INFLUENCE OF BEECH WOOD PRE-EXTRACTION ON BLEACHING AND STRENGTH PROPERTIES OF KRAFT PULPS

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Kraft pulps prepared from beech chips, with 10% wood weight loss, pre-extracted with green liquor solution, hot water and dilute oxalic acid, were more effectively delignified by a double-stage oxygen system in comparison with the reference pulp from original chips. The highest delignification efficiency was demonstrated for pulps prepared from dilute oxalic acid and hot water pre-extracted chips. The bleachability of oxygen delignified kraft pulps in the sequence $D_0(EO)D_1D_2$ was better in the case of the pulps from pre-extracted chips, first for those extracted with dilute oxalic acid and then for the hot water extracted ones. The consumption of ClO_2 in bleaching was lower for these pulps by about 40% and 20%, respectively, while for the pulp from green liquor solution pre-extracted chips it was lower only by about 5% compared with the reference pulp. Brightness reversion of the bleached pulps from pre-extracted chips was lower in comparison with the reference pulp, which correlates with lower content of hexenuronic acids. The loss of pulp yield in oxygen delignification and bleaching was of 1.4% for the pulp from dilute oxalic acid pre-extracted chips, 1.6% for the pulp from hot water pre-extracted chips, while in the case of the pulp from green liquor pre-extracted chips it was 2.4% and for the reference pulp – 2.5%. The beatability of bleached pulps from dilute oxalic acid and hot water pre-extracted chips was much worse than that of the bleached reference pulp, but in the case of the pulp from green liquor pre-extracted chips it was only slightly lower. The tensile index and burst index of the bleached pulps prepared from dilute oxalic acid and hot water pre-extracted chips were lower, while the tear index was higher, compared with those of the reference bleached pulp.

Keywords: beech wood, pre-extraction, kraft pulp, oxygen delignification, bleaching, hexenuronic acids

INTRODUCTION

The integrated forest biorefinery concept provides a promising opportunity for the development of the pulp and paper industry, as it represents a possibility to increase the profitability of an integrated pulp and paper mill. The implementation of the biorefinery concept in existing chemical pulp mills is regarded as a strategy for the sustainable co-production of paper, fuels, power and high value chemicals from diverse and heterogeneous lignocellulosic materials.[1] Currently used chemical pulping effectively removes a sizable fraction of the wood hemicelluloses into the black liquor, which is ultimately burned. The inability to capture a pure stream of hemicelluloses has limited the overall economic efficiency of the pulping process. Due to their branched nature, hemicelluloses are fairly reactive and can be extracted and converted into fuels or chemicals.[2,3] Unfortunately, conventional kraft pulping does not address at least one major aspect of commercial exploitation of lignocellulosic materials, namely, the use of extracted hemicelluloses.

The extraction of hemicelluloses before pulping can be carried out by alkaline or acidic treatment, by steam processing, or with hot water (autohydrolysis), which leads mainly to the generation of soluble oligomers or low-molecular weight polymers as major products. The amount of extracted hemicelluloses depends on the severity of the pre-treatment conditions. Since in pulp production hemicelluloses play an important role in determining the yield and pulp quality,[4] the economic limitation related to yield loss and/or poor pulp quality must be avoided.

The selection of the hemicelluloses extraction process is critical and depends on its efficiency, selectivity, and compatibility with existing pulping technology. The pre-extraction of hemicelluloses from hardwood chips with various

alkaline solutions prior to kraft pulping has been investigated.[5-7]Alkaline solutions are directly accessible in kraft mills, and for this reason they are very attractive to the industry. Therefore, much attention has been given to the study of green liquor and white liquor.

Green liquor (sodium carbonate and sodium sulphide), white liquor (sodium hydroxide and sodium sulphide) and caustic alkali can be used to extract hemicelluloses from wood chips without severely affecting the pulp yield and quality.[8-10] 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.[11] 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 the pulp production rate if the recovery cycle is the bottleneck. The environmental advantage of the extraction process is the reduction of the methanol content in black liquor by about 40%. Similar results were achieved for the pre-extraction of hemicelluloses from eucalyptus chips with green liquor prior to kraft pulping.[12] The pre-extracted chips were pulped much faster than original woodchips and 20% reduction of pulping chemicals was achieved.

Acid- and autohydrolysis are water-based methods that can be used to extract hemicelluloses from wood chips[5,13,14] before the pulping process. Acid-hydrolysis is usually carried out with inorganic acids at high temperatures. Autohydrolysis is driven by temperature, but the acetic acid released from xylan hydrolysis provides smooth acid conditions.[15,16] Wood acid hydrolysis promoted higher monosaccharides extraction yield, however, the autohydrolysis showed a less negative influence on pulp quality and overall yield.[14]

The process of hot water pre-extraction of hardwood before pulping to extract hemicelluloses is an environmentally friendly technology, which takes advantage of the readily available hemicellulosic component of hardwood species. Hot water extracts contain mainly xylose and other xylan-originated degradation products, such as xylans of lower degree of polymerization, xylose oligomers, acetic acid, and furfural. Kraft pulping and bleaching of hot water pre-extracted wood has several advantages and disadvantages with respect to conventional pulping and bleaching of original wood. An established advantage of extracted compared to non-extracted hardwood chips for kraft pulping is the reduced chemical charge and/or cooking time required to obtain bulkier pulp of similar kappa number, but lower strength properties.[17]Alternatively, the major drawbacks of performing an autohydrolysis stage prior pulping are the decreased pulp yield and limited strength of pulps, derived from cellulose depolymerisation and decreased residual xylan content. Van Heiningen and co-workers[18-22] suggest the integration of water prehydrolys is into alkaline pulping concepts to realize a biorefinery. 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.[23] Oxalic acid is one of the strongest organic acids known. It can catalyse the hydrolysis of hemicelluloses, while sparing cellulose. After mild pre-treatment, the cellulose enriched fraction can be used for papermaking.[24] Oxalic acid and diethyloxalate pre-extraction may result in a modified wood fibre, which has the potential to enhance physical properties, such as dimensional stability, but virtually no effect on mechanical performance.[25] The pulp yield and strength properties of kraft pulps from pre-extracted beech chips with dilute oxalic acid decreased with an increase in extracted wood and concentration of oxalic acid.[17]

The objective of our investigation was to compare oxygen delignification and bleaching efficiency of kraft pulps from beech chips pre-extracted with green liquor solution, hot water and dilute oxalic acid with those of the reference pulp from original chips, as well as the beatability and strength properties of bleached pulps.

EXPERIMENTAL

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 20×20×3 mm dimensions were used for laboratory pre-extraction and pulping experiments.

Methods

Hemicelluloses pre-extraction

Wood chips were extracted with 0.0825% oxalic acid (OA), hot water (W) and kraft green liquor

solution(GL) corresponding to 3% Na_2O charge on oven dry wood weight (ODW). 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 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 OD screened beech wood chips. The liquor-to-wood ratio was 4:1. The time to reach maximum extracting temperature of 160°C was 60 min and the dwell time at this temperature to remove 10% wood weight with green liquor was 48 min, with hot water – 30 min and with dilute oxalic acid– 20 min. After pre-extraction, the residual chips were used for kraft pulping.

Kraft pulping

Beech wood chips pre-extracted with 3% Na_2O charge of green liquor, hot water and 0.0825% oxalic acid were pulped after draining the extraction liquor without washing the chips. 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 of 4:1 at the required effective alkali (EA) charge. Effective alkali charge was 12% in kraft pulping of green liquor pre-extracted chips, 14% of hot water pre-extracted chips and 14.5% of dilute oxalic acid pre-extracted chips, while it was 15% (all as Na_2O) in reference kraft pulping. Reference kraft pulping of original beech wood chips was carried out at 170 °C. Heating time to this temperature from 100 °C was 90 min and the dwell time was 25 min. The kraft pulping of pre-extracted wood chips was performed at a constant temperature of 170 °C. Dwell time at this temperature was 30 min. The pulps were disintegrated in a laboratory pulper and thoroughly washed. Kappa number was determined after screening on a laboratory screen with 0.25 mm slots.

Oxygen delignification

The reference kraft pulp (Reference) prepared from original beech wood chips (kappa number of16.8), the pulp from green liquor pre-extracted chips (GLE) with kappa number of17, the pulp from hot water pre-extracted chips (WE) with kappa number of16.8 and the pulp from dilute oxalic acid pre-extracted chips (OAE) with kappa number of17.1 were used for oxygen delignification in two stages (OO). In the first stage of oxygen delignification, NaOH and $MgSO_4$ charges were of 1-2.5% and 0.15%, respectively. The experimental conditions of two-stage oxygen delignification are presented in Table 1.

Bleaching

The same bleaching conditions were applied for oxygen delignified kraft pulps of kappa number about 8, prepared from original and from pre-extracted beech chips. The bleaching sequence was $D_0(EO)D_1D_2$. The bleaching in individual stages was performed at 10% pulp consistency. The ClO_2 charge in D_0 stage was 0.7% ClO_2 (0.23 kappa factor), temperature 60 °C, reaction time 60 min and initial pH 2.5. The NaOH charge in EO stage was 1%, temperature 75 °C, pressure 0.3 MPa and reaction time 60 min. After the EO stage, each pulp was divided into four equal portions, which were then bleached in the D_1 stage with 0.4, 0.8, 1.2, and 1.6% ClO_2 charge. Each of the four resulting D_1 pulps was bleached in the D_2 stage with 0.3% ClO_2 charge. The D_1 and D_2 stages were conducted for 180 min at 80 °C and initial pH 4, and 4.5, respectively.

Table 1
Experimental conditions of two-stage oxygen delignification

Stage	1	2
Reaction time, min	30	60
Temperature, °C	90	100
Consistency, %	10	10
Pressure, MPa	0.6	0.3

Analyses

White liquor was prepared and analysed according to TAPPI test method T 624 cm-85. Kappa number of the pulp was determined according to ISO 302:2004 standard and hexenuronic acids according to T 282 pm-07. Pulp brightness was determined according to ISO 2470-1:2009 and brightness reversion according to TAPPI Useful Methods UM 200.The kraft pulps were beaten in a laboratory Jokro mill to 20,30, 40 and 50 °SR. Drainage resistance was determined according to ISO 5267-1 standard. Handsheets (80 g m^{-2}) were prepared on a Rapid Köthen sheet former, according to ISO 5269-2, and were tested for tensile index (ISO 1924-2), burst index (ISO 2758) and tear index (ISO 1974).

RESULTS AND DISCUSSION

Oxygen delignification

Additional removal of lignin from the pulp after pulping can be achieved by oxygen delignification, which under appropriate conditions of pressure, temperature, and alkali charge, results in effective delignification without

any significant influence on pulp yields. Oxygen delignification in two stages exploits the delignification reaction kinetics and allows maximum delignification of the pulp. To exploit the high selectivity of oxygen in lignin removal, two-stage oxygen delignification(OO) was used before bleaching the kraft pulps from original and pre-extracted beech chips.

The results of our previous papers[10,17] showed that, at the same beech wood weight loss in pre-extraction, the highest total monosaccharides content was achieved in hydrolysed OA and W extracts, while in hydrolysed GL extract the monosaccharides content was lower by about 2.5 times. At the same kappa number, the pulp yield from GL pre-extracted chips was about the same as that from the original chips. On the other hand, the pulp yields from W and OA pre-extracted chips were lower by about 4%.

In oxygen delignification experiments, kraft pulp from original beech chips (Reference), pulps from pre-extracted chips with green liquor (GLE), hot water (WE) and dilute oxalic acid pre-extracted chips (OAE) with 10% wood weight loss and with approximate kappa number of 17 were used. The delignification degree (in %) defined as the kappa number drop during oxygen delignification divided by initial kappa number prior to oxygen delignification increased with NaOH charge (Fig. 1). The delignification degree increased more in the case of the pulps from W and OA pre-extracted chips. The same effectiveness of oxygen delignification of these pulps was achieved at lower NaOH charge in comparison with the reference pulp, the delignification degree in this case was higher at the same NaOH charge. A delignification degree of 50% was reached for the pulp prepared from OA pre-extracted chips with 0.9% NaOH charge, the pulp from W pre-extracted chips with 1% NaOH charge, the pulp from GL pre-extracted chips with 1.7% NaOH charge and for the reference pulp with 2% NaOH charge. The delignification degree of the pulp from OA pre-extracted chips at 1% NaOH charge was 53%, of the pulp from W pre-extracted chips 50%, of the pulp from GL pre-extracted chips 40% and of the reference pulp was 32%. The results confirmed that the kraft pulps from pre-extracted chips responded better to oxygen delignification, first of all the pulps from OA and W pre-extracted chips.

The main factors affecting the hardwood kraft pulp oxygen delignification efficiency are kappa number and hexenuronic acids content. It is known that the kappa number of the pulp represents the content of lignin and hexenuronic acids. Hexenuronic acids are formed by base catalysed elimination of methanol from 4-O-methyl-D-glucuronoxylans during bulk delignification.[24]

The influence of NaOH charge on the hexenuronic acids content in oxygen delignification of kraft pulps from original and pre-extracted beech chips is shown in Fig. 2. The content of hexenuronic acids in the reference pulp was 58.5 mmol kg^{-1}, in the pulp from GL pre-extracted chips 46.5 mmol kg^{-1}, in the pulp from W and OA pre-extracted chips 32 mmol $kg^{-1}$and 29 mmol kg^{-1}, respectively. These results suggest that the content of hexenuronic acids in kraft pulps correlates with the xylan content. In our previous study,[10,17] we found that in pre-extraction of beech wood chips with W and OA by about twice more xylan was removed than with GL.

The content of hexenuronic acids slightly decreased with increasing the NaOH charge in oxygen delignication (Fig. 2).

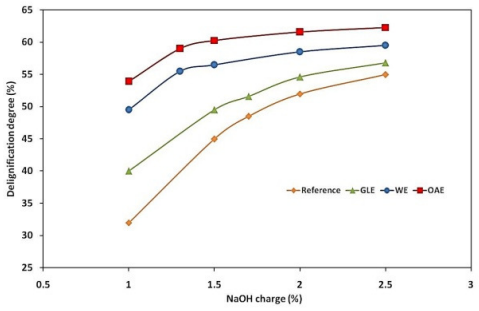

Figure 1: Delignification degree *versus* NaOH charge in OO stage of reference kraft pulp and of pulps prepared from chips pre-extracted with green liquor, hot water and dilute oxalic acid

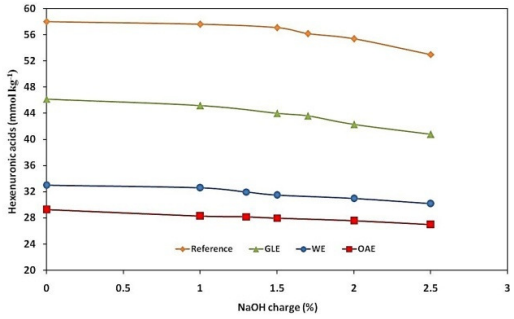

Figure 2: Hexenuronic acids content of reference kraft pulp and of pulps from chips pre-extracted with green liquor, hot water and dilute oxalic acid *versus* NaOH charge in OO stage

At 2.5% NaOH charge, the content of hexenuronic acids in the reference pulp and in the pulp from GL pre-extracted chips decreased by about 10%, whereas in the pulps from W and OA pre-extracted chips, a decrease by only about 3% was attained. Hexenuronic acids are relatively inert to oxygen delignification, so that a very small amount of hexenuronic acids is actually removed in the oxygen delignification stage.[25]

The overall oxygen delignification efficiency of the kraft pulps from original and pre-extracted chips was evaluated by the drop in kappa number in the oxygen stage. "True lignin kappa number" is the one derived only from lignin, after subtraction of the kappa number due to hexenuronic acids content, considering that 10mmol kg^{-1} hexenuronic acids equals one kappa number unit.[26] According to the approximate calculation based on the hexenuronic acids content, the lignin kappa number of the reference kraft pulp entering the OO stage was 10.95, that of the pulp from GL pre-extracted chips – 12.35, that of the pulp from W pre-extracted chips– 13.6 and that of the pulp from OA pre-extracted chips –14.2, while the kappa number of the kraft pulps determined by the standard method was about 17. The analysis of the hardwood data suggests that hexenuronic acids contribute by approximately 20 to 60% to the total kappa number for commercial hardwood kraft pulps.[27] Because in the OO stage only a small amount of hexenuronic acids was removed (Fig. 2), it was possible to observe that a larger amount of lignin was removed from the pulps prepared from W and OA pre-extracted chips in comparison with the reference pulp and the pulp from GL pre-extracted chips.

The higher oxygen delignification effectiveness of the beech wood kraft pulps from OA and W pre-extracted chips may be connected with better accessibility to oxygen due to lower hemicelluloses, respectively, xylan content in comparison with the reference pulp. This could be explained by the opening of the fibre supermolecular structure through the removal of hemicelluloses, allowing lignin to react more easily. These results correspond with the findings of other researchers.[28,29]

Bleaching

The same bleaching conditions were applied for bleaching of oxygen delignified kraft pulps from original and pre-extracted beech wood chips having a kappa number of about 8.5. These pulps were bleached by the sequences $D_0(EO)D_1$ and $D_0(EO)D_1D_2$, respectively, under the same conditions in individual stages. The consumption of ClO_2 in D_0, D_1 and D_2 stages was expressed as kappa factor defined as the consumption of active chlorine on kappa number unit of oxygen delignified pulp entering bleaching.

The relationships between the brightness of the pulps from original and pre-extracted chips and kappa factor in bleaching sequence $D_0(EO)D_1$ are shown in Figure 3. The brightness of the pulps increased with kappa factor for all the pulps prepared from original and pre-extracted beech wood chips. However, it is evident that the brightness of the pulps from OA and W pre-extracted chips is higher in comparison with that of the pulps from original and GL pre-extracted chips. This resulted in lower chemical consumption of ClO_2 in D_0 and D_1 stages at the same brightness level. A brightness of 88% ISO was reached for the pulp from OA pre-extracted chips at a kappa factor of 0.585, for the pulp from W pre-extracted chips at 0.69, for the pulp from GL pre-extracted chips at 0.78 and for the reference pulp at 0.8. The bleaching efficiency or bleachability of the pulp from OA pre-extracted chips was better by 26.9% than that of the reference pulp. The bleachability of the pulp from W pre-extracted chips was better by 13.8%, while that of the pulp from GL pre-extracted chips was better by only 2.5% than that of the reference pulp.

The brightness of the kraft pulps from original and pre-extracted chips after bleaching sequence $D_0(EO)D_1D_2$ at a different kappa factor is shown in Figure 4. The relationships for all the pulps were the same as in bleaching sequence $D_0(EO)D_1$ (Fig. 3), but the brightness at the same kappa factor was higher. A brightness of 89% ISO of the pulp from OA pre-extracted chips was achieved at a kappa factor of 0.5, of the pulp from W pre-extracted chips at 0.67, of the pulp from GL pre-extracted chips at 0.795 and of the reference pulp at a kappa factor of 0.84. The consumption of ClO_2 in the bleaching sequence $D_0(EO)D_1D_2$ of the pulp from OA pre-extracted chips was lower by 40.5% than that of the reference pulp. The consumption of ClO_2 in the bleaching of the pulp from W pre-extracted chips was lower by 20.2%, of the pulp from GL pre-extracted chips was lower only by 5.4% than of ClO_2 consumption in bleaching of the reference pulp.

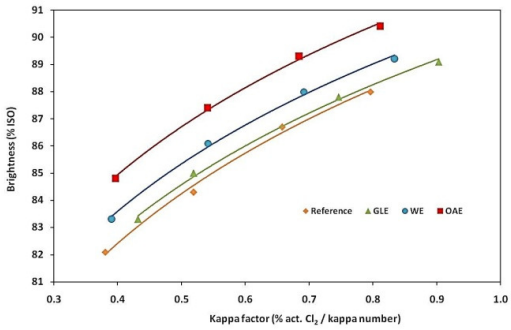

Figure 3: Brightness of reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips *versus* kappa factor in $D_0(EO)D_1$ sequence

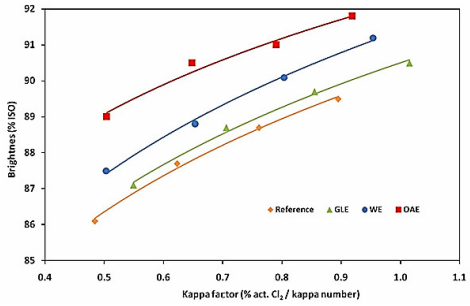

Figure 4: Brightness of reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips *versus* kappa factor in $D_0(EO)D_1D_2$ sequence

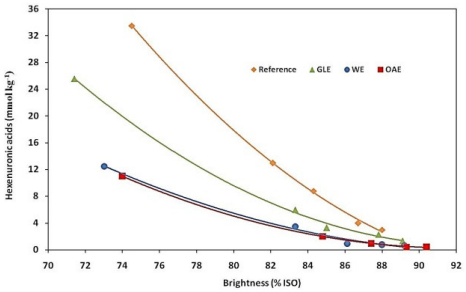

Figure 5: Hexenuronic acids content *versus* brightness of reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips bleached with the $D_0(EO)D_1D_2$ sequence

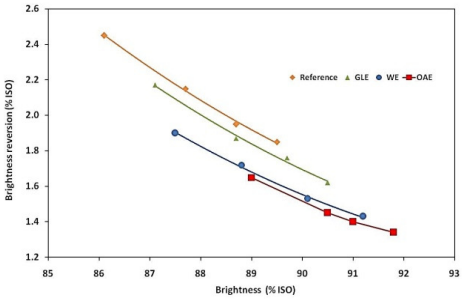

Figure 6: Brightness reversion *versus* brightness of reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips bleached with the $D_0(EO)D_1D_2$ sequence

The improved bleaching efficiency of the pulps from OA and W pre-extracted chips may be attributed to a lower content of hemicelluloses, thereby of hexenuronic acids, weaker lignin carbohydrate complex, an increase in the content of free phenolic hydroxyl groups of lignin, and a lower ash content.[30] Hexenuronic acids readily consume electrophilic reagents, such as chlorine dioxide. The results of our bleaching experiments also confirmed that the bleached pulps from pre-extracted chips contained less hexenuronic acid at the same brightness level in comparison with the reference pulp (Fig. 5).

High brightness and good brightness stability are desired properties of bleached hardwood kraft pulps. Brightness reversion or yellowing of a pulp represents a loss of brightness occurring after the bleaching, either in the drying or upon storage of the pulp. The relationship between brightness reversion and brightness of the pulps bleached with the sequence $D_0(EO)D_1D_2$ is shown in Figure 6.

Brightness reversion decreased in the following order: reference pulp >pulp from GL pre-extracted chips >pulp from W pre-extracted chips> pulp from OA pre-extracted chips. The lower brightness reversion of the bleached pulps prepared from pre-extracted chips than that of the reference pulp at the same brightness level correlates with the lower content of hexenuronic acids at the same brightness level (Fig. 5).The presence of hexenuronic acids in pulps is known to be a contributing factor to brightness reversion.[31]

Figure 7 compares the yields of unbleached and bleached reference kraft pulp and those of the pulps from GL liquor, W and OA pre-extracted beech wood chips. The pulping yields were found out from the kraft pulping delignification curve at a kappa number level entering into oxygen delignification stage. The yield of the unbleached pulp from OA pre-extracted chips was lower by 4.5%, of the pulp from W pre-extracted chips by 4%, of the pulp from GL pre-extracted chips by

0.3%, than the yield of the unbleached reference pulp. The overall yields of the bleached kraft pulps were calculated taking into account the pulp yield loss in bleaching. The overall yield of the bleached pulp from OA pre-extracted chips was lower by 3.4%, of the pulp from W pre-extracted chips by 3.1%, of the pulp from GL pre-extracted chips by 0.2%, in comparison with the yield of the bleached reference pulp. The loss in pulp yield during oxygen delignification and bleaching by the $D_0(EO)D_1D_2$ sequence of 1.4% for the pulp from OA pre-extracted chips, of 1.6% for the pulp from W pre-extracted chips, of 2.4% for the pulp from GL pre-extracted chips, and of 2.5% for the reference pulp. The loss in pulp yield upon bleaching was lower in the case of the unbleached pulp from pre-extracted chips with lower pulping yield.

The results showed that the lower the yield in kraft pulping the lower the yield loss in the bleaching process, this is connected with the lower content of hemicelluloses in the pulps from pre-extracted chips. In the bleaching process, the negative impact of OA and W pre-extraction on the overall yield of the bleached pulps decreased compared with the bleached reference pulp.

Beatability

The beating process changes several single fibre properties. The primary structural effects on fibres can be the result of internal fibrillation, external fibrillation, fines formation, fibre cutting, and straightening of fibres. The major effect of beating is a drastic increase of water uptake by the fibre material. The hydrodynamic volume of the fibres is increased substantially, so that filtration, *e.g.* in the sheet forming process, is severely hampered. This effect is used to characterize the effectiveness of beating by measuring drainage resistance.

Figure 8 shows the evolution of drainage resistance (in °SR) with the beating time of the bleached kraft pulps from original and pre-extracted beech wood chips. The beatability of the bleached pulps from pre-extracted chips was lower than that of the reference pulp. At 30 °SR, the beating time of the bleached pulps increased in the following order: reference pulp (23 min) < pulp from GL pre-extracted chips (24 min) <pulp from W pre-extracted chips (37 min) < pulp from OA pre-extracted chips (40 min).The bleached pulps from W and OA pre-extracted chips appeared to need more beating energy by about 60% and 70%, respectively, to attain the same drainage resistance compared to the bleached reference pulp, which is caused most likely by the lower content of hemicelluloses.

Strength properties

The structure and bonding of pulp in hand sheet depends on fibre properties such as fibrillation and also the density. Tensile strength of each pulp type therefore increases by beating (Fig. 9). There are indications that fibre/fibre joint strength also increases with beating due to changes in the physical structure of the fibre surface that makes new surfaces available of molecular bonding. Tensile strength of bleached pulps from pre-extracted chips was lower in comparison to the reference pulp at a same drainage resistance. At 30 °SR, tensile index of bleached pulps from original and pre-extracted chips were in the range 64-68 N m g^{-1}. The tensile index of the bleached pulps from W and OA pre-extracted chips was lower by about 6% in comparison to the reference pulp.

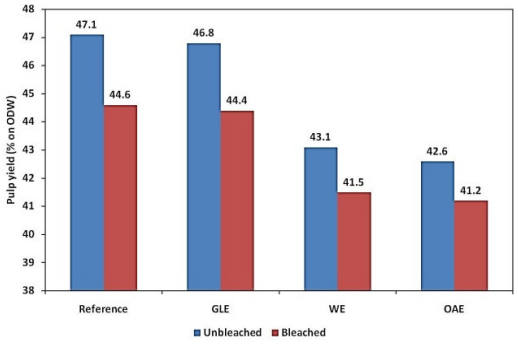

Figure 7: Yields of unbleached and bleached reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips

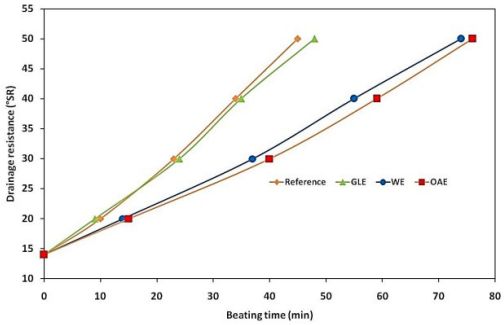

Figure 8: Drainage resistance *versus* beating time of bleached reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips

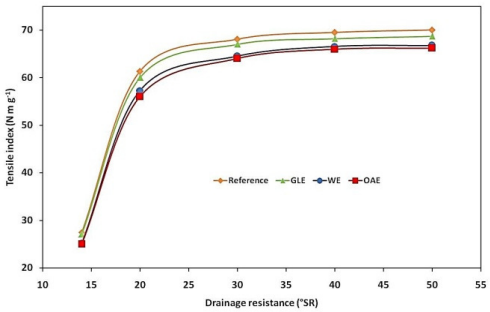

Figure 9: Tensile index *versus* drainage resistance of bleached reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips

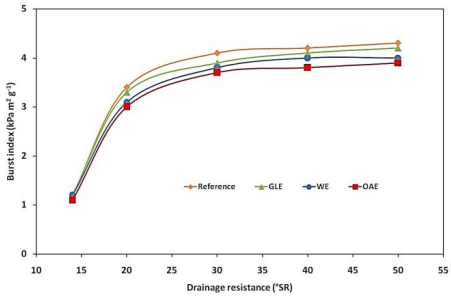

Figure 10: Burst index *versus* drainage resistance of bleached reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips

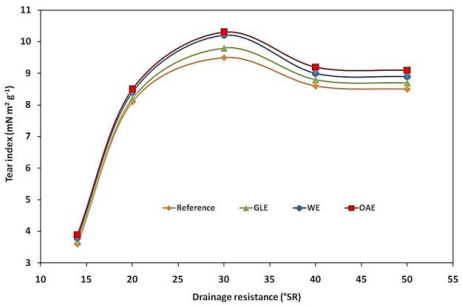

Figure 11: Tear index *versus* drainage resistance of bleached reference kraft pulp and of pulps prepared from green liquor, hot water and dilute oxalic acid pre-extracted chips

Corresponding relationships were also obtained for the burst index of the bleached pulps from original and pre-extracted chips (Fig. 10). At 30 °SR, the burst indexes of the bleached pulps were in the range of 3.7-4.1 kPa m^2g^{-1}. The difference between the burst indexes of the bleached pulps from W and OA pre-extracted chips and the reference pulp was of about 10%.

The results confirmed that the tensile and burst indexes of the bleached pulps increased with the beating degree in the whole region of the drainage resistance measured in this work, even if, for a drainage resistance greater than 30 °SR, the increase in the tensile and burst indexes is negligible, while the tear index increases substantially up to a drainage resistance of 30°SR, and then decreases (Fig. 11). At 30 °SR, the tear indexes of the bleached pulps were in the range of 9.5-10.3 mN m^2g^{-1}. The tear index of the bleached pulps from pre-extracted chips was higher in comparison with that of the reference pulp at the same drainage resistance. The tear index of the bleached pulps from W and OA pre-extracted chips was higher than that of the reference pulp by about 8%.

CONCLUSION

Under constant conditions of oxygen delignification, the kappa number reduction of the pulps from pre-extracted chips was higher in comparison with that of the reference kraft pulp. Consequently, the delignification efficiency of the pulps from pre-extracted chips was higher than that of the reference kraft pulp from original chips, first of all of the pulps from W and OA pre-extracted chips.

The bleachability of the pulps from OA and W pre-extracted chips, bleached by the $D_0(EO)D_1$ and $D_0(EO)D_1D_2$ sequences, was significantly better than that of the reference pulp, resulting in a decrease of the chlorine dioxide consumption required to reach the same brightness level. The bleachability of the pulp from GL pre-extracted chips was only moderately better than that of the reference pulp. The difference in the bleachability of these pulps was higher when the $D_0(EO)D_1D_2$ sequence was applied.

The bleached pulps from pre-extracted chips had a lower brightness reversion in comparison with the reference pulp at the same brightness level, which correlates with a lower content of hexenuronic acids.

The pulping yield of the unbleached pulps from pre-extracted chips was lower, which is connected with a lower content of hemicelluloses. The loss of pulp yield during oxygen delignification and bleaching using the $D_0(EO)D_1D_2$ sequence was much lower for the pulps from OA and W pre-extracted chips than for the reference pulp. The negative impact of OA and W pre-extraction in the bleaching process on the overall yield of the bleached pulps decreased in comparison with the bleached reference pulp.

The beatability of the bleached pulps from pre-extracted chips was lower than that of the reference pulp, mainly in the case of the pulps from OA and W pre-extracted chips.

The tensile and burst indexes of the bleached pulps from pre-extracted chips were lower than those of the bleached reference pulp. On the other hand, the tear index of the bleached pulps from pre-extracted chips was higher in comparison with that of the bleached reference pulp, first of all with that of the bleached pulps from OA and W pre-extracted chips.

The pre-extraction of beech wood hemicelluloses with OA and W before pulping improved the efficiency of pulping and bleaching, allowing to achieve high brightness, but the overall pulp yield was lower compared with those of the pulp from GL pre-extracted chips and of the reference pulp.

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