

**COMPARATIVE STUDY OF HEMICELLULOSES
EXTRACTION FROM BEECH AND OAK WOOD**

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

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ABSTRACT

Beech and oak wood chips were treated with dilute oxalic acid (0.0825 %), hot water and water solution of green liquor (3 % Na₂O charge on ODW) at elevated temperature in order to extract a part of hemicelluloses. The extractions were performed at 160°C, H-factor was changed in the range from 0 to 850 hrs. Dissolution rate of wood components was highest in case of extraction with dilute oxalic acid followed by extraction with hot water and green liquor solution. The extraction rate of oak chips was higher than of beech chips by all agents. The total content of monosugars in the hydrolysed extract of dilute oxalic acid was 7.6 % on ODW for beech and for oak 5.5 % on ODW, in hot water extract 6.5 % on ODW for beech and 4.1 % on ODW for oak, in green liquor extract was 2.8 % on ODW for beech and 2 % on ODW for oak, at 10 % wood weight loss. The xylose content in hydrolysed beech wood extracts represents about 79 % from the total monosugars content in all extracts, while in hydrolysed oak wood extracts only 49 %. Glucose content in hydrolysed extracts was in the range 0.165 % to 0.58 % on ODW; it was higher in dilute oxalic acid and hot water extracts. Lignin content in extracts was 0.8 to 3.8 % on ODW; it was higher for oak wood. Insoluble solids content was in the range 0.42 to 1.8 % on ODW; it was higher for oak wood and the highest content was in green liquor extracts. The beech wood is more suitable for pre-extraction of hemicelluloses prior to pulping than oak wood because the extracts contain more hemicelluloses.

KEYWORDS: Beech wood, oak wood, extraction, hemicelluloses, oxalic acid, hot water, green liquor.

INTRODUCTION

The global environmental concerns and the growing cost of fossil fuels stimulated the research and development of alternative products obtained from renewable resources. Lignocellulosic biomass is the most abundant class of renewable materials, accounting for about 50 % of all the biomass in the world (Wingren et al. 2003). It represents a useful and valuable

resource that could be used for production of biofuels and biochemicals. At present, intensive research takes place in application of hemicelluloses as raw materials for biofuels, high-value-added chemicals and materials.

The conventional pulping processes exploit only a part of the wood material. In the pulping process hemicelluloses are dissolved and degraded, they end up in black liquor where they are difficult to separate. A significant part of lignin and hemicelluloses are burnt in recovery boiler. However, the heating value of hemicelluloses is only about half of that lignin (Vakkilainen 1999). Therefore, it could be economically to convert the hemicelluloses to various value-added products (van Heiningen 2007). One option to convert a pulp mill into a pulp and biofuels and/or biochemicals produced by biorefinery processes requires the extraction of hemicelluloses from wood chips.

The isolation of hemicelluloses from various wood species has been already studied long time ago. Hemicelluloses, due to their lower degree of polymerization and the presence of branched side groups, can be more readily dissolved into aqueous solution than other components of the lignocelluloses complex. Many researchers have studied different methods, solvents, operating conditions and processes for extraction of hemicelluloses. Different properties and solubility of the wood hemicelluloses require different separation method. The presence of lignin as well as of lignin-carbohydrate complexes limits the hemicelluloses extraction from the wood cell wall matrix. The extensive hydrogen bonds between the individual polysaccharides components also inhibit their separation (Timell 1965, Sjöström 1993).

Many processes can remove hemicelluloses from lignocellulose. Alkaline, neutral and acidic solvent extraction of hemicelluloses are general chemical extraction methods that can be applied to isolate hemicelluloses from woods. It has been reported that hot water extraction, or autohydrolysis, is useful in generating a soluble carbohydrates (Thorp and Raymond 2004). The autohydrolysis process has attracted much interest during recent years, because it is an environmental sustainable technology and inexpensive compared to dilute mineral acid prehydrolysis. The depolymerisation of hemicelluloses is catalyzed by hydronium ions of water and naturally generated compounds such acetic acid, uronic and phenolic acids (Liu 2010).

Dilute acid pretreatments with sulphuric acid or sulphur dioxide have produced fermentable carbohydrates and pulp (Mosier et al. 2005, Söderström et al. 2003). Among dilute acid treatments, organic acids are thought to be more selective for the hydrolysis of β -(1,4)-glycosidic bonds than sulphuric acid, due to lower ability to cause glucose degradation (Lu and Mosier 2007). This research tested the hypothesis whether oxalic acid with its dual pKa could provide more efficient and specific hydrolysis of hemicellulose than could sulphuric acid. Oxalic acid is one of the strongest organic acids known. Due to its pKa's of 1.27 and 4.28, respectively, it can catalyse the hydrolysis of hemicelluloses while sparing cellulose. After mild pre-treatment, the cellulose enriched fraction can be used for papermaking (Green et al. 1991), or after more extensive pre-treatment, the residual solids can be hydrolyzed by cellulolytic enzymes to fermentable sugars for ethanol production.

Several technologies for removal of hemicelluloses from wood chips prior to pulping have been investigated (Al-Dajani and Tschirner 2008, Yoon and van Heiningen 2008, Mao et al. 2008). Selective removal of the hemicelluloses prior to pulping can be accomplished without degrading the wood fibres. The hemicelluloses extraction is conventionally used in the production of high-purity dissolving pulps. The removing of hemicelluloses prior to pulping is economically advantageous, less alkali charge may be required for pulping and the rate of delignification may be increased, or the bleaching chemical consumption may be reduced (Al-Dajani and Tschirner 2008, Yoon and van Heiningen 2008, Amidom et al. 2006, Kautto et al. 2010).

The goal of our investigation was to compare the influence of hardwood wood species and extraction agents on wood components dissolution rate and the extracts composition.

MATERIAL AND METHODS

Material

Beech wood (*Fagus sylvatica* L.) and oak wood (*Quercus robur* L.) mill chips were used in this study. Tab. 1 shows the chemical composition of beech and oak chips. Natural dirt was removed (Tappi test method T 265 cm-09) and chips of 20x20x3 mm dimensions were used for laboratory extraction experiments.

Tab. 1: Composition of beech and oak wood.

Component, % on ODW	Beech	Oak
Ash	0.49	0.36
Extractives	0.22	0.48
Total lignin, thereof:	25.75	28.52
Acid-soluble lignin	3.04	5.25
Klason lignin	22.71	23.27
Holocellulose	73.54	70.64
Alpha-cellulose	46.95	44.98
Hemicelluloses	26.59	25.66

Methods

Hemicelluloses extraction

Beech and oak wood chips were extracted with 0.0825 % oxalic acid (OA), hot water and water solution of green liquor with 3 % charge of total titratable alkali expressed as Na₂O on ODW (3 % GL). 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 (oven dry wood) screened beech and oak wood chips. The liquor-to-wood ratio was 4:1. Time to maximum extraction 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 of extraction were from 55 to 850 hrs. After extraction, the residual chips and liquor were separated on a 200 mesh nylon filter. The extraction liquor was collected and stored at 4°C for further analysis, while the residual chips from one laboratory autoclave were thoroughly washed with tap water and 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 (%).

Analyses

From air dried beech and oak wood sawdust was prepared in a rotary mill (type Brabender) according to Tappi method T 257 cm-02. The sawdust was separated on sieves into three fractions: 0.25, 0.25-0.4 and above 0.4 mm. The middle fraction was used for chemical analyses. Ash was determined according to Tappi T 211 om-07 and the content of extractives Tappi

T 204 om-07 methods. Klason lignin was determined according to Tappi T 222 om-02 and acid soluble lignin Tappi UM 250 methods. Holocellulose content was determined by a method based on Klauz procedure (Browning 1967) and alpha cellulose according to Tappi T 203 om-93 method. The hemicelluloses content was calculated as difference between the holocelluloses and alpha-cellulose content.

The pH of the hemicelluloses extracts was determined. To remove 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 % H₂SO₄ at 121°C in an autoclave was analysed for monosugars content (xylose, arabinose, glucose, galactose, mannose) by the HPLC method with a refractive index detector (Philips PU 4026), using a cation-exchange resin in Pb form as stationary phase and water (80°C) as mobile phase. The lignin content of hemicelluloses extract was measured by UV absorbance at 280 nm using an extinction coefficient of 20.3 L.g⁻¹.cm⁻¹ for hardwood (Alén and Hartus 1988).

RESULTS AND DISCUSSION

The conditions of beech and oak wood chips extraction with dilute oxalic acid, hot water and green liquor solution were selected according to our previous study (Fišerová and Opálená 2012). The extraction rate of wood components is one of the important parameters that influence the effectiveness of hemicelluloses pre-extraction prior to pulping process.

The wood weight loss of oak and beech species by extraction with dilute oxalic acid, hot water and green liquor solution (3 % Na₂O charge on ODW) increased with H-factor of extraction (Fig. 1). The relationship between wood weight loss and H-factor shows, that the extraction rate is higher for oak wood than for beech wood with all agents. The extraction rate increased as follows: 3 % GL < H₂O < 0.0825 % OA.

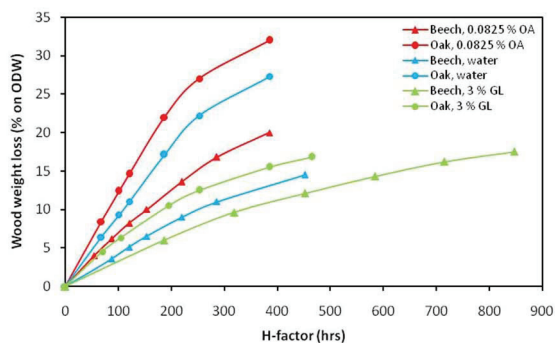


Fig. 1: Wood weight loss versus H-factor of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

The 10 % of oak wood weight loss was reached with 0.0825 % oxalic acid at H-factor 80 hrs, with hot water at 110 hrs and with 3 % green liquor at H-factor 185 hrs. The same of beech wood weight loss was reached with 0.0825 % oxalic acid at H-factor 150 hrs, with hot water at H-factor 250 hrs and with 3 % green liquor at H-factor 345 hrs. 10 % of wood weight loss represents a quantity of wood substance removed with near neutral solutions before the kraft pulping at which

yield and strength properties were approximately equal to a control pulp prepared from original wood chips (Goyal et al. 2007, Mao et al. 2008).

The dilute oxalic acid increased the rate of extraction by a factor of 1.2 for oak wood and 1.5 for beech wood in comparison with hot water and by a factor of 1.9 for oak wood and of 2.3 for beech wood in comparison with green liquor solution. Hot water increased the extraction rate by a factor of 1.6 for oak wood and of 1.5 for beech wood in comparison with green liquor solution. The results demonstrate that the amount of extracted wood components increased by addition of oxalic acid in water, which is in accordance with published results (Li et al. 2011).

The extraction rate of oak chips was higher than of beech wood by all agents. This is connected with morphology and chemical composition of wood species. The extraction rate of oak wood with dilute oxalic acid was 1.9 times higher than of beech wood, with hot water 2.3 times and with 3 % green liquor 1.9 times higher than of beech wood at H-factor 200 hrs.

Fig. 2 shows development of extract pH as a function of oak and beech wood weight loss for dilute oxalic acid, hot water and green liquor solution extraction. The pH of 3 % green liquor and hot water extracts decreased with increasing wood weight loss, but the pH of 0.0825 % oxalic acid extracts increased with increasing wood weight loss. These differences can be caused by increased content of acids in extract. At 10 % wood weight loss in extraction the pH of 3 % green liquor extract from beech wood was 6.7 and of oak wood extract 6.5. The pH of hot water extract from beech wood was 4 and from oak wood 3.8. The lowest pH values were achieved for 0.0825 % oxalic acid extracts, from beech wood 3.3 and from oak wood 3.2. The pH values at the same wood weight loss were higher for beech wood extracts than for oak wood extracts. From these follow that at equal weight loss of oak wood more acids were transferred into extracts than from beech wood.

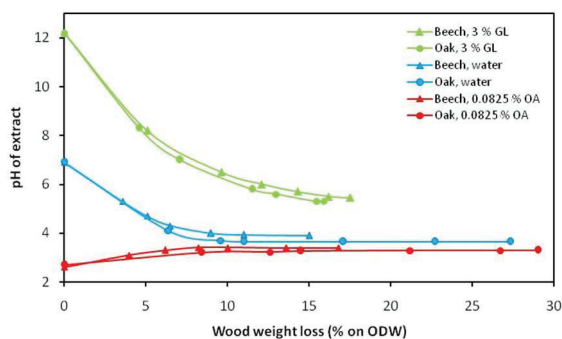


Fig. 2: pH of extract versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

The wood extracts contain dissolved hemicelluloses, minor amount of monosugars, lignin, insoluble solids (lignin condensation products), acetic acid, glucuronic acid, furfural, hydroxymethylfurfural and organic degradation products of wood components.

The content of hemicelluloses in extracts influences the economy of pre-extraction combined with a pulping process. The content of dissolved monosugars (xylose, arabinose, glucose, galactose and mannose) detected in the extraction liquor after hydrolysis increases with increasing beech and oak wood weight loss (Fig. 3). At 10 % wood weight loss in extraction the content of total monosugars in hydrolysed 0.0825 % oxalic acid extract of beech wood was 7.6 % on ODW and in hydrolysed oak wood extract was only 5.2 % on ODW. At equal wood weight loss the content

of total monosugars in hydrolysed water extract of beech wood was 6.5 % on ODW and in extract of oak wood was 4.1 % on ODW. Similarly, at 10 % wood weight loss in extraction the content of total monosugars in hydrolysed 3 % green liquor extract of beech wood was 2.8 % on ODW and in extract of oak wood was 2 % on ODW.

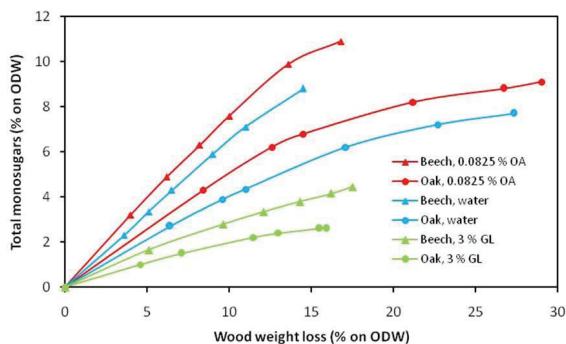


Fig. 3: Total monosugars content in hydrolysed extracts versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

The highest content of total monosugars at the equal wood weight loss was in hydrolysed 0.0825 % oxalic acid extract, it was lower in hot water extract and the lowest content of total monosugars was in hydrolysed 3 % green liquor extract from both wood species. At 10 % wood weight loss, the total monosugars content in hydrolysed dilute oxalic acid extract was higher by a factor of 1.3 for oak wood and a factor of 1.2 for beech wood in comparison with hot water extracts. The total monosugars content in hydrolysed dilute oxalic acid extract was higher by a factor of 2.7 for beech wood and by a factor of 2.6 for oak wood in comparison with green liquor extracts. The total monosugars content in hydrolysed hot water extract was higher by a factor of 2.3 for beech wood and by a factor of 2.05 for oak wood in comparison with green liquor extract.

The results demonstrate that at the equal wood weight loss the content of total monosugars in hydrolysed beech wood extracts was higher than in hydrolysed oak wood extracts regardless of applied agents. The beech wood has higher hemicelluloses content than oak wood (Tab. 1). The total monosugars content in hydrolysed dilute oxalic acid beech wood extract was 1.5 times higher than in oak wood extract, in hydrolysed hot water beech wood extract it was 1.6 times higher than in oak wood extract and in hydrolysed green liquor beech wood extracts it was 1.4 times higher than in oak wood extract at 10 % wood weight loss.

The hydrolysed extracts of beech and oak wood contain particularly xylose. Fig. 4 shows xylose content in hydrolysed extracts in dependence on wood weight loss. With increasing wood weight loss the xylose content in hydrolysed extracts increased similarly as the total monosugars content. At 10 % wood weight loss in extraction the highest xylose contents were in hydrolysed 0.0825 % oxalic acid extracts, from beech wood (6.0 % on ODW) and from oak wood (2.6 % on ODW), followed by xylose contents in hydrolysed hot water extracts, from beech wood (4.9 % on ODW) and from oak wood (2.0 % on ODW). The lowest xylose contents were in hydrolysed 3 % green liquor extracts, from beech wood (2.2 % on ODW) and from oak wood (0.95 % on ODW).

The highest xylose content at the equal wood weight loss was in hydrolysed 0.0825 % oxalic acid extract, it was lower in hot water extract and the lowest xylose content was in hydrolysed 3 % green liquor extract from both wood species. At 10 % wood weight loss, the xylose content in hydrolysed oxalic acid extract was higher by a factor of 1.2 for beech wood and of 1.3 for oak wood

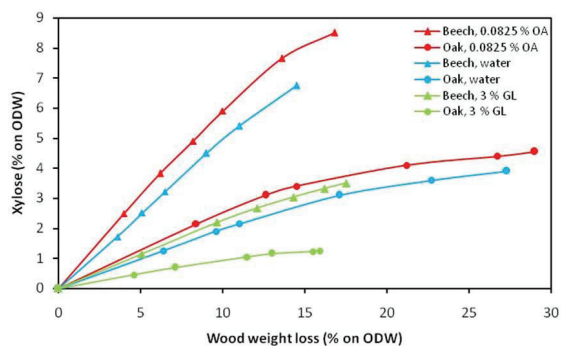


Fig. 4: Xylose content in hydrolysed extracts versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

in comparison with hot water extract. The xylose content in hydrolysed dilute oxalic acid extract was higher by a factor of 2.7 for beech and oak wood in comparison with green liquor extract. The xylose content in hydrolysed hot water extract was higher by a factor of 2.2 for beech wood and of 2.1 for oak wood and in comparison with green liquor extract.

The results demonstrate that at the equal wood weight loss the xylose content in hydrolysed beech wood extract was higher than in hydrolysed oak wood extract regardless of applied agents. At 10 % wood weight loss, the xylose content in hydrolysed dilute oxalic acid extract of beech wood was 2.3 times higher than in extract of oak wood, in hydrolysed hot water extract of beech wood was 2.45 times higher than in extract of oak wood and in hydrolysed green liquor extract of beech wood was 2.3 times higher than in extract of oak wood. The xylose content in hydrolysed extracts of beech wood represents about 77 % of the total monosugars content in extracts by all agents, while in hydrolysed extracts of oak wood only 49 %. These results confirmed that more xylan was extracted from beech wood than from oak wood.

Fig. 5 shows the dependence of glucose content in hydrolysed extracts on wood weight loss. With increasing wood weight loss the glucose content in hydrolysed extracts increased for both wood species. At 10 % wood weight loss in extraction with 0.0825 % oxalic acid glucose content in hydrolysed oak wood extract was 0.58 % on ODW and in hydrolysed beech wood extract 0.5 % on ODW. The glucose content in hydrolysed hot water oak wood extract was 0.54 % on ODW and in beech wood extract 0.45 % on ODW. The lowest glucose content was in hydrolysed green liquor oak wood extract (0.165 % on ODW) and in beech wood extract (0.24 % on ODW).

The glucose content in hydrolysed 0.0825 % oxalic acid extract of beech and oak wood was higher by a factor of 1.1 in comparison with hot water extract. The glucose content in hydrolysed 0.0825 % oxalic acid extract of beech wood was higher by a factor of 2.1 and by 3.5 for oak wood in comparison with green liquor extract. The glucose content in hydrolysed hot water extract was higher by a factor of 1.9 for beech wood and of 3.3 for oak wood in comparison with green liquor extract.

The higher content of glucose in hydrolysed dilute oxalic acid and hot water extracts could be caused by random chain cleavage of cellulose and hemicelluloses macromolecules during extraction at lower pH than by green liquor extraction.

With increasing beech and oak wood weight loss lignin content in extracts increased (Fig. 6). At 10 % wood weight loss the highest lignin content was in green liquor oak wood extract (3.8 % on ODW) and beech wood extract (1.25 % on ODW), it was lower in oak wood hot water

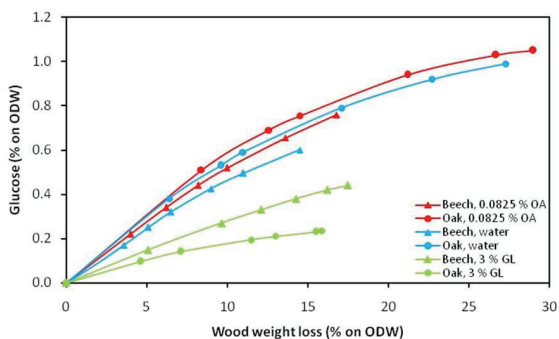


Fig. 5: Glucose content in hydrolysed extracts versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

extract (2.05 % on ODW) and beech wood extract (0.95 % on ODW). The lowest lignin content was in dilute oxalic acid oak wood extract (1.65 % on ODW) and beech wood extract (0.8 % on ODW). The lignin content in green liquor oak wood extract was 3 times higher than in beech wood extract; in hot water oak wood extract lignin content was 2.15 times higher than in beech wood extract. The lignin content in dilute oxalic acid oak wood extracts was 2.1 times higher than in beech wood extracts. Solubility of lignin was higher at higher pH of extraction solutions. The high solubility of oak wood lignin in all extraction agents can be connected with higher lignin content (mainly acid-soluble) in oak wood than in beech wood (Tab. 1).

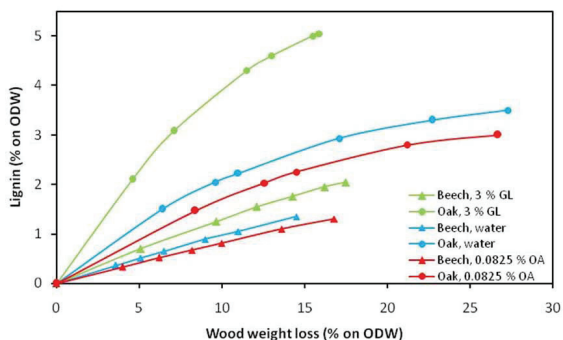


Fig. 6: Lignin content in extracts versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

Fig. 7 shows the dependence of insoluble solids content in extracts on beech and oak wood weight loss. Insoluble solids are condensation products of dissolved high molecular lignin. The content of insoluble solids in extracts increased with increasing wood weight loss.

At 10 % wood weight loss the highest insoluble solids content was in green liquor oak wood extract (1.83 % on ODW) and beech wood extract (1.44 % on ODW), followed in hot water oak wood extract (0.73 % on ODW) and beech wood extract (0.52 % on ODW). The lowest insoluble solids content was in dilute oxalic acid oak wood extract (0.61 % on ODW) and beech wood extract (0.42 % on ODW). The insoluble solids content in green liquor oak wood extract was 1.3 times higher than in beech wood extract, in hot water oak wood extracts was 1.4 times

higher than in beech wood extracts and in dilute oxalic acid oak wood extracts was 1.5 times higher than in beech wood extracts at the same wood weight loss. Higher insoluble solids content was in oak wood extracts than in beech wood extracts. The higher insoluble solids content in oak wood extracts in all extraction agents can be connected with higher lignin content in oak wood than in beech wood (Tab. 1).

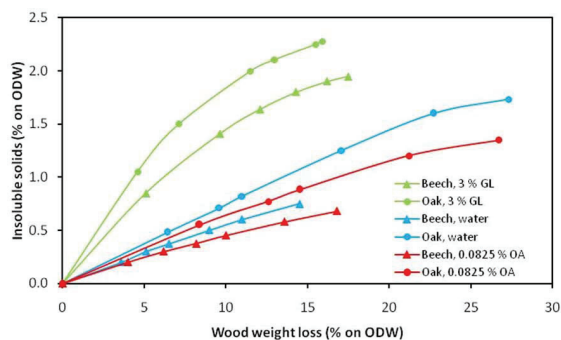


Fig. 7: Insoluble solids content in extracts versus wood weight loss of extraction with 0.0825 % oxalic acid, hot water and 3 % green liquor.

CONCLUSIONS

The results of beech and oak wood extraction using dilute oxalic acid, hot water and green liquor solution were used in order to select a wood species and a method of hemicelluloses extraction prior to the pulping for preparation of high value added products besides pulp.

The extraction rate of oak wood chips was higher than of beech wood by all agents which is connected with morphology and chemical composition of wood species. The extraction rate of oak wood with 0.0825 % oxalic acid was 1.9 times higher, with hot water 2.3 times and with green liquor 1.9 times higher than of beech wood.

Extraction of beech and oak wood with dilute oxalic acid and hot water is resulting in considerably higher dissolution of hemicelluloses, mainly xylan when compared with extraction by green liquor solution.

At 10 % wood weight loss was the content of total monosugars in hydrolysed beech wood extract was higher than in hydrolysed oak wood extract regardless of applied agents. The hemicelluloses content in beech wood is higher content than in oak wood. The total monosugars content in hydrolysed beech wood extracts was 1.4 to 1.6 times higher than in oak wood extracts.

At the same wood weight loss, the total monosugars content in hydrolysed dilute oxalic extract was higher by a factor about of 1.2 in comparison with hot water extract of both wood species. The total monosugars content in hydrolysed dilute oxalic acid extract was higher by a factor of about 2.6 for oak and beech wood in comparison with green liquor extract. The total monosugars content in hydrolysed hot water extract was higher by a factor about of 2.2 in comparison with green liquor extract.

The xylose content in hydrolysed beech wood extracts represents about 77 % from the total monosugars content in extracts by all agents, while in hydrolysed oak wood extracts only 49 %. The results confirmed that from beech wood more xylan is extracted than from oak wood.

Lignin content in green liquor extracts from oak wood was three times higher than from

beech wood, in hot water extracts 2.15 times and in dilute oxalic acid 2.1 times. The higher lignin content in oak wood extracts than in beech wood extracts can be explained with higher lignin content in oak wood.

The beech wood is more suitable for pre-extraction of hemicelluloses prior to pulping than oak wood because at the same wood weight loss the extracts contained more hemicelluloses. The highest content of hemicelluloses was in dilute oxalic acid extracts, less in hot water extract and the lowest in green liquor extracts.

A disadvantage of wood extraction by dilute oxalic acid and hot water is degradation of polysaccharides remaining in the extracted wood resulting in the following alkaline cooking process in decrease of yield and strength properties of pulp. It will be necessary to find out at which level of wood weight loss no significant degradation of polysaccharides occurs in the extracted wood.

Alkaline extraction agents promote alkaline degradation of the dissolved hemicelluloses and thus reduce the amount of monosugars, particularly xylose in hydrolysed extracts. The hemicelluloses content in green liquor extract is by half lower when compared with dilute oxalic acid and hot water extraction. The advantages of green liquor extraction are absence of significant degradation of polysaccharides in the extracted wood and availability of green liquor from the recovery cycle of a kraft pulp mill.

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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. Alén, R., Hartus, T., 1988: UV spectrophotometric determination of lignin from alkaline pulping liquor. *Cellulose Chem. Technol.* 22(6): 613-618.
3. Amidon, T.E., Bolton, T.S., Francis, R.C., Gratien, K., 2006: Effect of hot water pre-extraction on alkaline pulping of hardwoods. 2006 TAPPI Engineering, Pulping and Environmental Conf., electronic document, TAPPI Press, Atlanta, Session 57.
4. Browning, B.L., 1967: Holocellulose preparation. *Method of wood chemistry*. Vol. II, 1. Edition, New York, 396 pp.
5. Fišerová, M., Opálená, E., 2012: Hemicellulose extraction from beech wood with water and alkaline solutions. *Wood Research* 57(4): 505-514.
6. Goyal, G.C., Tan, Z., Yin, C., Marsolan, N., Amidon, T., 2007: Biorefinery – An Overview. ESPRAI Conference, New York, October 21, 2007, 6 pp.
7. Green, F., Larsen, M.J., Winandy, J.E., Highley, T.L., 1991: Role of oxalic acid in incipient brown-rot decay. *Material and Organism* 26(3): 191-213.
8. Kautto, J., Saukkonen, E., Henricson, K., 2010: Digestability and papermaking properties of prehydrolysed softwood chips. *BioResources* 5(4): 2502-2519.
9. Li, X., Cai, Z., Horn, E., Winandy, J.E., 2011: Oxalic acid pretreatment of rice straw particles and loblolly pine chips: Release of hemicellulosic carbohydrates. *Tappi J.* 10(5): 41-45.

10. Liu, S., 2010: Woody biomass: Niche position as a source of sustainable renewable chemicals and energy and kinetics of hot water extraction/hydrolysis. *Biotechnology Advances* 28(5): 563-582.
11. Lu, Y.L., Mosier, N.S., 2007: Biomimetic catalysis for hemicellulose hydrolysis in corn stover. *Biotechnol. Prog.* 23(1): 116-123.
12. Mao, H., Genco, J.M., van Heiningen, A.R.P., Zou, H., Luo, J., Pendse, H., 2008: Technical economic evaluation of a northern hardwood biorefinery using the „near-neutral“ hemicellulose pre-extraction process. TAPPI Engineering, Pulping and Environmental Conference, August 24-27, Portland, Oregon, 2008.
13. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005: Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresour. Technol.* 96(6): 673-686.
14. Sjöström, E., 1993: *Wood chemistry fundamentals and applications*. 2nd Edition, San Diego, Academic press.
15. Söderström, J., Pilcher, L., Galbe, M., Zacchi, G., 2003: Combined use of H₂SO₄ and SO₂ impregnation for steam pretreatment of spruce in ethanol production. *Appl. Biochem. Biotechnol.* 105-108: 127-140.
16. Timell, T., 1965: Wood hemicelluloses. II. *Advances in carbohydrate chemistry* 20: 409-483.
17. Thorp, B., Raymond, D., 2004: Forest biorefinery could open the door to bright future for P and P industry. *PaperAge* 120(7): 16-18.
18. van Heiningen, A.R.P., 2007: Converting a kraft pulp mill into an integrated forest products biorefinery. *TAPPSA J.* (May), 21-28.
19. Vakkilainen, E., 1999: Chemical recovery. In: *Chemical pulping*. J. Gullichsen, and C.-J. Fogelholm (eds.), Fapet Oy, Papermaking Sci. Technol. Ser. 6B, Ch. 11, B7-34.
20. Wingren, A., Galbe, M., Zacchi, G., 2003: Techno-economic evaluation of producing ethanol from softwood: Comparison of SSF and SHF and identification of bottlenecks. *Biotechnol. Progr.* 19(4): 1109-1117.
21. Yoon, S.H., van Heiningen, A., 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.

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

