CHANGES OF THE PINE WOOD (*PINUS SYLVESTRIS* L.) CHEMICAL COMPOSITION DURING WHITE- AND BROWN-ROT DECAY ORIGINATED FROM CHOSEN FUNGI SPECIES

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ABSTRACT

Scots pine wood (*Pinus sylvestris* L.) was submitted for controlled decay using two testing fungi species causing: brown-rot decay (*Coniophora puteana* (Schum.: Fr.) P. Karst.) and white-rot decay (*Trametes versicolor* (L.: Fr.) Pilát). The influence of fungi activity on wood chemical composition changes was examined. *Trametes versicolor* fungus (white-rot) simultaneously decomposes all of wood structural components – cellulose, hemicelluloses and lignin. The rate of cellulose and lignin content decrease is similar. Brown-rot decay does not cause lignin decomposition, only carbohydrates decompose. Fast cellulose decomposition takes place. Its rate is higher than wood mass-loss indicates. Research presented in this paper allows finding the correlation between the mass-loss of wood decayed by given fungus species and structural wood components content.

KEYWORDS: Pine wood, white-rot decay, brown-rot decay, chemical composition.

INTRODUCTION

Fungi in the first growth phase use spare substances (low molecular mass) gathered in wood. Hemicelluloses and cellulose with low polymerization degree are the next wood components which are decomposed by fungi (Krutul 1998, 1994, Krutul and Krasnodębska 1986). These compounds undergo fast decomposition from the reason of their chemical composition, significantly lower polymerization degree in comparison to alpha-cellulose and their distribution outside cellulose micelles. There is no accordance among different authors about the rate of particular wood components decomposition. Results in different papers are divergent. That is

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why there are different explanations of the fungi originated wood decomposition.

Variety of results obtained during the analysis of wood or trees decayed in natural environment by white-rot fungi proves that many different factors influence the rate and mechanism of decomposition. The same fungus species, depending on environmental conditions, may selectively decay lignin or simultaneously lignin with cellulose (Adaskaveg and Gilbertson 1986, Dill and Kraepelin 1986, Adaskaveg et al. 1990, Adaskaveg et al. 1995). Qualitative and quantitative changes of wood structural components during white-rot decay proceed slowly because of slow cellulose decomposition.

Brown-rot decay mechanism is quite different. Carbohydrates decomposition is fast, but hemicelluloses are decayed at first because they create the outside cover around the cellulose microfibers. Observed changes in cellulose content significantly indicate its decomposition (Ważny et al. 1963, Rogaliński and Kubiak 1967, Winandy and Morrell 1993), although some authors state that decomposition concern only cellulose molecules with low molecular mass in amorphous areas. Results of Flournoy et al. (1991) rather deny this thesis. These authors determined the cellulose polymerization degree in *Liquidambar styraciflua* during decay originated from *Postia placenta* fungus. Fast decrease of the cellulose polymerization degree was observed, from 1200 to 900, already after 5 % of wood mass-loss, to 750 after 10 % of mass-loss, 500 after 20 % of mass-loss and to cca 200 after 37 % of mass-loss. According to other authors (Curling et al. 2001, 2002a, b, Clausen and Kartal 2003), cellulose does not decompose until mass-loss on the level of 30 % - only hemicelluloses degrade then. Such a conclusion was stated basing on the observations of constant level of glucans content, but without determining the qualitative changes of cellulose.

Increase of 1 % NaOH soluble substances content is always observable after decay. It is an effect of the decomposition of hemicelluloses and low polymerization degree cellulose. Rate of such changes is different dependent on combination of fungus – wood species. Level of these substances content varies significantly from 15 to 60 % (Ważny et al. 1963, Rogaliński and Kubiak 1967, Winandy and Morrell 1993).

The aim of this paper is to determine the influence of test fungus acting causing brown-rot decay (*Coniophora puteana* (Schum.: Fr.) P. Karst.) and white-rot decay of wood (*Trametes versicolor* (L.: Fr.) Pilát) on qualitative and quantitative changes of the chemical composition of pine wood (*Pinus sylvestris* L.).

MATERIAL AND METHODS

Scots pine wood (*Pinus sylvestris* L.) samples without defects were collected from sapwood zone. Then they were submitted the controlled decay following modified procedure according to PN-EN-113 standard. Two species of testing fungi were the biological material: *Coniophora puteana* (Schum.: Fr.) P. Karst. (brown-rot decay) and *Trametes versicolor* (L.: Fr.) Pilát (white-rot decay).

Fungi rais was carried out on the maltose-agar culture medium. There were four samples for each fungus species and wood decay duration. Samples in raising vessels were placed in raising chamber for four months (*Coniophora puteana*) and twelve months (*Trametes versicolor*).

Every week four consecutive samples were taken from *Coniophora puteana* raising vessels. As for *Trametes versicolor*, four samples were taken from the raising vessel every week during the first month, every two weeks during the second month, and every four weeks during further months. Quite a number of samples with raising fungus exposition durations were obtained this way. It means also raising wood mass-loss caused by fungi.

Chemical analyses were performed on collected samples. About 0.3 mm thick shavings were collected using jointers from humidified samples. Shavings were then hand-crumbled. Fractions with dimensions $2 \times 1 \times 0.3$ mm were taken for analysis. Standard procedure consisting machine cutting, milling and sieving was not applied because wood demonstrates low cohesion and durability in advanced decomposition stage. Excessive mechanical disintegration could give unreliable results because of tiny shaving fractions.

Firstly, the moisture content was determined using drier-balance method. After drying, samples were extracted using chloroform (93 % v) – ethanol (7 % v) mixture in order to remove the extractives (Antczak et al. 2006). Prepared shavings were then analyzed for the content of cellulose, lignin and 1 % NaOH soluble substances, according to methods described in Kačík and Solár (1999), Krutul (2002). Reagents purity was compatible to analytical requirements and literature recipes.

RESULTS AND DISCUSSION

Changes of structural wood components content after white- and brown-rot decay are presented in the Figs. 1, 2, 3, 4.

Cellulose content changes

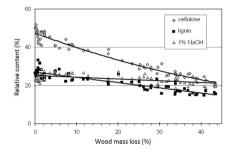
Cellulose, in wood decaying by white-rot *Trametes versicolor* fungi, undergoes slow decomposition (Fig. 1). Changes are of character similar to linear, 6-7 % of decomposed cellulose correspond to 10 % wood mass loss. Cellulose content changes were described by regression eq.: $y = 0.0064x^2 - 0.9508x + 51.585$, correlation coefficient R² = 0.9364.

Character of cellulose content changes is more violent during brown-rot decay (*Coniophora puteana*), what is presented in the Fig. 2. Significant decrease of cellulose content is observable already in the first stage of decay. 5 % of wood mass loss corresponds to 8 % decrease of cellulose content, 10 % of wood mass loss is connected with 20 % decrease of cellulose content. At the end of the experiment wood mass loss reached 30 % and cellulose content was only about 15 %. These changes are described with the regression eq.:

 $y = 0.0133x^2 - 1.5117x + 48.955$, with correlation coefficient $R^2 = 0.8957$.

Lignin content changes

Lignin is the wood component which also decomposes during white-rot decay (Fig. 1). Its content decreased slowly from 30 to 15 % correspondingly to wood mass loss from 0 to 45 %.



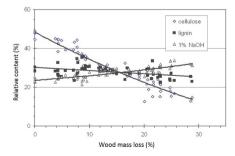


Fig. 1: Changes of structural components content in wood during white-rot decay (Trametes versicolor).

Fig. 2: Changes of structural components content in wood during brown-rot decay (Coniophora puteana).

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Character of these changes is similar to linear. It may be assumed that 50 % wood mass loss corresponds to 50 % decrease of lignin content. The dependence was described with the eq.: $y = 0.0024x^2 - 0.418x + 29.607$, with correlation coefficient $R^2 = 0.737$.

Changes of lignin content are not observable during brown-rot decay (Fig. 2).

1 % NaOH soluble substances content changes

Content of 1 % NaOH soluble substances (what means carbohydrates with low polymerization degree, in relation to cellulose) remain almost at the same level, which value is about 23 %. Eq.: y = -0.1374x + 27.357, $R^2 = 0.6114$.

Brown-rot decay causes fast decompotision of cellulose with simultaneous production of β - and γ -cellulose. Content of 1 % NaOH soluble substances (Fig. 2) raise with the rate similar to cellulose decomposition. It reaches the value of 35 % when wood mass loss equals 25 % (y = $0.0117x^2 + 0.1245x + 24.429$, R² = 0.8695).

Obtained results are consistent with common opinion about the scheme of white-rot decay. *Trametes versicolor* fungus simultaneously decompose all structural components – cellulose, hemicelluloses and lignin. Decreases of cellulose and lignin content are of similar character (Fig. 3).

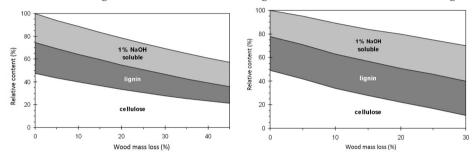


Fig. 3: Content of wood structural components during white-rot decay (Trametes versicolor). Fig. 4: Content of wood structural components during brown-rot decay (Coniophora puteana).

Only the content of 1 % NaOH soluble substances remained on the same level (about 23 %). These are low polymerization degree carbohydrates containing different cellulose degradation products. Our observations confirm common opinion about the enzymatic control of fungi activity: in case of white-rot decay enzymes generation (stimulation and inhibition) is controlled, in the form of feedback, by the saccharides level. According to Eriksson et al. (1990) cellobiose is this saccharide. The content of small-molecule polysaccharides on the constant level confirms this theory, because 1 % NaOH soluble substances are the intermediate products between cellulose and cellobiose.

Lignin content does not change during brown-rot decay. Changes in the content of can be observed in the Fig. 4.

Only carbohydrates decompose as a result of brown-rot decay. Rate of the cellulose decomposition is very fast, faster than it arises from wood mass loss. Cellulose depolymerization takes place together with the increase of the content of 1 % NaOH soluble substances (which are, among others, cellulose depolymerization products). Brown-rot decay mechanism is up till now unknown, but there are no premises that it is able to control the generation of depolymerization factors. Nowadays different authors present the opinion that enzymes interact with other chemical factors (Green et al. 1980, Highley and Murmanis 1985, Highley et al. 1988, Highley et al. 1994a, b, Green and Highley 1997). These factors generated by fungi probably cause "uncontrolled" cellulose decomposition which exceed fungus demand for nutrients.

CONCLUSIONS

Trametes versicolor fungus (white-rot decay) simultaneously decomposes all wood structural components – cellulose, hemicelluloses and lignin. Rates of cellulose and lignin decomposition are similar.

The content of small-molecular carbohydrates stays on the constant level, what indicates uniform cellulose depolymerization and exploitation of decomposition products by fungus.

Lignin decomposition is not observable during brown-rot decay, only carbohydrates degrade. Fast cellulose decomposition takes place. Its rate is faster than it arises from wood mass loss.

Cellulose decomposition, apart from the decay kind, occurs from the beginning of fungi development in wood.

Performed analyses allow determination of the correlation between wood mass loss during decay caused by given fungus species and the content of wood structural components.

REFERENCES

- 1. Adaskaveg, J.E., Gilbertson, R.L., 1986: In vitro decay studies of selective delignification and simultaneous decay by the white rot fungi *Ganoderma lucidum* and *G. tsugae*. Can. J. Bot. 64(8): 1611-1619.
- Adaskaveg, J.E., Gilbertson, R.L., Blanchette, R.A., 1990: Comparative studies of delignification caused by *Ganoderma* species. Applied and Environmental Microbiology 56(6): 1932-1943.
- 3. Adaskaveg, J.E., Gilbertson, R.L., Dunlap, M.R., 1995: Effects of incubation time and temperature on in vitro selective delignification of silver leaf oak by *Ganoderma colossum*. Applied and Environmental Microbiology 61(1): 138-144.
- 4. Antczak, A., Radomski, A., Zawadzki, J., 2006: Benzene substitution in wood analysis. Annals of Warsaw Agricultural University. Forestry and Wood Technology 58: 15-19.
- Clausen, C.A., Kartal, S.N., 2003: Accelerated deterioration of brown-rot decay: Comparison of soil block test, chemical analysis, mechanical properties, and immunodetection. Forest Products Journal 53(11/12): 90-94.
- Curling, S.F., Clausen, C.A., Winandy, J.E., 2001: The effect of hemicellulose degradation on the mechanical properties of wood during brown rot decay. Document of The International Research Group on Wood Preservation (Stockholm Sweden). Document No. IRG/WP 01-20219, 11 pp.
- 7. Curling, S.F., Clausen, C.A., Winandy, J.E., 2002a: Experimental method to quantify progressive stages of decay of wood by basidiomycete fungi. International Biodeterioration and Biodegradation 49(1): 13-19.
- Curling, S.F., Clausen, C.A., Winandy, J.E., 2002b: Solid wood products relationships between mechanical properties, weight loss, and chemical composition of wood during incipient brown-rot decay. Forest Products Journal 52 (7/8): 34-39.
- 9. Dill, I., Krapelin, G., 1986: Palo podrido: Model for extensive delignification of wood by *Ganoderma applanatum*. Applied and Environmental Microbiology 52(6): 1305-1312.
- Eriksson, K.-E., Blanchette, R.A., Ander, P., 1990: Microbial and enzymatic degradation of wood and wood components. Springer Verlag, Berlin, Heidelberg, New York, Hong Kong, London, Milan, Paris, Tokyo, 407 pp.
- Flournoy, D.S., Kirk, T.K., Highley, T.L., 1991: Wood decay by brown-rot fungi: Changes in pore structure and cell wall volume. Holzforschung 45(5): 383-388.

WOOD RESEARCH

- 12. Green, N.B., Dickinson, D.J., Levy, J.F., 1980: A biochemical explanation for the observed patterns of fungal decay in timber. Document No. IRG/WP 1111, 16 pp.
- 13. Green, III.F., Highley, T.L., 1997: Mechanism of brown-rot decay: Paradigm or Paradox. International Biodeterioration and Biodegradation 39(2/3): 113-124.
- 14. Highley, T.L., Murmanis, L.L., 1985: Involvement of hydrogen peroxide in wood decay by brown-rot and white-rot fungi. Document No. IRG/WP 1256, 21 pp.
- 15. Highley, T.L., Ibach, R.E., Kirk, T.K., 1988: Properties of cellulose degraded by the brown rot fungus, *Postia placenta*. Document No. IRG/WP 1350, 9 pp.
- Highley, T.L., Clausen, C.A., Croan, S.C., Green, III.F., Illman, B.L., Micales, J.A., 1994a: Research on biodeterioration of wood, 1987-1992. I. Decay mechanisms and biocontrol. Research paper FPL-RP-529, 20 pp.
- Highley, T.L., Micales, J.A., Illman, B.L., Green, III.F., Croan, S.C., Clausen, C.A., 1994b: Research on biodeterioration of wood, 1987-1992. II. Diagnosis of decay and in-place treatments. Research paper FPL-RP-530, 7 pp.
- Kačík, F., Solár, R., 1999: Analytical wood chemistry. (Analytická chémia dreva). Technical University of Zvolen, 368 pp (in Slovak).
- Krutul, D., 1994: Variation in cellulose content in the stem of pine wood (*Pinus silvestris* L.). (Udzial celulozy i drewna poznego w pniu sosny (*Pinus silvestris* L.). Annals of Warsaw Agricultural University, Forestry and Wood Technology 45: 43-49 (in Polish).
- Krutul, D., 1998: Distribution of cellulose and lignin on the cross- and longitudinal-section of the Scots pine stem (*Pinus sylvestris* L.). 12th Scientific Conference of Wood Technology Faculty, Warsaw University of Life Sciences. Pp 149-154 (in Polish).
- Krutul, D., 2002: Exercises of wood chemistry and chosen problems of organic chemistry. (Cwiczenia z chemii drewna oraz wybranych zagadnień chemii organicznej). Warsaw University of Life Sciences (in Polish).
- Krutul, D., Krasnodębska, B., 1986: Analysis of cellulose and latewood content in the pine stem. 2nd Scientific Conference of Wood Technology Faculty, Warsaw University of Life Sciences. Pp 85-93 (in Polish).
- 23. Rogaliński, K., Kubiak, M., 1967: Decay of pine wood under the influence of the fungi Merulius lacrymans Wulf., Poria vaporaria (Pers.) Fr. and Gleophyllum sepiarium (Wulf.) Karsten. (Rozkład drewna sosny pod wpływem działania grzybów Merulius lacrymans Wulf., Poria vaporaria (Pers.) Fr. i Gleophyllum sepiarium (Wulf.) Karsten). Sylwan 111(12): 11-25 (in Polish).
- 24. Ważny, J., 1963: Colour reactions application for the analysis of fungi decaying wood. Folia Forestalia Polonica S.B. 5: 63–78 (in Polish).
- 25. Winandy, J.E., Morrell, J.J., 1993: Relationship between incipient decay, strength, and chemical composition of Douglas-fir heartwood. Wood and Fiber Science 25(3): 278-288.

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