ON THE RELATIONSHIP BETWEEN WOOD FIBRE WALL SWELLING, CHARGED GROUPS AND DELAMINATION DURING REFINING

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ABSTRACT

The influence of sulphonic and carboxylic acid groups in combination with the effect of counter ion form, on the swelling capacity of mechanical pulp fibres was studied by means of water retention value (WRV) measured in the temperature range from 25 to 95°C. Mechanical pulp fibres (TMP) were treated with hydrogen peroxide and/or sodium sulphite during conditions resembling those used in chemimechanical and bleaching processes commonly used in the industry. In conventional chemimechanical processes sulphite treatment is used before refining while peroxide treatment can be utilized both before and after refining. In this study we did however also use sulphite after peroxide treatment. When subjecting sodium sulphite treated pulps to a subsequent hydrogen peroxide step, all pulps show a decrease in sulphonic acid groups, which could be owed to dissolution of highly charged lignin. Pulps treated with a high hydrogen peroxide charge (4%), showed a loss in carboxylic acid groups during subsequent treatment with sodium sulphite. This loss is probably due to dissolution of highly charged fibre material such as demethylated pectins. Both increased degree of sulphonation and carboxylation of the lignin reduces the softening temperature by means of reducing the degree of cross-linking in the lignin matrix. This softening probably improves the compressibility of the fibre pads in the sample holders of the WRV centrifuge, which would counteract an otherwise expected increasing WRV-value due to increased swelling potential. This makes it difficult to see clear trends in WRV as a function of increase in degree of sulphonation and carboxylation. When changing counter ion form from proton or calcium form to sodium form there is however always a clear increase in WRV in the range from 20 to 30%.

KEYWORDS: Swelling, Fibre Wall, Water Retention Value, High-Yield Pulp, Ionic Form.

INTRODUCTION

The swelling properties of the wood matrix play an important role when manufacturing high-yield pulps. The fibre wall is only able to swell to a small extent when water-saturated at room-temperature. Increasing the temperature [1, 2, 3] leads to increased fibre wall swelling due to the softening of lignin, which also will give room for the swelling potentials of hemicelluloses and the amorphous part of cellulose. Softening of lignin is also influenced by chemical treatments, such as carboxylation and sulphonation [4, 5]. Defibrating wood chips at different states of swelling will produce fibres and pulps with different combinations of qualities and at different energy demands [6, 7]. This is explained by the fact that the fractures will occur in different areas of the fibre walls depending on where the weakest position is situated. The position of the weakest point will be influenced by the degree of swelling and softening of the wood polymers in the fibre wall [8, 9].

Native wood contains carboxylic acid groups that are located mainly in the hemicelluloses [10, 11]. Supplementary acidic groups can be added to the lignin by oxidative treatments and sulphonation creating carboxylic acid groups and sulphonic acid groups respectively [10-13]. The sulphonic groups are relatively strong acids having a pK_a value of ~1, while carboxylic groups are weak acids having a pK_a value of 3.5 – 5 in hemicellulose and oxidized lignin. When acid groups are dissociated, i.e. are in their ionized form, the proton can be exchanged for other counter ions. It is known that the type of counter ion will influence the swelling ability of the fibre wall [5, 7, 14 -19]. For carboxymethylated sulphite and Kraft pulps, depending on type of counter ion, the following order of swelling is proposed: $Al^{3+}<H^+<Ca^{2+}<Mg^{2+}<Li^+<Na^+$ [20, 21]. Divalent and trivalent ions provide less swelling than monovalent counter ions, due to their ability to bind

into two or more acid groups, thus holding the polymer chains together. Protons are an exception as they form very strong intermolecular bonds i.e. hydrogen bonds. Addition of soluble salt, which increases the ionic strength, has a negative effect on the fibre wall swelling due to screening of the electrostatic repulsion between the charged groups [7, 22-24].

Improved understanding regarding how to optimise the degree of swelling in the wood fibre wall may be a way to reduce the energy demand in the refining process. The forces necessary to achieve fibrillation (internal as well as external) are greatly influenced by the swelling properties of the fibre wall. The degree and position of swelling is also the main cause to where in the wood matrix the fibre separation will take place. Refining of wood chips in different state of swelling will result in mechanical pulp fibres with different optical and mechanical properties. In this study the effect of carboxylic acid groups, sulphonic acid groups and ionic counter ion on high-yield pulps is evaluated by means of measurements of their water retention values at elevated temperatures.

EXPERIMENTAL

Materials
A commercial unbleached spruce TMP taken from the blow line directly after the first chip-refining step was used as raw material. Prior to the experimental work, the pulps were washed with DTPA and then the fine material of the pulps was removed. Four pulp samples were first treated with hydrogen peroxide and after a washing step, further treated with sodium sulphite. Another four pulp samples were treated in the opposite way; first with sodium sulphite and then with hydrogen peroxide. Subsequent to chemical treatment the pulps were converted to proton, sodium and calcium form.

Methods
For chemical treatment of the pulp samples, a modified wing defibrator consisting of a double mantled vessel was used as mixer and reactor, see Fig. 1. When performing trials with sodium sulphite, the wing defibrator was preheated to 130°C. 150 g of pulp (o.d.) was placed inside the wing defibrator and preheated for 2 minutes at a rotor speed of 60 rpm. The rotor speed was then increased to 750 rpm during one minute while the chemicals were added to the defibrator via a nozzle. The reaction time in the wing defibrator was 5 minutes at a rotor speed of 60 rpm. The chemical treatment was stopped by means of washing with deionised water. The sodium sulphite charges used were 10 and 40 g/kg at pH9 and a pulp consistency of 20 %.
When performing trials with hydrogen peroxide, the wing defibrator was preheated to 90°C. 150g of pulp (o.d.) was placed inside the wing defibrator and preheated for 10 minutes at a rotor speed of 60 rpm. The rotor speed was then increased to 750 rpm during one minute while the chemicals were added to the defibrator via a nozzle. The reaction time in the wing defibrator was 15 minutes at a rotor speed of 60 rpm. The chemical treatment was stopped by means of washed with deionised water. The hydrogen peroxide charges were 10 or 40 g/kg with a sodium hydroxide charge factor of 0.6 to the hydrogen peroxide charge at a pulp consistency of 20%. DTPA and sodium silicate were also added at a charge of 10 g/kg and 20 g/kg respectively.
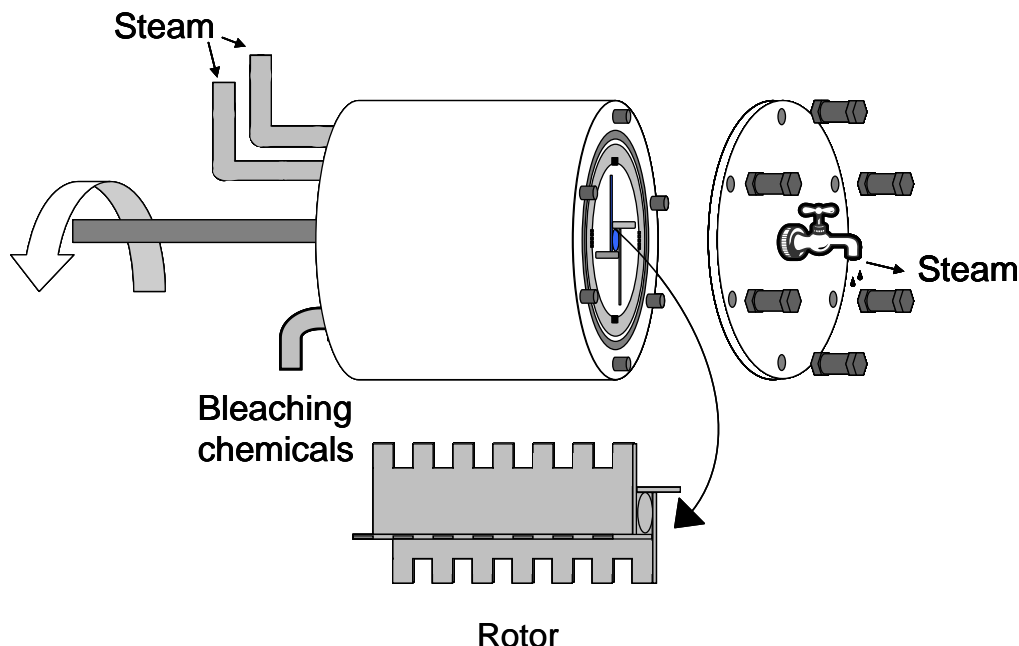
Fig. 1 – Wing defibrator used for chemical treatment of the pulps. The rotor was modified so that the fibres were not refined during mixing.

In addition to their reference form, all pulps were ion exchanged into H^+, Na^+ and Ca^2 form. All pulps were first converted to the proton form by treatment with 0.1M HCl for one hour. It should be emphasized that it is of uttermost importance to wash chemimechanical pulps that contain sulphonic acid groups at low enough pH, as in this case with 0.1 M HCl, in order to ensure that the sulphonate groups are transferred to their proton form. Excess acid was then gently washed out using deionised water. The sodium form was obtained by treatment of 0.1M NaCl for one hour at pH 8.5, followed by gentle washing with deionized water. In the case of calcium the pulps were soaked in 0.1M of calcium chloride and the pH was adjusted to 9.5 with calcium oxide. After soaking for 24h the pulps were washed with deionised water.

Water retention value (WRV) was measured according to SCAN-C 62:00 with exception that the methodology was further developed in order to take the influence of temperature level into consideration and also to keep temperature constant during the measurement [3]. The experiments were performed at temperatures of 25, 75 and 95°C, in such a way that the pulp suspension, sample holders and rinsing water were pre-heated to the measurement temperatures before the centrifugation.

RESULTS AND DISCUSSION

In most conventional production systems for bleached chemimechanical pulp (BCTMP) the wood is subjected to alkaline sulphite treatment before defibration/refining followed by bleaching by means of alkaline peroxide treatment. There are also systems where alkaline peroxide treatment is utilized both before and after defibration/refining often called alkaline peroxide mechanical pulp (APMP).

In this model study we have evaluated the charge levels in terms of degrees of sulphonation and carboxylation of a conventional thermomechanical pulp (TMP) treated with 10 g/kg Na_2SO_3 (Low Sulphite – LP) and 40 g/kg Na_2SO_3, (High Sulphite – HS) as well as with 10 g/kg H_2O_2 (Low Peroxide – LP) and 40 g/kg H_2O_2, (High Peroxide - HP) see Table 1. The degree of carboxylation increased twice as much in the HP case as in the LP case and the degree of sulphonation increased twice as much in the case of HS as in the case of LS roughly according to plan.

Table 1 – Charge in pulp after the first treatment step utilizing a wing defibrator as mixer and reactor. The charge of the DTPA washed, untreated TMP was 102 µmol/g.
LP = Low Peroxide charge, 10 g/kg   **HP = High Peroxide charge, 40 g/kg,**
LS = Low Sulphite charge, 10 g/kg   **HS = High Sulphite charge, 40 g/kg.**

	Change in charge in first treatment		
Sample	**Total charge**	**Carb. groups**	**Sulph. groups**
	[µmol/g fibres]	[µmol/g fibres]	[µmol/g fibres]
LP	158	56	-
HP	272	169	-
LS	135	-	33
HS	223	-	120

Each of the four pulps; LS, HS, LP and HP were subjected to a second treatment in such a way that each pulp that was sulphite treated in the first step was peroxide treated in the second step and each pulp that was peroxide treated in the first step was sulphite treated in the second step. Charge levels in terms of carboxylic groups as well as sulphonate groups were measured on the resulting eight pulps here called; LP-LS, LP-HS, HP-LS, HP-LS, LS-LP, HS-LP, LS-HP and HS-HP, see Table 2.

Table 2 – Charge in pulp after the second treatment step. LP/HP = Low/High hydrogen peroxide charge, LP/HP = Low/High sodium sulphite charge.

			Change in charge in second treatment		
Sample	**Total charge**	**Sulfonic groups**	**Carb. groups**	**Sulph. groups**	**Total**
	[µmol/g fibres]	[µmol/g fibres]	[µmol/g fibres]	[µmol/g fibres]	[µmol/g fibres]
LP-LS	187	13	16	13	29
LP-HS	269	16	94	16	110
HP-LS	178	16	-109	16	-93
HP-HS	259	17	-30	17	-12
LS-LP	152	19	-2	-14	17
HS-LP	192	16	138	-104	34
LS-HP	213	21	90	-12	78
HS-HP	247	22	123	-99	24

The data shows that when subjecting the primary stage low peroxide charge treated pulps to a second stage alkaline sodium sulphite treatment, not only sulphonic acid groups but also some carboxylic acid groups were created. This may be due to reactions of alkali with lignin [18]. While pulps treated with the high peroxide charge in the primary stage, showed a loss in carboxylic acid groups when treated with alkaline sodium sulphite. A possible explanation might be that highly charged material such as pectins are demethylated [19] and dissolved also some highly charged lignin might be dissolved. When subjecting pulps treated with alkaline sodium sulphite in the primary stage to hydrogen peroxide, treatment as a secondary stage the sulphonic acid group content decreases to a level of ~16-22 µmol/g fibres regardless of the initial amount of sulphonic acid groups present in the pulps. This could is most probably due to dissolution of highly charged lignin most probably concentrated to the surfaces of the surfaces of the treated TMP fibres.

A prerequisite for swelling of wood and mechanical pulps is softening (3). Modification of the swelling and softening properties of each of the wood polymers (lignin, hemicelluloses and cellulose) can to a large extent control the position of where the weakest part of the wood matrix will be situated. Moreover, the weakest part of the wood matrix is where the fibre separation will take place when producing mechanical

pulps. Most probably the efficiency of the external and internal fibrillation of the fibre walls is also influenced by how the swelling and softening properties are controlled. The energy demand to produce mechanical pulps is to a great deal determined by the combination of position of fibre-fibre separation together with the efficiency of the external and internal fibrillation. The most important parameters that influence the wood matrix and wood fibres' ability to swell are temperature, pH, ionic form of and the amount of charged groups in the hemicelluloses and lignin of the cell walls.

Water retention value (WRV) is a measure of the capacity of the pulp (fibre network) to retain water during centrifugation and is strongly correlated to the swelling ability of wood pulp fibres. According to standard, the water retention value of pulps is measured at 23°C. In high-yield pulps as thermomechancial and chemimechanical pulps where lignin is present, the standard method is of minor interest both due to that the forming and pressing unit processes in reality are performed at temperatures ranging from 50 to 90°C and even more important due to the fact that the amorphous cross linked lignin polymer has a softening temperature of ~75°C. High-yield pulps are normally refined, i.e. defibrated and fibrillated at temperatures well above the softening temperature of lignin, so in order to take into account of the contribution to swelling from lignin, water retention measurement should also be made at those temperatures. Increasing the temperature leads to a decrease in water retention value due to that the viscosity of water is reduced with increasing temperature. When rising the temperature, the viscosity of water is lowered, thus the water is transported out of the fibres more easily. At elevated temperatures the effect of counter ion is more prominent, see Fig. 2, especially for highly charged pulps.
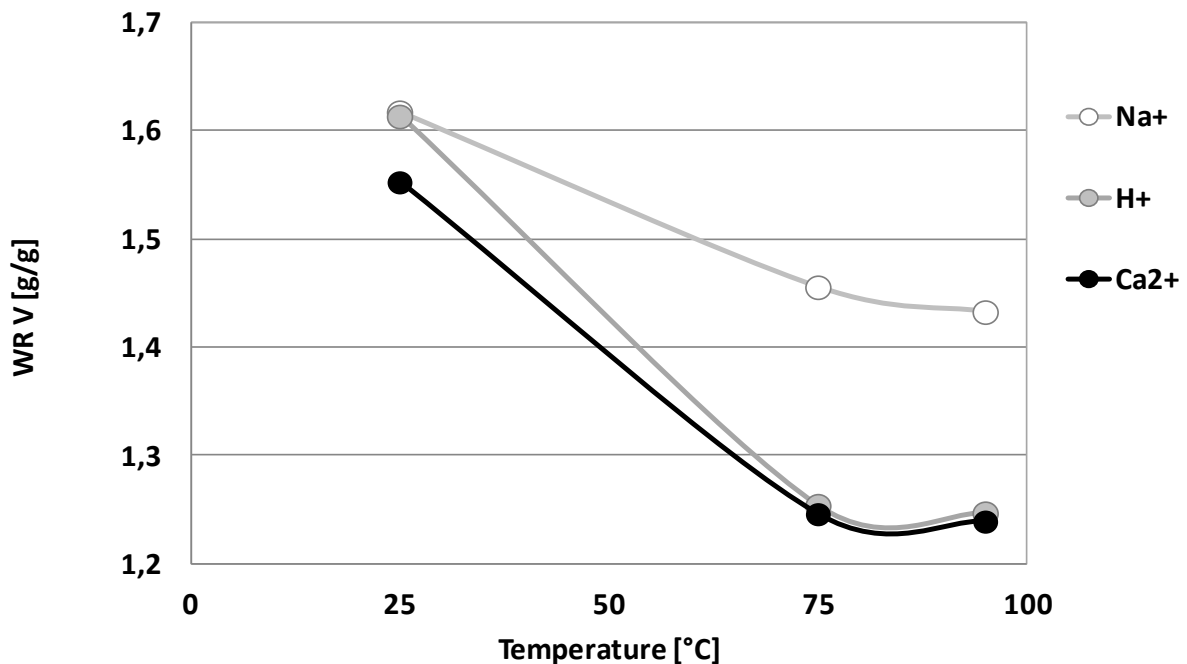
Fig. 2 – Influence of ionic form of peroxide treated TMP fibres, Na^{+} and Ca^{2+} as undissociated (H^{+}), total charge level of 269 µmol/g on the water retention value in a temperature interval of 25 to 95°C.

It has been known [3, 4] that the softening of the wood matrix increases with an increasing number of charged groups. As mentioned above, softening of the wood matrix is a prerequisite to swelling in wood material. Introducing charged groups into the lignin polymer, for instance by sulphonation, opens up its rigid structure promoting swelling. However, at high temperatures this softening increases the compressibility of the fibre pad employed in the water retention measurements rendering lower water retention values. The four samples in Fig. 3 having a water retention value above 1.5 all have been treated

with the higher hydrogen peroxide charge. The sulphonic acid group content was at about the same level for all samples.
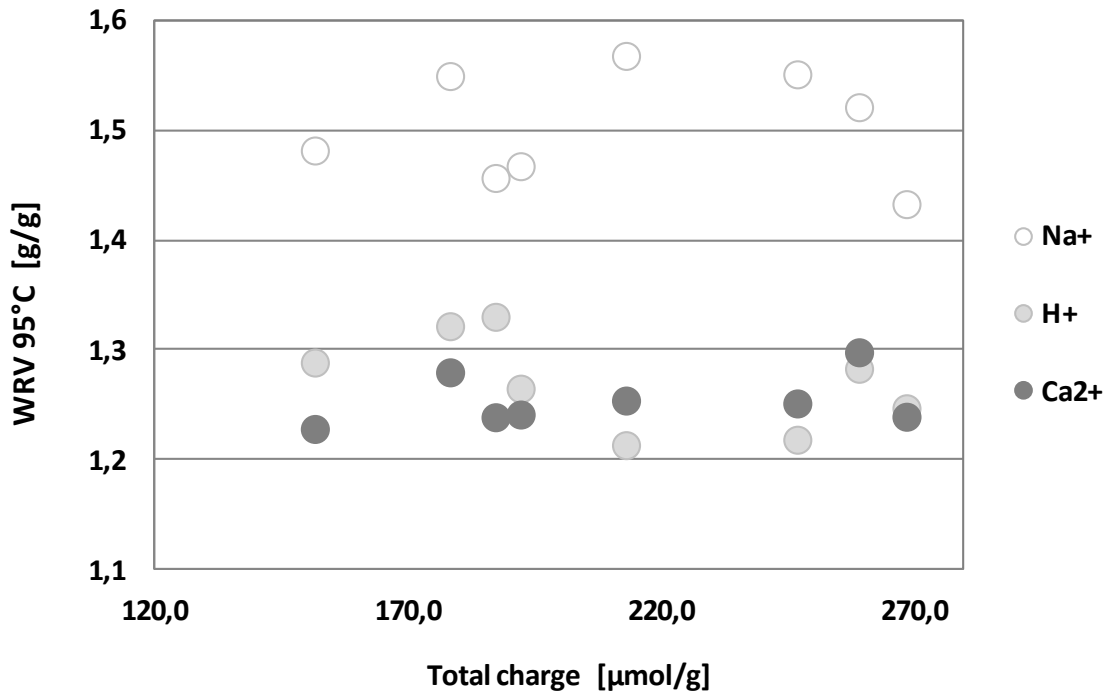
Fig. 3 – Water retention value measured at 95°C as a function of the total acidic group charge of pulp with different counter ions.

These data show that regardless of charge level the mechanical pulp fibres in calcium form or proton form has WRV-values measured at 95°C in the range 1.2 – 1.35 g/g. If the same pulp fibres are tested in their sodium form the WRV values measured at 95°C is in the range 1.4 – 1.6 g/g. It was expected that the WRV, i.e. swelling potential, should be lower for calcium and proton form samples, but not that there shouldn´t be any difference when increasing charge. One should however remember that both sulphonation and carboxylation of lignin reduces the softening temperature by means of reducing the degree of cross linking in the lignin. This does actually improve the compressibility of the fibre pad in the sample holders in the WRV centrifuge at 3000g. The increased compressibility will counteract the increased swelling potential and thus give no clear change in WRV. In the case of sodium form we can see a vague tendency to increase and then decrease when charge level is increased, most probably due to the similar combined effect of improved compressibility due to softening and improved swelling potential due to increased charge density. Early published data shows that swelling propensity due to addition of alkaline sulphite can actually be estimated during chip refining provided that the machine is equipped with thorough gap distance measurement and that the sampling rate is fast enough [27]. The increase in gap distance, when adding 0.5% alkaline sulphite at constant thrust load (nominal pressure), is about 10%. In this case the wood fibres are actually both sulphonated and changed into sodium form simultaneously, i.e. we cannot distinguish between the influences of change in charge level from the influence of ionic form. It is however interesting that the WRV data and the refiner gap measurement data seam to support each other.

CONCLUSIONS

Studies on how carboxylic and sulphonic groups, counter ion, pH and temperature influence swelling properties during refining are important to improve the understanding the mechanisms regarding internal and external fibrillation during refining. When subjecting sodium sulphite treated pulps to a subsequent hydrogen peroxide step, all pulps show a decrease in sulphonic acid groups, which could be owed to dissolution of highly charged lignin. Pulps treated with a high hydrogen peroxide charge (4%), showed a loss in carboxylic acid groups during subsequent treatment with sodium sulphite. This loss is probably due to dissolution of highly charged fibre material such as demethylated pectins. Both increased degree of sulphonation and carboxylation of the lignin reduces the softening temperature by means of reducing the degree of cross-linking in the lignin matrix. This softening probably improves the compressibility of the fibre pads in the sample holders of the WRV centrifuge, which would counteract an otherwise expected increasing WRV value due to increased swelling potential. This makes it difficult to see clear trends in WRV as a function of increase in degree of sulphonation and carboxylation. When changing counter ion form from proton or calcium form to sodium form there is however always a clear increase in WRV in the range from 20 to 30%. Knowledge regarding the behaviour of swelling is a key to get ideas regarding how to modify the present high yield pulping processes in order to reduce the energy demand in the refiners, and also how to tailor make the manufacturing of mechanical pulp fibres with different optical and mechanical properties. Water retention value measurements at elevated temperature and the detailed assessment of charged groups provides information to some degree, but further studies for a deeper understanding regarding how to measure and interpret the combined softening and swelling phenomena are recommended.

REFERENCES

1. Höglund, H., Bäck, R., Falk, B. and Jackson, M., Thermopulp – a new energy efficient mechanical pulping process", Pulp Pap Can, 98(6):T215-222 (1997).

2. Eriksson, I., Haglind, I., Lidbrandt, O. and Salmén, L., "Fiber swelling favoured by lignin softening", Wood Sci Techno., 25:135-144 (1991).

3. Fjellström, H., Engstrand, P. and Htun, M., "Aspects of fibre wall swelling in high-yield pulp", Proceedings, The 4th International Conference on Pulping, Papermaking and Biotechnology, November 7-9, Nanjing, China p. 1183 (2012).

4. Atack, D. and Heitner, C., "Dynamic mechanical properties of sulphonated Black spruce", Trans Tech Sec, CPPA., 5(4):99-108 (1979).

5. Salmén, L., "Influence of ionic groups and their counterions on the softening properties of wood materials", J Pulp Pap Sci, 21(9):310-315 (1995).

6. Hammar, L.Å., Htun, M., Ottestam, C., Salmén, L. and Sjögren, B., "Utilizing the ionic properties of the wood polymers in mechanical pulping", J Pulp Pap Sci, 22(6):219-223 (1996).

7. Lindström, T. and Carlsson, G., "The effect of chemical environment on fiber swelling", Svensk Papperstidning, 85(3):R14-20 (1982).

8. Salmén, L. and Pettersson, B., "The primary wall: important for the fibre separation in mechanical pulping", Cellul Chem Technol, 29:331-337 (1995).

9. Konn, J., Pranovich, A., Fardim, P. and Holmbom, B., "Characterisation and effects of mew anionic groups formed during chemimechanical pulping of spruce", Colloids Surf. A: Physicochem Eng Aspects, 296:1-7 (2007).

10. Sjöström, E., Jansson, J., Haglund, P. and Enström, B., "Acidic groups in wood and pulp as measured by ion exchange", J Polym Sci, 5(11):211-241 (1965).

11. Sjöström, E., "The origin of charge on cellulosic fibres", Nordic Pulp Pap Res J, 4(2):90-93 (1989).

12. Gierer, J. and Imsgard, F., "Reactions of lignin with oxygen and hydrogen peroxide in alkaline media", Svensk Papperstidning, 80(16):510-518 (1977).

13. Agnemo, R. and Gellerstedt, G., "The reactions of lignin with alkaline hydrogen peroxide. Part II: Factors influencing decomposition of phenolic structures", Acta Chem Scan, B33:337-342 (1979).

14. Sundberg, A., Pranovich, A. and Holmbom, B., "Distribution of Anionic Groups in TMP Suspensions", Journal of Wood Chemistry and Technology, 20(1): 71-92 (2000).

15. Laine, J., Lovgren, L., Stenius, P. and Sjoberg, S., "Potentiometric titration of unbleached kraft cellulose fibre surfaces", Colloids Surf. 88: 277-287 (1994).

16. Nyrén, V. and Back, E., Acta Chem. Scand. 12:1516 (1958).

17. Lloyd, J.A. and Home, C.W., "The determination of fibre charge and acidic groups of radiate pine pulps", Nord. Pulp Paper Res. J. 1:48-58 (1993).

18. Thornton, J., Ekman, R., Holmbom, B. and Eckerman, C., "Release of potential "anionic trash" in peroxide bleaching of mechanical pulp", Pap. Puu 75:426-433 (1993).

19. Zhang, Y., Sjogren, B., Engstrand, P. and Htun, M., "Determination of charged groups in mechanical pulp fibres and their influence on pulp properties", J. Wood Chem. Technol.14(1):83 (1994).

20. Scallan, A.M. and Grignon, J., "The effect of cations on pulp and paper properties", Svensk Papperstidning, 82(2):40-47 (1979).

21. Lindström, T., "Chemical factors affecting the behaviour of fibres during papermaking", Nord Pulp Paper Res J, 7(4):181-192 (1992).

22. Nedelcheva, M.P. and Yuriev, V., Nauch Tr Leningrad Lesotekh Akad , 121:74 (1969).

23. Nelson, P.F. and Kalkipsakis, C.G., "The behaviour of salts of a carboxymethylated eucalypt kraft pulp", Tappi, 47(3):170-176 (1964).

24. Grignon, J. and Scallan, A.M., "Effect of pH and neutral salts upon the swelling of cellulose gels", J Appl Polym Sci, 25:2829-2843 (1980).

25. Konn, J., "Process Chemistry in Chemithermomechanical Pulping", Doctoral Thesis, ISBN: 9789521217968 (2006).

26. Konn, J., Pranovich, A. and Holmbom, B., "Dissolution of fibre material in alkaline pretreatment and refining of spruce CTMP" Holzforschung 60:32-39 (2006).

27. Engstrand P., Karlström A. and Nilsson L., "The impact of chemical addition on refining parameters" Int. Mech. Pulp Conf., Ottawa, Canada, CPPA, p. 281 (1995).