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Partial hydrolysis of ash wood by hot-water pretreatment

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Abstract: *Partial hydrolysis of ash wood by hot water pretreatment.* Hot water pretreatment of ash wood (*Fraxinus excelsior* L., 39 years old) chips at the temperatures 160, 180 and 200 °C in the time range within 30-240 min has been carried out. Released nascent organic acids (e.g. formic, acetic and levullinic) moved pH values of solutions into the acidic ranges from 4.89 (160 °C; 30 min) to 3.00 (200 °C; 60 min). The polysaccharide portion of ash wood was released into the solutions in both monosaccharide and in the higher measure as low-molecular fragments of polysaccharides (oligomers). There were determined all sugars (pentoses and hexoses) in hydrolysates which are typical for hardwood (D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose and L-rhamnose) and volatile substances (acetic acid, 2-furaldehyde, methanol and propionic acid). Maximum concentration of sugars in both monomeric and oligomeric forms altogether was present in hydrolysates at mild condition (160 °C, 120 min). Acetic acid and 2-furaldehyde were predominant in solutions from volatile compounds.

Keywords: ash, hydrothermal pretreatment, hydrolysate, polysaccharides, 2-furaldehyde

INTRODUCTION

Hydrolysis processes are important part of technological processes for production of cellulosic bioethanol. They are used for both pretreatment of lignocellulosics biomass (hydrolysis of the hemicelluloses) and creation of D-glucose from cellulose. Hydrolysis steps can be performed by dilute acids, concentrated acid or enzymatically (Gnansounoun Pandey, 2009; Laxman, Lachke 2009).

Prehydrolysis is used in preference to remove hemicelluloses prior to the production of kraft-dissolving pulps, especially those produced from hardwoods, too. Recent efforts were directed toward the production of liquid fuels or chemical from hardwoods for recovery of xylose and its oligomers (Garrote, Domínguez, Parajó 1999a, Sun, Cheng 2002).

The hemicelluloses are hydrolyzed to water-soluble oligomers or to individual sugars by acid hydrolysis (Garrote, Domínguez, Parajó 1999a,b).

The hydrothermal pretreatment uses water as a hydrolysis medium (autohydrolysis). Hydronium ions which are generated from both water and nascent organic acids (predominantly formic and acetic acids) catalyse the hemicellulose depolymerization to monomeric sugars and oligosaccharides. Those protons then break the heterocyclic ether bonds between the sugar monomers in the polymeric chains formed by the hemicelulluloses and the cellulose (Garrote et al. 1999a).

Rapid and efficient fermentation of the hydrolysates is limited because of acid pretreatment (autohydrolysis) forms inhibitors such as acetic acid, furfural and compounds formed from lignin (Palmqvist, Hahn-Hägerdal 2000a, b,).

In the paper there is studied the influence of hydrothermal treatment (autohydrolysis) on dissolution of ash wood (*Fraxinus excelsior* L.).

MATERIAL AND METHODS

Wood samples

The specimens (chips) sizes 2×2×10 mm were prepared from the trunk wood of 39-year-old ash tree (*Fraxinus excelsior* L.).

Analysis of wood

The amount of extractives soluble in the mixture 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

Ash wood chips samples (2 g) were treated with distilled water into the stainless autoclaves under these conditions: temperature – 160, 180 and 200 °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_2 (Kačík, Výbohová, Kačíková 2007).

Monosaccharides and oligosaccharides released from wood (after hydrolysis of glycoside bonds in liquor by 4 % (w/w) of H_2SO_4 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

Wood is primarily composed of cellulose, hemicelluloses, and lignin. Used ash wood chemical composition was: 5.28 % extractives, 77.85 % holocellulose, 38.86 % cellulose and 17.42 % lignin.

Under hot water conditions, the hemicelluloses and cellulose (primarily amorphous portion) are hydrolyzed, producing short chain sugar polymers, sugars, and sugar breakdown products.

The acetic acid with other so-called nascent acids (mostly formic, uronic and others) influence the hydrolysates acidity, reaction media pH values (Tab. 1) and hydrolysis processes in wood and in liquors, respectively.

The above mentioned acids release protons that break the heterocyclic ether bonds between the sugar monomers in the polymeric chains formed by the hemicelluloses and the cellulose. A quantitative hydrolysis of the hemicelluloses can be performed almost without damage to cellulose because the bonds in hemicelluloses are weaker than in cellulose (Bobleter 1994).

Tab. 1 Prehydrolysates pH value

Temperature (°C)	Time (min)	pH
160	30	4.89
	60	3.55
	120	3.33
	240	3.21
180	30	3.32
	60	3.08
	120	3.03
	240	3.05
200	30	3.17
	60	3.00
	120	3.04
	240	3.07

The hydrothermal treatments of lignocellulosics are suitable for hemicelluloses dissolution. The resulting liquors from autohydrolysis of aspen wood contained a mixture of monomeric sugars (D-xylose, L-arabinose, D-glucose, D-mannose, D-galactose and L-rhamnose), and sugar oligomers.

Water prehydrolysis provided mostly soluble xylan oligosaccharides. The portion of these substances decreased with increased temperature and time of prehydrolysis.

Figures 1 and 2 illustrate the times and temperatures to maximum yields of monosaccharides and total amount of released saccharides (mono- and oligosaccharides) in the prehydrolysates.

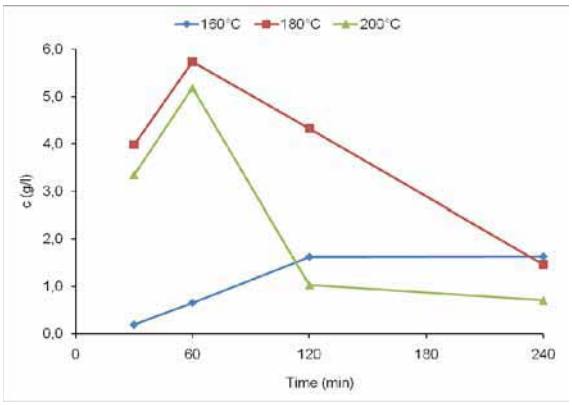


Fig. 1 Influence of temperature and reaction time on the concentrations of released monosaccharides from ash wood.

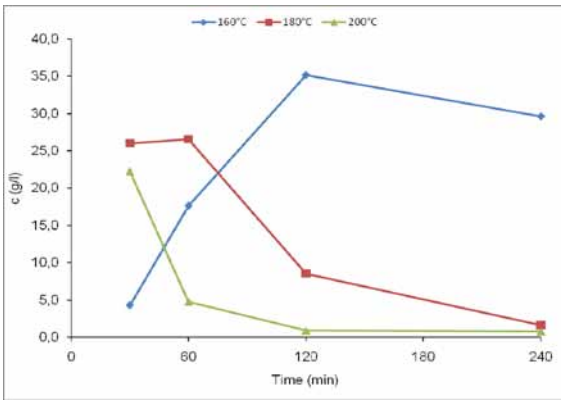
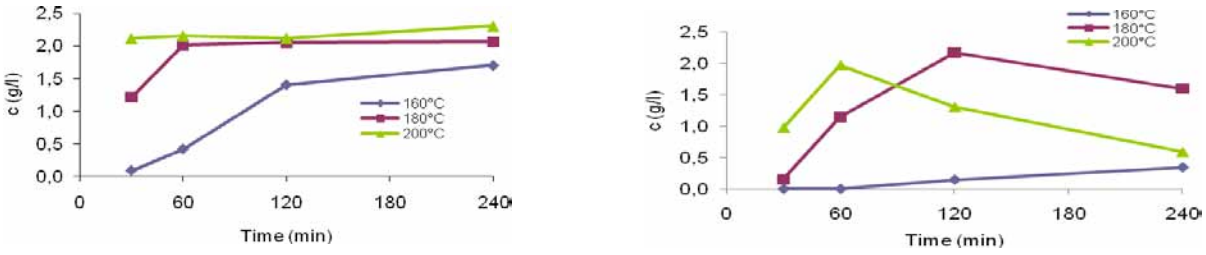


Fig. 2 Influence of temperature and reaction time on the concentration of released mono- and oligosaccharides from ash wood.

The treatment conditions at 160 °C and 120 min are optimal for obtaining xylooligosacharides in high yield from ash.

Acetic acid and sugar-decomposition products (2-furaldehyde, methanol, propionic acid) were determined in prehydrolysates in the 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 (Bobleter 1994, Garrote et al. 1999b).

Acetic acid and 2-furaldehyde (pentose dehydration product) were found to be ones of the main volatile products of ash hydrothermal treatment (Fig. 3a,b).



a *b*

Fig. 3a,b Concentration of volatile compounds in prehydrolysates, a - acetic acid, b - 2-furaldehyde.

CONCLUSIONS

Hydrothermal treatment under mild conditions (160-200 °C, reaction time 30-240 min, liquor to solid ratio 4:1 (ml/g)) caused impact on dissolution of ash (*Fraxinus excelsior* L.). Obtained liquors contained a mixture of oligosaccharides (mostly xylooligosacharides), monosaccharides (mainly xylose, glucose, arabinose) and decomposition products of sugars and lignin (volatile compounds – methanol, acetic acid, propionic acid and 2-furaldehyde).

The treatment conditions at 160 °C and 120 min are optimal for obtaining xylooligosacharides in high yield from ash wood. It was found that the formation of these compounds depends on the autohydrolysis conditions (reaction time, temperature).

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Streszczenie: Częściowa hydroliza drewna jesionu w gorącej wodzie. Drewno jesionu (*Fraxinus excelsior* L., 39 lat) traktowano w temperaturach 160, 180 oraz 200 °C w czasie 30-240 min. Określono odczyn hydrolizatu, zawartość cukrów oraz substancji lotnych w zależności od temperatur oraz czasów.

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