*, *C. odorata*, *G. arborea* and *T. grandis*), the application of FA did not provide additional protection against decay (Figure 3). Nonetheless, NPsAg decreased weight loss in species with low WPG (*H. alchornoides*, *C. odorata*, *G. arborea* and *T. grandis*) providing additional protection to them when added to FA.

## 4. Conclusions

Upon furfurylation, wood species such as *V. ferruginea, V. grandis, C. odorata, S. saman* and *E. cyclocarpum* showed WPG values higher than 25%, while *H. alchornoides*, *C. odorata*, *G. arborea* and *T. grandis* showed WPG values lower than 20%. The 25% WPG value was considered a critical limit in the furfurylation of tropical species studied with the purpose of increasing thermal stability, water absorption and decay resistance. Yet, regarding hardness, improvement was achieved when WPG exceeded 35%.

FA treatment with the addition of NPsAg also improved the properties of wood for WPG values over 25%. However, no changes were observed compared to using a plain FA treatment regarding thermal stability, water absorption, hardness, and decay resistance. Nevertheless, the main consequence of adding NPsAg to FA was its effective added decay resistance in species with WPG under 20%, which is of great importance for the improvement of wood durability.

## Authors' contribution

J. Gaitán-Alvarez: tree cutting, wood material sampling, determination of wood properties, running the data analysis; A. Berrocal: laboratory experiments, data analysis; C. Lykidis: analysis of the results, editing and review of the paper; R. Moya: designing of the experiment, tree sampling, writing the paper, coordinating the research project; G.I. Mantanis: overall design of the experiment, writing the paper, final review and final editing of the paper.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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