FOLIA FORESTALIA POLONICA
Seria B, zeszyt 23, 1992

# INFRARED SPECTROSCOPIC STUDIES OF HOLOCELLULOSE AND LIGNIN FROM DEGRADED WOOD

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Results of infrared spectroscopic studies on holocellulose and lignin preparations taken from wood of different kinds and degrees of degradation were presented.

It was found that holocellulose taken from pine and beech wood, cooked in NaOH is highly deacetylated. Also the 30 - 70% increase in degree of oxidation of pine and beech lignin from the wood cooked in NaOH and pine lignin from the wood decomposed by fungi was noted.

## INTRODUCTION

Infrared spectroscope studies of wood and its chemical components were carried out by many researchers (O'Connor 1971, Hergert 1971). These examinations are still being used and developed to provide deep qualitative and quantitative characteristics of wood and its components (Supiński, Dziurzyński 1988, Geles et al. 1989, Niemz et al. 1989, Wienhaus et al. 1989). This paper presents the results of infrared spectroscopic examinations of holocellulose and lignin preparations taken from wood of different kinds and degrees of degradation.

## MATERIAL AND METHODS

The tests were caried out on holocellulose and lignin preparations taken from pine and beech wood degraded in the following processes: cooking in NaOH, hydrolysis in $H_2SO_4$ and decay by *Coriolus versicolor*

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* Fungal decays were performed in mycological laboratory of Institute of Chemical Wood Technology at agreement of Prof. Dr. K. Lutomski.

L. ex Fr. Quel. and *Coniophora puteana* Schum. ex Fr./Karst. fungi *. Samples of 3×20×30 mm were subjected to degradation. Alkalic cooking was carried out in laboratory autoclaves with NaOH solution at 1.2 moldm$^{-3}$ concentration, at a temperature of 438 K, for 2 hrs at liquor to wood ratio 5 : 1. Acid hydrolysis was made in glass flasks unter a reflux condenser using 0.6 moldm$^{-3}$ at 373 K, for 6 and 30 hrs at liquor to wood ratio 5 : 1. Solid residues of cooking and hydrolysis were washed with hot water to neutral reaction. Decay with *Coriolus versicolor* and *Coniophora puteana* was carried out in Kolle flasks containing agar-agar medium. The decomposition was carried out in chamber in the following conditions: temp. 295 K, time 120 - 300 days, relative humidity 65 - 70%, in dispersed daylight.

The decomposed wood was ground to sawdust fraction 0.5 - 1.0 mm and its chemical composition was determined (Fig. 1). Lignin was determined with Tappi T 13 m method and holocellulose using 10% peracetic acid at temp. 365 K in time of 20 min. for beech and 45 min. for pine (Haas, Schoch, Ströhle 1955). Detailed descriptions of the decomposition processes and determinations of chemical composition of the wood are given in Dziurzyński (1984). Losses in mass of the wood from which holocellulose and lignin preparations were obtained are presented in Table 1.

The IR spectra were obtained as follows: holocellulose and lignin preparations were ground in vibrator M. v. Ardenne, C. Z. Jena. The batch of 400 mg was roasted at 823 K KBr and 2.00±0.05 mg of the ground

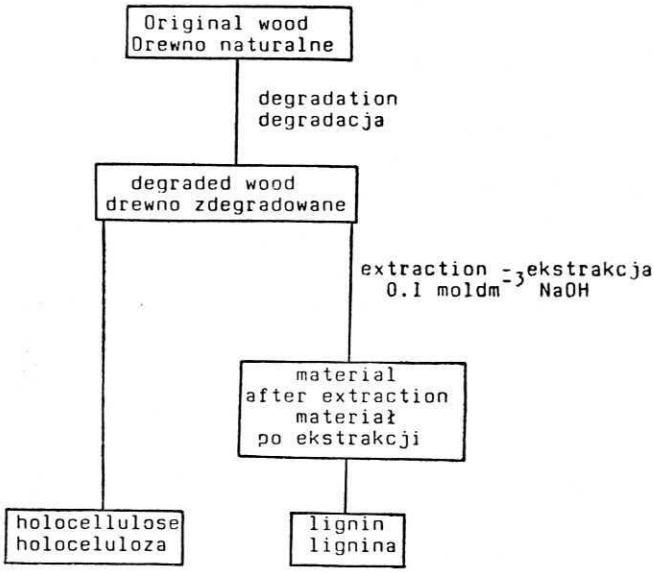


Fig. 1. Scheme for obtaining holocellulose and lignin preparations
Rys. 1. Schemat otrzymywania preparatów holocelulozy i ligniny

Table 1

Holocellulose and lignin content and mass losses depending on the degradation method (Dziurzyński 1984)

Zawartość holocelulozy i ligniny oraz ubytki masy drewna w zależności od rodzaju degradacji (Dziurzyński 1984)

| Decomposing factor Czynnik rozkładający | Pine – Sosna | | | | Beech – Buk | | | |
|---|---|---|---|---|---|---|---|---|
| | time of decomposition czas rozkładu | mass loss ubytek masy (%) | content zawartość (%) | | time of decomposition czas rozkładu | mass loss ubytek masy (%) | content zawartość (%) | |
| | | | lignin lignina | holocell holocel | | | lignin lignina | holocell holocel |
| – | 0 | 0 | 27.6 | 67.4 | 0 | 0 | 23.5 | 69.5 |
| NaOH T=438 K | 2 h | 33.3 | 22.0 | 74.6 | 2 h | 52.0 | 8.2 | 84.3 |
| $H_2SO_4$ T=373 K | 30 h | 31.6 | 36.4 | 63.5 | 6 h | 42.7 | 34.5 | 62.5 |
| *C. versicolor* T=295 K | 300 d | 28.7 | 19,7 | 61.9 | 120 d | 63.0 | 17.5 | 60.5 |
| *C. puteana* T=295 K | 220 d | 63.0 | 34.4 | 11.5 | 250 d | 57.0 | 10.8 | 21.2 |

preparation was homogenized in the same vibrator. Then a sample of 200.0 mg of homogenized mixture was tableted in PW-20 tableter using hydraulic press at 100 kp for 10 min. The spectra were recorded with spectrophotometer Specord IR 75, C. Z. Jena. The parameters of spectra recording were as follows: slit program 1.5, excitation 3 s, speed of paper shift 7.5 mm/100 $cm^{-1}$, speed of spectrum shift 113 $cm^{-1}$/min. Permeability of minimum spectra of lignin at 1850 $cm^{-1}$ and holocellulose at 2250 $cm^{-1}$ was assumed $95 \pm 3\%$. Quantitative analysis of lignin spectrum was carried out assuming lines connecting the minima 670 and 1850 $cm^{-1}$ and 1850 and 3700 $cm^{-1}$ as the base. For holocellulose the spectrum base constituted the lines connecting the minima 760 and 1900 $cm^{-1}$ and 2300 and 3900 $cm^{-1}$.

## RESULTS AND DISCUSSION

Absorbances of IR spectra of holocellulose and lignin preparations are given in Tables 2 and 3. In beech holocellulose (Table 2) the absorbance of 1230 and 1730 $cm^{-1}$ bands is about three times greater than in pine holocellulose and is a measure of the number of acetic groups (O'Connor 1971, Karklin et al. 1971). The absorbance of 1230 $cm^{-1}$ band of the holocellulose obtained from the wood cooked in NaOH decreases by 36 - 50% while that of 1730 $cm^{-1}$ one falls as much as two to six times. This is due to strong deacetylation of holocellulose in the process. The absorbances of these bands of holocellulose from the wood hydrolysed in $H_2SO_4$ decrease to a lesser degree, i.e. deacetylation is lower. In the

Table 2

**Absorbances of IR spectrum bands of holocellulose separated from wood degraded by chemical and biological factors**
**Absorbancje pasm widma IR holocelulozy wyodrębnionej z drewna zdegradowanego czynnikami chemicznymi i biologicznymi**

| Origin of holocellulose / Pochodzenie holocelulozy | | | Absorbances – Absorbancje | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 890 | 1030 | 1100 | 1170 | 1230 | 1310 | 1380 | 1430 | 1630 | 1730 | 2880 | 3400 $cm^{-1}$ |
| Pine Sosna | original wood drewno wyjściowe | | 0.07 | 0.28 | 0.26 | 0.22 | 0.14 | 0.14 | 0.16 | 0.15 | 0.03 | 0.09 | 0.14 | 0.29 |
| | degraded wood drewno zdegradowane | NaOH | 0.07 | 0.22 | 0.21 | 0.17 | 0.09 | 0.10 | 0.12 | 0.11 | 0.04 | 0.03 | 0.10 | 0.16 |
| | | $H_2SO_4$ | 0.09 | 0.35 | 0.30 | 0.25 | 0.13 | 0.14 | 0.16 | 0.15 | 0.03 | 0.03 | 0.13 | 0.29 |
| | | *C. versicolor* | 0.05 | 0.21 | 0.20 | 0.17 | 0.10 | 0.10 | 0.12 | 0.12 | 0.03 | 0.06 | 0.11 | 0.20 |
| | | *C. puteana* | 0.11 | 0.41 | 0.35 | 0.29 | 0.16 | 0.17 | 0.19 | 0.18 | 0.05 | 0.05 | 0.15 | 0.33 |
| Beech Buk | original wood drewno wyjściowe | | 0.10 | 0.46 | 0.38 | 0.31 | 0.24 | 0.17 | 0.22 | 0.18 | 0.02 | 0.18 | 0.14 | 0.33 |
| | degraded wood drewno zdegradowane | NaOH | 0.11 | 0.35 | 0.31 | 0.27 | 0.12 | 0.15 | 0.17 | 0.16 | 0.04 | 0.03 | 0.14 | 0.29 |
| | | $H_2SO_4$ | 0.11 | 0.50 | 0.46 | 0.37 | 0.19 | 0.20 | 0.23 | 0.20 | 0.04 | 0.05 | 0.18 | 0.43 |
| | | *C. versicolor* | 0.09 | 0.37 | 0.32 | 0.26 | 0.19 | 0.15 | 0.19 | 0.16 | 0.04 | 0.14 | 0.12 | 0.28 |
| | | *C. puteana* | 0.09 | 0.48 | 0.41 | 0.29 | 0.22 | 0.18 | 0.21 | 0.18 | 0.03 | 0.10 | 0.16 | 0.36 |

**Table 3**

Absorbances of IR spectrum bands of lignin separated from wood degraded by chemical and biological factors
Absorbancje pasm widma IR ligniny wyodrębnionej z drewna zdegradowanego czynnikami chemicznymi i biologicznymi

| Origin of lignin / Pochodzenie ligniny | | | Absorbances – Absorbancje | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 850 | 1030 | 1080 | 1140 1120 | 1210 | 1270 | 1310 | 1410 | 1450 | 1510 1505 | 1600 | 1710 | 2880 | 2910 | 3400 $cm^{-1}$ |
| Pine Sosna | original wood drewno wyjściowe | | 0.10 | 0.37 | 0.30 | 0.33 | 0.39 | 0.46 | | 0.26 | 0.36 | 0.41 | 0.22 | 0.10 | 0.17 | 0.24 | 0.26 |
| | degraded wood drewno zdegradowane | NaOH | 0.11 | 0.34 | 0.30 | 0.33 | 0.40 | 0.44 | | 0.27 | 0.35 | 0.39 | 0.24 | 0.17 | 0.21 | 0.28 | 0.26 |
| | | $H_2SO_4$ | 0.11 | 0.38 | 0.30 | 0.35 | 0.45 | 0.51 | | 0.30 | 0.39 | 0.46 | 0.25 | 0.12 | 0.19 | 0.25 | 0.25 |
| | | *C. versicolor* | 0.11 | 0.37 | 0.30 | 0.36 | 0.41 | 0.45 | | 0.27 | 0.36 | 0.41 | 0.23 | 0.13 | 0.19 | 0.26 | 0.25 |
| | | *C. puteana* | 0.11 | 0.31 | 0.26 | 0.28 | 0.32 | 0.34 | | 0.22 | 0.28 | 0.31 | 0.21 | 0.14 | 0.22 | 0.26 | 0.23 |
| Beech Buk | original wood drewno wyjściowe | | 0.11 | 0.44 | 0.52 | 0.61 | 0.54 | 0.43 | 0.45 | 0.38 | 0.54 | 0.51 | 0.35 | 0.15 | 0.25 | 0.36 | 0.28 |
| | degraded wood drewno zdegradowane | NaOH | 0.07 | 0.27 | 0.32 | 0.35 | 0.39 | 0.33 | 0.28 | 0.26 | 0.38 | 0.34 | 0.25 | 0.21 | 0.27 | 0.38 | 0.18 |
| | | $H_2SO_4$ | 0.09 | 0.30 | 0.35 | 0.40 | 0.40 | 0.34 | 0.32 | 0.28 | 0.39 | 0.38 | 0.27 | 0.12 | 0.20 | 0.24 | 0.18 |
| | | *C. versicolor* | 0.08 | 0.32 | 0.37 | 0.41 | 0.40 | 0.35 | 0.33 | 0.29 | 0.40 | 0.40 | 0.26 | 0.12 | 0.17 | 0.25 | 0.19 |
| | | *C. puteana* | 0.07 | 0.27 | 0.33 | 0.37 | 0.34 | 0.28 | 0.29 | 0.25 | 0.34 | 0.32 | 0.23 | 0.14 | 0.17 | 0.23 | 0.18 |

holocellulose from the wood degraded by fungi deacetylation is almost absent. The only exception is holocellulose from pine wood degraded by *C. versicolor* where considerable falls in the absorbance of 1230 and 1730 $cm^{-1}$ bands can be found. Differences in absorbance of the remaining bands of IR spectra of holocellulose can reach the value of up to 50% (Table 2). These are not large differences considering the fact that repeatability of IR spectra averages 18.6%.

In case of lignin (Table 3) significant differences in IR spectra can be observed between the pine and beech lignin. In the pine lignin the band 1310 $cm^{-1}$ does not accur as compared with the beech one. Strong band of the pine lignin at 1080 $cm^{-1}$ is observed in beech only on the slope of the 1120 $cm^{-1}$ band. These differences appear because the structure of phenylpropane skeleton of the pine lignin is a guaiacyl system while that of beech is siringil/guaiacyl one (Hergert 1971). Also the difference in absorbance of the 1270 and 1120 $cm^{-1}$ bands being a measure of the number of methoxyl groups is specific for the pine and beech lignin (Faix, Schweers 1974). This difference is positive for the pine lignin and negative for the beech lignin. This fact is reflected in the results of determinations of metoxyl groups with classic methods: the content of these groups is higher in the beech lignin than in the pine one. In the pine and beech lignin also the ratio of absorbance of the 2910 and 3400 $cm^{-1}$ bands is different. For the pine lignin this ratio averages 1.03 while for the beech one 1.47. This is due to a greater number of C-H groups in the beech lignin.

Analysing IR absorbances of lignin in relation to the method of its degradation, the band 1710 $cm^{-1}$ is worth noticing. Absorbance of this band increases in the pine and beech lignin from the wood cooked in NaOH and pine lignin from the wood decomposed by fungi by 30 - 70%. This proves oxidation of this lignin. Similar changes in lignin oxidation were found neither in wood hydrolysed in $H_2SO_4$ nor in beech wood decomposed by fungi.

## CONCLUSIONS

1. Holocellulose separated from the wood cooked in NaOH is highly deacetylated. In the holocellulose of the wood hydrolysed in $H_2SO_4$ deacetylation was observed in a lesser degree while in that from the wood decomposed by fungi it was almost absend.

2. Cooking of pine and beech wood in NaOH and decomposition of pine wood by fungi brings about an increase in the degree of lignin oxidation by 30 - 70% as compared to that from natural wood.

Received in September 1991

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## BADANIA SPEKTROSKOPOWE W PODCZERWIENI HOLOCELULOZY I LIGNINY DREWNA ZDEGRADOWANEGO


### Streszczenie

Wykonano badania spektroskopowe w podczerwieni preparatów holocelulozy i ligniny sosny i buka, wyodrębnionych z drewna naturalnego oraz drewna zdegradowanego w procesach: roztwarzania NaOH, hydrolizy $H_2SO_4$, rozkładu przez grzyby *Coriolus versicolor* oraz *Coniophora puteana*.

Stwierdzono, że holoceluloza wyodrębniona z drewna roztworzonego w NaOH jest silnie zdeacetylowana. W holocelulozie drewna hydrolizowanego $H_2SO_4$ deacetylacja zaszła w mniejszym stopniu, a w holocelulozie drewna rozłożonego przez grzyby prawie nie wystąpiła. Roztwarzanie drewna sosny i buka w NaOH oraz rozkład drewna sosny przez grzyby powoduje wzrost stopnia utlenienia ligniny o 30 do 70% w stosunku do ligniny drewna naturalnego.