

HOT WATER AND OXALIC ACID PRE-EXTRACTION OF BEECH WOOD INTEGRATED WITH KRAFT PULPING

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ABSTRACT

Combination of pre-extraction with kraft pulping was applied to beech chips in order to use hemicelluloses for biofuels or chemicals production. The extraction with hot water and dilute oxalic acid solutions was performed at 160°C. The oxalic acid increased the rate of extraction by a factor of 2 to 3.2. The content of total monosugars, xylose and glucose in hydrolysed extracts was higher while the content of lignin and insoluble solids in extracts was lower compared to hot water extract. At the same kappa number the pulp yield from pre-extracted chips was lower in comparison with the control pulp. The pulp yield decreased with increase of extracted wood, at Kappa number 20 and 5 % wood weight loss the yield decreased by 2.5 to 5 %, at 10 % wood weight loss by 7 to 11.5 %. The effective alkali charges in the pulping process of pre-extracted chips were by 0.5 to 1 % lower than in the control pulping. The pulp strength properties from pre-extracted pulps were lower compared to the control pulp. The tensile index of pulps from pre-extracted chips with 5 % wood weight loss decreased by 4 to 8.5 %, with 10 % wood weight loss by 10 to 16 % in comparison with control pulps at the same kappa number. The tear index of pulps from pre-extracted wood decreased similarly. Pre-extraction of beech wood with lower concentration of oxalic acid (0.0825 %) is preferable to hot water pre-extraction because the kraft pulp yield and strength properties are higher at the same wood weight loss.

KEYWORDS: Beech wood, pre-extraction, hot water, oxalic acid, hemicelluloses, kraft pulping, tensile index, tear index.

INTRODUCTION

The process of converting biomass to simple chemical compounds is named biorefining (Kamm and Kamm 2004). One biorefining variant is „value prior pulping“ (VPP), which involves the separation of non-cellulosic carbohydrates from wood chips before traditional chemical or mechanical pulping (Thorp and Raymond 2004).

The specific hemicelluloses are partially extracted through a prehydrolysis process. In this way, a raw material is obtained for bioethanol or other chemical feedstocks. The remaining

solids (cellulose, residual hemicelluloses, and lignin) are then the raw material for pulp or fibre products (Kamm and Kamm 2004). Successful application of VPP requires that only the desired components be removed from the wood and those components and the final pulp are not degraded in the process. VPP optimization requires a balance between potential yield loss, paper property changes and capital investments and any increased revenue from marketing a by-product.

Many processes have been proposed for extracting carbohydrates from wood (Kenealy et al. 2006). Pretreatments with dilute sulphuric acid or sulphur dioxide have produced fermentable carbohydrates and pulp (Clark and Mackie 1987) (Boussaid et al. 2000) (Söderström et al. 2003) (Mosier et al. 2005). Hot water extraction or autohydrolysis is useful for generating a soluble carbohydrate extract (Thorpe and Raymond 2004). Water hydrolysis of wood as a pretreatment stage before alkaline pulping is seen as an opportunity to approach the ideals of a forest biorefinery. In water hydrolysis the degradation products of primarily hemicelluloses and some other wood components are mainly dissolved in liquid phase and they also escape partly as gas.

White-rot fungi create or attach carboxylic acid groups (oxalate esters) on carbohydrates in wood. Since oxalic acid is a dicarboxylic acid, attachment of one acid group in an ester bond leaves the second carboxylic acid free. Attachment or creation of carboxylic groups increases the influx of water and swelling of wood, which results in energy savings during refining. Acid groups on fibre surfaces can also increase binding between fibres and improve the tensile and burst strength of paper products (Hunt et al. 2004).

It has been shown that oxalic acid breaks down hemicelluloses, resulting in a reduction in refining energy (Kenealy et al. 2007) (Meyer-Pinson et al. 2004). The major advantages reported for pre-extraction using oxalic acid or diethyl oxalate are reduced refining energy (35-55 %) and improved strength (Green et al. 1991). The use of oxalic acid is also reported to reduce brightness loss in comparison with water (autohydrolysis) and mineral acids pretreatment (Kenealy et al. 2006).

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 their decreased 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 hemicelluloses 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 pretreatment, the cellulose enriched fraction can be used for papermaking (Green et al. 1991), or after more extensive pretreatment, the residual solids can be hydrolyzed by cellulolytic enzymes to fermentable sugars for ethanol production.

Oxalic acid and diethyloxalate pre-extraction may result in a modified wood fibre that has potential to enhance physical properties such as dimensional stability but it has virtually no effect on mechanical performance. This treatment greatly lowers the energy required to refine pine chips into fibres (Mosier et al. 2005).

The goal of our investigation was to compare the influence of hot water and dilute oxalic acid solutions on composition of beech wood extracts and the follow up kraft pulping process of pre-extracted wood.

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, or with 0.0825 and 0.165 % oxalic acid (OA) water solution. The pre-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 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 35 min. The H-factors of pre-extraction were from 55 to 287 hrs. The H-factors were calculated based on the Arrhenius equation combining the effect of time and temperature similarly to H-factor in kraft pulping (Sixta 2007). 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 (%).

Kraft pulping

Pre-extracted beech wood chips of others autoclaves 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 experiments. White liquor of 25 % sulphidity plus fresh water was added to pre-extracted chips to obtain a liquor-to-wood ratio 4:1 at the required effective alkali (EA) charge. Effective alkali charge was 14 % for pulping of hot water pre-extracted chips, 14.5 % for oxalic acid pre-extracted chips and 15 % (all as Na₂O) 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 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. Dwell time at this temperature was in range of 15 to 60 min, and the corresponding H-factors were in range of 230 to 918 hrs. 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 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, 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).

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. The 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

Hemicelluloses pre-extraction

The conditions of beech wood chips pre-extraction with hot water and dilute oxalic acid solutions 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 dilute oxalic acid solutions and increased as follows: H₂O < 0.0825 % OA < 0.165 % OA. The 10 % of wood weight loss was reached with hot water at H-factor 253 hrs, with 0.0825 % OA at 154 hrs and with 0.165 % OA at 77 hrs. The oxalic acid increased the rate of extraction by a factor of 2 to 3.2. The results demonstrate that the amount of extracted wood components increased by addition of oxalic acid in hot water, which is in accordance with published results (Li et al. 2011). 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).

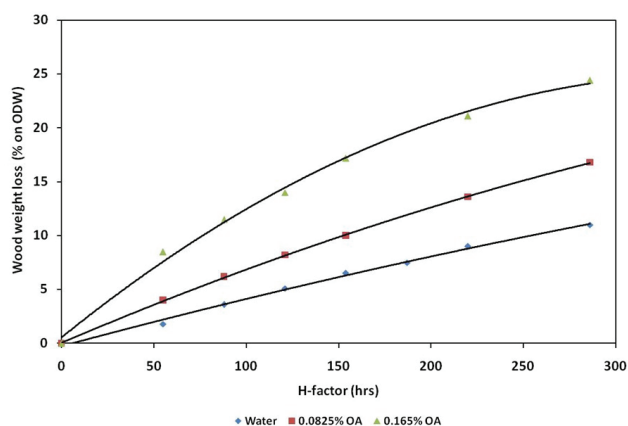


Fig. 1: Wood weight loss versus H-factor of pre-extraction.

Fig. 2 shows development of extract pH as a function of H-factor for hot water and oxalic acid solutions pre-extraction. The pH of hot water extracts decreased with increasing H-factor, but the pH of oxalic acid extracts increased with H-factor. Hot water extract pH decreased from 7 to 3.9, pH of 0.0825 % OA extract increased from 2.6 to 3.4 and pH of 0.165 % OA extract increased from 2.35 to 2.8. At 10 % wood weight loss in pre-extraction pH of hot water extract was 4.0, pH of 0.0825 % OA extract 3.4 and pH of 0.165 % OA extract 2.45. In the case of hot water pre-extraction acidity is developed by splitting off of O-acetyl groups and uronic acid in hemicelluloses resulting in formation of acetic acid and other organic acids.

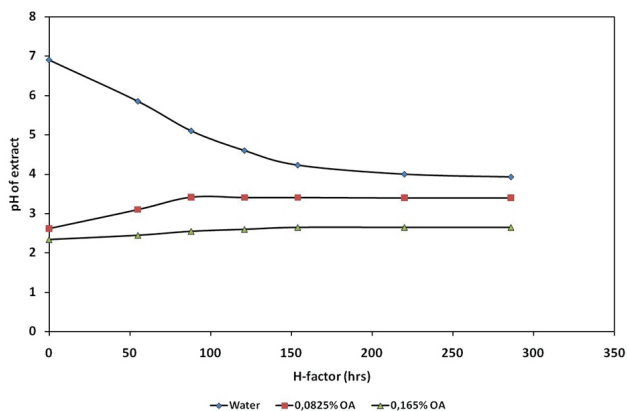


Fig. 2: pH of extract versus H-factor of pre-extraction.

The extracts contain dissolved oligosaccharides, minor amount of monosaccharides, lignin, insoluble solids (condensation products), acetic acid, glucuronic acid, furfural, hydroxymethylfurfural and organic degradation products of wood components. The content of dissolved monosugars (xylose, arabinose, glucose, galactose and mannose) that are detected in the extraction liquor following hydrolysis increases with increasing wood weight loss in pre-extraction (Fig. 3).

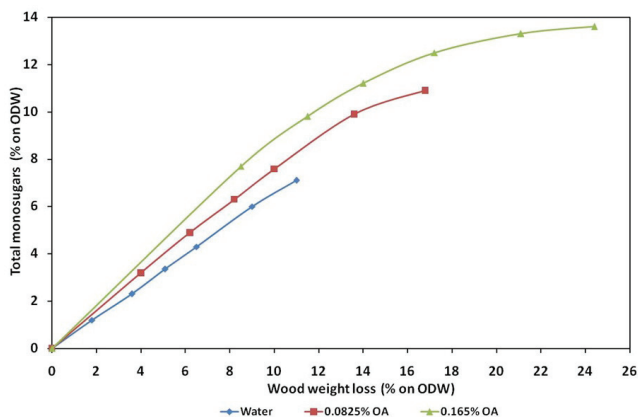


Fig. 3: Total monosugars content in hydrolysed extracts versus wood weight loss.

The highest content of total monosugars at the equal wood weight loss was in hydrolysed 0.165 % OA extract, then in 0.0825 % OA extract and the lowest was in hydrolysed hot water extract. At 10 % wood weight loss in pre-extraction the highest content of total monosugars was in hydrolysed 0.165 % OA extract (8.8 % on ODW), then in hydrolysed 0.0825 % OA extract (7.6 % on ODW) and the lowest was in hydrolysed hot water extract (6.5 % on ODW).

The hydrolysed extracts from beech 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 pre-extraction the highest xylose content was in hydrolysed 0.165 % OA extract (7.2 % on ODW), then in hydrolysed 0.0825 % OA extract (6.0 % on ODW) and the lowest xylose content was in hydrolysed hot water extract (4.9 % on ODW). Results confirmed that oxalic acid pre-extraction is more selective towards xylan extraction than hot water pre-extraction. The xylose content in hydrolysed hot water extracts represents 75 %, in 0.0825 % OA extracts 78 % and in hydrolysed 0.165 % OA extracts up to 82 % from the total monosugars content.

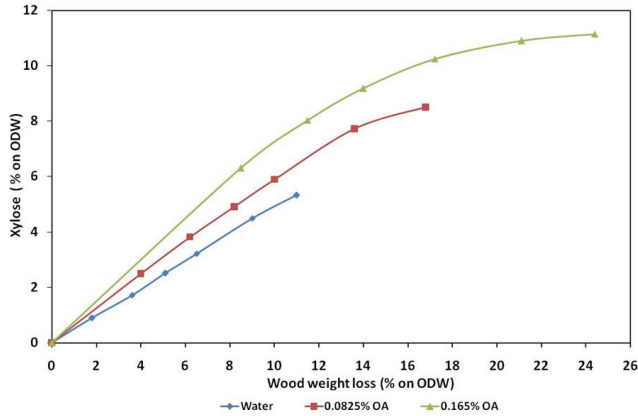


Fig. 4: Xylose content in hydrolysed extracts versus wood weight loss.

Fig. 5 shows the dependence of glucose content in hydrolysed extracts on wood weight loss. With increasing wood weight loss and with increasing concentration of the oxalic acid solutions the glucose content in hydrolysed extracts increased. At 10 % wood weight loss in pre-extraction with hot water the glucose content was 0.45 % on ODW, in pre-extraction with 0.0825 % OA was 0.5 % on ODW and with 0.165 % OA was 0.59 % on ODW. The higher content of glucose in hydrolysed oxalic acid extracts could be caused by random chain cleavage of cellulose and hemicelluloses macromolecules during pre-extraction that was higher than by hot water pre-extraction.

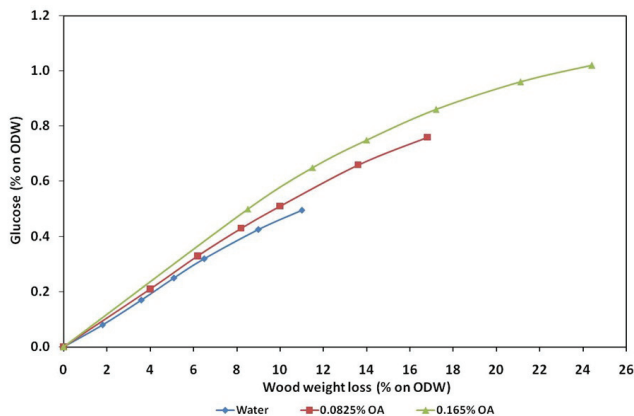


Fig. 5: Glucose content in hydrolysed extracts versus wood weight loss.

With increasing wood weight loss in pre-extraction lignin content in extracts increased (Fig. 6). At 10 % wood weight loss the lignin content was in hot water extract 0.92 % on ODW, in 0.0825 % OA extract was 0.8 % on ODW and in 0.165 % OA extract lignin content was 0.72 % on ODW. Solubility of lignin was higher at higher pH of pre-extraction solutions.

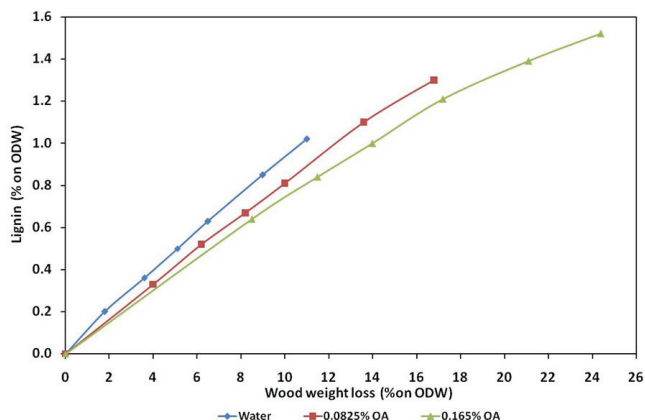


Fig. 6: Lignin content in extracts versus wood weight loss.

Fig. 7 shows the dependence of insoluble solids content in extracts on 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 insoluble solids content in hot water extract was 0.56 % on ODW, in 0.0825 % OA extract was 0.41 % on ODW and in 0.165 % OA extract insoluble solids content was 0.39 % on ODW. The formation of insoluble solids increased with higher pH of pre-extraction solutions.

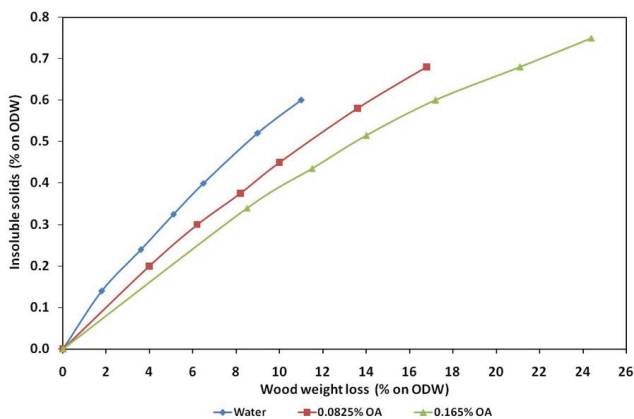


Fig. 7: Insoluble solids content in extracts versus wood weight loss.

Kraft pulping

The extraction solution type and wood weight loss has influence on the kraft pulp yields 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 degradation of cellulose. Yield of kraft pulps prepared from beech chips pre-extracted with hot water or with 0.0825 % OA and 0.165 % OA solution at 5 % and 10 % of wood weight loss were compared to the kraft control pulps from original beech chips.

The relationship between total pulp yield and kappa number of kraft pulps prepared from original beech chips and pre-extracted chips at 5 % wood weight loss is shown in Fig. 8. The pulp yields of pre-extracted chips were lower in comparison with the kraft control pulp (Kraft control) at the same kappa number. At kappa number 20, the yield of pulp from chips pre-extracted with 0.0825 % OA (0.0825 % OA-KP) was 47.2 % on ODW, pre-extracted with hot water (Water-KP) was 46.7 % on ODW and pre-extracted with 0.65 % OA (0.165 % OA-KP) was 46 % on ODW. The pulp yield from original chips (Kraft control) was 48.4 % on ODW at same kappa number.

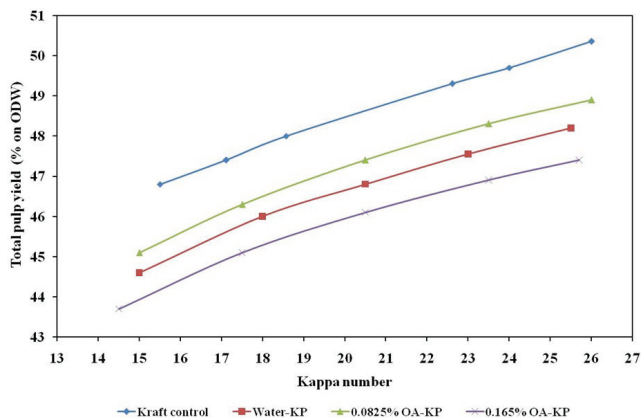


Fig. 8: Total pulp yield versus kappa number of pulps from original beech chips and pre-extracted chips at 5 % wood weight loss.

Fig. 9 shows the relationship between total pulp yield and kappa number of kraft pulps prepared from original and pre-extracted beech chips at 10 % of wood weight loss. At kappa number 20, the yield of pulp from chips pre-extracted with 0.0825 % OA was 45 % on ODW, with hot water was 44.2 % on ODW and with 0.165 % OA was 42.9 % on ODW. The increasing wood weight loss in pre-extraction from 5 to 10 % results in decrease of pulp yield by about 2.2 % on ODW for 0.0825 % OA, 2.5 % on ODW for hot water and 3.1 % on ODW for 0.165 % OA solution.

The results show that addition of small amount of oxalic acid (0.0825 %) increases the rate of hot water pre-extraction (Fig. 1) and does not have significant negative influence on pulp yield. On the other hand, at higher concentration of oxalic acid (0.165 %) in pre-extraction, pulp yields were lower compared with hot water pre-extraction. Pulp yield decrease is most probably a result of very low pH of extracts with 0.165 % OA concentration (Fig. 2).

At the same kappa number the yield of pulp from pre-extracted chips was lower compared to the kraft pulp control, which was caused by removal of the wood substance in the pre-extraction stage. At 5 % of wood weight loss in pre-extraction pulp yields were lower by 1.2 % on ODW to 2.4 % on ODW than pulp yields from original chips at kappa number 20. Similarly, at 10 % of wood weight loss the pulp yields were lower by 3.4 % on ODW to 5.5 % on ODW.

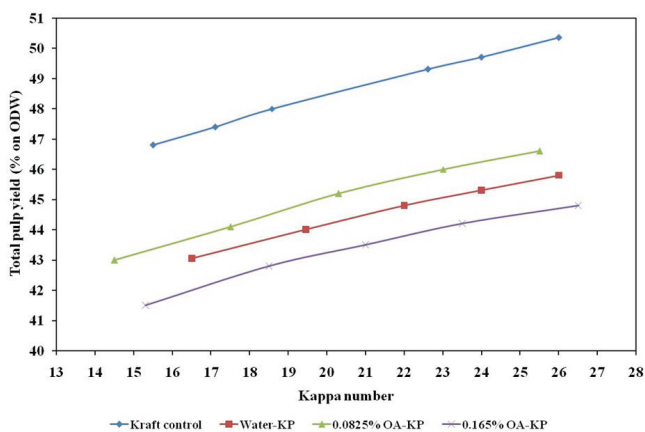


Fig. 9: Total pulp yield versus kappa number of pulps from original beech chips and pre-extracted chips at 10 % wood weight loss.

The lower yield of kraft pulps prepared from 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.

Polysaccharides, particularly cellulose undergo degradation in alkaline conditions due to peeling reactions, where reducing end-groups of the cellulose chains are cleaved off, and 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.

For the hot water pre-extracted chips the required EA charge in the follow up kraft pulping process was 14 % on ODW and for oxalic acid solutions pre-extracted chips was 14.5 % on ODW for obtaining the same kappa number. In kraft control pulping of original beech chips EA charge was 15 % on ODW. The lower EA charge in kraft pulping of pre-extracted chips is related to extraction of hemicelluloses which consume a large part of alkali in the kraft control pulping process.

Kraft pulp properties

Tensile index and tear index of kraft pulps (kappa number 14–26.5) prepared from original and pre-extracted chips with hot water, 0.0825 % OA and 0.165 % OA at 5 % and 10 % wood weight loss were determined at a beating degree 30°SR.

Tensile index of kraft pulps prepared from original and pre-extracted chips at 5 % wood weight loss increased with kappa number (Fig. 10). The results show that tensile index of kraft pulps prepared from pre-extracted chips is lower than that of the kraft control pulp at the same kappa number. Tensile index of pulp prepared from chips pre-extracted with 0.0825 % OA decreased by about 4 %, from hot water pre-extracted chips by about 6 % and from chips pre-extracted with 0.165 % OA by about 8.5 % when compared with kraft control pulp at the same kappa number.

The corresponding relationship between tensile index and kappa number of kraft pulps from original chips and pre-extracted chips with 10% extracted wood is shown in Fig. 11. In comparison with kraft control pulp at the same kappa number tensile index of pulp prepared from chips pre-extracted with 0.0825 % OA decreased by about 10 %, pulp from hot water pre-

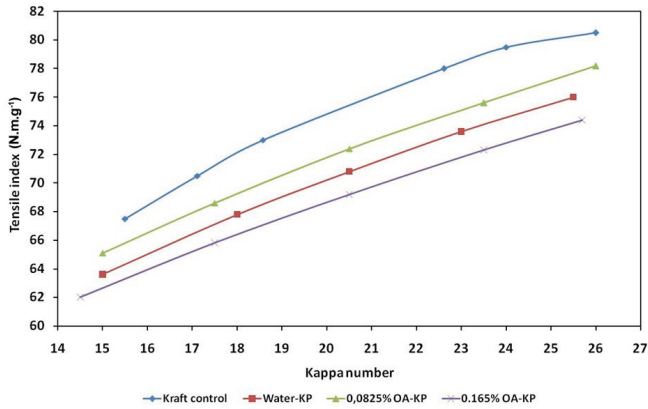


Fig. 10: Tensile index versus kappa number of pulps from original beech chips and pre-extracted chips at 5 % wood weight loss.

extracted chips by about 12.5 % and from chips pre-extracted with 0.165 % OA by about 16 %.

Thus, it appears that tensile index of the pulps prepared from pre-extracted chips correlates roughly with total pulp yield and, consequently with hemicelluloses content (Figs. 8, 9) because the tensile index is a function of inter-fibre bonding strength.

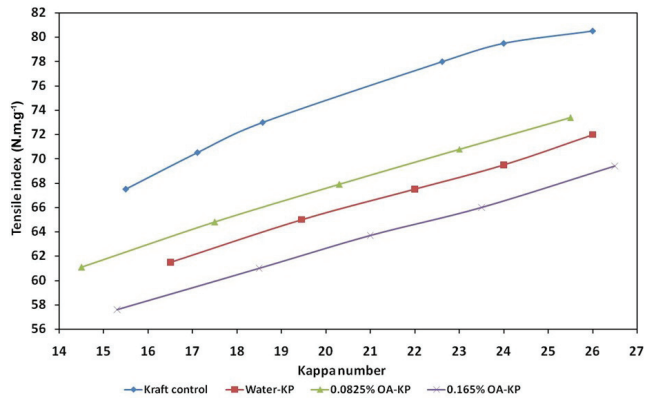


Fig. 11: Tensile index versus kappa number of pulps from original beech chips and pre-extracted chips at 10 % wood weight loss.

Tear index is dependent on the total number of fibres participating in sheet rupture, fibre length, fibre strength and number and strength of fibre-to-fibre bonds. Tear index of kraft pulp from original and pre-extracted chips with 5 and 10 % extracted wood decreased with increasing kappa number (Fig. 12, 13). Tear index of pulps prepared from pre-extracted chips with 5 % extracted wood were lower by about 1-2 % as of kraft control pulps at the same kappa number (Fig. 12). Tear index decreased more (about 2.5-6 %) if the pulps were prepared from pre-extracted chips with 10 % of wood weight loss (Fig. 13).

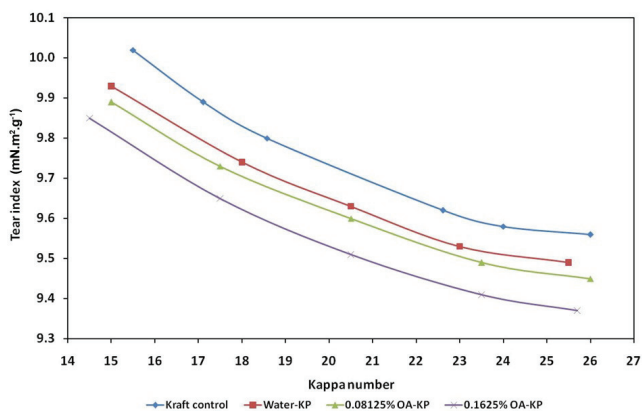


Fig. 12: Tear index versus kappa number of pulps from original beech chips and pre-extracted chips at 5 % wood weight loss.

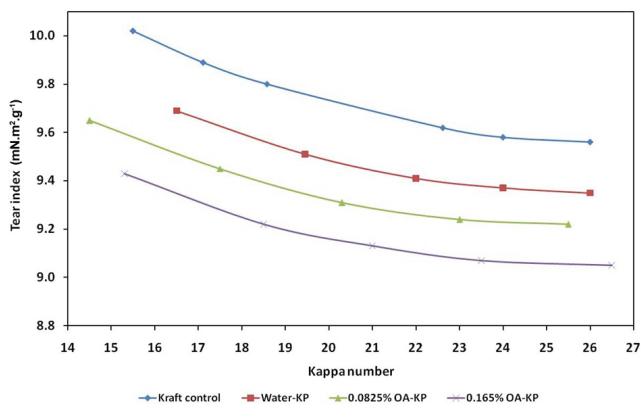


Fig. 13: Tear index versus kappa number of pulps from original beech chips and pre-extracted at 10 % wood weight loss.

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 (Fig. 5).

It is possible to conclude that pulp strength properties are influenced by wood weight loss and property of extraction solution. The pulp strength properties decreased with increasing of wood weight loss in pre-extraction.

CONCLUSIONS

The results of this study showed that pre-extraction of beech wood with hot water and dilute oxalic acid solutions are the promising methods to extract hemicelluloses from beech wood prior to kraft pulping in order to produce by-products besides pulp. Addition of a small amount

of oxalic acid increases the rate of extraction and the content of hemicelluloses in extracts in comparison with hot water at the same amount of extracted wood.

Pre-extraction of beech wood with oxalic acid is more selective to xylan extraction, with higher content of xylose in hydrolysed extract and with lower content of lignin and insoluble solids in extract in comparison with hot water extract.

At the same kappa number the yield of pulp from pre-extracted chips was lower than the yield of kraft control pulp. Pulp yield decreased with increasing level of wood extraction. The lower yield is attributed to removal of hemicelluloses and to increased sensitivity of cellulose towards alkaline degradation.

The pulp strength properties from the hot water and dilute oxalic acid pre-extracted beech chips are lower compared to kraft control pulp. The strength properties decreased with increasing amount of extracted wood.

Pre-extraction of hemicelluloses prior kraft pulping can increase the capacity of kraft pulp mill (as it decreases dwell time of the chips in a digester), but reduces the pulp yield, which means higher wood consumption. The strength of the pulp from pre-extracted chips is not acceptable for production of paper with very high strength.

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