

## Hot-water prehydrolysis of willow wood

MARTA LAUROVÁ

Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology, Technical University in Zvolen, Slovak Republic

**Abstract:** A pretreatment of various renewable lignocellulosic sources is very important step when producing pulp, bioethanol and other technically important chemicals. Hot water prehydrolysis of willow wood chips (*Salix alba* L., 15 years old) at the temperature of 180 °C in the time range of 30-240 min has been carried out. The maximum sugar concentration was found in the solution at 60 min. Concentration of acetic acid and 2-furaldehyde in hydrolysates increased at first, but after 120 min decreased. Their concentrations were approximately twelve times higher than concentrations of methanol and propionic acid.

*Keywords:* willow, hydrothermal pretreatment, carbohydrates, 2-furaldehyde, bioethanol

### INTRODUCTION

Lignocellulosics biomass is the most abundant natural renewable resource and it is one of the preferred choices for the production of bioethanol, but as a substrate for a bioethanol production it has the physical and chemical barriers in its complex structure, which resists hydrolysis (crystalline portion of cellulose, degree of polymerization cellulose, lignin content and its association with cellulose, in surface area). It is required to cellulose biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars (Mosier et al. 2005, Sun, Cheng 2002).

The pretreatment is the first step in the conversion of biomass to ethanol. The aim of hydrolysis processes at lignocellulosics pretreatment is predominant removing both hemicelluloses and partially lignin portions and increasing the porosity of lignocellulosic materials. Many different pretreatments have been proposed and developed. Physical, physico-chemical, and biological processes have been used. A pretreatment combines any two or all of these pretreatments (Kumar et al. 2009, Sun, Cheng 2002).

Prehydrolysis can be realized in water (autohydrolysis) or by mineral acids (acid hydrolysis). One of the most common physicochemical pretreatment methods is liquid hot water (LHW) treatment (autohydrolysis). The LHW process uses compressed, hot liquid water (at pressure above the saturation point) to hydrolyze the hemicellulose. Xylose recovery is high (88-98%), and no acids or chemical catalyst are needed in this process, which makes it attractive economically and environmentally. However, the development of the LHW process is still in the laboratory stage (Laxman, Lachke 2009).

Hot-water pretreatment is an important tool for practical cellulose conversion processes, and it is the theme of this paper.

### MATERIAL AND METHODS

#### *Wood samples*

The specimens (chips) sizes 2×2×10 mm were made from trunk wood from 15-year-old willow tree (*Salix alba* L.).

#### *Analysis of wood*

The amount of extractives soluble in the mixture of toluene-ethanol (1:2) was determined in accordance with ASTM Standard D 1107-96 (1998), the amount of cellulose by Seifert method (Seifert 1960) and the amount of holocellulose by Wise method (Wise et al. 1946). Lignin amount was determined in accordance with ASTM Standard D 1106-96 (1998).

### *Hydrothermal treatment of wood*

Willow wood chips samples (2 g) were treated with distilled water into the stainless autoclaves under these conditions: temperature – 180 °C, time – 30, 60, 120 and 240 min. The wood /water ratio was 1:4 (g/ml).

### *Analyses of hydrolysates*

At the end of the treatments, reaction products were cool and the solid residues were recovered by filtration. The samples of liquors were used for direct GC determination of volatile compounds (methanol, acetic acid, propionic acid, 2-furaldehyde) under 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 – N<sub>2</sub> (Kačík, Výbohová, Kačíková 2007).

Monosaccharides and oligosaccharides released from wood (after hydrolysis of glycoside bonds in liquor by 4 % (w/w) of H<sub>2</sub>SO<sub>4</sub> at 100 °C for 4 hours) were determined in the form of aldonitrilacetates by GC method on Fisons 8310 DPFC GC (Kačík, Kačíková 2009).

Prehydrolysates pH values were determined by a potentiometric method with pH meter (inoLab pH 720, WTW GmbH).

## RESULTS AND DISCUSSION

The average composition of 15-year-old willow wood used in this study as a raw material was following (dry weight basic): 73.15 % of holocellulose, 40.45 % of cellulose, 20.07 % of lignin and 6.49 % 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.

**Tab. 1 Hydrolysates pH value at 180 °C**

t (min)	30	60	120	240
pH	3,38	3,26	3,03	3,02

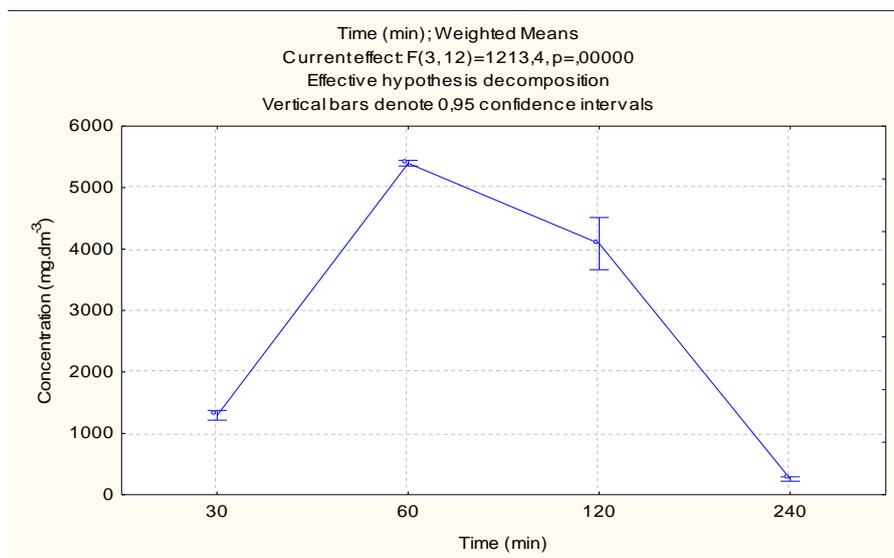
The increase of the hydrolysates acidity causes next degradation of wood matter and the glycosidic bonds in the polysaccharides are cleaved. The hemicelluloses are hydrolysed to soluble sugars (Laurová, Kačík 2009a,b, Laurová, Kačík, Sivák 2009). The resulting liquors contained a mixture of monosaccharides and oligosaccharides of D-xylose, L-arabinose, D-glucose, D-mannose, D-galactose and L-rhamnose, which are typical for hardwoods.

The highest yield of the released sugars from wood was found at the time of the hydrolysis in 60 min. Figure 1 and 2 illustrate the time of maximum yields of monosaccharides and total amount of released saccharides (mono- and oligosaccharides) in the prehydrolysates. At the biggest yields of the saccharides (60 min) approximately one quarter of the carbohydrate amount is present in the form of monosaccharides and other residue in the form of oligosaccharides or low molecular weight polysaccharides.

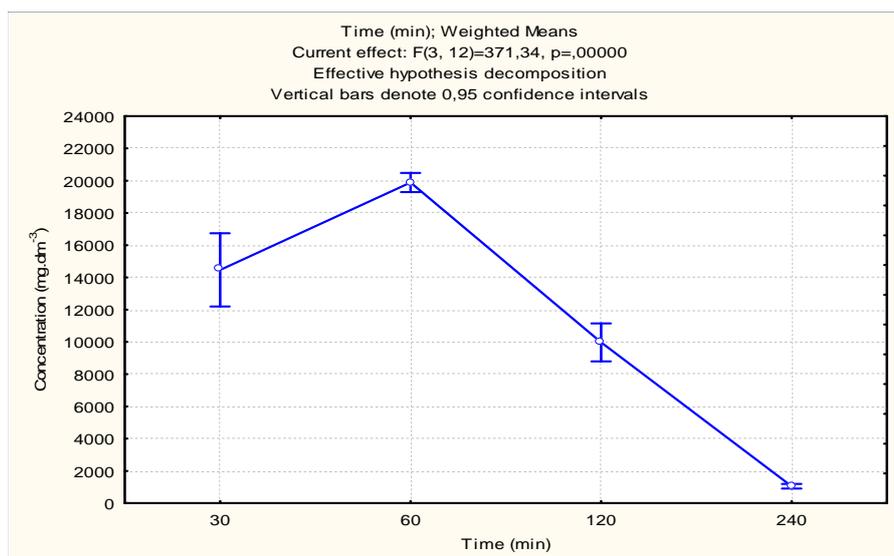
For hardwoods, in which the major hemicellulose is 4-*O*-methylglucuronoxylan, the resulting prehydrolysates contain large quantities of xylose and xylooligomers (Conner 1984). Water prehydrolysis provided mostly soluble both xyloligosaccharides and low molecular weight polysaccharides of D-glucose, too (Fig. 3). The portion of these substances into prehydrolysates increased to 60 min and then their amount decreased.

Acetic acid and other decomposition products (2-furaldehyde, methanol, propionic acid) were determined in prehydrolysates in form of volatile products. It was found that the formation rate of these compounds depends on the autohydrolysis conditions (temperature

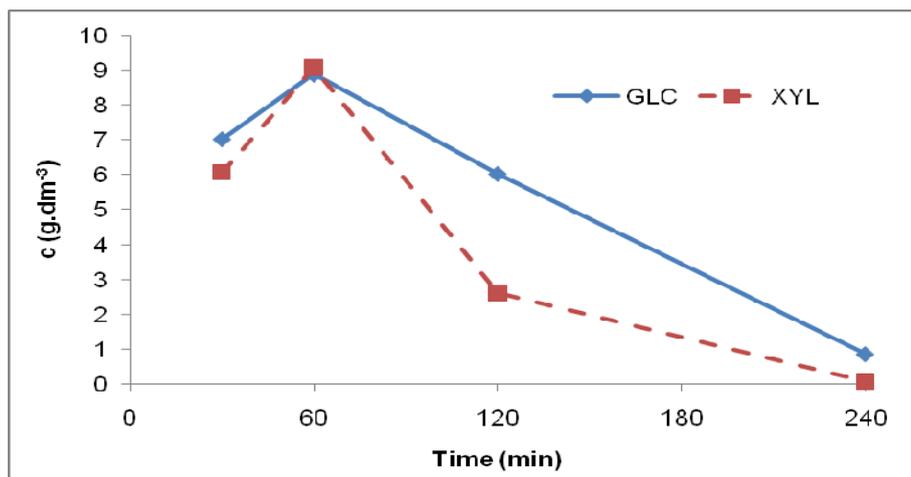
and reaction time) in agreement with previous reports (Kačík, Výbohová, Kačíková 2007, Laurová, Kačík 2009a,b, Laurová, Kačík, Sivák 2009).



**Fig. 1** Influence of reaction time on the concentrations of released monosaccharides from willow wood.

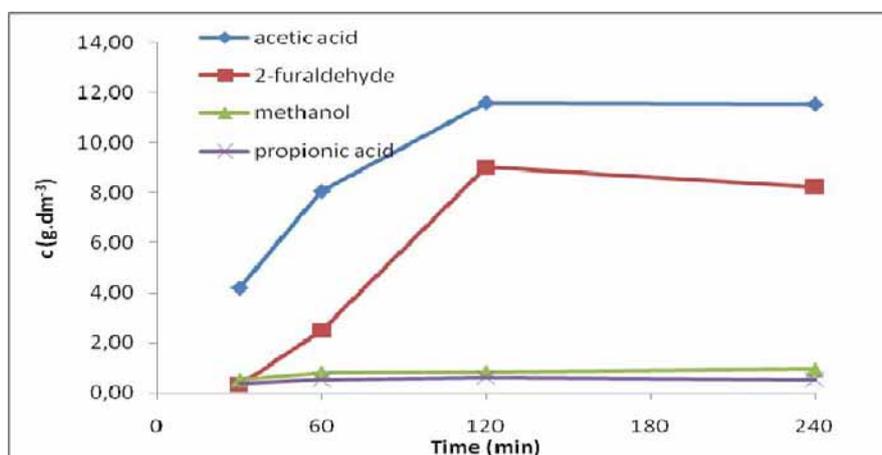


**Fig. 2** Influence of reaction time on the concentration of released mono- and oligosaccharides from willow wood.



**Fig.3** Concentrations of mono- and oligosaccharides of D-xylose and D-glucose in prehydrolysates.

Acetic acid and 2-furaldehyde (pentose dehydration product) were found to be ones of the main volatile products of willow hydrothermal pre-treatment (Fig. 4).



**Fig. 4** Concentration of volatile compounds in prehydrolysates

In hardwoods there are 3-5 % of acetyl groups ( $\text{CH}_3\text{CO}-$ ), they give acetic acid at the hydrolysis. The acetic acid amount increases mainly at the first 120 min of the hydrolysis. 2-Furaldehyde arises by pentose dehydration and it can be isolated as a valuable product at the certain conditions. Its concentration increased to 120 min and then decreased due to the condensation reactions.

## CONCLUSIONS

The maximal amount of oligosaccharides released from willow wood under the mild conditions of hot-water prehydrolysis was achieved at 180 °C in the time of 60 min. The presence of oligosaccharides and low-molecular polysaccharides in hydrolysates was approximately four times higher than monosaccharides. Concentrations of the acetic acid and 2-furaldehyde as the main volatile products increased at the first 120 min of the prehydrolysis.

## REFERENCES

1. Laxman, Ryali Seeta, Lachke, Anil H. 2009. Bioethanol from Lignocellulosic Biomass: Part I Pretreatment of the Substrates. In: Handbook of Plant - based Biofuels. Ed. By Willow ok Pandey, CRC Press. p. 121-139.
2. Conner, A. H. 1984. Kinetic modelling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood and fiber science, vol. 16 (2), pp. 268-277.
3. Kačík, F., Výbohá, E., Kačíková, D. 2007. Volatile compounds arising at hydrolysis of birch wood. In *Acta Facultatis xylologiae Zvolen*, Zvolen: Technická univerzita vo Zvolene, vol. 49 (2), pp. 39-46.
4. Kačík, F., Kačíková, D. 2009. Determination of carbohydrates in lignocellulosics by gas chromatography of aldonitrilacetates. In: *Folia Forestalia Polonica*, vol. 40, series B - Wood Science, pp. 61-66.
5. Kumar, P., Barret, D. M., Delwiche M. J., Stroeve, P. 2009. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. In: *Ind. Eng. Chem. Res.*, vol. 48, pp. 3713-3729
6. Laurová, M., Kačík, F. 2009a. Permanent changes to structure and properties of beech and willow wood after hydrothermal plasticization. Part II. chemical changes. In: *Folia Forestalia Polonica*, vol. 40, series B - Wood Science, pp. 15-22.
7. Laurová, M. Kačík, F. 2009b. Arising of saccharides and volatile compounds at poplar wood (*Populus tremula* L.) prehydrolysis. In: *Acta Facultatis Forestalis*, vol. 51 (3), pp. 153-161.
8. Laurová, M. Kačík, F., Sivák, J.: Water prehydrolysis of willow wood (*Salix alba* L.). In: *Acta Facultatis Xylologiae*, vol. 51 (1), pp. 19-26.
9. Mosier, N., Wyman Ch., Dalec, B., Elander, R., Lee, Y.Y., Holtzapf, M., Ladisch, M. 2005. Features of promising technologies for pretreatment of lignocellulosic biomass In: *Bioresource Technology*, vol. 96 (6), pp. 673-686.
10. Sun, Y., Cheng, J. 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. In: *Bioresource Technology*, Vol. 83 (1), pp. 1-11.
11. Seifert V. K. 1960. Zur Frage der Cellulose-Schnellbestimmung nach der Acetylaceton- Methode. In: *Das Papier*, vol. 14, pp. 104-106.
12. Wise L. E., Murphy M., D'Addieco A. A. 1946. Chlorite holocellulose, its fractionation and bearing on summative wood analysis and on studies on the hemicelluloses. In: *Paper Trade Journal*, Vol. 122 (35), pp. 35-34.
13. ASTM Standard D 1106-96: Standard test method for acid insoluble lignin in wood (1998).
14. ASTM Standard D 1107-96: Standard test method for ethanol toluene solubility of wood (1998).

**Acknowledgement:** This work has been supported by the Slovak Scientific Grant Agency under the contract No. VEGA 1/0490/09.

**Streszczenie:** Wstępna hydroliza drewna wierzb w gorącej wodzie. Drewno wierzb (*Salix Alba* L., 15 lat) traktowano w temperaturze 180°C w czasie 30-240 min. Określono zawartość wybranych substancji w zależności od temperatur oraz czasów.

Corresponding author:

assoc. prof. Marta Laurová  
Department of Chemistry and Chemical Technologies, Faculty of Wood Sciences and Technology,  
Technical University in Zvolen, T.G. Masaryka 24, 960 53 Zvolen, Slovak Republic.  
e-mail: laurova@vsld.tuzvo.sk, www.tuzvo.sk