

VODNÁ PREDHYROLÝZA DREVA VRBY BIELEJ (*Salix alba* L.)

WATER PREHYDROLYSIS OF WILLOW WOOD (*Salix alba* L.)

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ABSTRACT

A pretreatment of various renewable lignocellulosic sources is very important step at production of pulp, bioethanol and other technical important chemicals. In this study, there was investigated formation of saccharides, as well as both carbonyl and volatile products, during water prehydrolysis of willow wood at 160–200 °C. The maximal sugars yield was found at the mild conditions of hydrolysis (160 °C, 240 min). Decomposition of monosaccharides into acetic acid and furfural was found in a large extent at higher temperatures.

Key words: willow, hydrolysis, saccharides, carbonyl compounds, gas chromatography

ÚVOD

A pretreatment of lignocellulosic biomass at the production of pulp, bioethanol and other technical important chemicals, has significant influence on yields of these products. The various physical, physico-chemical and biological processes of pretreatment are using for this purpose at present [1, 2]. The water prehydrolysis of biomass (by saturated water steam and hot high-pressure water) can be considered as an environmentally friendly technology, where it is not necessary to add some of chemicals [3].

The water pretreatments of lignocellulosic materials have got a different effect on their main components, depending on the operational conditions. The pretreatment main goal is to remove lignin and hemicelluloses, to decrease cellulose crystallinity and to increase porosity of the lignocellulosic material [1].

Extractives, hemicelluloses and water-soluble lignin are released from wood in the temperature range 150–230 °C. The cellulose crystalline fraction depolymerises at the higher temperatures (210–280 °C) [4, 5].

Hydronium ions, which are generated from both water and nascent organic acids (predominantly formic and acetic acids), catalyse the hemicellulose and cellulose depolymerization. However, the physicochemical characteristics of cellulose (linear configuration, high polymerization degree and crystalline structure) make hydrolyzation more difficult than hemicelluloses [4].

The hemicelluloses are hydrolyzed to water-soluble oligomers or to monomeric sugars [3, 4, 6, 7, 8, 9, 10, 11, 12].

Prehydrolysates obtained by hydrothermal pretreatment of lignocellulosic materials 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), usually. It was found, that the formation of these compounds

depends on the autohydrolysis conditions (reaction time, temperature) [12]. An acetic acid, furfural and compounds formed from lignin are inhibitors of fermentation of the hydrolysates [13, 14, 15].

Changes to main components of wood are significantly reflected in permanent changes to physical and mechanical properties of wood [16, 17].

The aim of this work was the study of the hydrothermal pretreatment influence on dissolution of willow (*Salix alba* L.) wood. The effects of temperature and reaction time on the concentration of released monomeric sugars, oligosaccharides, sugar- and lignin-degradation products into hydrolysates were assessed.

EXPERIMENTAL

Material

Wood samples preparation

The samples from the trunk wood of 33 years old willow (*Salix alba* L.) were chipped to the dimensions $2 \times 2 \times 10$ mm.

Wood analyses

The amount of extractives soluble in the mixture toluene-ethanol (1:2) was determined in accordance with ASTM Standard D 1107-967 [18], the amount of cellulose by Seifert method [19] and the amount of holocellulose by Wise method [20]. Lignin amount was determined in accordance with ASTM Standard D 1106-9610 [21].

Hydrolysis

Wood chips (2 g) were put into the stainless autoclaves with internal volume 12 cm^3 and they were refilled by distilled water. The solid/liquor ratio was 1:4.

The prehydrolysis was performed in the thermostat at the temperatures 160, 180 and 200 °C. The time of treatment was 30, 60, 120 and 240 min. Then the autoclave was cooled into the temperature 20 °C and the hydrolysate was filtrated.

Hydrolysates analyses

pH value

Hydrolysates pH values were determined by the potentiometric method with pH meter inoLab pH 720 (WTW GmbH).

Saccharides

Monosaccharides and oligosaccharides released from wood (after hydrolysis of glycoside bonds in liquor by 4 % (w/w) H_2SO_4 at 100 °C for 4 hours) were determined in the form of aldonitrilacetates by GC method [22] in the following conditions: column – 5 % PEGA Chromaton N-AW-DMCS (0.16-0.2 mm) $240 \text{ cm} \times 0.35 \text{ cm}$, column temperature – 200 °C, injector temperature – 260 °C, detector temperature 250 °C, detector – FID, carrier gas – N_2 .

Carbonyl compounds

Total amount of released carbonyl compounds was determined by gravimetric method in form of 2,4-dinitrophenylhydrazones (2,4-DNPH) [22].

Volatile compounds

The volatile compounds in the hydrolysates (methanol, acetic acid, propionic acid, 2-furaldehyde) were determined by the method of GC [23] at the following conditions: column – Chromosorb 102 (80–100 mesh) 120 cm × 0.35 cm, column temperature – 195 °C, injector temperature – 250 °C, detector temperature – 250 °C, detector – FID, carrier gas – N₂.

RESULTS AND DISCUSSION

The average composition of the 33 years old willow used in this study as raw material was following (dry weight basic): 79.90 % of holocellulose, 44.00 % of cellulose, 20.12 % of lignin and 5.95 % of extractives.

During the water pretreatment of willow wood, various acid compounds were released. The acetic acid with other nascent acids (mostly formic, uronic) influence the hydrolysates acidity, reaction media pH values (Tab. 1) and hydrolysis processes in wood and in liquors.

Table 1: Hydrolysates pH value

Temperature (°C)	Time (min)			
	30	60	120	240
160	4.65	3.78	3.58	3.44
180	3.95	3.49	3.21	3.12
200	3.63	3.11	3.09	3.10

The increase of the hydrolysates acidity causes next degradation of wood matter and the glycosidic bonds in the polysaccharides are cleaved. The hemicelluloses are hydrolysed to soluble sugars. 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.

At the temperature 160 °C the monosaccharide amount in the hydrolysates increased during the total time range (Fig. 1). At the higher temperatures (180 °C) the maximum yield of monosaccharides was determined during 120 min of the hydrolysis. The highest concentration of monosaccharides in hydrolysates was observed at the temperature 200 °C and the time of the hydrolysis 60 min. It is in accordance with 2-furaldehyde amount increase in the hydrolysates (tab. 5).

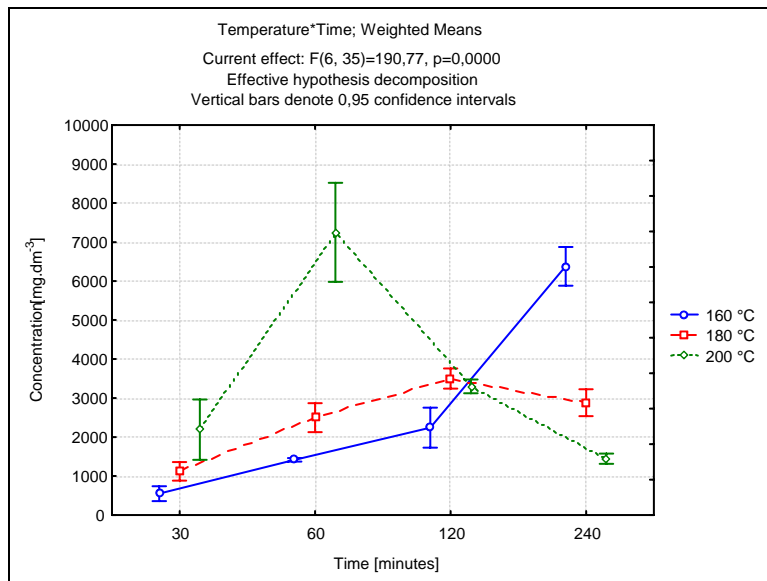


Fig. 1 Concentration of monosaccharides in hydrolysates (mg.dm⁻³)

The different trend we can see at the determination of total sugar amount (sum of the mono- and oligosaccharides) in hydrolysates determined after the hydrolysis of glycoside bonds by 4 % sulphuric acid (Fig. 2).

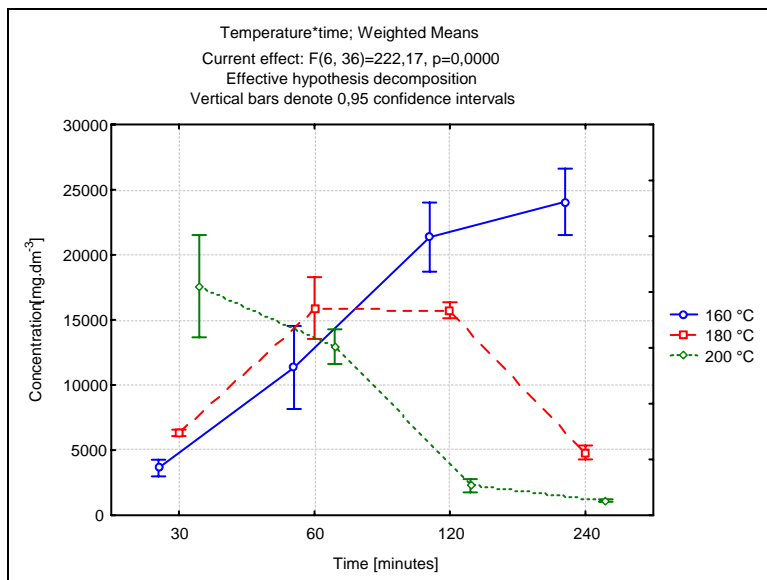


Fig. 2 Concentration of monosaccharides in hydrolysates after hydrolysis of glycoside bonds by 4 % H₂SO₄ (sum of the mono- and oligosaccharides) (mg.dm⁻³)

The biggest yield of the released sugars from wood was found at the temperature 160 °C and at the time of the hydrolysis 240 min. These results are in good agreement with values found by prehydrolysis of beech [24].

Depolymerisation of oligosaccharides and low-molecular polysaccharides to monosaccharides takes place at the higher temperatures (180 and 200 °C), predominantly (Tab 2).

Tab. 2 Total content of saccharides (TS) to monosaccharides (MS) ratio

Temperature (°C)	Time (min)			
	30	60	120	240
160	6.6	8.0	9.5	3.8
180	5.7	6.4	4.5	1.7
200	8.0	1.8	0.7	0.8

This fact is in good agreement with results obtained at prehydrolysis of aspen and alder [11, 12].

For hardwoods, in which the major hemicellulose is 4-*O*-methylglucuronoxylan, the resulting prehydrolysates contain large quantities of xylose and xylooligomers. The D-xylose, D-cellulose, L-arabinose and D-galactose were present in greater amounts. The concentration of D-xylose was smaller than concentration of D-glucose in whole temperature range (Tab. 3).

Tab. 3 Ratio of concentrations XYL* /GLC* in hydrolysates

Temperature (°C)	Time (min)			
	30	60	120	240
160	0.06	0.30	0.60	0.63
180	0.13	0.49	0.58	0.05
200	0.48	0.63	0.31	0.18

* After hydrolysis of glycosidic bonds by 4 % H₂SO₄.

However, under more drastic conditions secondary reactions occur which result in the formation of furfural, hydroxymethyl furfural and their precursors by the dehydration of pentose and hexose sugars. 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 200 °C (Tab. 4).

Tab. 4 Mass yields of 2,4-DNPH of carbonyl compounds (g.dm⁻³)

Temperature (°C)	Time (min)			
	30	60	120	240
160	2.20	5.78	9.85	15.45
180	4.75	8.40	16.85	17.23
200	8.93	12.80	18.43	18.18

The amount of volatile substances in the prehydrolysates, increased with reactions temperature and time in most cases (tab. 5). Acetic acid was dominant. This fact is in good accord with the production of sugars and their decomposition products (e.g. 2-furaldehyde).

Tab. 5 Concentration of volatile compounds in prehydrolysates (g.dm⁻³)

Temperature (°C)	Time (min)	Compounds			
		Methanol	Acetic acid	Propionic acid	2-Furaldehyde
160	30	0.16	0.33	0.10	0.03
	60	0.19	0.70	0.18	0.07
	120	0.40	2.42	0.43	0.32
	240	0.43	5.90	0.72	1.45
180	30	0.19	0.54	0.14	0.12
	60	0.49	4.27	0.62	0.72
	120	0.61	7.26	0.80	4.71
	240	0.69	7.89	0.66	5.94
200	30	0.32	1.87	0.55	0.36
	60	0.68	7.38	0.95	5.34
	120	0.74	8.59	0.81	4.81
	240	0.75	7.66	0.64	2.15

CONCLUSIONS

At the mild conditions of willow wood water prehydrolysis the maximal oligosaccharides release was achieved at the 160 °C (240 min). This fact is in a good agreement with high content effective inhibitor of hydrolysis processes – furfural, presented in liquors at higher temperatures (180, 200 °C). The presence of oligosaccharides and low-molecular polysaccharides in hydrolysates was approximately four times higher than monosaccharides.

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SÚHRN

Príspevok sa zaoberá vodnou predhydrolyzou vrby bielej (*Salix alba* L.) v teplotnom rozmedzí 160 až 200 °C. V hydrolyzátoch boli metódou plynovej chromatografie (GC) identifikované a kvantifikované uvoľnené monosacharidy, oligosacharidy a nízkomolekulové fragmenty polysacharidov z dreva, ako aj prchavé produkty autohydrolyzy (kyselina octová a propionová, 2-furaldehyd a metanol).

Maximálne zmeny v zložení polysacharidového podielu dreva nastali pri teplote 160 °C po 240 minútach vodnej predhydrolyzy. Do roztoku sa uvoľňoval predovšetkým hemicelulózový podiel spolu s nascentnými kyselinami, ktoré katalyzovali depolymerizačné reakcie pentózanov a hexózanov a dehydratačné reakcie monosacharidov v dreve a v hydrolyzátoch. Zvýšením reakčnej teploty na 180, resp. 200 °C, prevládali deštruktívne reakcie monosacharidov za vzniku najmä mimoriadne reaktívneho 2-furaldehydu, ktorého koncentrácia v hydrolyzátoch so zvyšujúcou sa teplotou a predĺžovaním času predúpravy narastala.

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