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RESISTANCE OF THERMALLY OR CHEMICALLY AND THERMALLY PRETREATED MAPLE WOOD (*ACER PSEUDOPLATANUS L.*) TO THE FUNGUS SERPULA LACRYMANS*

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Maple wood impregnated primarily by water solutions of sulphuric acid with concentrations from 0 % to 2,5 % was thermally treated at temperatures of 160 or 190 °C within the time frame of 3 hrs. Subsequently it was exposed to a biodegradation by the brown-rot fungus *Serpula lacrymans* for the duration of 1 month. The rotting of wood was slowed down only in those situations when the thermal pretreatments of wood were combined with its pretreatmet of a relatively higher concentrations of the acid.

Key words: Thermolytic reactions, thermally pretreated wood, chemically pretreated wood, sulphuric acid, charring, toxic substances, maple wood, brown-rot fungus *Serpula lacrymans*

INTRODUCTION

On the basis of practice experiences we know that a wood rotting can be stopped by flame or high temperature as a consequence of wood sterilization (immediate protection) and char formation (long-term protection).

The spores and mainly the mycelia of fungi are not thermostable. They can be destroyed at relatively low temperatures usually ranging from 45 to 105 °C. However, such thermic sterilization has just a short-term effect. On the other

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hand, in a situation if substances with toxicity to fungi could simultaneously be formed, the wood (trees, wooden products) would be less accessible for the following biodegradation processes.

The first part of this work deals with the basic thermolytic reactions in the lignin-polysaccharidic complex of wood due to which some toxic substances acting against fungi could be formed, as well. Second part of this work presents one of our model experiments aimed at resistance of thermally pretreated maple wood to fungi, i.e. the resistance of pretreated maple wood against the brown-rot fungus *Serpula lacrymans*.

THERMOLYTIC REACTIONS IN WOOD AND POSSIBILITIES FOR CREATION OF TOXIC SUBSTANCES

The course of various thermolytic reactions (homolytic and heterolytic) in wood depends mainly on quantities of heat and oxygen transport into wood and on catalytic additives in wood.

On the basis of many experiments (Sandermann and Augustin 1963, Nassar and Mackay 1984, Shafizadeh 1984, Košík 1987, Rychlý 1995), in which the techniques of thermal analysis (DTA, TG, DTG), gas chromatography, IR- and NMR-spectroscopy, cone calorimeter method, oxygen index test, and other methods have been used, it is evident that hemicellulose is the most thermo-unstable and lignin is the most thermo-stable component of wood.

The exothermic reactions, accompanied, for example, with levoglucosan and combustible volatiles formation from cellulose, are inhibited by various fire retardants (Woo and Schniewind 1987, Reinprecht and Mihálik 1988, Košík et al. 1989, Balog 1995).

Acids: - H_2SO_4, H_3PO_4, ..., and their salts: - $[NH_4]_2SO_4$, $NH_4H_2PO_4$, ..., catalyze in polysaccharides the hydrolysis of glycosidic bonds random depolymerization, and also the dehydration reactions creation of intermediate products (2-furaldehyde and other furan derivatives, levoglucosenone and other pyran derivatives, various olefinic and aromatic structures) which are important in char formation. Aromaticity and graphitelike ringing of the char is accompanied with a reduction of the hydrogen and oxygen ratios to carbon. These reactions are competetive to levoglucosan formation and retard flaming combustion of wood.

In the following points the thermolytic reactions in all polymers of wood (hemicelluloses, cellulose, and lignin) with regard to a temperature of 300 C are briefly summarized, analogously to the idea of Shafizadeh (1984)*.

a) At temperatures below 300 °C the following reactions are dominant:

- random hydrolytic and thermooxidative scission of bonds in wooden polymers which is connected with reduction in their degree of polymerization;
- elimination of water;

* Shafizadeh (1984) classified the thermolythic reaction in cellulose with regard to a temperature of 300 °C. On the basis of this brief review of thermolytic reaction in wood components it is evident that during thermal degradation of wood also substances with a toxic effect on fungi can be formed. The most toxic substances for fungi are quinones, furan derivativer, phenols, higher aromatic compounds, but in specific situations can also be formed other substances even with a higher toxicity.

- hydrolytic elimination of acetic acid from acetylated hemicelluloses;
- cleavage of C-C alkyl-alkyl bonds as well as of C_{β}-O-C_4 β-aryl ether or C_{α}-O-C_4 α-aryl ether bonds in lignin;
- cleavage of aryl-glycosidic bonds between lignin and hemicelluloses;
- formation of free radicals;
- recombination of free radicals; e.g. due to disproportionation of two phenoxy radicals can be formed more toxic benzoquinones (p-benzoquinone, ...);
- formation of carbonyl, carboxyl, and hydroperoxide groups;
- creation of lactones,
- evolution of CO and CO_2;
- production of a charred residue.

b) At temperatures above 300 C the following reactions are dominant:

- depolymerization of cellulose by transglycosylation mechanism, and perhaps by others, as well (Blažej and Košík 1985), when the levoglucosan (1,6-anhydro-β-D-glukopyranose) but also others anhydromonosaccharides are formed;
- cleavage of C-C, C-O, and other bonds which is connected with evolution of various lower molecular volatile products (H_2O, CO, CO_2, methanol, formaldehyde, acetaldehyde, furan, ...), including free radicals; e.g. in lignin the C-O-CH_3 aryl-methyl ether bonds, C-C alkyl-aryl bonds, or C-C bonds in aromatic ring are cleaved;
- repolymerization of degradation products arisen from lignin-polysaccharidic complex on tar condensate aromatic products and solid charred residues which contain a high portion of carbon.

RESISTANCE OF THERMALLY PRETREATED MAPLE WOOD TO THE BROWN-ROT FUNGUS SERPULA LACRYMANS

MATERIAL AND METHODS

The model experiments have been carried out with the selected specimens of maple log (*Acer pseudoplatanus* L.) with a cross-section of 15 mm x 15 mm (tangential x radial).

Firstly, the sound specimens with a length of 400 mm were subjected to thermal or combined chemical and thermal degradation processes and subsequently their both ends with a length of 30 mm were exposed to a biodegradation processes by the brown-rot fungus *Serpula lacrymans.*

I. Thermal (chemical and thermal) pretreatment of specimens

With the aim to model a presence of some fire retardants (e.g. amonium sulphate $[NH_4]_2SO_4$) in wood and also to expedite the charring process, the tested specimens were at first impregnated (Δp = 0,8 MPa, τ = 3 hours, T = 20 °C) with water or water solutions of sulphuric acid:

C_{H2SO4} = 0 %, 0.1 %, 0,25 %, 0,5 %, 1 % or 2,5 %.

The mass retention of sulphuric acid into maple specimens (R_{H2SO4} [%]) increased proportionally with the rise of the acid concentration (C_{H2SO4}) (table 1).

Table 1
Tabela 1

Retention (R) of sulphuric acid into maple specimens
Zawartość (R) kwasu siarkowego w próbkach klonu

C_{H2SO4} [%]	0	0.1	0.25	0.5	1.0	2.5
T_1 = 160°C R_{H2SO4} [%]	0	0.09	0.22	0.46	0.71	1.83
T_2 = 190°C R_{H2SO4} [%]	0	0.11	0.18	0.38	0.83	1.75
Σ R_{H2SO4} [%]	0	0.10	0.20	0.42	0.77	1.79

Note: R_{H2SO4} = (mass of H_2SO_4 determined in specimens before thermal treatment / mass of original specimens in the oven dry state) x 100 [%]
Uwaga: R_{H2SO4} =(masa H_2SO_4 oznaczona w próbkach przed obróbką termiczną / masa początkowa próbek w stanie suchym) x 100 [%]

Impregnated specimens were conditioned to a moisture content level of w 25 % - 30 % and then thermally treated within the time frame of τ = 3 hours in the laboratory drying-kiln WS 100 at two different temperatures: T_1 = 160°C or T_2 = 190 °C (table 2).

Table 2
Tabela 2

Losses of mass (Δm_T - arithmetic mean) of maple specimens caused by the thermal or chemical and thermal treatments

Ubytek masy (Δm_T - średnia arytmetyczna) próbek klonu pod wpływem obróbki termicznej lub chemicznej i termicznej

C_{H2SO4} [%]	0	0.1	0.25	0.5	1.0	2.5
T_1 = 160°C Δm_T [%]	0.32	0.67	1.02	1.98	7.32	17.45
T_2 = 190°C Δm_T [%]	1.12	1.80	2.03	3.21	22.62	28.51

Note:
Uwaga:
$\Delta m_T = [(m_o - m_T / m_o]. 100$ [%]
where: m_o - the mass of the original specimen in the oven dry state
m_o - masa początkowa próbki, w stanie suchym
m_T - the mass of the thermally treated specimen in the oven dry state
m_T - masa próbki po obróbce termicznej w stanie suchym
The calculation of Δm_T is connected with a negligible error as a presence of the sulphuric acid in specimens. This error was not regarded:
- partly due to the relatively low amount of the acid (R_{H2SO4}) in original specimens (table 1);
- partly because the amount of evaporated acid during a thermall exposition was not determined.

Obliczenie Δm_T jest związane z nieznacznym błędem wynikającym z obecności kwasu siarkowego w próbkach. Błędu tego nie uwzględniono:
- z powodu stosunkowo niskiej zawartości kwasu (R_{H2SO4}) w próbkach pierwotnych (tabela 1);
- z powodu nie wyznaczenia ilości kwasu odparowanego podczas obróbki termicznej

II. Biodegradation of thermally pretreated specimens

The mycological tests were carried out in laboratory conditions using the brown-rot fungus *Serpula lacrymans* (Wulf. ex Fr.) Schroet. as a testing organism:

- Thermally pretreated specimens with the dimension of 15 x 15 x 30 mm were situated into 1 litre Kolle's flasks on the fungous mycelium which had been grown on the agar-malt cultivating soil.

Note: Totally 144 specimens (12 series each with 12 specimens) were subjected to the mycological test.

- Incubating temperature $T = 20 \pm 1\ ^{o}C$.
- Exposure time $\tau = 1$ month.

The mycological tests were evaluated on the basis of the mass losses of specimens (Δm_F) caused only due to the fungus activity (table 3, fig. 1 and 2).

Determination of Δm_F :

$$\Delta m_F = \frac{m_F - m_F}{m_T} \cdot 100\ \%$$

where:

m_F - the mass of the thermally treated and then mycologically tested specimen in the oven dry state

m_T - the mass of the thermally treated specimen in the oven dry state.

Table 3
Tabela 3

Mycological test carried out with the pretreated maple specimens and evaluated by the losses of mass (m_F - arithmetic mean) caused by the fungus *Serpula lacrymans* (1 month)
Wyniki testu mykologicznego wykonanego na próbkach klonu nasyconych kwasem siarkowym - oznaczono ubytki masy (m_F - średnia arytmetyczna) pod wpływem grzyba *Serpula lacrymans* po 1 miesiącu

C_{H2SO4} [%]	0	0.1	0.25	0.5	1.0	2.5
$T_1 = 160^oC$ Δm_T [%]	4.05	4.81	5.97	3.95	1.75	0
$T_2 = 190^oC$ Δm_T [%]	3.72	5.47	5.10	3.00	0.94	0

Note: $\Delta m_{F\ (untreated\ maple)} = 4{,}2\%$
Uwaga: $\Delta m_{F\ (klon\ nienasycony)} = 4{,}2\%$

RESULTS AND DISCUSSION

The biodegradation process (caused by the brown-rot fungus *Serpula lacrymans*) in thermally pretreated maple specimens was not in the majority of cases more apparently inhibited by the thermal (chemical and thermal) effects (table 3, fig. 1 and 2).

Only in those situations when the thermal treatment was carried out with specimens which contained already a higher amount of sulphuric acid, the rotting was slowed down (c_{H2SO4} = 1 %) or not even began (c_{H2SO4} = 2.5 %). These inhibition effects could have been caused not only as a consequence of toxic substances (carbonized wood, free radicals, quinones,...) formed in thermally degraded maple, but probably also due to a very low acidity in wood substance which is unsuitable for fungi.

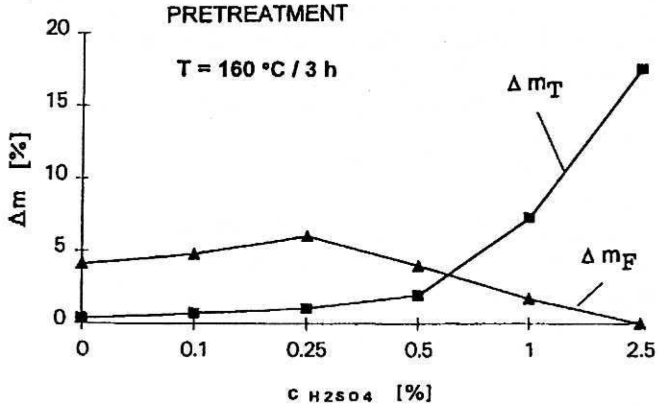

Fig. 1 Losses of mass (Δm) in maple wood:
Rys. 1 Ubytki masy (Δm) drewna klonu
Δm_T - during the thermic degradation process [T_1 = 160 °C / 3 hours];
Δm_T - podczas rozkładu termicznego [T_1 = 160 °C / 3 hours];
Δm_F - during the subsequent biological degradation process with the fungus *Serpula lacrymans* [T = 20 °C / 1 month]
Δm_F - podczas późniejszego procesu biodegradacji pod wpływem grzyba *Serpula lacrymans* [T = 20 °C / 1 miesiąc]

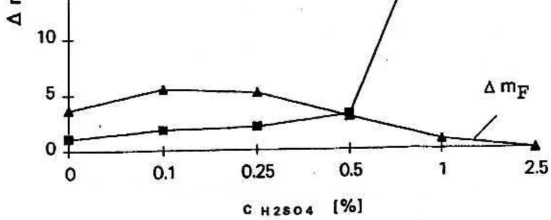

Fig. 2 Losses of mass (Δm) in maple wood:
Rys. 2 Ubytki masy (Δm) drewna klonu
Δm_T - during the thermic degradation process [T_1 = 190 °C / 3 hours];
Δm_T - podczas rozkładu termicznego [T_1 = 190 °C / 3 hours];
Δm_F - during the subsequent biological degradation process with the fungus *Serpula lacrymans* [T = 20 °C / 1 month]
Δm_F - podczas późniejszego procesu biodegradacji pod wpływem grzyba *Serpula lacrymans* [T = 20 °C / 1 miesiąc]

On the other hand, a gentle increasing of biodegradation processes was obtained in those situations when the thermally treated maple wood (treated at both temperatures: 160 °C or 190 °C) contained a lower amount of sulphuric acid (C_{H2SO4} = 0,1 % or 0,25 %). This result can be explained by a catalytic action of sulphuric acid on hydrolytic reactions in polysaccharides (Košík et al. 1989). The created oligosaccharides are inducers of cellulases (Eriksson et al. 1990). Simultaneously they can be faster deteriorated by extracellular enzymes of fungi on watersoluble di- and monosaccharides which are subsequently metabolized inside the fungi mycelia on carbon dioxide and water.

RECAPITULATION

The problem referring to biodegradation of pretreated wood, which was intentionally or non-intentionally exposed to the primary thermal or chemical and thermal effects, has over the last years been permanently the print of our interest with the aim to anticipate relations among the abio- and biodegradation processes (Reinprecht 1996).

The results of this work confirmed that a wood primary treated by abiotic agents can be more or less accessible for subsequent attack by fungi. Biodegradation processes are usually accelerated in a consequence of depolymerization reactions in a lignin-polysaccharidic matrix of wood and inhibited due to formation of toxic agents.

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REFERENCES

Balog K. (1995): Reakcia celulózových materiálov na oheň a proces horenia. [Habilitačná prácal], Technical University in Zvolen, Zvolen, 94 p.

Blažej A., Košík M. (1985): Fytomasa ako chemická surovina. (Phytomass as a raw material), Veda, Bratislava, 402 p.

Eriksson K-E. L., Blanchette R.A., Ander P. (1990): Microbial and enzymatic degradation of wood and wood components. Springer Series in Wood Science, Berlin Heidelberg, 407 p.

Košík M. (1987): Reakcie zložiek dreva pri termolytickom a hydrolytickom pôsobení a ich vplyv na selektívnos procesu. [Doktorská dizertačná prácal, Slovak Technical University - ChTF, Bratislava, 131 p.

Košík M., Šurina I., Micko M. (1989): Thermolytic reactions of cellulose II. Hydrolysis and thermoxidation. Folia Forestalia Polonica, Ser. B, 20: 82-89.

Nassar M. M., Mackay G. D. M. (1984): Mechanism of thermal decomposition of lignin. Wood Fiber, 16: 441-453.

Reinprecht L., Mihálik A. (1988): K problematike úlohy fosforu a lignínsacharidickej skladby na priebeh termických analýz dreva. (On problem of the function of phosphorus and lignin-saccharidic composition in the course of thermal analyses of wood), In: Wood Burning '88, VŠLD Zvolen: 185-197.

Reinprecht L. (1996): Procesy degradácie dreva. (Processes of wood degradation), Technical University in Zvolen, 150 p.

Rychlý J. (1995): Príspevok k štúdiu vznietenia a horenia polymérov. [Doktorská dizertačná prácal, Institution of polymers - SAV, Bratislava, 141 p.

Sandermann W., Augustin H. (1963): Chemische Untersuchungen über die thermische Zersetzung von Holz - Erste Mitteilung: Stand der Forsung. Holz Roh- Werkstoff, 21: 256-268.
Shafizadeh F. (1984): The chemistry of pyrolysis and combustion. In: The chemistry of solid wood (ed. Rowell,R.M), Adv. Chem. Ser., 207, Am. Chem. Soc., Washington: 489-529.
Woo J. K., Schniewind A. P. (1987): Thermal degradation of wood treated with fire retardants I. DSC-analysis. Holzforschung, 41: 305-313.

ODPORNOŚĆ DREWNA KLONU (*ACER PSEUDOPLATANUS L.*) NA DZIAŁANIE GRZYBA *SERPULA LACRYMANS* PO WSTĘPNEJ OBRÓBCE TERMICZNEJ ORAZ PO OBRÓBCE CHEMICZNEJ I TERMICZNEJ

Streszczenie

Drewno klonu, wstępnie nasycone kwasem siarkowym o stężeniu 0-2,5% ogrzewano w temperaturze 160 i 190C w ciągu 3 godz. Próbki poddano następnie działaniu grzyba *Serpula lacrymans* w czasie 1 miesiąca. Proces biodegradacji został zahamowany tylko w przypadku, kiedy obróbka termiczna drewna była połączona z działaniem kwasu o wyższych stężeniach.

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