

PERMANENT CHANGES TO STRUCTURE AND PROPERTIES OF BEECH AND ASH WOOD AFTER ITS HYDROTHERMAL PLASTICIZATION PART II. CHEMICAL CHANGES

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SYNOPSIS. Hydrothermal treatment of wood has a variety of impacts on wood components. This article presents chemical changes in ash and beech wood resulting from influence of autohydrolysis. Depending on the operational conditions used in the experiment, polysaccharides (mainly hemicellulose portion – primarily xylans, and amorphous portion of cellulose) are depolymerised to mono- and oligomers. Sugars in monomeric form are, as a result of hydrolysis processes, dehydrated to low-molecular carbonyl compounds (e.g. 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde). Water-soluble lignin concurrently undergoes degradation reactions. In the hydrolysates there were determined syringaldehyde and vanillin.

KEY WORDS: ash, beech, hydrothermal treatment, saccharides, carbonyl compounds

INTRODUCTION

The hydrothermal treatment of wood uses water as plasticization medium. This treatment causes various chemical changes in materials, depending on the operational conditions. For example, carbohydrates (hemicelluloses and cellulose) and water-soluble lignin undergo depolymerisation reactions. Hemicelluloses are hydrolysed to water-soluble oligomers or to monomeric sugars (autohydrolysis) (CONNER 1984, GARROTE et AL. 1999 a, b, GARROTE and PARAJÓ 2002, CARVALHEIRO et AL. 2004, PARAJÓ et AL. 2004, LAUROVÁ and KUČEROVÁ 2005).

Hydronium ions, which are generated from both water and nascent organic acids (predominantly formic and acetic acids), catalyse hemicelluloses and cellulose depolymerisation. These protons then break heterocyclic ether bonds between monomeric sugars in polymeric chains formed by hemicelluloses and cellulose. The reaction mechanism of hydrothermal degradation of cellulose is essentially the same as described above for hemicelluloses. However, the physicochemical characteristics

of cellulose (linear configuration, high polymerisation degree and crystalline structure) make its hydrolysis more difficult than in case of hemicelluloses (GARROTE et AL. 1999 a).

Hydrolysates obtained by hydrothermal treatment of lignocellulosic materials can contain low-molecular products which are generated by destruction both of lignin and monomeric sugars, e.g. carbonyl compounds, alcohols and carboxylic acids (2-furaldehyde, 5-hydroxymethyl-2-furaldehyde (HMF), methanol, acetic and levulinic acid, propionic acid, syringaldehyde, vanillin). It was found that the formation of these compounds depends on the autohydrolysis conditions (reaction time, temperature) (KAČÍK 2001, KAČÍK et AL. 2008). Acetic acid, furfural and compounds formed from lignin are inhibitors of fermentation of the hydrolysates (DELGENES et AL. 1996, PALMQVIST and HAHN-HÄGERDAL 2000 a, b).

Changes to main components of wood are significantly reflected in permanent changes to physical and mechanical properties of wood (KÚDELA 2005).

In our research we studied the influence of hydrothermal treatment (autohydrolysis) on dissolution of ash (*Fraxinus excelsior* L.) and beech (*Fagus sylvatica* L.) wood. Release of monomeric sugars, oligosaccharides, sugar- and lignin-degradation products into hydrolysates was measured.

MATERIAL AND METHODS

Testing material

The first group of test specimens (samples) 20 × 20 × 30 mm in size were prepared from ash (*Fraxinus excelsior* L.) logs, the second, with dimensions of 2 × 2 × 10 mm were prepared from beech logs (*Fagus sylvatica* L.).

Hydrothermal treatment of wood

Ash wood samples were immersed in distilled water in the stainless autoclaves under following conditions: temperature – 100, 120, 140 and 160°C, time – 1 and 2 hours. The wood (weight)/water (volume) ratio was 1:4 (g/ml).

Beech wood samples were treated with distilled water into the stainless autoclaves under following conditions: temperature 160°C, time – 30, 60, 120, 180, 240, 300 and 360 min. The wood /water ratio was 1:4 (g/ml).

Analyses of hydrolysates

At the end of the hydrothermal treatment, reaction products were cooled and solid residues were recovered by filtration.

Monosaccharides and oligosaccharides released from wood (after hydrolysis of glycoside bonds in liquor by 4% (w/w) H₂SO₄ at 100°C for 4 hours) were determined in form of aldonitrilacetates by GC method (KAČÍK and SOLÁR 2000) in the

following conditions: column – 5% PEGA Chromaton N-AW-DMCS (0.16-0.2 mm) 240 cm-0.35 cm, column temperature – 200°C, injector temperature – 260°C, detector temperature 250°C, detector – FID, carrier gas – N₂. Total amount of released carbonyl compounds was determined by gravimetric method in form of 2,4-dinitrophenylhydrazones (2,4-DNPH) (KAČÍK and SOLÁR 2000).

Carbonyl compounds such as 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, levulinic acid, formaldehyde, acetaldehyde, syringaldehyde and vanillin were identified and determined by the high-performance liquid chromatography (HPLC) after dissolution of their 2,4-dinitrophenylhydrazones in a mixture methanol-tetrahydrofuran (1:1) (KAČÍK et AL. 2006).

Detector: DAD

Column: Chromolith Performance RP-18e

Temperature: 35°C

Mobile phase: methanol (22 vol.%) : aqua (58 vol.%) : tetrahydrofuran (20 vol.%)

Mobile phase flow: 2 ml/min.

RESULTS AND DISCUSSION

Plasticization by hydrothermal treatment is the oldest and often used method for improvement of mechanical and physical properties of wood. During hydrothermal treatment of wood, various compounds are released into hydrolysates. The hydrothermal treatments of lignocellulosic materials are suitable for hemicelluloses dissolution. Carbohydrates were released into liquors mainly in form of monosaccharides (Table 1).

Table 1. Concentration of monosaccharides in hydrolysates, obtained after hydrothermal plasticization of ash wood, before (a) and after (b) hydrolysis of glycoside bonds by 4% H₂SO₄ (sum of mono- and oligosaccharides)

Temperature [°C]	Time [h]	Concentration [g·dm ⁻³]	
		monosaccharides (a)	monosaccharides (b)
100	1	0.235	0.329
	2	0.374	0.506
120	1	0.423	0.507
	2	0.730	0.892
140	1	0.562	0.631
	2	1.153	1.367
160	1	1.816	3.361
	2	4.231	5.987

Increasing amounts of sugars in hydrolysates resulted in ash wood weight loss, and in enhanced wood shrinkage (KÚDELA 2009). The resulting liquors contained a mixture of monosaccharides D-xylose, L-arabinose, D-glucose, D-mannose, D-

-galactose, L-rhamnose and D-ribose, which are typical for hardwoods. Their total concentration in hydrolysates increased with increasing temperature and hydrolysis time. Monosaccharide D-glucose, which was created from glucomannans and amorphous portion of cellulose, was the main monomeric sugar product in the autohydrolysis over the 100-140°C temperature range. The concentration of D-xylose, which was created by depolymerizations of xylans, was smaller than concentration of D-glucose. Its concentration increased steadily with reaction time. However, at the temperature of 160°C, water hydrolysis provided mostly soluble xylan. Hydrolysis of xylans was dominant (Table 2).

Table 2. Ratio of concentrations (XYL/GLC) in hydrolysates

Temperature [°C]	XYL/GLC		XYL*/GLC*	
	1 hour	2 hours	1 hour	2 hours
100	0.005	0.003	0.017	0.014
120	0.005	0.001	0.013	0.011
140	0.002	0.045	0.059	0.319
160	0.289	1.323	1.842	2.853

*After hydrolysis of glycoside bonds by 4% H₂SO₄.

The results show that the conditions – temperature 160°C and time 2 hours, are optimal for obtaining maximum yields of monosaccharides and total amount of released saccharides (mono- and oligosaccharides) from ash wood, respectively (Tables 1 and 2). Besides hemicellulose-derived sugars, the hydrolysates contained sugar- and lignin- dehydration products, too. It was found that the formation rate of these compounds depends on the autohydrolysis conditions. The highest mass yields of 2,4-DNPH of carbonyl compounds were observed at the temperature of 160°C and the time of the hydrolysis of 2 hours (Table 3).

Table 3. Mass yields of 2,4-DNPH of carbonyl compounds

Temperature [°C]	Mass yields [g]	
	1 hour	2 hours
100	0.0053	0.0074
120	0.0077	0.0110
140	0.0147	0.0312
160	0.0421	0.0815

Carbonyl compounds 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, levulinic acid, acetaldehyde, formaldehyde, syringaldehyde and vanillin were detected by chromatographic methods HPLC in the form 2,4-DNPH (Table 4).

Concentration of furfural, a pentose degradation product, increased with reactions temperature and time. This fact corresponded to the maximal production of xylo-oligosaccharides. The 5-hydroxymethyl-2-furaldehyde formed by dehydration reactions of hexoses was present in lower amounts than furfural. Levulinic acid is a weak acid, and it is formed when HMF is broken down by degradation (dehydration) reactions. Generation of this substance and both acetaldehyde and

Table 4. Concentration of carbonyl compounds in hydrolysates

Time/temperature [hour/°C]	Concentration of carbonyl compounds [mg·dm ⁻³]						
	2-furaldehde	5-hydroxymethyl- 2-furaldehde	acetaldehde	formaldehde	levulinic acid	syringaldehde	vanillin
1/100	4	1	1	1	2	2	6
1/120	7	3	1	2	3	4	12
1/140	26	2	6	6	4	22	48
1/160	121	42	39	25	36	335	44
2/120	6	3	1	2	3	3	11
2/140	18	5	5	4	7	11	26
2/140	52	10	18	13	6	46	126
2/160	304	159	150	17	53	3 341	2 009

formaldehde was relatively low. In aqueous media, lignin can undergo degradation reactions depending on the operational conditions. Table 3 shows that the yields of both products syringaldehde and vanillin increased at the reaction temperature 100 to 140°C slowly. Their maximal production found was obtained at 160°C almost.

For comparison, in the hydrolysates obtained after beech hydrothermal treatment at a temperature of 160 °C, there were identified and determined the same carbonyl compounds. The portion of these substances increasing with increased temperature and time of hydrolysis (Table 5).

Table 5. Concentration of carbonyl compounds in hydrolysates

Time [min]	Concentration of carbonyl compounds [mg·dm ⁻³]						
	2-furaldehde	5-hydroxymethyl- 2-furaldehde	acetaldehde	formaldehde	levulinic acid	syringaldehde	vanillin
30	1	1	–	1	–	3	4
60	5	6	1	1	4	7	15
120	341	9	4	3	6	6	24
180	1 154	80	37	8	7	48	130
240	1 425	86	59	10	8	57	166
300	1 448	72	60	11	9	40	117
360	1 699	72	89	12	9	60	103

In the first phase of plasticization (30-60 min) mainly the compounds from lignin macromolecule are released into the solution. In the next phases, substantial degradation of carbohydrates takes place and 2-furaldehyde is formed predominantly. Concentration of HMF decreased after 300 min of treatment because it was decomposed into low-molecular products. These toxic products are removed, e.g. during pretreatment of lignocellulosic materials, from hydrolysates by various detoxification methods (JÖNSSON et AL. 1998, LARSSON et AL. 1999, JÖNSSON et AL. 2001, CARVALHO et AL. 2006).

CONCLUSIONS

Hydrothermal treatment caused effect on chemical changes in both ash (*Fraxinus excelsior* L.) and beech (*Fagus sylvatica* L.) wood.

Ash wood (*Fraxinus excelsior* L.) subjected to hydrothermal treatment at temperatures from 100 to 160°C is liable to chemical changes. Amorphous portion of cellulose is released into the solution as D-glucose over the whole temperature range. Degradation of the main portion of hemicelluloses (xylans) starts predominantly at a temperature of 160°C.

With ongoing plasticization, monosaccharides and lignin in ash wood are subjected to further decomposition. The resulting substances such as 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, levulinic acid, formaldehyde, acetaldehyde, syringaldehyde and vanillin were quantitatively determined in the hydrolysates. Their content increased gradually with increasing temperature.

Beech wood (*Fagus sylvatica* L.) under mild conditions of water treatment (160°C) degraded into low-molecular products, which were released into hydrolysates. The concentration of 2-furaldehyde in hydrolysates was prevailing and increased with increasing treatment time. Carbonyl compound 5-hydroxymethyl-2-furaldehyde, after 300 min of treatment, decomposed into low-molecular products analogous to those obtained in case of beech wood.

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