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Chemical alterations of pine wood saccharides during heat sterilisation

František Kačík[a,*], Pavel Šmíra[b], Danica Kačíková[c], Veronika Vel'ková[c], Andrea Nasswettrová[b], Vladimír Vacek[d]

[a] Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, 960 53 Zvolen, Slovakia
[b] Thermo Sanace, Chamrádová 475/23, 718 00 Ostrava-Kunčičky, Czech Republic
[c] Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, 960 53 Zvolen, Slovakia
[d] Department of Mathematics and Descriptive Geometry, Faculty of Wood Sciences and Technology, Technical University in Zvolen, T. G. Masaryka 24, 960 53 Zvolen, Slovakia

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ABSTRACT

Alterations in saccharides during heat sterilisation of pine wood (*Pinus sylvestris* L.) were investigated. The mass loss, extractives, lignin, cellulose, holocellulose and hemicelluloses were determined. Changes in saccharides were evaluated by the determination of monosaccharides in wood, size exclusion chromatography (SEC) as well as Fourier transform infrared (FTIR) spectroscopy. During heat sterilisation of pine wood the slight mass loss, an increase in extractives and a decrease in lignin and polysaccharides were observed. Hemicelluloses are degraded approximately twice as fast as cellulose. The degree of polymerisation of cellulose decreases approximately by 10% and it increases in holocellulose (by approx. 8%) as a result of a faster degradation of shorter hemicellulose chains. FTIR spectroscopy shows that sterilisation results in the deacetylation of cellulose and the formation of new carbonyl groups, an increase in the total crystallinity index (TCI) and a decrease in the lateral order index (LOI) and the hydrogen-bond intensity (HBI).

1. Introduction

Wood as a natural biodegradable material is permanently exposed to degradation processes of the environmental, chemical and microbial character. Particularly due to the biological degradation (wood-destroying fungi and insects) significant changes in its physical, mechanical and chemical properties occur. The range of damage depends on the environment in which the material is situated and on processes it is exposed to. A long-term action especially of biotic factors can finally result in the loss of function of wood as a structural element or the whole structure. Wood-destroying insects are considered the worst form of degradation of wooden parts of a building. The formation of larval frass often results in the loss of structural integrity of the infested wood and financial losses due to the need for treatment and/or replacement of the damaged wood (Heijari et al., 2008; Popescu, Tibirna, & Vasile, 2009; Yokoyama et al., 2009).

For the purpose of lengthening the durability of wooden parts of new constructions as well as historical buildings, various methods for their protection are searched for, e.g. traps of wood-destroying insects (Reddy, 2007; Reddy, Fettkother, Noldt, & Dettner, 2005), chemical treatments of wood with insecticides (Hagler & Blackmer, 2007; Hertel, 1997) and/or thermal modification of wood at the temperature of 160–260 °C improving its dimensional stability and biological resistance (Esteves, Domingos, & Pereira, 2008; Esteves & Pereira, 2009). A more moderate form of thermal wood protection is also its heat sterilisation. It is a practical and environmentally friendly treatment to kill pests in solid wood materials and prevent the transfer of pests between regions, states and continents. Current regulations for heat sterilisation of solid wood packaging materials require a minimal core temperature of 56 °C for 30 min, and of the firewood at least 71 °C for a minimum of 75 min (Wang, 2010; Wang, Bergman & Mace, 2010). At the thermal protection of wood in building structures against pests, wood is treated with air heated to the temperature of 120 °C where the temperature of 55–60 °C must be achieved in the cross-section of the wood for the period of 1 h. It is sufficient for the coagulation of proteins and killing the wood-destroying insects and at the same time the

* Corresponding author. Tel.: +421 45 5206 524; fax: +421 45 5321 811.
E-mail address: kacik@tuzvo.sk (F. Kačík).

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quantity of terpenes found in wood, which is then less attractive to insects, is reduced (Kacik et al., 2012; Kacik, Smira, Kacikova, Reinprecht, & Nasswettrova, 2014).

A disadvantage of thermally treated wood is the deterioration of its mechanical properties, due to which the use of wood modified in this way in some applications, in particular as a structural material, is limited. The decrease of strength properties is closely related to the chemical changes of main wood components (Boonstra, Van Acker, Tjeerdsma, & Kegel, 2007).

Most information about changes in mechanical, physical and chemical properties at temperatures used in the process of wood modification (160–260 °C) are available and data for lower temperatures are rare. The aim of our research was therefore to determine alterations in chemical and physical properties of pine wood caused by temperatures which are used at thermal protection of wooden structures.

2. Material and methods

2.1. Sample characteristics and treatment

Scots pine (*Pinus sylvestris* L.) wood at the age of 100 years was used. Three boards, 1000 × 180 × 25 mm (length × width × thickness), were conditioned at a temperature of 20 ± 2 °C and 65 ± 5% relative humidity to the moisture content of about 12%. Each of the boards was divided into three identical parts, where one of them was the reference sample, and the other ones were thermally treated. Heat treatment was applied to the experimental samples in a laboratory type heating oven Memmert UNB 200 controlled at an accuracy of ±1 °C under atmospheric pressure at the temperature of 60 °C and 120 °C. Once the target temperature had been reached, the temperature was held constant for 10 h. The mass loss (ML) was determined after cooling down the board in the dry environment.

2.2. Chemical analyses

Reference (untreated, denoted as 20 °C) and thermally modified samples were mechanically disintegrated to sawdust, and the fraction of the size 0.5–1.0 mm was extracted in the Soxhlet apparatus with a mixture of ethanol and toluene according to the ASTM Standard Test Method for Ethanol – Toluene Solubility of Wood D1107-96. Lignin content was determined according to the ASTM Standard Test Method for Acid-Insoluble Lignin in Wood D1106-96. Holocellulose was determined using the method of Wise, Murphy, and D'Addieco (1946), and cellulose by the Seifert method (Seifert, 1956). Hemicelluloses were calculated as a difference between holocellulose and cellulose. All measurements were performed on four replicates per sample. Data were presented as percentages of oven-dry weight per unextracted wood.

2.3. Size exclusion chromatography (SEC)

Samples of cellulose and holocellulose were derivatized using phenyl isocyanate to obtain tricarbanilates which were dissolved in tetrahydrofuran prior to size exclusion chromatography (SEC) analysis. The derivatives were prepared according to procedure described previously (Kacik, Kacikova, Jablonsky, & Katuscak, 2009). SEC analyses were performed at 35 °C with tetrahydrofuran at a flow rate of 1 ml min^{-1} on a two PLgel, 10 μm, 7.5 × 300 mm, MIXED B columns preceded by a PLgel, 10 μm, 7.5 × 50 mm, GUARD column. Two tricarbanilate derivatives were prepared for each sample and each derivative was analysed twice.

2.4. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the wood surface were recorded on Nicolet iS10 FT-IR spectrometer equipped with Smart iTR using attenuated total reflectance (ATR) sampling accessory attached ZnSe crystal (Thermo Fisher Scientific). The spectra were registered at an absorbance mode (A) from 4000 to 400 cm^{-1} at a spectral resolution of 4 cm^{-1}, and 64 scans were used. Measurements were performed on four replicates per sample. Crystallinity of cellulose indexes were calculated according to O'Connor, DuPré, and Mitcham (1958) for lateral order index (LOI, A_{1422}/A_{896}), (Nelson & O'Connor, 1964) for total crystallinity index (TCI, A_{1369}/A_{2918}) and (Nada & Hassan, 2000) for hydrogen bond intensity (HBI, A_{3336}/A_{1336}).

2.5. Statistical analysis

For all parameters, multiple comparisons were first subjected to an analysis of variance (ANOVA) and significant differences between average values of control and treated samples were determined using Duncan's multiple range test at a *P*-value of 0.05.

3. Results and discussion

3.1. Chemical changes

The mass loss (ML) of wood during its thermal treatment is one of the most important characteristics and it is commonly used for expressing a change in the quality of treated wood. ML depends on wood species, environment, temperature and time of heating. The published data for pine wood were found in the range from 0.4% (2 h, 190 °C) to 7.3% (12 h, 210 °C) (Esteves, Marques, Domingos, & Pereira, 2007), ML rapidly increased at higher temperatures (260 °C) and it reached the value of 18.5% after 15 min and 30% after an hour of heating (Bourgois & Guyonnet, 1988). A correlation between temperature and ML was determined at the temperature range of 20–237 °C during the thermal treatment of spruce wood (Kacikova, Kacik, Cabalova, & Durkovic, 2013) according to which the calculated mass losses at the temperatures of 60 and 120 °C are 0.17% and 0.52%. Slightly higher values measured in this work (0.21% and 0.64%) can be caused by a higher ratio of extractive substances in pine wood (5.80%) compared to spruce wood (2.17%) (Table 1).

During thermal treatment the amount of extractives increases significantly (Table 1). The increase in extractives at higher temperatures was found out in various types of hardwood as well as softwood species (Esteves, Graca, & Pereira, 2008; Esteves, Videira, & Pereira, 2011; Nuopponen, Vuorinen, Jamsa, & Viitaniemi, 2003; Peters, Fisher, & Fischer, 2008). The composition of extractives changes at higher temperatures – some disappear and new ones are formed. These changes can influence some properties of thermally modified wood, e.g. wettability (Esteves, Domingos, & Pereira, 2008; Manninen, Pasanen, & Holopainen, 2002; Nuopponen et al., 2003).

Hemicelluloses are changing at thermal treatment as the first ones of the main wood components, and at relatively low temperatures. Their degradation starts with deacetylation and the formed acetic acid acts as a catalyst of depolymerisation reactions and further accelerates the degradation of polysaccharides. Acid-catalysed reactions result in the formation of formaldehyde, 2-furaldehyde and other aldehydes (Nuopponen, Vuorinen, Jamsa, & Viitaniemi, 2004; Rowell, 2012; Sivonen, Maunu, Sundholm, Jamsa, & Viitaniemi, 2002; Tjeerdsma, Boonstra, Pizzi, Tekely, & Militz, 1998). The significant decrease of holocellulose and hemicellulose yields (Table 1) is in agreement with results of other authors who discovered at thermal treatment on various wooden

Table 1
Mass loss and yields of extractives and main wood components of heat-treated pine wood. Data represent mean percentages of oven dry weight ± standard deviations.

Temperature (°C)	Mass loss (%)	Extractives (%)	Lignin (%)	Holocellulose (%)	Cellulose (%)	Hemicelluloses (%)
20	0.00 ± 0.00	5.80 ± 0.08	24.34 ± 0.04	74.66 ± 0.09	44.15 ± 0.11	30.51 ± 0.19
60	0.21 ± 0.01	7.94 ± 0.09	23.81 ± 0.07	72.48 ± 0.13	43.53 ± 0.16	28.96 ± 0.28
120	0.64 ± 0.02	12.47 ± 0.10	22.92 ± 0.05	66.56 ± 0.14	40.94 ± 0.25	25.62 ± 0.36

Table 2
Relative amounts and yield of monosaccharides in the samples of pine wood (%). Data represent means ± standard deviations.

Temperature (°C)	GLC	XYL	GAL	ARA	MAN	Yield
20	68.09 ± 0.17	6.74 ± 0.12	1.87 ± 0.24	5.11 ± 0.43	18.18 ± 0.34	71.45 ± 0.61
60	69.37 ± 0.52	6.18 ± 0.11	1.85 ± 0.14	4.86 ± 0.38	17.74 ± 0.13	68.63 ± 0.58
120	71.21 ± 0.09	5.06 ± 0.16	1.34 ± 0.04	4.75 ± 0.14	17.64 ± 0.22	63.33 ± 0.80

Note: GLC = D-glucose, XYL = D-xylose, GAL = D-galactose, ARA = L-arabinose, MAN = D-mannose.

species that hemicelluloses are degraded more easily than cellulose and xylans were degraded from hemicelluloses in the most easiest way (Alen, Kotilainen, & Zaman, 2002; Esteves, Graca, & Pereira, 2008; Zaman, Alen, & Kotilainen, 2000). Unlike reported results, we observed changes in saccharides even at lower temperatures (60 and 120 °C) (Table 1).

During thermal treatment the relative quantity of glucose in pine wood increases, while quantities of non-glucose saccharides decrease due to the faster degradation of hemicelluloses compared to cellulose; the changes are significant (Table 2). Pentosans are degraded faster than hexosans and xylans degrades in the fasted way at both applied temperatures, which is consistent with the findings for thermally modified pine and spruce wood (Gonzalez-Pena, Curling, & Hale, 2009). However, there is a significant decrease in the yields of saccharides, which is in agreement with results of cellulose and hemicelluloses determination which are given in Table 1.

3.2. Degree of polymerisation (DP) and molecular weight distribution (MWD)

Cellulose is more resistant to thermal action compared to hemicelluloses (the decrease in the yield of cellulose was 7.27% and hemicelluloses 16.03% of the original values), as reported in the literature (Bourgois, Bartholin, & Guyonnet, 1989; Yildiz, Gezer, & Yildiz, 2006). A significant decrease in the degree of polymerisation (DP) occurs at the temperature of 60 °C and increasing the temperature to 120 °C does not cause any significant decrease of DP (Table 3). The molecular weight distribution (MWD) curves (Fig. 1) shows that the decrease in DP at 60 °C is caused by the split of high-molecular-weight fractions of cellulose. Fractions with the medium molecular weight are split up at the temperature of 120 °C, forming shorter chains results an increase of polydispersity (PD), but not in a significant decrease in DP. The cellulose degradation does not only depend on temperature, but also on the duration of treatment. Fengel (1966) determined in cellulose isolated from thermally treated spruce wood that during 24-h lasting heating at the temperature of 120 °C the degree of polymerisation was relatively constant (DP ~700) and it sharply dropped (DP ~300) when the temperature was increased to 200 °C. After 90-min thermal treatment of spruce wood, the cellulose DP is constant up to the temperature of approx. 160 °C and it rapidly decreases when the temperature is increased above 220 °C (Kacikova et al., 2013).

In holocellulose samples, a significant change in DP does not occur at 60 °C, which can be explained by the simultaneous splitting of longer chains of cellulose and shorter chains of hemicelluloses which mutually compensate. Apart from cellulose, where DP decreases at the temperature of 120 °C, DP in holocellulose increases due to the faster splitting of hemicelluloses with the molecular weight of approx. 15,500 and the quantity of cellulose chains with higher molecular weights increases approx. within the range of 250,000–1,100,000 (Fig. 2, Table 4).

3.3. Fourier transform infrared (FTIR) spectroscopy

In the cellulose chain there are three hydroxyl groups available for interaction with other hydroxyl groups, forming secondary valence bonds. This hydrogen-bonding network plays a significant role with respect to crystallinity and chain structure (Siroky, Blackburn, Bechtold, Taylor, & White, 2010). Considering the chain mobility and bond distance, the hydrogen bond intensity (HBI) of

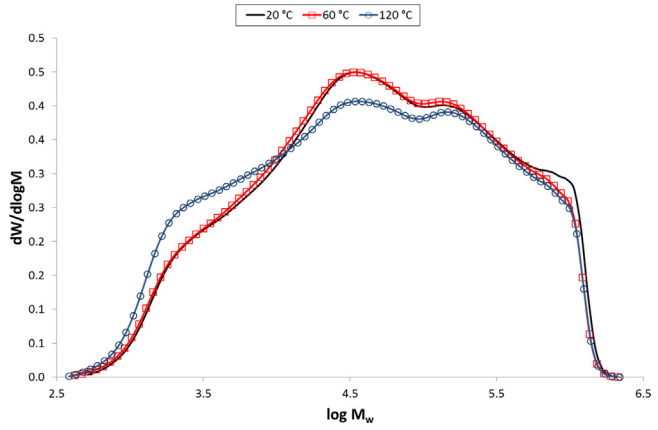

Fig. 1. Molecular weight distribution of cellulose before and after thermal treatment of pine wood.

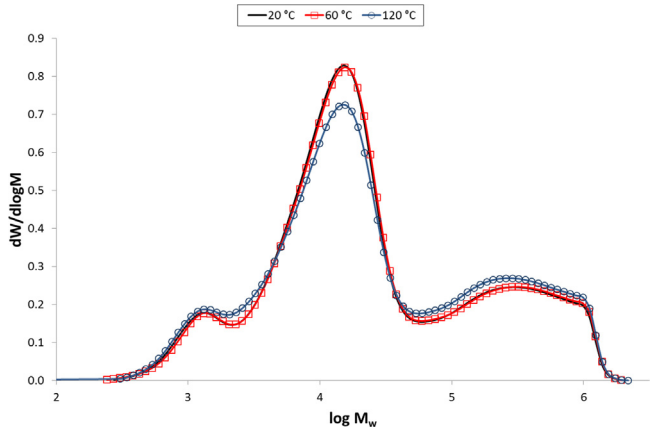

Fig. 2. Molecular weight distribution of holocellulose before and after thermal treatment of pine wood.

Table 3
Results of macromolecular characteristics of cellulose from heat-treated pine wood. Data represent means ± standard deviations.

Temperature (°C)	M_n	M_w	M_z	PD	DP
20	15,474 ± 647	217,496 ± 5252	643,727 ± 19316	14.08 ± 0.82	1343 ± 32
60	13,804 ± 315	198,223 ± 4126	613,306 ± 4798	14.36 ± 0.05	1224 ± 25
120	11,694 ± 112	196,443 ± 1897	606,702 ± 6268	16.80 ± 0.31	1213 ± 12

Note: M_n = number average molecular weight (MW), M_w = weight average MW, M_z = z average MW, PD (polydispersity) = M_w/M_n), $DP_w = M_w/162$.

Table 4
Results of macromolecular characteristics of holocellulose from heat-treated pine wood. Data represent means ± standard deviations.

Temperature (°C)	M_n	M_w	M_z	PD	DP
20	8537 ± 230	154,551 ± 1013	637,827 ± 3018	18.11 ± 0.38	954 ± 6
60	8343 ± 389	154,214 ± 3911	640,130 ± 6839	18.50 ± 0.41	952 ± 24
120	7603 ± 690	167,379 ± 1594	653,212 ± 4944	22.14 ± 1.80	1033 ± 10

Note: M_n = number average molecular weight (MW), M_w = weight average MW, M_z = z average MW, PD (polydispersity) = M_w/M_n), $DP_w = M_w/162$.

cellulose is closely related to the crystal system and the degree of intermolecular regularity, that is, crystallinity, as well as the amount of bound water (Oh, Yoo, Shin, & Seo, 2005).

During thermal treatment of pine wood the signal intensity slightly decreases approximately at 3400 cm^{-1} (OH-stretching, or intra-molecular hydrogen bonds in cellulose) as well as at the band around the wavenumber of 2900 cm^{-1} (C—H bonds in cellulose) (Rosa, Rehman, de Miranda, Nachtigall, & Bica, 2012). The decrease in band intensity at 1728 cm^{-1} is caused by deacetylation of hemicelluloses and simultaneously intensity at 1719 cm^{-1} slight increase, which suggests the formation of new carbonyl groups. Similar effect was observed at the thermal treatment of spruce and pine wood (Kotilainen, Toivanen, & Alen, 2000), beech and pine wood (Tjeerdsma & Militz, 2005) and beech and ash wood (Windeisen, Baechle, Zimmer, & Wegener, 2009). Splitting-off of acetyl groups reduces the band intensity at 1245 cm^{-1}, which was also observed by Windeisen et al. (2009); Windeisen, Strobel, and Wegener (2007) during the thermal treatment of ash and beech wood. The decrease in intensity at 1644 cm^{-1} is caused by the decrease in quantity of adsorbed water due to heating of pine wood, which is in agreement with results obtained from thermal modification of spruce wood (Chung, Lee, & Choe, 2004; Yildiz & Gumuskaya, 2007). Bands at wavenumbers of 1160 and 1103 cm^{-1} (antisymmetric bridge oxygen stretching or C=O and C=C stretching and CH_2 rocking) (Baeza & Freer, 2001) as well as at 1053 cm^{-1} (asymmetric in-plane ring stretching) (Chung et al., 2004; Yildiz & Gumuskaya, 2007) increase at the temperature of 60 °C and decrease at the temperature of 120 °C (Table 5).

Our results show that the value of total crystallinity index (TCI) increases during thermal modification of pine wood due to the faster degradation of the amorphous fraction of cellulose, as confirmed in more studies (Chung et al., 2004; Yildiz & Gumuskaya, 2007). However, cellulose crystallinity increased with thermal modification due to degradation of its amorphous part and it is related not only to temperature but also time of thermal treatment (Wikberg & Maunu, 2004), e.g. Bhuiyan, Hirai, and Sobue (2000) found out that the degree of crystallinity of spruce wood increased during the initial stage of heat treatment and decreased at the advanced stages. The cellulose lateral order intensity (LOI) and hydrogen bond intensity (HBI) in our experiments slightly decrease during heating (Table 6).

It is known, that the crystallinity of cellulose influences the thermal stability of wood. It can therefore be presumed that cellulose with higher values of TCI, LOI and HBI will have a higher thermal stability (Poletto, Pistor, Zeni, & Zattera, 2011; Poletto, Zattera, Forte, & Santana, 2012). On the other hand, some authors found out that the thermal stability of cellulose depends especially on the crystallinity index, the size of crystals and the degree of polymerisation (Kim, Eom, & Wada, 2010; Newman, 1999; Poletto, Pistor, Zeni, & Zattera, 2011). Poletto, Zattera, et al., 2012 and Poletto, Zattera, & Santana, 2012) have recently shown that higher extractive contents in the wood accelerate the degradation process and promote an increase in the conversion values at low temperatures and cellulose crystallinity inhibits wood degradation. The increase in cellulose crystallinity influences physical properties, e.g. wettability which reduces during thermal modification of wood because the quantity of hydroxyl groups accessible for water adsorption is reduced (Boonstra & Tjeerdsma, 2006; Wikberg & Maunu, 2004). This phenomenon is also supported by faster degradation of hemicelluloses. From our results an increase of thermal stability of cellulose in the treated pine can be predicted.

Table 5
FT-IR absorbances of cellulose samples isolated from pine wood.

Wavenumber (cm^{-1})	Temperature (°C)		
	20	60	120
3336	0.0412	0.0382	0.0374
2895	0.0124	0.0112	0.0093
1728	0.0042	0.0037	0.0028
1644	0.0036	0.0031	0.0028
1456	0.0101	0.0089	0.0082
1429	0.0143	0.0136	0.0132
1368	0.0191	0.0186	0.0182
1334	0.0190	0.0182	0.0179
1316	0.0227	0.0219	0.0214
1280	0.0103	0.0099	0.0099
1260	0.0103	0.0098	0.0091
1247	0.0101	0.0096	0.0091
1202	0.0054	0.0520	0.0520
1160	0.0300	0.0320	0.0290
1103	0.0610	0.0620	0.0600
1053	0.1055	0.1065	0.1061
897	0.0166	0.0171	0.0172
810	0.0018	0.0015	0.0015

Table 6
FT-IR crystallinity ratio and hydrogen bond intensity for the cellulose samples.

Temperature (°C)	A1368/A2898 (TCI)	A1429/A897 (LOI)	A3336/A1336 (HBI)
20	1.5403	0.8614	1.8150
60	1.6607	0.7953	1.7443
120	1.9570	0.7674	1.7477

4. Conclusions

From experimental results obtained at heat sterilisation of pine wood can be concluded that a slight mass loss, an increase in extractive substances and a decrease in contents of main wood components – lignin and polysaccharides – take place. Changes

in saccharides occurred at relatively low temperatures (60 and 120 °C). Hemicelluloses are degraded approximately twice as faster as cellulose. The degree of polymerisation (DP) of cellulose decreases approximately by 10% and it increases in holocellulose (by approximately 8%) as a result of a faster degradation of shorter hemicellulose chains. FTIR shows that modification results in the deacetylation of cellulose and the formation of new carbonyl groups, an increase of the total crystallinity index (TCI) and a decrease in the lateral order index (LOI) and the hydrogen-bond intensity (HBI). These changes can result in increased resistance to pests and to improve the dimensional and thermal stability of wood. A slight deterioration of mechanical properties is not an obstacle to the use of thermally modified wood for structural purposes.

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