Publication VI

Mikhail Iakovlev, Eero Hiltunen, and Adriaan van Heiningen. 2010. Paper technical potential of spruce SO_2-ethanol-water (SEW) pulp compared to kraft pulp. Nordic Pulp and Paper Research Journal, volume 25, number 4, pages 428-433.

Paper technical potential of spruce SO_2-Ethanol-Water (SEW) pulp compared to kraft pulp

Mikhail Iakovlev, Eero Hiltunen, and **Adriaan van Heiningen**

KEYWORDS: Brightness, Drainability, Paper quality, Physical properties, *Picea abies*, SEW pulp, SO_2-ethanol-water, Spruce, Strength properties

SUMMARY: Pulp mills will in the future no longer be only pulp production processes, but biorefineries, producing also green fuels and chemicals. In this context, the SO_2-ethanol-water (SEW) process is highly interesting, as it enables better fractionation of the wood components in a biorefinery concept. However, the pulp produced must as well be competitive with the conventional pulps.

In this study, the pulp properties of softwood SEW pulps were compared to kraft pulps. The SEW pulps possess good tensile, z-directional strength and higher brightness before bleaching. However, the limiting factors for SEW pulp utilization in conventional papermaking are low fibre strength, slow dewatering and high density. Nevertheless, these factors are not as crucial, for instance, in tissue production. Moreover, high density is even advantageous in specialty paper grades, while nanocellulose production would benefit from the decrease in beating energy consumption due to the low fibre strength and high fibre swelling.

ADDRESSES OF THE AUTHORS: Mikhail Iakovlev (mikhail.iakovlev@tkk.fi), **Eero Hiltunen** (eero.hiltunen@tkk.fi) and **Adriaan van Heiningen*** (avanheiningen@umche.maine.edu): Aalto University, School of Science and Technology, Department of Forest Products Technology, P.O.Box 16300, 00076 Aalto, Espoo, Finland. *also University of Maine, Department of Chemical and Biological Engineering, Orono, ME, USA.
Corresponding author: Mikhail Iakovlev

SO_2-ethanol-water (SEW) pulping may be considered as a fractionation process in a forest biorefinery enabling fast removal of lignin and hemicelluloses from different biomass species producing cellulose-rich solid residue, i.e. pulp (Primakov 1961; Westmoreland, Jefcoat 1991; Iakovlev et al. 2009). The SEW pulping chemistry is similar to that of acid sulfite cooking (similar pH of the liquor and temperatures, sulfur dioxide as delignification agent), therefore it is expected that SEW pulp would exhibit similar properties as acid sulfite pulp. Yet unlike sulfite and kraft cooking, SEW process does not employ any base leading to appreciable simplification of the recovery plant and the opportunity of its profitable use in small mills (Iakovlev et al. 2007). Another advantage of SEW process is elimination of the impregnation stage due to the very high penetration rate of ethanol through the cell wall. Contrary to kraft cooking, where the dissolved carbohydrates are mostly degraded to hydroxyacids, and to sulfite cooking, in which around 10-20% of the dissolved monosaccharides are oxidized to aldonic acids by hydrosulfite anions, SEW process preserves the carbohydrates in the spent liquor. This concentrated low-molecular weight sugar solution is a promising feedstock for further chemical and biochemical treatment (Iakovlev, van Heiningen 2009).

At present, kraft pulp dominates the paper and board products market, so potential alternative pulps should be compared with it. Acid sulfite, having a significantly smaller market size, and kraft pulps are substantially different with respect to their beating behaviour, and paper mechanical strength and optical properties. It is also known that many acid-based organosolv pulps behave similar to acid sulfite pulps, i.e. they have higher beatability, higher densities, lower tear strength and higher brightness compared to kraft pulps (Young 1994).

Pulp beating is known to promote the formation of macropores in fibre cell wall (Maloney, Paulapuro 1999). Sulfite pulps have considerably higher cell wall pore volume (i.e. fibre swelling) and lower cell-wall cohesion compared to kraft pulps and that explains the fact that sulfite pulps beat much faster (Stone, Scallan 1968). Another explanation for the lower beatability of kraft pulp according to Page (1983) is that paracrystalline regions of cellulose become amorphous during cooking in a cellulose-swelling medium, e.g. alkaline solutions. On the contrary acid sulfite (and SEW) liquors are not swelling agents for cellulose. The higher fraction of amorphous cellulose in kraft pulp leads to higher energy absorption during beating and thus to lower beating rate.

Many models relate fibre and interfibre bond properties to the tensile strength of paper, though their validity can be seriously questioned (Alava, Niskanen 2008). Hence we based our analysis of tensile strength on the following observations reported in literature: while having weaker fibres the acid sulfite pulps are known to have higher fibre swelling, activation (i.e. drying stresses) and interfibre bonding than kraft pulps (Hiltunen et al. 2002). Drying stresses connect fibre swelling and fibre shrinkage to the elastic modulus and tensile strength of paper (Alava, Niskanen 2008). The tensile strength of paper is determined during fracture of the sheet and depends on fibre segment activation, interfibre bonding and fibre strength (Niskanen 2000; Hiltunen 2003).

Tensile strength is somewhat higher for kraft pulps compared to acid sulfite pulps (at the same freeness). However, kraft pulps exhibit considerably higher tear strength (Rydholm 1965) which is explained by higher fibre strength and by lower interfibre bonding. It is also related to the higher amount of the amorphous cellulose in kraft pulp (Page 1983).

Sulfite pulps are known to be brighter and exhibit higher bleachability than kraft pulps (Rydholm 1965). The reason for higher brightness of sulfite pulps in comparison with kraft pulps is absence of strong chromophores such as quinones and stilbenes which are present in kraft pulps. Better bleachability of sulfite pulps in comparison with kraft pulps is explained by lower amount of lignin-carbohydrate bonds which are mostly hydrolyzed in acidic conditions. Another explanation (Backa et al. 2005; Antonsson et al. 2003) is that even if lignin-carbohydrate complexes (LCC) are present in sulfite pulp they are more reactive in bleaching compared to the kraft LCC because of greater importance of "peeling delignification". Also hexenuronic acids which are not present in acid sulfite pulps consume high amounts of bleaching chemicals as fully bleached kraft pulps are produced.

In the present study the paper technical properties for sheets made from SEW and kraft pulps are compared.

Materials and Methods

Air dried Norway Spruce chips (*Picea abies*, dry matter content 92.9%) were screened using the screens O45; //8; //6; //4 and //2 mm. The fractions from the screens //4 and //2 mm were collected together and used for cooking.

The SEW pulping liquor preparation comprised of injecting gaseous sulfur dioxide into 55% ethanol-water solution, and the SO_2 concentration was controlled by increase in the weight of the solution. Deionized water and ethanol ETAX A (96.1 v/v %) were used. The concentration of SO_2 was 12 w/w %. The kraft pulping liquor sulfidity was 35.0% and the active alkali charge was 21.0% (as NaOH) on wood.

500 o.d. g of the chips and the liquor at a liquor-to-wood ratio of 6 l/kg were placed in 20 bombs (220 ml each) and the cooking was accomplished in a silicon oil bath. The SEW pulp was produced at 135°C (±1°C) in 70 minutes. The kraft pulping comprised of impregnation at 120°C for 70 minutes, heating-up to 170°C for 20 minutes and cooking at 170°C for 125 minutes.

At the end of the cooking, the bombs were rapidly removed from the bath and put into cold water. After cooling, the pulp was removed from the bombs and placed into a washing sock. After squeezing the spent liquor the SEW pulp was washed 2 times with 40% ethanol-water solution (4 ml/g pulp) at 60°C and finally 2 times with deionized water (40 ml/g pulp) at room temperature (Iakovlev et al. 2009), while the kraft pulp was washed 4 times with deionized water (40 ml/g pulp) at room temperature. Visually the SEW pulp did not contain any rejects, contrary to kraft, and therefore it was not screened. The kraft pulp was screened using 0.35 mm screen. The resulting pulps were analyzed for yield and kappa number using SCAN-C 1:00, intrinsic viscosity in CED using SCAN-CM 15:99. Fibre Saturation Point (FSP) was measured according to the solute exclusion technique (Stone et al. 1968; Maloney 2000). The accuracy of Aalto University FSP method is considered to be ~0.03 g/g with three parallel measurements. Fibre length and coarseness were measured by Metso/Kajaani FibreLab device. The pulps properties are given in *Table 1*.

Table 1. Unbeaten pulp properties.

Pulp	SEW	Kraft
Kappa number	42.8	40.0
Unscreened yield, %	53.3	49.3
Rejects, % on pulp	no*	0.3
Intrinsic viscosity in CED, ml/g	1160	1350
Fibre length (lw), mm	2.78	2.99
Coarseness, mg/m	0.217	0.172
FSP, g/g	1.36	1.24

*visual evaluation

The pulps were beaten in a PFI mill at 10% stock consistency (300 g) at a load of 3.4 kg/cm, difference between the two beating elements speed was 6.0 m/s (ISO 5264-2:2002). Drainability of pulp was measured by ISO 5267-1:1999 (Schopper-Riegler method). Handsheets (approx. grammage 60 g/m^2) were prepared from unbeaten and beaten pulps using a KCL-model (square) sheet machine and deionized water (ISO 5269-1:2005) and tested for grammage (ISO 536:1995), density (ISO 534:1988), zero-span (ISO 15361:2000), tensile (ISO 1924-2:1994), tear (ISO 1974:1990, Elmendorf method), burst (ISO 2758:1983) and internal bond (Scott-bond) strength (T569 pm-00), ISO brightness (ISO 2470:1999), opacity, light scattering and absorption coefficients (ISO 9416:1998).

Results and Discussion

The SEW pulp has lower fibre length and higher coarseness than kraft pulp (*Table 1*). We do not have an explanation for the difference in the fibre length (the raw material batch was the same). Higher coarseness of the SEW pulp is probably a consequence of the higher yield.

The drainage resistance of the SEW pulp increases much faster during beating than that of the kraft pulp (*Table 2*, *Fig 1*) indicating the lower cell-wall strength of the former. Higher SR indicates higher fibre swelling and higher water removal resistance in a paper machine. The SEW pulp also has a higher FSP than kraft (*Table 1*). This shows that SEW pulp has higher cell-wall pore volume and (single) fibre swelling.

Dry zero-span for the SEW pulps is fluctuating around 150 (Nm/g), while for the kraft pulp it is around 180 (Nm/g) (*Fig 2*). The slight increase of zero-span of kraft pulp with beating is due to fibre straightening (Mohlin, Alfredsson 1990). It can be also related to real fibre strengthening (Hiltunen et al. 1999) or to the influence of bonding on the measurement. In any case the value for SEW pulp is clearly lower than for kraft pulp meaning the former has weaker fibres.

Density is higher for the SEW pulp sheets than for kraft if plotted against number of beating revolutions (*Fig 3*), which indicates higher bonded area (RBA) for the SEW pulps (at the same beating energy). However, at constant drainability the density of the SEW pulp sheets is about the same as that of kraft (*Fig 4*).

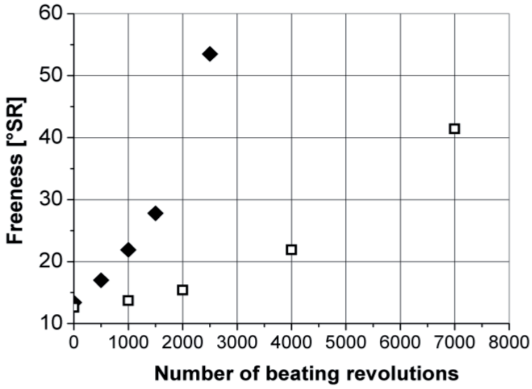

Fig 1. Freeness versus number of beating revolutions: ◆ – SEW; □ – kraft pulps.

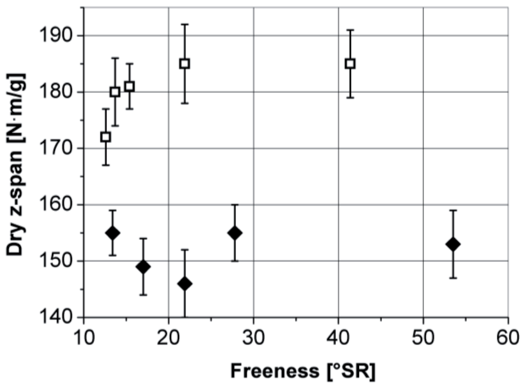

Fig 2. Dry zero-span versus freeness: ◆ – SEW; □ – kraft pulps.

Table 2. Pulp sheets properties.

Pulp	SEW					Kraft				
Number of beating revolutions	0	500	1000	1500	2500	0	1000	2000	4000	7000
Freeness, °SR	13.4	17.0	21.9	27.8	53.5	12.6	13.7	15.4	21.9	41.4
Apparent density, kg/m^3	529	664	662	687	752	459	543	592	656	705
95% confidence level, kg/m^3	*±9*	*±2*	*±2*	*±4*	*±1*	*±2*	*±1*	*±1*	*±1*	*±1*
Tensile index, (N·m)/g	36.3	60.1	64.7	68.4	82.7	34.0	63.6	77.4	96.2	109
95% confidence level, (N·m)/g	*±1.8*	*±2.5*	*±2.0*	*±2.8*	*±2.4*	*±2.0*	*±2.3*	*±2.1*	*±4.0*	*±2*
Tear index, (N·m^2)/kg	9.25	7.62	6.79	6.36	5.54	23.4	22.2	16.4	13.0	11.8
Burst index, kN/g	2.76	4.57	4.95	5.66	6.03	2.74	5.28	6.93	8.03	9.51
Internal bond strength, J/m^2	102	249	333	409	615	62.1	109	165	280	382
95% confidence level, J/m^2	*±6*	*±6*	*±13*	*±17*	*±24*	*±9.4*	*±3*	*±3*	*±22*	*±23*
Dry z-span, (N·m)/g	155	149	146	155	153	172	180	181	185	185
95% confidence level, (N·m)/g	*±4*	*±5*	*±6*	*±5*	*±6*	*±5*	*±6*	*±4*	*±7*	*±6*
ISO brightness, %	46.5	42.8	41.9	40.9	37.4	24.4	23.0	21.9	20.6	19.2
95% confidence level, %	*±0.2*	*±0.2*	*±0.3*	*±0.4*	*±0.6*	*±0.1*	*±0.2*	*±0.2*	*±0.3*	*±0.2*
Opacity, %	82.9	81.1	79.7	75.4	71.8	97.6	96.3	95.3	93.8	92.1
Light scatter, m^2/kg	25.1	19.4	17.4	16.0	12.7	23.3	18.6	17.2	15.6	13.7
Light absorption, m^2/kg	2.83	2.73	2.62	2.49	2.44	12.2	10.6	10.6	10.6	10.4

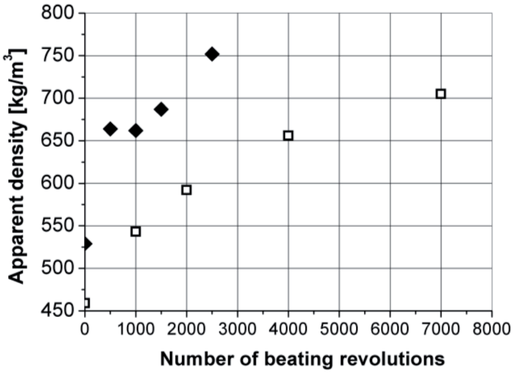

Fig 3. Apparent density versus number of beating revolutions: ◆ – SEW; ☐ – kraft pulps.

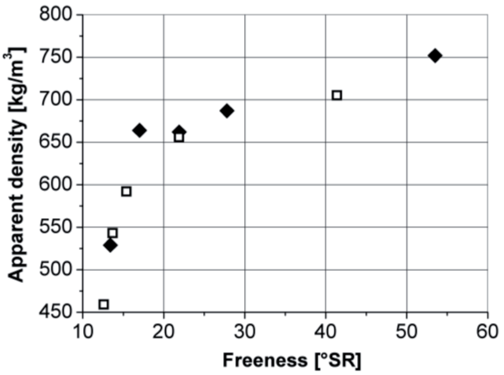

Fig 4. Apparent density versus freeness: ◆ – SEW; ☐ – kraft pulps.

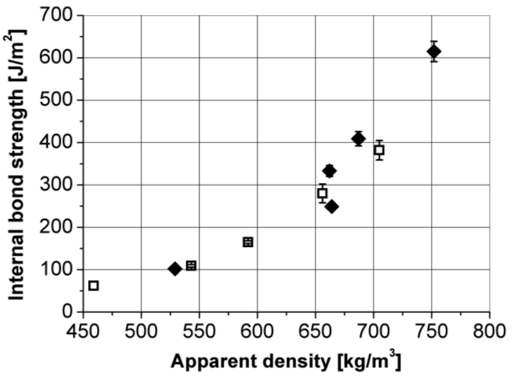

Fig 5. Internal bond strength versus apparent density: ◆ – SEW; ☐ – kraft pulps.

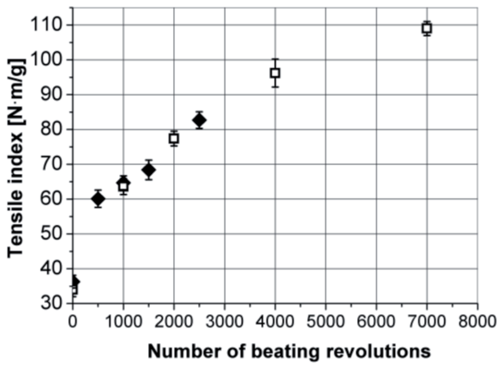

Fig 6. Tensile index versus number of beating revolutions: ◆ – SEW; ☐ – kraft pulps.

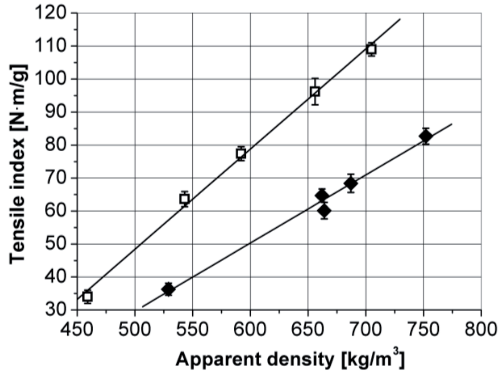

Fig 7. Tensile index versus apparent density: ◆ – SEW; ☐ – kraft pulps.

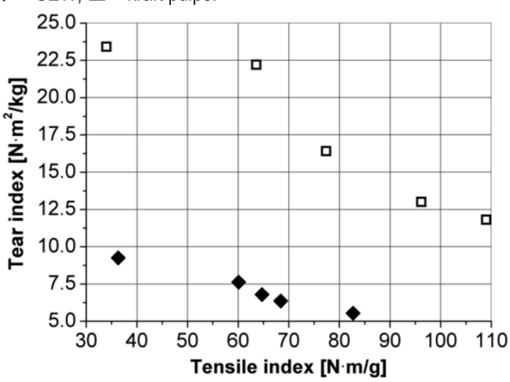

Fig 8. Tear index versus tensile index: ◆ – SEW; ☐ – kraft pulps.

Internal bond (Scott-bond) strength develops clearly quicker during beating for SEW pulp (*Table 2*). This shows that SEW pulp has higher interfibre bonding than kraft at the same beating energy. However, at constant sheet density, Scott bond strength is about the same for both pulps (*Fig 5*).

The SEW and kraft pulp tensile index development follows the same curve if plotted versus beating duration (*Fig 6*), thus showing that tensile strength of SEW pulp sheets is as good as that of kraft sheets at the same beating energy.

However, when tensile strength is plotted versus density (*Fig 7*), SEW pulp has poorer tensile strength than kraft pulp. Exact reasons for this are difficult to determine as tensile strength is a complex function of three factors: activation, bonding and fibre strength. In this study SEW pulp seems to have higher activation (FSP), higher bonding (Scott-bond) and lower fibre strength (zero-span) than kraft pulp.

Tear index of the SEW pulps is considerably lower than that of kraft (*Fig 8*). It is known that high fibre length increases tear strength, and according to Seth (1996) also high fibre coarseness increases tear strength. We assume that length and coarseness effects compensate for each other in this study. Thus the difference in tear index is most likely mainly due to the lower fibre strength of SEW pulp (and to minor extent also because of higher interfibre bonding of SEW pulp sheets at the constant beating energy).

Low tear strength probably leads to low flaw-resisting ability (fracture energy) of paper/board. This is because both tear strength and fracture energy are known to depend on fibre length, fibre strength and interfibre bonding. Thus roughly similar trend for fracture energy during beating can be expected as has been shown to be the case for mechanical-chemical pulp mixtures (Hiltunen 2003). However, tear strength is nowadays considered far less important for paper runnability as thought traditionally as is explained in a recent paper physics study (Uesaka 2005).

The higher brightness (*Fig 9*) and lower light absorption of the SEW pulp indicate its better optical properties despite a slightly higher kappa number (*Tables 1, 2*). Poorer opacity of the SEW pulp is probably because of higher brightness since these properties depend on each other. The light scattering coefficient decreases during beating, causing a decrease in brightness, for both SEW and kraft pulps due to the reducing of free surface area in the sheet as density increases (*Fig 9*, *Table 2*).

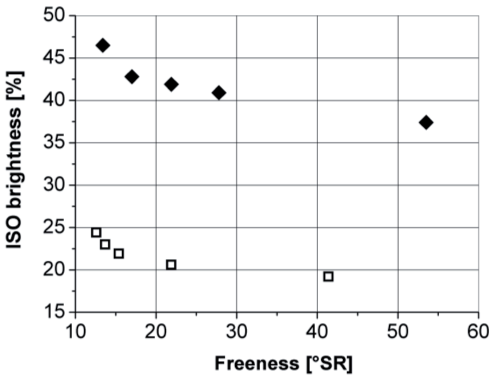

Fig 9. ISO brightness versus freeness: ◆ – SEW; ☐ – kraft pulps.

Certain issues on technical suitability of SEW pulp for paper production can be discussed. A significant problem for SEW pulp is slow dewatering leading to production capacity problems in fast and large paper and board machines. Nevertheless, the water removal properties seem less crucial, for example, in tissue production and smaller specialty paper machines. This is demonstrated in Central Europe where sulfite pulp is being currently used as a raw material in tissue production. It is related to the fact that the low grammage of tissue makes water removal easier than in heavier grades.

Higher density (poorer bulk) is a disadvantage in many paper/board grades (e.g. uncoated fine papers) but is an advantage in some specialty paper grades like greaseproof papers, release paper. Also in some cases in coated printing papers a dense enough structure for base paper is preferred before coating in order to control coating colour absorption. In production of greaseproof papers sulfite pulp is sometimes used as it is densified with lower beating energy consumption than kraft. Old, small and slow machines that are typically used for production of greaseproof papers seem evidently to have more flexibility to the dewatering resistance of pulp than large machines.

In the production of nano/microfibrillar cellulose from chemical pulp the high energy needed to break fibres into fibrils is of high concern. Because of the low fibre strength and low beating energy consumption, SEW pulp could be suitable for nanocellulose production. In addition, increased fibre swelling (internal fibrillation) could also lead to easier breaking of loosened internal fibre wall structure into fibrils. In fact sulfite pulp is being currently used as raw material for nanocellulose in some research projects for these reasons.

We can summarize the comparison between SEW and kraft pulps as follows:

1. SEW pulp beats faster than kraft pulp (SR, sheet density) which means slower dewatering at the same beating energy consumption and lower beating energy consumption for achieving the same sheet density.
2. SEW pulp has clearly weaker fibres than kraft as indicated by lower zero-span and tear strength.
3. SEW pulp has clearly higher interfibre bonding than kraft pulp at the same beating energy level as indicated by higher Scott-bond strength and higher density. At constant sheet density Scott-bond strength is about the same.
4. SEW pulp has lower tensile strength than kraft at constant density, but the same tensile strength at constant beating energy consumption was reached for both pulps.
5. Unbleached SEW pulp is considerably brighter than unbleached kraft pulp.

Conclusions

In general SEW pulp is similar to acid sulfite pulp. It beats easily which implies lower beating energy consumption to achieve certain density or fibre swelling level and lower investments needed for the beating equipment. It has excellent z-directional strength and good tensile strength but low tear strength. High brightness before bleaching is a clear advantage of the SEW pulp which allows avoiding long bleaching sequences.

One significant problem of SEW pulp is poor water removal properties leading to production capacity problems at fast and large paper and board machines. However, the water removal properties seem to be less crucial, for instance, in tissue production and small specialty paper machines.

High sheet density of SEW pulp is an advantage in certain specialty papers like greaseproof and release paper.

As SEW pulp is cost-effective and based on the obtained results it may be stated that this pulp is suitable for many paper and board grades, however, not for all. It has potential in some specialty grades, tissue and new applications such as nanocellulose production.

Acknowledgements

We thank Timo Pääkkönen for his help with the laboratory work, Myrtel Kåll for fibre length and Leena Nolvi for FSP measurements. Financial support of TEKES through the FiDiPro program is greatly appreciated.

Literature

Alava, M. and Niskanen, K. (2008): Chapter 5: In-plane tensile properties, In: Niskanen, K. (ed.), Paper Physics (2nd ed.), Publ. Finnish Paper Engineer's Association, Jyväskylä, Finland, pp. 181.

Antonsson, S., Lindström, M.E. and Ragnar, M. (2003): A comparative study of the impact of the cooking process on oxygen delignification, Nord. Pulp Paper Res. J., 18(4), 388.

Backa, S., Gustavsson, C., Lindstroem, M.E. and Ragnar, M. (2005): On the nature of residual lignin, Cellulose Chemistry and Technology, 38(5-6), 321.

Hiltunen, E., Laine, J.E. and Paulapuro, H. (1999): Effect of fibre charge on refining of softwood kraft pulp, PTS-Symposium PAPIERFASERSTOFF-TECHNIK: Brachliegende Potentiale beim Einsatz von Faser- und Hilfstoffen, Dresden, Germany, April 14-15, 1999, PTS, München, 1999, pp. 19, 19E and 19-1 to 19-10.

Hiltunen, E., Kettunen, H., Laine, J.E. and Paulapuro, H. (2002): Behaviour of reinforcement fibres in TMP-based paper, Paperi Puu, 84(4), 269.

Hiltunen, E. (2003): On the beating of reinforcement pulp, Doctoral Thesis, Helsinki University of Technology, Laboratory of Paper Technology, Reports, Series A16, Espoo, Finland, 65 pages + 8 publications as appendix.

Iakovlev, M., van Heiningen, A. and Pylkkänen, V. (2007): SO_2-ethanol-water pulping of softwoods, In: Proceedings of the 6th Biennial Johan Gullichsen Colloquium, Espoo, Finland, November 15, 2007, pp. 39.

Iakovlev, M., Pääkkönen, T. and van Heiningen, A. (2009): Kinetics of SO_2-ethanol-water pulping of spruce, Holzforschung, 63, 779.

Iakovlev, M. and van Heiningen, A. (2009): Mass balances and dissolution kinetics of hemicelluloses during SO_2-ethanol-water (SEW) pulping of spruce, In: Proceedings of 15th ISWFPC Conference, Oslo, Norway, June 15-18.

Maloney, T. and Paulapuro, H. (1999): The formation of pores in the cell wall, J. Pulp and Paper Sci., 25(12), 430.

Maloney, T. (2000): On the pore structure and dewatering properties of the pulp fiber cell wall, Doctoral Thesis, Helsinki University of Technology, Acta Polytechnica Scandinavica, Chemical Technology Series No. 275, Espoo, Finland 2000, 52 pages + 7 publications as appendix, p. 11.

Mohlin, U-B. and Alfredsson, C. (1990): Fiber deformation and its implications on pulp characterisation, Nordic Pulp Paper Res. J. 5(4):172.

Niskanen, K. (2000): Kraft fibers in paper – effect of beating, 10th International Conference CELLUCON 1998, Turku, Finland, Woodhead Publ., Cambridge, UK, 2000, pp. 249-260.

Page, D.H. (1983): The origin of the differences between sulfite and kraft pulps, J. Pulp Paper Sci., 9(1), 15.

Primakov, S.F. (1961): Delignification of various wood species with aqueous-alcoholic solutions of SO_2, Nauchn. Tr. Vses. Nauchn.-Issled. Inst. Tsellyulozn.-Bumazhn. Prom., 47, 69.

Rydholm, S. (1965): Pulping processes, Interscience publishers, New York – London – Sydney, pp. 361, 439, 1156.

Seth, R.S. (1996): Optimizing reinforcement pulps by fracture toughness, Tappi J., 79(1), 170.

Stone, J.E., Scallan, A.M., and Abrahamson, B. (1968): Influence of beating on cell wall swelling and internal fibrillation, Svensk Papperstidning, 19(10), 687.

Stone, J.E. and Scallan, A.M. (1968): Effect of component removal upon the porous structure of the cell wall of wood. III. Comparison between the sulfite and kraft processes, Pulp Paper Mag. Can., 69(12), 69.

Uesaka, T. (2005): Principal factors controlling web breaks in pressrooms – Quantitative evaluation, Appita J., 58, 425.

Westmoreland, R.A. and Jefcoat, I.A. (1991): Sulfur dioxide-ethanol-water pulping of hardwoods, Chemical Engineering Communications, 104, 101.

Young, R.A. (1994): Comparison of the properties of chemical cellulose pulps, Cellulose (London), 1(2), 107.

Manuscript received May 17, 2010

Accepted August 18, 2010