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Selected properties of beech wood degraded by brown-rot fungus *Coniophora puteana*

Svojstva bukova drva nakon djelovanja gljive *Coniophora puteana*, uzročnice smeđe truleži

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ABSTRACT • This paper reveals the alteration of selected physical and chemical properties of non-tension beech wood exposed to short- and medium-term degradation by the brown-rot fungus *Coniophora puteana*. The fungus caused a gradual mass loss and a significant decrease in wood density by the decay progression. Biodegradation increased the contents of polar extractives in wood markedly, it caused a substantial removal of cellulose and it relatively increased the contents of lignin in wood. The above mentioned alterations of beech wood were reflected in an expressively increased rate of wood/water interactions, influenced its permeability and the rate of surface swelling. Wood colour turned to brown, and its lightness was reduced after 60-day degradation. The chemical analyses, VIS and FTIR spectra confirmed significant chemical changes of beech wood.

Key words: beech wood, *Coniophora puteana*, physical properties, VIS and FTIR spectra

SAŽETAK • U radu se objašnjavaju određene promjene fizikalnih i mehaničkih svojstava netenzijske, zdrave bukovine nastale kratkotrajnim i srednjetrojnim djelovanjem gljive *Coniophora puteana*, uzročnice smeđe truleži. Gljiva je tijekom svog razvoja i napredovanja prouzročila postupni gubitak mase i znatno smanjila gustoću bukovine. Biorazgradnjom se izrazito povećao sadržaj polarnih ekstraktiva, nestalo je celuloze i relativno se povećao sadržaj lignina u drvu. Navedene promjene bukovine očitovale su se izrazito povećanom interakcijom vode i drva, odnosno utjecale su na njegovu permeabilnost i veličinu površinskog bubrenja. Boja drva postala je smeđa, a sjaj je nakon 60 dana izlaganja gljivi smanjen. VIS i FTIR spektralne kemijske analize potvrdile su znatne kemijske promjene bukovine.

Ključne riječi: bukovina, *Coniophora puteana*, fizička svojstva drva, VIS i FTIR spektrometrija

1 INTRODUCTION

1. UVOD

Besides the benefits resulting from conversion of plant substrates into organic portion of forest and agri-

cultural soil, the activity of brown-rot fungi in technical practice is undesired, especially if construction materials made from wood are attacked. Degradation of wood substance in this case results in a deep loss of polysaccharides portion of wood, and sometimes also of

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lignin. The physico-mechanical properties of wood are gradually reduced with the development of biodegradation, even in a relatively short time of the process (Reinprecht, 1991a,b; Reinprecht, 1994). The accompanying phenomena of the brown-rot are the mass loss, decrease in density, change of colour and lightness, loss of cohesion, shrinkage and increased fragility of wood (Fengel, Wegener, 1984).

The effect of brown-rot and moulds on wood as a raw material in the pulp and paper production is highly undesired, due to reduced yield of pulp, its diminished quality and increased consumption of pulping chemicals (Šutý, 1982; Bergman, 1985).

The aim of this paper was to judge the alterations in the chemical composition and selected physical properties of beech wood occurring in the course of short and medium-term degradation by the brown-rot fungus *Coniophora puteana*. This paper represents a continuation of the previous research focused on pre-treatment of hard wood species by white-rot fungi prior to pulping.

2 MATERIALS AND METHODS

2. MATERIJALI I METODE

A 60 cm long section of the tree trunk was taken from its middle part. From this section a prism of non-tension wood with dimensions of 3x3x60 cm, (longer dimension parallel with grain) was prepared. The position of the prism was approximately 6 cm from the section circumference. The age of the tree was 82 years. The dimensions of specimens prepared from the prism were 3x3x1 cm. The shorter dimension was parallel, and the longer ones were perpendicular to grain. From the specimens a comparable series, each comprising 5 pieces, were prepared. A criterion of selection was the number of annual rings, density and position of the specimens in the prism. A small number of specimens in a series (5) were due to from some long lasting analyses of the selected physical properties of wood. This is why the contribution was focused on the estimation of trends and not on the precise data from a numerous series of the compared specimens.

2.1 Biodegradation

2.1. Biorazgradnja

The brown-rot fungus *Coniophora puteana* (Schum. Ex. Fr.) P. Karst BAM 273 was used for degradation. The fungus was grown on a malt-agar nutrient medium. The degradations were carried out in Kolbe flasks at 22 °C for 15, 30 and 60 days. The model decay was stopped by a 2-hour immersion of the specimens into 99 % methanol. The specimens were dried in two steps. The first step - careful air drying was followed by drying in a dessicator over P₂O₅; and both procedures were performed at the ambient temperature.

2.2 Measurements and analyses

2.2. Mjerenja i analize

- mass loss of the specimens was determined gravimetrically,

- density of the specimens was determined in their absolutely dry states,
- coefficients of permeability in axial direction were determined by using the method of Regiňáč et al. (1977),
- kinetics of facial swelling was determined according to the contact method with PC data processing (Solár et al, 2005),
- colour of wood samples was estimated with the spectrometer Conica Minolta CM-2600 D in the range of 360 – 740 nm. From each series comprising 5 specimens, 60 shots were taken in total. The spectra were evaluated in co-ordinates of the colour space „CIELAB“. The “differential spectra” represented a difference between the spectra of biodegraded and sound beech wood. Moisture content of the samples was 4.5 %,
- extractives of medium polarity were determined by extraction with benzene/ethanol (2:1 v/v) mixture in a Soxhlet apparatus; time of extraction was 8 h,
- cellulose was determined by using the method of Kürschner and Hoffer (K-H), and 3 delignification steps were performed,
- lignin in wood and residual lignin in the cellulose preparations were determined by TAPPI Standards T-13m method,
- nitrobenzene oxidation (NB) of extractive-free wood (4.0 ml of 2M NaOH and 0.25 ml of C₆H₅NO₂ on 200 mg of wood meal) were performed at 180°; time of oxidation was 2.5 h; the finals were analysed by HPLC, using an UV detector with the optimised wavelength,
- total hydrolysis of extractive-free wood meals was performed by using the method of Seaman et al. (1954) and mono-saccharides were determined by GLC of their aldnitrile-acetates,
- FTIR spectra were obtained by Nicolet Magna 750 spectrometer using KBr technique; difference spectra were expressed as a difference between the spectra of biodegraded and sound wood in their absolutely dry states.

Methods of chemical analyses are described in detail in the book by Kačík and Solár 1999.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

3.1 General data and chemical analyses

3.1. Osnovni podaci i kemijske analize

As given in Tab. 1, the degradation of beech wood by the brown-rot fungus *C. puteana* led to its marked mass loss, decrease in density and alterations in its chemical composition, almost proportional to the time of fungal action.

The reduction in density of biodegraded beech wood is in accordance with its mass loss, and the variability of data is low.

Table 1 Mass loss, density, BA extract and the contents of lignin and cellulose in sound beech wood and beech wood degraded by *C. puteana* (%)

Tablica 1. Gubitak mase, gustoća, BA ekstrakt te sadržaj lignina i celuloze u zdravom drvu bukve i drvu razorenom gljivom *C. puteana* (u %)

Basic statistics <i>Osnovna statistika</i> Component <i>Komponenta</i>	Sound wood <i>Zdravo drvo</i>	15-day degradation <i>Nakon 15 dana truljenja</i>	30-day degradation <i>Nakon 30 dana truljenja</i>	60-day degradation <i>Nakon 60 dana truljenja</i>
Mass loss, % <i>gubitak mase, %</i>	0	11.11	25.89	46.41
<i>n</i>	-	5	5	5
<i>v</i> , %	-	10.27	14.23	7.03
Density, g·cm ⁻³ <i>gustoća</i>	0.6629	0.5569	0.4753	0.3784 ?
<i>n</i>	5	5	5	3
<i>v</i> , %	0.950	2.622	3.972	3.655
BA extract <i>BA ekstrakt</i>	0.91	2.47	3.48	7.76
Lignin – <i>lignin</i>	22.43 (22.23)**	23.97 (20.78)	28.04 (20.47)	37.36 (18.47)
Cellulose – <i>celuloza</i>	51.96 (51.48)	48.73 (42.26)	43.68 (31.89)	33.57 (16.59)

- An approximate value due to deformation of specimens and crack formation during degradation and drying.
- *Približna vrijednost zbog promjene oblika uzoraka i pukotina nastalih nakon truljenja i sušenja.*

**Data in brackets express content of the component recalculated relative to mass of wood before degradation, taking into considering mass loss and BA extract of wood. Correction of cellulose contents on lignin has not been performed due to its low contents in K-H cellulose preparations (0.2 – 0.3 %).

***Podaci u zagradama predočuju udio pojedine komponente u odnosu prema masi drva prije biorazgradnje, uzevši u obzir gubitak mase i BA ekstrakt drva. Korekcija udjela celuloze u odnosu prema ligninu nije napravljena zbog njezina malog udjela pri-*

As shown in Tab. 1, the action of *C. puteana* led to a relative increase in the lignin portion in the extractive-free biodegraded wood. The obtained data, when related to initial mass of wood prior to biodegradation, indicate, however, the proceeding removal of lignin, which equalled 16.9 % after 60 days of decay. Degradation of lignin by the brown-rot may result from action of H₂O₂, H₂O₂/Fe²⁺ and Mn³⁺/oxalate complexes taking part in the polyoses degradation instead of the lacking enzyme exo-β-glucanase (Eriksson et al, 1990; Reinprecht, 1996).

The content of cellulose in beech wood was markedly reduced with the development of biodegradation, and a 60-day action of *C. puteana* resulted in a 33.6 % removal of this component (Tab. 2). The rate of cellulose decomposition slowed down moderately after a 30-day decay (Tab. 2). More detailed data concerning the degradation of polysaccharides by the brown-rot fungus are given in Tab. 2.

The data in Tab. 2 confirmed a high rate of degradation of cellulose and glucomannans. The rate of xylenes and other hemicelluloses decomposition was appa-

Table 2 Relative representation of anhydro-saccharides in hydrolysates of extractive-free beech wood (in %)

Tablica 2. Relativna zastupljenost anhidro-saharida i hidrolizata ekstrahirane bukovine (u %)

Component <i>Sastojak</i>	Sound wood <i>Zdravo drvo</i>	15-day degradation <i>Nakon 15 dana truljenja</i>	60-day degradation <i>Nakon 60 dana truljenja</i>
Glucan	47.04 (45.56)*	42.84 (37.15)	33.95 (16.78)
Mannan	0.87 (0.86)	0.56 (0.49)	0.44 (0.22)
Xylan	15.07 (14.93)	14.13 (12.25)	12.72 (6.29)
Arabinan	1.17 (1.16)	1.03 (0.89)	1.04 (0.51)
Rhamnose side units	0.75 (0.74)	0.68 (0.59)	0.61 (0.30)
Galactan	traces – <i>u tragovima</i>	traces – <i>u tragovima</i>	traces – <i>u tragovima</i>

* Data in brackets represent the contents of polysaccharides expressed relative to mass of wood before biodegradation.

* *Podaci u zagradama označavaju relativan sadržaj polisaharida (šećera) u odnosu prema masi drva prije truljenja.*

Table 3 Yield of nitrobenzene oxidation (NB) products of native lignin in sound and biodegraded extractive-free beech wood (in % of lignin in wood)**Tablica 3.** Produkt oksidacije nitrobenzenom (NB) sastojaka prirodnog lignina u zdravoj bukovini i natruloj ekstrahiranoj bukovini (u % u odnosu prema ligninu)

Oxidation product <i>Oksidirani sastojak</i>	Sound wood <i>Zdravo drvo</i>	Wood degraded for 15 days <i>Drvo nakon 15 dana truljenja</i>	Wood degraded for 60 days <i>Drvo nakon 60 dana truljenja</i>
3,4-dihydroxybenzaldehyde <i>3,4-dihidroksibenzaldehid</i>	0.249	0.320	0.216
p-hydroxybenzaldehyde <i>p-hidroksibenzaldehid</i>	0.223	0.250	0.213
Vanillic acid – <i>vanilna kiselina</i>	1.329	1.311	1.183
Syringic acid – <i>siringilna kiselina</i>	3.509	3.483	3.287
Vanilline – <i>vanilin</i>	13.722	12.856	12.001
Syringaldehyde – <i>siringil aldehid</i>	34.206	31.958	27.841
Total of products – <i>suma produkata</i>	53.234	50.178	44.740
S/G ratio – <i>omjer S/G</i>	2.493	2.486	2.320
S/G ratio incl. aromatic acids* <i>omjer S/G, uključujući aromatične kiseline</i>	2,506	2.502	2.361

* weight ratio of Σ syringyl aldehyde + syringic acid to Σ vanilline + vanillic acid* *Maseni udio Σ siringil aldehida + siringilna kiselina u odnosu prema Σ vanilinu + vanilnoj kiselini.*

rently milder. A deep removal of polyoses from the cell walls modifies their micro structure, sub-micro structure as well polarity, and may partly explain the altered physical and mechanical properties of wood attacked by the applied brown-rot fungus. Lower portions of “glucan” in the wood hydrolysates compared to the corresponding contents of cellulose may result from residual non-cellulosic polyoses and lignin present in the K-H cellulose preparations (data shown in Tab. 2)

HPLC of the nitrobenzene oxidation products of the extractive-free beech wood meals gave the data concerning the alterations of “in vitro” lignin due to the action of *C. puteana* (Tab. 3).

Chromatography of the oxidation products of lignin in the compared samples of beech wood pointed out a reduction in the total yield of aromatic aldehydes and aromatic carboxylic acids with the time of biodegradation. This phenomenon may result from coupling of phenoxi-, and quinonmethide radicals arising in the enzymatic degradation of lignin in a substrate. In this case, however, also a relative enrichment of lignin for more cross-linked structures might play some role. The reduced S/G ratio in lignin, apparent after a 60-day biodegradation, indicates a faster decomposition of syringyl units in lignin and enrichment of wood for the not yet degraded middle lamellae lignin.

3.2 Physical properties

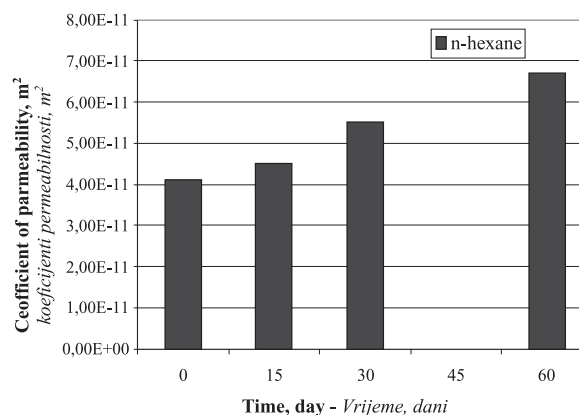
3.2. Fizička svojstva

A positive influence of biodegradation on wood permeability and its interactions with different media as ethanol-water, craft and NSSC liquors, water (Solár et al. 2001), respectively, might result from a rapid decrease in density of biodegraded wood (Tab. 1). The achieved results confirmed this assumption for a non-polar medium n-hexane (Fig. 1). The measure-

ments of axial permeability of beech wood with water as a medium failed due to the formation of cracks on the surface of biodegraded specimens.

As shown in the histogram in Figure 1, biodegradation increased wood permeability proportionally to the time of fungal attack. The increase in this property may result from the diminished density and increased porosity of the biodegraded material. The obtained data, however, are of an informative value only, due to a small number of specimens in a series of the compared samples.

Figure 2 illustrates an increase in the kinetics of the first phase of facial swelling of the biodegraded beech wood. A short-term action of *C. puteana* had the most apparent effect on the swelling kinetics, and the corresponding rate constant of surface swelling repre-

**Figure 1** Coefficients of axial permeability of sound beech wood and beech wood degraded by *C. puteana* ($n = 5$; $w_{\text{inic.}} = 4.5\%$; $v_{\text{coeff.}} = 30$ to 40%)

Slika 1. Koeficijent permeabilnosti u longitudinalnom smjeru zdrave bukovine i bukovine nakon razgradnje (truljenja) proizročenoga gljivom *C. puteana* ($n = 5$; $w_{\text{inic.}} = 4.5\%$; koef. varijacije = $30 - 40\%$)

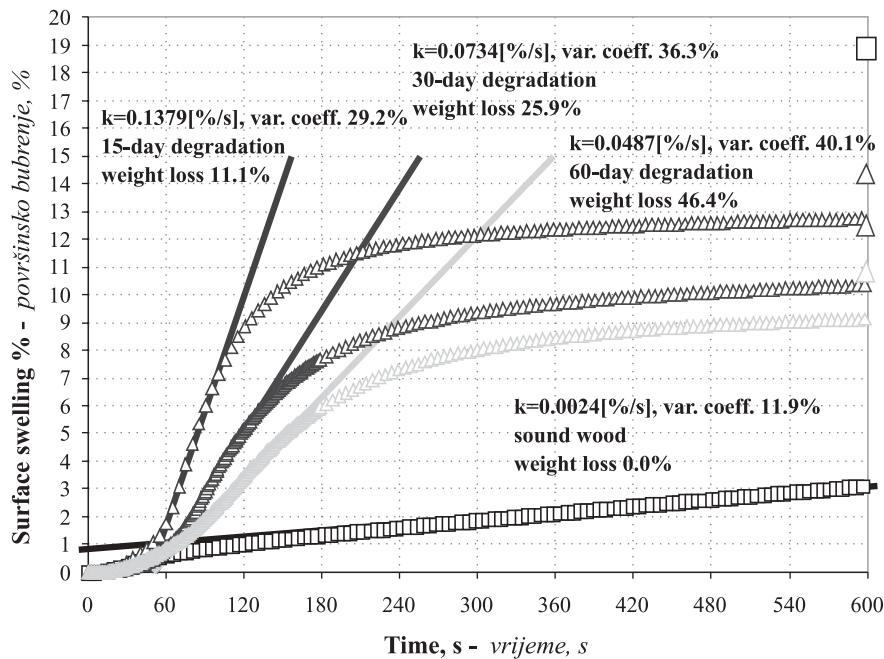


Figure 2 Kinetic plots and relative rate constants of the first phase of facial swelling of beech wood as a function of time of degradation by *C. puteana*; $n = 5$; $w_{mic.} = 4.5\%$; medium: water; $t = 20\text{ }^{\circ}\text{C}$ (marks on the right co-ordinate y correspond to a 24-hour swelling)

Slika 2. Kinetička slika površinskog bubrenja i relativna konstanta porasta u početnoj fazi bubrenja bukovine u ovisnosti o vremenu izlaganja gljivi *C. puteana*; $n = 5$; $w_{mic.} = 4,5\%$; medij: voda; $t = 20\text{ }^{\circ}\text{C}$ (oznake na desnoj ordinati predočuju 24-satno bubrenje)

sents a 57 multiple of the value found for sound material. Biodegradation prolonged to 30 and 60 days, respectively, led to a drop in the rate constants of beech wood facial swelling, which equalled only a 20 multiple of the value determined for sound wood after 60-day degradation. The reduction in the initial rate of facial swelling due to prolonged biodegradation might follow from the increase in the content of less polar lignin. The diminished density of the degraded samples may also play a role in this case. The final values of surface swelling of beech wood attacked by *C. puteana* were considerably lower than that of sound wood.

An increase in the rate of “wood/water” interactions, expressed by the kinetics of facial swelling of beech wood degraded by the brown-rot fungus, may influence negatively its dimensional stability and lead to crack formation in contact of dry wood with polar media.

The action of the brown-rot caused also changes in the optical properties of beech wood (Figs. 3, 4 and 5).

As shown in Fig. 3, the short-term 15-day action of *C. puteana* caused a negligible shift in the colour of beech wood from red to green. Longer degradation caused a reverse effect on its colour, and a regular shift from green to red colour became more apparent (co-ordinate a^*). The initial stages of the brown-rot were accompanied by an unexpectedly slight increase in the lightness of beech wood that was followed by a deep drop after a 60-day degradation equalling 5.5 % of the scale in co-ordinate L^* .

Fig. 4 illustrates lightness and colour of the biodegraded material in co-ordinates L^* and b^* .

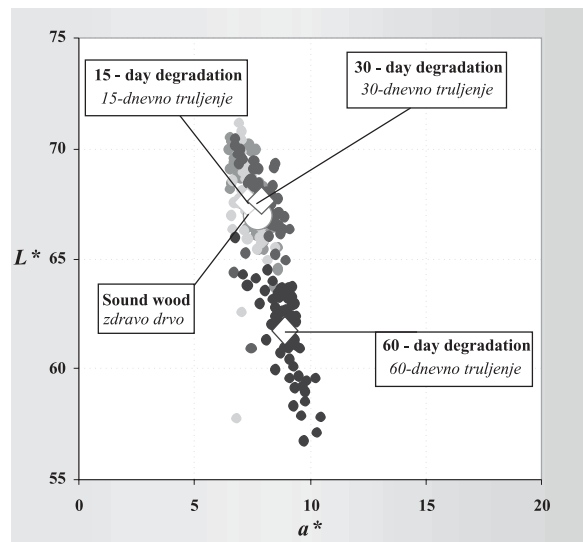


Figure 3 Lightness (L^*) and colour of wood in co-ordinate a^* of the CIELAB colour space (var. coeff. L^* : sound wood – 2.66 %, 15 days degr. – 2.91 %, 30 days degr. – 2.32 %, 60 days degr. 3.26 %; var. coeff. a^* : sound wood – 8.53 %, 15 days degr. – 5.49 %, 30 days degr. – 7.68 % and 60 days degr. – 8.03 %)

Slika 3. Svjetlina (L^*) i koordinata boje drva (a^*) u koordinatnom sustavu analize boje CIELAB (koef. varijacije L^* : zdravo drvo – 2,66 %, 15-dnevno truljenje – 2,91 %, 30-dnevno truljenje – 2,32 %, 60-dnevno truljenje 3,26 %; koef. varijacije a^* : zdravo drvo – 8,53 %, 15-dnevno truljenje – 5,49 %, 30-dnevno truljenje – 7,68 %, 60-dnevno truljenje – 8,03 %)

Fig 4 expresses a slight increase in the lightness of the compared samples of beech wood in initial stages of the brown-rot and an apparent decrease in this property after a 60-day biodegradation. At the same time, a shift was recorded in the colour of wood from blue to

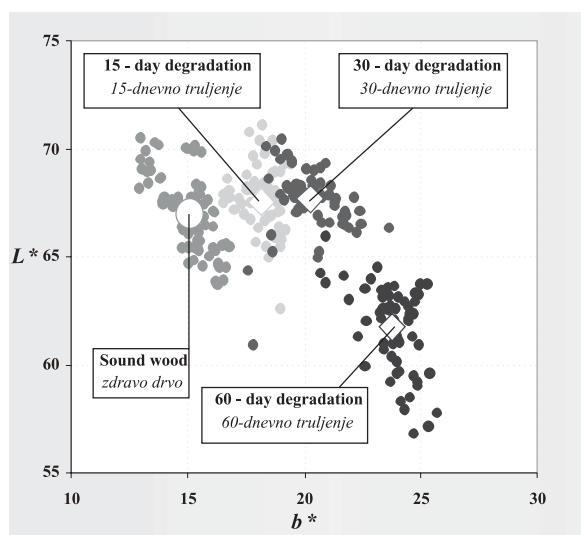


Figure 4 Lightness (L^*) and colour of sound beech wood and beech wood degraded by *C. puteana* (L^*) expressed in the co-ordinate b^* (var. coeff. L^* : sound wood – 2.66 %, 15 days degr. 2.91 %, 30 days degr. – 2.32 %, 60 days degr. 3.26 %; var. coeff. b^* : sound wood 6.64 %, 15 days degr. – 4.03 %, 30 days degr. – 6.12 % and 60 days degr. – 4.57 %)

Slika 4. Svjetlina (L^*) i koordinata boje drva (b^*) zdrave i gljivom *C. puteana* razorene bukovine (koef. varijacije L^* : zdravo drvo – 2,66 %, 15-dnevno truljenje 2,91 %, 30-dnevno truljenje – 2,32 %, 60-dnevno truljenje 3,26 %; koef. varijacije b^* : zdravo drvo 6,64 %, 15-dnevno truljenje – 4,03 %, 30-dnevno truljenje – 6,12 %, 60-dnevno truljenje – 4,57 %)

yellow (9 % of the scale in co-ordinate b^*) - almost proportional to the time of biodegradation.

Fig. 5 represents the VIS differential reflex spectra of beech wood expressing the difference between the averaged spectra of the biodegraded and sound wood. Each spectrum used for their construction represented the mean of 60 spectra taken from the surface of the compared samples.

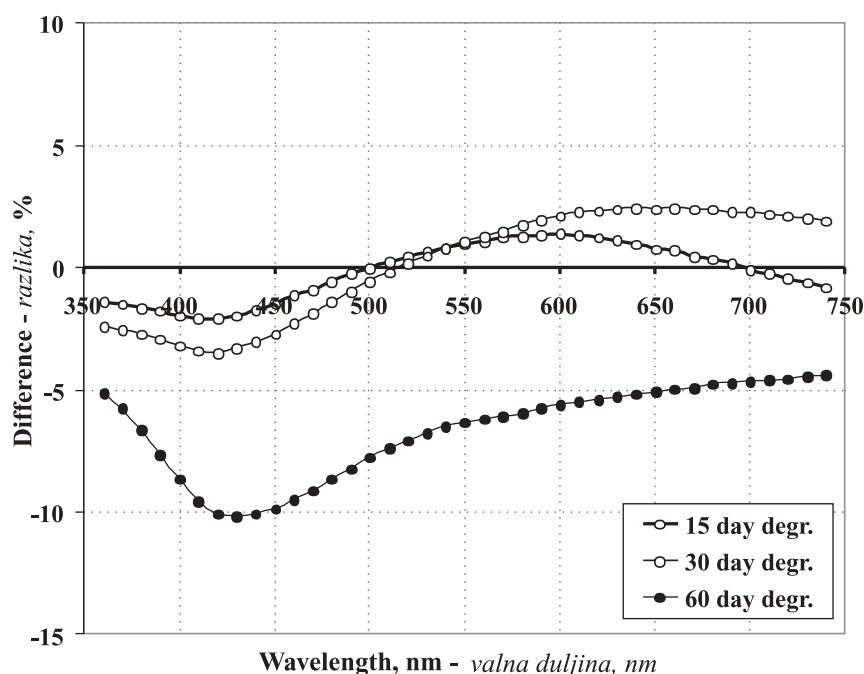


Figure 5 Differential reflex spectra of beech wood degraded by *C. puteana*

Slika 5. Spektar diferencijalnog odsjaja bukovine razorene gljivom *C. puteana*

A small maximum in the visible range of light (λ_{\max} of approximately 600-650 nm) in the spectra of 15 and 30 days biodegraded wood indicate a reduced absorption of light in the range of 500-700 nm, compared to that of sound wood. This observation is in good accordance with the increased lightness of the short-term biodegraded material. On the other hand, the both short-term degraded samples exhibited moderate minima in the region of 360 to 500 nm, thus confirming the increased light absorption in this area. A longer, 60-day biodegradation led to a decrease in the light reflection from the specimens surface within the whole range of the monitored wavelength. A considerably reduced reflection (or increased absorption) of light in the region of 360-760 nm with a minimum at 425-430 nm possibly results from the new chromophores formation, especially in lignin. Increased content of lignin, contributing to absorption at 450 nm (Wilcox, 1975) in the biodegraded wood plays undoubtedly a significant role in the colour alterations of wood due to the brown-rot.

Absorption FTIR spectra and differential spectra of extractive-free and absolutely dry wood meals of beech wood are shown in Figs. 6 and 7.

In the spectra of biodegraded wood (Fig. 6) a decrease can be seen in the associated hydroxyl groups (band at 3420 cm^{-1}) and in C-H vibrations (bands at 2923 and 2852 cm^{-1} – stretch. and bend. modes) of $-\text{CH}_2-$ and $-\text{CH}_3$ groups in wood with the time of brown-rot. The alterations are milder in the spectrum of wood degraded for 15 days, and marked in the spectrum of 60-day degraded wood. Reduction of these bands is the result of removal of polysaccharides, as well as de-methylation of lignin.

A moderately increased absorbance of the peak at wave number of 1760 cm^{-1} (β -keto group, C-O in esters and carboxyl acids) after a 15-day degradation (Figs. 6

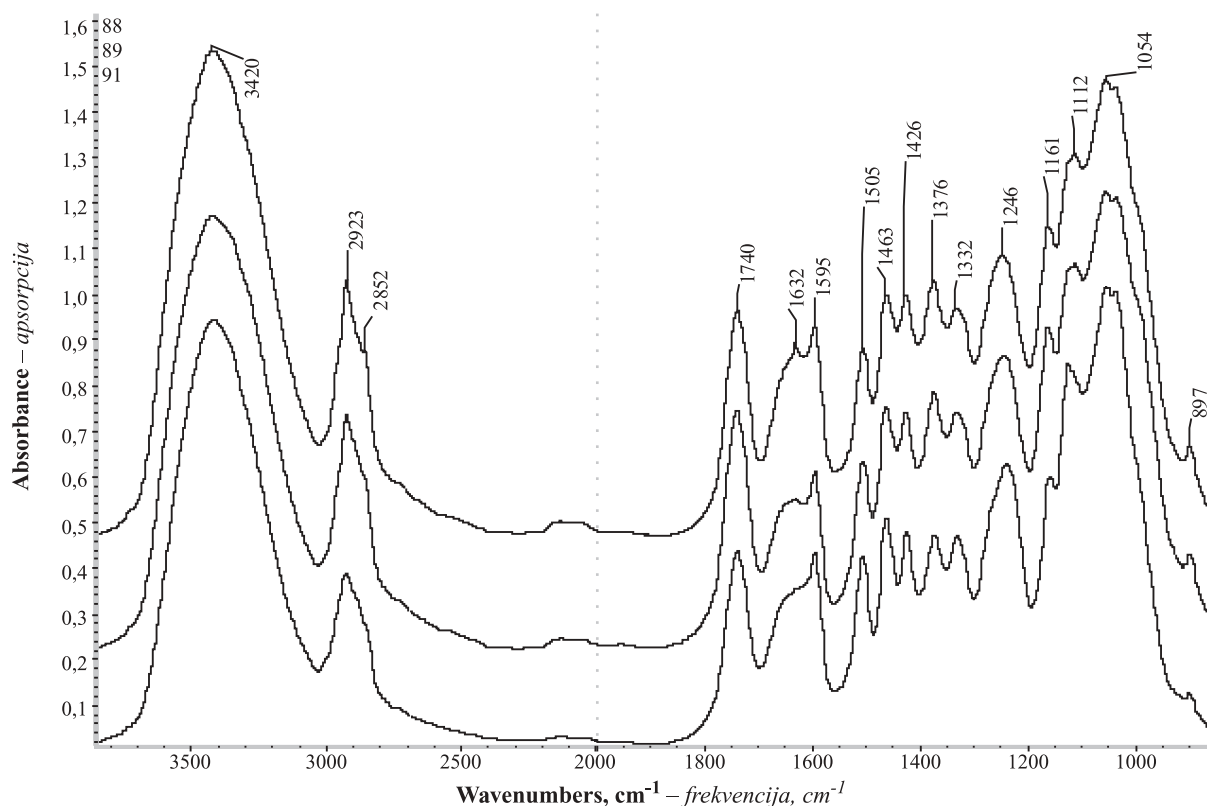


Figure 6 FTIR spectra of sound beech wood and beech wood biodegraded by *C. puteana* (Samples: 88 – sound beech wood; 89 – 15 days degraded wood; 91 – 60 days degraded wood)

Slika 6. FTIR spektr zdrave bukovine i bukovine razorene gljivom *C. puteana* (uzorak: 88 – zdrava bukovina; 89 – drvo nakon 15 dana truljenja; 91 – drvo nakon 60 dana truljenja)

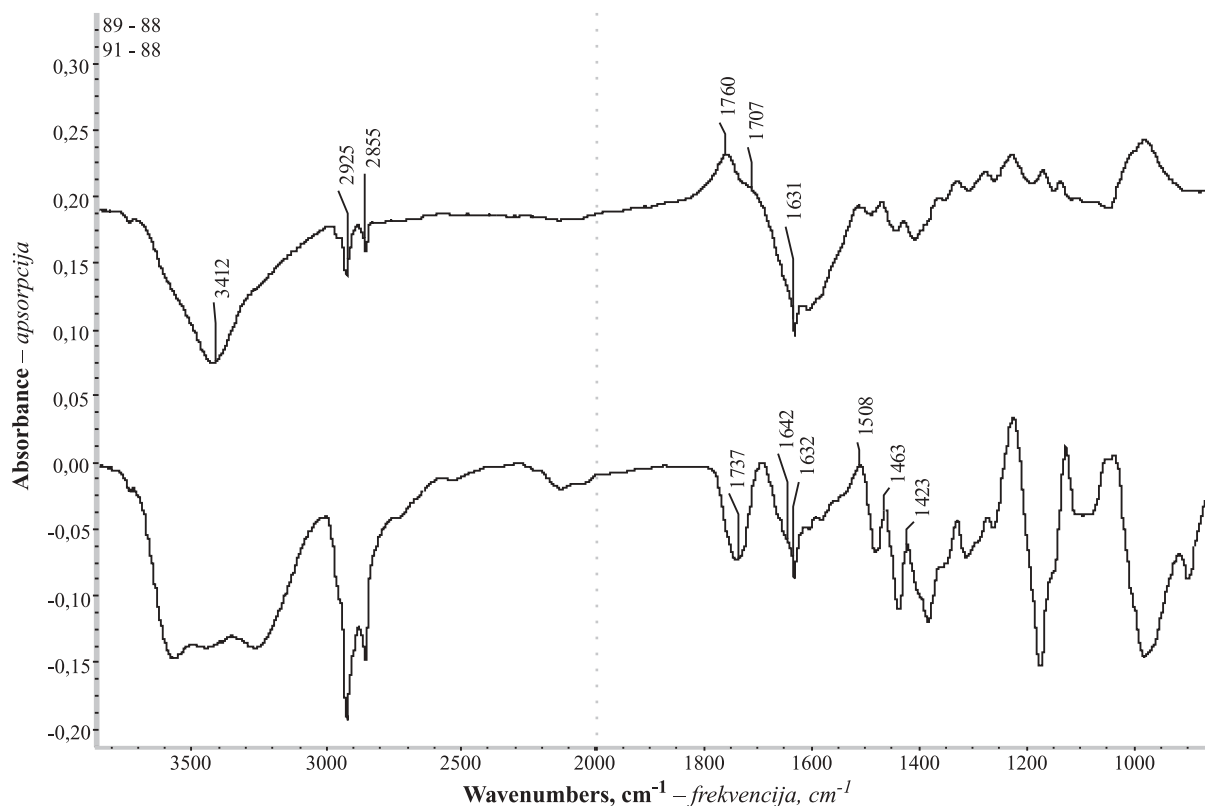


Figure 7 Difference FTIR spectra of beech wood biodegraded by *C. puteana* (89 – 88: spectrum of beech wood degraded for 15 days; 91 – 88: spectrum of 60-days degraded beech wood)

Slika 7. Razlike FTIR spektra bukovine razorene gljivom *C. puteana* (89 – 88: spektar bukovine nakon 15 dana truljenja; 91 – 88: spektar bukovine nakon 60 dana truljenja)

and 7) may point out at the relative stability of 4-O-methyl glucurono-xylanes in initial stages of the brown-rot. A prolonged 60-day action of *C. puteana* caused marked reduction of the band at 1740 cm^{-1} . This observation confirms the degradation of glucurono-xylanes connected with splitting of acetyl groups and 4-O-methyl glucuronic acids side units (data agree with the reduced contents of xylanes in biodegraded wood).

In the spectra of biodegraded wood a decrease in the absorbance of the composed band at 1632 cm^{-1} was observed. This band comprises absorption of α -CO groups conjugated with p-hydroxi -substituted aromatic ring and o-, p-quinone structures in lignin.

An intensive broad minimum in the region of $1700\text{--}1508\text{ cm}^{-1}$ in the difference spectrum of 15-day degraded wood, and a smaller one in the spectrum of a 60-day degraded wood may hint at the continuous decomposition and formation of various chromophoric structures with the development of brown-rot.

Reduction of the band at 1595 cm^{-1} in the spectra of both biodegraded samples (a composed maximum comprising the aromatic ring stretching, associated with aromatic C-C stretch. mode in lignin, and carboxylate ion C=O stretch. in uronic acids) indicates a cleavage of the side branches of 4-O-methylglucuronic acid from glucurono-xylanes.

The absorbance of a peak at 1505 cm^{-1} did not change apparently, despite the relative increase of lignin in the biodegraded wood with the time of degradation. This observation might imply the formation of o-quinoid structures in lignin due to its oxidative de-methylation.

The band at 1463 cm^{-1} (aromatic ring vibration and C-H deformation) did not change apparently due to biodegradation, and possibly represents the not-yet-attacked lignin in biodegraded wood.

A decrease in the absorbance of bands at 1426 and 1375 cm^{-1} in the spectra of biodegraded wood indicates partial degradation of lignin. The former band may be attributed to aromatic skeletal vibrations, the latter one comprises symmetric C-H deformations, phenolic O-H deformations and C-O stretching mode.

A slightly diminished maximum at 1332 cm^{-1} (syringyl ring breath. with C-O stretch.) results from degradation of syringyl units in lignin, which is in conformity with the NB oxidation data.

Maxima arising at 1225 cm^{-1} in the difference spectra of biodegraded samples (Fig. 7) may imply the formation of new phenolic hydroxyl groups in lignin, especially after a 60-day influence of brown-rot.

A slight reduction of a small band at 1161 cm^{-1} (ring breathing with C-O stretching, and C-O stretching in tertiary alcohol) implies a possible degradation of guaiacyl structures in lignin (conformity with the NB oxidation data).

A number of minima in the region of wave numbers of $1000\text{--}1430\text{ cm}^{-1}$ in the difference spectra is connected with a diminished concentration of O-H and C-O linkages (bending frequency) in the degraded wood resulting from the preferential removal of carbohydrates. The following sources were used for the interpretation of

absorption bands in FTIR spectra: Sarkanen and Ludwig, 1971; Kováč and Leško, 1980; Fengel and Wegener, 1984 and Faix and Banhoff, 1988.

4 CONCLUSIONS

4. ZAKLJUČCI

The experimental data concerning properties of non-tension beech wood degraded by brown-rot fungus *Coniophora puteana* led to the following conclusions:

- degradation of beech wood by brown-rot *C. puteana* under experimental conditions resulted in its marked mass loss and decrease in its density, proportional to time of fungal action,
- the rate of cellulose and non-cellulosic polysaccharides decomposition was increasing with the time of biodegradation, especially in an interval between 30 and 60 days; the side L-rhamnose units in hemicelluloses seemed to be the most resistant,
- content of lignin in extractive-free biodegraded beech wood was rising relative to time of degradation, however recalculation of its content to wood before degradation confirmed decomposition of this bio-polymer in an unexpected degree,
- NB oxidation data confirmed preferential degradation of syringyl structures of "in vitro" lignin due to the action of brown-rot fungus, and the diminished yield of products of NB oxidation indicate lignin condensation via coupling of its radical intermediates arising in the process of biodegradation,
- biodegradation of beech wood increased its axial permeability for n-hexane and markedly influenced the rate of wood/water interactions expressed outwards by the steeper fast pseudo-linear phase of its facial swelling,
- the most apparent effect on the swelling kinetics of beech wood had a 15-day action of *C. puteana* leading to 57 multiply increased value of the relative rate constant of its facial swelling,
- early stages of biodegradation of beech wood led to unexpectedly slight increase in its lightness, and only a moderate shift was recorded in the colour of wood from blue to yellow,
- a longer 60-day action of *C. puteana* apparently reduced lightness of beech wood, and caused a slight shift in its colour from green to red, and a more intensive one from blue to yellow,
- VIS and FTIR spectra confirmed alterations in the basic wood constituents due to biodegradation, however the spectra did not explain satisfactorily the formation of new chromophores responsible for its optical properties.

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