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CHANGES IN CHEMICAL COMPOSITION OF SPRUCE SOLID WOOD AND SPRUCE CARDBOARD UNTER THE INFLUENCE OF *CONIOPHORA PUTEANA* (SCHUM. EX FR.) KARST. FUNGUS

Kazimierz Lutomski

Wood Chemical Technology Institute of the Poznań Agricultural Academy

The spruce wood and unbleached cardboard (*Picea abies* (L) Karst.) were subject to the action of *Coniophora puteana* (Schum. ex Fr.) Karst. fungus during 7, 14, 21 and 28 days. Changes in weight and contents of cellulose, lignin, pentosanes and weak alkali soluble substances were determined as well as their reactivity with alkalis as compared to indecomposed materials. It was found that basic chemical composition and dynamics of decomposition of solid spruce wood and cardboard obtained from that material are comparable.

INTRODUCTION

Research on new fungicides and chemical wood protection products requires a simple and fast method of determining fungicidal properties of those compounds and substances. Block method, applied in Europe, is of little value for screening tests dur to its great labour consumption, large quantities of materials to be used and almost 6-months research period. The research under discussion requires fast testing of large number of various combinations.

In literature we can find descriptions of different laboratory methods enabling to obtain data on biological activity towards fungi of substances unknown in this respect in time shorter than that of the block method. Those methods use various materials and assessment criteria of tested preparation effectiveness [1, 7, 9, 19, 20, 22]. Research on chemical products for wood protection carried on for a long time in the Wood Protection and Preservation Laboratory, IChTD/AR in Poznań was all inspiration to work out the simple if possible way of determining fungicidal properties of potential fungicides. Assumptions and initial results of testing that method were presented by Lutomski and Spława-Neyman in specialistic conferences on problems of wood protection [10, 13, 14]. The essential methodical point is the use of carboard of unbleached spruce pulp as sampling material. Its basic advantage, as opposed to the solid wood, is the ease of getting large number of samples uniform in structure, easily saturated and etc. It can be stated, that this method to a high degree meets the requirements of fast screening tests of wood protection products, defined by Dickinson [5] and Richardson [16].

To explain the process of decomposition of wood substance contained in unbleached spruce cardboards caused by fungi, the research was done on changes in contents of cardboard basic chemical constituents under the influence of specific species of fungus responsible for brown rot of wood, being a basic test grade in that kind of research. Further aim of that work was an attempt to find an additional criterion for objective assessment of the degree of decomposition of lignocellulose substance under the action of fungi. Weight losses are not always a sufficient basis for determining the fact of initiation of cardboard destruction process by fungi [12]. For comparison tests were also made to determine those changes in spruce wood.

MATERIALS AND TESTING METHODS

For testing needs samples of unbleached spruce cardboard were drawn in the shape of discs, 18 mm in diameter and 2.4 - 2.5 mm thick. Material basis weight was 1175 g/m^2. Spruce wood samples (*Picea abies* (L.) Karst.) had the density of 440 ± 10 kg/m^3 and dimensions of $15 \times 15 \times 4$ mm (that last size was taken along fibres).

Thus prepared samples were subjected to 8-hour extraction with methylene chloride [18], dried to solids at a temp. 105 ± 1°C, weighted, sterilized with steam at 1.2 MPa and place on 120 mm Petri dishes filled with a mycelium of standard graft *Coniophora puteana* (Schum. ex Fr.) Karst. cultured on the nutrient agar and malt. Samples, 6 pcs in one dish were laid on glass plates 2 mm high and about 12 mm in diameter. Dishes with samples were kept in a thermostat at 21 ± 1°C and 80 ± 5% air relative humidity for 7, 14, 21 and 28 days. For each variant of material and testing period 8 dishes i.e. 48 dishes were taken.

When the foreseen time passed, the samples were removed, cleaned of superficial mycelium, weighed, dried in open air for 48 hours and for next 24 hours in the air stream at 40 - 50°C and at 105°C to obtain dry matter. After drying the samples were weighed and measured in respect of their moisture content and weight losses.

Thus obtained material was mechanically crushed and a fraction of 1.0 - 2.0 mm was used for further chemical analyses. The following important constituents of tested materials were determined: the contents of cellulose, lignin, pentosanes, weak alkali soluble substances. Besides, the determination of material reactivity to alkalis was made. Cellulose content was determined by Seifert acetylacetone method [15]. Thus determined cellulose is practically free from hemicellulose and lignin. Quantitative determination of lignin in material being tested was made by Tappi method [15], whereas pentozane content was estimated by Tollens method [15]. The amount of substances soluble in weak alkalis

Table 1 - Tabela 1

Content of basic chemical constituents in spruce solid wood (*Picea abies* (L.) Karst.) and unbleached spruce cardboard

Zawartość podstawowych składników chemicznych w drewnie świerka (*Picea abies* (L.) Karst.) i nie bielonej tekturze świerkowej

Constituent Składnik	Wood Drewno	Cardboard Tektura
	Content – Zawartość %	
Cellulose Celuloza	50.37	49.51
Lignin Lignina	29.18	28.74
Pentozans Pentozany	13.07	11.41
Soluble in 1% NaOH Rozpuszczalne w 1% NaOH	11.93	9.12

was defined acc. to Sieber [15], with the use of 1% water solution of sodium hydroxide. A characteristic feature of lignocellulose substance decaying under the action of brown-rot fungi is its reactivity with alkalis [8]. This is the amount of ml of 0.1n NaOH reacting with 0.1 g of tested substance. That determination was made as follows: about 0.1 g of precisely weighed material was put into the conical flask and 50 ml of 0.1n NaOH added. It was heated under reflux condenser in the boiling water bath for two hours. After cooling the whole was titrated with 0.1n HCl. Number of militres of 0.1n NaOH absorbed by 0.1 g of tested substance was calculated. A novelty introduced to that method was potentiometric titration with the use of glass general-purpose electrode and electromagnetic stirrer.

Table 1 and Figures 1 - 6 show results of six determinations.

RESULTS

Results of testing the content of basic chemical constituents of spruce solid wood and spruce cardboard are shown in Table 1. They can be summed up with a statement that those materials have similar content of cellulose and lignin. Slightly lower amounts of pentosanes and constituents soluble in weak alkalis found in the cardboard are caused by technological processes applied during the production of pulp.

After seven days of test fungus action the samples were partially covered with superficial mycelium and weight losses found in both the materials varied by about 0.4%. Solid wood was characterized by a higher rate of decomposition than spruce cardboard. Likewise, higher quan-

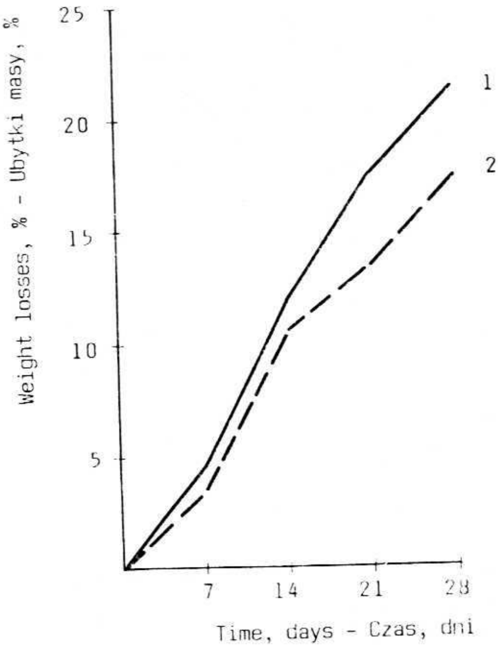

Fig. 1. Changes in spruce solid wood and spruce cardboard weight under the action of *Coniophora puteana fungus*

Rys. 1. Zmiany masy drewna i tektury świerkowej pod wpływem grzyba *Coniophora puteana*

1 — wood (drewno), *2* — cardboard (tektura)

titative changes in wood were observed in determining the cellulose content. In the week of testing quantitative changes of lignin and pentosanes were insignificant as it was observed by Seifert [18]. However, solubility in 1% sodium hydroxide markedly increased and that growth was slightly higher in case of cardboard. It indicates that in that time enzymes had better access to structural elements of material as broken as spruce pulp.

The next seven days of tests showed further growth of percentage losses in wood and cardboard weight. The dynamics of those changes for both the materials was similar, which can be clearly seen in Fig. 2.

Among the constituents, the cellulose decomposed faster than pentosanes. The rate of decay of cellulose contained in solid wood was higher than that of cardboard cellulose (Fig. 3). Visual examination of samples

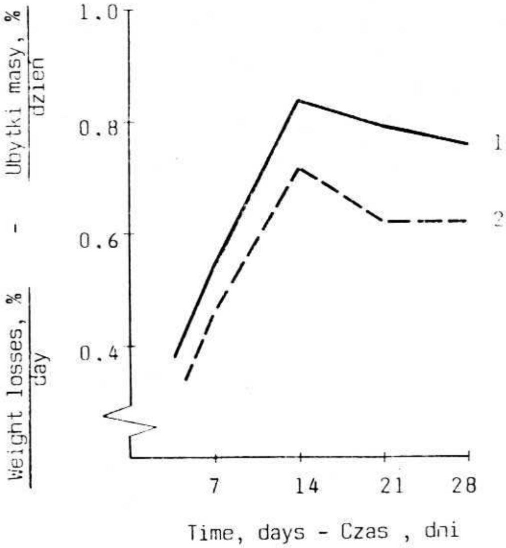

Fig. 2. Dynamics of spruce solid wood and spruce cardboard decomposition under the action of *Coniophora puteana* fungus

Rys. 2. Dynamika rozkładu drewna i tektury świerkowej pod wpływem grzyba *Coniophora puteana*

1 — wood (drewno), *2* — cardboard (tektura)

discovered the presence of brown spots and over-colouring in both the materials which is attributed by W a ż n y [21] to the separation of metoxyl groups from lignin.

The period under discussion was characterized by considerable growth of alkali solubility of tested samples which exceeded 38% for wood and 31% for cardboard. The rate of solubility changes was 3.8% and 2.6% a day, respectively. According to S e i f e r t [18] that phenomenon is connected with the gradual increase of intermediate products of cellulose and hemicellulose decomposition in the base as well as with passing certain part of lignin into the soluble form. It can be partially proofed by the dark colouring of 1% NaOH water solutions used in the determination of alkali solubility.

After 21 days of testing the samples of spruce solid wood and cardboard distinctly changed their colour into dark brown and were easily crushed. At the same time, the drop in test fungus decomposing activity was observed, which can be clearly seen in Fig. 2. There was a decrease in the rate of sample decomposition, expressed in terms of weight losses per day. The change is more visible in case of spruce cardboard. That way, there revealed a property characteristic of wood destructive fungi and previously observed among other by Schultze-Dewitz [17] and Seifert [18] which consists in strong decomposition of lignocellulose substance and accumulation of big amounts of intermediate products of decay in the base. Those products are further depolymerized and assimulated by mecelium. It is also evidenced by the further growth of base solubility in alkalis. The solubility for both the materials tested reached the maximum at 20% weight losses.

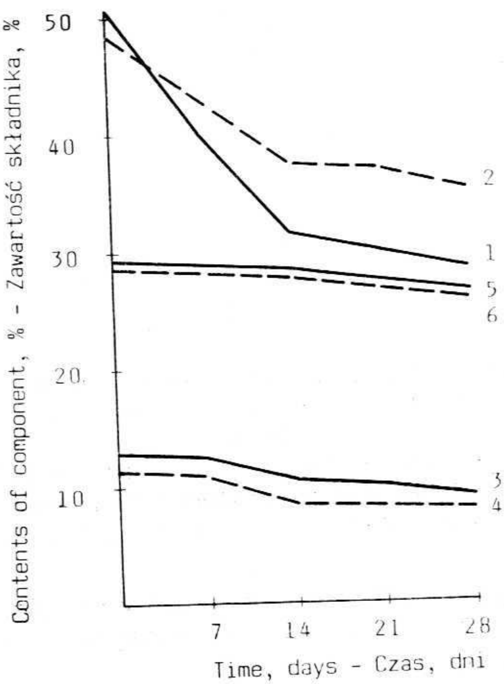

Fig. 3. Changes in contents of spruce solid wood and spruce cardboard basic constituents under the action of *Coniophora puteana* fungus

Rys. 3. Zmiany zawartości w drewnie i tekturze świerkowej podstawowych składników pod wpływem grzyba *Coniophora puteana*

1 — wood cellulose (celuloza w drewnie), *2* — cardboard cellulose (celuloza w tekturze) 3 — wood pentosanes (pentozany w drewnie), *4* — cardboard pentosanes (pentozany w drewnie) *5* — wood lignin (lignina w drewnie), *6* — cardboard lignin (lignina w tekturze)

After 28 days of test fungus activity, the samples of spruce wood and cardboard were dark brown, brittle and lost their original fibrous structure. Fig. 2 shows the drop in rate of decomposition whereas Fig. 3 and 4 present the decrease in the rate of cellulose quantitative changes.

On reaching the maximum after 21 days of decomposition the alkali solubility decreased and that drop was smaller in case of spruce cardboard than of solid wood. With regard to the amount of 0.1n NaOH absorbed by substances tested, the repeated growth of that index was observed after 28 days of decomposition. It can be the evidence of the growing amount of acid substances separated from the mycelium into the base or the presence in the base of higher amount of organic acids being the products of lignocellulose material decomposition.

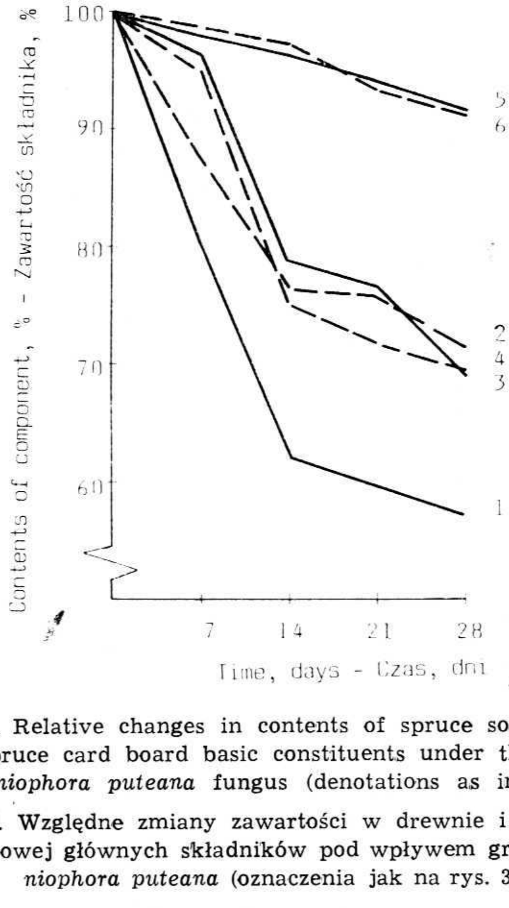

Fig. 4. Relative changes in contents of spruce solid wood and spruce card board basic constituents under the action of *Coniophora puteana* fungus (denotations as in Fig. 3)

Rys. 4. Względne zmiany zawartości w drewnie i tekturze świerkowej głównych składników pod wpływem grzyba *Coniophora puteana* (oznaczenia jak na rys. 3)

Thus presented results indicate that the tested substances, i.e. spruce solid wood and cardboard have similar chemical constitution and differences observed are contained within the bounds of the measuring error. It is confirmed by the statistical analysis of the results. Weight losses and changes in chemical constitution of both kinds of lignocellulose substance subjected to the action of test fungus are also similar. In this connection, the cardboard made of unbleached wood pulp can be acknowledged as coordinate material, comparable with solid wood for tests in mycological research. Its greatest advantages are a big ease of drawing samples, high saturation power and before mentioned structural homogeneity.

Test results, presented above, were obtained in natural material free from any chemicals to protect it from decay. In fast methods of testing those preparations it is essential to choose proper criterion to judge the degree of the decomposition of material devided into samples. Most often weight losses are taken into account, but those are rather small in short

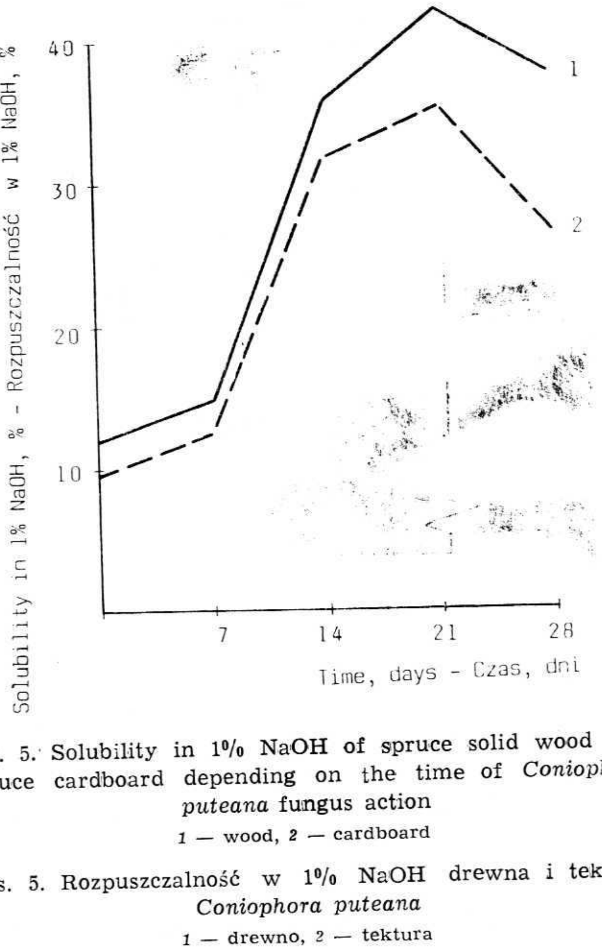

Fig. 5. Solubility in 1% NaOH of spruce solid wood and spruce cardboard depending on the time of *Coniophora puteana* fungus action

1 — wood, 2 — cardboard

Rys. 5. Rozpuszczalność w 1% NaOH drewna i tektury *Coniophora puteana*

1 — drewno, 2 — tektura

period of mycelium action [11]. It was observed that quantitative changes of lignocellulose materials under the influence of fungi are always preceded by quantitative ones. Brown-rot fungi cause fast depolymerization of cellulose and the products of decomposition are assimilated in the further course of the process. The determination of cellulose quantitative and qualitative changes in the decomposed wood is not simple, requires special chemical reagents is troublesome in realization. Research done by K e r n e r [9], L u t o m s k i [10, 11, 12], S c h u l t z e - D e w i t z [17] and S e i f e r t [16] showed that rot decay fungi cause fast growth of

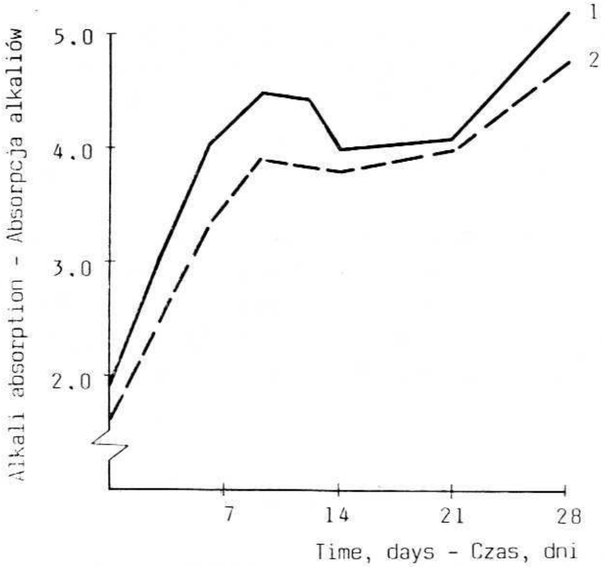

Fig. 6. Alkali absorption of spruce solid wood and spruce cardboard depending on the *Coniophora puteana* fungus action time

Rys. 6. Absorpcja alkaliów przez drewno i tekturę świerkową w zależności od czasu działania grzyba *Coniophora puteana*

1 — wood (drewno), *2* — cardboard (tektura)

consituents soluble in alkalis. On the other hand, K a w a s e [8] drew attention to the quick changing property of those materials, such as their reactivity with alkalis and defined it as „alkali consumption". It should be understood as total amount of alkalis reacting with defined amount of biologically decomposed organic substance. As a result of decomposition process acid chemical compounds and substances are generated and react with alkalis added. Their number depends on the degree of decomposition of the organic material. It was found that spruce solid wood and spruce cardboard subjected to the action of *Coniophora puteana* fungus reacted with alkali to a similar degree. Amounts of 0.1n NaOH used by 0.1 g of decomposed substance of both the materials are twice as large at 5 - 10% weight losses as compared with sound wood.

With regard to the ease and simplicity of performing the analysis as well as fast determination of alkali reactivity of the decomposed wood, particularly in the initial phase of the process, that feature can be considered as a simple and fast diagnostic measure enabling to confirm univocally the fact of initiating the decay of lignocellulose substance by brown-rot fungi. It can be especially helpful in case of small weight losses below 5%.

When developing the method described by Kawase [8] in the research under discussion we applied potentiometric titration. It enabled us to determine precisely the point of neutralization of the solution being titrated, without the need of using not easily accessible fluorescent indicators. That procedure was extorted by dark colouring of tested solutions.

By the way, the idea has arisen to use that colour property of alkaline solution for the assessment of the degree of organic substance decomposition in laboratory tests. That conception, consisting in colorimetric measurement of alkaline extracts of the decomposed lignocellulose material, would make the evaluation of test results more objective.

CONCLUSIONS

The cardboard of unbleached wood pulp can be recognized as coordinate material to the solid wood for samples in tests on fungicidal properties of wood protection products. The similar content of basic constituents in both the materials and their changes under the influence of *Coniophora puteana* test fungus cans speak for that. Alkali solubility and reactivity of decomposed substance are chemical features which would be first affected by the brown type decay. That last property can be good diagnostic feature, particularly, in initial phases of brown rot of lignocellulose materials.

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ZMIANY SKŁADU CHEMICZNEGO DREWNA I TEKTURY ŚWIERKOWEJ POD WPŁYWEM GRZYBA *CONIOPHORA PUTEANA* (SCHUM. EX FR.) KARST.

Streszczenie

Drewno świerka (*Picea abies* (L.) Karst.) oraz niebieloną tekturę z takiego drewna poddano działaniu grzyba *Coniophora puteana* (Schum. ex Fr.) Karst. w czasie 7, 14, 21 i 28 dni. W rozłożonym materiale oznaczono zmiany masy oraz zawartości celulozy, ligniny, pentozanów, składników rozpuszczalnych w 1% NaOH i reaktywność z alkaliami. Zmiany masy, ich dynamika i zmiany zawartości badanych składników obu materiałów, z niewielkimi tylko różnicami, były zbliżone. Szybkość zmian zawartości celulozy i rozpuszczalności w alkaliach drewna była większa w drewnie w pierwszych dwóch tygodniach rozkładu. Stwierdzono też nieco większy wzrost reaktywności z alkaliami drewna litowego w porównaniu z tekturą. Z punktu widzenia składu chemicznego i jego zmian pod wpływem rozkładu brunatnego, tektura z niebielonego ścieru może być uznana za równorzędny z drewnem litym materiał na próbki w badaniach mykologicznych chemicznych środków ochrony drewna.

Authors address
Prof. dr hab. Kazimierz Lutomski
Akademia Rolnicza w Poznaniu
Instytut Chemicznej Techn. Drewna
ul. Wojska Polskiego 38/42, 60-637 Poznań