

The effect of increased pulp yield using additives in the softwood kraft cook on the physical properties of low-grammage handsheets

Hafizur Rahman, Mikael E. Lindström, Peter Sandström, Lennart Salmén and Per Engstrand

KEYWORDS: H-factor, Kappa number, Polysulfide, Tensile index, Thermoporosimetry, Wet- Zero span, Z strength.

ABSTRACT: The effect of increasing the pulp yield by the addition of sodium borohydride (NaBH₄) or polysulfide (PS) in softwood kraft cooking, i.e. enhancing the retention of glucomannan, on the physical properties of low-grammage handsheets was studied. In addition to the yield improvement, an increase in tensile index was observed, especially at lower degrees of beating. These higher yield pulps showed an increase in pore volume, indicating an increased degree of swelling of the fibres. Presumably, the increased flexibility of the fibres affects the bonding strength and leads to the higher tensile index observed.

ADDRESSES OF THE AUTHORS:

Hafizur Rahman (hafizur.rahman@sca.com or hafrah@student.miun.se), SCA R & D Centre, Sidsjövägen 2, P.O. Box 716, SE-851 21 Sundsvall, Sweden; **Mikael E. Lindström** (mil@kth.se), KTH Royal Institute of Technology, Teknikringen 26, SE-100 44 Stockholm, Sweden; **Peter Sandström** (peter.sandstrom@sca.com), SCA R & D Centre, Sidsjövägen 2, P.O. Box 716, SE-851 21 Sundsvall, Sweden; **Lennart Salmén** (lennart.salmen@ri.se), Research Institutes of Sweden, RISE Bioeconomy/Cellulose Science & Technology, Drottning Kristinas Väg 61, P.O. Box 5604, SE-114 86 Stockholm, Sweden; **Per Engstrand** (per.engstrand@miun.se), FSCN Mittuniversitetet, SE-851 70 Sundsvall, Sweden.

Corresponding author: Hafizur Rahman

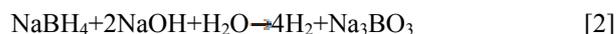
Introduction

In the paper industry, kraft pulp fibres are the most important raw material for the production of virgin paper, board and many other applications. Kraft pulps are produced from hardwood, softwood and annual plants. It is well known that the properties of bleached pulps depend not only on the raw material but also on the pulping process, the extent of delignification and the bleaching sequences. The carbohydrate chemistry of alkaline cooks involves a number of complicated reactions. The most challenging part of a kraft cook is to remove the lignin while minimizing the losses of cellulose and hemicellulose. The degradation of lignin, cellulose and hemicellulose depends on the chemical conditions in the kraft cook, and the overall pulp yield can be increased by using different additives in the kraft cook (Aurell, Hartler 1965a; Paavilainen et al. 1989). The overall yield also affects the physical properties of the paper product (Antonsson et al. 2009a). Yield-increasing additives to stabilise glucomannan (Rydholm 1965) can

be either reducing or oxidizing chemicals. A reducing additive is sodium borohydride (NaBH₄), which yields stable alcohol groups (Rydholm 1965; Gulsoy, Eroglu 2011) and sodium borate according to the reaction (Rydholm 1965), Eq 1.

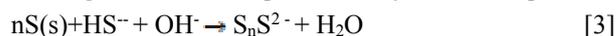


At the same time a side reaction occurs, Eq 2.



The most important advantage of using NaBH₄ is the significant yield increase, but there are other advantages such as energy savings during refining and an increase in pulp brightness (Gulsoy, Eroglu 2011).

An oxidizing chemical additive is polysulfide which can be produced by adding elemental sulfur to white liquor (Rydholm 1965; Lindgren, Lindström 1995), when the following reaction takes place already at 70°C, Eq 3.



Polysulfide can also be produced by the atmospheric oxidation of a mixture of white and black liquor (Rydholm 1965). Polysulfide sulfur in the cooking liquor stabilises hemicellulose at lower temperatures (100°C-120°C) by oxidizing the reducing end groups of the polysaccharides into alkali-stable aldonic acids, and this reduces the carbohydrate degradation in kraft cooking (Hägglund 1946). It has been shown that oxidation of the end-groups in carbohydrate chains make them stable against endwise peeling by hydroxide (OH⁻) ions during cooking. Polysulfide addition has also been found to have an slightly positive effect on delignification when cooking to low kappa numbers (Lindström, Teder 1995).

Up to a certain level, the yield increases in proportion to the concentration of the reducing and oxidizing chemicals (Rydholm 1965). The gain in pulp yield for both sodium borohydride and polysulfide cooking is directly due to an increased hemicellulose (glucomannan) yield in the kraft pulp (Rydholm 1965; Gullichsen, Fogelholm 1999). It has been reported that a higher content especially of glucomannan can be achieved with an increased hydroxide ion (OH⁻) concentration, but this reduces the amount of xylan retained (Aurell, Hartler 1965b; Brännvall, Lindström 2007).

In general, during kraft cooking, the alkaline peeling reaction of the aldehyde end groups of the carbohydrate molecules leads to the dissolution of short chains of cellulose and hemicellulose. Cellulose is relatively resistant to alkaline degradation, as was seen in early studies on pulp yield (Aurell, Hartler 1965b; Gustavsson, Waleed 2000). The chemical composition of the pulp greatly affects fibre strength. Increases in both cellulose (Gurnagul et al. 1992) and hemicellulose (Spiegelberg 1966) content have been reported to lead to an increase in

fibre strength. Hemicelluloses on the fibre surface are more effective for bonding between fibres (Mohlin, Teder 2002; Danielsson, Lindström 2005).

The physical properties, especially the tensile index, are important parameters for low grammage sheets where the tensile strength of a paper depends primarily on the degree of bonding between fibres. The tensile strength increases with increasing fibre length, fibre strength and fibre joint strength. Fibre length is very dependent on the raw material, where hardwood has shorter fibres than softwood. The tensile strength is also very dependent on the amount of hemicellulose in the pulp, but the relation between fibre strength and hemicellulose content is not linear (Mohlin, Teder 2002). A positive correlation between fibre strength and cellulose content may be found up to 70-80% cellulose content (Page et al. 1985), since the cellulose is the backbone of the fibre wall and the main contributor to fibre strength. Softwood kraft pulps usually have above 75% cellulose content (Mohlin, Teder 2002). Thus, up to a certain level, an increase in cellulose content is expected to increase the overall strength of the fibre material (Salmén 1993). The Wet Zero-span test is a fast method that can be used to determine single fibre strength properties (Mohlin, Alfredsson 1990; Clark 1994; Cowan 1994).

Hemicellulose is required for sufficient softening of the fibre wall and it also plays a role in bonding. A higher hemicellulose content increases the fibre joint strength. The bonding ability of fibres in paper is usually described by the bonded area and the bonding strength between fibres (Laine, Stenius 1997), and the Z-strength is the best method for measuring bonding strength (Koubaa, Koran 1995). An increase in fibre-to-fibre bonding leads to an increase in Z-strength (Singh 2007). In addition, the fibre-fibre joint strength increases with increasing surface charge of the fibres due to increased surface swelling (Torgnysdotter 2006). Pulps with a higher surface charge have been shown to give stronger fibre joints and surface softness is of primary importance for utilisation of the joint strength (Forsström, Torgnysdotter 2005). It has been suggested that a surface charge determination can give a measure of the openness and ability of the fibres to form strong joints (Andreasson et al. 2003). Retention of hemicelluloses, i.e. increasing the hemicellulose content in a pulp, results in greater swelling of the high-yield kraft pulp, and an increase in swelling generally improves the fibre bond area and should also affect the pore volume of the fibre wall (Stone et al. 1969). The pore volume in the cell wall can be determined by differential scanning calorimetry (DSC) (Maloney, Paulapuro 2001).

Materials and Methods

A mixture of Spruce (*Picea abies*), 70%, and Pine (*Pinus sylvestris*), 30%, chips was obtained as industrial chips from SCA Östrand mill, Sundsvall, Sweden. The chips were screened and the fraction with a thickness of 2-8 mm was retained. Knots and bark were removed by hand. The chips were dried at room temperature in the summer (June-July) of 2015 and the dry solids content was determined (approximately 91%, when dried at 105°C).

Preparation of pulps

Kraft pulps were prepared in a laboratory digester (1L) with a capacity of 100g of dry chips. The cooking conditions were effective alkali 20% (as NaOH), sulfidity 35%. The liquor/wood ratio was adjusted to 4:1. The chips were impregnated with cooking liquor by increasing the temperature from 70°C to 160°C at a rate of 1°C/min. The duration of the treatment at the maximum temperature was varied depending on the target kappa number, i.e. 35 (± 2 units) and 40. The white liquor and black liquor were taken directly from the Östrand mill. Two different additives: polysulfide 2% or sodium borohydride (NaBH_4) 1% calculated on wood dry chips were charged. The temperature was kept at 160°C for the remainder of the cooking time until the H-factor for the target kappa number was reached. The pulps were then screened in cold water on a sieve plate with 0.15 mm slot width. The screening was done with backwater reversal. For the yield determination, the dry solids content of the wet screened pulps and the amount of dry shives/reject were measured after using a halogen moisture analyzer drying at 105°C overnight. The kappa number (ISO 302:2014) was measured on three replicates of each pulp according to the standard method SCAN-C 1:77. In order to simplify the experimental procedure, bleaching was done in a single bleaching stage with powerful chlorine-dioxide (ClO_2) for all pulps produced and tested in this work and the charge was calculated as kappa number $\times 4$ (acl/ton of pulp). Pulps produced by this procedure will not have full brightness i.e. 88% ISO but most of the lignin is removed. Thus, the purpose was here eliminating most of the effect of lignin (and extractives) on different properties. This is important as almost all softwood kraft pulps for tissue applications are bleached. The bleaching conditions were: pulp consistency 10%, temperature 25°C, and time 18 h. The pulp was washed with de-ionised water after bleaching.

Sheet Preparation and Physical Testing

For the preparation of laboratory sheets of 20g/m² and 60 g/m² the bleached pulps were beaten in a PFI mill (ISO 5264-2: 2011) at different beating levels: 0, 500, 1000 and 2000 revolutions. Drainability was determined as the Schopper-Riegler ($^{\circ}\text{SR}$) value (ISO 5267-1999). Handsheets with a grammage of 20g/m² and 60 g/m² were prepared according to ISO 5269-2:2004 with normal tap water using a conventional sheet former with a surface area of 0.0211m². The density, tensile strength (ISO 1924-3), Z-strength (ISO 1,4 MPa) (Mohlin, Teder 2002) and wet Zero-span tensile strength (ISO 15361) of the handsheets were determined. The sheet grammage and thickness were determined according to ISO 5270. All physical properties were determined at 23°C \pm 1°C and 50% \pm 2% relative humidity according to ISO 187. 5-8 samples were measured and the mean value was calculated. The percentage increase in tensile index and Z strength were calculated from interpolated curves for each condition.

Instruments

The carbohydrate analysis was performed by a GC-method (Theander, Westerlund 1986). The contents of

the five principal, neutral monosaccharides arabinose, galactose, glucose, xylose and mannose were determined according to SCAN-CM 71:09 using a Gas Chromatography-Flame Ionization Detector (GC-FID). The analyses were done on a HP (Hewlett Packard) 6890 with a BPX 70 column (12 m, 0.32 μm I.D. and 0.25 μm film thickness). The samples were hydrolyzed with 72% sulfuric acid (H_2SO_4) using a two-step technique. The hydrolyzed sample was reduced, acetylated and the resulting alditol acetates of the monosaccharides were determined by GC. The alditol acetate content of each mono-carbohydrate was recalculated to polysaccharide assuming that the ratio of glucose to mannan in softwood glucomannan is 1.0:3.5 and that all other polysaccharides present were cellulose and xylan (Antonsson et al. 2009b).

Conductometric titration was used to determine the total charge of the fibre material (Wågberg et al. 1985) i.e. the amount of carboxyl and sulfonic acid groups on the cellulose fibres. The acid groups are first put into proton form by reducing the pH and the suspension is then titrated with a NaOH (0.01M) solution. To minimize the effect of Donnan-equilibrium, i.e. the differences in pH between bulk solution and fibre wall, NaCl (0.01M) was added. In addition, N_2 gas was bubbled through the test solution during titration to remove any disturbing O_2 and CO_2 .

Polyelectrolyte titration was carried out to determine the surface charge according to the method described by Wågberg et al. (1989). The excess of polymer in the solution was titrated with an anionic potassium polyvinyl sulphate polymer (KPVS), which together with a cationic indicator, toluidine blue, gave a colour shift from blue to pink at the end point of the titration. A highly charged and high molecular weight cationic polymer, poly-(dimethyldiallylammonium) chloride, "polyDADMAC" ($1 \times 10^5 < M_w < 3 \times 10^5$) was absorbed to the fibre material. Here, a slightly less charged and significantly smaller polymer, poly (1, 5 -dimethyldiallyl-1, 5-diazaundecamethylene) bromide, "polybrene" ($M_w \approx 8 \cdot 10^3$) was used.

To determine the pore size distribution of the pulp fibres, differential scanning calorimetry (DSC) using the thermoporosimetry technique was employed (Maloney, Paulapuro 2001). Measurements were made using a TA Q1000 DSC instrument equipped with a refrigerated cooling system (RCS). To integrate the melting peaks, Analysis 2000, version 4.0 C software was used. N_2 was used as carrier gas at a rate of 50 ml min^{-1} . The technique is based on the fact that water retained within small pores shows a depressed melting temperature due to the increased pressure of water in cavities with a curved interface. The mean pore diameter (D) is calculated from the Gibbs-Thomson equation, Eq 4.

$$D = \frac{-4V_m \sigma_{is}}{\Delta H_m \ln \frac{T}{T_0}} = -\frac{k}{T} \quad [4]$$

where V_m is the molar volume of ice, σ_{is} is the surface energy at the ice-water interface, T_0 is the melting point of water at normal pressure, T_m is the melting temperature and ΔH_m is the latent heat of melting.

The melting temperatures between -33 and -0.1°C corresponding to calculated pore diameters between 1.3 and 431 nm were studied in accordance with earlier studies (Fahlén, Salmén 2005). Samples of unbeaten kraft pulp were analysed at a moisture content of $3\text{-}10 \text{ g}\cdot\text{g}^{-1}$ using a sample size of $0.5\text{-}3 \text{ mg}$. All measurements were made in triplicate and the average pore volume ($\text{ml}\cdot\text{g}^{-1}$) was calculated.

Results and Discussion

Total yield

Under the conditions used in this study, the addition of NaBH_4 during the first part of the kraft cook (NaBH_4 – kraft pulp) resulted in a greater yield increase than the addition of polysulfide (PS – kraft pulp). Fig 1 shows that at a kappa number of 35 ± 2 the yield increase for the NaBH_4 – kraft pulp was 4%-units and for PS – kraft pulp 2.5%-units.

Table 1 shows that glucomannan content was highest in the NaBH_4 – kraft pulp, 14.8%, compared to the PS – kraft pulp with 10.8% and the reference pulp with 9.0%. According to Wang et al. (2005) Sodium borohydride reduces the aldehyde end groups in the hemicellulose to stable alcohol end groups while polysulfide oxidises the aldehyde end groups to carbonyl end groups, and reduced end group is more stable towards peeling than an oxidised end group. As the aldehyde group in cellulose is also reduced the yield of the NaBH_4 -kraft pulp is due to both an increase in cellulose, 2%, and in glucomannan, 3%, content based on wood.

Physical properties

The tensile index was evaluated on 20 g/m^2 and 60 g/m^2 handsheets at low PFI-beating degrees, 0 - 2000 revolutions. Fig 2 shows the effect of increasing the pulp yield on the tensile index for the 20 g/m^2 sheets. The tensile index increase observed for the NaBH_4 – kraft pulp compared to the reference kraft pulp was greater than that for the PS – kraft pulp. In both cases, the percentage increase in tensile index decreased with increasing beating.

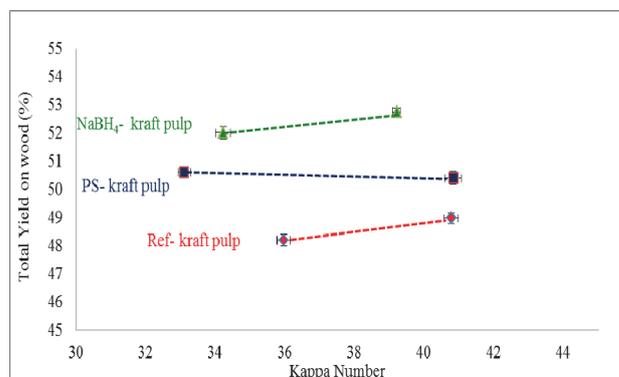


Fig 1 - Total yield on wood (%) vs. kappa number after kraft cooking with two different alkali charges. For polysulfide (PS) 2% was added and for sodium borohydride (NaBH_4) 1% based on dry wood chips.

Table 1 - The relative carbohydrate composition and yield of the respective pulps

Kraft pulp	Estimated relative Composition (%)					Yield on wood (%)				
	Cellulose	Gluc- mannan	Galactan +Arabinose	Xylan	Total Hemi cellulose	Cellulose	Gluc- mannan	Galactan +Arabinose	Xylan	Total Hemi cellulose
Ref	80.4	9.0	1.5	9.1	19.6	34.1	3.8	0.6	3.9	8.3
PS (2% on dry wood chips)	78.5	10.8	1.5	9.2	21.6	35.5	4.9	0.7	4.2	9.8
NaBH ₄ (1% on dry wood chips)	77.2	14.8	1.2	6.9	22.8	36.1	6.9	0.5	3.2	10.6

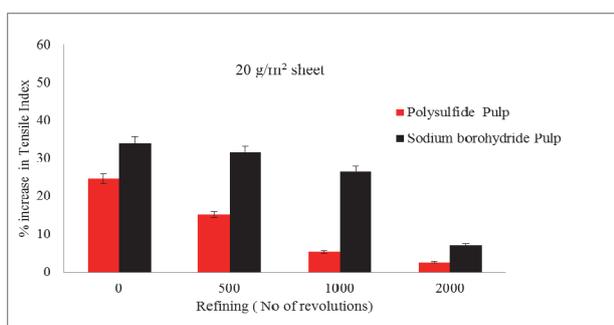


Fig 2 - Percentage increase in tensile index compared to reference pulp at different PFI-beating levels for 20 g/m² sheets plotted from the experimental data of interpolated curves as described under experimental.

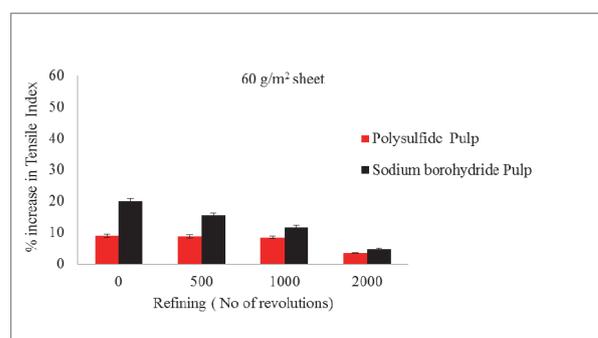


Fig 3 - Percentage increase in tensile index compared to reference pulp at different PFI-beating levels for 60 g/m² sheets plotted from the experimental data of interpolated curves as described in experimental.

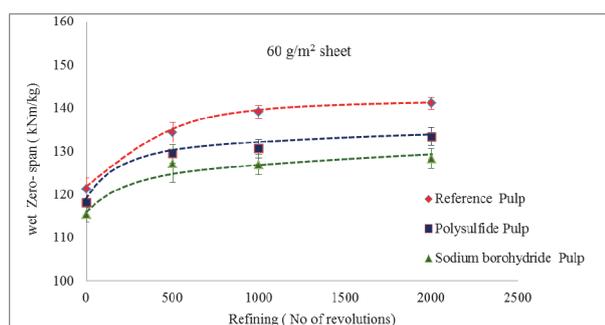


Fig 4 - Wet Zero-span versus number of beating revolutions for 60 g/m² sheet of three different kraft pulps.

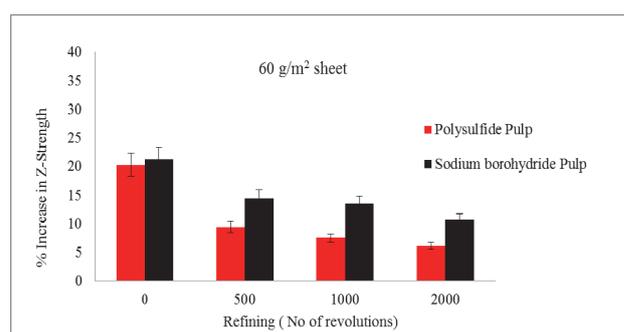


Fig 5 - Percentage increase in Z-strength at four different beating levels for NaBH₄ and PS-pulps from interpolated curves described in the experimental.

Table 2 - The estimated Zero-span strength at 1000 PFI rev.

Pulp	Total Yield (%) (Cellulose + Hemicellulose)	Cellulose Yield (%)	Zero-span (kNm/kg)	Zero-span of cellulose
Ref	42.4	34.1	139.1	173.0
PS	45.3	35.5	130.6	166.5
NaBH ₄	46.8	36.1	126.9	164.3

Fig 3 shows the corresponding data for the 60 g/m² handsheets. The same trend is observed as for the 20 g/m² handsheets, although the percentage increase in tensile index is much less than for the 20 g/m² sheets.

The fact that the addition of sodium borohydride or polysulfide to the first part of the cook influences the tensile index more for 20 g/m² paper sheets than for 60 g/m² sheets is probably due to the fact that there are fewer fibres in the fibre network forming the paper, so that the joint strength between the fibres is more important in the 20 g/m² paper sheets than in the 60 g/m² papers, where there are more fibres present to form fibre interactions.

Fig 4 shows the wet Zero-span for 60 g/m² sheets plotted against degree of refining for the three different pulps. The addition of NaBH₄ or PS lowered the wet Zero-span strength and NaBH₄ had a greater effect than the PS treated.

One explanation for the lower wet Zero-span for the higher yield NaBH₄-pulp and PS-pulp, may be that these paper sheets contain fewer fibres per gram of paper since the pulps contain more hemicellulose. For the NaBH₄-pulp this amounts to an 8% difference from the reference pulp. As cellulose is the load-bearing component of the fibre the Zero-span value may be related to the effective cellulose content (the cellulose content per g of pulp) by the ratio of total yield per cellulose yield, as given in Table 2. Still, after compensation for the pulp yield, the reference pulp seemed to have the strongest fibres, and the tensile index increase with addition of both NaBH₄ and PS cannot be explained by an increase in fibre strength.

Table 3 - Charge analysis of unbeaten pulps

Pulp	Total Charge ¹		Surface Charge ²	
	Mean Value (µeq/g)	Standard Deviation (±)	Mean Value (µeq/g)	Standard Deviation (±)
Ref	79.0	0.91	15	0.10
PS	108.0	0.35	18	0.07
NaBH ₄	95.0	1.84	15	0.33

¹ Determined by polyelectrolyte adsorption (Polybrene, $M_w \approx 8 \cdot 10^3$) around pH 7.5

² Determined by polyelectrolyte adsorption (Poly-DMDAAC, $M_w > 3 \cdot 10^3$) around pH 7.5

An increase in the bonded area between fibres and an increase in the strength of the bond can increase the fibre joint strength. In this study, the fibre joint strength in the 60 g/m² sheets has been estimated by measuring the z-strength. As shown in *Fig 5*, the z-strength of both the NaBH₄ – kraft pulp and the PS – kraft pulp was greater than that of the reference pulp at all refining levels. There seems thus to be a correlation between the increase in z-strength and the increase in tensile strength index (*Fig 2*), suggesting that the observed tensile index increase for the NaBH₄ –kraft pulp and the PS – kraft pulp could be due to an increase in fibre joint strength.

An increase in hemicellulose content in a kraft pulp is generally considered (Saukkonen 2014) to increase the swelling of the fibre, and thus increase the fibre surface flexibility and increase the bonding potential as a result of a larger bonded area (Rydholm 1967; Schönberg et al.2001; Hannuksela et al. 2004).

Earlier studies have reported a correlation between the fibre joint strength and the fibre surface charge (Forsström, Torgnydotter 2005). In the present study, no increase in surface charge was observed, see *Table 3*.

Increasing the amount of hemicellulose in the fibre wall counteracts the aggregation of cellulose during the drying of the fibre (Salmén, Olsson 1998; Larsson, Salmén 2014). A less aggregated fibre wall has a greater flexibility and can lead to an increase in the fibre joint strength. An increase in the total charge, as seen in the case of the NaBH₄-pulp and the polysulfide pulp (*Table 3*) may also lead to a greater swelling of the fibre, and a greater degree of sheet consolidation. Earlier studies have also shown a relationship between the swelling behaviour and the hemicellulose content of a kraft pulp (Young, Rowland 1933; Saukkonen 2014). The swelling in water is also strongly related to the porosity of the fibre wall (Berthold, Salmén 1997).

Fig 6 shows that the pore volumes of both the NaBH₄ and the PS- kraft pulps were somewhat higher than that of the reference pulp, especially for the NaBH₄ -pulp. This supports the hypothesis that these high-yield pulps may have a higher fibre flexibility that may result in stronger bonds leading to an increase in tensile index for the sheets.

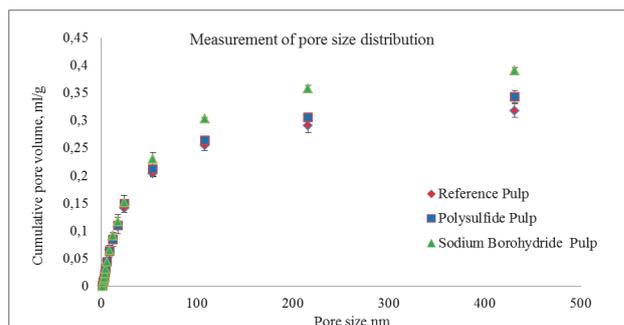


Fig 6 - Cumulative pore volume as a function of pore diameter from thermoporosimetry measurements on unbeaten kraft pulps.

Conclusions

Increasing the pulp yield by the addition of NaBH₄ or PS in softwood kraft cooking, i.e. increasing the retention of glucomannan, showed a positive effect on the strength of low- grammage sheets, especially at a low degree of beating. The most significant improvement was seen in the case of the tensile index. These high-yield pulps showed an increase in pore volume indicating an increase in the degree of swelling of the fibre. This increase in flexibility of the fibres presumably leads to increased bond strength, resulting in the higher tensile index of these pulps.

Acknowledgements

The authors thank SCA R&D centre, Sundsvall for support and guidance in the laboratory and also thank Östrand mill for supplying chips and cooking chemicals, and RISE/Bioeconomy, Stockholm for supporting some of the laboratory tests. This work was conducted under the auspices of the Forest as a Resource Industrial College (FORIC) at Mid- Sweden University, and the Knowledge foundation in collaboration with SCA Forest Products and Mid Sweden University financially supported the study.

References

- Andreasson, B., Forsström, J. and Wågberg, L. (2003): The porous structure of pulp fibres with different yields and its influence on paper strength, *Cellulose*, 10(2), 111.
- Antonsson, S., Henriksson, G. and Lindström, M.E. (2009a): The influence of lignin and xylan on some kraftliner pulp properties, *Nord. Pulp Paper Res. J.* 24(4), 403-408.
- Antonsson, S., Karlström, K. and Lindström, M.E. (2009b): Applying a novel cooking technique to produce high kappa number pulps-the effect on physical properties, *Nord. Pulp Paper Res. J.* 24(4), 415-420.
- Aurell, R. and Hartler, N. (1965a): Kraft Pulping of pine Part I "The changes in composition of the wood residue during the cooking process", *Svensk Papperstidn*, 68(3), 59.
- Aurell, R. and Hartler, N. (1965b): Kraft Pulping of pine Part II "The changes in composition of the wood residue during the cooking process", *Svensk Papperstidn*, 68(4), 97-102.
- Berthold, J. and Salmén, L. (1997): Effect of mechanical and chemical treatments on the pore size distribution in wood pulps examined by inverse size-exclusion chromatography, *J. Pulp Paper Sci.* 23, 245-253.

- Brännvall E.** and **Lindström M.E.** (2007): The hemicellulose composition of pulp fibres and their ability to endure mechanical treatment, *Tappi*, 6(10), 19-24.
- Clark, J. d' Å.** (1994): *Paper Trade J.* 118(1), 29, *Tappi Standard T 231 m.*
- Cowan, W.F.** (1994): Comparing Wet Zero-Span Tensile Testing with Conventional Laboratory Pulp Evaluation, *Process and Product Quality Conference, Proceeding (Tappi)*, 47-50.
- Danielsson, S.** and **Lindström, M.E.** (2005): Influence of birch xylan adsorption during kraft cooking on softwood pulp strength, *Nord. Pulp Paper Res. J.* 20 (4), 436-441.
- Fahlén, J.** and **Salmén L.** (2005): Ultrastructural changes in a holocellulose pulp revealed by enzymes, thermoporosimetry and atomic force microscopy, *Holzforschung*, Vol. 59, 589-597.
- Forsström, J.** and **Torgnysdotter, A.** (2005): Influence of fibre/fibre joint strength and fibre flexibility on the strength of papers from unbleached kraft fibres, *Nord. Pulp Paper Res. J.* 20 (2).
- Gullichsen, J.** and **Fogelholm, C.J. (eds).** (1999): *Chemical Pulping, Papermaking Science and Technology Book & A, Fapet Oy, Helsinki.*
- Gulsoy, S.K.** and **Eroglu, H.** (2011): Influence of Sodium Borohydride on Kraft Pulping of European Black Pine as a Digester Additive, *Ind. Eng. Chem. Res.* 50 (4), 2441-2444.
- Gurnagul, N., Page, D. H.** and **Paice M. G.** (1992): The effect of cellulose degradation on the strength of wood pulp fibres, *Nord. Pulp Paper Res. J.* 7 (3), 152-154.
- Gustavsson, C.** and **Waleed, W.** (2000): The influence of cooking conditions on the degradation of hexenuronic acid, xylan, glucmannan and cellulose during kraft cooking of soft wood, *Nord. Pulp Paper Res. J.* 15 (2), 160.
- Hannuksela, T., Holmbom, B., Mortha, G.** and **Lachenal, D.** (2004): Effect of sorbed galactoglucomannans and galactomannans on pulp and paper handsheet properties, especially strength properties, *Nord. Pulp Paper Res J.* 19(2), 237-244.
- Hägglund, E.** (1946): Allmän översikt över verksamheten vid Svenska Träforsknings-institutets Träkemiska avdelning och Cellulosaindustriens Centrallaboratorium under år 1945, *Svensk Papperstidning*, 49 (9), 191-204.
- Koubaa, A.** and **Koran, Z.** (1995): Measure of the internal bond strength of paper/board, *Tappi*, Vol. 3, 103-111.
- Laine J.** and **Stenius P.** (1997): Effect of charge on the fibre and paper properties of bleached industrial kraft pulps, *Paperi Ja Puu*, 79 (4).
- Larsson, P. T.** and **Salmén, L.** (2014): Influence of cellulose supra-molecular structure on strength properties of chemical pulp, *Holzforschung*, 68(8), 861-866.
- Lindgren, C.** and **Lindström M.E.** (1995): Thermal decomposition of inorganic polysulfides at kraft cooking conditions, *Nord. Pulp Paper Res J.* 10(1), 041-045.
- Lindström, M.E.** and **Teder A.** (1995): The effect of polysulfide pretreatment when kraft pulping to very low kappa numbers, *Nord. Pulp Paper Res J.* 10(1), 008-011.
- Maloney, T.C.** and **Paulapuro, H.** (2001): Thermoporosimetry of pulp fibres, *The science of papermaking, 12th Fundamental research symposium. Oxford, UK, Sep 17-21, Vol. 2, 897-926.*
- Mohlin, U. B.** and **Teder, A.** (2002): Importance of cellulose/hemicellulose ratio for pulp strength, *Nord. Pulp Paper Res. J.* 17 (01), 014-019.
- Mohlin, U.B.** and **Alfredsson, C.** (1990): Fibre deformation and its implications in pulp characterization, *Nord. Pulp Paper Res. J.* 5 (4), 172-179.
- Paavilainen, L.** (1989): Effect of Sulfite cooking Parameters on the papermaking Potential of Pulp Fibres, *Paperi Puu*, 71(4), 356-363.
- Page, D.H., Seth, R.S.** and **El-Hosseiny, F.** (1985): *Strength and Chemical Composition of Wood Pulp Fibers, The Eighth Fundamental Research Symposium, Oxford, Vol.1, 77-91.*
- Rydholm S.** (1965): *Pulping processes, Interscience publishers, John wiley and sons, New York, London, Sydney, 635-644.*
- Rydholm, S.** (1967): Relationship of pulp and paper properties, In: *Pulping Processes, Rydholm, S. (ed.), Interscience Publishers, New York, USA, 1152-1166.*
- Salmén, L.** (1993): Responses of Paper Properties to Changes in Moisture Content and Temperature, In C.F. Baker (Ed) *Products of Papermaking. Pira International, 369-430.*
- Salmén, L.** and **Olsson, A.M.** (1998): Interaction between hemicelluloses, lignin and cellulose: structure-property relationships, *J. Pulp paper Sci.* 24, 99-103.
- Saukkonen E.** (2014): Effects of the Partial Removal of Wood Hemicellulose on the properties of the Kraft pulp, Ph.D.Thesis, Lappeenranta University of Technology, Finland.
- Schönberg, C., Oksanen, T., Suurnäkki, A., Kettunen, H.** and **Buchert, J.** (2001): The importance of xylan for the strength properties of spruce kraft pulp fibres, *Holzforschung*, 55(6), 639-644.
- Spiegelberg, H.** (1966): Effect of hemicelluloses on mechanical properties of individual pulp fibres, *Tappi*, 49 (9), 388-396.
- Singh, S.p.** (2007): Relationship of z-tensile strength with in-plane strength properties of paper, *Ind. Chem. Technol.* 14, 317-320.
- Stone, J.E., Treiber, E.** and **Abrahamson, B.** (1969): Accessibility of regenerated cellulose to solute molecules of a molecular weight of 180 to 2×10^6 , *Tappi*, 52, 108-110.
- Torgnysdotter, A.** (2006): Fibre/ fibre joints; Their Characterization and Influence On Different Paper Strength Properties, Ph.D. Thesis (ISSN 1652-2443), University of Royal Institute of Technology (KTH), Stockholm.
- Theander O.** and **Westerlund E.A.** (1986): Studies on dietary fibre 3, improved procedure for analysis of dietary fibre, *J. ric. Food Chem.* 34, 330-336.
- Wang, Y., Azhar, S., Lindström, M.E.** and **Henriksson, G.** (2005): Stabilization of Polysaccharides During Alkaline Pretreatment of Wood Combined with Enzyme-Supported Extractions in a Biorefinery. *Wood Chemi. Technol.* 35 (2), 91-101.
- Wågberg, L., Ödberg, L.** and **Nordmark, G.** (1989): Charge determination of porous substrates by polyelectrolyte adsorption&. Part 1. Carboxymethylated, bleached cellulosic fibres, *Nord. Pulp Paper Res. J.* 04(2), 071-076.

Wågberg, L., Winter, L. and Lindström, T (1985): Determination of ion-exchanged capacity of carboxymethylated cellulose fibers using colloid and conductometric titrations, In V. Punton (Ed) Papermaking Raw Materials, Mech. Eng. Publ. Ltd. London, Vol. 2, 917-923.

Young, G.H. and Rowland, B.N. (1933): The relation between hydration capacity and pentosan content of softwood pulps, Paper Trade Journal, 97(15), 44-46.

Manuscript received May 18, 2017

Accepted July 1, 2017

Appendix

Table-The absolute values of the tensile index for the 20 g/m² and 60 g/m² sheets

Sheet Grammage	Kraft Pulps	Tensile index (kNm/kg)							
		0 PFI		500 PFI		1000 PFI		2000 PFI	
		MV	SD (±)	MV	SD (±)	MV	SD (±)	MV	SD(±)
20 g/m ²	Ref	14.8	0.03	40.4	0.17	41.1	0.14	61.1	0.09
	PS	18.7	0.10	44.5	0.06	48.3	0.15	62.6	0.09
	NaBH ₄	19.7	0.33	52.0	0.50	59.5	0.80	65.8	0.60
60 g/m ²	Ref	29.2	0.09	59.8	0.17	70.8	0.17	88.1	0.33
	PS	31.8	0.84	63.8	0.69	76.7	0.64	91.1	0.33
	NaBH ₄	35.0	0.08	68.8	0.15	79.1	0.74	92.1	0.50