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Effect of Combined Steam and Heat Treatments on Extractives and Lignin in Sapwood and Heartwood of Turkey Oak (*Quercus cerris* L.) Wood

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Combined treatment with steam and heat was imposed on green Turkey oak (*Quercus cerris* L.) wood, both for sapwood and heartwood. Steaming was carried out in an autoclave at 100, 120, or 130 °C, and then a portion of the samples was heated in an oven for 2 h at 120 or 180 °C. Extraction with ethanol provided the greatest extractive contents in sapwood, and the extractive quantity decreased as the heating temperature was increased to 180 °C. In contrast, extraction with dichloromethane provided the greatest extractive content in heartwood, and no sizeable differences were found among the various treatments. Lignin amounts increased with rising treatment temperatures combined with steaming at 100 and 120 °C until the greatest value of 31.1% lignin content was reached. However, the lignin content decreased as the steaming temperatures rose to 130 °C. In all the combined treatments, the lignin content was greater in heartwood than in sapwood. Moreover, both steaming and heating applied individually produced no significant effect on lignin content.

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INTRODUCTION

In general, hydrothermal treatments of wood induce a temporary or permanent change and improve some wood characteristics. The actions of steam and heat on wood are complex because they involve changes in the physical and chemical nature of the wood microstructure and in the cell wall components. Steam causes swelling of the material accompanied by hydrolysis of certain compounds and solvation of various extractives. On the other hand, thermal treatment causes progressive degradation of the constituents of the wood cells, leading to the formation of numerous substances whose nature depends on the wood species, the samples size, and the process conditions.

Many studies have shown that the combination of high temperature and steam may cause changes in the chemical composition of wood (Fengel and Wegener 1989; Kosikova *et al.* 1999). The changes in chemical composition and wood structure in thermal processes are mainly caused by the degradation of hemicelluloses, cellulose, and lignin, which directly influences the physical and chemical properties of the wood (Stamm 1956, Weiland and Guyonnet 2003; Boonstra and Tjeerdsma 2006; Hill 2006; Esteves and Pereira 2009).

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The effect of hydrothermal treatment on chemical modification of locally grown, intermediate hardwood species such as Turkey oak (*Quercus cerris* L.), has not been studied very much. The natural range of this species is from Southern Europe to South-western Asia. Turkey oak wood could represent an important resource for mountain economies. However, low quality factors cause this kind of wood to be considered only for the lowest-valued use, *i.e.* as firewood. The principal limiting factors include the following: low dimensional stability, elevated internal tension, strong swelling and shrinkage, and low durability, mainly in sapwood (Giordano 1981). Also, a difficulty in gluing (Lavisci *et al*. 1991) and a not very appealing surface color (Tolvaj and Molnart 2006) have precluded, up to now, penetration of this wood in the furniture market. Nevertheless, the color change is often viewed positively, especially in hardwoods, for which there is a strong difference between heartwood and sapwood, such as Turkey oak.

No data have been reported in the literature concerning the different chemical components between heartwood and sapwood for Turkey oak wood, although Lavisci *et al*. (1991) have reported that the nature and concentration of extractives for this kind of wood are quite different, principally in terms of the insoluble fraction. Turkey oak might be a valuable commercial wood, but its value is often degraded by a variety of stains, most of which are due to extractives such as tannins in the wood. These stains often can be prevented by working with wet wood and high-temperature steaming.

Lignins are complex polymers made up of *p*-hydroxyphenyl, guaiacyl, and syringyl units in various proportions, depending on the botanical type of the trees. In hardwood species, such as oak species, lignin is composed of syringyl and guaiacyl units, with a trace of *p*-hydroxyphenyl groups (Assor *et al*. 2009). Konovalova *et al*. (2007) have stated that oak wood lignin of the guaiacyl type is located primarily in the middle lamella and, to a small extent, in ray parenchyma cells and in the walls of ring vessel elements. In contrast, syringyl lignin is located in the libriform fiber walls and in the latewood portion.

The physical and chemical properties of lignin play an important role against the invasion of pests and pathogens; while for the forest product industries, lignin is considered one of the major barriers to an efficient extraction of cellulose fibers for pulp and paper production (Novaes *et al*. 2010). The same authors have reported that lignin has greater energy content than either cellulose or hemicelluloses.

Several studies support the theory that lignin content increases with heat treatment (Zaman *et al*. 2000; Esteves *et al*. 2008). Esteves and Pereira (2009) have suggested that the apparent increase in lignin content upon thermal treatment of wood could not be considered pure lignin. In fact, numerous researchers have hypothesized that polycondensation reactions occur in the cell wall of other components, with consequent polymerization, thus increasing the apparent lignin content (Esteves and Pereira 2009). On the other hand, the increase in lignin content may not imply the formation of lignin during the process but rather the reduction of the amounts of other wood components (Kamdem *et al.* 2002)

Another aspect that should not be underestimated is the possibility of using lignin as a processing stabilizer for polystyrene and polyethylene (*i.e.* as a chemical that can be used during the processing of these polymers) instead of conventional organic stabilizers, which are toxic and more expensive (Pucciariello *et al*. 2004). Considering that this polymer will likely be used in the industrial sector in the future, one could then consider the possibility of inducing new polymerization in the wood by means of hydrothermal treatments, leading to significant increases in the availability of lignin. However,

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although lignin has been tried in various fields, it is still difficult to make use of. One reason for this failure, as indicated by Funaoka *et al*. (1990), is the complexity of lignin structures.

Rowe and Conner (1979) have stated that extractives may influence most of the properties of wood and the performance of wood products because they can protect wood from decay and affect the degree to which the color changes upon exposure to light, the odor of the wood, and the accent of the grain pattern. Extractives may also have an influence in gluing, finishing, papermaking, and in contributing to the corrosion of metals in contact with wood. In addition, the extractives have been shown to contribute to the dimensional stability of wood. Furthermore, they may have an influence in terms of health hazards. For example, the resin, tannic acid, pigment, *etc*. are considered to be responsible for the color change in wood (Sundqvist 2004). In a study by Esteves and Pereira (2009) most of the extractives disappeared or were degraded during heat treatment, especially the more volatile compounds.

Ding *et al*. (2011) found for Mongolian pine wood that there was an increase in the extractives content after heat treatment: 2.8% in the control sample, 3.2% in the sample treated in atmospheric steam, and 3.5% in pressurized steam. In contrast, González-Peña *et al*. (2004) investigated the effect of extractives on thermo-treated wood degradation and did not find any significant differences compared to controls.

The technological properties of lignin (durability, strength, *etc*.) and the extractives (paintability, glueability) have a primary importance. Therefore, for the direct use of these components as a material for usage, the distribution and the quantity in the different parts of the wood (sapwood and heartwood) are the most important factors for its characterization and use.

The main goal of this work was to evaluate the effect of different combinations of steaming and heating treatment conditions on the quantitative determination of extractives and lignin in Turkey oak green wood.

MATERIAL AND METHODS

Samples Preparation

The wood material used came from four trees growing in a high Turkey oak forest located in the Basilicata Region (Southern Italy). Green lumber pieces were used in order to avoid the possibility that natural or artificial drying might influence the characteristics of the wood (Esteban *et al*. 2005). Boards were cut radially from the logs, and nonstandard plainsawn specimens were extracted with the annual rings tangentially oriented. The wood specimens measured $50 \times 6 \times 180$ mm (in the tangential, radial, and longitudinal directions, respectively). Sapwood and heartwood were distinguished for each treatment. Twelve different treatments were performed on randomly selected samples, as indicated in Table 1.

A total of 160 samples, 40 for each treatment, equally distributed between heartwood and sapwood, were initially used for the Control (Ctrl) conditions, steaming at 100 °C (ST100), steaming at 120 °C (ST120), and steaming at 130 °C (ST130) (Table 1). After that, 40 samples were used for the first combined treatments: 10 for Ctrl+heating at 120 °C (H120), 10 for ST100+H120, 10 for ST120+H120, and 10 for ST130+H120 (Table 1). The other 40 samples were used for the second combined treatments: 10 for Ctrl+heating at 180 °C (H180), 10 for ST100+H180, 10 for ST120+H180, and 10 for

ST130+H180 (Table1). The remaining samples (80 specimens) were used for the other treatments: 20 for Ctrl, 20 for ST100, 20 for ST120, and 20 for ST130 (Table 1).

Table 1. The Twelve Treatments and the Number of Specimens

Treatment	Steaming Temperature (°C)	Pressure (bar)	Heating Temperature (°C)	Initial number of samples	Final number of samples
Ctrl	-	-	-	40	20
ST100	100	-	-	40	20
ST120	120	1	-	40	20
ST130	130	1.7	-	40	20
Ctrl+H120	-	-	120		10
ST100+H120	100	-	120		10
ST120+H120	120	1	120		10
ST130+H120	130	1.7	120		10
Ctrl+H180	-	-	180		10
ST100+H180	100	-	180		10
ST120+H180	120	1	180		10
ST130+H180	130	1.7	180		10

Steaming Processes

Treatments of green wood were carried out at different temperatures and pressures by indirect steaming inside an autoclave (model Vapormatic 770/A). The instrument was sterilized by means of vertical charging, which was completely automatic, thermo-regulated, and controlled. The autoclave was equipped with a closed stainless steel basket (240 × 190 mm in diameter and height, respectively) and a microprocessor, which permitted the programming of various times and temperatures (from 100 to 130 °C). The maximum capacity of the autoclave was 23 L.

The cycles were the following:

ST100. From an ambient temperature (*T*) of about 24 °C, the *T* was increased to 100 °C over 20 min and was held constant at 100 °C for 20 min. Next, the T was decreased to 50 °C over 180 min. The total time was 220 min.

ST120. From an ambient *T* of about 24°C, the *T* was increased to 100 °C over 20 min and was held constant at 100 °C for 10 min to eliminate the residual air. Next, the *T* was increased to 120 °C over 20 min and was held constant at 120 °C for 60 min. Finally, the *T* was decreased to 100°C over 40 min and to 50°C over 180 min. The total time was 330 min.

ST130. From an ambient *T* of about 24 °C, the *T* was increased to 130 °C over 30 min and was held constant at 130 °C for 10 min. Similar to the ST120 treatment, the *T* was decreased to 100 °C over 60 min and to 50 °C over 180 min. The total time was 280 min.

Heat Treatment

A portion of the original samples used in the autoclave was then treated for 2 h in a small heating unit controlled with ±1 °C sensitively under atmospheric pressure, using two different heat cycles: 120 and 180 °C. Next, the samples were cooled and weighed.

For determination of the extractive and lignin content, three random samples for each treatment and type of wood (sapwood and heartwood) were chosen. For the following determinations, 6 g was taken from each of the 24 samples (12 from sapwood

and 12 from heartwood), extracted and ground with a small rotary blade machine. Additional experimental information is described in Todaro *et al*. (2012).

Determination of Extractives

The determination of extractives was quantified using the modified TAPPI CPPA G 13 method as described in Solvent Extractives in Pulp (1997). This method determines the amount of solvent-soluble, non-volatile material in wood and pulp. As reported in the method, two different solvent systems may be employed: dichloromethane or ethanol; the first gives lower amounts of extractives, while extraction with ethanol gives reproducible results and includes some additional compounds. The extraction apparatus consisted of a 250 mL flask, a Soxhlet tube (40 mm in diameter), and a 300 mm Hallihan cooler. Cellulose thimbles (medium porosity and size of 33×80 mm) were used to filter the samples. For each of the 24 samples, the solvents used were ethanol and dichloro-methane, respectively. After extraction the material was dried using a rotary evaporator connected to a vacuum pump (Vacuubrand PC3001). For each extraction, 2 g of material was placed in a cellulose thimble, which was covered with a cotton ball to prevent loss of the wood. Each extraction was carried out for 7 h; then, the solution was dried (up to a pressure of 20 mbar) in a previously weighed 25 mL flask. Finally, it was possible to calculate the extraction percentage by weighing the flask containing the residue.

Determination of the Lignin

The lignin determination was quantified by using a modified TAPPI T13 m-54 (1954) method. The Klason lignin content was determined from the amount of precipitate formed after sulfuric acid attack on the extractive-free material.

Each sample (1 g) was dried and transferred to a 50 mL beaker. Then, 15 mL of 72% H_2SO_4 was added. Subsequently, the samples were allowed to stand for 2 h in a 20 °C water bath, with frequent stirring. The samples were then washed with a total of 560 mL of water into a 1 L beaker so that the H_2SO_4 concentration was diluted to 3%. The beaker was covered with a large watch glass, and the mixture was refluxed for 4 h, maintaining a constant volume by adding water. The solution was then filtered by using a vacuum system (Vacuubrand PC3001 model) with a polyvinyldifluoride (PVDF) membrane. The resulting residue was dried in an oven set at 45 °C for 12 h. Samples were then removed from the oven, cooled, and weighed by using a balance having 0.001 g accuracy. The lignin content was determined by comparing the weight of the residue remaining with the original weight of material.

RESULTS AND DISCUSSION

Extractives

The quantities of extractives with ethanol were found to be substantially greater than those obtained with dichloromethane (Fig. 1). These results can be explained by considering the polar nature of the compounds present in the lignin and extractives. Dichloromethane is a relatively nonpolar solvent ($\mathcal{E} = 8.9$; $E_T = 41.1$), while ethanol is more polar ($\mathcal{E} = 24.5$; $E_T = 51.9$) (Reichardt 1979).

When ethanol was used as the solvent (Fig. 1), a greater content of extractives was found in sapwood treated with ST120+H120 (9.9%), followed by ST130+H120 (8.9%). Turkey oak sapwood and heartwood showed considerable differences in terms of

extractives using both methods. The interpretation of this result is quite complicated; a likely hypothesis may be that more complex tannins exist in heartwood than in sapwood (Roux 1957; Hillis 1968). Rowe and Conner (1979) have reported a particularly notable contrast for oak wood between the components of sapwood and heartwood.
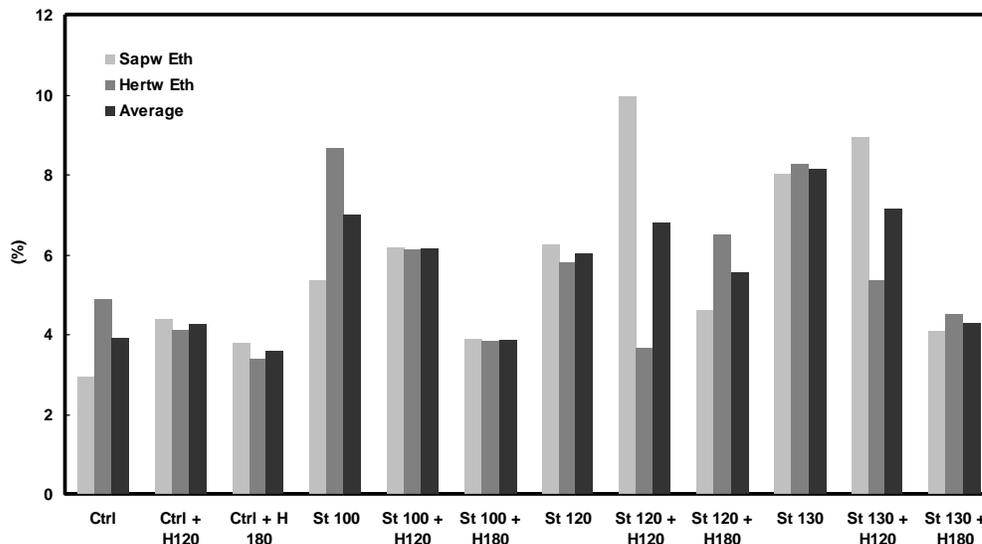

Fig. 1. Extractives content using ethanol with sapwood (Sapw Eth), heartwood (Hertw Eth), and average values for all treatments

In terms of average values, the quantity of extractives appeared to increase with steaming treatment. Nevertheless, a decrease resulted under the most extreme process conditions (in combination with heating to 180 °C) (Fig. 2). The greatest quantity of extractives was obtained with steaming at 130 °C without heating. It is important to note that with the combination of steaming and heating to 180 °C, the extractive percentage obtained dropped sharply in all samples, leading to the assumption that a fixed amount of extractive remained. The cause of this drop should be investigated.
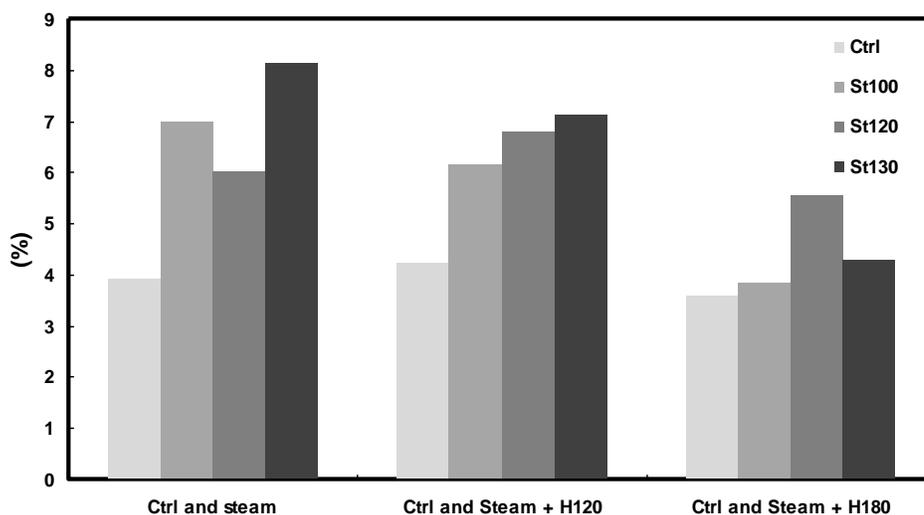

Fig. 2. Influence of combined treatment on average extractive content

The effect of steaming on wet Turkey oak wood, which is particularly difficult to treat, was not completely clear in this study. An explanation for these results could involve the presence of pressurized steam in the experiment to which the green wood was submitted (Ding *et al*. 2011). As suggested by Rowe and Conner (1979) for oak wood species, a complete understanding of the phenomena of stain or other problems for Turkey oak wood will be attainable only when information regarding the chemistry of heartwood and sapwood extractives has progressed considerably.

Assor *et al*. (2009) have confirmed that the softening of wood begins between 50 and 100 °C, depending on various parameters and species. The authors stated that the presence of water in wood during steaming certainly affects degradation of the components of the wood by promoting hydrolysis, particularly in the presence of acetic acid, in addition to creating conditions favorable for the condensation of lignin.

Esteves *et al*. (2008) have reported that the extractives content increases significantly with mass loss, followed by a decrease, despite the fact that most of the original extractives disappeared from the treated wood.

While a clear pattern was displayed when ethanol was used, confusing and unclear results were obtained when dichloromethane was used (Fig. 3). In any case, the quantity of extractives in heartwood was clearly greater than that in sapwood. These results can be understood by considering that heartwood has a greater amount of nonpolar extractives than sapwood. This hypothesis should be further investigated. Hillis (1968) has reported that heartwood presents more phenolic-type extractives (*e.g.* flavonoids), while sapwood contains starch, soluble sugars, and triglycerides. As reported by Santana *et al.* (2009), polar solvents give high extraction efficiencies. However, they also extract other undesirable polar compounds present in the samples. With a nonpolar solvent, such as dichloromethane, the extraction of phenols would require a previous acidic digestion of the analytes.
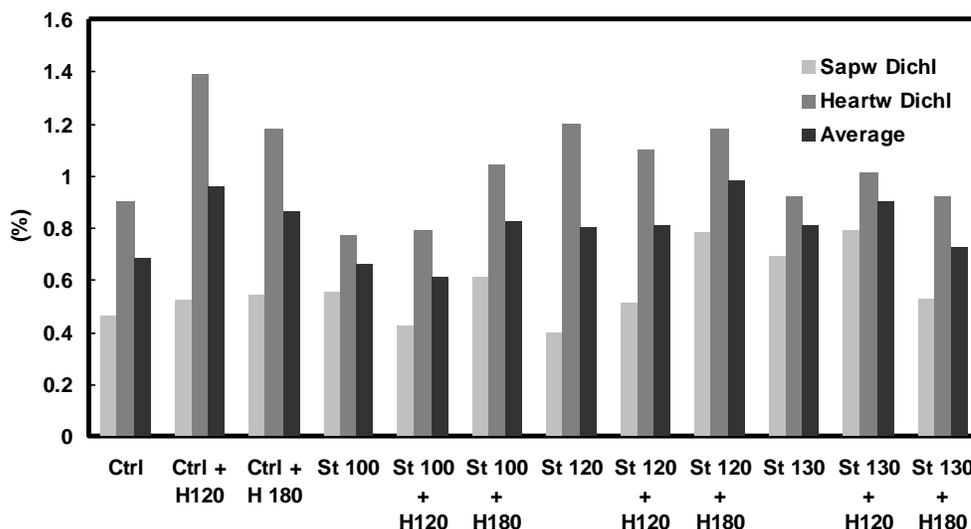

Fig. 3. Extractive content using dichloromethane in sapwood (Sapw Dichl), heartwood (Heartw Dichl), and average value for all treatments

Hillis (1968) has stated that extractives are mostly detectable in rays and that they can also form coatings on the cell wall and on the pits, or they can penetrate the cell wall itself. These different locations inside the tree are one reason why one solvent extraction

cannot extract all the extractives at once and why the use of several solvents of different polarity can increase the total removal of extractives (Caron 2010).

Our results using dichloromethane showed no noteworthy results regarding the influence of different steaming or heating methods. The amount of extractives obtained with dichloromethane seemed to be independent of treatments, similar to reports by González-Peña *et al*. (2004).

Lignin

When comparing sapwood and heartwood (Fig. 4), the lignin contents were always greater in heartwood, with the only exceptions coming from samples treated only with heat (Ctrl+H120 and Ctrl+H180). Similar results were found by Wahab *et al*. (2011) in *Acacia* hybrid wood treated with hot oil, where the lignin content of heartwood was greater than that in sapwood.
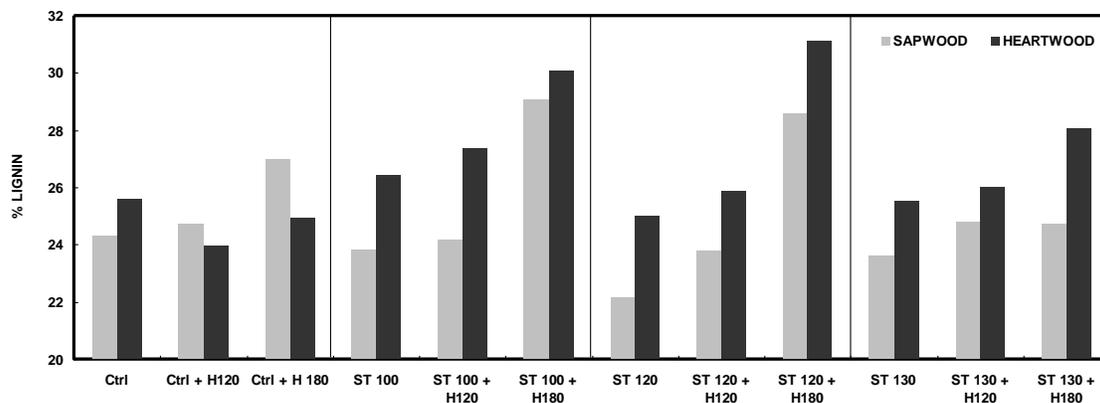

Fig. 4. Lignin content in sapwood and heartwood for all treatments

The differences in chemical composition in the wood, in terms of extractives, cellulose, and hemicellulose (Cao *et al*. 2012) content, could be due to the lignin concentration in sapwood and heartwood.

The greatest percentage of lignin was found in samples treated with a combination of steaming at 100 and 120 °C and heating to 180 °C. In samples treated with the combination ST100+H180, the amounts of lignin were 29.1% from sapwood and 30.1% from heartwood, while samples treated with ST120+H180 yielded 28.6% of lignin from sapwood and 31.1% from heartwood. The minimum amount of lignin was obtained from samples treated only with steaming, mainly at 120 and 130 °C.

According to Bourgois and Guyonnet (1988), Zaman *et al*. (2000), and Andersons *et al*. (2009), the percentage of lignin content is positively related to the increase of heating temperature (Fig. 4). Moreover, this relationship for Turkey oak was observed only with high temperature heating and a previous steaming treatment.

In fact, by comparing all of the lignin content values to untreated samples (Ctrl), the greatest lignin extractions were obtained with the combination of steaming and heating at 180 °C. Even when the steaming temperature was increased to 130 °C, the lignin content decreased (Fig. 5). With the combination of steaming at 120 °C and heating to 180 °C, it was possible to extract 21.5% more lignin than untreated samples. Moreover, it was observed that both steaming and heating applied individually produced no positive or substantial effect. The amount of lignin in the steamed wood (partially in

ST 100, totally in ST 120 and ST130) decreased compared to the Ctrl, principally in sapwood.
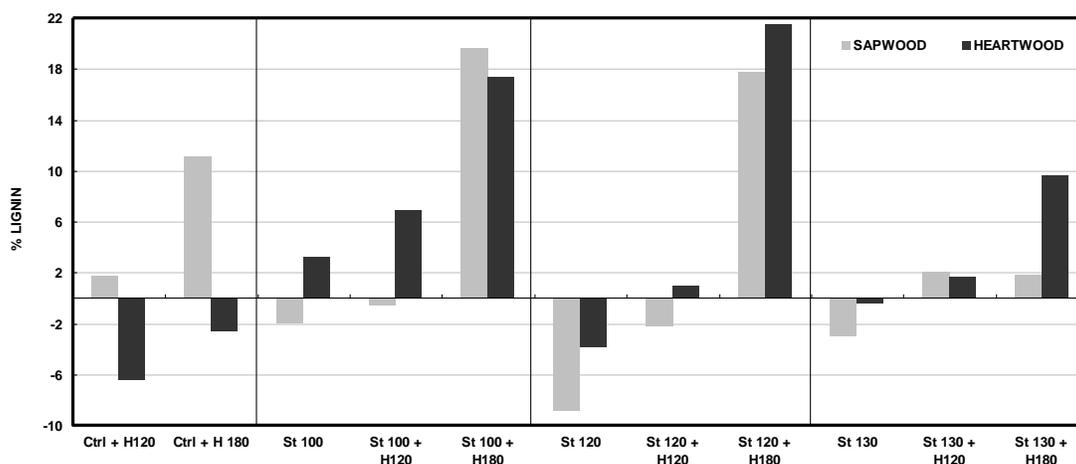

Fig. 5. Relative lignin content compared to Ctrl in sapwood and heartwood

These results have been confirmed in a recent paper by Dashti *et al*. (2012) for *Quercus infectoria*. These authors also found a reduction of lignin content and high-lighted the difference in terms of permeability and diffusion coefficient between sapwood and heartwood. In addition, they stated that the presence of tyloses in heartwood, of which Turkey oak is filled, has a significant effect on the final impact of steaming treatment on lignin content, probably due to reduction of cellular wall structure destruction, which lowers the water vapor diffusivity rate through wood.

Funaoka *et al*. (1990) have indicated that water contained in wood accelerates the condensation of lignin because water decreases the softening temperature of lignin, allowing the flow of lignin at a lower temperature.

Further analysis of the results indicated that steaming should not exceed 120 °C. Indeed, increasing the temperature up to a maximum of 180 °C increased the amount lignin extracted, but when the samples were treated with steam exceeding more than 120 °C, the amount of lignin extracted decreased (Fig. 5).

The increasing amount of lignin content with heat treatment could be due to some of the thermal degradation products of carbohydrates likely being trapped in the lignin (Yildiz *et al*. 2006). Several authors have reported the formation of condensation products and possible cross-linkage between lignin and polysaccharides (Funaoka *et al*. 1990; Košíková *et al*. 1999; Sivonen *et al*. 2002). As reported by Assor *et al*. (2009), lignins are strictly associated with noncellulosic polysaccharides that form so-called lignin-carbohydrate complexes (LCCs).

In fact, the loss of polysaccharide material during heat treatment leads to an increase in the lignin content of the wood. These results have also been reported by Wahab *et al*. (2011). Kamdem *et al*. (2002) have suggested that the increase in lignin conten is probably due to the reduction of other wood components and does not imply that new lignin is formed. Andersons *et al*. (2009) also established that the lignin content increases due to the degradation of compounds that are not thermally stable.

Steam can have different effects on the structure of lignin. It can promote hydrolysis reactions on polysaccharides (Fengel and Wegener 1989), causing an increase of alcoholic aliphatic functional groups that are able to react with the lignin scaffold.

Similarly, the presence of water at high temperatures can cause oxidation reactions with the formation of new alcoholic functional groups on the lignin structure. Water can also induce hydrolysis of saccharides, which increase the amount of lignin due to reactions of these new alcohols with lignin itself. Furthermore, thermal treatment can induce reorganization of the lignin by increasing its cross-linked structure due to simple reorganization of the structure and/or oxidation processes (Huang *et al*. 2012).

It is evident that hydrothermal treatment promotes an increase of the amount of lignin recovered in the samples. It is also apparent that the main effect was obtained with heartwood (Fig. 4 and Fig. 5), while sapwood gave an increase in the amount of lignin only under the most drastic conditions (ST100+H180; ST1200+H180). Thus, the steam treatment induced alteration of the wood compounds, increasing the effect of the thermal treatment in the heartwood.

In sapwood we observed a progressive reduction in the amount of lignin from ST100+H180 to ST130+H180; while with heartwood, no clear effect was evident (Fig. 5). In this case, extensive hydrolysis of polysaccharides caused by hot water can produce an increase in the cross-linked structure of lignin (Funaoka *et al*. 1990; Košíková *et al*. 1999). The "new" cross-linked lignin forms a structure more resistant to analytical determination.

It is noteworthy that the steam treatment at 130 °C and the thermal treatment at 180 °C gave a lower amount of lignin. It is difficult to explain this result. We hypothesize that with these conditions, reorganization of the lignin structure allowed the formation of a more rigid cross-linked structure that is more resistant to the acidic treatment used in the determination of lignin.

CONCLUSIONS

The aim of this study was to understand how 12 different hydrothermal treatment conditions influence the extractive and lignin content of Turkey oak (*Quercus cerris* L.), one of the forest species with the largest planted area in Southeastern Europe. Up until now, this species has been inadequately investigated.

1. The quantities of extractives found with ethanol were substantially greater than those obtained with dichloromethane. These results can be explained by considering the polar nature of the compounds present in the lignin and extractives.

2. In contrast to ethanol, by using dichloromethane, the quantity of extractives was greater from heartwood than from sapwood. In terms of average value, the quantity of extractives appeared to increase with the steaming treatment. Nevertheless, the amount of extractive content decreased when steam was combined with heat at the extreme temperature of 180 °C.

3. Uniform results for lignin content were found for sapwood and heartwood. The most lignin was found in samples subjected to combined treatments of moderate steaming (100 to 120 °C) and extreme heating (180 °C). In ST120+H180 treatment, a 21.5% increase in the amount of lignin was obtained compared to the untreated samples.

4. In all samples subjected to combined treatments, the content of lignin in heartwood was greater than lignin content in sapwood. Moreover both steaming and heating

applied individually produced no positive and sizeable effect on lignin content compared to the control.

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