WOOD RESEARCH
59 (4): 2014
557-570

INFLUENCE OF GREEN LIQUOR AND HOT WATER PRE-EXTRACTION OF HARDWOODS ON KRAFT PULPING

Mária Fišerová, Elena Opálená
Pulp and Paper Research Institute
Bratislava, Slovak Republic

(Received May 2014)

ABSTRACT

Mixed hardwood chips were pre-extracted with green liquor and hot water prior to kraft pulping. The hot water extraction rate was higher by a factor of 1.3 compared to extraction with green liquor solution corresponding to 3 % Na_2O charge on ODW. The total monosaccharides content in hydrolysed hot water extract was approximately twice higher than in hydrolysed green liquor extract at the same wood weight loss. The total kraft pulp yield decreased with increase of wood weight loss in pre-extraction. Pulp yield from green liquor pre-extracted chips was approximately the same as from original chips, while pulp yield from hot water pre-extracted chips at 10 % wood weight loss was by about 4 % lower. Addition of 0.1 % AQ in kraft pulping of pre-extracted chips increased total pulp yield by about 1%. Effective alkali charge in kraft pulping was reduced by 3 % in kraft pulping of green liquor pre-extracted chips, and by 1 % of hot water pre-extracted chips in comparison with original chips. The fibre characteristics of kraft pulps from green liquor pre-extracted chips at 10 % wood weight loss were only slightly lower as of kraft control pulps at the same kappa number. Fibre strength (FS number), length (L number) and bonding ability (B number) of pulps from hot water pre-extracted chips were lower by about 3 %, and by about 6 % respectively for bonding ability as fibre characteristics of kraft control pulps. Strength properties of pulps from pre-extracted chips showed similar dependencies. Tensile index of pulps from hot water pre-extracted chips decreased by about 12 %, burst index by about 15 % and tear index by about 5.5 % in comparison with kraft control pulps at a same kappa number.

KEYWORDS: Mixed hardwoods, pre-extraction, green liquor, hot water, hemicelluloses, kraft pulping, anthraquinone, fibre characteristics, strength properties.

INTRODUCTION

The implementation of biorefinery in an existing pulp mill is regarded as a strategy for the sustainable co-production of paper, fuels, power and high value chemicals from various lignocellulosic raw materials (Carvalheiro et al. 2008). The final pulp yield and quality from pre-extracted chips should be preserved even in combination with the hemicelluloses pre-extraction process. However, in order to maintain the pulp yield and minimise the loss of pulp strength, the presence of hemicelluloses is necessary in the fibre matrix (Yoon et al. 2008, Mosello et al. 2010). Therefore, the optimised conditions are always a compromise between hemicelluloses extraction and the quality of the pulp obtained from pre-extracted wood. The pre-extracted wood enriched mainly in cellulose and lignin which will be processed in kraft pulping. Integration of a hemicelluloses pre-extraction process into a pulp mill should cause minimal changes in the final properties of the pulp, which is the main product, and minimal disruption to the normal operation (Yoon et al. 2008, Mendes et al. 2009, Helmerius et al. 2010).

Alkaline pre-extraction is well suited for combination with kraft pulping, since there will be no great change in pH, can be carried out at lower temperatures and pressure than pulping and maintain pulp yield and strength (Al-Dajani and Tschirner 2008, Helmerius et al. 2010, Jun et al. 2012). It has been reported that alkaline extraction would be more suitable for hemicelluloses extraction from hardwoods than softwoods (Helmerius et al. 2010, Walton et al. 2010). This is based on the fact that during kraft pulping, the hemicelluloses are degraded by the alkaline peeling reaction and most of glucomannans in the softwood are degraded while xylan in the hardwood is more stable and solubilised as oligomers (Fardim and Duran 2004, Patt et al. 2006, Schild et al. 2010).

Green liquor (sodium carbonate and sodium sulphide), white liquor (sodium hydroxide and sodium sulphide) and caustic can be used to extract hemicelluloses from wood chips without severely affecting the pulp yield and quality (Yoon et al. 2011, Walton et al. 2010). A technical economic evaluation of the near neutral hemicelluloses extraction process with green liquor from mixed southern hardwood chips was published by researchers of Maine University (Mao et al. 2008). In this analysis an attempt was made to determine the economic feasibility of building a commercial biorefinery that is co-located at an existing kraft pulp mill and is fully integrated with the mill in terms of mass and energy. The recovery cycle is off-loaded because the amount of organics in black liquor is reduced and less white liquor is needed for pulping. These changes would allow increasing pulp production rate if the recovery cycle is the bottleneck. Environmental advantages of the extraction process are reduction of methanol content of the black liquor by about 40 %.

Hot water pre-extraction of hemicelluloses is a cheap and environmentally friendly process, corrosion problems are limited and no sludge is generated in comparison to the dilute acid and alkaline extraction process (Walton et al. 2010). The main advantages of hot water pre-extraction compared to dilute acid or alkali pre-extraction is that the wood is treated in less severe conditions. The mechanism of hot water hydrolysis is based on cleavage of O-acetyl and uronic acid substitutions that results in formation of acetic and other organic acids. This is a self-catalysed reaction at lowering the extract pH to the range of 3-4 (Garrote and Parajó 2002). Depending on the length and temperature of extraction, the final extracted wood yield ranges from 70 to 95 % of original wood. Under the too mild conditions of hot water pre-extraction a low quantity hemicelluloses is solubilised (Lei et al. 2010, Vila et al. 2011).

The hot water hydrolysis is selective to hemicelluloses whereas cellulose is retained in pre-extracted chips and shows improved susceptibility to further treatment due the structural changes of the lignocellulosic matrix (Garrote and Parajó 2002, Lei et al. 2010). The residual polysaccharides in hot water pre-extracted wood are then more susceptible to peeling and dissolution typical of alkaline pulping. In consequence of this, hot water pre-extraction causes a significant and permanent loss in pulp yield and paper strength in subsequent kraft pulping (Yoon et al. 2008, Liu et al. 2009, Mendes et al. 2011). The hot water pre-extracted chips of sugar maple and Brazilian eucalyptus were easier to pulp and bleach but the pulps had worse response to refining and lower strength properties in comparison to the control pulps (Goyal et al. 2007).

Hardwoods extract contain mainly xylose and other xylan-originated degradation products such as xylans of lower polymerization degree, xylose oligomers, acetic acid and furfural. After hydrolysis of polysaccharides, the monosaccharides can be used as a fermentation medium for production of biofuels (ethanol, propanol and butanol) and biopolymers (lactic acid for polylactic acid and polyhydroxyalkanoates (Amidon et al. 2008). According several authors hemicelluloses in the extract could be a base for manufacture of high added value products (Carvalheiro et al. 2008, van Heiningen 2006). Therefore, interest to extract hemicelluloses from chips before pulping and to utilise extracted hemicelluloses has greatly increased in recent years.

The objective of our investigation was to compare of green liquor and hot water impact on hemicelluloses pre-extraction and subsequent kraft pulping and pulp properties of mixed hardwoods.

MATERIAL AND METHODS

Material

Mixed hardwood chips were used in this study. The mixture contained about 50 % beech (*Fagus sylvatica* L.), 20 % oak (*Quercus robur* L.), 6 % turkey oak (*Quercus cerris* L.), 6 % aspen (*Populus tremula* L.), 4 % black locust (*Robinia pseudoacacia* L.), 4 % hornbeam (*Carpinus betulus* L.), 3.5 % ash (*Fraxinus excelsior* L.), 3.5 % poplar (*Populus alba* L.) and 3 % maple (*Acer platanoides* L.). Natural dirt was removed (Tappi test method T 265 cm-09) and the chips of 20x20x3 mm dimensions were used for laboratory pre-extraction and kraft pulping experiments.

Methods

Hemicelluloses pre-extraction

Mixed hardwood chips were extracted with kraft green liquor solution corresponding to 3 % Na_2O charge (3 % GL) on oven dry wood (ODW) and hot water. Green liquor of total titratable alkali (TTA) 121.7 g Na_2O/L (156 g Na_2CO_3/L, 35 g Na_2S/L and 3.5 g NaOH/L) was received from a 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 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-factor of pre-extraction varied from 50 to 450 hrs. After pre-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 extraction yield and wood weight loss. After determination of pre-extracted chips weight the extraction yield (%) on original chips was calculated. The difference between weight (ODW) of original and pre-extracted chips was the wood weight loss (%).

Kraft pulping

Pre-extracted mixed hardwood chips of the other autoclaves were pulped after draining the extraction liquor without chips washing. The volume of residual extraction liquor in chips was about 1/3 of the total liquor. The kraft pulping experiments were performed similarly to the pre-extraction. White liquor of 25 % sulphidity plus fresh water was added to obtain a liquor-to-wood ratio 4:1 at the required effective alkali (EA) charge. Effective alkali charge was 12 % and 12.5 %, 14 % and 14.5 % respectively in kraft pulping experiments of pre-extracted chips and 15 % (all as Na_2O) in kraft control pulping. 0.1 % AQ (anthraquinone) was added in pulping of pre-extracted chips. The kraft control pulping experiments of original beech wood chips were carried out at 170°C. The heating time to this temperature from 100°C was constantly 90 min and the dwell time was in range 30 to 60 min. The corresponding H-factors changed from 432 to 1122 hrs. The kraft pulping experiments of pre-extracted wood chips were performed at constant temperature of 170°C. The dwell time at this temperature was in range of 15 to 60 min, and the corresponding H-factors were in range 230 hrs to 918 hrs. Pulps were disintegrated in a laboratory pulper and thoroughly washed. The wet pulps were placed in a refrigerator for measurement of total pulp yield. Reject content, kappa number and strength properties of pulps were determined after screening on a laboratory screen with 0.25 mm slots.

Analyses

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 original hemicelluloses extract and the extract after one hour hydrolysis with 4 % H_2SO_4 at 121°C in an autoclave was analysed for monosaccharides 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.

White liquor was prepared and analysed according to TAPPI test method T 624 cm-85. The effective alkali concentration of the final black liquor was determined according the modified SCAN-N 33:94 method. Kappa number of pulp was determined according to ISO 302:2004 standard.

The zero-span tensile strength of mixed hardwood kraft pulps was measured by a Pulmac Inc. Zero-Span 1000 apparatus according to ISO 15361:2000 standard. The results were expressed as FS number, L number and B number:

FS number (N/cm) = Avg. > 10 wet zero-span tensile tests normalized to 60 $g.m^{-2}$.

L number (%) = Avg. > 10 re-wet short (0.40 mm) span tensile tests/Avg. > 10 re-wet zero span tensile tests.

B number (%) = Avg. 10 dry short (0.40 mm) span tensile tests/Avg. 10 re-wet short span (0.40 mm) tensile tests.

The kraft pulps were beaten in a laboratory Jokro mill to 30 °SR. Beating degree of pulps was determined according to ISO 5267-1:1999 standard. Handsheets (80 $g.m^{-2}$) were prepared on a Rapid Köthen sheet former according to ISO 5269-2:2004 and were tested for tensile index (ISO 1924-2:2008), burst index (ISO 2758:2001) and tear index (ISO 1974:2012).

RESULTS AND DISCUSSION

Hemicelluloses pre-extraction

The conditions of mixed hardwood chips pre-extraction with green liquor solution with 3 % Na_2O charge on ODW and hot water were selected according to our previous study (Fišerová and Opálená 2012). The wood weight loss by pre-extraction increased with H-factor (Fig. 1). The relationship between wood weight loss and H-factor shows, that the extraction rate is higher with hot water than with green liquor solution. The 10 % of wood weight loss was reached with hot water at H-factor 210 hrs and with 3 % green liquor solution at H-factor 265 hrs. The hot water increased the rate of extraction by a factor of 1.3 in comparison with green liquor solution. 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 hardwood chips (Goyal et al. 2007, Mao et al. 2008).

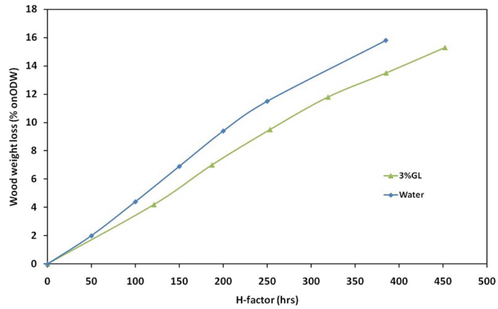

Fig. 1: Wood weight loss versus H-factor of pre-extraction with 3 % green liquor charge and hot water.

Fig. 2 shows development of green liquor and hot water extract pH as a function of wood weight loss. At 10 % wood weight loss in pre-extraction hot water extract pH was 4 and pH of green liquor extract was 6.9. In the case of hot water pre-extraction acidity is developed by splitting off of O-acetyl groups and uronic acid of hemicelluloses resulting in formation of acetic acid and other organic acids.

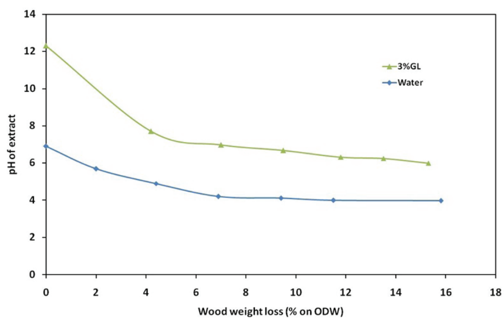

Fig. 2: pH of extract versus wood weight loss in pre-extraction with 3 % green liquor charge and hot water.

The extracts contain dissolved oligosaccharides, minor amount of monosaccharides, lignin, insoluble solids (condensation products), acetic acid, glucuronic acid, furfural, hydroxymethylfurfural, organic degradation products, and residual salts if green liquor was used. The total content of monosaccharides (xylose, arabinose, glucose, galactose and mannose) detected in the extracts after hydrolysis increases with increasing wood weight loss in pre-extraction as shown on Fig. 3.

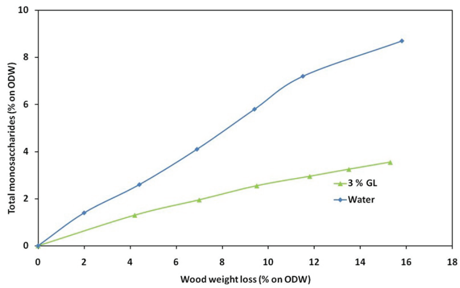

Fig. 3: Total monosaccharides content in hydrolysed extract versus wood weight loss in pre-extraction with 3 % green liquor charge and hot water.

A higher content of total monosaccharides at equal wood weight loss was in hydrolysed hot water extract. At 10 % wood weight loss in hydrolysed hot water extract the total monosaccharides content was 6.25 % on ODW and in hydrolysed green liquor extract 2.6 % on ODW. The same content of monosaccharides was in hydrolysed hot water extract at 4.5 % wood weight loss.

At the same wood weight loss, the total monosaccharides content in hydrolysed green liquor extract was approximately twice lower than in hydrolysed hot water extract, this correlates with higher pH of green liquor solution. At these conditions, lignin solubility is higher (Fišerová et al. 2013a) as well degradation reactions of polysaccharides are more intensive at generation of saccharinic acids and other products (Tunc and van Heiningen 2011).

The hydrolysed hemicellulose extracts from mixed hardwoods 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 monosaccharides content (Fig. 3). At 10 % wood weight loss in pre-extraction xylose content in hydrolysed hot water extract was 4.7 % on ODW, and in hydrolysed green liquor extract 2 % on ODW. The xylose content in hydrolysed extracts represents about 75 % from the total monosaccharides content.

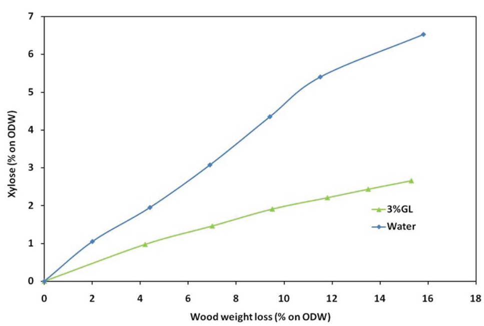

Fig. 4: Xylose content in hydrolysed extract versus wood weight loss in pre-extraction with 3 % green liquor charge and hot water.

Kraft pulping

The goal of pre-extraction is to obtain a relatively high yield of hemicelluloses in extract, but at the same time to minimize degradation of cellulose. The total yield of kraft pulps prepared from mixed hardwood chips pre-extracted with green liquor and hot water at 5 and 10 % of wood weight loss were compared to the kraft control pulps from original mixed hardwood chips.

The relationship between total pulp yield and kappa number of kraft pulps prepared from original, 3 % green liquor charge and hot water pre-extracted mixed hardwood chips is shown in Fig. 5. The total pulp yields of pre-extracted chips were lower in comparison with original chips at the same kappa number. At kappa number 20, the yield of pulp from chips pre-extracted with 3 % green liquor charge at 5 % wood weight loss [5 % GLE-KP (12.5 % EA)] was 47.2 % on ODW and at 10 % wood weight loss [10 % GLE-KP (12 % EA)] was 47 % on ODW. The total pulp yield from original chips [Kraft control (15 % EA)] was 47.5 % on ODW at the same kappa number. The total yield of pulp from chips pre-extracted with hot water at 5 % wood weight loss [5 % WE-KP (14.5 % EA)] was 45.7 % on ODW and at 10 % wood weight loss [10 % WE-KP (14 % EA)] was 43.5 % on ODW. Total pulp yields from chips pre-extracted with 3 % green liquor charge were lower by 0.2 % and 0.5 % respectively than the yield of kraft control pulp at the same kappa number. On the other hand, yields of pulps prepared from chips pre-extracted with hot water were significantly lower (by 1.8 %, and 4 % respectively) than the yield of kraft control pulps.

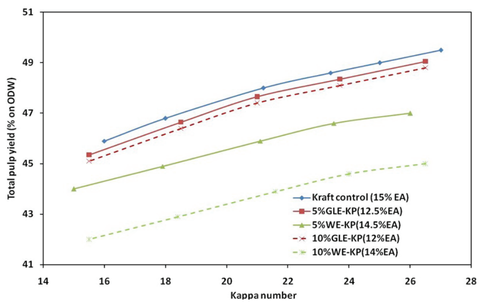

Fig. 5: Total pulp yield versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 5 % and 10 % wood weight loss.

Significantly lower total pulp yield was obtained from hot water pre-extracted chips. Similar results were achieved in our previous experiments (Fišerová et al. 2013b) and by other researchers (Liu et al. 2009, Mendes et al. 2011). Hot water extract pH and pulp yields were lower than from green liquor pre-extracted chips (Fig. 2). Polysaccharides, particularly cellulose undergo degradation in alkaline conditions due to peeling reactions, where reducing end-groups of the cellulose chains are cleaved off, due to random alkaline hydrolysis. In acidic conditions of pre-extraction, hydrolysis causes formation of the new reducing end-groups, which results in severe yield loss in subsequent alkaline pulping.

The results showed that the extraction agent and wood weight loss has influence on the kraft pulp yield prepared from pre-extracted chips. The lower yield of kraft pulps prepared from hot water pre-extracted chips is attributed both to the removal of hemicelluloses during the pre-extraction and to the increased sensitivity of polysaccharides towards alkaline degradation as a result of acidic conditions in pre-extraction.

Effective alkali charge was reduced in kraft pulping of pre-extracted chips, but more in case of green liquor pre-extracted chips. Hot water pre-extracted chips were delignified with 14.5 % EA, and 14 % EA charge respectively, whereas chips pre-extracted with 3 % green liquor charge were delignified with 12.5 % EA, and 12 % EA charge only at 5 %, and 10 % wood weight loss. In kraft control pulping of original hardwood chips EA charge was 15 %. Lower EA charge in kraft pulping was applied due to wood weight loss in pre-extraction. Additional reasons for lower EA charge in pulping is higher pH of green liquor extract (approximately 1/3 extract in dissolution of hemicelluloses volume enters into pulping) and lower lignin content in pre-extracted chips (Fišerová et al. 2013b). At the same kappa number pulp yields were higher due to lower alkali consumption in dissolution of hemicelluloses.

Addition of AQ in kraft pulping

AQ is an important catalyst that has been used widely in alkaline pulping for its effectiveness in acceleration of delignification and increasing pulp yield. AQ was added into kraft pulping of chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss (Fig. 6). Total pulp yield from green liquor pre-extracted chips increased by addition of 0.1 % AQ into pulping by 0.8 % whereas same addition of AQ into kraft pulping of hot water pre-extracted chips increased total pulp yield by 1 % at kappa number 20 in comparison to pulping without AQ addition. The pulp yields from green liquor pre-extracted chips prepared with addition of AQ were higher by 0.3 % than pulp yields of kraft control pulp at the same kappa number, while the pulp yields from hot water pre-extracted chips were lower by 3 %.

The results confirmed the higher stabilizing effect of AQ as oxidative agent on reducing end groups of polysaccharides in kraft pulping of hot water pre-extracted chips in comparison with green liquor pre-extracted chips. This probably may be connected with higher content of reducing polysaccharides end groups of hot water pre-extracted mixed hardwood chips.

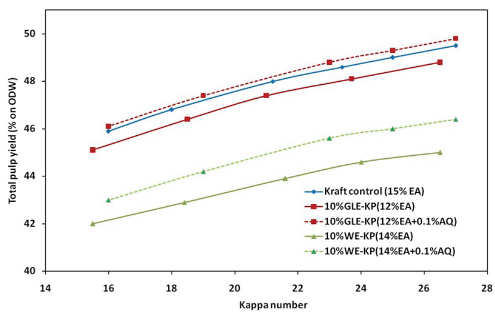

Fig. 6: Total pulp yield versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss, followed by kraft pulping with and without addition of 0.1 % AQ.

Fibre characteristics of kraft pulps

Single fibre strength and length, also the ability of the fibres to swell and form inter-fibre bonds are very important for the strength of pulp. In the pulp and paper industry, zero-span tensile strength testing of pulp handsheets is often considered as an indicator of mean fibre strength. Fibre characteristics of kraft pulps are expressed as FS number (fibre strength), L number (fibre length) and B number (bonding ability).

The relationships between FS number (Fig. 7), L number (Fig. 8) and B number (Fig. 9) and kappa number of kraft pulps prepared from original chips [Kraft control (15 % EA)], 3 % green liquor charge [10 % GLE-KP (12 % EA)] and hot water [10 % WE-KP (14 % EA)] pre-extracted mixed hardwood chips at 10 % wood weight loss show similar development.

The fibre strength (FS number) of kraft control pulps from original chips are the highest at the same kappa number (Fig. 7). Influence of green liquor pre-extraction on fibre strength of mixed hardwood pulps is insignificant. The fibre strength of pulps from hot water pre-extracted were by about 3 % lower as the fibre strength of kraft control pulps at the same kappa number.

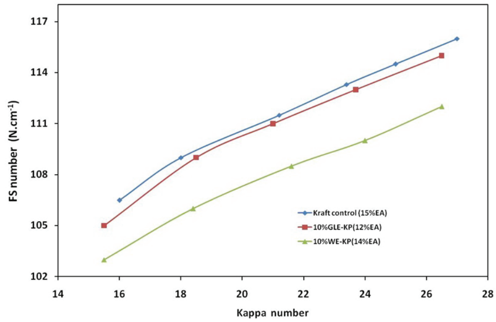

Fig. 7: FS number versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

Fibre length (L number) of pulps from hot water pre-extracted mixed hardwood chips is by about 6 % lower in comparison with kraft control pulps at the same kappa number, while L number of pulps from green liquor pre-extracted chips is only slightly lower (Fig. 8).

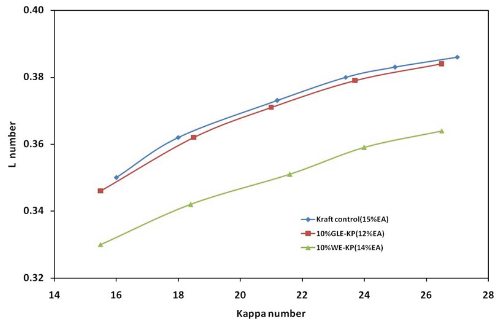

Fig. 8: L number versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

The dependence of bonding ability expressed as B number on kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss is shown on Fig. 9. The fibre bonding ability of kraft pulps was influenced by the extraction agent. The fibre bonding ability of pulps from hot water pre-extracted pulps is lower by about 6 % in comparison with kraft control pulps at the same kappa number. On the other hand, the bonding ability of pulps from green liquor pre-extracted chips differs slightly. The fibre bonding ability of pulps correlates with the total pulp yield (Fig. 5).

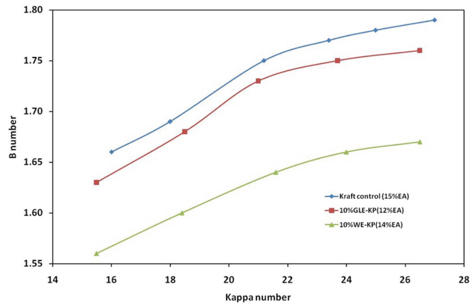

Fig. 9: B number versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

Strength properties of kraft pulps

Tensile index, burst index and tear index of kraft pulps (kappa number 15.5-27) prepared from original, 3 % green liquor charge and hot water pre-extracted chips at 10 % wood weight loss were determined at a beating degree 30°SR.

Tensile index of kraft pulps prepared from original and pre-extracted mixed hardwood chips increased with kappa number (Fig. 10). The results show that tensile index of kraft pulps prepared from chips pre-extracted with green liquor at 10 % wood weight loss was slightly lower (by about 1 %) than that of the kraft control pulp at the same kappa number. Tensile index of kraft pulps prepared from hot water pre-extracted chips was by about 12 % lower compared with kraft control pulp at the same kappa number.

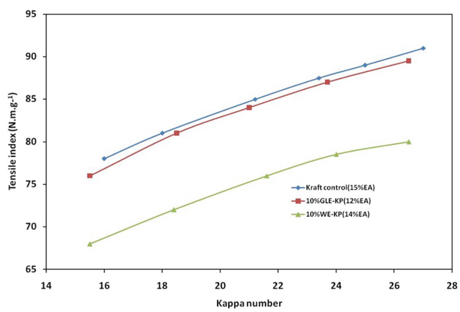

Fig. 10: Tensile index versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

The burst index of kraft pulps prepared from pre-extracted chips has a similar development with kappa number than the tensile index (Fig. 11). Burst index of pulps prepared from green liquor pre-extracted chips at 10 % wood loss was by about 2 % lower than that of the kraft control pulp at the same kappa number, while burst index of pulps from hot pre-extracted chips was by about 15 % lower.

The higher value of tensile and burst index of kraft pulps prepared from green liquor pre-extracted chips correspond with higher total pulp yield (Fig. 5) and, consequently, with higher hemicelluloses content in comparison with pulps from hot water pre-extracted pulps. It can be concluded that these parameters are particularly a function of inter-fibre bonding strength. The results indicate that the mild alkaline pre-extraction has no negative effect on bonding ability.

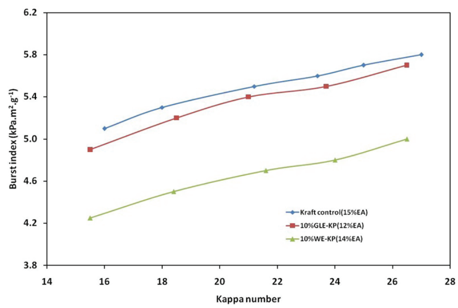

Fig. 11: Burst index versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

Tear index of kraft pulp from original chips and chips pre-extracted with 3 % green liquor charge and hot water decreased with increasing kappa number (Fig. 12). Tear index of pulps prepared from green liquor pre-extracted chips at 10 % wood loss was slightly lower (about 0.7 %) than that of the kraft control pulp at the same kappa number. Tear index of pulps prepared from chips pre-extracted with hot water was by about 5.5 % lower than that of kraft control pulp at same kappa number.

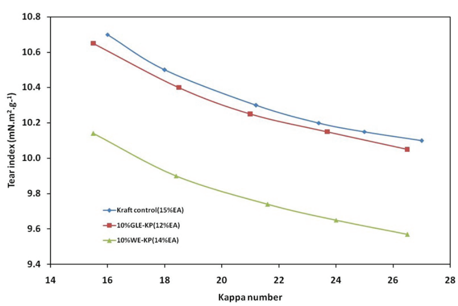

Fig. 12: Tear index versus kappa number of kraft pulps from original and mixed hardwood chips pre-extracted with 3 % green liquor charge and hot water at 10 % wood weight loss.

The results suggest that the tear index decreased with degradation of cellulose in pre-extraction which reduces fibre strength. This corresponds with lower pH value of extract (Fig. 2) and higher content of glucose in extract (Fišerová and Opálená 2012). Tear index is dependent on the total number of fibres participating in sheet rupture, fibre strength, fibre length and number and strength of fibre-to-fibre bonds. It is possible to conclude that pulp strength properties are influenced by properties of extraction solution and wood weight loss (Fišerová et al. 2013b). However negative impact of hot water pre-extraction on tensile, burst and tear strength was confirmed.

CONCLUSIONS

Pre-extraction of hemicelluloses from mixed hardwoods can be applied prior to kraft pulping in order to use extracted hemicelluloses for biofuels or chemicals production. The total monosaccharides content in hydrolysed green liquor extracts was markedly lower as in hydrolysed hot water extracts at the same wood weight loss. Approximately the same total monosaccharides content was in hydrolysed hot water extract at 4.5 % wood weight loss as in hydrolysed green liquor extract at 10 % wood weight loss. Hot water increased the rate of extraction by a factor of 1.3 in comparison with green liquor.

A major advantage of the green liquor pre-extraction of mixed hardwoods is that the pulp yield and properties of pulp remain essentially the same as that of kraft control pulp from original chips. The pulp yield from hot water pre-extracted chips was lower in comparison with the yield of kraft control pulp at the same kappa number. The pulp yield decreased with increase of extracted wood amount, at 5 % wood weight loss by about 1.8 % and at 10 % wood weight loss by about 4 %. Addition of 0.1 % AQ in pulping of hot water pre-extracted chips increased total pulp yield by about 1 % and 0.8 % of pulps from green liquor pre-extracted chips.

Fibre characteristics as fibre strength (FS number), length (L number) and bonding ability (B number) of kraft pulps prepared from green liquor pre-extracted chips at 10 % wood weight loss were only gently lower than of kraft pulps from original chips. Fibre strength of pulps from hot water pre-extracted chips was by about 3 %, while fibre length and bonding ability by about 6 % lower as of pulps from original chips at the same kappa number. Tensile, burst and tear index of pulps from green liquor pre-extracted chips were approximately the same as from original wood chips, while tensile index of pulps from hot water pre-extracted chips was lower by about 12 %, burst index by about 15 % and tear index by about 5.5 % compared with the kraft control pulps at the same kappa number.

Potential benefit of hemicelluloses pre-extraction with green liquor is reduction of alkali charge in the pulping process from 15 to 12 % EA. The advantage of green liquor pre-extraction is availability of green liquor from the recovery cycle. Disadvantages of green liquor pre-extraction compared to hot water pre-extraction process is lower hemicelluloses content in the extract and that the extract contains inorganic salts from green liquor.

Hot water extraction releases higher amount of hemicelluloses but does so at expense of kraft pulp yield, fibre characteristics and strength properties of pulp. The strength properties of the pulp from hot water pre-extracted chips are not acceptable for production of very high strength paper.

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 1: Alkaline extraction. Tappi J. 7(6): 3-8.

2. Amidon, T.E., Wood, C.D., Shupe, A.M., Wang, Y., Graves, M., Liu, S., 2008: Biorefinery: Conversion of woody biomass to chemicals, energy and materials. J. Biobased Materials and Bioenergy 2: 100-120.
3. Carvalheiro, F., Duarte, L.S., Girio, F.M., 2008: Hemicellulose biorefineries: A review on biomass pretreatment. Journal of Scientific and Industrial Research 67: 849-864.
4. Fardim, P., Duran, N., 2004: Retention of cellulose, xylan, and lignin in kraft pulping of *Eucalyptus* studied by multivariate data analysis: Influence of physicochemical and mechanical properties of pulp. Journal Brazil Chemistry Society 15(4): 514-522.
5. Fišerová, M., Opálená, E., 2012: Hemicelluloses extraction from beech wood with water and alkaline solutions. Wood Research 57(4): 505-514.
6. Fišerová, M., Opálená, E., Illa, A., 2013a: Comparative study of hemicelluloses extraction from beech and oak wood. Wood Research 58(4): 543-554.
7. Fišerová, M., Opálená, E., Stankovská, M., 2013b: Influence of hemicelluloses pre-extraction on kraft pulping. Papír a celulóza 68(4): 108-112.
8. Garrote, G., Parajó, J.C., 2002: Non-isothermal autohydrolysis of *Eucalyptus* wood. Wood Science and Technology 36: 111-123.
9. Goyal, G, Tan, Z., Yin, C., Marsolan, N., Amidon, T.E., 2007: Biorefinery-An Overview. In Proceedings of the 3rd International Conference on Eucalyptus Pulp, 2007, Belo Horizonte, Brazil. Pp 232-238.
10. Van Heiningen, A., 2006: Converting a kraft mill into an integrated forest biorefinery. Pulp Paper Canada 107(6): 38-43.
11. Helmerius, J., von Walter, J.V., Rova, U., Berglund, K.A., Hodge, D.B., 2010: Impact of hemicelluloses pre-extraction for bioconversion on birch Kraft pulp properties. Bioresource Technol. 101(15): 5996-6005.
12. Jun, A., Tschirner, U.W., Tauer, Z., 2012: Hemicellulose extraction from aspen chips prior to kraft pulping utilizing kraft white liquor. Biomass and Bioenergy 37: 229-236.
13. Lei, Y., Li, J., Sun, R., 2010: Effect of hot water extraction on alkaline pulping of bagasse. Biotechnology Advances 28: 609-612.
14. Liu, S., Mishra, G.K., Amidon, T.E., Gratien, K., 2009: Effect of hot-water extraction of woodchips on kraft pulping of eucalyptus woodchips. J. Biobased Mater. Bioenergy 3: 363-369.
15. Mao, H., Genco, J.M., van Heiningen, A., Pendse, H., 2008: Technical economic evaluation of a hardwood biorefinery. Using the „near-neutral“ hemicellulose pre-extraction process. J. Bio-based Materials and Bio-energy 2(2): 1-9.
16. Mendes, C.V.T., Carvalho, M.G.V.S., Baptista, C.M.S.G., Rocha, J.M.S., Soares, B.I.G., Sousa, G.D.A., 2009: Valorisation of hardwood hemicelluloses in kraft pulping process by using an integrated biorefinery concept. Food Bioprod. Process 87(3): 197-207.
17. Mendes, C.V.T., Rocha, J.M.S., Sousa, G.D.A, Graça, M., Carvalho, M.G.V.S., 2011: Extraction of hemicelluloses prior to kraft cooking: A step for an integrated biorefinery in the pulp mill. O Papel 72(9): 79-83.
18. Mosello, A.Z., Tahir, P., Resalati, H., Shamsi, S.R.F, Mohmamed, A.Z., 2010: A review of literatures related of using kenaf for pulp production (beating, fractionation a recycled fiber). Modern Applied Science 4(9): 21-29.
19. Patt, R., Kordsachia, O., Fehr, J., 2006: European hardwoods versus *Eucalyptus globulus* as raw material for pulping. Wood Science and Technology 40: 39-48.
20. Schild, G., Sixta, H., Testova, L., 2010: Multifunctional alkaline pulping, delignification and hemicelluloses extraction. Cellulose Chem. Technol. 44(1-3): 35-45.

21. Tunc, M.S., van Heiningen, A., 2011: Characterization and molecular weight distribution of carbohydrates isolated from autohydrolysis extract of mixed southern hardwoods. Carbohydr. Polym. 83(1): 8-11.
22. Vila, C., Romero, J., Francisco, J.L., Garrotte, G., Parajó, J.C., 2011: Extracting value from *Eucalyptus* wood before kraft pulping: Effect of hemicelluloses solubilization on pulp properties. Bioresource Technology 102(8): 5251-5254.
23. Walton, S.L., Hutto, D., Genco, J.M., Walsum, G.P., van Heiningen, A.R.P., 2010: Pre-extraction of hemicelluloses from hardwood chips using an alkaline wood pulping solution followed by kraft pulping of the extracted wood chips. Industrial and Engineering Chemistry Product and Research 49(24): 12638-12645.
24. Yoon, S.H., Macevan, K., 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(6): 22-27.
25. Yoon, S.H., Tunc, M.S., van Heiningen, A., 2011: Near-neutral pre-extraction of hemicelluloses and subsequent kraft pulping of southern mixed hardwoods. Tappi J. 11(1): 7-15.

Mária Fišerová, Elena Opálená
Pulp and Paper Research Institute
Lamačská Cesta 3
841 04 Bratislava
Slovak Republic
Corresponding autor: fiserova@vupc.sk