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REDUCTION OF YIELD LOSS IN KRAFT PULPING OF HOT WATER PRE-EXTRACTED BEECH WOOD

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ABSTRACT

The effect of polysaccharides stabilizing agent on kraft pulp yield from hot water pre-extracted beech chips was investigated. Total pulp yield from hot water pre-extracted chips exhibit a linear decrease with increasing wood weight loss, while the yield of total monosaccharides in hydrolysed extracts increased. Following that in laboratory pulping experiments pre-extracted chips with 10 % wood weight loss were used at which the total pulp yield decreased by 4.2 % in comparison with original beech chips. As reductive agent in the intermediate step sodium borohydride (SBH) in a mild alkaline sodium sulphide (SS) solution was used. The combination of reductive treatment with addition of oxidative agent anthraquinone (AQ) in kraft pulping of hot water pre-extracted wood chips increased total yield pulp by 2.7 %. Combined simultaneous application of reductive and oxidative agents in kraft pulping of hot water pre-extracted chips increased pulp yield by 2.3 %. Both methods of pulp yield improvement have positive effect on tensile strength, but the intermediate step treatment of hot water pre-extracted chips caused slight reduction in tear strength. From economic standpoint application of polysaccharides stabilizing agents in kraft pulping is preferable to an intermediate step, even though by application of an intermediate step the yield of monosaccharides increased by about 2 % and effective alkali charge in the pulping process decreased by 3 %.

KEYWORDS: Beech wood, hot water pre-extraction, monosaccharides, sodium borohydride, anthraquinone, kraft pulping, strength properties.

INTRODUCTION

Pre-extraction of hemicelluloses from wood prior to pulping has recently gained increased attention in the pulp and paper industry, but the lack of clear understanding of influence of pre-extraction on pulp properties is one of the barriers to its commercial implementation. Since the hemicelluloses content directly affects the surface properties of pulp fibres, for all that is very important to find out how pre-extraction process can impact pulp fibre quality. The heating value of polysaccharides is only half that of lignin, therefore combustion of dissolved hemicelluloses in black liquor is not their optimal economical utilization (Heiningen 2006). The hemicelluloses can be used in addition to pulp for the production of higher value-added products exceeding more than 20 times their fuel value.

Hot water was found to be an effective solvent in the extraction of hemicelluloses from wood chips (Yoon et al. 2008). Advantage of this process is that no chemicals other than water are involved, no problems of equipment corrosion, no necessary sludge treatments or acid recycling, and there is a good yield of saccharides solutions and low by product formation (Al-Dajani et al. 2009). Hot water pre-extraction produces oligomers and monomers, which are dissolved in extract, but it also partly degrades polymers in the chips. The residual partly degraded polysaccharides in hot water pre-extracted wood are more susceptible to peeling and dissolution typical of alkaline pulping, primarily due the presence of a large number of reducing end groups formed during autohydrolytic cleavage of the glycosic bonds mostly catalyzed by released acetic acids from wood. In consequence of this, hot water pre-extraction caused a significant and permanent loss in pulp yield and paper strength in subsequent kraft pulping (Yoon et al. 2008, Liu et al. 2009). The hot water pre-extracted chips of sugar maple and Brazilian eucalyptus were easier to pulp and bleach but the pulps had worse refinability and lower strength properties in comparison to control pulps (Goyal et al. 2007).

Since the value of pulp is still the most important concern in the pulp and paper industry, this economic limitation related to yield loss caused by hemicelluloses pre-extraction emphasizes the need to search for an alternative or modification to the existing kraft process for its transition to integrated forest biorefineries. In acidic conditions, hydrolysis causes formation of the new reducing end groups, which results in severe yield loss in subsequent alkaline pulping. Therefore, it is conceivable that there is room for optimization of the pulping conditions to minimize such degradation. While the decrease of polymerization degree in hot water pre-extraction is irreversible, conversion of the reducing end-groups, namely carbonyl groups, to other functional groups by oxidation, reduction or derivatization before alkaline pulping or in situ could decelerate further degradation to certain extent (Mänttäri et al. 2011).

Chemical additives can be used in pulping to reduce reactions of polysaccharides or increase reactivity of lignin. The method of increasing pulp yield is to stabilize the polysaccharides with regard to peeling by treating the carbonyl end group with oxidizing or reducing agent. Additives that have been tried previously include sodium dithionite, SBH, polysulfide, hydrogen sulphide, AQ, and surfactants (Courchene 1998).

Polysulfide and AQ are well-known pulping additives to increase pulp yield. Polysulphide and AQ oxidize the reducing end groups of polysaccharides to aldonic acid groups, thus stabilizing the polysaccharides against peeling reactions. AQ additionaly accelerates the delignification rate of pulping (Teder 1969, Dimmel et al. 2003).

One important modifications of the kraft process is the pretreatment of hot water pre-extracted wood chips with reducing agent, such as SBH, under the mild alkaline conditions prior to kraft pulping (Meller 1963). The presence of SBH would be expected to have a large effect unless the hemicelluloses were degraded too extensively during the water pre-extraction. The stabilization of polysaccharides of wood chips by pretreatment with SBH is attributed to the reaction by which the terminal aldehyde end groups are reduced to primary alcohols (MacDonald and Franklin 1969).

The effect of end group stabilizing additives such as SBH, AQ and anthraquinone-2-sulphonic acid sodium salt on the rates of the yield loss reactions in the prehydrolysis-soda AQ process of cotton linters was investigated (Testova et al. 2014). SBH and anthraquinone-2-sulphonic acid sodium salt ensured a cellulose yield gain of 13 and 11 %, respectively, compared to the control pulping. Both stabilization agents decreased the content of the reducing end groups, while in the case of anthraquinone-2-sulphonic acid sodium salt stabilization a 25 % increase in carboxyl group content compared to reference was also observed. The addition of end group stabilizers resulted in a significant decrease in the peeling-to-stopping rate constant ratio.

The effect of kraft pulping process modification integrated with hemicelluloses pre-extraction on properties of pulp produced from softwood chips were investigated (Yoon et al. 2011). Three process modifications were designed to improve the yield recovery capability of kraft pulping preceded by hot water pre-extraction including oxidative, oxidative-reductive, and oxidative followed by oxidative-reductive.

The goal of our investigation was to compare influence of oxidizing and reducing agents on polysaccharides reducing end group stabilization of hot water pre-extracted beech chips. Two stabilization pathways were applied, namely, oxidation to aldonic acids by AQ in kraft pulping and reduction to alditols by SBH which was perfomed in an intermediate step before kraft pulping with addition of AQ. Application of SBH and AQ was carried out also together in kraft pulping of hot water pre-extracted beech chips.

MATERIAL AND METHODS

Material

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

Methods

Hemicelluloses pre-extraction

Wood chips were extracted with hot water in a series of six laboratory autoclaves, each of 0.75 L volume. The autoclaves were filled with 100 g ODW (oven dry weight) screened beech 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 15 to 48 min to attain 5, 10 and 15 % wood weight loss. 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 wood weight losses. After determination of extracted chips weight and the solids the pre-extraction yield (%) on original chips was calculated. The difference between weight of original and pre-extracted chips was the wood weight loss (%).

Intermediate step

The hot water pre-extracted beech chips at 10% of wood weight loss were treated with 5 % charge of SS and the mixture of SBH (0.5 %) in a mild alkaline solution of SS (5 %) at a temperature 140°C for 90 min. The other conditions were identical as in the pre-extraction experiments.

Kraft pulping

Pre-extracted beech wood chips without or with intermediate step were pulped after draining the extraction liquor without chips washing. Volume of the residual extraction liquor in chips was about 1/3 of the total liquor. The kraft pulping experiments were performed similarly to the pre-extraction or intermediate step treatment experiments. White liquor of 25 % sulphidity plus fresh water was added to pre-treated chips to obtain a liquor-to-wood ratio 4:1 at the required effective alkali (EA) charge. Effective alkali charge was 13.5, 14 and 14.5 % for pulping of hot water pre-extracted chips, 12, and respectively 11 % for pulping of chips after intermediate step treatment and 15 % (all as Na_2O) in kraft control pulping. 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 the range 30 to 60 min. The kraft pulping experiments of pre-extracted wood chips were performed at constant temperature of 170°C. Dwell time at this temperature was in range of 15 to 60 min. Unless otherwise specified, in the kraft pulping experiments also 0.1 % AQ was added. Pulps were disintegrated in a laboratory pulper and thoroughly washed and total pulp yield determined. Reject content, kappa number and strength properties of pulps were determined after screening on a laboratory screen with 0.25 mm slots.

Analyses

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 liquors were prepared and analysed according to TAPPI test method T 624 cm-85. Kappa number of pulp was determined according to ISO 302: 2004 standard. 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) and tear index (ISO 1974: 2012).

RESULTS AND DISCUSSION

Pre-extraction effect on monosaccharides and pulp yield

The extraction solution type and wood weight loss has influence on kraft pulp yields and strength properties prepared from pre-extracted chips. The goal is to obtain a relatively high yield of hemicelluloses in extract, but at the same time to minimize pulp yield and strength loss.

The conditions of beech wood chips pre-extraction with hot water were selected according to our previous study (Fišerová and Opálená 2012). The content of total monosaccharides (xylose, arabinose, glucose, galactose and mannose) that are detected in the extraction liquor following acid hydrolysis increases with increasing wood weight loss in pre-extraction (Fig. 1). As expected, a linear relationship was observed between total monosaccharides content in hydrolysed extracts and weight loss of beech chips measured after hot water pre-extraction (R^2=0.998) indicating that the wood weight loss could be an important control parameter which makes the monosaccharides content of the hydrolysed extracts predictable in a reasonable way.

Total yield of kraft pulps prepared from beech chips pre-extracted with hot water at 5, 10 and 15 % of wood weight loss (WE) were compared to the kraft control pulps (Kraft control) from original beech chips (Fig. 2). Pulp yields of pre-extracted chips were lower in comparison with the kraft control pulp at the same kappa number. The total pulp yield at a given kappa number decreased as the hot water pre-extraction level increased. At kappa number 20, the yield of pulp from pre-extracted chips at 5 % wood weight loss was by 1.7 %, at 10 % by 4.2 % and at 15 %

wood weight loss was by 6.2 % lower in comparison with kraft control pulp. The pulp yield from original chips was 48.4 % on ODW at same kappa number.

The lower pulp yield is attributed both to the removal of hemicelluloses during the pre-extraction and to the increased vulnerability of polysaccharides towards alkaline degradation as a result of acidic conditions at pre-extraction.

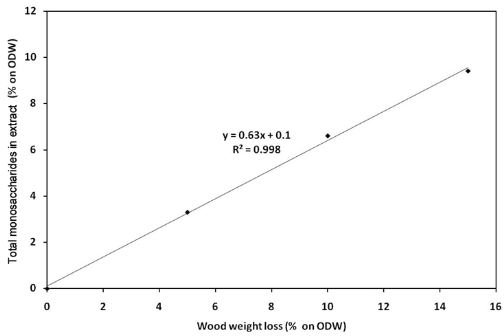

Fig. 1: Total monosaccharides content in hydrolysed extracts versus wood weight loss.

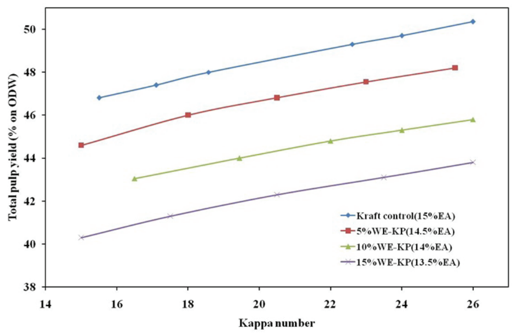

Fig. 2: Total pulp yield versus kappa number of pulps from original and hot water pre-extracted beech chips at 5, 10 and 15 % wood weight loss.

Total pulp yields at kappa number 20 plotted against total monosaccharides content in hydrolysed extracts is shown on Fig. 3. The pulp yield decreased significantly as the total monosaccharides in hydrolysed extracts increased, it means with increased wood weight loss in extraction process (Fig. 1). The linear relationship observed between total pulp yields and total monosaccharides content in hydrolysed extracts ((R^2=0.993) was analogous to wood weight loss ((R^2=0.998)).

The results confirmed that with hot water it was not possible to extract a significant amount of hemicelluloses from beech wood chips without also causing a sizable loss in yield of the kraft pulp. On the present, pulp is the most important product in the pulp and paper industry, this economic limitation related to yield loss caused by hemicelluloses pre-extraction emphasizes the need to search for an alternative pulping process or modification of the kraft pulping process enabling transition to integrated forest biorefineries. Stabilization of polysaccharides was performed as an intermediate step and/or during kraft pulping of hot water pre-extracted beech chips.

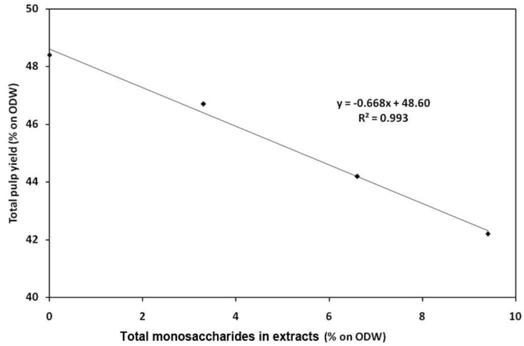

Fig. 3: Total pulp yield at kappa number 20 versus total monosaccharides in hydrolysed extracts from original and hot water pre-extracted beech chips at 5, 10 and 15 % wood weight loss.

Intermediate step stabilization

Effect on pulp yield

At kraft pulping of hot water pre-extracted wood chips, the residual polysaccharides were extensively degraded and dissolved in the alkaline pulping liquor, primarily due to the presence of a large amount of reducing end groups formed during the auto hydrolytic cleavage of the glycosidic bonds mostly catalysed by acetic acids released from wood.

Therefore, the effect of SBH as polysaccharides end group reducing agent on kraft pulp yield improvement of hot water pre-extracted beech chips at 10 % wood weight loss were studied. The pre-extracted chips were treated in an intermediate step with SBH under alkaline conditions. To maximize reducing effectiveness, SBH was dissolved in a mild alkaline solution of SS and this mixture was used as treatment liquor for polysaccharides end group stabilization of hot water pre-extracted beech chips prior to kraft pulping with AQ addition. SS undergoes hydrolysis in aqueous solutions, which is governed by pH-dependent equilibrium, to generate hydroxide ion, hydrogen sulphide and hydrosulphide ions. Since the pKa value of hydrogen sulphide is about 7 at room temperature, the amount of un-ionized hydrogen sulphide should be significant at the near-neutral or mild alkaline pH level of the intermediate step. Therefore, it is possible to assume that additional end group stabilization can also be taking place by the thiolation with hydrogen sulphide, derived from SS, by which some aldehyde end groups of polysaccharides are reduced to thioalditols (Vinje and Worster 1969). The beneficial effect of SS on kraft pulp yield of water pre-extracted wood chips was confirmed (Yoon et al. 2009).

In order to investigate the presumed beneficial effects of SS on kraft pulp yield, the water pre-extracted beech chips at 10 % wood weight loss were treated with 5 % charge of SS in the intermediate step and with addition of 0.1 % AQ in kraft pulping (Fig. 4). The addition of AQ increased pulp yield from water pre-extracted chips by 1 %, while intermediate treatment with SS increased the pulp yield by 1.6 % at the same kappa number. It can be speculated that treatment with SS increased the pulp yield by about 0.6 %.

Influence of intermediate treatment using the mixture of SS (5 %) and SBH (0.5 %) on kraft pulp yield of hot water pre-extracted chips with addition of 0.1 % AQ in pulping is presented on Fig. 4. The total pulp yield of water pre-extracted beech chips treated with SBH in a mild alkaline SS solution was by 2.7 % higher in comparison with hot water pre-extracted chips at the same kappa number. Considering about 1.6 % pulp yield gain after the treatment of water pre-extracted chips with SS and addition of AQ in pulping, then treatment with addition of SBH increased the pulp yield by 1.1 % at the same kappa number. The results confirmed the stabilizing effect of reductive treatment with SBH in a mild alkaline solution of SS on polysaccharides of hot water pre-extracted beech chips against alkaline hydrolysis in the subsequent kraft pulping stage. The results are in accordance with the results obtained for pre-extracted southern pine chips (Yoon et al. 2009).

Double extraction of beech chips using SBH in a mild alkaline (SS) solution after hot water extraction showed about 2 % higher total monosaccharides yield than of a simple extraction with hot water and the wood weight loss was increased by 7 %. In addition effective alkali charge was reduced in kraft pulping by about 3 %.

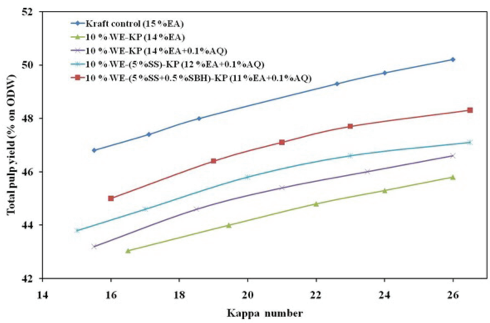

Fig. 4: Total pulp yield versus kappa number of pulps from original and hot water pre-extracted beech chips at 10 % wood weight loss treated in intermediate stage with SS, the mixture (SS+SBH) and addition of AQ in kraft pulping.

Effect on pulp properties

Handsheets were prepared from kraft pulps beaten to 30°SR from original beech chips, hot water pre-extracted chips (10 % wood weight loss) without and with intermediate polysaccharides stabilization with SS and the mixture SS with SBH (SS+SBH). On Fig. 5 tensile index and tear index of kraft pulps are compared at kappa number 20. The tensile index of the kraft pulp from hot water pre-extracted chips was approximately 12 % lower than of the kraft control pulp. At application of AQ in kraft pulping of hot water pre-extracted chips tensile index increased by 7 %. The tensile index of pulps from chips after polysaccharides stabilizing in the intermediate step was approximately 9 %, respectively 11 % higher than that of the pulp from hot water pre-extracted pulp. The tensile index of kraft pulps correlates roughly with total yield and, consequently, with hemicelluloses content in pulps (Fig. 4). These results indicate that the intermediate treatment of hot water pre-extracted chips has a positive effect on inter-fibre bonding capabilities of kraft pulps, because tensile index is a function of inter-fibres bonding strength.

However, pulps from the chips treated with polysaccharides stabilizers showed somewhat reduced tear resistance than pulps from hot water pre-extracted chips. The tear index of the kraft pulp from water pre-extracted chips was approximately 6 % lower than of the kraft control pulp. The tear index of pulps from chips after polysaccharides stabilizing intermediate treatment was approximately 7 % lower than of the pulp from hot water pre-extracted chips. This trend can be commonly encountered in most high-yield pulping process. In a high-yield process, further loading of polysaccharides on the fibres with an increasing amount of hemicelluloses would reduce the proportion of cellulose and the number of fibres in the sheet to critical levels, thereby lowering the tear resistance (Clark 1985).

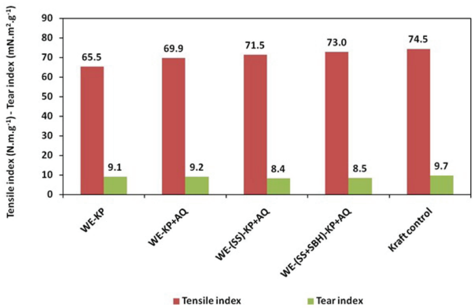

Fig. 5: Comparison of tensile index and tear index of pulps (kappa number 20) beaten to 30°SR from original and hot water pre-extracted beech chips at 10 % wood weight loss treated in intermediate step with SS, the mixture (SS+SBH) and addition of AQ in kraft pulping.

The reductive modification of hot water pre-extracted beech chips kraft pulping using SBH in a mild alkaline SS solution in the intermediate step clearly showed a promising effects on preserving pulp yield and handsheet strength properties even though 10 % wood mass was dissolved in hot water pre-extraction process.

The combination of treatment with SBH (0.5 %) in a mild alkaline SS (5 %) solution, and addition of 0.1 % AQ in kraft pulping of hot water pre-extracted beech chips caused about 65 % recovery of pulp yield loss in the subsequent kraft pulping in comparison with kraft control pulping of original beech chips. No significant changes in strength properties was observed for pulps prepared from a chips after reductive stabilization of polysaccharides preceded by hot water pre-extraction, except slight reduction in tear strength.

Stabilization in pulping

Effect on pulp yield

Preliminary results confirmed that SBH is an effective polysaccharides stabilizing additive for hot water pre-extracted chips in following kraft pulping. The application of SBH in an intermediate step is costly for its use on a technical scale in the pulp and paper industry. Therefore, laboratory experiments were performed with addition of SBH in the kraft pulping process instead of performing a separate stage before pulping. Further, additions of AQ and SBH in pulping experiments were tested.

The relationship between total pulp yield and kappa number of kraft pulps from original and hot water pre-extracted beech chips at 10 % wood weight loss with addition of AQ, SBH and their mixture in kraft pulping is shown on Fig. 6. Kraft pulp yields from hot water pre-extracted chips were increased after addition of 0.5 % SBH in the pulping process by 1.7 %, while addition of 0.1 % AQ increased the pulp yields by 1 % at the same kappa number.

Application of the mixture SBH and AQ in pulping resulted in increased pulp yield by 2.3 % (Fig. 6). The results suggest, that addition of AQ reduced the stabilization effect of SBH (Fig. 4). This effect may be explained by a competing reaction occurring between SBH and carbonyl groups of AQ confirmed by colour change from light yellow to red upon the heat-up of the alkali-AQ-SBH mixture (Testova et al. 2014).

The application of reducing agent SBH (0.5 %) with oxidative agent AQ (0.1 %) in kraft pulping process of hot water pre-extracted beech caused about 55 % recovery or improvement of pulp yield in comparison with kraft control pulp.

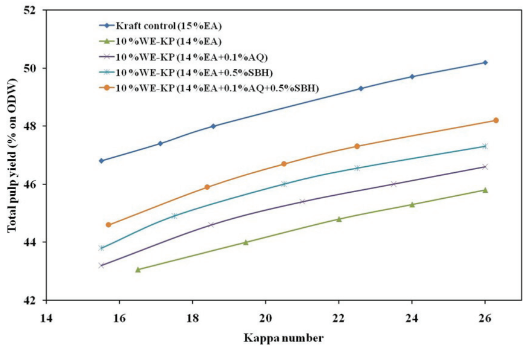

Fig. 6: Total pulp yield versus kappa number of pulps from original and hot water pre-extracted beech chips at 10 % wood weight loss with addition of AQ, SBH and the mixture (AQ+SBH) in kraft pulping.

Effect on pulp properties

Handsheets were prepared from kraft pulps (kappa number 20), from original and hot water pre-extracted beech chips at 10 % wood weight loss with addition of AQ, SBH and the their mixture in kraft pulping. On Fig. 7 tensile index and tear index of kraft pulps beaten to 30°SR are presented. The tensile index of kraft pulp from hot water pre-extracted chips increased with addition AQ, SBH and their mixture in pulping process. The tensile index of kraft pulps correlates roughly with total yield, and respectively with hemicelluloses content (Fig. 6). These results indicated that addition of oxidative or reductive agent and their mixture in kraft pulping had a positive effect on recovery of interfibre bonding capabilities and fibre flexibility of kraft pulps from hot water pre-extracted chips.

The tear index of pulps from hot water pre-extracted chips prepared with addition of polysaccharides stabilizers into the pulping process was approximately the same as of pulps from hot water pre-extracted chips (Fig. 7).

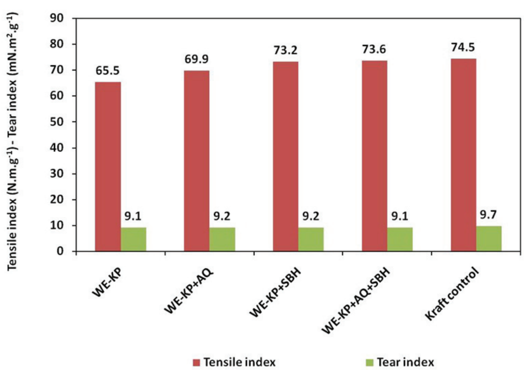

Fig. 7: Comparison of tensile index and tear index of pulps (kappa number 20) beaten to 30 °SR, from original and hot water pre-extracted beech chips at 10 % wood weight loss with addition of AQ, SBH and the mixture (AQ +SBH) in kraft pulping.

CONCLUSIONS

Beech wood chips were pre-extracted with hot water and subjected to conventional and modified kraft pulping. Total pulp yield from water pre-extracted chips exhibit a linear decrease with increasing wood weight loss, while the yield of total monosaccharides in hydrolysed extracts increased. Handsheets properties decreased; therefore papers produced from pulps of hot water pre-extracted chips will exhibit lower strength properties. The lower kraft pulp yield is attributed both to the removal of hemicelluloses during the pre-extraction and to the presence of a large amount of reducing end groups in polysaccharides formed during the autohydrolytic cleavage of glycosidic bonds mostly catalysed by released acetic acids from wood.

The treatment of hot water pre-extracted beech chips at 10 % wood weight loss with SBH in alkaline SS solution in intermediate step and addition of AQ in pulping on kraft pulp yield showed increased pulp yield by 2.7 % in comparison with the kraft pulp yield of hot water pre-extracted chips at the same kappa number. The SBH should be used with a low-alkalinity SS solution for treatment of hot water pre-extracted beech chips to maximize its effectiveness at stabilizing residual polysaccharides against alkaline degradation in the subsequent kraft pulping.

The application of reducing SBH with oxidizing agent AQ in kraft pulping of hot water pre-extracted beech chips at 10 % wood weight loss confirmed stabilizing effect on polysaccharides because the pulp yield increased by 2.3 % in comparison with kraft pulp yield from hot water pre-extracted chips at the same kappa number.

The lower kraft pulp yield at application of a mixture of SBH and AQ in the pulping of hot water pre-extracted beech wood chips showed a reduced stabilization effect of SBH in comparison with SBH application in the intermediate step. This effect may be explained by a competing reaction of these agents.

The modification of hot water pre-extracted beech wood chips kraft pulping had positive effect on tensile index while tear index was unchanged or slightly reduced.

In spite of lower improvement of pulp yield at application of SBH with AQ in the pulping process is this polysaccharides stabilizing way of hot water pre-extracted chips economically preferable to an intermediate treatment step with SBH in a mild alkaline SS solution, and addition AQ in kraft pulping.

However, SBH is still so costly that it is desirable to find a way to minimize or replace its use in order to economically justify its use on a technical scale in the pulp and paper industry.

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