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# THE INFLUENCE OF TIME AND TEMPERATURE OF BEECH WOOD (*FAGUS SYLVATICA* L.) HEAT TREATMENT IN SUPERHEATED STEAM ON THE CARBOHYDRATES CONTENT

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## ABSTRACT

The influence of time (2, 6, 10 h) and temperature of beech wood (*Fagus sylvatica* L.) heat treatment in superheated steam (160 °C, 220 °C) on the carbohydrates content was examined. Carbohydrates were divided into two groups basing on the molecular mass. Holocellulose, cellulose and α-cellulose were qualified to the group of high molecular mass. Hemicelluloses, 1 % NaOH soluble substances and β + γ cellulose were qualified to the group of low molecular mass. Significant changes in the chemical composition of beech wood take place in the temperature of 220 °C and treating time of 6 and 10 hours. Hemicelluloses content decreases from 37 % to about 4 % in these conditions. Holocellulose content decreases from 84 % to 52 % and α-celulose content from 38 % to 18 %.

KEYWORDS: Heat treatment, superheated steam, carbohydrates, beech.

## INTRODUCTION

Optimal parameters of the heat treating process must be selected for heat species. High treatment temperature causes series of changes in properties of carbohydrates present in wood. The number of chemical processes follows the heat treatment (Rowell 2002, Yildiz and Gumukaya 2007). The most important are:

- hemicelluloses degradation with monosaccharides forming, which may undergo the

reverse condensation reactions and form strongly branched polysaccharides;
- crosslinking between carbohydrates macromolecules and between carbohydrates and lignin molecules;
- the increase of cellulose crystallinity.

Reactions and processes mentioned above lead to change of structural and non structural wood components content (Parysek and Zakrzewski 2006, Zawadzki et al. 2007, Yildiz et al. 2006). Hemicelluloses are the wood structural component which is the least resistant for temperature changes. Hemicelluloses degradation rate in the temperature of 150 °C is four times higher in relation to cellulose (Stamm 1956). It is the result of (among others) the low polymerization degree of hemicelluloses. Formic and acetic acids, which are formed mainly from O-acetyl-galactoglucomannan under the influence of the temperature, accelerate and catalyze the hydrolysis of hemicelluloses and amorphous cellulose (Kollmann and Fengel 1965). In the temperature of 150 °C the apparent change of carbohydrates content is observed. It is mainly caused by carbohydrates hydrolysis to monosaccharides and then their dehydratation to cyclic furan-type compounds (Fengel and Wegener 2003).

## MATERIAL AND METHODS

One single board isolated from the beech wood (*Fagus sylvatica* L.) was examined. Fifty six samples with size of 40 x 40 x 170 mm were isolated. Samples were marked and divided into seven groups of eight with similar density. Each group contained samples from perimeter- and pith-adjacent wood zone. First group was the comparative one (control). Second, third and fourth were treated in the temperature of 160 °C corespondingly 2, 6 and 10 hours. Fifth, sixth and seventh group were treated in the temperature of 220 °C with the same duration variants. The heat treatment process was divided into three stages. Samples drying in the temperature of 105 °C during 3 hours and then 130 °C during 12 hours was the first stage. Then adequate volume of boiling water introduced into applied laboratory dryer and treating temperature was increased by 15 °C each hour until the assumed temperature was reached. Then samples were treated during next 2, 6 or 10 hours. In the third stage samples were cooled and leaved in the exiccator until the constant mass was reached.

Samples were disintegrated after treatment and sieved. Fraction passing the sieve with 1.0 mm and remaining on 0.5 mm mesh sieve was taken for analysis. Samples were extracted with ethanol-chloroform (93/7) (v/v) (Antczak et al. 2006) mixture and then analysis of carbohydrates were performed (Krutul 2002, Kačik and Solár 1999).

Following analysis were performed: holocellulose content using sodium chlorite, 1 % NaOH soluble substances, cellulose content with Kürschner-Hoffer method, α-cellulose content using 17.5 % NaOH.

## RESULTS AND DISCUSSION

The chemical composition of examined treated samples differs from control samples as it was shown in the Tab. 1. Changes in chemical composition are observable especially for higher temperature and longer treating duration. The most significant content decrease in relation to original value is observed for hemicelluloses. Cellulose content decreases significantly only at 220 °C after 10 hours treatment.

*Tab. 1: The influence of time and temperature of heat treatment in superheated steam on carbohydrates content in beech wood (Fagus sylvatica L.)*

| Group number | Temperature (°C) | Time (h) | Density (g.cm$^{-3}$) | Content in extracted wood (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Holocellulose* | Cellulose* | α-cellulose in wood* | Hemicelluloses** | 1 % NaOH soluble subst.* | β + γ cellulose* |
| 1. | Control | | 0.70±0.03 | 84.1 ± 0.7 | 46.7 ± 4.8 | 38.5 ± 4.0 | 37.4 ±5.5 | 15.6 ± 0.6 | 8.2 ± 0.8 |
| 2. | 160 | 2 | 0.661±0.021 | 82.8 ± 0.3 (73.7)*** | 47.5 ± 2.5 (42.3) | 38.5 ± 1.6 (34.3) | 35.3 ±2.7 (31.4) | 16.2 ± 0.6 (14.4) | 9.1 ± 1.2 (8.0) |
| 3. | 160 | 6 | 0.66±0.03 | 81.6 ± 0.3 (72.6) | 46.7 ± 2.8 (41.6) | 36.6 ± 2.0 (32.6) | 34.9 ± 2.9 (31.0) | 19.0 ± 0.4 (16.9) | 10.1 ± 0.8 (9.0) |
| 4. | 160 | 10 | 0.66±0.03 | 80.7 ± 0.2 (71.8) | 45.6 ± 2.2 (40.6) | 36.3 ± 1.8 (32.3) | 35.1 ± 2.3 (31.2) | 17.1 ± 2.2 (15.2) | 9.3 ± 0.5 (8.3) |
| 5. | 220 | 2 | 0.617±0.026 | 58.7 ± 0.4 (45.2) | 53.3 ± 1.7 (41.0) | 35.6 ± 1.2 (27.4) | 5.4 ± 2.1 (4.2) | 28.0 ± 0.1 (21.6) | 17.7 ± 1.8 (13.6) |
| 6. | 220 | 6 | 0.618±0.021 | 57.1 ± 0.5 (40.0) | 52.5 ± 2.0 (36.8) | 19.1 ± 2.1 (13.4) | 4.6 ± 2.5 (3.2) | 32.8 ± 1.7 (23.0) | 33.3 ± 2.2 (23.4) |
| 7. | 220 | 10 | 0.614±0.025 | 52.2 ± 1.1 (36.5) | 48.3 ±1.5 (33.8) | 18.2 ± 1.1 (12.7) | 3.9 ± 2.6 (2.7) | 36.6 ± 0.9 (25.6) | 30.1 ± 1.6 (21.1) |

*average content
**the hemicelluloses content was found by subtracting cellulose from holocellulose content
***values in brackets calculated in relation to sample mass before heat treatment

Results in the Tab. 1 are divided to two factors. One of them was molecular mass of analysed substances – high molecular mass (holocellulose, cellulose, α-cellulose) and low molecular mass (hemicelluloses, 1 % NaOH soluble substances and β + γ cellulose). Second of them were parameters of treatment – temperature (160 and 220 °C) and time (2, 6, 10 hours).

Heat treatment in the temperature of 160 °C does not cause significant changes in the content of holocellulose, cellulose and α-cellulose in beech wood (Fig. 1). The holocellulose content after 2 hours treatment decreases by 1.5 % in relation to control sample, after 10 hours – by 4.0 %. The cellulose content after 6 hours treatment does not change and after 10 hours treatment decreases by 2.4 %. The α-cellulose content after 10 hours treatment decreases by 5.7 %. Generally the temperature of 160 °C does not cause significant changes of hogh molecular polysacharides.

Changes in hemicelluloses, 1 % NaOH soluble substances and β + γ cellulose content after treatment in the temperature of 160 °C are presented in the Fig. 2. These are substances of relatively low molecular masses. Hemicelluloses content was calculated by subtracting cellulose from holocellulose content. It decreases in relation to the control sample (by 6 % for duration 10 h). Content of substances soluble in 1 % NaOH increases by almost 10 % after 10 hours treatment. There is also observable increase of β + γ cellulose content. It is probably connected with the degradation of hemicelluloses and cellulose chains of low polymerisation degree, mainly amorphous cellulose. Obtained results are similar with literature. Melcer et al. (1990) found that hemicelluloses degraded the fastest at 120 °C from among structural wood components. Sanderman and Augustin (1964) reported thet pentosans degradation varied from 8 % at 170 °C to 100 % at 350 °C. Noticeable decreases in the content of polysaccharides occur at temperatures above 150 °C (Fengel 1967).

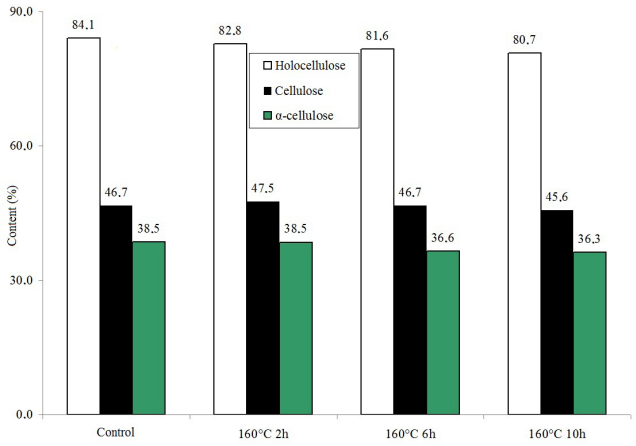


*Fig. 1: Holocellulose, cellulose and α–cellulose content in beech wood treated in 160 °C in relation to control samples*

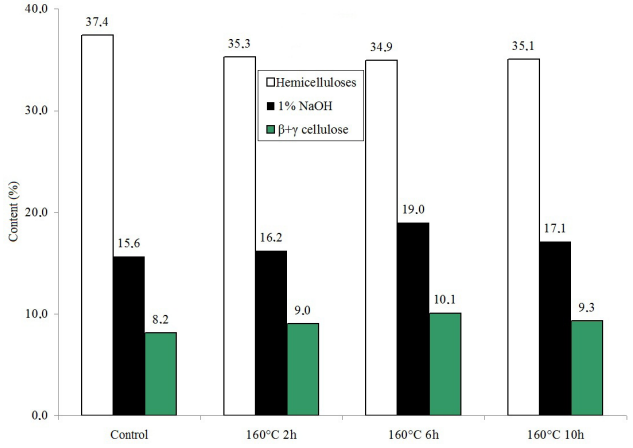


*Fig. 2: Hemicelluloses, 1 % NaOH soluble substances and β + γ cellulose content in beech wood treated in 160°C in relation to control samples*

Holocellulose content decreases significantly after treatment in the temperature of 220 °C (Fig. 3). It is 30 % lower after 2 h of treatment in relation to the control sample.

Increasing of treatment duration causes further decrease of holocellulose content, but it is not so significant (11 % for 10 h of treatment in relation to the result for duration 2 h, what means 37 % decrease in relation to the control sample).

Cellulose content after 2 h of treatment in the temperature of 220 °C is about 14 % higher than in the control sample. Subsequent treatment causes the decrease of cellulose content by about 1.5 % for 6 h duration and 9 % for 10 h duration in relation to the result obtained after 2 h of treatment.

Initial increase of cellulose content is obviously caused by the reduction of total sample mass after treatment. This increase is not observed for content values calculated in relation to the sample mass before treatment (values in brackets in the Tab. 1). Cellulose content decrease with the time of treatment in 220 °C testifies that significant changes in the cellulose structure occur. These are probably the decomposition of amorphous cellulose to furan-type compounds, among others to hydroxymethylfurfural.

These data are confirmed by the analysis of other high molecular mass compounds. The content of α-cellulose decreases with time of treatment (after 10 h of treatment it is almost 50 % lower than after 2 h of treatment, and 53 % lower than in the control sample). It testifies that in this temperature cellulose chains undergo progressive degradation.

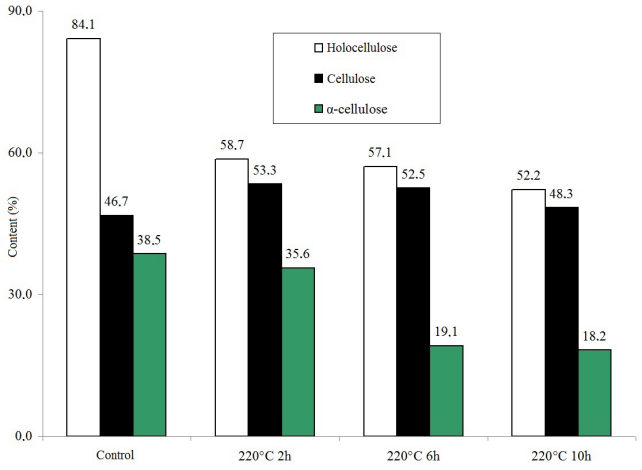


*Fig. 3: Holocellulose, cellulose and α-cellulose content in beech wood treated in 220 °C in relation to control samples*

Fig. 4 presents changes of the content of relatively low polymerisation degree carbohydrates after treatment in the temperature of 220 °C. Hemicelluloses content after treatment is about seven times lower than in the control sample and decreases with the treating time. Simultaneously 1 % NaOH soluble substances content increases (by 79 % after 2 hours of treatment, 110 % after 6 and 135 % after 10 hours) in relation to control sample. Content of β + γ cellulose increases from 8 % in control sample to about 30 % in samples treated 6 and 10 hours, what is caused by hemicelluloses and cellulose (including α-cellulose) degradation.

Higher temperature and time of modification causes the most significant changes in chemical composition. Generally, the content of holocellulose, cellulose, α-cellulose and hemicelluloses decreases. Content of 1 % NaOH soluble substances and β + γ cellulose increases. These tendencies are especially observable in case of results calculated in relation to the sample mass before treatment, when the mass loss does not influence results. These results show that the temperature of 160 °C has an observable infuence on the chemical composition of beech wood.

Hemicelluloses content decreases below 3 % at 220 °C. Mitchel et al. (1953) reported that the hemicelluloses in douglas fir decompsed at 220 °C faste that α – cellulose. They also found that, under these conditions, the hemicelluses decomposed mainly to carbon dioxide and water with the formation of very little condensation products. Aoyama (1996) reported that a large percentage of the hemicelluloses from bamboo were solubilized at temperatures between 170 and 206 °C.

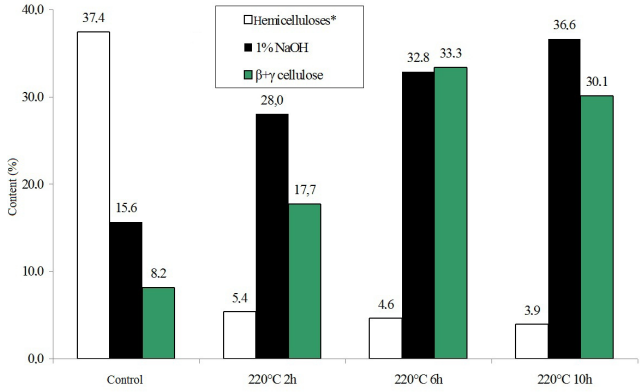


*Fig. 4: Hemicelluloses, 1 % NaOH soluble substances and β + γ cellulose content in beech wood treated in 160 °C in relation to control samples*

Results also show significant decrease of cellulose content with temperature increase. Temperature raise causes cellulose crystallinity increase (Stamm 1964, Shafizaded 1984, Fengel and Wegener 2003) which initially makes the cellulose more resistant to temperature influence. Significant decrease of the cellulose polymerisation degree takes place not before exceeding 200 °C ant it causes degradation. 1.6-anhydro-beta-D-glucopyranose is the most important proct of the cellulose decomposition. Furan-type cyclic compounds and 2-hydroxyethanal are also formed.

## CONLUSIONS

1. Heat treatment in the temperature of 160 °C does not cause changes in high molecular mass carbohydrates content (in the range of standard deviation) and causes relatively small changes in the content of low molecular carbohydrates. Hemicelluloses undergo deacylation and then degradation to monosaccharides in this temperature. Dehydratation to cyclic furan-type compounds is the following process.
2. Heat treatment in the temperature of 220 °C causes significant changes in the content of high molecular mass carbohydrates (especially α-cellulose). These changes probably refers to amorphous cellulose and consist in the decrease of polymerisation degree. In consequence, the content of β + γ cellulose increases.
3. Heat treatment in the temperature of 220 °C significantly influences also the content of low molecular mass carbohydrates (mainly hemicelluloses). These changes are analogous to processes descripted in Conclusion 1, but their rate is much higher. Almost total hemicellulose transformation into low molecular mass products takes place in these conditions.
4. The most significant changes in chemical composition of beech wood takes place after 10 h of treatment in 220 °C. Hemicelluloses and α-cellulose (mainly amorphous) undergo degradation in this temperature. As the result, content of 1 % NaOH soluble substances and β + γ cellulose increases.

## REFERENCES


1. Antczak, A., Radomski, A., Zawadzki, J., 2006: Benzene substitution in wood analysis. Annals of Warsaw Agricultural University, Forestry and Wood Technology 58: 15-19.
2. Aoyama, M., 1996: Steaming treatment of bamboo grass. II. Characterization of solibilized hemicellulose and enzymatic digestibility of water-extracted residue. Cellulose Chemistry and Technology 30: 385-393.
3. Fengel, D., Wegener, G., 2003: Structure and ultrastructure. In: Wood chemistry ultrastructure reactions. Walter de Gruyter, Berlin, Germany.
4. Fengel, D., 1967: On the changes of the wood and its components within the temperature range up to 200 ˚C . Part IV: The behaviour of cellulose in sprucewood under thermal treatment. Holz als Roh- und Werkstoff 25: 102-111.
5. Kačik, F., Solár, R., 1999: Wood analytical chemistry. Technical University in Zvolen.
6. Kollmann, F., Fengel, D., 1965: Änderungen der chemischen Zusammensetzung von Holz durch thermische Behandlung. Holz als Roh- und Werkstoff 23(12): 461-468.
7. Krutul, D., 2002: Exercises of wood chemistry and chosen problems of organic chemistry. Wydawnictwo SGGW, Warszawa.
8. Mitchell, R.L., Seaborg, R.M., Millett, M.A., 1953: Effect of heat on the properties and chemical composition of Douglas-Fir wood and its major components. J. Forest Prod. Res. Soc. 3(4): 38 pp.
9. Melcer, I., Melcerova, A., Kačik, F., Šindler, J., Vargicova, K., Sertic, V., 1990: Changes in the properties of beech wood. Drevo 59(4): 255-260.
10. Parysek, M., Zakrzewski, R., 2006: Investigations on the chemical composition of pine wood subjected to hydrothermal modification. Folia Forestalia Polonica, seria B, zeszyt 37: 23-31.
11. Rowell, R., Lange, S., McSweeny, J., Davis, M., 2002: Modification of wood fiber using steam. Wood Science and Engineering Department, Oregon State University Corvalis, USA. Pp 606-615.
12. Sandermann, W., Augustin, H., 1963: Chemical investigations on the thermal decomposition of wood. Part II: Investigations by means of the differential thermal analysis. Holz als Roh- und Werkstoff 21: 305-315.
13. Shafizadeh, F., 1984: The chemistry of solid wood. R.M. Rowel1 (ed), Advances in Chemistry Series No. 207, American Chemical Society, Washington, DC. Pp 489-530.
14 Stamm, A.J., 1956: Thermal degradation of wood and cellulose. Ind. Eng. Chem. 48(3): 413-417.
15. Stamm, A. J., 1964: Wood and cellulose science. The Ronald Press Co., New York.
16. Yildiz, S., Gezer, E.D., Yildiz, U., 2006: Mechanical and chemical behavior of spruce wood modified by heat. Building and Environment 41: 1762-1766.
17. Yildiz, S., Gumukaya, E., 2007: The effects of thermal modification on crystalline structure of cellulose in soft and hardwood. Building and Environment 42: 62–67.
18. Zawadzki, J., Grześkiewicz, M., Gawron, J., Zielenkiewicz, T., 2007: Chemical behavior of pine wood (*Pinus sylvestris* L.), modified by heat. Annals of Warsaw Agricultural University, Forestry and Wood Technology 62: 380-383.

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