

HEMICELLULOSES EXTRACTION FROM BEECH WOOD WITH WATER AND ALKALINE SOLUTIONS

MÁRIA FIŠEROVÁ, ELENA OPÁLENÁ
PULP AND PAPER RESEARCH INSTITUTE
BRATISLAVA, SLOVAK REPUBLIC

(RECEIVED OCTOBER 2011)

ABSTRACT

Beech wood chips were treated with water and water solutions of alkaline chemicals at elevated temperature in order to extract a part of hemicelluloses. The extractions were performed at 160°C, chemicals charge 3 % Na₂O on o.d. wood; H-factor was changed in the range from 0 to 850 hrs. Dissolution rate of wood components was highest in case of extraction with water followed by extraction with NaOH solution, green liquor (GL), sodium acetate (NaAc), NaHCO₃ and Na₂CO₃. With increasing H-factor pH of extracts decreased; highest decrease was in extraction with water followed by extraction with solutions of NaAc, NaOH, GL, Na₂CO₃ and NaHCO₃. At of 10 % wood weight loss pH of extract decreased in extraction with water to 3.9 whereas in extraction with NaAc to pH 5.1, with NaOH to 5.5, Na₂CO₃ to 5.6, with GL to 6.4 and with NaHCO₃ to pH 6.6. Under these conditions the total content of sugars in the hydrolysed extract after extraction with water was 6.1 % on o.d. wood; out of this xylose content was 4.6 % on o. d. wood. In extraction with solutions of NaOH, GL, NaAc, NaHCO₃, Na₂CO₃ the total content of sugars was in the range 2.05 to 3.3 % on o.d. wood and xylose content was 1.85 to 2.85 % on o.d. wood. In extraction with alkaline solutions glucose content in hydrolysed extracts was 0.24 to 0.34 % on o.d. wood, what is approximately by half lower than in extraction with water. Lignin content in extracts was 0.8 % to 1.2 % on o.d. wood; insoluble solids content was in the range 0.55 % to 1.8 % on o.d. wood.

KEYWORDS: Beech wood, autohydrolysis, alkaline extraction, hemicelluloses, xylose, glucose, lignin, insoluble solids, furfural.

INTRODUCTION

Pulp mills offer a more effective utilisation of renewable resources. Implementation of biorefinery concepts has the potential to strengthen the competitiveness of the pulp and paper industry by diversification of products. In the kraft process, in addition to lignin a large fraction of the hemicelluloses is dissolved in the black liquor stream during the cooking procedure (Bhaskaran and von Koeppen 1970). These modified, solubilised biopolymers in the black liquor

stream and their degradation products are typically concentrated and combusted to generate heat and power requirements for the kraft pulp mill. Polysaccharides such as hemicelluloses have a low heating value ($13.6 \text{ MJ}\cdot\text{kg}^{-1}$) compared with lignin $27.0 \text{ MJ}\cdot\text{kg}^{-1}$ (van Heiningen 2006a). Considering that the heating value of hemicelluloses is considerably lower than of lignin, extracting the hemicelluloses before the pulping stage and production of high value products from extracted hemicelluloses has the potential to improve overall economics of a pulp mill.

Hemicelluloses can be used directly in polymeric form for novel industrial applications such as biopolymers (Ebringerova et al. 1994), hydrogels (Gabrielii et al. 2000), or thermoplastic xylan derivatives (Jain et al. 2000), or once hydrolysed, they can serve as a source of sugars for fermentation to fuels, such as ethanol, or chemicals, such as 1,2,4-butane-triol, a less hazardous alternative to nitroglycerine (Niu et al. 2003). Top value added chemicals that can be produced from sugars in the extract are: 1.4 diacids (succinic, fumaric and malic); furan-2.5-dicarboxylic acid; 3-hydroxy propionic acid; aspartic acid; glutaric acid; glutamic acid; itaconic acid; levulinic acid; 3-hydroxybutyrolactone; glycerol; sorbitol; and xylitol/arabinitol (Carvalho et al. 2008).

Removal of hemicelluloses in a pure form from wood involves hydrolysis of covalent bonds (ester and ether) which link the hemicelluloses to lignin. The ester bonds are easily cleaved by alkali, while the ether linkage under these conditions is much more stable (Sjöström 1993). Xylan, the main hardwood hemicellulose is removed primarily by dissolution rather than degradation, although deacetylation occurs when treated with an caustic solution.

Pre-extraction of hemicelluloses from biomass can be accomplished under different conditions. There are several extraction methods such as steam explosion, organic solvents, alkalis, dilute acids, enzyme treatment, and water extraction (autohydrolysis). Autohydrolysis is the most common commercial procedure, because water is the only reagent making it environmentally friendly (Caparros et al. 2007) (Yoon et al. 2008) (Leschinsky et al. 2009a). During the autohydrolysis process hydronium ions split off from acidic compounds (e.g. acetic, uronic and phenolic acids) released from biomass, lowers the pH of the extract to a range 3-4 (Al-Dajani et al. 2009). The rate of hydrolysis of the wood carbohydrate polymers are directly affected by the hydronium ion concentration (Springer and Harris 1985). This makes autohydrolysis similar to acid hydrolysis in the way that it leads to unwanted side reactions at elevated temperatures.

Acid pre-extraction cause random chain cleavage in cellulose and hemicelluloses, the extracted wood components have lower degree of polymerization (DP) and more reducing end-groups. Subsequent kraft pulping conditions of extracted wood promotes increased solubility and peeling reactions and significant yield loss (Yoon and van Heiningen 2008) (Al-Dajani et al. 2009).

Other methods of hemicelluloses extraction prior to pulping include near-neutral pre-extraction (van Heiningen and Tunc 2005), (van Heiningen 2006b) (Mao et al. 2008) and alkaline pre-extraction at moderate temperature (Al-Dajani and Tschirner 2008) (Zang et al. 2008).

Pre-extraction of wood with alkaline solutions results lower yields of hemicellulose extracts in comparison with autohydrolysis but has positive effect on subsequent kraft pulping conditions in terms chemical charge, and reaction time (Al-Dajani and Tschirner 2008).

Hardwoods contain a higher proportion of total carbohydrates to lignin compared with softwoods as well as a more open vascular structure, which renders hardwoods more amenable to chemical pre-treatment (Polizeli et al. 2005). The European beech (*Fagus sylvatica* L.) is the most important commercial hardwood species in central and southern Europe and its hemicelluloses consists of primarily acetated 4-O-methyl glucuronoxylan (xylan).

The alkaline peeling reaction degrades glucomannan, the dominant softwood hemicelluloses, rapidly under alkaline conditions, while de-acetylated, solubilised oligomeric xylan is more stable due to the 4-O-methyl glucuronic acid side chains. Thus, alkali pre-extraction should be more suitable for hemicelluloses extraction from hardwood rather than softwoods (Simonson 1965).

Near-neutral (GL) and alkali pre-extraction of hemicelluloses from wood can be considered as well-integrated with existing alkaline process such as kraft pulping, since it will lower alkali charge, although the effectiveness of hemicelluloses extraction and recovery is not well-documented for combining pulp production with conversion of hemicelluloses into high added value products (Mao et al. 2008).

The goal of our investigation was to compare influence of water and different alkali solutions on beech wood components dissolution rate prior to kraft pulping process and to determine the content of sugars, lignin, insoluble solids and furfural in extracts.

MATERIAL AND METHODS

Material

Beech wood (*Fagus sylvatica* L.) mill chips were used in this study. The natural dirt was removed (Tappi test method T 265 cm-09) and the chips of 20x20x3 mm dimensions were used for laboratory extraction experiments.

Hemicellulose extraction

Wood chips were extracted with water and solutions of chemicals containing 3 % Na_2O charge on oven dry wood (ODW). The charge of chemicals was: NaOH (3.87 g on 100 g ODW), Na_2CO_3 (5.128 g on 100 g ODW), NaHCO_3 (8.1 g on 100 g ODW), NaAc (13.5 g $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$ on 100 g ODW). The green liquor with total titratable alkali 121.7 g $\text{Na}_2\text{O/L}$ (156 g $\text{Na}_2\text{CO}_3/\text{L}$, 35 g $\text{Na}_2\text{S/L}$ and 3.5 g NaOH/L) was received from kraft pulp mill. The extraction experiments were performed in a series of six laboratory autoclaves, each of 0.75 L volume. The autoclaves were filled with 100 g ODW screened beech wood chips. The liquor-to-wood ratio was 4:1. The time to maximum extracting temperature 160°C was constantly 60 min and the dwell time at this temperature was in the range of 0 to 120 min. The H-factors were calculated by application of the Arrhenius equation combining the effect of time and temperature similarly to H-factor in kraft pulping (Sixta 2006).

After extraction, the residual chips and liquor were separated using a 200 mesh Nylon filter. The extract liquor was collected and stored at 4°C for further analysis, while the residual chips were thoroughly washed with tap water and then air-dried for determination of wood weight losses. After determination of extracted chips weight and the solids, the extraction yield (%) on original chips was calculated. The difference between weight of original and extracted chips was the wood weight loss (%).

Analysis of hemicelluloses extract

The pH of the hemicelluloses extracts was determined. To remove the insoluble solids, the extract was centrifuged for 60 min at 4500 rpm and the supernatant was collected for analysis. The weight of insoluble solids in the extract was determined after drying at 105°C. The original hemicelluloses extract and the extract after one hour hydrolysis with 4 % H_2SO_4 at 121°C in an autoclave was analysed for sugars content (xylose, arabinose, glucose, galactose, mannose) by the HPLC method using as stationary phase a cation-exchange resin in Pb form, water

(80°C) as mobile phase and a refractive index detector (Philips PU 4026). The lignin content of hemicelluloses extract was measured by UV-Vis absorbance at 280 nm using an extinction coefficient of 20.3 L.g⁻¹.cm⁻¹ for hardwood (Alén and Hartus 1988). Furfural in the extract was determined using a spectrophotometric method (Al-Showiman 1998).

RESULTS AND DISCUSSION

Hemicelluloses extraction

In order to assess the potential of using xylose contained in beech wood 4-O-methyl glucuronoxylan as a feedstock for bioconversion to fuels or chemicals with high added value, a number of laboratory experiments were performed with beech wood. The beech wood chips were extracted using alkaline solutions and hot water (autohydrolysis). At same conditions beech wood chips were extracted with green liquor generated in the chemical recovery system of a kraft pulp mill. Green liquor (GL) mainly consists of Na₂CO₃ and Na₂S; a minor component of green liquor is NaOH. For comparison water solutions of Na₂CO₃ and NaOH were used for extraction. It is known, that during extraction with green liquor (Chen 2009) the wood acids, in particular acetic acid, will react with Na₂CO₃ to produce NaAc (sodium acetate) and CO₂. The generation of a gas, CO₂, which is insoluble at neutral or acidic conditions, will cause problems in practical operations. NaAc solution was used as an alternative alkali source to replace Na₂CO₃ in extraction of hemicelluloses with green liquor, because it forms a near neutral buffer solution with acetic acid without the release of a gas. In industrial practise the NaAc solution could be prepared in a separate vessel by neutralizing acetic acid recovered from wood extract. NaHCO₃ solution was used as a buffer to neutralize the acetic acid released by deacetylation of hemicelluloses.

The wood weight loss in extraction with water and solution of alkalis increases with increasing H-factor. The rate of wood dissolution increased as follows: Na₂CO₃ < NaHCO₃ < NaAc < GL < NaOH < H₂O (Fig. 1).

The rate of wood components dissolution up to an H-factor 400 hrs was higher than at higher H-factor values. This is related to dissolution of highly branched hemicelluloses. Further dissolution of hemicelluloses is slower. The relationship between wood weight loss and H-factor shows, that presence of acids in water extraction significantly increases the rate of extraction. For example an H-factor 400 hrs autohydrolysis extracts 16 % ODW, extraction with NaOH solution 11.5 % ODW, with GL 11.1 % ODW, with NaAc 10.1 % ODW, with NaHCO₃ 8.2 % ODW and with Na₂CO₃ 6 % ODW.

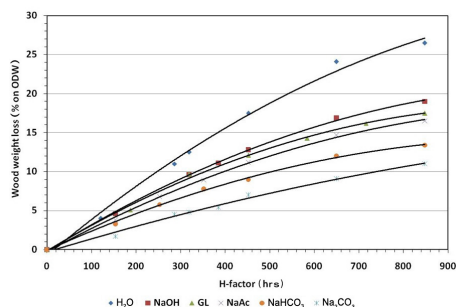


Fig. 1: Wood weight loss versus H-factor of extraction.

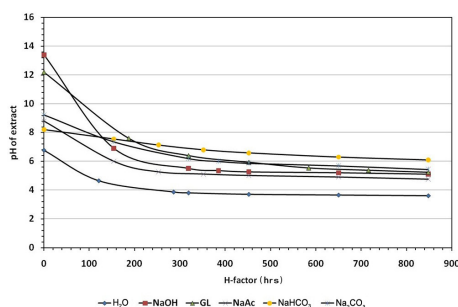


Fig. 2: pH of extract versus H-factor.

Fig. 2 shows the development pH of the extract liquor as a function of H-factor for water and solutions of NaOH, GL, NaAc, NaHCO₃, and Na₂CO₃. The pH of extract liquors decreased with increasing H-factor. At beginning of extraction pH decreased significantly with all agents except of NaHCO₃. After reaching an H-factor about 150-200 hrs pH of extract decreased slightly in the flowing sequence: NaHCO₃ > Na₂CO₃ > GL > NaOH > NaAc > H₂O. The change of the extract pH depends on the ability of the used chemicals to neutralise the generated acids.

Fig. 3 shows the pH of the extract liquor and the H-factor of beech wood chips extraction with water and solutions of NaOH, GL, NaAc, NaHCO₃, Na₂CO₃ at 10 % wood weight loss. This is an optimal extracted weight of wood with green liquor, when mechanical properties of kraft pulp prepared from pre-extracted wood are as good as that of the kraft pulps produced from original wood (Mao 2007). In extraction with water pH of extract decreased to a lowest value (3.9) whereas H-factor required for extraction of 10 % wood weight was the lowest (263 hrs). This is related to the acetic acid generated in autohydrolysis which is reducing significantly pH of extract and speeds up hydrolysis of wood hemicelluloses. At an extraction of 10 % wood weight with solution of NaOH extract pH decreased to 5.5 (H-factor 320 hrs), in extraction with green liquor pH of extract decreased to 6.4 (H-factor 346 hrs), with solution of NaAc pH of extract decreased to 5.1 (H-factor 391 hrs), with NaHCO₃ solution pH decreased to 6.6 (H-factor 497 hrs) and with Na₂CO₃ solution pH of extract decreased to 5.6 (H-factor 734 hrs).

Fig. 4 shows pH of extracts at beginning and after of 10 % wood weight loss by extraction of beech wood chips using water and solutions of NaOH, GL, NaAc, NaHCO₃ and Na₂CO₃. Most significant was decrease of pH in extraction with NaOH (decrease by 7.5) followed by decrease of pH by 5.8 points in extraction with green liquor, in extraction with NaAc by 3.7 points and water by 2.9 points. In extraction with solution of NaHCO₃ pH decreased by 1.6 points only as the solution of NaHCO₃ neutralises the hydroxonium ions liberated from the wood and keeps pH near to neutral value. From the other chemicals used for extraction the highest pH was observed in extraction with green liquor.

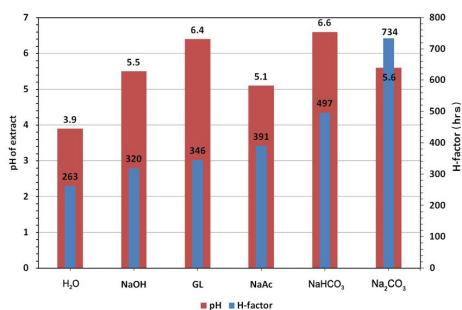


Fig. 3: H-factor and pH of extracts at 10 % wood weight loss in extraction.

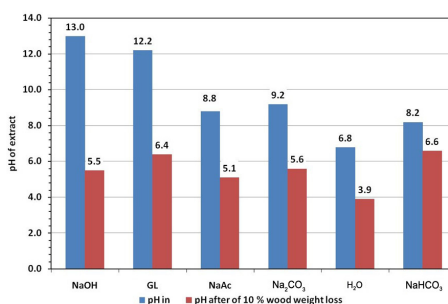


Fig. 4: Comparison of extract pH at beginning and after of 10 % wood weight loss by extraction.

Extract analysis

The hemicelluloses extraction experiments resulted in extracted liquors containing particularly dilute oligosaccharides, minor amount of monosaccharides, lignin, insoluble solids (condensation products), acetic acid, glucuronic acid, furfural, hydroxymethylfurfural, organic degradation products, and residual salts of the alkaline chemicals used. Acetic acid and furfural are the products that are formed during acid degradation of hardwood xylan. The content of

dissolved component sugars (xylose, arabinose, glucose, galactose and mannose) that are detected in the extraction liquor following hydrolysis increases with wood weight loss (Fig. 5).

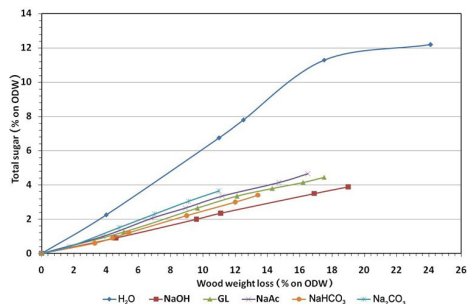


Fig. 5: Total sugar content in hydrolysed extracts versus wood weight loss.

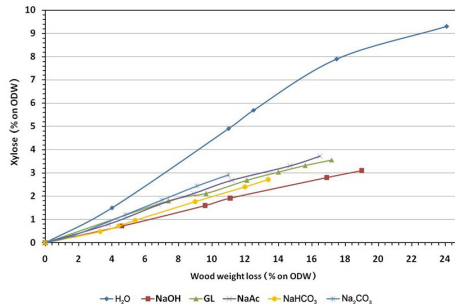


Fig. 6: Xylose content in hydrolysed extracts versus wood weight loss.

The hydrolysed extracts from hardwoods contain particularly xylose. Fig. 6 shows xylose content in hydrolysed extracts in dependence of wood weight loss. The dependence is analogous as the determined total sugar content in hydrolysed extracts. With increasing wood weight loss xylose content in hydrolysed extracts increased similarly as the total sugar content as xylose represents about 76 % of total sugar content in hydrolysed extracts. At an extraction of 10 % of wood weight xylose content in the hydrolysed water extract was 4.6 % on ODW. However, in extract of NaOH, GL, NaAc, NaHCO₃ and Na₂CO₃ solution xylose content was in the range just from 1.85 % to 2.85 % on ODW.

Fig. 7 shows dependence of glucose content in hydrolysed extracts on wood weight loss. With increasing wood weight loss glucose content in hydrolysed extracts increased at the most in extraction with water. At 10 % wood weight loss in extraction glucose content in hydrolysed extract was 0.55 % on ODW. At extraction with solutions of NaOH, GL, NaAc, NaHCO₃ and Na₂CO₃ glucose content was in the range from 0.24 % to 0.34 % on ODW. Glucose content in hydrolysed extracts decreased in dependence of extraction agent in following sequence: H₂O > NaAc > NaOH > Na₂CO₃ > GL > NaHCO₃. The higher content of glucose in hydrolysed water extracts could be caused by random chain cleavage in cellulose and hemicelluloses during acid extraction of wood.

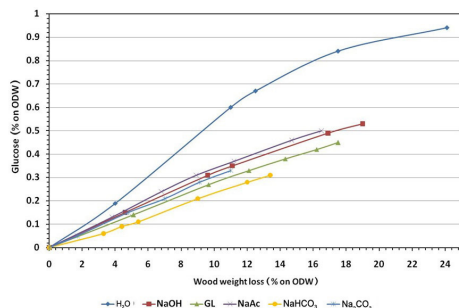


Fig. 7: Glucose content in hydrolysed extracts versus wood weight loss.

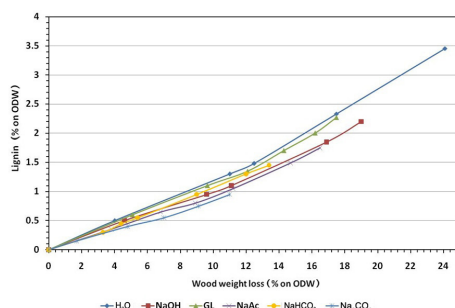


Fig. 8: Lignin content in extracts versus wood weight loss.

Glucose content is higher in water extracts than in alkaline extracts of beech wood. The reason is that the acetic acid split off from acetyl groups of hemicelluloses during water extraction leads to more extensive hydrolysis and dissolution of glucomannan. Another source of glucose detected after extract hydrolysis is starch (Tunc and van Heiningen 2011). The alkaline conditions promote degradation of dissolved glucomannan and glucan or starch and this reduces the amount of glucose detected in alkaline extracts.

Fig. 8 shows the relationship between lignin content in extracts and wood weight loss. With increasing wood weight loss lignin content in extracts increased. At 10 % wood weight loss lignin content in extracts was in the range from 0.8 % to 1.2 % ODW. Lignin content decreased depending on the applied extraction chemicals in the following order: H_2O > GL > NaHCO_3 > NaOH > NaAc > Na_2CO_3 .

A variety of compounds (e.g. aromatic, polyaromatic, phenolic and aldehydic) may be released from the lignin fraction in the extraction process. Some of the dissolved lignin degradation products remain soluble in the extract, while degradation products characterised by a higher molecular weight precipitate upon cooling (Leschinsky et al. 2009b). Content of insoluble solids increased with increasing amount of wood weight loss (Fig. 9). A larger amount of insoluble solids was formed at beginning of extraction approximately up to 10 % wood weight loss in extraction. At extraction of 10 % wood weight content of insoluble solids in extracts was in the range from 0.55 % to 1.8 % on ODW. Insoluble solids in extracts decreased in dependence of applied extraction agent in the sequence: NaOH > Na_2CO_3 > GL > NaAc > NaHCO_3 > H_2O . In water extract after cooling only 0.55 % insoluble solids on ODW were found.

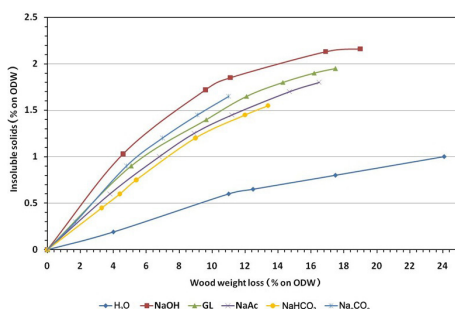


Fig. 9: Insoluble solids content in extracts versus wood weight loss.

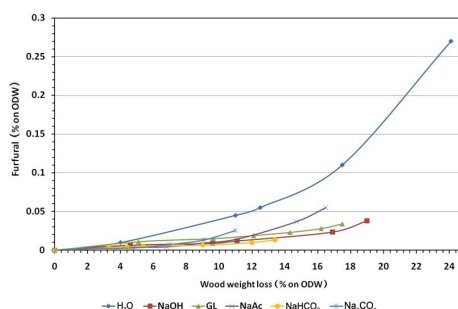


Fig. 10: Furfural content in extracts versus wood weight loss.

Subsequently to hemicelluloses hydrolysis, pentose sugar monomers may dehydrate to furfural. Similarly, hexose sugars may degrade during extraction of hemicelluloses to hydroxymethylfurfural. Furfural and hydroxymethylfurfural content in extracts depends on applied extraction agents and extraction conditions. These compounds can be used as raw material for production of value added chemicals. Fig. 10 shows the relationship between furfural content in extract and wood weight loss. In water extraction of beech wood with increasing wood weight loss furfural content in extracts increased markedly. At 10 % wood weight loss furfural content in extracts was in the range from 0.01 % to 0.04 % on ODW.

CONCLUSIONS

The results of beech wood extraction using green liquor, NaOH, Na₂CO₃, NaHCO₃ and NaAc solutions were compared with hot water extraction in order to select a method of hemicelluloses extraction for preparation of value added products from xylose or furfural and simultaneously to utilize the extracted wood for kraft pulp manufacture.

Extraction of beech wood with hot water is resulting in considerably higher dissolution of wood components, mainly xylan when compared with extraction by alkali solutions. A disadvantage of wood extraction by water is degradation of polysaccharides remaining in the extracted wood resulting in the following alkaline cooking process decrease of yield and strength properties of pulp. In view of the high xylose yield in the hydrolysed water extract it will be necessary to find out at which level of extraction degree no significant degradation of polysaccharides occurs in the extracted wood.

Alkaline extraction agents promote alkaline degradation of the dissolved hemicelluloses and thus reduce the content of sugars particularly xylose in hydrolysed extracts.

Out of tested extraction agents good results were obtained in extraction of beech wood with green liquor. In extraction with green liquor pH decreases to the near neutral region and the rate of wood components dissolution is high. However, xylose yield is about by half lower when compared with hot water extraction. The advantages of green liquor extraction is absence of significant degradation of polysaccharides in the extracted wood and availability of green liquor from the recovery cycle of a kraft pulp mill.

ACKNOWLEDGMENT

This work was supported by the Slovak Research and Development Agency under contract No. APVV-0367-10.

REFERENCES

1. Al-Dajani, W.W., Tschirner, U., 2008: Pre-extraction of hemicelluloses and subsequent kraft pulping. Part I. Alkaline extraction. Tappi J. 7(6): 3-8.
2. Al-Dajani, W.W., Tschirner, U., Jensen, T., 2009: Pre-extraction of hemicelluloses and subsequent kraft pulping. Part II. Acid and autohydrolysis. Tappi J. 8(9): 30-37.
3. Alén, R., Hartus, T., 1988: UV spectrophotometric determination of lignin from alkaline pulping liquor. Cellulose Chem. Technol. 22(6): 613-618.
4. Al-Showiman, S.S., 1998: Furfural from some decorative plants grown in Saudi Arabia. Journal of Scientific & Industrial Research 57(12): 907-910.
5. Bhaskaran, T.A., von Koeppen, A., 1970: The degradation of wood carbohydrates during sulphate pulping. Holzforschung 24(1): 14-19.
6. Caparros, S., Ariza, J., Garrote, G., Lopez, F., Diaz, M.J., 2007: Optimization of *Paulownia fortunei* L. autohydrolysis – organosolv pulping as a source of xylooligomers and cellulose pulp. Ind. Eng. Chem. Res. 46(2): 623-631.
7. Carvalheiro, F., Duarte, L.C., Gírio, F.M., 2008: Hemicellulose biorefineries: A review on biomass pre-treatments. Journal of Scientific & Industrial Research 67(11): 849-864.
8. Chen, X., 2009: Hemicellulose pre-extraction of hardwood. A Dissertation, The University of Maine, USA, August 2009.

9. Ebringerová, A., Hromádková, Z., Kačuráková, M., Antal, M., 1994: Quarternized xylans: Synthesis and structural characterization. *Carbohydrate Polymers* 24(4): 301-304.
10. Gabrieli, I., Gatenholm, P., Glasser, W.G., Jain, R.K., Kenne, L., 2000: Separation, characterization and hydrogel-formation of hemicelluloses from aspen wood. *Carbohydrate Polymers* 43(4): 367-374.
11. Jain, R.K., Sjöstedt, M., Glasser, W.G., 2000: Thermoplastic xylan derivatives with propylene oxide. *Cellulose* 7(4): 319-336.
12. Leschinsky, M., Weber, H.K., Patt, R., Sixta, H., 2009a: Formation of insoluble components during autohydrolysis of *Eucalyptus globulus*. *Lenzinger Berichte* 87: 16-25.
13. Leschinsky, M., Sixta, H., Patt, R., 2009b: Detailed mass balance of autohydrolysis of *Eucalyptus globulus* at 170°C. *BioResources* 4(2): 687-703.
14. Mao, H., 2007: Technical evaluation of a hardwood biorefinery using the “near-neutral” hemicelluloses extraction process. Master’s Thesis, University of Maine, USA.
15. Mao, H., Genco, J.M., van Heiningen, A.R.P., Pendse, H., 2008: Abstracts of Papers. Nordic Wood Biorefinery Conference, Stockholm, March 11-13, 2008. Pp 16-29.
16. Niu, W., Molefe, M.N., Frost, J.W., 2003: Microbial synthesis of the energetic material precursor 1,2,4-butanetriol. *J. Am. Chem. Soc.* 125(43): 12998-12999.
17. Polizeli, M.L.T.M., Rizzatti, A.C.S., Monti, R., Terenzi, H.F., Jorge, J.A., Amorim, D.S., 2005: Xylanases from fungi: Properties and industrial applications. *Appl. Microbiol. Biotechnol.* 67(5): 577-591.
18. Simonson, R., 1965: The hemicelluloses in sulphate pulping process. Part 3: The isolation of hemicelluloses fractions from birch sulphate cooking liquors. *Sven. Papperstidn.* 68(8): 275-280.
19. Sixta, H., 2006: Multistage kraft pulping. In: *Handbook of pulp*. H. Sixta, ed., Wiley-VCH, Weinheim. Pp 325-365.
20. Sjöström, E., 1993: *Wood chemistry: Fundamentals and applications*. 2nd Edition, Academy Press Inc., San Diego, 293 pp.
21. Springer, E.L., Harris J.F., 1985: Procedures for determining the neutralizing capacity of wood during hydrolysis with mineral acid solutions. *Ind. Eng. Chem. Prod. Res. Dev.* 24(3): 485-489.
22. Tunc, M.S., van Heiningen, A.R.P., 2011: Characterization and molecular weight distribution of carbohydrates isolated from autohydrolysis extract of mixed southern hardwoods. *Carbohydr. Polym.* 83(1): 8-13.
23. van Heiningen, A.R.P., Tunc, M.S., 2005: Abstracts of Papers. 229th ACS National Meeting, San Diego, CA, USA, March 13-17, 2005. Pp CELL-209.
24. van Heiningen, A.R.P., 2006a: Abstracts of Papers. PAPTEC 92nd Annual Meeting, 2006. Pp C167-C176.
25. van Heiningen, A., 2006b: Converting a kraft pulp mill into an integrated forest biorefinery. *Pulp Pap. Can.* 107(6): 38-43.
26. Yoon, S.-H., MacEwan, K., van Heiningen, A.R.P., 2008: Hot-water pre-extraction from loblolly pine (*Pinus taeda*) in integrated forest products biorefinery. *Tappi J.* 7(6): 27-32.
27. Yoon, S.-H., van Heiningen, A.R.P., 2008: Kraft pulping and papermaking properties of hot water pre-extracted loblolly pine in an integrated forest products biorefinery. *Tappi J.* 7(7): 22-27.
28. Zang, Z., Chi, C., Liu, X., 2008: Abstracts of Papers. 10th European Workshop on Lignocellulosic and Pulp EWLP, Stockholm, 2008.

MÁRIA FIŠEROVÁ, ELENA OPÁLENÁ
PULP AND PAPER RESEARCH INSTITUTE
LAMAČSKÁ CESTA 3
841 04 BRATISLAVA
SLOVAK REPUBLIC
Corresponding autor: fiserova@vupc.sk