

The Effect of Heat Treatment on the Chemical Composition of Ash Wood

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Common ash (*Fraxinus excelsior* L.) wood was heat treated in an oven at temperatures of 160, 180, and 200 °C, and under atmospheric pressure in the presence of air for a duration of 3, 6, 9, and 12 h. The impact of heat treatment on the chemical composition of wood was studied. The extractives content initially increased up to 200 °C and 3 h. However, with extended treatment duration it decreased. Hemicellulosic monosaccharide (D-xylose) degraded under all treatment conditions and resulted in a decrease of holocellulose content. In the case of lignin, demethoxylation and the formation of more condensed structures were observed. This led to an increase in lignin content at temperatures of 180 and 200 °C. The oxidation process already began at 160 °C. This resulted in the formation of new carbonyl or carboxyl groups that contributed to color change, *i.e.*, wood darkening. From the beginning the increase in the cellulose crystallinity was observed, and then it decreased. The maximum was reached at the temperatures of 160, and 180 °C for 9 h of treatment and at the temperature of 200 °C for 6 h.

Keywords: Heat treatment; Ash wood; Lignin; Holocellulose; Saccharides; FTIR spectroscopy

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INTRODUCTION

The heat treatment of wood is an environmentally friendly process to enhance properties such as color, dimensional stability, or resistance to microbiological attack (Hill 2006; Esteves and Pereira 2009; Tolvaj *et al.* 2014). While various heat treatment processes have been used, the main differences are seen in the process conditions (temperature, duration, process steps, oxygen or nitrogen atmosphere, steaming, wet or dry process, use of oils, steaming schedules, *etc.*) (Militz 2002; Bazyar 2012).

The alteration of some physical and mechanical properties of wood, *e.g.*, color, density, equilibrium moisture content, toughness, modulus of elasticity, modulus of rupture, and abrasion resistance due to heat treatment are mentioned in several studies. These alterations are highly dependent upon the treatment conditions and wood species and are closely related to the changes of the chemical constituents of wood during the thermal treatment (Boonstra *et al.* 2007; Niemz *et al.* 2010; Da Silva *et al.* 2013; Kačíková *et al.* 2013; Dzurenda 2014; Tankut *et al.* 2014; Cademartori *et al.* 2015; Candelier *et al.* 2016; Kučerová *et al.* 2016; Zawadzki *et al.* 2016; Zielenkiewicz *et al.* 2018).

The application of heat on wood results in dehydration, hydrolysis, oxidation, depolymerization, and the degradation of wood components. At low temperatures between

20 and 100 °C, water and volatile extractives are removed from wood. At temperatures up to 100 °C, important chemical reactions take place in wood. Deacetylation of hemicelluloses occurs at the beginning of the treatment. The presence of acetyl groups that are thermally labile and lead to the formation of acetic acid is a significant factor in the thermal degradation of hemicellulose. Depolymerization reactions of less ordered carbohydrates (hemicelluloses and amorphous cellulose) are catalyzed by the acetic acid (Candelier *et al.* 2016), which leads to the formation of oligosaccharides and monosaccharides. Consequently, these saccharides are dehydrated to form furfural and hydroxymethyl furfural (Tjeerdsma and Militz 2005). Changes in the hemicellulose content and structure result in the loss of bending and tensile strength. Degradation of the cellulose macromolecule is considered as the main factor affecting the loss in tensile strength (Boonstra *et al.* 2007). The formation of colored degradation and oxidation products from the hemicelluloses and extractives results in wood darkening. The intensity of the discoloration depends on the intensity of the heat (Bekhta and Niemz 2003; Kačík and Kubovský 2011; Chen *et al.* 2012).

The thermal stability of wood depends on the proportion of chemical components in the wood species. According to Fengel and Wegener (1984), hardwoods are less thermally stable than softwoods. In general, the proportion of hemicelluloses in hardwoods is higher in comparison to softwoods. Regarding the non-glucosic sugar units present in wood, the proportion of pentosans (xylose and arabinose) in hardwoods is higher than the proportion of hexosans (glucose, galactose, and mannose), where pentosans are more susceptible to thermal degradation. Moreover, hardwoods have more acetyl groups than softwoods. The presence of acetyl groups leads to the formation of acetic acid, thus causing an acid-catalyzed degradation of polysaccharides.

An increase in heating severity causes chain scission of the cellulose with a concomitant decrease in the cellulose degree of polymerization and the degree of crystallinity. Crystalline cellulose degrades at temperatures ranging from 300 to 340 °C. However, the amorphous regions of cellulose are more susceptible to thermal degradation. These regions most likely exhibit similar thermal behavior as the hexose components of hemicelluloses (Kim *et al.* 2001).

The lignin thermally decomposes over a broad temperature range. This is because various oxygen functional groups in the lignin macromolecule have different thermal stabilities and their scission occurs at different temperatures (Brebú and Vasile 2010). In the initial stages of heating, the decomposition of lignin due to the reduction of structural units bound by aryl-ether bonds was observed (Kačíková *et al.* 2008; Windeisen and Wegener 2008). At the higher treatment temperatures, cross-linking and the condensation reactions occurred and led to an increase in the proportion of lignin in the wood (Nuopponen *et al.* 2004; Hill 2006; Windeisen and Wegener 2008; Kačík *et al.* 2016). An increase in the relative content of lignin during heat treatment can also be caused by degradation of the hemicelluloses and cellulose (Wikberg and Maunu 2004; Tumen *et al.* 2010; Da Silva *et al.* 2013).

Common ash (*Fraxinus excelsior* L.) wood is solid, hard, and exceeds common standards in toughness and flexibility. Due to these superb properties, it is one of the most valuable species of timber (Klement *et al.* 2008). Heat-treated ash wood is used for cladding and decking in moist environments, *e.g.*, in bathrooms, saunas, and exterior.

The aim of this study is to explain the chemical changes of ash wood during the process of heat treatment under various process conditions (temperature and time). The content of extractives, lignin, and holocellulose was determined using the conventional

analytical methods. To determine the content of the main saccharides (glucose and xylose), high-performance liquid chromatography (HPLC) was used. Furthermore, chemical changes in wood were monitored using Fourier transform infrared (FTIR) spectroscopy as well.

EXPERIMENTAL

Materials

Common ash (*Fraxinus excelsior* L.) wood used in the research was from Central Slovakia. Samples were prepared from one trunk to lower the variability of properties. The samples were defect-free with dimensions of 32 mm × 32 mm × 120 mm (width × thickness × length). The samples were divided into 13 groups. Twelve groups were heat treated under defined conditions, and one group was left without treatment (control sample). Before heat treatment, all of the samples were oven dried at 103 ± 2 °C, and their weight was measured.

Methods

Heat treatment

Twelve groups, with each having 15 samples, were heat treated in a laboratory oven under atmospheric pressure in the presence of air. The treatment was performed for 3, 6, 9, and 12 h at three different temperatures of 160, 180, and 200 °C. The time for reheating the oven to the required temperature after inserting the samples was 10 min. After the treatment, the samples were placed in a desiccator over silica gel, where they were cooled and reweighed. The mass loss due to heat treatment was calculated.

Chemical analyses

The wood samples were mechanically disintegrated to sawdust. Fractions of 0.5 to 1.0 mm were extracted in a Soxhlet apparatus with a mixture of ethanol and toluene, according to ASTM D1107-96 (2013). The lignin content was determined according to ASTM D1106-96 (2013) and the holocellulose content was determined according to Wise *et al.* (1946).

The qualitative and quantitative analyses of the saccharides were performed according to the National Renewable Energy Laboratory (NREL) (Sluiter *et al.* 2011). An Agilent 1200 HPLC chromatograph (Agilent Technologies, Santa Clara, CA, USA) equipped with an Aminex HPX-87P column and refractive index detector were used in the analyses. The analysis at 80 °C used ultrapure water as an eluent at a flow rate of 0.5 mL/min. Glucose and xylose were detected and quantitatively determined using cellobiose as an internal standard. Two samples were hydrolyzed in parallel and each hydrolysate was analyzed twice.

FTIR spectroscopy

The FTIR spectra of the wood and cellulose isolated according to the Seifert method (Seifert 1956) were recorded on a Nicolet iS10 FTIR spectrometer equipped with the Smart iTR attenuated total reflectance (ATR) sampling accessory with diamond crystal (Thermo Fisher Scientific, Madison, WI, USA). The spectra were measured in the wavenumber range from 4000 to 650 cm^{-1} . A resolution of 4 cm^{-1} and 64 scans per sample were used. Six measurements were performed per sample and the average spectra were determined and evaluated. The OMNIC 8.0 software (Thermo Fisher Scientific, Madison, WI, USA)

was used to evaluate the spectra. Total Crystallinity Index (A_{1370}/A_{2900}) according to Nelson and O'Connor (1964) was determined to estimate cellulose crystallinity.

RESULTS AND DISCUSSION

Wood darkening was the most visible effect of the heat treatment (Fig. 1). The intensity of discoloration increased with increasing heat treatment temperature and duration. Wood darkening is often explained as being due to the formation of oxidation and degradation products from the wood components (Bekhta and Niemz 2003; Chen *et al.* 2012). According to Srinivas and Pandey (2012), the decrease in lightness indicates that many components that absorb visible light are formed during the heat treatment. Some authors (Hon and Minemura 2001; Poncsak *et al.* 2006; Esteves *et al.* 2008) explained that there is the formation of low molecular weight sugars *via* the degradation reactions of hemicelluloses and the formation of quinones *via* the oxidation reactions. Chen *et al.* (2012) mentioned that the condensation reactions of lignin and some extractives and the formation of byproducts contribute to the increase of red tone intensity on the wood sample. Additionally, color darkening occurs with increasing lignin amount in the heat-treated wood structure (Ates *et al.* 2009).

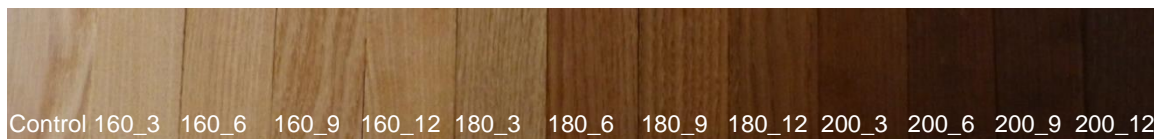


Fig. 1. The impact of treatment conditions (temperature (160 to 200 °C) and time (3 to 12 h)) on the color of ash wood

Wood heating resulted in a reduction in the mass of samples. The extent of mass loss depended on the temperature and time of treatment. The data shown in Table 1 represented the direct effect of heating with no effect on the moisture content. A considerable increase in mass loss was associated with the loss of macromolecular components. Regarding the chemical characteristics, changes in extractives and lignin content, and a decrease in the content of holocellulose with an increase in severity of the treatment were observed.

Considering the chemical components of wood, the extractives were the wood component that was the most affected by the heat treatment. In untreated wood, a 3.8% extractives content was determined. The initial decrease in extractives content when heat treatment at 160 °C was conducted could have been due to the removal of volatiles. Subsequently, the content of extractives increased. A duration of 3 h of heat treatment at a temperature of 200 °C caused an increase in the extractives content to 6.9%. This was attributed to the release of degradation products of lignin and saccharides in the extraction mixture, or by their condensation reactions with the extractives originally present in untreated wood. This result was comparable to other studies (Wang *et al.* 2015; Severo *et al.* 2016). According to Pelaez-Samaniego *et al.* (2014), the decrease in extractives in more severe conditions could be due to the cracking and devolatilization of lignin intermediates or due to the formation of extra char by further polycondensation. Strong positive correlations between the total color difference and the extractives content were found by Kučerová *et al.* (2016) and Čabalová *et al.* (2018). Following the mentioned finding, the

fact that an increased content of extractives can be one of the causes of wood darkening was concluded.

Table 1. Mass Loss and Chemical Characteristics of Heat-treated Ash Wood

Temperature (°C)	Time of Treatment (h)	Mass Loss (%)	Extractives (%)	Lignin (%)	Holocellulose (%)
20	-	-	3.80 ± 0.17 (3.80)	22.16 ± 0.32 (22.16)	79.53 ± 0.28 (79.53)
160	3	0.26 ± 0.15	3.59 ± 0.30 (3.58)	21.85 ± 0.69 (21.79)	78.11 ± 0.61 (77.91)
	6	1.44 ± 0.13	4.95 ± 0.39 (4.88)	21.14 ± 0.28 (20.84)	75.40 ± 0.16 (74.32)
	9	1.69 ± 0.21	4.21 ± 0.25 (4.14)	21.22 ± 0.34 (20.86)	74.77 ± 0.05 (73.51)
	12	1.95 ± 0.15	4.26 ± 0.42 (4.18)	21.17 ± 0.12 (20.76)	72.67 ± 0.48 (71.25)
180	3	2.92 ± 0.87	4.33 ± 0.53 (4.20)	22.19 ± 0.22 (21.54)	72.25 ± 0.27 (70.14)
	6	3.20 ± 0.82	4.56 ± 0.34 (4.41)	22.60 ± 0.29 (21.88)	70.84 ± 0.07 (68.57)
	9	4.60 ± 0.61	5.33 ± 0.42 (5.08)	23.05 ± 0.37 (21.99)	65.81 ± 0.09 (62.78)
	12	5.79 ± 0.53	5.42 ± 0.36 (5.11)	23.36 ± 0.14 (22.01)	62.12 ± 0.14 (58.52)
200	3	8.04 ± 0.85	6.86 ± 0.59 (6.31)	24.03 ± 0.11 (22.10)	60.89 ± 0.09 (56.00)
	6	13.91 ± 0.95	6.63 ± 0.47 (5.71)	28.27 ± 0.44 (24.34)	53.87 ± 0.14 (46.38)
	9	16.99 ± 0.43	6.26 ± 0.55 (5.20)	30.28 ± 0.26 (25.14)	56.70 ± 0.10 (47.07)
	12	18.48 ± 0.59	6.06 ± 0.61 (4.94)	30.84 ± 0.82 (25.14)	57.42 ± 0.31 (46.81)

Note: Data represents mean values ± standard deviations; numbers in parentheses represent mean percentage of oven-dry weight prior to thermal treatment

In untreated wood, a 22.2% lignin content was determined. The heat treatment at a temperature of 160 °C resulted in a slight decrease in the lignin content. This was caused by the degradation reactions supporting the production of various phenolic breakdown products (Hill 2006). However, the lignin content increased by conducting heat treatment at the temperatures of 180 and 200 °C. This may have been the consequence of the condensation reactions of lignin with hemicelluloses cleavage products or of lignin macromolecule cross-linking (Nuopponen *et al.* 2004; Wikberg and Maunu 2004; Tumen *et al.* 2010; Da Silva *et al.* 2013). An increase in lignin content contributes to the increase in total color difference (Kačíková *et al.* 2013; Kučerová *et al.* 2016).

Holocellulose is the total polysaccharide fraction of wood consisting of cellulose and hemicelluloses, which was 79.5% in the untreated ash wood. The content of holocellulose decreased due to heating. The decrease was more noticeable at higher temperatures. To explain the described changes, the content of D-glucose and D-xylose (Table 2) was determined. Following these results, the fact that the degradation of hemicelluloses had already started at 160 °C can be concluded. In comparison to hemicelluloses, cellulose is more thermally stable, especially due to its crystalline

structure. The obtained results were supported by previously published data (Alen *et al.* 2002; Brito *et al.* 2008; Esteves *et al.* 2008; González-Pena *et al.* 2009; De Moura *et al.* 2012; Gawron *et al.* 2014; Wang *et al.* 2015; Kučerová *et al.* 2016).

Table 2. Content of Main Monosaccharides in Heat-treated Ash Wood

Treatment		D-Glucose (%)	D-Xylose (%)
Temperature (°C)	Time (h)		
20	-	40.30 ± 0.12 (40.30)	18.05 ± 0.12 (18.05)
160	3	40.75 ± 0.22 (40.65)	17.33 ± 0.15 (17.29)
	6	39.76 ± 0.21 (39.19)	17.17 ± 0.16 (16.92)
	9	40.46 ± 0.19 (39.78)	16.40 ± 0.10 (16.12)
	12	39.78 ± 0.24 (39.01)	15.59 ± 0.19 (15.29)
180	3	41.39 ± 0.23 (40.18)	16.00 ± 0.23 (15.53)
	6	42.07 ± 0.32 (40.72)	15.45 ± 0.24 (14.96)
	9	42.22 ± 0.21 (40.28)	13.80 ± 0.21 (13.17)
	12	42.04 ± 0.16 (39.61)	12.79 ± 0.25 (12.05)
200	3	42.30 ± 0.21 (38.90)	12.30 ± 0.19 (11.31)
	6	42.11 ± 0.15 (36.25)	9.15 ± 0.25 (7.88)
	9	42.86 ± 0.29 (35.58)	8.75 ± 0.24 (7.26)
	12	43.03 ± 0.48 (35.08)	7.08 ± 0.33 (6.36)

Note: Data represents mean values ± standard deviations; numbers in parentheses represent mean percentage of oven-dry weight prior to thermal treatment

A decrease in hemicellulose content - a highly hydrophilic polymer - reduces the free hydroxyl groups. It results in an increase in dimensional stability and decay resistance of heat-modified wood (Dubey *et al.* 2012; Li *et al.* 2016). The relationship between polysaccharidic fraction and physical and/or mechanical properties of heat-treated wood has been studied by many researchers so far. Significant power law regressions for the content of hemicelluloses with modulus of elasticity (MOE), modulus of rupture (MOR), and lightness were found by Kačíková *et al.* (2013). Strong positive loadings for lightness, blue-yellow chromatic coordinate, equilibrium moisture content, and contents of holocellulose and xylose were observed by Čabalová *et al.* (2018). In addition, strong positive correlations for the MOR and the MOE with the glucose and xylose content were detected by Kučerová *et al.* (2016).

Further valuable information was provided by FTIR spectroscopy. The differential spectra (Fig. 2) showed changes in the wood components caused by heat treatment. These are presented in the fingerprint region (1800 to 800 cm⁻¹), where most of the specific vibrations occurred. The intensity of the changes varied depending upon the treatment

conditions. The comparison of differential spectra showed that the heating temperature had a greater influence on the peak intensities than the time of heat treatment.

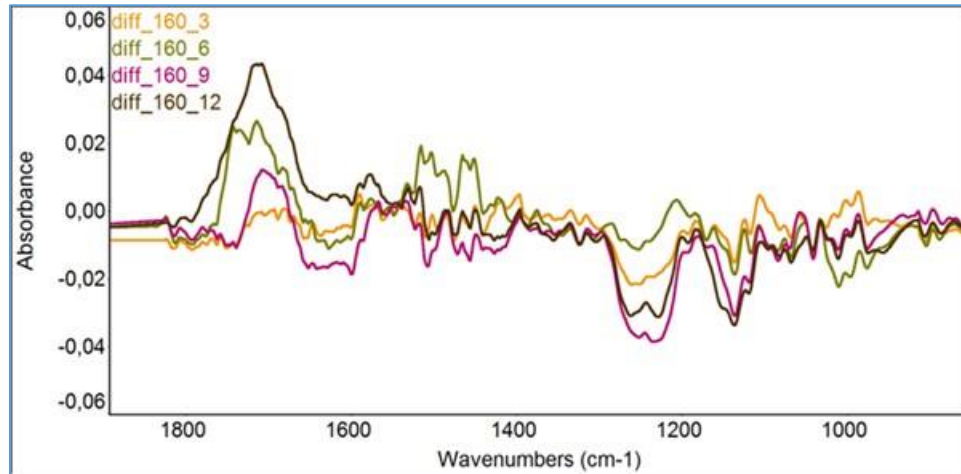


Fig. 2(a). Differential FTIR spectra of heat-treated ash wood at 160 °C

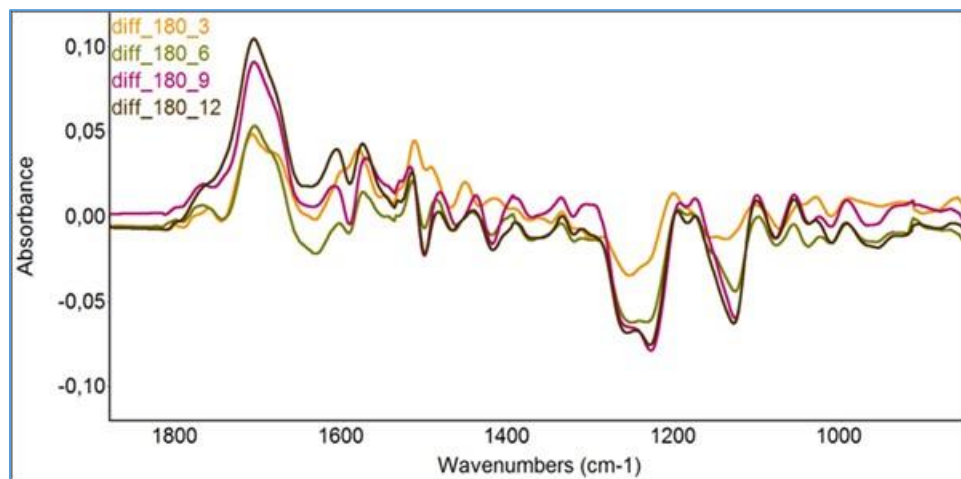


Fig. 2(b). Differential FTIR spectra of heat-treated ash wood at 180 °C

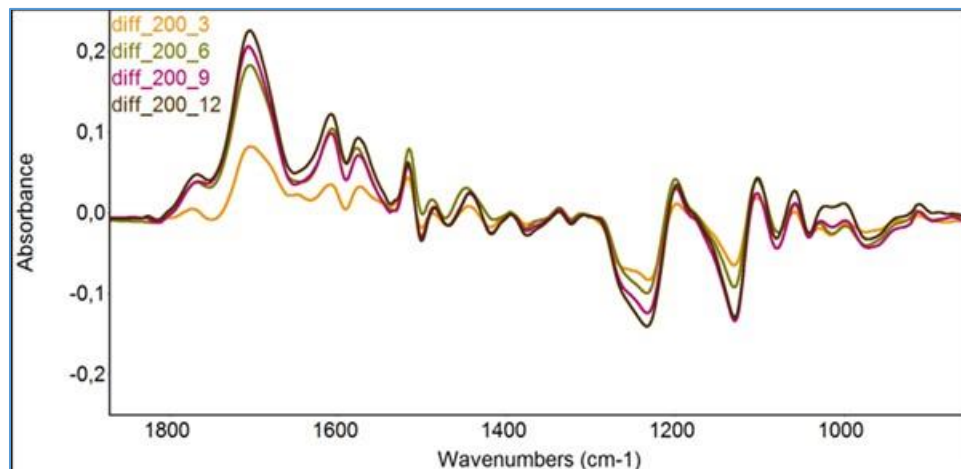


Fig. 2(c). Differential FTIR spectra of heat-treated ash wood at 200 °C

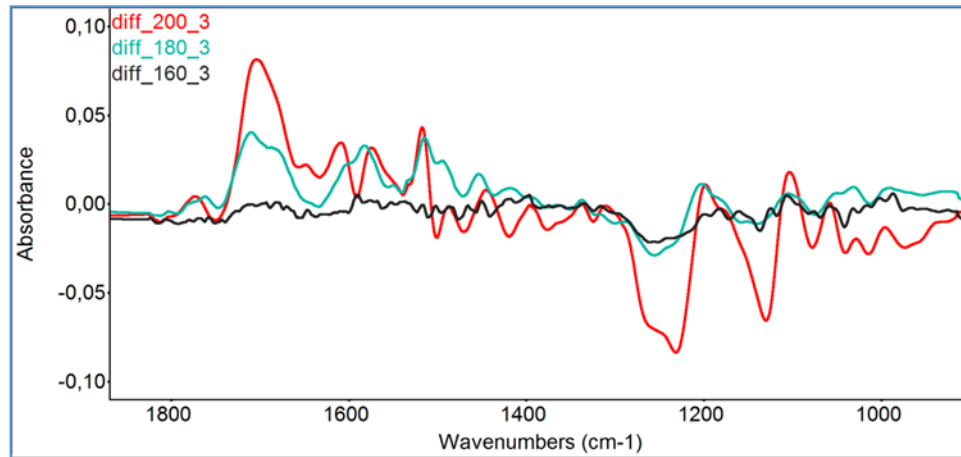


Fig. 2(d). Differential FTIR spectra of ash wood heat-treated for 3 h

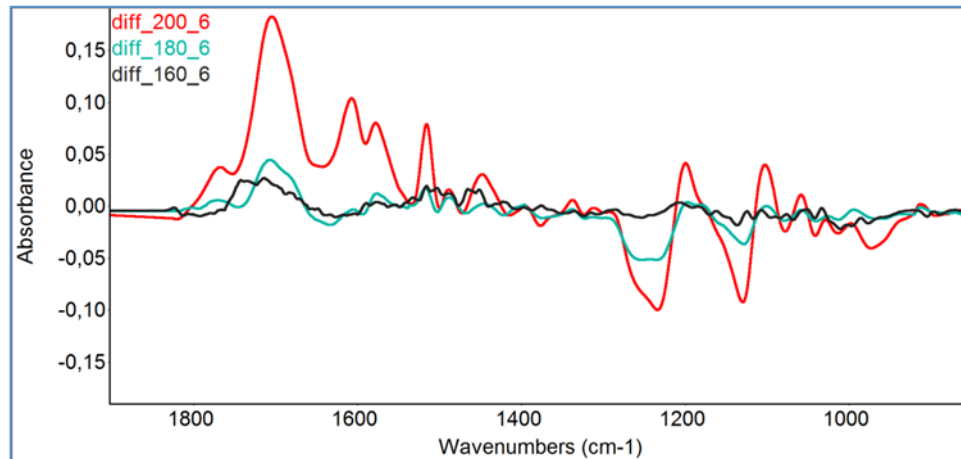


Fig. 2(e). Differential FTIR spectra of ash wood heat-treated for 6 h

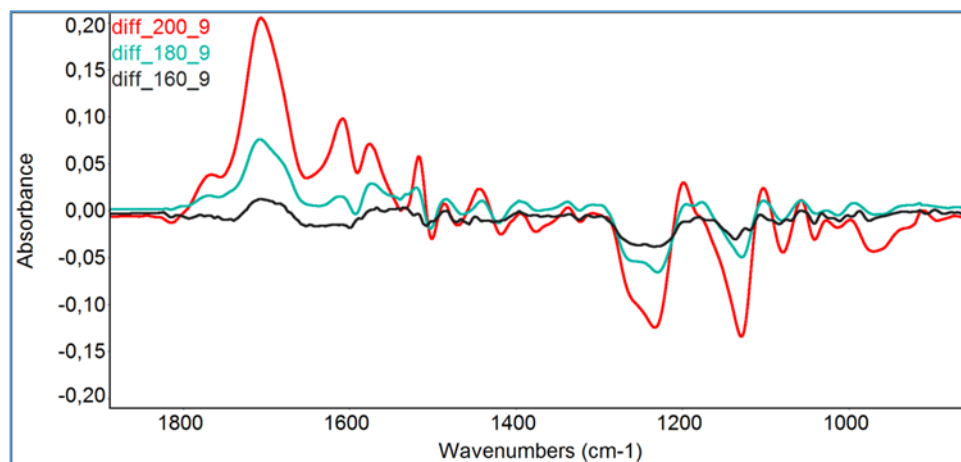


Fig. 2(f). Differential FTIR spectra of ash wood heat-treated for 9 h

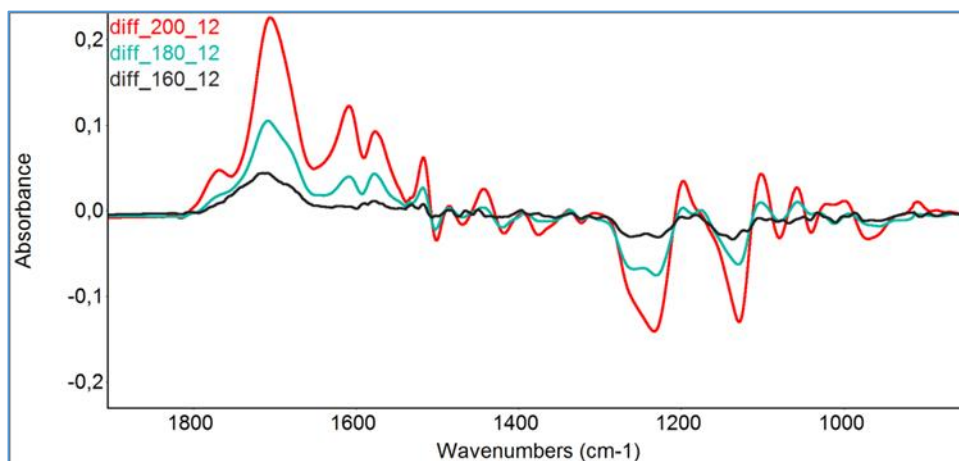


Fig. 2(g). Differential FTIR spectra of ash wood heat-treated for 12 h

The absorption peak at 1732 cm^{-1} corresponded to the unconjugated C=O stretching vibrations in lignin, and the carbonyl and carboxyl groups in hemicelluloses. During the process of the heat treatment of wood, the intensity increased. This may have been caused by the oxidation processes, by the opening of the glucopyranose ring, or by the cleavage of β -alkyl-aryl ether linkages in lignin (Windeisen *et al.* 2009; Esteves *et al.* 2013; Özgenc *et al.* 2017). Furthermore, with increasing treatment severity, the shift in a maximum to smaller wavenumbers was observed. According to Esteves *et al.* (2013), this may be due to an increase in carbonyl or carboxyl groups in the wood components by oxidation. Their formation contributed to the darkening of thermally loaded wood (Chen *et al.* 2012).

The peak at 1593 cm^{-1} was assigned to the aromatic skeletal and C=O stretch vibrations. This peak in treated wood broadened to approximately 1597 cm^{-1} and its intensity increased. The broadening of this peak suggested that there was an increase in structural diversity around the aromatic rings. The increase in the intensity of this peak may be due to an increase in the relative content of lignin in treated wood (Esteves *et al.* 2013; Cademartori *et al.* 2015; Wang *et al.* 2015).

Aromatic ring stretching vibrations are demonstrated also by the absorption band at 1506 cm^{-1} . According to Hon and Shiraishi (2000), this wavenumber is typical for hardwood lignin that consists of guaiacyl (G) and syringyl (S) units. Due to the thermal load, it shifted to 1512 cm^{-1} , which is typical for guaiacyl units. Mentioned shifting was reported also by other authors (Windeisen *et al.* 2009; Tuong and Li 2010; Wang *et al.* 2015) and may be caused by the demethoxylation of lignin.

Another absorption band representing lignin was located at a wavenumber 1459 cm^{-1} (aromatic C-H deformation and asymmetric bending of $-\text{CH}_3$ and $-\text{CH}_2$). Its intensity increased with increasing severity of treatment. Similar change in beech wood was observed also by Özgenc *et al.* (2017). However, in spectra of spruce and pine wood, the decrease in its intensity was found by cited authors.

The peak at 1420 cm^{-1} correlated to the asymmetric C-H deformations in hemicelluloses and lignin. The intensity slightly decreased after treatment over the temperature of $160\text{ }^\circ\text{C}$.

At the wavenumber of 1232 cm^{-1} (syringyl ring and C-O stretching in lignin and xylan), a decrease in peak intensity and broadening was observed. This suggests that xylan degraded and a more condensed structure of lignin was formed (Esteves *et al.* 2013).

The degradation of hemicelluloses was also evident in the decreased intensity of the peak at 1370 cm^{-1} (C–H deformation in carbohydrates) and at 1156 cm^{-1} (C–O–C vibration in carbohydrates), respectively. Hemicelluloses are the most thermally labile of the macromolecular cell wall components. When wood is heated, hemicelluloses degrade first, resulting in the formation of various volatile compounds (Hill 2006).

The absorption peak with the maximum at 1325 cm^{-1} in the spectrum of untreated wood was the result of the overlapping of three different peaks. Two of these peaks were assigned to cellulose (at 1332 cm^{-1} for OH in plane bending, and at 1316 cm^{-1} for CH_2 wagging), and the third was assigned to lignin (around 1329 cm^{-1} for the S-ring plus G-ring condensed). Heat treatment resulted in the broadening of peaks in this section of the spectra.

The intensity of the peak at 896 cm^{-1} (β -(1,4)-glycosidic linkage, and C-H deformation in cellulose) showed no considerable changes. Özgenc *et al.* (2017) found that change of this peak intensity depends on wood species. Whereas no change was observed in beech wood, there was a decrease in its intensity in softwood species.

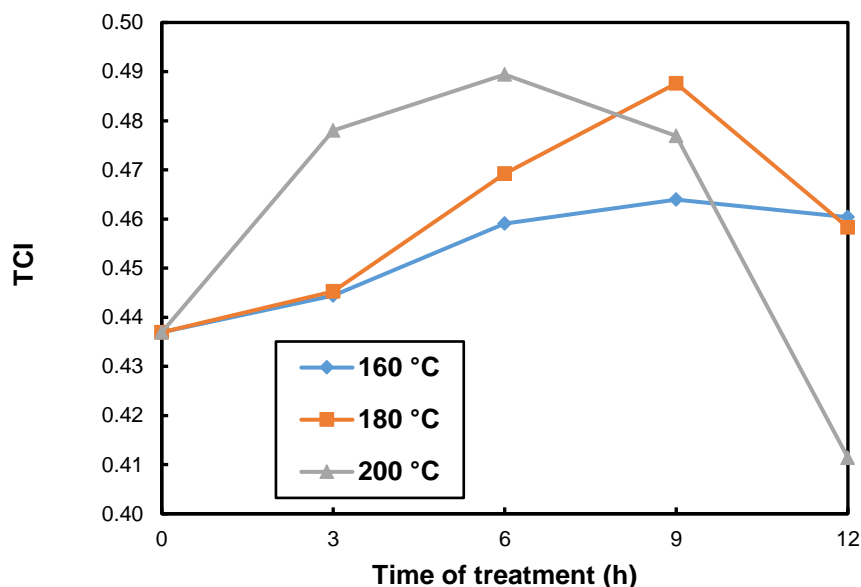


Fig. 3. Total Crystallinity Index of cellulose

During the initial stage of heat treatment, the degree of cellulose crystallinity increased. At the later stages a decrease was observed (Fig. 3). Crystallinity changes are more considerable at higher temperatures. The maximum crystallinity was found after 9 h of treatment at the temperatures of 160, and 180 °C or after 6 h at 200 °C. The initial increase in crystallinity could be caused by degradation of amorphous regions, and rearrangement or reorientation of quasicrystalline regions of cellulose. On the other hand, the decrease in cellulose crystallinity could be due to increased numbers of chain scission reactions that increased the amorphous character of cellulose (Bhuiyan *et al.* 2000; Kong *et al.* 2017). Higher crystallinity of cellulose results in low chemical reactivity, higher thermal stability, and higher tensile strength (Hill 2006; Poletto *et al.* 2012).

CONCLUSIONS

1. Considerable changes in the polysaccharides were caused by the heat treatment of ash wood. The content of holocellulose decreased already during the 3 h heat treatment at a temperature of 160 °C, which was caused by the degradation of less thermally stable hemicelluloses. It was evident that there was a decrease in D-xylose content in the heat-treated wood and that there were changes in intensity of hemicellulosic characteristic bands in the FTIR spectra. The intensity of degradation increased with increased severity of heating.
2. The lignin content slightly decreased at the beginning, at a temperature of 160 °C, while at higher temperatures it increased. In the lignin macromolecule, the demethoxylation and the formation of more condensed structures were observed.
3. The initial increase in the content of extractives may have been caused by the release of degradation products of the main wood components in the extraction mixture or by their condensation reactions with the extractives originally present in the untreated wood.
4. New carbonyl or carboxyl groups were formed due to oxidation under all treatment conditions. This may have contributed to wood darkening during heat treatment.
5. From the beginning an increase in the cellulose crystallinity was observed, and then it decreased. The maximum was reached at the temperatures of 160 and 180 °C for 9 h of treatment and at temperature of 200 °C for 6 h.

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