




## Article

# Physical and Chemical Changes in Hydrothermally Modified Wood

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**Abstract:** In this study, the simulation of artificial conditions, containing various chemical additives similar to a bog environment, was hypothesised as a relatively short way to develop a more sustainable wood product with better properties. This study aimed to determine how hydrothermal treatment with different iron additives with and without tannic acid, performed at 100 °C for 75 h, changed the mass and density of wood of different tree species (*Pinus sylvestris* L., *Picea abies* (L.) H. Karst., *Pseudotsuga menziesii* (Mirb.) Franco, *Juglans regia* L., and *Acer platanoides* L.); total phenolic compounds in biobased solvents after the hydrothermal processing and iron concentration in different wood layers. We also aimed to determine the wood chemical composition using Fourier-transform infrared technique. The study results showed that the softwood samples were more susceptible to hydrothermal modification than the hardwood samples, indicated by minorly different intensities on infrared spectra. The FTIR results showed bands of hardwood and softwood samples which along with the spectral characterisation of the wood constituents, which can further be utilized for creating a larger FTIR spectral database of wood samples for their identification. The factors with the most significant effect on the hydrothermal modification were tannic acid and inorganic Fe<sub>3</sub>O<sub>2</sub> salt, used as an additive. The results indicated the suitability of inorganic Fe<sub>3</sub>O<sub>2</sub> salt and tannic acid combination applied in this type of modification, because a higher concentration of iron was distributed on the inner and intermediate sublayers of wood samples. The hydrothermal modification approach to anchor tannic acid–Fe macromolecules in wood shown in this study has promising capabilities and may attract interest in the field of wood protection against weathering.

**Keywords:** iron oxides; iron salt; tannic acid; total phenolic compounds; mass loss; wood density



**Citation:** Varnagirytė-Kabašinskiė, I.; Pukalskiė, M.; Šilinskas, B.; Škėma, M.; Aleinikovas, M. Physical and Chemical Changes in Hydrothermally Modified Wood. *Forests* **2021**, *12*, 1771. <https://doi.org/10.3390/f12121771>

Academic Editor: Luis García Esteban

Received: 11 November 2021

Accepted: 13 December 2021

Published: 14 December 2021

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## 1. Introduction

Wood, chemically described as a polymeric composite of cellulose, hemicellulose, and lignin, is an economically important renewable resource widely used as an environmentally friendly material with properties suitable for industry and the private sector. Despite good natural wood properties, the requirements for wood or wood-based construction products are growing. The biodegradability, dimensional nonstability under varying moisture contents, and degradability by ultraviolet (UV) light often limit the use of natural wood and its products. Under outdoor exposure conditions, wood undergoes the photooxidation or photochemical degradation process: the colour changes, followed by the loss of fibres, and surface erosion is often observed [1–3]. The wood properties change due to internal chemical reactions, and wood strength is lost as it biologically degrades due to oxidation, hydrolysis, and dehydration reactions [4,5].

Different wood modification processes, such as thermal modification at elevated temperatures, chemical acetylation with acetic anhydride, furfurylation with furfural

alcohol, or treating with modifying resins, using pressure methods, etc., often create value-added wood products [4,6–13]. The modified wood and wood products are widely used in different interior and exterior applications [14,15].

Chemical wood modification is costly and time-consuming, and requires fastidious processing. Therefore, heat treatment is one of the more appropriate solutions due to its cost-effectiveness and environmental friendliness. Previous studies indicated that heat treatment affects wood colour stability when it is exposed to UV radiation, and improves biological durability and dimensional stability [3,16–18]. Along with the thermal processing of wood, different biobased extracts, oils, waxes, resins, and phenolic compounds, as natural preservatives, can be additionally used. Generally, such complex wood treatment could be an alternative to protect wood against wood destructive organisms and weathering degradations. Additionally, it does not cause toxicity to the environment [19,20].

Wood contains many phenolic compounds, such as lignin and tannin. The main phenolics contained in tree wood and bark are hydrolysable and condensed tannins, which are the combinations of simple phenols, such as pyrogallol and ellagic acid, and of esters of sugar, primarily glucose, along with gallic and digallic acids. The tannins act as agents with metals because both have the potential to oxidize the phenol groups (antioxidant) and to complex the metal by ortho-diphenol complexation. The biological activity of tannins is linked to their antioxidant property [21,22]. According to Dai and Mumper (2010) [23], plant phenolics are involved in the defence process against UV radiation, pathogens, parasites, and predators, and contribute to plants' colour. Therefore, these compounds act as predominant contributors to wood fragrance and durability. Often, iron ions are used in the qualitative analyses of various phenolic compounds because iron ions react easily with the phenolics producing colouring substances.

Following the sustainable supply of forest products, it becomes important to test different wood modifications to obtain high-value wood products. The development of wood products is also a challenge for maintaining environmental sustainability and protecting the environment [24]. Based on specific natural processes, it has been observed that trees in the bog environment have undergone a chemical change over the years. The bogwood can be obtained from any tree species that naturally grow in the bog or nearby bog, including oak and pine. Under acidic conditions, wood tannins react with iron salts and other minerals, which gradually change wood colour to dark brown or black. The anaerobic conditions and low oxygen protect the wood from decay, increase wood hardness, and weaken the decomposition process. Overall, naturally modified wood is characterised by good quality, high resistance to environmental conditions, and similarity to the most expensive tropical tree species. Despite the challenging extraction conditions, rarity, and costliness, the use of bogwood in science and industry is quite extensive. Due to the high durability of wood, dendrochronologists can obtain information on long-term changes in climate or tree growth conditions; due to its special aesthetic qualities and natural colour it is highly valued in the furniture industry, woodworking, and carvings. The simulation of a specific bog environment for wood ecomodification was hypothesised as an accelerated way to develop a sustainable wood product. Grosse et al. (2019) [25], aiming to improve the wood properties, treated wood with lactic acid-based treatments with the addition of chestnut tannins. Their results showed increased biological resistance and product persistence of modified wood.

This study was based on the search for environmentally friendly wood modification technologies to improve the physical and chemical properties of wood. The aim of this study was to determine the influence of different thermal treatments with additives  $\text{Fe}_2\text{O}_3$  or  $\text{FeCl}_3$  in combination with tannic acid on the following issues: (1) the changes of mass, volume, and density of wood, obtained from different tree species—*Pinus sylvestris* L., *Picea abies* (L.) H. Karst., *Pseudotsuga menziesii* (Mirb.) Franco, *Juglans regia* L., and *Acer platanoides* L.; (2) the changes of total phenolic compounds (TPC) in biobased solvents after the hydrothermal processing of different tree species wood; (3) the changes of Fe

concentration in different wood layers; and (4) to analyse wood chemical composition using Fourier-transform infrared (FT-IR) technique.

## 2. Materials and Methods

The wood samples obtained from Scots pine (*Pinus sylvestris*), Norway spruce (*Picea abies*), Douglas fir (*Pseudotsuga menziesii*), walnut (*Juglans regia*) and Norway maple (*Acer platanoides*) were used to determine the influence of different hydrothermal treatments with additives Fe<sub>2</sub>O<sub>3</sub> or FeCl<sub>3</sub> with and without tannic acid. The sets of 20 wood samples of 20 × 20 × 30 mm dimensions from each tree species were exposed to the following treatments: H<sub>2</sub>O + 16 g FeCl<sub>3</sub>; H<sub>2</sub>O + 16 g FeCl<sub>3</sub> + 50 g tannic acid; H<sub>2</sub>O + 16 g Fe<sub>2</sub>O<sub>3</sub>; H<sub>2</sub>O + 16 g Fe<sub>2</sub>O<sub>3</sub> + 50 g tannic acid; H<sub>2</sub>O + no additives (control). It was assumed that the selected additives and their concentrations were the lowest possible concentrations to cause the least impact on the environment, therefore, these solvents were assessed as biobased solvents. The wood samples were immersed into the biobased solvents and boiled at a constant temperature of 100 °C in a laboratory pot for 75 h (hereafter, hydrothermal treatment). More specific details about the experiment were provided in Aleinikovas et al. (2021) [26].

For the assessment of the concentrations of extractible phenolics, the biobased solvents with Fe<sub>2</sub>O<sub>3</sub> or FeCl<sub>3</sub> and with or without tannic acid after the processing of each tree species were sampled into individual laboratory test tubes and transported to the laboratory. The chemical study was focused to compare the concentrations of extractible phenolics from pine, spruce, fir, walnut, and maple. Total phenolic compounds in the biobased solvents after processing were semiquantitatively evaluated with a Folin–Ciocalteu reagent [27]. According to this procedure, the commercial reagent was diluted with distilled water at a ratio of 1:10. The reaction mixture was prepared by mixing 150 µL of tested solvent after thermal treatment, 750 µL of Folin–Ciocalteu reagent solution, and 600 µL of 7.5 percent sodium carbonate solution. The absorption was read after 60 min at λ = 765 nm. The samples were prepared in triplicate for each analysis and the mean value of absorbance was obtained. The same procedure was repeated for the standard solution of gallic acid, and the calibration line was construed ( $y = 10.8386x + 0.036$ ,  $R^2 = 0.993$ ). The TPC was expressed in mg gallic acid equivalents (GAE) per 1 kg of tested wood species after processing.

For the assessment of mass and volume changes of wood samples, all wood samples were oven-dried to constant weight before and after the treatment processing, and then the mass and volume of the samples were measured.

For the assessment of Fe concentration in wood, the treated wood samples were removed from the biobased solvents and prepared following this scheme: each sample was cut into three subsamples/layers, representing the outer, intermediate, and inner wood layers with the thickness of 2 mm per layer. Total Fe concentration was analysed by inductively coupled plasma optical emission spectroscopy according to the LST EN ISO 16968:2015.

The aromatic structure intensities and functional group identification of untreated (control) and treated wood samples were studied using Fourier-transform infrared (FT-IR) technique. FT-IR spectroscopy has often been used to investigate wood chemical composition. This method requires a simple sample preparation, is nondestructive, and uses a small sample amount. The FT-IR analyses were separately performed on the wood samples of each tested wood species. The FT-IR measurements with attenuated total reflection technique (ATR) were recorded using a Bruker Vertex 70 v (Bruker Daltonic, Bremen, Germany) spectrometer equipped with a diamond crystal ATR cell as a sample holder. The wood samples were sliced by microtome. The FT-IR spectra of wood samples were acquired in the range of 400–3800 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. The instrument chamber was evacuated below 350 Pa during spectra acquisition to eliminate interference from CO<sub>2</sub> and water vapor bands. The resulting spectra were an average of 300 scans (100 scans at three random points). The spectra were normalized, and baseline corrections were made.

To determine the significant differences of wood parameters, the content of total phenolic compounds, and Fe concentration in different wood layers between different treatments, ANOVA and Tukey's Studentized Range (HSD) test were used. The different letters next to the mean values show statistically significant differences at  $p < 0.05$  between the treatments. The obtained data were analysed using the statistical package SAS 9.4 (SAS Institute Inc., Wake County, NC, USA).

### 3. Results and Discussion

#### 3.1. Changes of Wood Mass, Volume and Density after Treatment

The hydrothermal processing itself, when the control treatment without additives was used, caused wood mass loss by 4.2–5.3 percent for pine, spruce, and maple, and by 9.2–10.4 percent for fir and walnut wood (Table 1). When wood samples were treated with  $\text{Fe}_2\text{O}_3$ , the mass of wood samples decreased slightly by 2–4 percent for all species, except spruce wood, which mass did not change. When wood samples were treated with the pure additive  $\text{Fe}_2\text{O}_3$ , the mass of wood samples decreased by 3.5–5.8 percent for all species, except fir wood, which decreased by 15.0 percent. The treatment with the additives  $\text{Fe}_2\text{O}_3$  and tannic acid responded to the relatively slight mass loss for spruce, fir, maple, and walnut. The highest loss of mass was fixed in the wood treated with the pure additive  $\text{FeCl}_3$ . The difference from the untreated wood of the same species ranged from 13.7–15.6 percent for pine, spruce, fir, and walnut to 20.7 percent for maple.

The thermal processing and different treatments caused the different responses of wood volume (Table 1). After the control treatment, wood volume decreased by 1.8–2.6 percent for fir and maple, 7.7–10.1 percent for pine, spruce, and walnut. Pure  $\text{Fe}_2\text{O}_3$  induced wood volume reduction from 2.6–3.8 percent for fir, maple, and walnut to 7.6–8.4 percent for pine and spruce. In this case, the addition of tannic acid caused higher wood volume reduction only for maple wood. The thermal processing with the pure additive  $\text{FeCl}_3$  reduced wood volume by 9.2–11.4 percent for all species, except fir, in which volume decreased only by 3.8 percent. When tannic acid was added together with  $\text{FeCl}_3$ , the wood volume decrease was slightly reduced. The obtained changes in wood density were different both between different treatments and between tree species (Table 1). The control treatment caused the increase in pine and spruce wood density, the decrease in fir wood density, and had no impact on maple and walnut wood density. Similar changes in wood density were obtained after the treatment with the additive  $\text{Fe}_2\text{O}_3$ , showing the increased wood density of pine and spruce. The thermal treatment with the additive  $\text{FeCl}_3$  decreased the wood density of all tree species. The highest changes of 10.5–12.1 percent from untreated wood were obtained for the fir and maple wood.

The mass loss of hydrothermally treated wood is often found due to wood thermal degradation [28,29]. Different studies showed contradictory data obtained from different wood treatment experiments: the data varied due to wood species, initial moisture contents, and treatment intensities. Tenorio and Moya [28] studied mass loss along with heat treatment and found its dependence on wood species, specifics of the drying process, and treatment intensity. Chaouch et al. [30] found that hardwoods (*Fagus sylvatica* L., *Populus nigra* L., *Fraxinus excelsior* L.) were more sensitive to thermal degradation than softwoods (*Pinus sylvestris* L., *Abies pectinate* Lam.), as demonstrated by the higher mass losses recorded for the same treatment duration. Only small mass losses were observed due to vaporization of volatile extractives and of bound water absorbed on the wood fibres until 160 °C and thermal degradation began at higher temperatures [30]. Earlier findings also indicated that wood species of lower densities generally are more resistant to thermal treatment than those of higher density, and this was explained by the intrinsic thermal properties of each wood species.

**Table 1.** Changes of wood mass, volume and density after treatment. Different letters a, b, c, d and e given next to the mean value show statistically significant differences between the treatments for each tree species at  $p < 0.05$  ( $n = 20$ ).

Treatment *	Changes (Percent) of Wood Parameters		
	Mass	Volume	Density
Scots pine <i>Pinus sylvestris</i> L.			
Control	$-5.3 \pm 0.3^c$	$-9.2 \pm 2.6^b$	$+4.4 \pm 3.1^c$
Fe <sub>2</sub> O <sub>3</sub>	$-4.1 \pm 0.7^d$	$-7.6 \pm 1.3^{bc}$	$+3.9 \pm 1.7^c$
FeCl <sub>3</sub>	$-15.6 \pm 0.8^a$	$-11.1 \pm 1.3^a$	$-5.0 \pm 1.9^a$
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	$+3.8 \pm 2.7^e$	$-5.9 \pm 3.1^c$	$+10.4 \pm 5.2^d$
FeCl <sub>3</sub> + tannic acid	$-8.9 \pm 1.1^b$	$-7.9 \pm 1.3^b$	$-1.1 \pm 1.8^b$
Norway spruce <i>Picea abies</i> (L.) H. Karst.			
Control	$-4.8 \pm 0.4^c$	$-7.8 \pm 2.3^b$	$+3.3 \pm 2.7^b$
Fe <sub>2</sub> O <sub>3</sub>	$-5.8 \pm 0.5^{bc}$	$-8.4 \pm 2.7^{ab}$	$+3.0 \pm 3.2^b$
FeCl <sub>3</sub>	$-13.7 \pm 2.5^a$	$-10.5 \pm 2.1^a$	$-3.6 \pm 3.0^a$
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	$-0.6 \pm 0.1^d$	$-3.7 \pm 0.8^b$	$-5.0 \pm 1.1^c$
FeCl <sub>3</sub> + tannic acid	$-6.4 \pm 0.7^b$	$-7.8 \pm 1.1^b$	$+1.5 \pm 1.3^b$
Douglas fir <i>Pseudotsuga menziesii</i> (Mirb.) Franco			
Control	$-10.4 \pm 1.2^b$	$-1.8 \pm 0.7^b$	$-8.7 \pm 1.3^b$
Fe <sub>2</sub> O <sub>3</sub>	$-15.5 \pm 1.5^a$	$-3.8 \pm 0.9^a$	$-12.1 \pm 2.0^a$
FeCl <sub>3</sub>	$-15.5 \pm 1.5^a$	$-3.8 \pm 0.9^a$	$-12.1 \pm 2.0^a$
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	$-4.5 \pm 1.1^c$	$-0.7 \pm 0.9^c$	$-3.9 \pm 1.2^c$
FeCl <sub>3</sub> + tannic acid	$-10.8 \pm 1.5^b$	$-1.9 \pm 0.8^b$	$-9.1 \pm 1.9^b$
Norway maple <i>Acer platanoides</i> L.			
Control	$-4.2 \pm 0.5^d$	$-2.6 \pm 0.7^d$	$-1.7 \pm 0.8^c$
Fe <sub>2</sub> O <sub>3</sub>	$-3.5 \pm 1.1^d$	$-2.6 \pm 0.6^d$	$-1.0 \pm 1.4^c$
FeCl <sub>3</sub>	$-20.7 \pm 1.4^a$	$-11.4 \pm 1.7^a$	$-10.5 \pm 1.8^a$
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	$-6.3 \pm 0.6^c$	$-7.0 \pm 1.2^c$	$+0.8 \pm 1.6^d$
FeCl <sub>3</sub> + tannic acid	$-14.5 \pm 1.4^b$	$-9.2 \pm 2.2^b$	$-5.8 \pm 2.8^b$
Walnut <i>Juglans regia</i> L.			
Control	$-9.2 \pm 1.5^b$	$-10.1 \pm 1.4^a$	$+1.1 \pm 2.3^c$
Fe <sub>2</sub> O <sub>3</sub>	$-4.3 \pm 0.7^c$	$-3.3 \pm 1.5^c$	$-1.0 \pm 2.0^{bc}$
FeCl <sub>3</sub>	$-13.9 \pm 1.9^a$	$-9.2 \pm 1.4^{ab}$	$-5.2 \pm 3.1^a$
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	$-3.4 \pm 0.8^c$	$-3.7 \pm 1.5^c$	$+0.4 \pm 2.1^b$
FeCl <sub>3</sub> + tannic acid	$-9.8 \pm 2.0^b$	$-8.1 \pm 1.3^b$	$-1.9 \pm 3.3^b$

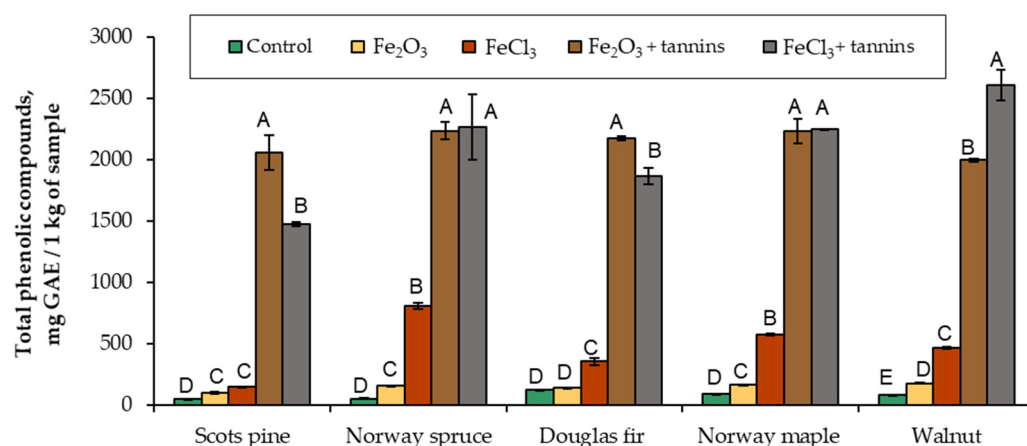
\* Note: the plus and minus signs, + and −, given next to the values indicate the increase and the decrease in the value.

### 3.2. Chemical Changes of Solutions, Used for Hydrothermal Wood Treatments

The biobased solvents, obtained after the thermal treatment using the different additives (Fe<sub>2</sub>O<sub>3</sub>; FeCl<sub>3</sub>, and tannic acid) and the control without additives, were chemically analysed for the solvent pH and the content of the total phenolic compound. The pH values of control wood biobased solvents were in the range of 3.05–3.84, depending on wood species (data not shown). The pH values of biobased solvents with FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> additives after hydrothermal treatment decreased around 5.8 percent and 9.2 percent with respect to the control sample of FeCl<sub>3</sub>. The reduction in pH values indicated that changes arose from the strong acidity and the solid–solid reaction and formation of acidic functional groups on the surface of the wood. Acidic conditions may act as a depolymerization catalyst that further increases decomposition causing loss of mass, density, and mechanical properties. This result can be confirmed from the mass loss data shown in Table 1, where the mass of pine wood samples decreased 15.6 percent, spruce wood 3.7 percent, fir 15.5 percent, maple 20.7 percent, and walnut 13.9 percent, indicating significant reactions and changes in carbon skeleton structures from the transformation of organic matter in aqueous

phase via temperature and acidic hydrolysis [31]. In addition, the components such as proteins or polysaccharides also began to hydrolyse at a hydrothermal temperature higher than 100 °C, which also affected changes in pH values of analysed biobased solvents. The solvents with Fe<sub>2</sub>O<sub>3</sub> additive showed different results with respect to the control sample. In this case, the pH values of the solvents decreased by 0.5–2.6 percent. The obtained results showed a similar trend to the mass loss data (see Table 1), where mass loss ranged between 4.1 and 5.8 percent, (except for fir wood, where mass decreased 15.5 percent). A similar tendency was observed in the solvents obtained after wood treatment with tannic acid.

The total polyphenol content of biobased solvent samples was analysed by the Folin–Ciocalteu method (Figure 1). The measured exchanges of total phenolic compounds (TPC) have different behaviour depending on the wood species studied. In general, the increased content of TPC in the solvents was observed in all tested samples with different additives with respect to the control sample. The content of TPC in the solvents with FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> additives depended only on wood species. Differences were observed of analysed solvents with Fe<sub>2</sub>O<sub>3</sub> additive, where TPC concentration did not increase significantly with respect to the control sample. Unfortunately, we could not find any similar results to compare with the data published previously. However, these results indicate the hypothesis that solvent-soluble compounds during thermal processing can cause an accumulation of the discoloured compounds on the surface due to migration from the inner wood when the solvent evaporates. This reaction is usually caused by a chemical interaction between iron ions and wood compounds, such as hydrolysable tannins, which form nonextractable compounds and increase the stain and durability of wood [32]. Meanwhile, the TPC concentration in the solvents with FeCl<sub>3</sub> additive increased about 1.5–2.3-fold with respect to the control samples. This indicates solubilization of the phenolic compounds found in wood, depending on pH media. Temperature and acidic medium might encourage hydrolysis associated with the release of certain phenolic compounds that are not initially soluble in water (for example, condensed tannin) or partially hydrolysed lignin fragments. Furthermore, the hydrolysis may also depend on wood species as in the case of phenolic compounds [33]. The kinetics of the reactions depends on hydrolysis as well as the mass transfer of the water to the molecules and the diffusion of the molecules from the wood to the solution [34]. The combined influence of FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> and tannic acid showed that determined TPC contents were similar, except for the solvents obtained from pine and fir samples, where the TPC extraction contents significantly increased in the solvents with Fe<sub>2</sub>O<sub>3</sub> and tannic acid additives. The concentrations of TPC were 0.8–1.3-fold higher than in biobased solvents with FeCl<sub>3</sub> and tannic acid additive, compared with FeCl<sub>3</sub> without additives. In the case of spruce, maple, and walnut, a minor variation was observed between the tested biobased solvents with Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> and tannic acid additive, although this was not significant when observed on the experimental field. Usually, water, iron, and phenolic substances enrich the colour of the wood. When iron dissolves in water, iron ions are produced since wood is an acidic substance, and together with iron ions undergoes partial hydrolysis in an exothermic reaction. The strongly acidic solution may accelerate ionization by oxygen, in this case, iron ions react with hydroxyl groups in phenolic compounds in wood and promote a dark colour and durability of the wood [32].



**Figure 1.** Content of total phenolic compounds (mg GAE—gallic acid equivalent/1 kg of the sample after processing) in the solvents after different treatments of different tree species. Bars show standard deviation of mean; different letters given above the bar show statistically significant differences between the treatments for each tree species at  $p < 0.05$  ( $n = 3$ ).

### 3.3. Fe Concentration in Treated Wood

Tannins, extracted from wood material, have good compatibility and may form covalent bonds with hydroxyl groups on the surface of wood fibres. In this study, we used tannic acid, FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in an aqueous solution to improve some properties of wood. It is expected that this simple, green technology can improve the functionality of wood by attracting iron ions from water to some extent. The concentration of iron in the wood after different treatments showed large variability between the treatments and wood species (Table 2). In this section, the emphasis was put on the analysis of the modification effect of the iron complex on the wood surface, where a sublayers analysis was performed every 2 mm. Compared to the control samples, the content of Fe ions increased 3–15-fold in the intermediate layer, and 2–8-fold in the inner layer, depending on the different tree species. After hydrothermal treatment with FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> additives, the content of iron on the outer surface of the wood increased significantly compared to the control. For instance, on the outer layer of pine wood the concentration of iron increased 77- and 48-fold, maple wood 42- and 12-fold, and walnut wood 29.6- and 15.8-fold, respectively. In general, the obtained results showed that a higher concentration of iron was accumulated on the surface when wood samples were treated with the Fe<sub>2</sub>O<sub>3</sub> additive. According to Wang et al. (2015) [35] and Zhang et al. (2012) [36], thermal treatment could enhance the magnetic properties of Fe<sub>2</sub>O<sub>3</sub> and positive charges on surface hydroxyl groups, which were composed by the protonation and deprotonation. New active sites could be formed through electrostatic interaction with positive charges and attract iron ions. Slightly different results were obtained from wood samples treated with FeCl<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> with tannic acid. The concentration of iron on the outer wood surface was lower compared to the wood species treated without tannic acid additive. For instance, the amount of iron ions on the layer of spruce wood treated with Fe<sub>2</sub>O<sub>3</sub> was 2.2-fold higher than that treated with Fe<sub>2</sub>O<sub>3</sub> with tannic acid additive. However, the concentration of iron ions in the intermediate and inner layers were 2.6- and 2.2-fold higher than wood treated with Fe<sub>2</sub>O<sub>3</sub> with tannic acid additive, respectively. The same tendencies were observed for other studied wood species. It showed interesting interactions by forming complexes of tannic acid and metal ions. Unfortunately, we could not find any similar results to compare with the data published previously. However, according to Ma et al. (2020) [37], a tannic acid and metal complex was able to generate rough hierarchical structures on the surface of the wood. A study by Huang et al. (2020) [38] showed that ferrous sulphate reacted with tannic acid to form a complex of ferrous–tannic acid. This complex was unstable and was easy to oxidize to form ferric tannate composite, which resulted in the coexistence of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the composites immobilized on wood fibres. Tannic acid–Fe complexes may adhere to the surface of

wood fibres via strong covalent bonds [38]. There, abundant phenolic hydroxyl groups on the surface of tannic acid make the tannin–Fe complex on the surface of the modified material more hydrophilic. Therefore, it is possible that Fe<sup>2+</sup> ions may be absorbed into intermediate and inner wood layers due to the chelation properties of tannic acid, and the ability to form the tannin–Fe complex.

**Table 2.** Mean Fe concentration (mg kg<sup>−1</sup>) in sublayers (outer, intermediate, and inner wood layers with the thickness of 2 mm per layer) after the thermal treatment. Different letters a, b, c, d and e given next to the mean value show statistically significant differences between the treatments for each tree species at  $p < 0.05$  ( $n = 20$ ).

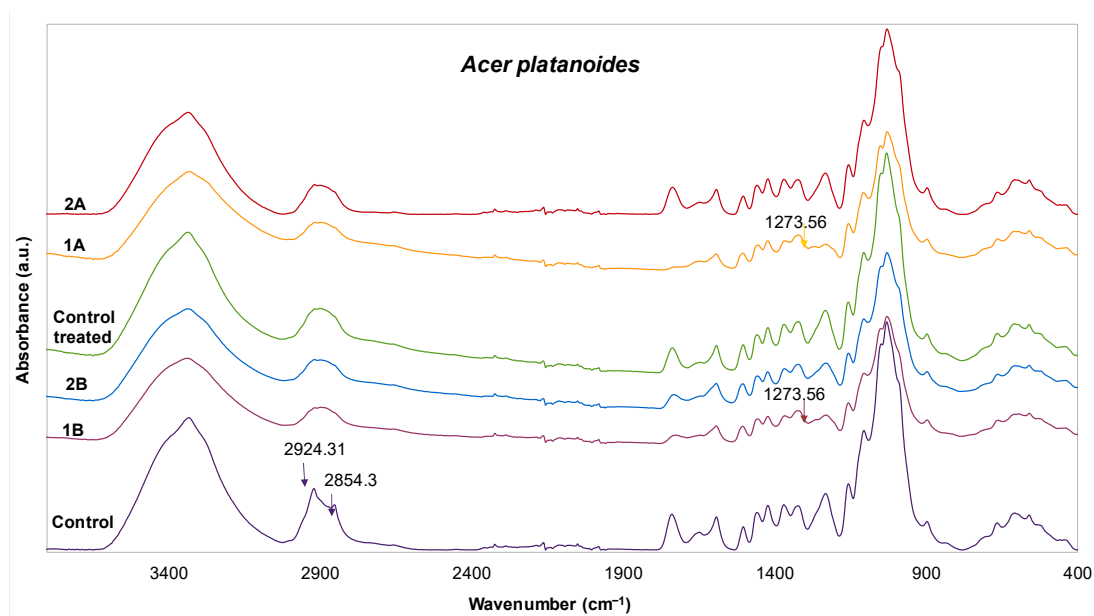
Treatments	Mean Fe Concentration (mg kg <sup>−1</sup> )		
	Outer Sublayer	Intermediate Sublayer	Inner Sublayer
Scots pine <i>Pinus sylvestris</i> L.			
Control *	111.40 ± 3.70 <sup>d</sup>	111.40 ± 3.70 <sup>d</sup>	111.40 ± 3.70 <sup>d</sup>
Fe <sub>2</sub> O <sub>3</sub>	8548.48 ± 1925.16 <sup>a</sup>	473.60 ± 32.44 <sup>c</sup>	372.59 ± 37.68 <sup>b</sup>
FeCl <sub>3</sub>	5358.97 ± 426.94 <sup>b</sup>	653.31 ± 141.13 <sup>b</sup>	322.49 ± 12.79 <sup>c</sup>
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	3903.08 ± 1481.83 <sup>c</sup>	1080.95 ± 87.68 <sup>a</sup>	876.34 ± 52.31 <sup>a</sup>
FeCl <sub>3</sub> + tannic acid	3224.85 ± 393.19 <sup>c</sup>	585.27 ± 91.34 <sup>b</sup>	383.67 ± 22.98 <sup>b</sup>
Norway spruce <i>Picea abies</i> (L.) H. Karst.			
Control	45.00 ± 0.48 <sup>d</sup>	45.00 ± 0.48 <sup>d</sup>	45.00 ± 0.48 <sup>d</sup>
Fe <sub>2</sub> O <sub>3</sub>	12,453.94 ± 2096.81 <sup>a</sup>	354.39 ± 78.38 <sup>d</sup>	324.36 ± 26.11 <sup>c</sup>
FeCl <sub>3</sub>	8589.60 ± 1161.92 <sup>b</sup>	1703.88 ± 371.60 <sup>b</sup>	763.20 ± 143.67 <sup>b</sup>
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	5608.70 ± 700.68 <sup>c</sup>	937.37 ± 126.64 <sup>c</sup>	770.43 ± 128.01 <sup>b</sup>
FeCl <sub>3</sub> + tannic acid	7510.81 ± 1209.56 <sup>b</sup>	2798.82 ± 823.61 <sup>a</sup>	1094.26 ± 108.84 <sup>a</sup>
Douglas fir <i>Pseudotsuga menziesii</i> (Mirb.) Franco			
Control	103.85 ± 2.48 <sup>d</sup>	103.85 ± 2.48 <sup>d</sup>	103.85 ± 2.48 <sup>e</sup>
Fe <sub>2</sub> O <sub>3</sub>	14,189.04 ± 2520.21 <sup>a</sup>	751.68 ± 155.74 <sup>b</sup>	565.20 ± 63.27 <sup>b</sup>
FeCl <sub>3</sub>	4457.39 ± 715.83 <sup>b</sup>	685.24 ± 60.76 <sup>b</sup>	405.52 ± 19.01 <sup>c</sup>
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	4059.72 ± 410.19 <sup>b</sup>	1365.48 ± 64.82 <sup>a</sup>	1157.76 ± 7.03 <sup>a</sup>
FeCl <sub>3</sub> + tannic acid	2888.95 ± 218.92 <sup>c</sup>	500.15 ± 36.90 <sup>c</sup>	325.58 ± 28.54 <sup>d</sup>
Norway maple <i>Acer platanoides</i> L.			
Control	37.61 ± 3.01 <sup>e</sup>	37.61 ± 3.01 <sup>d</sup>	37.61 ± 3.01 <sup>d</sup>
Fe <sub>2</sub> O <sub>3</sub>	15,966.13 ± 1495.33 <sup>a</sup>	9327.27 ± 1129.27 <sup>a</sup>	7851.80 ± 651.68 <sup>a</sup>
FeCl <sub>3</sub>	4794.83 ± 1364.64 <sup>b</sup>	988.27 ± 312.80 <sup>b</sup>	608.28 ± 73.77 <sup>bc</sup>
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	3265.34 ± 451.30 <sup>c</sup>	943.79 ± 173.76 <sup>bc</sup>	707.02 ± 126.17 <sup>b</sup>
FeCl <sub>3</sub> + tannic acid	1851.71 ± 367.27 <sup>d</sup>	492.28 ± 117.50 <sup>cd</sup>	407.38 ± 44.58 <sup>c</sup>
Walnut <i>Juglans regia</i> L.			
Control	196.00 ± 8.74 <sup>d</sup>	196.00 ± 8.74 <sup>d</sup>	196.00 ± 8.74 <sup>e</sup>
Fe <sub>2</sub> O <sub>3</sub>	5808.97 ± 3140.73 <sup>a</sup>	516.66 ± 100.55 <sup>c</sup>	243.80 ± 18.63 <sup>d</sup>
FeCl <sub>3</sub>	3113.23 ± 365.63 <sup>bc</sup>	791.47 ± 65.74 <sup>b</sup>	614.88 ± 10.11 <sup>b</sup>
Fe <sub>2</sub> O <sub>3</sub> + tannic acid	4260.61 ± 643.11 <sup>b</sup>	1576.83 ± 47.91 <sup>a</sup>	1179.18 ± 66.29 <sup>a</sup>
FeCl <sub>3</sub> + tannic acid	2185.00 ± 189.69 <sup>c</sup>	828.16 ± 127.60 <sup>b</sup>	566.69 ± 6.42 <sup>c</sup>

\* The data for the control treatment were obtained from one wood sample, not from its separate layers because no Fe was added to the control treatment; the obtained minor Fe concentration in the control indicates the background Fe concentration.

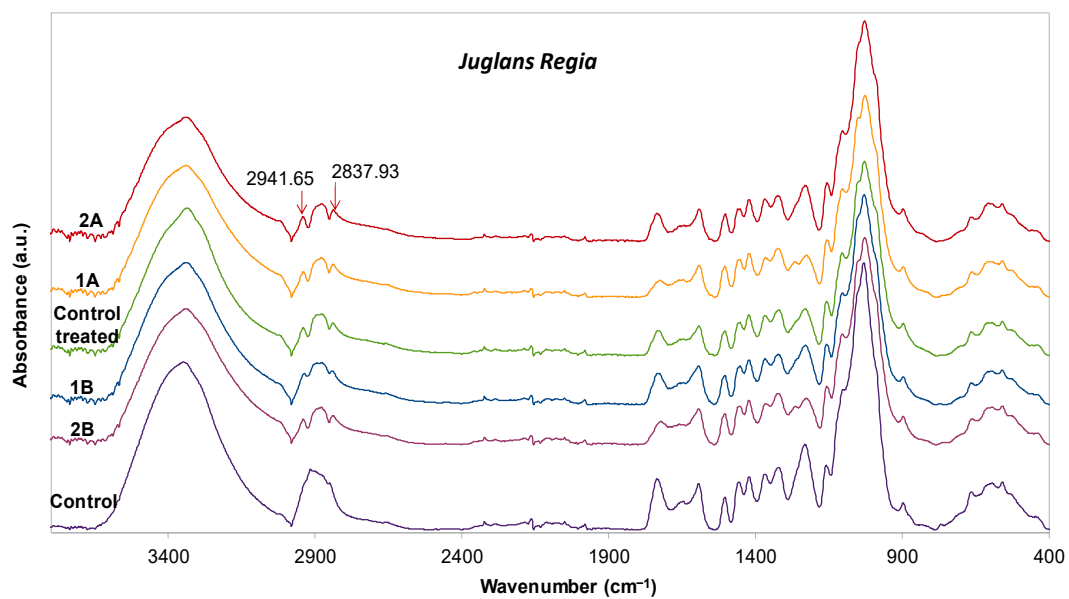
### 3.4. FTIR Analysis of Wood Samples

Hydrothermal treatment with various additives was used to increase hardwood and softwood functionality. The FTIR spectra of obtained control and studied hardwood and softwood samples indicated the fingerprint regions (Figures 2–6).

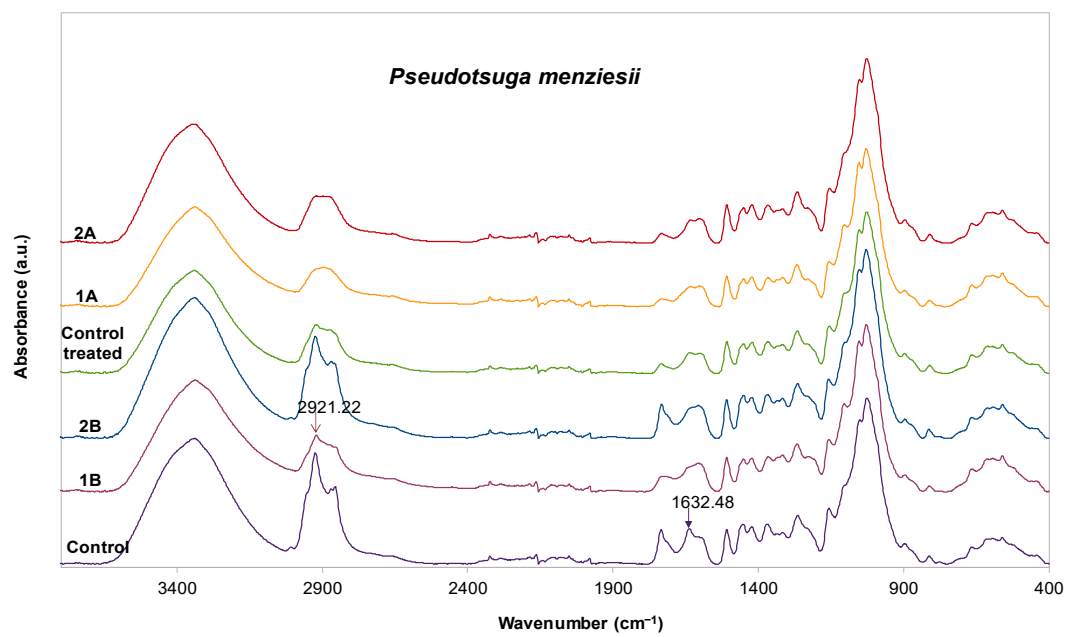




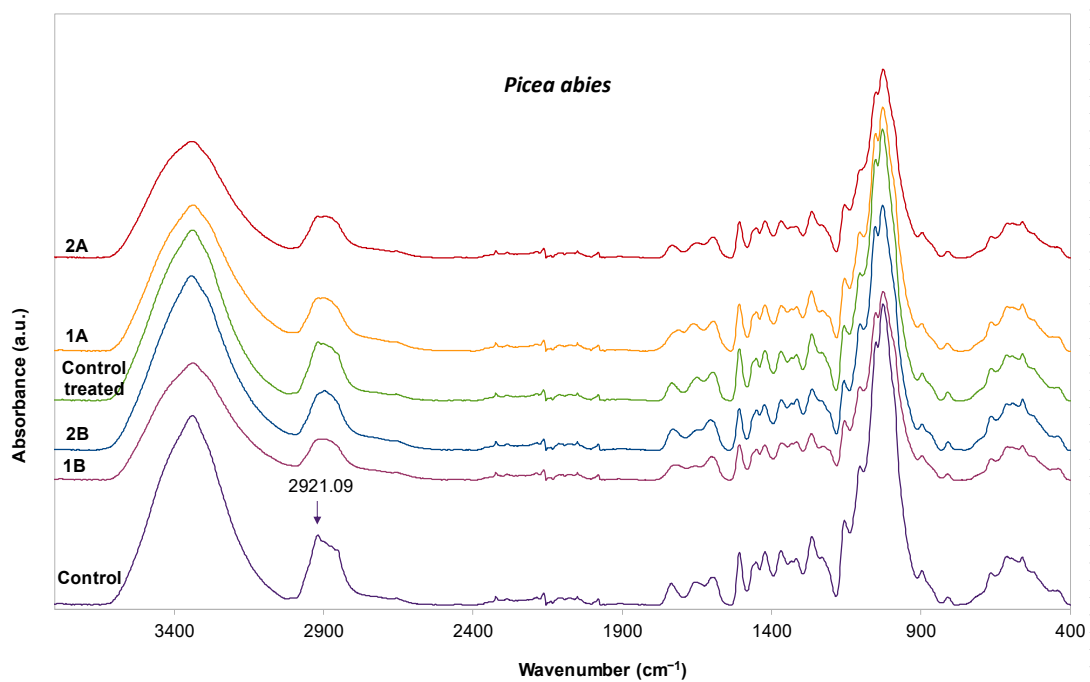
**Figure 2.** Spectral band assignments of the main spectral peaks observed in the Norway maple wood FTIR spectra. 1A— $\text{Fe}_2\text{O}_3$ ; 2A— $\text{FeCl}_3$ ; 1B— $\text{Fe}_2\text{O}_3$  + tannic acid; 2B— $\text{FeCl}_3$  + tannic acid.



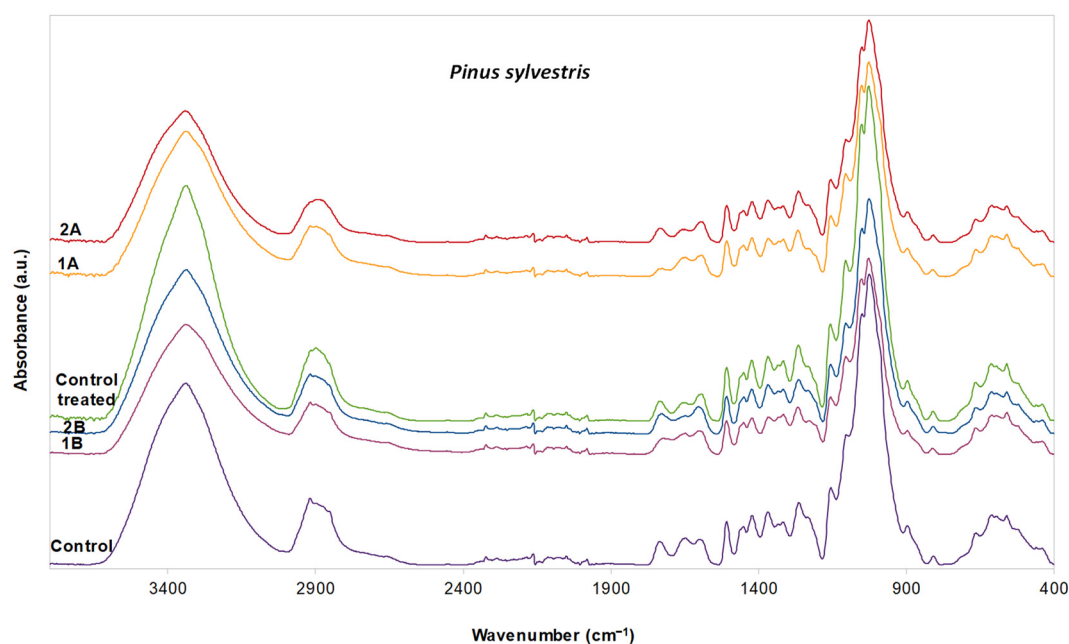
**Figure 3.** Spectral band assignments of the main spectral peaks observed in the walnut wood FTIR spectra. 1A— $\text{Fe}_2\text{O}_3$ ; 2A— $\text{FeCl}_3$ ; 1B— $\text{Fe}_2\text{O}_3$  + tannic acid; 2B— $\text{FeCl}_3$  + tannic acid.



**Figure 4.** Spectral band assignments of the main spectral peaks observed in the Douglas fir wood FTIR spectra. 1A— $\text{Fe}_2\text{O}_3$ ; 2A— $\text{FeCl}_3$ ; 1B— $\text{Fe}_2\text{O}_3$  + tannic acid; 2B— $\text{FeCl}_3$  + tannic acid.



**Figure 5.** Spectral band assignments of the main spectral peaks observed in the Norway spruce wood FTIR spectra. 1A— $\text{Fe}_2\text{O}_3$ ; 2A— $\text{FeCl}_3$ ; 1B— $\text{Fe}_2\text{O}_3$  + tannic acid; 2B— $\text{FeCl}_3$  + tannic acid.



**Figure 6.** Spectral band assignments of the main spectral peaks observed in the Scots pine wood FTIR spectra. 1A— $\text{Fe}_2\text{O}_3$ ; 2A— $\text{FeCl}_3$ ; 1B— $\text{Fe}_2\text{O}_3$  + tannic acid; 2B— $\text{FeCl}_3$  + tannic acid.

Due to the complexity of the wood, many characteristic peaks in the fingerprint region of the spectra made it complicated to assign all spectral peaks to their constituents. Analysed samples showed infrared spectra with the same profile, whereas the positions of the main bands remained the same, and only minor intensities occurred with respect to different wood samples. Small shifts were observed as a function between the treated and untreated wood samples (Figures 2–6). The characteristic signal bands' assignments of the main peaks, observed in the fingerprint region, which ranged between 3500 and 400  $\text{cm}^{-1}$ , were made on the basis of the literature data (Table 3). The bands at O–H stretching band were at 3500–3000  $\text{cm}^{-1}$  and did not significantly change during the thermal treatment. Notable observations include a broad band at 3300 and 2921  $\text{cm}^{-1}$ , which were attributed to the hydroxyl groups in phenolic and aliphatic structures of the cellulose. The bands between 2924 and 2854  $\text{cm}^{-1}$ , arising predominantly from CH stretching in aromatic methoxyl groups and in methyl and methylene groups of side chains [39], were particularly clear for the control samples of maple, spruce, and fir. The bands from 1400 to 1800  $\text{cm}^{-1}$  were assigned to the aromatic nature of the structure. Compared the FTIR spectrum of the control samples with wood samples treated with  $\text{FeCl}_3$  and  $\text{Fe}_2\text{O}_3$  and tannic acid additives, peaks of phenolic (O–H) deformation region were slightly more broadened than in the control samples. These changes occurred due to changes in Fe–tannic acid complexation. Complexes that are formed between Fe ions and phenolic groups with the presence of hydroxyl groups increase the stability of the complexes and form a stable metal–polyphenol complex coating which had a high affinity. A possible mechanism of ion change could be considered as  $\text{Fe}^{3+/2+}$  attaching hydroxyl groups donating electrons to metal ions [40,41]. The consisted Fe–tannin complex strongly binds carbohydrate-binding proteins, which are usually rich in residues featuring aromatic side chains. Therefore, the affinity between the Fe–tannin complex and carbohydrates is attributed to Van der Waals force and hydrophobic interactions, suggesting that hydrophobic interactions play an important role in the formation of surface-bound units [42]. According to Grasel et al. (2015) [43] and Falcão et al. (2013) [44], the C–O vibrations of condensed tannins can be seen at 1375–1365; 1160–1155 and 1075–1065  $\text{cm}^{-1}$ , while hydrolysable tannins at 1315–1290; 1200–1170 and 1035–1025  $\text{cm}^{-1}$ . According to our data, hydrolysable tannins together with their Fe complexes can be seen according to C–O stretch vibrations at 1315–1105  $\text{cm}^{-1}$ .

The bands located at 1507 and 1593  $\text{cm}^{-1}$ , which purely comprise aromatic skeletal vibrations of benzene rings, were recorded as the characteristic peaks of lignin. A vibration region ranged from 1150 to 1300  $\text{cm}^{-1}$  stretching C–O vibrations, and more speciality recorded near 1230  $\text{cm}^{-1}$  which referred to syringyl lignin. According to Saha et al. (2019) [45] in hardwoods usually, the guaiacyl–syringyl type of lignin is predominant, while in softwoods, guaiacyl type lignin is common. The peak at 1273  $\text{cm}^{-1}$  was caused by guaiacyl lignin. Ramage et al. (2017) [46] and Sharma et al. (2020) [47] reported that softwood and hardwood differ in their chemical composition, with various forms of lignin components such as guaiacyl or syringyl units, hemicelluloses such as xylan, glucomannan, and mannose constituent and wood extractives. Our research partially substantiated this statement.

**Table 3.** The characteristic signal bands assignments of the main peaks of softwood and hardwood after hydrothermal treatment.

Frequency Range ( $\text{cm}^{-1}$ )	Attribution of the Absorption Bands	Attributed to	Reference
3300	C–H	Phenolic and aliphatic structures	[49,50]
2924; 2854	Aromatic C–H stretch	Methoxyl groups and in methyl and methylene groups	[47,51]
1630–1635	COO stretching, absorbed OH, and conjugated C–O	Cellulose, lignin	[47]
1510	C=C	Lignin	[52]
1593	Aromatic skeletal and C=O stretch vibration	Lignin	[48]
1050–1250	C–O–C	Carbohydrates and cellulose	[52]
1026; 1050–1250	C–O–C stretching vibration (hemicellulose, cellulose, lignin)	Cellulose and hemicellulose	[47,48]
1230	C–O–C symmetric stretching and OH plane deformation	Syringyl lignin	[45]
1273	C–C	Guaiacyl lignin structure	[45,53]

The largest values of FT-IR spectra were assigned to absorption bands between 1050–1250  $\text{cm}^{-1}$ , which gave bands C–O–C bridges in cellulose and hemicelluloses. Moreover, there was C–O bands (1026 and 1050  $\text{cm}^{-1}$ ) stretching, usually attributed to cellulose and hemicellulose. These peaks were assigned to the C=O and COO asymmetric tension vibrations in the aromatic rings and aromatic skeletal and the C=O stretch vibration, respectively [48].

In general, during wood treatment, only the minor part of lignin was shifted. Lignin was affected during hydrothermal treatment enriched with inorganic/organic components, which is the probable reason for the increased intensity of this peak. FTIR spectra of this study may assume that used additives during hydrothermal treatment may have an influence on lignin shift, however, it can be concluded that increased temperature may affect examined wood during the hydrothermal process.

#### 4. Conclusions

The simulation of artificial conditions, containing various chemical additives close to the bog environment, was hypothesized as a relatively short way to develop a more sustainable wood product. As the objective of this study was to test different wood modification treatments, searching for environmentally friendly technology, the impact of the phenolic substance—tannic acid—naturally found in wood, especially oak wood, was also tested. The potential of FTIR spectroscopy combined with other chemometric methods was evaluated to show the influence of additives such as  $\text{Fe}_2\text{O}_3$  and  $\text{FeCl}_3$  in combination

with tannic acid on wood samples. It was observed that the softwood samples were more susceptible to hydrothermal modification than the hardwood samples, indicated by minor different intensities on infrared spectra. FTIR results showed bands of hardwood and softwood samples, which along with the spectral characterization of the wood constituents, can further be utilized for creating a larger FTIR spectral database of wood samples for their identification. The factors with the most significant effect on the hydrothermal modification were tannic acid and inorganic  $\text{Fe}_3\text{O}_2$  salt used as the additive. The results indicated the suitability of the inorganic  $\text{Fe}_3\text{O}_2$  salt and tannic acid combination applied in this type of modification because the higher concentration of iron was distributed on the inner and intermediate sublayers of wood samples. The hydrothermal modification approach to anchor tannic acid–Fe macromolecules in wood shown in this study has promising capabilities and may attract interest in the field of wood protection against weathering.

**Author Contributions:** Conceptualization, I.V.-K., M.P. and M.A.; formal analysis, I.V.-K., M.P. and B.Š.; investigation, M.P., B.Š. and M.Š.; methodology, M.P., B.Š. and M.A.; software, B.Š.; supervision, M.A.; visualization, I.V.-K. and M.P.; writing—original draft preparation I.V.-K. and M.P.; writing—review and editing, B.Š., M.Š. and M.A. All authors have read and agreed to the published version of the manuscript.

**Funding:** This project received funding from the European Regional Development Fund (project No 01.2.2-LMT-K-718-01-0021) under grant agreement with the Research Council of Lithuania (LMTLT).

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors thank Antanas Baltrušaitis and Lina Beniušienė for their contribution to the development of a wood-modification technology process and their valuable comments.

**Conflicts of Interest:** The authors declare no conflict of interest.

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