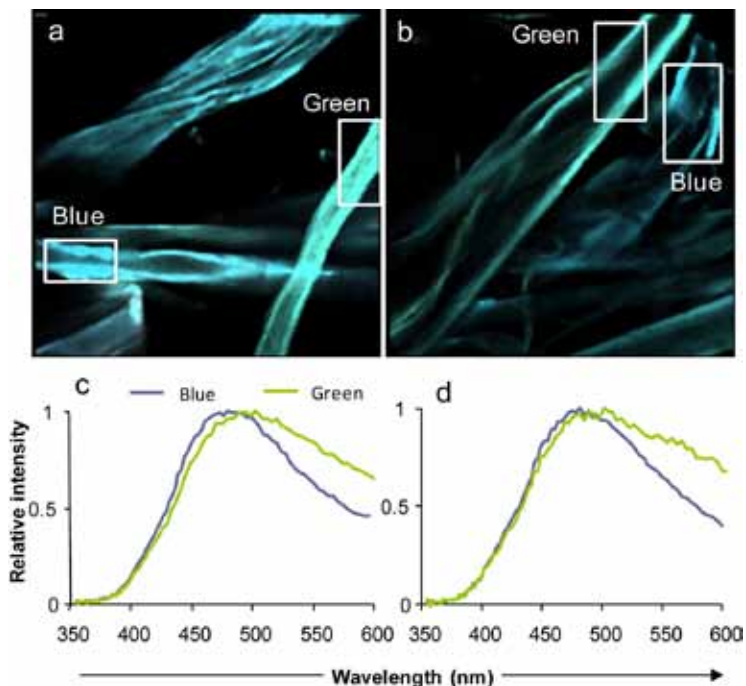


CRUW Mechanical Pulping

Sub-project 3: Effect of sulphite pre-treatment and high intensity refining on spruce TMP pulps produced at the Braviken mill

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Intern rapport nr 7 (begränsad spridning)

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Summary

The effects of pressurized compressive chip and low dosage sulphite pre-treatments were evaluated for production of thermomechanical pulp in mill scale trials using Norway spruce (*Picea abies*) at the Braviken paper mill (Holmen Paper AB, Sweden). The aim of the study was to provide knowledge leading to the improvement of energy efficiency during the production of mechanical pulps suitable for news and improved new grade papers. Pulps produced in the mill trials were characterized using conventional pulp and paper testing and by advanced methods including image analysis, FTIR with multivariate analysis, Simons staining with statistical analysis, spectral imaging and HCL fibre cleavage.

Sulphite pre-treatment gave a linear dose response in tensile index and light scattering with addition of sulphite ($\geq 1.2\%$ Na_2SO_3). The maximum in tensile index and light scattering at a sulphur content of 0.2% (as Na_2SO_3) reported previously was not found in this mill study. Low dosage sulphite pre-treatment increased delamination/internal fibrillation of fibres indicating increased fibre flexibility. These fibres produced denser sheets with higher tensile index and slightly reduced light scattering at certain specific energy consumption. The specific energy consumption needed to produce pulp at a certain tensile index was reduced by 320 kWh/BDT (15%) for chips pre-treated with $\sim 1.2\%$ Na_2SO_3 compared with untreated chips. This gave a reduction in light scattering for sulphite pre-treated pulps when compared at equal tensile index.

Image analysis of fibre cross-sections provided information of the composition of the total fibre population, fibre cross-sectional compactness as well as effects of sulphite treatment. Results showed a fairly constant fibre population (40% early-/60% latewood) existing in all samples and for higher energy to cause greater fibre splitting of untreated fibres particularly of latewood fibres. Increasing the amount of sulphite reduced fibre splitting with less severe fibre delamination for pulps refined at 1820 and 1850 kWh/ADT. Sulphite treatment seemed in general to induce more refining of early- than latewood fibres. SEM observation on fibres revealed high degree of deformation along the fibre axis that could also be seen on the fibre cross-sections analyzed.

FTIR analyses indicated that the highest degree of sulphonation (10 kg/BDT) gave rise to different fibre separation mechanisms during refining compared with the reference unsulphonated pulps providing a different fibre surface and thereby mechanical properties. Multivariate analysis of FTIR spectra suggested the exposed fibre surface to be richer in hemicellulose for sulphonated pulped fibres. This could provide for a better binding surface and higher strength for paper. However, no clear pattern of differences in the distribution images and therefore the microdistribution of xylan were determined.

Statistical analysis of the Simons' staining of fibres indicated that both the energy input and chip pre-treatment significantly induced wall delamination and internal fibrillation (D/IF) of pulp fibres. It was shown that the fibre development of pulp 10(1580) (with lowest SEC) gained via improved wall D/IF was almost similar to that shown for pulp 00(1850) (with highest SEC). This indicates that an energy efficient refining can be obtained with 10 kg/BDT sulfite pre-treatment prior to refining and will produce the most flexible fibres.

Spectral imaging showed sulphite treatment of impressarefiner chips to improve the optical properties of pulps with a clear dose-response shown at both higher and lower SEC levels, the former having the largest effect on whiteness. Photochemical effects of sulfonation using reflectance intensities showed complex results regarding lignocellulosic autofluorescence. Unlike wood, impressarefiner chips and pulp fibres showed a clear blue-shifted fluorescence maximum characteristic for a shortened conjugated system indicating that both the chipping and Impressafiner pretreatment induced a minor degradation of the lignocellulosic matrix that can be measured using spectral imaging. Refining however, increased the red edge fluorescence of the sulfonated whole long fibre fraction with a similar effect on the lignin fluorescence of wood.

Using the HCL method of fibre analysis no significant trend for the effect of sulphite treatment was noted and only minor differences in fibre length were detected.

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Stig Bardage, SLU, Uppsala

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Anne-Mari Olsson, Lennart Salmén, Innventia, Stockholm

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Dinesh Fernando and Geoffrey Daniel, SLU, Uppsala

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Jonas Hafrén, SLU Uppsala, Erik Nelsson, Holmen Paper AB Norrköping, Hans C. Gerritsen and Arjen N. Bader, Utrecht University The Netherlands

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Paul Ander, SLU, Uppsala

Background

During the production of news grade and improved news grade papers it is desirable to reach high opacity at sufficient strength properties with a minimal use of electrical energy. For this purpose, the thermomechanical pulp (TMP) process provides pulp with a suitable combination of light scattering and strength properties (Höglund and Wilhelmsson 1993). However, the use of electrical energy in this process is high.

One approach for reducing the use of electrical energy in the TMP process is chip pre-treatment prior to refining. Various types of pre-treatment techniques have been evaluated throughout the history of TMP, including: mechanical pre-treatment (Frazier and Williams 1982), sulphite pre-treatment (Atack *et al.* 1978), alkaline hydrogen peroxide pre-treatment (Bohn and Sferrazza 1989), oxalic acid pre-treatment (Akhtar *et al.* 2002), enzymatic pre-treatment (Peng *et al.* 2005) and others. However, so far, no chip pre-treatment technique has been widely adapted in mill scale production of TMP from spruce.

In 2008 Holmen Paper AB started a new TMP line at the Braviken paper mill with an ambition to increase pulp quality and decrease energy consumption. Included in this installation was the first mill scale Impressafiner operating on 100% spruce chips. The Impressafiner is a pre-treatment screw-press where chips are compressed at high strain in a pressurized environment. During the compression, water and extractives are pressed out of the chips. An impregnation step is located directly after the compression zone. The liquor uptake for chips in this position is high, which makes it a suitable process step for addition of chemicals.

Low dosage sulphite pre-treatment was chosen as a first candidate for this evaluation. It has been observed that low dosage sulphite pre-treatment gives a maximum in tensile index and light scattering at a sulphur content of ~0.2% (as Na₂SO₃) compared to other sulphite dosages at equal specific energy consumption (Axelson and Simonson 1982; Westermark *et al.* 1987; Svensson *et al.* 1994). The low sulphur content needed to reach this effect is an attractive feature of this pre-treatment concept. Low sulphur content implies low sulphite dosage and therefore less yield loss and low chemical costs.

Chemi-thermomechanical pulping

During the production of CTMP from softwood, wood chips are usually impregnated with 2-4% Na₂SO₃ at pH 9-10 and pre-heated at 120-140 °C with a retention time of 2-15 min. This usually yields sulphur contents in the range 0.4-1.2% (as Na₂SO₃) prior to refining (Lindholm and Kurdin 1999). The major chemical mechanism for sulphonation of wood under these conditions is the

introduction of sulphonate groups into benzylic (α -) carbon of phenyl propane units in lignin (Lindholm and Kurdin 1999). The introduction of sulphonate groups in the lignin polymer affects the dynamic mechanical properties of wood. In the sulphur content range 0.3 to 2.8% (as Na_2SO_3), the softening temperature of black eastern spruce (*Picea mariana*) was decreased by about 2 °C for every 0.1% increase in sulphur content (as Na_2SO_3) (Atack *et al.* 1978) (Figure 1).

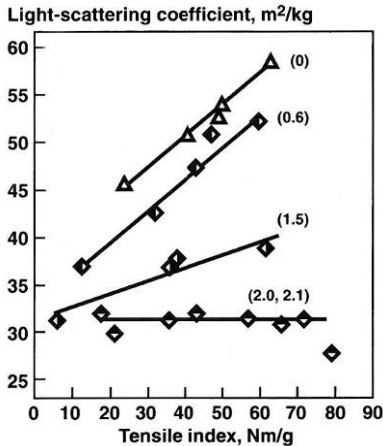


Figure 1. Light scattering vs. tensile index for different sulphonate content (% $-\text{SO}_3^-$) denoted in brackets (1% $-\text{SO}_3^- = 1.57\% \text{Na}_2\text{SO}_3$) (Atack *et al.* 1980).

Sulphonation under CTMP conditions shifts fibre separation towards the middle lamella so that separation occurs predominantly in the area of the primary cell wall and middle lamella (Lai and Iwamida 1993). Fibre separation in the area of the middle lamella is favourable for products such as paper board and tissue where the objective is to produce pulp with high bulk and low amount of shives at a certain Scott bond (paper board) or tensile strength (tissue) (Höglund and Wilhelmsson 1993). Such pulps are however not suitable for printing grade papers due to the inferior light scattering in relation to tensile index (Höglund and Wilhelmsson 1993). Atack *et al.* (1980) measured the relationship between light scattering and tensile index for different degrees of sulphonation (Figure 1) and attributed the lower light scattering for sulphonated pulps to an extensive collapse of long fibres and lower amounts of fines.

LOW DOSAGE SULPHITE PRE-TREATMENT

Low dosage sulphonation (sulphur content < 0.4% as Na_2SO_3) under slightly alkaline conditions prior to refining has been shown to affect pulp properties differently compared to the effects seen in the dosage range of the CTMP process (Axelson and Simonson 1982). A maximum was observed for both tensile index

and light scattering at 0.2% sulphur content (as Na_2SO_3) when compared at certain specific energy consumption (Figure 2). Similar results were later obtained by Westermarck *et al.* (1987) and Svensson *et al.* (1994).

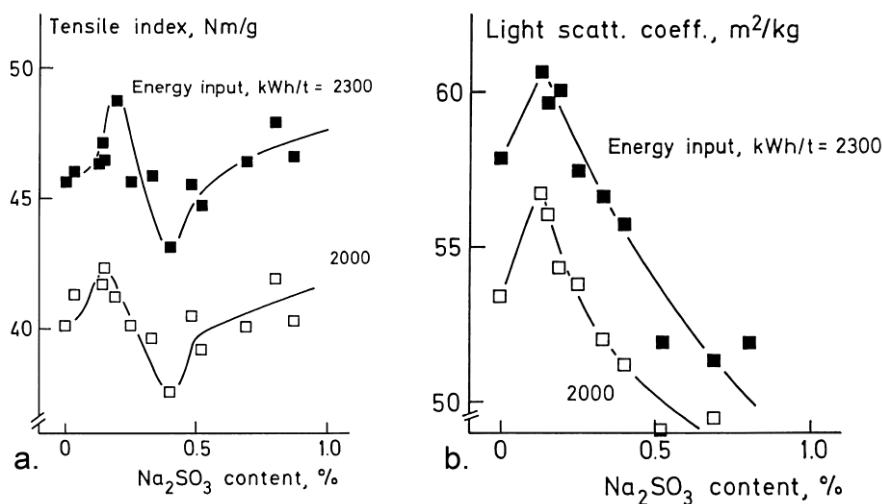


Figure 2. Tensile index (a) and light scattering (b) vs. sulphur content (as Na_2SO_3) at certain specific energy consumption. A maximum in tensile index and light scattering was observed at a sulphur content of 0.2% (as Na_2SO_3) (Axelson and Simonson 1982).

The explanation offered by Axelson and Simonson (1982) to the maximum in tensile index and light scattering was that a sulphur content of 0.2% (as Na_2SO_3) gave a suitable decrease in the softening temperature in relation to the temperature and frequency of the breaker bar section and the refining zone of the refiner used in the study.

It was later found that there is a selective sulphonation of the primary cell wall layer for low sulphite dosages (Westermarck *et al.* 1987). It was also found that sulphonation affects the softening temperature of the middle lamella and the primary cell wall layer differently. As the softening temperature of middle lamella is decreased by sulphonation, the softening temperature of the primary cell wall layer is increased from a value below that of the middle lamella. The high protein content of the primary cell wall is suggested as the explanation to the differences between the primary cell wall layer and middle lamella (Östberg and Salmén 1988). However, relating this effect to the maximum in tensile index observed by Axelson and Simonson (1982) is rather speculative.

By comparing the microscopic appearance of fibre-fibre fractures for wood with different sulphur contents, it was possible to relate the tensile index maximum at a

sulphur content of 0.2% (as Na₂SO₃) with fibre surfaces where the middle lamella was almost completely removed. These surfaces also had very thin, thread-like fragments that were not present at higher sulphonation levels (Westermarck *et al.* 1987, Johansson *et al.* 1997).

Experimental

MATERIALS AND METHODS

A mill scale trial was conducted at the Braviken paper mill, Holmen Paper AB, Norrköping, Sweden. The raw material used was a mixture of round wood and sawmill chips from 100% Norway spruce (*Picea abies*).

CHIP PRE-TREATMENT

Figure 3 outlines details of the chip pre-treatment equipment used in the trial. For production of chips and pulps with chip pre-treatment, chips were fed from the chip washer to a steaming bin (90 °C, ~15 min.) through a rotary valve to the pressurised RT-conveyor (1.8 barg, 3-10 sec). Thereafter chips were compressed in the Impressafiner with geometrical compression ratio 2.7:1 and specific energy consumption 20-28 kWh/bdt and directly submerged in the impregnator (liquor uptake: 0.9-1.8 m³/bdt) and transferred to the refiner pre-heater (10-15 min, no steam added). Before refining, both reference and pre-treated chips were fed through a plug screw into the steam pressurized environment where chips are pre-heated prior to refining (4.6 barg, ~155 °C, ~6 sec). Samples of reference chips were collected after the chip wash. Samples of pre-treated chips were taken out after the impregnator.

Addition of sulphite

Sulphite was added to chips by mixing concentrated solutions of sodium bisulphite (NaHSO₃) and sodium hydroxide (NaOH) into the continuous flow of impregnation liquid. The solution was passed through a static mixer after which the pH was measured. The solution was then absorbed by the chips in the impregnator. The addition of NaHSO₃ was controlled by the Impressafiner production rate, which was determined by the rotational speed of the ingoing screw conveyor. The addition of NaOH was adjusted to render an impregnation solution with pH 9. Sulphite doses are given as percent Na₂SO₃ on oven dried basis.

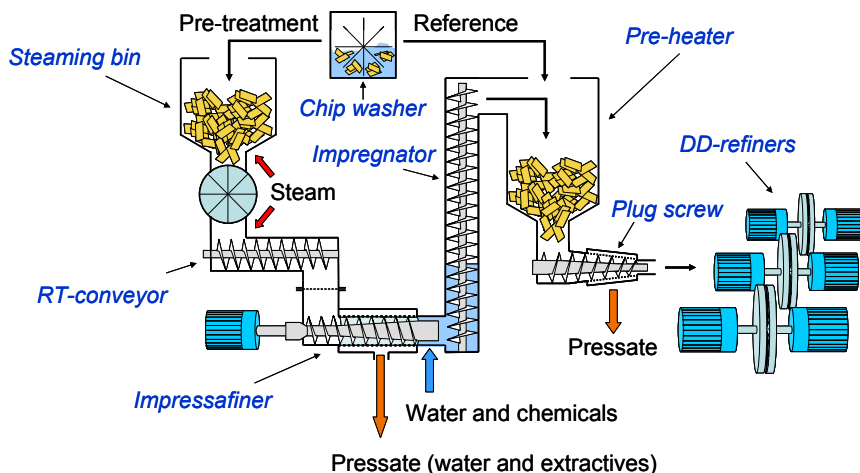


Figure 3. Detailed description of the chip pre-treatment equipment located in the double disc line. After the chip wash, it is possible to direct chips to the pre-treatment equipment or to the pre-heater.

DOUBLE DISC REFINING

Pulps were produced in RGP68DD (double disc) refiners (Metso) using p-(DN72N816-817) and c-segments (DO52B036-037). There are three parallel primary DD-refiners in the line. The refiner plates were 72" in diameter and rotated at 1500 rpm each in opposite directions. The refiner housing pressure was 4.6 barg and the dilution water was controlled by an automatic consistency controller based on the production rate and motor power. The production rate was calculated from pulp flow and pulp consistency in the standpipe situated directly after the blow line. The set point for the plate gap was controlled by an automatic specific energy consumption controller based on production rate and motor power. Pulp samples were collected from the blow line directly after the refiner.

ADDITION OF SULPHITE

Sulphite was added to chips by mixing concentrated solutions of sodium bisulphite (NaHSO_3) and sodium hydroxide (NaOH) into the continuous flow of impregnation liquid. The solution was passed through a static mixer after which the pH was measured. The solution was then absorbed by the chips in the impregnator. The addition of NaHSO_3 was controlled by the Impressafiner production rate, which was determined by the rotational speed of the ingoing screw conveyor. The addition of NaOH was adjusted to render an impregnation solution with pH 9. Sulphite doses are given as percent Na_2SO_3 on oven dried basis.

TRIAL

Pulp samples were collected after the double disc refiner for different refining

energy consumptions (1750-2100 kWh/bdt) and dosage of Na₂SO₃ (0, 0.12, 0.24, 0.61 and 1.21%). The chemical additions and Impressafiner settings are presented in *Table 1*. During the trial, the raw material composition was changed from the normal 50/50 blend to 30% sawmill and 70% round wood chips. After impregnation, the temperature of the chips was 62 °C. The production rate over the refiner was 8.6 bdt/h and the blow line consistency after refining was 30-32%.

Samples of chips and pulp were allowed to cool down to room temperature for a few hours before they were frozen. The samples were then analysed for sulphur content (SCAN-CM 57:99).

Table 1. Chemical additions and Impressafiner settings for sulphite pre-treatment

| Na ₂ SO ₃ added (%) | NaHSO ₃ (kg/bdt) | NaOH (kg/bdt) | Compression ratio | SEC Impressafiner (kWh/bdt) | Impregnation water |
|---|--------------------------------|------------------|----------------------|-----------------------------------|-----------------------|
| 0.00 | 0 | 0 | 2.7:1 | 18 | Fresh water |
| 0.12 | 1 | 0.3 | 2.7:1 | 18 | Fresh water |
| 0.24 | 2 | 0.6 | 2.7:1 | 18 | Fresh water |
| 0.61 | 5 | 1.4 | 2.7:1 | 18 | Fresh water |
| 1.21 | 10 | 3.8 | 2.7:1 | 18 | Fresh water |

ANALYSES

Five pulp samples were collected during a period of 12 min. for each process setting (i.e. for each mechanical pre-treatment setting, chemical dose or specific energy consumption). The samples were mixed, frozen and analysed three times using the following conventional methods: Hot disintegration (ISO 5263-3), length weighted fibre length and shives (Eurocon PulpEye), Canadian standard freeness (CSF) (ISO 5267-2), Rapid Köthen labsheets without white water circulation (ISO 5269-2, DIN 54358), density (ISO 534), tensile index and elongation (ISO 1924-2), tear index (ISO 1974), specific light scattering coefficient and light absorption coefficient (ISO 9416) and brightness (ISO 2470).

Additional analyses were also performed on chosen pulps, including: extractive (SCAN-CM 49:03) and sulphur content (SCAN-CM 57:99), fibre charge of whole pulp (SCAN-CM 65:02), Bauer McNett fractionation (SCAN-CM 6:05), Simons' staining according to Fernando and Daniel (2010) and spectra of the diffuse reflectance factor (ISO 2469). The pH was also measured for some of the pulps by the following method. Twelve gram high consistency pulp (~30% dry content) was diluted with 60 mL deionized water. The sample was dewatered in a Büchner funnel after 15 min. and the pH measured on the eluate.

Results and discussion

SULPHONATION REACTIONS

The amount of sulphur found in chips without sulphite addition was 60 mg/kg (*i.e.* 0.02% as Na₂SO₃), which originates from the natural sulphur content in wood. Pulps without sulphite addition had a sulphur content of 210-240 mg/kg (*i.e.* 0.08-0.09% as Na₂SO₃) (Figure 4), which originates from the natural sulphur content in wood and also sulphur containing compounds in the refiner dilution water. The refiner dilution water is a mix of fresh water and paper machine white water which may contain sulphur containing compounds originating from the dithionite bleaching step further down the process.

The temperature of the chips after impregnation was 62 °C at which sulphonation reactions are expected to be rather slow. Chip samples were collected directly after the impregnation and were then allowed to cool down to room temperature for a few hours before they were frozen. Much of the sulphonation of chip samples probably occurred after the samples were collected. Approximately 60-80% of added sulphite was chemically bound to chips, where the lowest dosage had the highest conversion ratio (*Figure 4*).

After impregnation, chips were fed to the pre-heater which may be better described as a retention bin since steam is normally not added in this position. The retention time in the pre-heater was 10-15 min. and the temperature of the chips did not change during this time. It is assumed that some sulphonation occurred here. Some of the added sulphite was removed from the chips in the plug screw prior to the refiner. Sulphonation reactions occur more rapidly in the pressurised environment after the plug screw (~155 °C, 6 sec) and most of the sulphonation reactions are likely to have occurred here and during refining. The pulp samples were allowed to cool down for a few hours before they were frozen and some sulphonation reactions may also have occurred during that time.

Approximately 55-70% of added sulphite was found as sulphur content in pulp after refining. However if the sulphur content of sulphite pre-treated pulps are subtracted by the amount of sulphur found in pulp produced without sulphite addition the conversion ratio is only 37-50%.

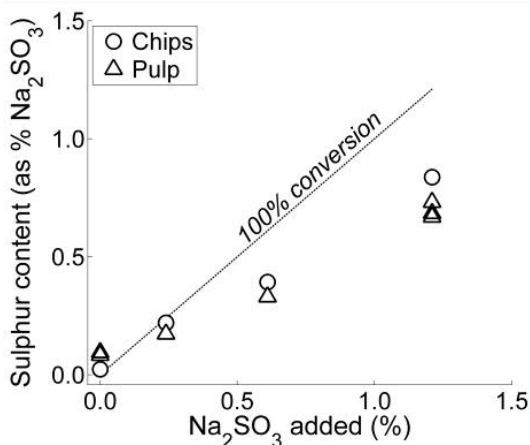


Figure 4. Sulphur content in chips and pulp (as % Na₂SO₃) vs. % Na₂SO₃ added.

MICROSCOPY STUDY OF SULPHONATED CHIPS

Chips pre-treated in the Impressafiner without sulphite addition typically showed two types of cracking/splitting in the chip structure: i) splits located between both the fibres and rays running along the interphase between the middle lamella-primary wall regions and the secondary wall layer (*i.e.* S1) (*Figure 5a*, arrows); and ii) splits located in fibres at the interphase between middle lamella, primary cell wall and inner secondary wall layers (S1/S2) (*Figure 5b*, arrows).

Introduction of sulphite at pH 9 into the impregnation liquid resulted in irregular and mild swelling of the secondary wall into the cell lumen for all dosages (*i.e.* 0.12-1.21% Na₂SO₃) (*Figure 5c-f*). Swelling of the secondary S2 wall layer into the fibre lumen was most obvious in the latewood fibres as reflected by the inward buckling of the S2 and S3 wall layers (*Figure 5c*, arrows). Additional effects of sulphite addition noted were an overall loss of chip and fibre integrity (*Figure 5d, f*). It was not possible to determine any major differences in morphological effects between cross-sections from the different dosages of sulphite addition.

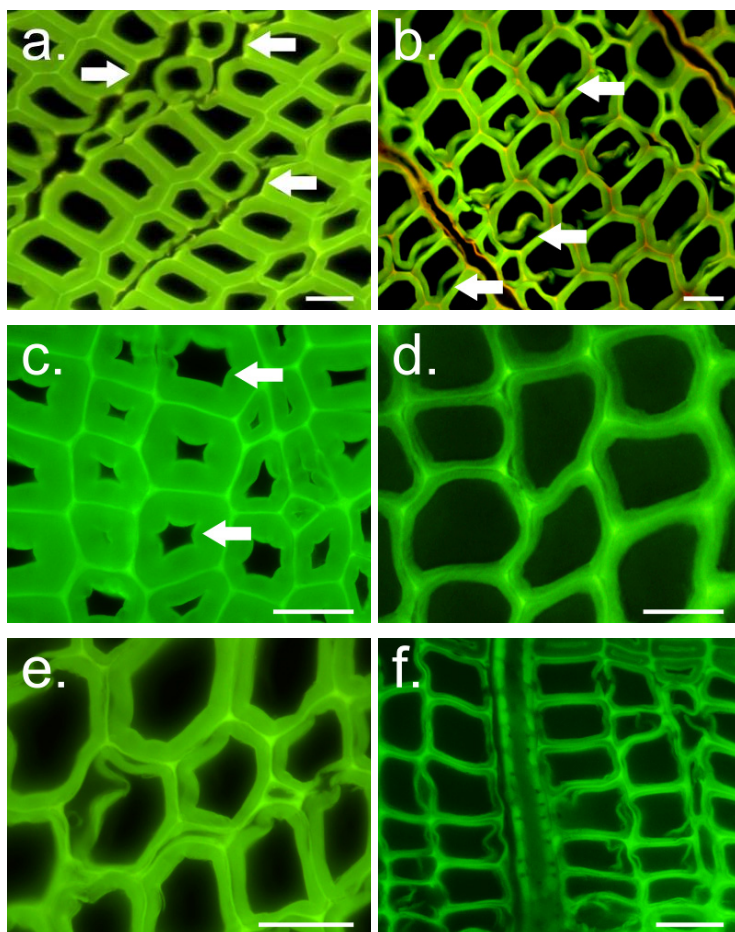


Figure 5. Transverse sections from chips pre-treated in the Impressafiner (a) and (b) and with different additions of Na_2SO_3 . (c) 0.12%, (d) 0.24%, (e) 0.61%, (f) 1.21%. (a) and (b) were also presented in and are presented here again to enable comparison between mechanical pre-treatment and pre-treatment with sulphite addition. It should be noted that the compression ratio in the Impressafiner was 3.6:1 for (a) and (b) and 2.7:1 for (c)-(f). Bars: a-f = 20 μm .

These observations indicate that the Impressafiner pre-treatment opens up the internal structure of the chips, inducing cracks and splits between the cellular elements thereby allowing for a more rapid influx of the impregnation fluid. Our previous work (Nelsson *et al.*, 2012) with Impressafiner pre-treated chips showed that they were able to absorb more water compared to non-pre-treated chips. The changes in internal structure caused by the Impressafiner pre-treatment may therefore lead to more rapid and even sulphonation throughout the chips. It is also possible that the impregnation fluid is redirected to additional impregnation

pathways through the cracks and splits produced during mechanical pre-treatment. It may be speculated that such a change in the impregnation pathway could also affect the sites of sulphonation (*i.e.* the distribution of sulphonation reactions between the middle lamella, primary and secondary cell walls). However, further studies are needed in order to confirm if such an effect actually exists.

PULP PROPERTIES

The most prominent effect of sulphite pre-treatment was an increase in tensile index (*Figure 6a*). The highest dose of sulphite (*i.e.* 1.21% Na₂SO₃) increased the tensile index with 7.6 Nm/g compared to non-sulphonated pulps at specific energy consumption 1950 kWh/bdt. When compared at tensile index 47 Nm/g, the specific energy consumption was reduced with ~320 kWh/bdt (*i.e.* ~15%) for pulps pre-treated with 1.21% Na₂SO₃ compared with non-sulphonated pulps.

The relationship between density and tensile index was not affected by sulphonation (*Figure 6b*). Light scattering was slightly reduced (*i.e.* 1.6 m²/kg) by the highest sulphite addition compared to non-sulphonated pulps at equal specific energy consumption (*Figure 6c*). However, when compared at equal tensile index, the highest dosage of sulphite (1.21% Na₂SO₃) had a light scattering that was 9.1 m²/kg lower than for non-sulphonated pulps (*Figure 6d*). Of the 9.1 m²/kg, 7.6 m²/kg was a result of the reduction in specific energy consumption needed to reach similar tensile index.

Fibre length was not affected by addition of sulphite when compared at similar specific energy consumption (*Figure 6e*). This is somewhat surprising since there are numerous reports from pilot scale trials showing increased fibre length for sulphite pre-treated pulps when refined at equal specific energy consumption (Argyropoulos and Heitner 1991; Atack *et al.* 1980; Axelson and Simonson 1982). However, Chagaev *et al.* (2005) showed that fibre length was not affected by sulphite pre-treatment during high intensity refining.

The two highest dosages of sulphite (*i.e.* 0.61, 1.21% Na₂SO₃) reduced the shive content at the lower energy level (*i.e.* ~1780 kWh/bdt) compared to non-sulphonated pulps (*Figure 6f*).

Axelson and Simonsson (1982) reported a maximum in tensile index and light scattering at a sulphur content of 0.2% (as Na₂SO₃), which was later confirmed by Westermark *et al.* (1987) and Svensson *et al.* (1994). In our study, tensile index and light scattering followed linear relations with the amount of sulphite added without any maximum in the low dose range (*Figure 6a, c*).

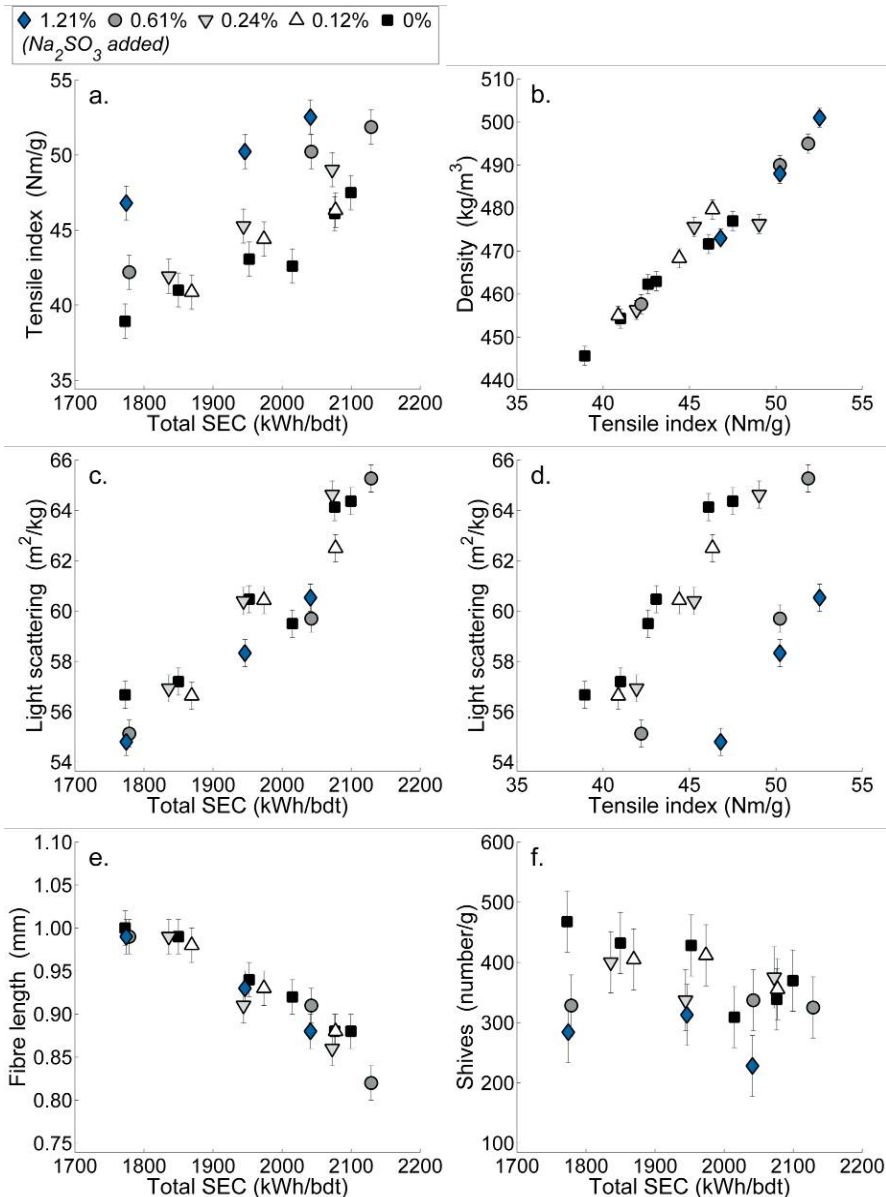


Figure 6. Tensile index (a), light scattering (c), fibre length (e) and shives (f) vs. specific energy consumption and density (b) and light scattering (d) vs. tensile index for different additions of Na_2SO_3 . Error bars show 95% confidence intervals.

The difference in results between this study and previous studies are outlined in Figure 7. All studies were performed using Norway spruce at similar pH.

However, our study was performed using a different impregnation technique (i.e. Impressafiner pre-treatment) and with a mill scale high intensity refiner. The explanation for the maximum in tensile index and light scattering offered by Axelson and Simonson (1982) was that a sulphur content of 0.2% (as Na_2SO_3) gave a suitable decrease in the softening temperature in relation to the temperature and frequency of the breaker bar section and the refining zone of the refiner used in the study. It is therefore assumed that the different results obtained in this study are caused by the different refining conditions. Nevertheless, it is not possible to rule out the effects of the Impressafiner pre-treatment as a cause to these differences through opening up the chip structure for chemical influx as described earlier.

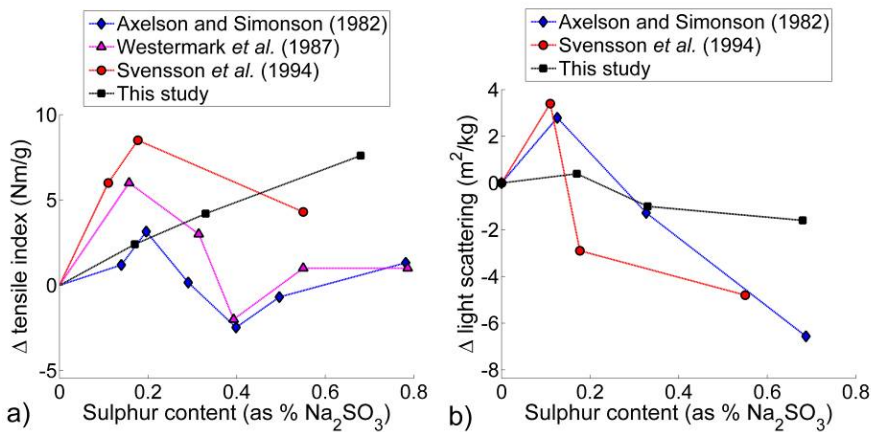


Figure 7. Comparison of changes in tensile index (a) and light scattering (b) at certain specific energy consumption vs. sulphur content (as % Na_2SO_3) for different studies. The lines between data points in (a) and (b) do not symbolise linear relations between data points.

FIBRE PROPERTIES

Table 2 shows detailed properties for six individual pulps produced with different dosage of sulphite at two energy levels. The addition of 1.21% Na_2SO_3 at pH 9 increased the pulp pH from ~ 5.7 to ~ 7.2 after refining. For the low energy pulps (1780 kWh/bdt) fibre charge was increased by 40 mmol/kg by the addition of 1.21% Na_2SO_3 which corresponds to an increase in sulphonic acid groups of 0.5% (as Na_2SO_3).

Distribution of the Bauer-McNett fractions was not significantly affected by addition of sulphite at certain specific energy consumption (Table 2). The proportion of the fine (< 200) and 16-30 fractions did not change in any distinct way in response to either increased refining energy or degree of sulphonation. The

proportion of the fine fraction (< 200) is expected to increase when the refining energy is increased, although the lack of a correlation between the two may be explained by the rather uncertain measurement of the fine fraction. By applying a linear regression model to the data in *Table 2*, it was possible to show that only the specific energy consumption and not the degree of sulphonation had a significant effect on the proportion of the > 16 fraction (Not shown).

Table 2. Pulp properties for different refining energies and dosage of Na₂SO₃

| | | | | | | | |
|---|----------------|------|------|------|------|------|------|
| Total SEC (kWh/bdt) | | 1780 | 1780 | 2080 | 2080 | 2040 | 2040 |
| Na₂SO₃ added (%) | | 0.00 | 1.21 | 0.00 | 0.24 | 0.61 | 1.21 |
| Sulphur in pulp after refining as Na₂SO₃ (%) | | 0.08 | 0.67 | 0.09 | 0.17 | 0.33 | 0.68 |
| Pulp pH after refining | | 5.72 | 7.01 | 5.75 | 6.00 | 6.31 | 7.23 |
| Fibre charge in whole pulp (mmol/kg) | | 70 | 110 | 71 | 80 | 95 | 96 |
| Bauer-McNett fractions (%) | <200 | 24.9 | 22.7 | 25.1 | 27.4 | 26.6 | 26.3 |
| | 30-200 | 27.9 | 28.6 | 32.0 | 31.9 | 30.7 | 31.3 |
| | 16-30 | 23.5 | 24.1 | 24.2 | 23.0 | 23.3 | 24.3 |
| | >16 | 23.7 | 24.6 | 18.7 | 17.7 | 19.4 | 18.1 |
| Degree of D/IF of Fibre Cell Walls (Simons' staining of Bauer-McNett 16-30 fraction) (%) | High | 16.8 | 29.3 | 24.5 | 22.8 | 29.0 | 39.0 |
| | Low | 26.3 | 26.3 | 27.5 | 26.8 | 28.0 | 26.3 |
| | Non | 57.0 | 44.5 | 48.0 | 50.5 | 43.0 | 34.8 |
| Fibre length (mm) | | 1.00 | 0.99 | 0.88 | 0.86 | 0.91 | 0.88 |
| Density (kg/m³) | | 446 | 473 | 472 | 476 | 490 | 501 |
| Tensile index (Nm/g) | | 38.9 | 46.8 | 46.1 | 49.0 | 50.2 | 52.5 |
| Light scattering (m²/kg) | | 56.7 | 54.8 | 64.1 | 64.6 | 59.7 | 60.5 |

Fernando and Daniel's (2010) version of Simons' staining of the 16-30 fraction was used to assess the degree of delamination/internal fibrillation (D/IF) of the pulps (*Table 2*). Sulphite pre-treatment showed an effective increase in D/IF. Simons' staining measures the accessibility of interior surfaces in the fibre cell wall through selective staining of fibres containing pores larger than 5 nm (Yu *et al.* 1995). This type of internal fibre development has been shown earlier to correlate positively with the whole pulp tensile index (Stone *et al.* 1968; Fernando *et al.* 2011). Stone *et al.* (1968) suggested that this correlation was a result of an increased flexibility and collapsibility for fibres with increased D/IF. Fibre flexibility and collapsibility have been described as dependent on the fibre dimensions (fibre cell wall thickness and fibre width) together with the elasticity (Young's modulus) of the fibre cell wall (Paavilainen 1993). Increasing the amount

of pores larger than 5 nm in the fibre cell wall (as measured by Fernando and Daniel's (2010) method of Simons' staining) should correlate with a decrease in the elasticity of the fibre cell wall and thereby with increasing flexibility and collapsibility of the fibre.

By using a linear regression model it was possible to show that the percentage of fibres with high D/IF was significantly increased by both increased specific energy consumption and increased degree of sulphonation. An increase in the pulp sulphur content by 0.1% (as Na₂SO₃) gave an equivalent increase in the percentage of fibres with high D/IF as increasing the refining energy with 100 kWh/bdt.

The effective increase in D/IF caused by sulphonation is probably the explanation to the increase in tensile index and density for sulphite pre-treated pulps. However, an increase in fibre charge is also known to increase these properties (Barzyk 1997). The increase in density could also explain the lower light scattering at certain amount of fine material for the sulphonated pulps when compared to non-sulphonated pulps. When a sheet is densified without changing the amount of fine material or the degree of external fibre fibrillation, less light reflective surfaces are available to scatter light. It should be noted that a large range of the pore sizes measured by Simons' staining are much too small to scatter light in the visual spectra. For detailed information on the Simons staining see *Appendix 3*.

Optical properties

Sulphite pre-treated pulp had lower light absorption compared to non-sulphonated pulps (*Figure 8a*). The decrease in light absorption resulted in increased brightness (*Figure 8b*) even though there was a slight decrease in light scattering for sulphite pre-treated pulps. Brightness is measured as the diffuse reflectance factor using a filter or a mathematical function having an effective wavelength of 457 nm. The light absorption is calculated from the diffuse reflectance factor and opacity measured with a filter or calculated with a mathematical function having an effective wavelength of 557 nm.

In *Figure 9a*, the diffuse reflectance factor is presented for the wavelength range 420-700 nm. Spectra for pulps from two different refining energy levels, with and without sulphite pre-treatment are shown. The diffuse reflectance factor was higher for sulphite pre-treated pulps. *Figure 9b* shows the difference in spectra (by subtraction) between sulphonated and non-sulphonated pulps for the two different refining energy levels. The difference was most pronounced between 450 and 550 nm, corresponding to a region where lignin has a high optical activity. This can be explained by degradation of chromophoric structures in lignin during sulphonation. For detailed information on the optical properties see *Appendix 4*.

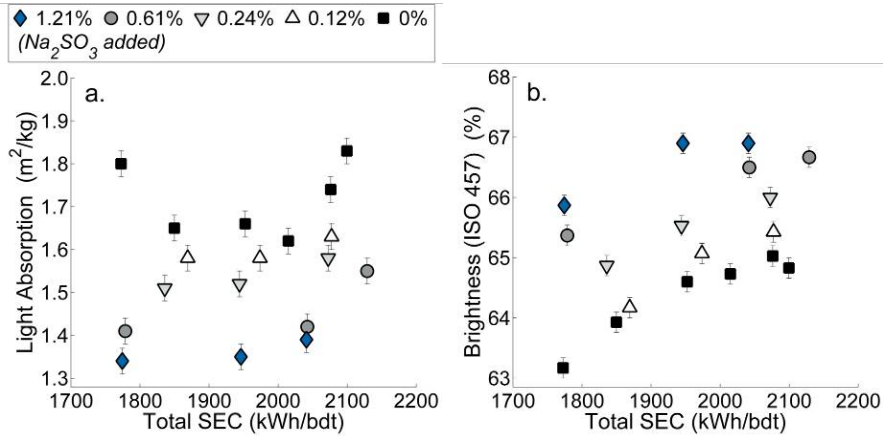


Figure 8. Light absorption (a) and brightness (b) vs. total specific energy consumption for different additions of Na_2SO_3 . Error bars show 95% confidence intervals.

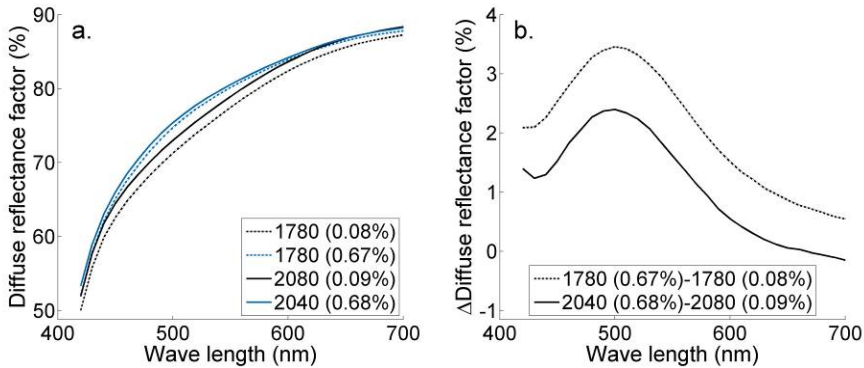


Figure 9. a) Diffuse reflection intensity measured over 420-700 nm for four of the pulps included in Table 2. The legend shows total specific energy consumption and sulphur content as % Na_2SO_3 in brackets. b) Difference in diffuse reflection intensity between sulphonated and non-sulphonated pulps measured over 420-700 nm.

Conclusions

Sulphite pre-treatment gave a linear dose response in tensile index and light scattering with the addition of sulphite (up to an addition of 1.2% Na₂SO₃). The maximum in tensile index and light scattering at sulphur content of 0.2% (as Na₂SO₃) reported by Axelson and Simonson (1982) was not seen in this mill study. Low dosage sulphite pre-treatment increased delamination/internal fibrillation of fibres indicating increased fibre flexibility. These fibres produced denser sheets with higher tensile index and slightly reduced light scattering at certain specific energy consumption. The specific energy consumption needed to produce pulp with a certain tensile index was reduced by 210-320 kWh/bdt (12-15%) for chips pre-treated with ~1.2% Na₂SO₃ compared to chips pre-treated without chemicals. However, this led to a reduction in light scattering for sulphite pre-treated pulps when compared at equal tensile index.

References

- Akhtar, M., Swaney, R. E., Horn, E. G., Lentz, M. J., Scott, G. M., Black, C. C., Houtman, C. J., Kirk, T. K. Method for producing pulp. WO 02/075043 A1. 9/2002.
- Argyropoulos, D. S., Heitner, C. (1991) Ultra-high-yield pulping part VII: The effect of pH during impregnation on the quality of lightly sulphonated CTMP. *J. Pulp Pap. Sci.* 17(5):137-143.
- Atack, D., Heitner, C., Stationwala, I. M. (1978) Ultra high yield pulping of eastern black spruce. *Svensk Papperstidn.* 81(5):164-176.
- Atack, D., Heitner, C., Karnis, A. (1980) Ultra high yield pulping of eastern black spruce. Part 2. *Svensk Papperstidn.* 83(5):133-141.
- Axelson, P., Simonson, R. (1982) Thermomechanical pulping with low addition of sulfite Part 1. Effects of mild sulfite treatment of spruce chips prior to defibration. *Svensk Papperstidn.* 85(15):R132-R139.
- Barzyk, D., Page, D. H., Ragauskas, A. (1997) Acidic group topochemistry and fibre-to-fibre specific bond strength. *J. Pulp Pap. Sci.* 23(2):J59-J61.
- Bohn, W. L., Sferrazza, M. J. (1989) Alkaline peroxide mechanical pulping, a revolution in high yield technology. In: *Proceedings of the Int. Mech. Pulp. Conf.*, Helsinki, June 6-8, 184-200.
- Chagaev, O., Heitner, C., Hellstern, M. (2005) The effects of sulphonation and high-intensity refining on the ultra-high-yield pulping of spruce. *Pulp Pap. Canada* 106(12):65-70.
- Fernando, D., Daniel, G. (2010) Characterisation of spruce thermomechanical pulps at the fibre cell wall level: a method for quantitatively assessing pulp fibre development using Simons' stain. *Tappi J.* 9(10):47-55.
- Fernando, D., Muhic', D., Engstrand, P., Daniel, G. (2011) Fundamental understanding of pulp property development under different thermomechanical pulp refining conditions as observed by a new Simons' staining method and SEM observation of the ultrastructure of fibre surfaces. *Holzforschung*, 65(6):777-786.

- Frazier, W. C., Williams, G. J. (1982) Reduction of specific energy in mechanical pulping by axial pre-compression of wood. *Pulp Pap. Canada* 83(6):87-92.
- Höglund, H., Wilhelmsson, K. (1993) The product must determine the choice of wood type in mechanical pulping. In: *Proceedings of the 18th Int. Mech. Pulp. Conf.*, Oslo, June 15-17, 1-22.
- Johansson, L., Peng, F., Simonson, R. (1997) Effects of temperature, sulfonation on shear deformation of spruce wood. *Wood Sci. Technol.* 31(2):105-117.
- Lai, Y. Z., Iwamida, T. (1993) Effects of chemical treatments on ultra-high-yield pulping. 1. Fiber separation. *Wood Sci. Technol.* 27(3):195-203.
- Lindholm, C.A., Kurdin, J.A. (1999) Chemimechanical pulping. In: *Papermaking Science and Technology, Mechanical pulping*. 223-249. Helsinki : Fapet Oy.
- Nelsson, E., Sandberg, S., Hildén, L., Daniel, G. (2012) Pressurised compressive chip pre-treatment of Norway spruce with a mill scale Impressafiner. *Nord. Pulp Pap. Res. J.* 27(1):56-62.
- Paavilainen, L. (1993) Conformability flexibility and collapsibility of sulfate pulp fibers. *Pap. Puu.* 75(9-10):689-702.
- Peng, F., Ferritus, R., Ångsås, U. Method of producing mechanical pulp and the mechanical pulp thus produced. US 2005/0241785A1. 11/03/2005.
- Stone, J. E., Scallan, A. M., Abrahamson, B. (1968) Influence of beating on cell wall swelling and internal fibrillation. *Svensk Papperstidn.* 71(19):687-694.
- Svensson, E., Engstrand, P., Htun, M., Svensson, B. (1994) A better balance between shives content and light-scattering properties of TMP/CTMP by SO₂ gas-phase impregnation prior to defibration. *Nord. Pulp Pap. Res. J.* 9(3):167-171.
- Westermarck, U., Samuelsson, B., Simonsson, R., Pihl, R. (1987) Investigation of a selective sulfonation of wood chips. Part 5. Thermomechanical pulping with low addition of sulfite. *Nord. Pulp Pap. Res. J.* 2(4):146-151.
- Yu, X., Minor, J. L., Atalla, R. H. (1995) Mechanism of action of Simons' stain. *Tappi J.* 78(6):175-180.
- Östberg, G., Salmén, L. (1988) Effects of sulfonation on properties of different cell wall layers. *Nord. Pulp Pap. Res. J.* 3(1):8-12.

APPENDIX 1. FIBRE POPULATION ANALYSIS BASED ON FIBRE CROSS-SECTIONS FROM PULP FIBRES OBTAINED FROM BAUER-McNETT FRACTION 30

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Summary

The effect of chip pre-treatment with sulphite before refining was investigated in a trial on the B-line in the Braviken mill, 2009-12-14. Sulphite was added to the impregnator, placed directly after the impress refiner, in dosages of 1, 2, 5 and 10 kg/BDT at pH 9. Pulp samples were obtained from the blow line after DD2.

Fibre populations from Bauer-McNett fraction 30 of pulps produced from untreated and sulphite pre-treated wood chips were analysed using fluorescent microscopy and image analysis. The pulp fractions were analysed for earlywood and latewood fibre content as well as of non-split and split fibre content. Furthermore, fibre cross-sectional compactness and severe delamination of the fibre wall of non-split fibres were also analysed.

Experimental

PULP SAMPLES

Six pulps were chosen by the CRUW scientists for further analysis (*Table 1*). The pulps were subjected to fractionation in a Bauer-McNett apparatus and samples of the 30 fraction were collected.

Table 1. Some properties of the pulps studied and number of fibres from Bauer-McNett 30 fraction image analysed

| Pulp nr | Specific energy (kWh/ADT) | Sulphite concentration (kg/BDT) | Sulphonation (mmol/kg) | Number of fibres analysed |
|---------|---------------------------|---------------------------------|------------------------|---------------------------|
| 1 | 1580 | 0 | 6,549 | 274 |
| 2 | 1580 | 10 | 53,017 | 524 |
| 3 | 1820 | 5 | 26,197 | 908 |
| 3 | 1820 | 10 | 54,265 | 644 |
| 5 | 1850 | 0 | 7,485 | 1143 |
| 6 | 1850 | 2 | 13,722 | 554 |

TRANSVERSE FIBRE MORPHOLOGY

Pulp fibres were aligned according to Reme *et al.* (2002). Moist fibre bundles were rapidly frozen with liquid Nitrogen and freeze-dried prior to embedding in a water soluble polymer (Technovit[®]). Samples were sectioned transversally using a rotary

microtome (Leica RM 2265) to a thickness of 2,0 µm. Pulp fibre cross-sections were observed under UV-light using a fluorescence microscope (Leica DMRE) at a magnification of 200x. Lignin auto-fluorescence images were obtained using a blue filter (510 nm wave length), acquired with a CCD camera and stored digitally. Pulp fibre cross-sections morphology was analysed by means of computerised image analysis.

IMAGE ANALYSIS

Measurements were performed automatically with the software ImagePro PLUS (Media Cybernetics). The features used to differentiate the pulps were:

- **Number of split fibres**
- **Number of non-split fibres**
- **Cross-sectional compactness:** measurements performed on non-split fibres divided the fibre population into earlywood and latewood. Results show also how the fibre population is being refined by changes in the frequency at different cross sectional compactness classes. Cross sectional compactness is defined as:

$$= \frac{4\pi A}{P^2}$$

A = transverse fibre wall area

P = transverse fibre perimeter

- **Severe delamination:** detects splits in the fibre wall by counting the number of cavities in fibre cross section.

More information on these measurement methods can be found in the CRUW Internal Report nr 1.

Analysis of cross-sectional compactness, and severe delamination were performed on the non-split fraction of the pulp samples. Detection of non-split and split fibres was based on the presence or not of the fibre lumen.

Cross-sectional compactness values up to 0.5 refer to earlywood fibres and values higher than 0.5 refer to latewood fibres.

For the detection of severe delamination of fibre walls the image analysis reveals if there is more than one hole (lumen) present in the fibre cross-section and by that values higher than 1 refer to increasing numbers of severe fibre wall splits.

Results

Samples contained approximately 40 % earlywood fibres and 60 % latewood of the non-split fibres fraction (*Table 2*). These results also indicate that the number of fibres analysed for each pulp may be considered as representative. Generally, higher energy input resulted in more fibre splitting. Between pulps without sulphite treatment (pulps 1 and 5) fibre splitting was increased with 10% due to refining energy. The effect of the sulphite treatment on fibre splitting of fibres refined at 1580 KWh/ADT was marginal. Increasing amounts of sulphite resulted in less fibre splitting of pulps refined at 1820 and 1850 KWh/ADT. However, pulp 6 refined at 1850 KWh/ADT and treated with 2 kg sulphite/BDT showed practically the same amount of split fibres as for pulp 4 refined at 1820 KWh/ADT and treated with 10 kg sulphite/BDT. This may indicate that at high energy inputs less amounts of sulphite are needed to achieve equivalent pulp properties.

Table 2. Image analysis of non-split and split fibre populations of the pulp samples

| Pulp nr | Specific energy (kWh/ADT) | Sulphite conc. (kg/BDT) | Total nr | Fibres | | Non-split fibres | |
|---------|---------------------------|-------------------------|----------|---------------|-----------|------------------|---------------|
| | | | | Non-split (%) | Split (%) | Latewood (%) | Earlywood (%) |
| 1 | 1580 | 0 | 274 | 62,04 | 37,96 | 58,82 | 41,18 |
| 2 | 1580 | 10 | 524 | 61,83 | 38,17 | 57,72 | 41,28 |
| 3 | 1820 | 5 | 908 | 55,95 | 44,05 | 61,61 | 38,39 |
| 4 | 1820 | 10 | 644 | 59,01 | 40,99 | 60,26 | 39,74 |
| 5 | 1850 | 0 | 1143 | 52,14 | 47,86 | 59,23 | 40,77 |
| 6 | 1850 | 2 | 554 | 59,75 | 40,25 | 60,42 | 39,58 |

CROSS-SECTIONAL COMPACTNESS

Cross-sectional compactness results are presented in *Figures 1 and 2*.

The fibre cross-sectional compactness frequency distributions of pulps subjected to the same refining energy are similar and determined mostly by the refining energy. Slight changes in the frequency distributions are due to effects of the sulphite treatment.

For pulps subjected to the same refining energy the sulphite treatment seems to make latewood fibres less affected by refining, more fibres fall into higher frequency classes (thicker fibre walls), while earlywood fibres may be more affected as the lower frequency classes decrease after the treatment.

The sample from pulp 1 with no sulphite treatment shows the typical bimodal distribution shown by softwoods (Reme et al., 2002). Sulphite (i.e. 10 kg/m³) addition in pulp 2 promoted the preservation of latewood fibres as more fibres fall into higher classes of cross-sectional compactness (latewood fibres are not as refined as in pulp 1). On the contrary, it seems that the thinnest earlywood fibres are being more refined, and some even refined to destruction (i.e. no fibres in class

0.1). This is also valid for the other pulps studied. Sulphite treatment seems to induce more refining of earlywood fibres and less refining of latewood fibres.

SEVERE DELAMINATION

Delamination of the fibre cell walls occurs during refining at the micro- and ultrastructural levels. Only the largest and more obvious delaminations can be detected by image analysis at this relatively low magnification (200x).

Results for severe delamination are presented in *Figures 3 and 4*.

Looking at the results for all fibres in the pulp samples studied (*Figure 3*) it appears that pulps subjected to sulphite treatment show less severe delamination compared to untreated pulps. Despite specific refining energy, severe delamination of earlywood fibres decreases with sulphite treatment (*Figure 4*). For latewood fibres the effect is a little less clear. For pulps refined at 1580 KWh/ADT the treatment with 10 kg sulphite/BDT lead to a slight increase in severe delamination of the fibre wall. Nevertheless, as a whole it seems that treatment of pulps with increasing concentrations of sulphite lead to less occurrence of severe delamination of the fibre wall. These observations are in agreement with data on the amount of split fibres in the pulp samples treated at 1820 and 1850 KWh/ADT presented in *Table 2*.

Conclusions

Image analysis of the pulp sample was successfully accomplished. The number of fibres analysed for each pulp may constitute representative samples as the amount of earlywood and latewood in the samples are fairly constant (approx. 60% earlywood and 40% latewood). Image analysis allowed for comparison of different non-treated and sulphite treated pulp samples refined at different energy inputs.

Generally, higher energy input resulted in more fibre splitting. The frequency distributions of fibre cross-sectional compactness for pulps subjected to the same refining energy are similar and determined mostly by the refining energy.

Some effects of sulphite treatment on the pulps could be detected. Latewood fibres seem to be less affected by refining when treated with sulphite while earlywood fibres appear to be more affected. Increasing amounts of sulphite addition resulted in less fibre splitting of pulps refined at 1820 and 1850 KWh/ADT. Possibly, addition of low amounts of sulphite (i.e. 2 kg sulphite/BDT) to pulps refined at 1850 KWh/ADT and higher input energies may have the same effect as higher concentrations of sulphite at lower refining energies.

As a whole it seems that pulp treatments with increasing concentrations of sulphite lead to less severe delamination of the fibre wall. Furthermore, sulphite treatment seems in general to induce more refining of earlywood fibres and less refining of latewood fibres.

Previous results have shown that pulp fibres may collapse differently along the fibre axis (Bardage *et al.*, 2002). EM observation on the pulp studied revealed high degree of deformation along fibres that could also be seen on the fibre cross-sections analysed. It is still a very difficult task to evaluate the collapse of single fibres and more method development is needed. Therefore measurements of fibre collapse were not included in this report.

References

- Bardage, S.L., Daniel, G. and Singh, A. (2002). Three-dimensional analysis of the collapse behavior of kraft-cooked Norway spruce fibres. *Wood and Fibre Science*, 34(3): 382-390.
- Fernando, D., Daniel, G., Muhic´ D., Olsson, A-M., Salmén, L. 2011. Effect of using low-energy segments for producing TMP pulps at Braviken. CRUW Internal Report nr 6. Mechanical Pulping 1:
- Reme, P.A. and Helle, T. (2002). Assessment of transverse dimensions of wood tracheids using SEM and image analysis. *Holz als Roh- und Werkstoff* 60: 277–282.

Bauer-McNett fraction 30

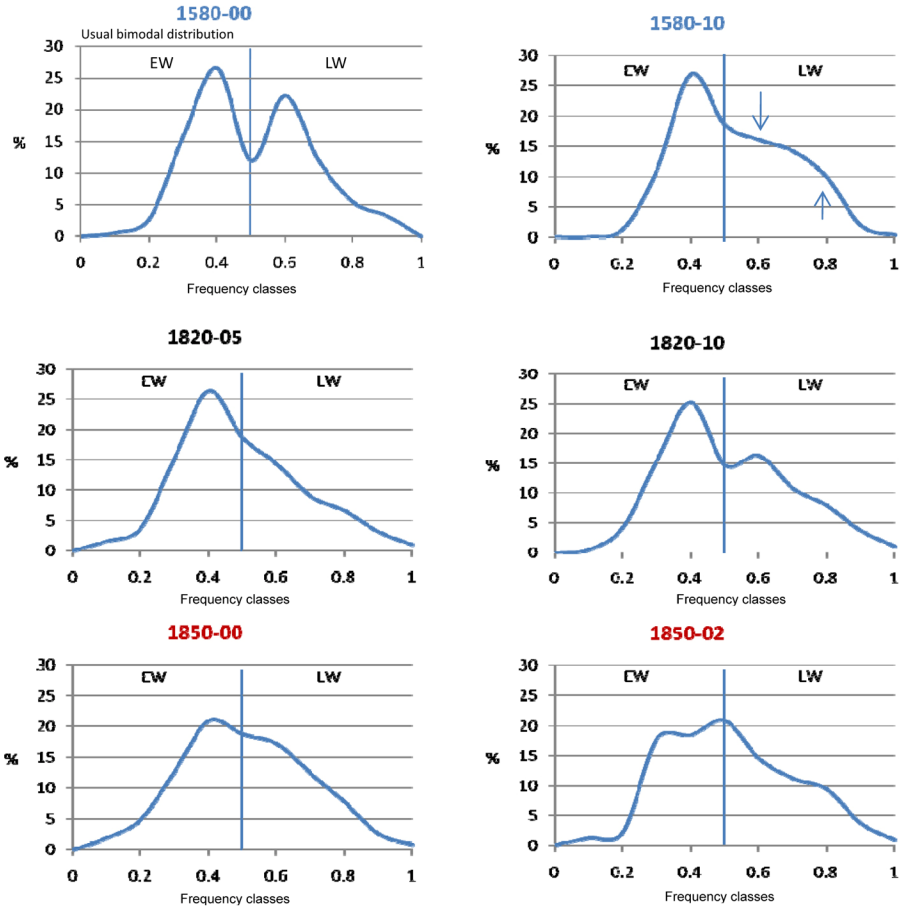


Figure 1. Cross-sectional compactness of samples from Bauer-McNett fraction 30 of the pulp studied. Pulp denomination = (Refining energy)-(sulphite concentration). EW = earlywood fibres; LW = latewood fibres

Bauer-McNett fraction 30

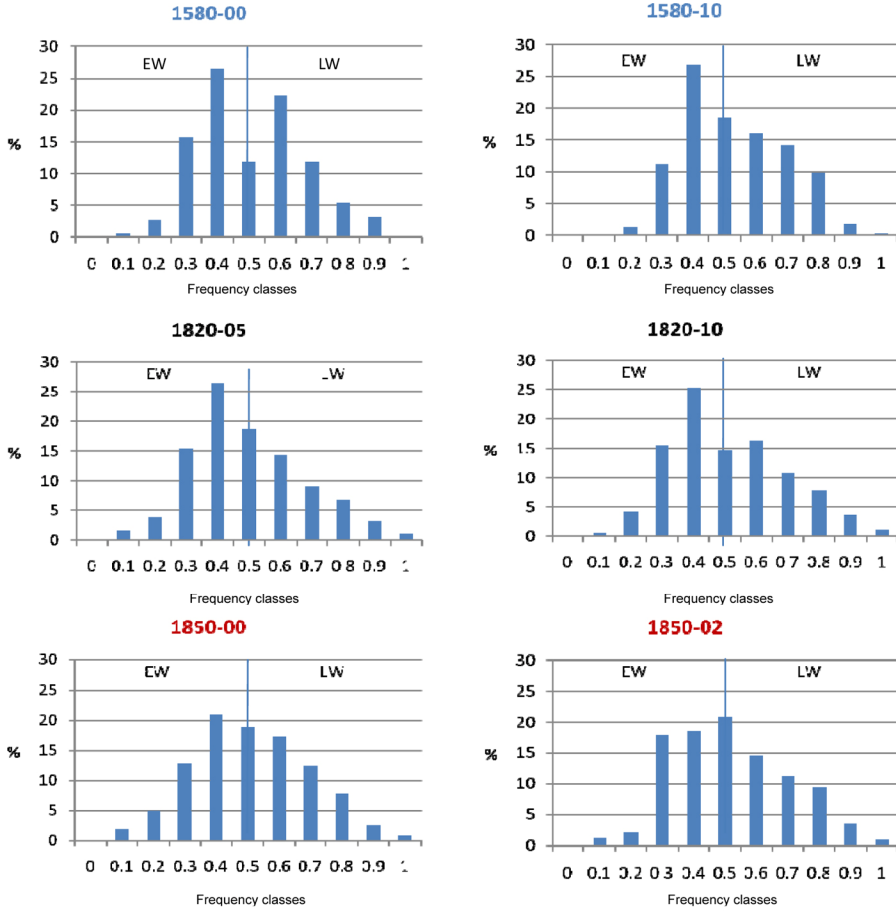


Figure 2. Cross-sectional compactness of samples from Bauer-McNett fraction 30 of the pulp studied. Pulp denomination = (Refining energy)-(sulphite concentration). EW = earlywood fibres; LW = latewood fibres

Bauer-McNett fraction 30

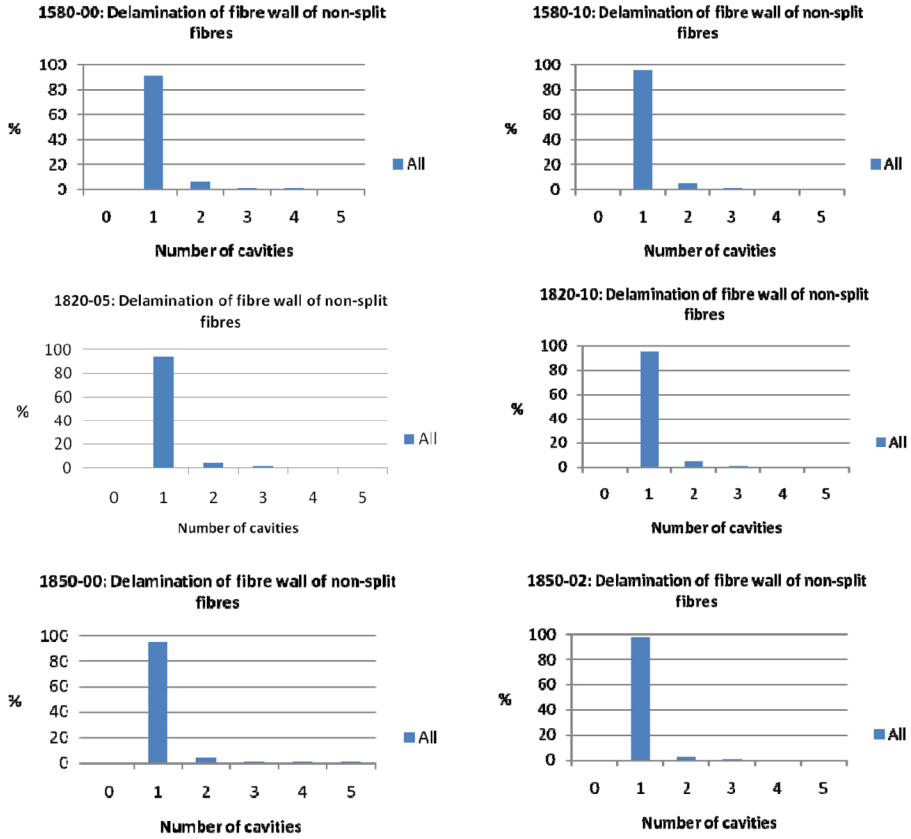


Figure 3. Severe delamination of samples from Bauer-McNett fraction 30 of the pulp studied. Pulp denomination = (Refining energy)-(sulphite concentration).

Bauer-McNett fraction 30

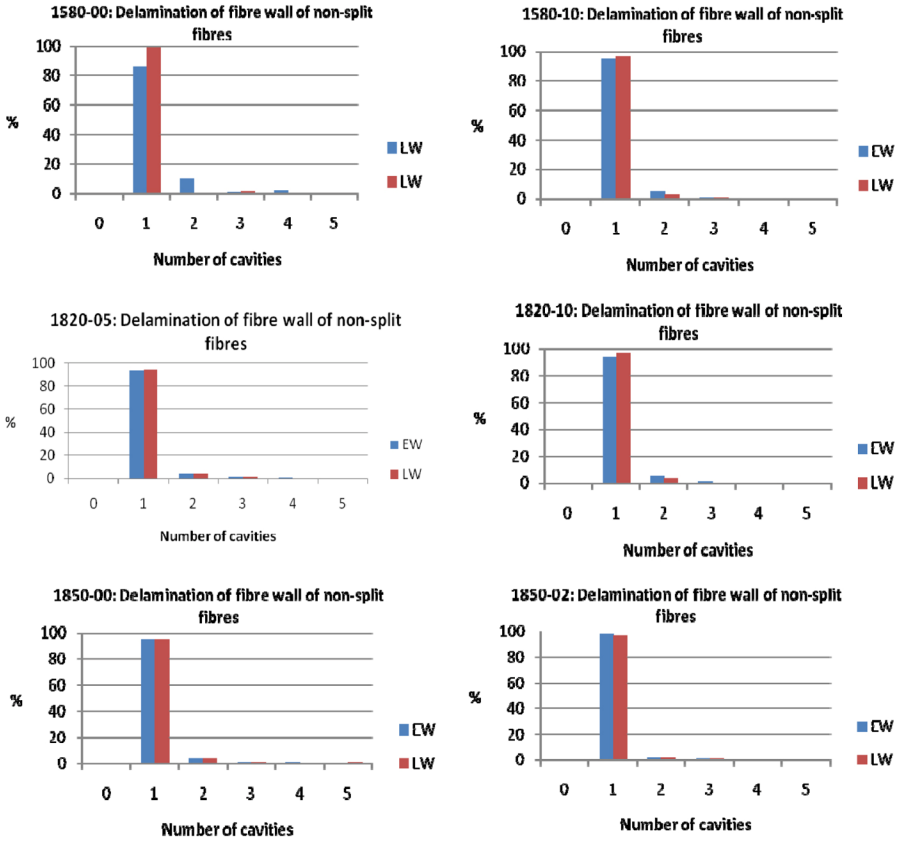


Figure 4. Severe delamination of samples from Bauer-McNett fraction 30 of the pulp studied. Pulp denomination = (Refining energy)-(sulphite concentration). EW = earlywood fibres; LW = latewood fibres

APPENDIX 2. EVALUATION OF SURFACE COMPOSITION BY FTIR MICROSCOPY

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Material

Single fibres were prepared from the TMP pulps refined at 1580, 1820 and 1850 kWh/ton. Pulps made both with and without sulphonation were tested. The fibres were dried and glued onto glass slides. Both earlywood and latewood fibres were prepared. 10 fibre samples were analysed for each pulp.

Methods

SURFACE MEASUREMENTS

The surface composition of the fibre surfaces were analysed by FTIR microscopy measurements using a Spectrum Spotlight 400 FTIR Imaging System (Perkin Elmer Inc, Shelton, CT, USA). FTIR ATR (Attenuated total reflection) was used. Over a length of 100 μm covering the total fibre width, spectra were acquired with a resolution of one spectrum from each sub-area of 1.56 by 1.56 μm using an array MCT detector. A CCD camera was used to display the area of interest before it was irradiated with IR light. From these images the fibres were defined as earlywood or latewood fibres. In *Figure 1* the image before and after measurement on the same fibre is shown.

The overall surface composition was achieved as an average spectrum calculated from all the sub-areas.

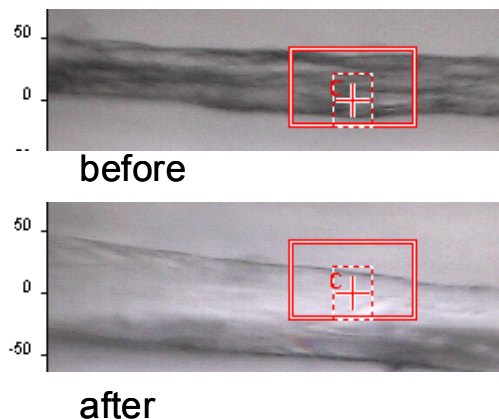


Figure 1. Image of one fibre before (upper image) measurement and after (lower image) measurement. The red square indicates the area of measurement.

EVALUATION

The IR Spectra were processed by the software Spotlight 1.5.1, HyperView 2.0 and Spectrum 6.2.0 (Perkin Elmer Inc., Shelton, CT, USA). The spectra were corrected by applying an atmospheric correction function to minimize the effects of CO₂ and H₂O. An ATR correction compensated for the effect of the ATR crystal. The whole matrix of spectra was automatically baseline corrected in the Hyper View program.

The average spectra were analysed with multivariate analysis using SIMCA-P+ 11 (Umetrics). From a PCA analysis the principal components that separate the different pulps were identified in scoreplots, and in loading plots significant wave numbers for this separation are shown.

Results

MULTIVARIATE ANALYSIS

In score plots grouping of samples can be identified. In *Figure 2* a score plot for principal components 3 and 6 show a separation of fibres with high degree of sulphonation (i.e. 1580-10 and 1820-10) from those with low (11820-05, 1850-02) or no sulphonation (1580-00, 1850-00). No separation between fibres with different refining energy could be found in the multivariate analysis, and no separation either between earlywood and latewood.

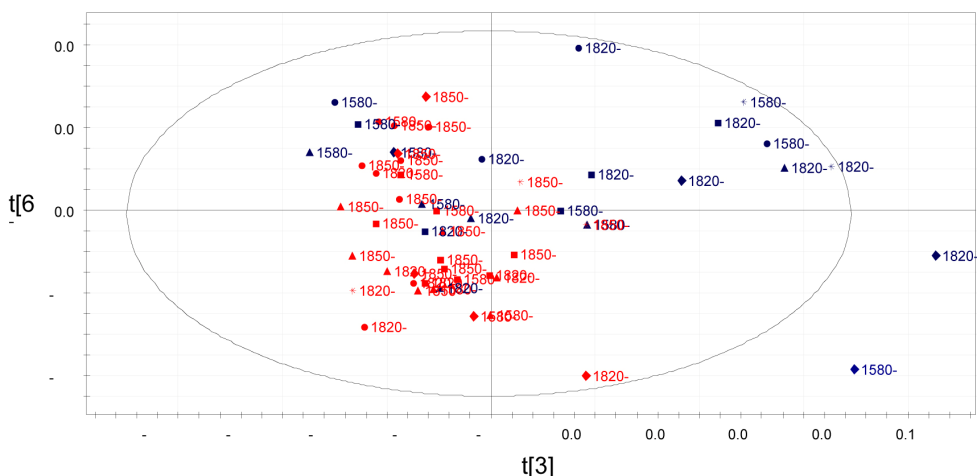


Figure 2. Score plot of principal components 3 and 6. Red marks correspond to no or low degree of sulphonation and blue marks corresponds to the pulps of high degree of sulphonation 1580-10 and 1820-10.

For every principal component there is a loading plot showing the significant spectrum for this component. In *Figure 3* the loading plots for principal components 3 and 6 are shown together with one of the average spectra from a fibre. From the score plot a higher degree of sulphonation is equivalent to a higher value of both component 3 and 6. This means that in the loading plot positive values comes with higher degree of sulphonation. Important peaks where both the principal components show the same behaviour are at wavenumber 1752 cm^{-1} corresponding to the C=O bond in xylan, and at 810 cm^{-1} corresponding to glucomannan. Since these scores are positive in the loadings plot, sulphonated fibres have more of these components.

Earlier measurements (Stevanic and Salmén 2008) of sulphonated primary wall material showed changes in pectin vibrations at 1643 cm^{-1} . In the loadings plot for component 3 there is a negative peak at 1640 cm^{-1} showing less pectin in the surface of sulphonated fibres. In component 6 this is not shown.

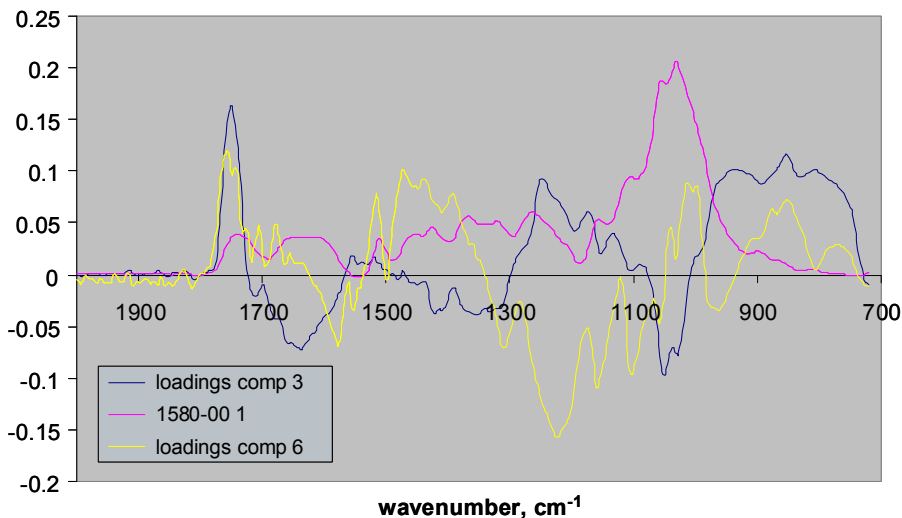


Figure 3. Loading plot for principal component 3 and 6 together with a fiber spectrum.

Intensity maps for different wavenumbers can be made to visualize the distribution of components. As an example, the distributions of xylan (1752 cm^{-1}), glucomannan (810 cm^{-1}) and pectin (1640 cm^{-1}) for the pulps 1580-00 and 1580-10 are shown in *Figure 4*. To compensate for different overall intensity of the spectra, the analysed peak height was normalized to the total absorbance from 1800 cm^{-1} to 800 cm^{-1} . From these maps no clear pattern can be seen.

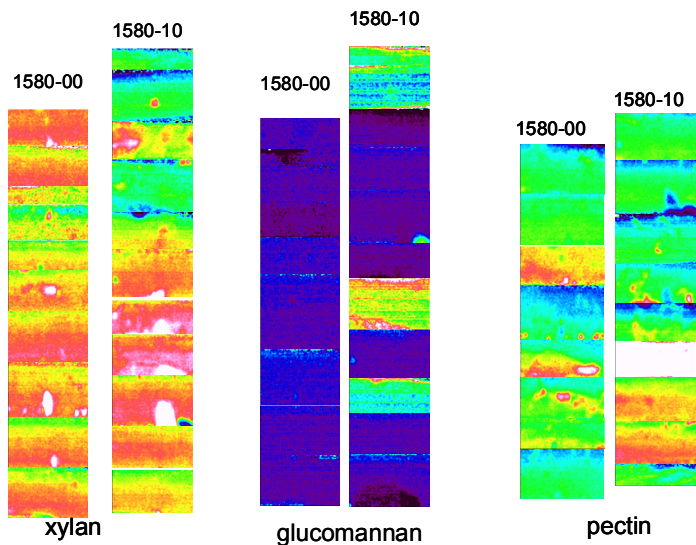


Figure 4. Distribution image of xylan, glucomannan and pectin in sulphonated 1580-10 and unsulphonated 1580-00 fibres.

Conclusions

The highest degree of sulphonation seems to give different fibre separation during refining, than unsulphonated pulps giving a different fibre surface and therefore other mechanical properties. The multivariate analysis of the FTIR spectra suggests that the surface is richer in hemicellulose for the sulphonated fibres. This could provide for a better binding surface and higher strength for the paper. However, no clear pattern of differences in the distribution images and therefore the micro-distributions of xylan were seen.

References

1. Stevanic, J.S. and Salmén, L. (2008). Interactions among components in the primary cell wall of Norway spruce (*Picea abies* (L.) Karst); Effect of a low sulphonation pretreatment. *J Pulp Paper Sci.* 34(2):107-112.

APPENDIX 3. FERNANDO AND DANIEL'S METHOD OF SIMONS' STAINING FOR UNDERSTANDING FIBRE DEVELOPMENT AT THE CELL WALL LEVEL DURING TMP PROCESSING OF SULFONATED CHIPS

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Background

Wood fibres behave differently during mechanical pulping processes like thermomechanical pulping (TMP) depending on the process conditions/treatments. These changes govern the pulp and paper properties of the final product. For example, internal structural modifications to the native fiber wall known as delamination/internal fibrillation (D/IF) are thought to be a prerequisite pulp fibre characteristic in mechanical pulps (MP). Fiber wall D/IF makes stiff wood fibres flexible, a basic fibre property that not only governs physical (e.g. strength) and optical properties of pulp and handsheets but also contributes to improved paper formation (Fernando *et al.*, 2011).

The new microscopy method of Simons' staining developed by Fernando and Daniel (2010) allows visualization and quantification of fibre development concerning degree of wall D/IF of MP fibres occurred during processing, as well as statistical analysis of whole pulp fibre populations of different MPs for the degree of D/IF developed in the fibres. The method readily measures the degree of wall D/IF of fibres in a given pulp based on the colour reaction of single fibres to Simons' stain (SS). SS is a two-colour dye consisting of a low- and high molecular weight polymeric mixture of direct blue (DB) and orange (DO) dyes used previously for visualizing changes in pulp fibre fibrillation and mechanical damage of beaten fibres (Simons 1950; Koljonen and Heikkurinen 1995). Depending on the severity and/or the extent of fibre wall D/IF occurred due to processing and/or process conditions/treatment, fibres in a pulp stain differentially from blue to yellow/orange. The method, based on the colour reaction to SS, identifies and categorizes the whole pulp fibre population of a MP into five major sub-fibre populations (S-FP) with the data on the latter used for evaluation and statistical analysis of MPs.

In the present study, the effect of chip pre-treatment with low dosages of sulfite prior to TMP refining was investigated by analyzing and characterizing sulfonated TMP fibres at the cell wall level using Fernando and Daniel's method of SS.

EXPERIMENTAL

Samples of Norway spruce (*Picea abies* (L) Karst) TMPs produced following sulfite pre-treatment of chips during a mill-scale trial at Holmen Paper (Braviken, Sweden) were used for the present study. The trial was as a step towards reducing the energy consumption during production of TMPs. Six never-dried pulp samples were selected for detailed microscopy study using the SS method representing pulps produced at extreme refining condition of energy input from main dosages of sulfite (i.e. 0, 2, 5 and 10 kg/bdt) treated chips (*Figure 1*).

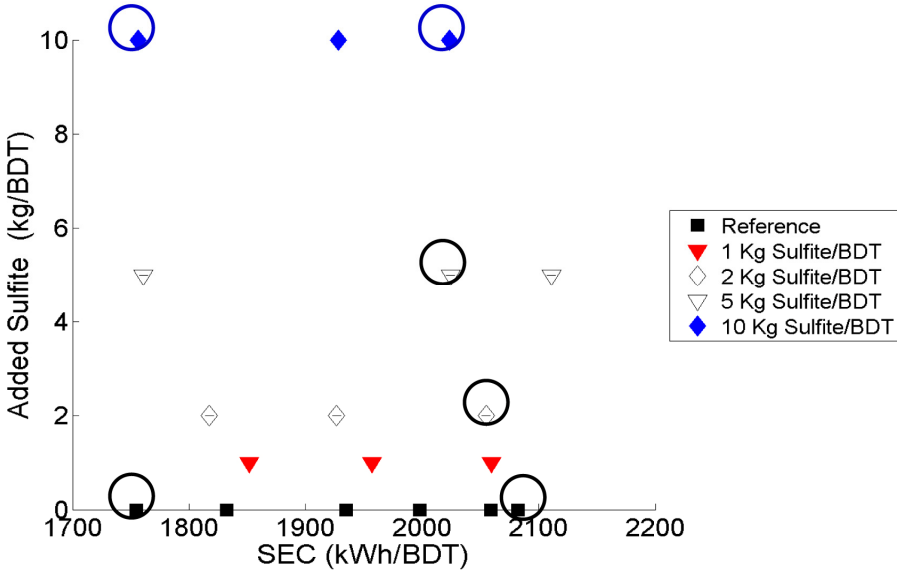


Figure 1. Different levels of the sulfite dosages used during chip pre-treatment prior to refining and the varying levels of energy input applied during the trial. Circles on the graph represent the TMP samples used during the present study.

SIMONS STAINING

TMP fibres were characterized using Fernando and Daniel's method of SS as described previously (Fernando and Daniel 2010) in order to understand fibre behavior at the cell wall level as a consequence of the chip pre-treatments with different sulfite dosages. Data obtained on D/IF of pulp fibre walls using a Leica DMLB light microscope were summarized in a bar graph and further analyzed statistically.


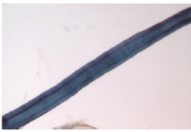
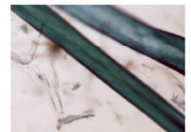
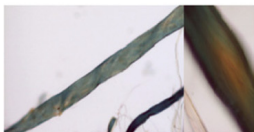

Non-parametric statistical procedure Ordinal Logistic Regression (OLR) test was performed on these categorical data of colour reaction to SS in order to assess differences in the degree of pulp fibre wall D/IF of the six sulfonated TMPs used. Data were analyzed using SAS computer software (SAS/STAT, Version 9.1 for

windows (XP-Pro platform), SAS Institute Inc., Cary, NC, USA) (Fernando and Daniel 2010).

Results and Discussion

Based on the degree of fibre wall D/IF in a MP induced as a result of process treatments (i.e. different levels of sulfite pre-treatment and energy input), the whole pulp fibre population of sulfonated TMP can be categorized into five S-FPs as summarized in the *Table 1* (Fernando and Daniel 2010). As described by the authors, these five S-FP's showed ordinality in the degree of fibre wall D/IF from lowest S-FP1 to the highest S-FP5. This information is used in the OLR procedure during statistical analysis of the six TMPs.

Table 1. Summary of S-FPs present in a MP identified with Fernando and Daniel's method of SS and the different levels in the degree of fibre wall D/IF they reflect

| S-FP category | Color reaction of fibers | Fiber development | Illustrations |
|---------------|--------------------------------------|---|--|
| S-FP1 | Light blue | Almost untreated at fiber wall level (i.e. no D/IF) |  |
| S-FP2 | Dark blue | Mild fiber modification |  |
| S-FP3 | Green | Development of both small and large pores with some weak D/IF |  |
| S-FP4 | Yellow/orange along < ½ fiber length | Fibers well treated with moderate D/IF |  |
| S-FP5 | Yellow/orange along > ½ fiber length | Fibers extensively treated with major D/IF |  |

(From Fernando and Daniel (2010), TAPPI J.)

EFFECT OF SULFITE PRE-TREATMENT OF CHIPS PRIOR TO REFINING ON FIBRE WALL D/IF

A summary of preliminary results of SS for pulps produced with sulphite pre-treated chips is presented in *Figure 2*. Here, the five S-FP's present in a sulfonated TMP were classified into three major contrasting groups of “non D/IF”, “low D/IF” and “high D/IF”. S-FPs light blue and dark blue were combined to form the non D/F group and S-FP4 and S-FP5 to form the high D/F group. The S-FP3 was considered as the category “low D/IF” which is the middle group. Group “non D/IF” represents non-treated or the least treated fibre population, group “low D/IF” moderately treated fibres and group “high D/IF” for the most severely treated fibre population in a given TMP type (Fernando and Daniel 2010).

It was apparent that pulps refined with high SEC following highest dosage of sulphite (10 kg) pre-treatment contained the most flexible fibres dominated by treated fibres comprising ca. 65% of the whole fibre population and the majority of which were in group high D/IF (39% of total fibres, *Figure 2*). As expected, low energy input without chemical pre-treatment generated the least developed pulps during the trial where the untreated fibre population was 57% with lowest proportion of the group high D/IF (16%). Interestingly, the SS method revealed the behaviour of two pulps 00(1850) and 10(1580) where more or less similar fibre development concerning wall D/IF were shown by the two pulps (52% and 55% treated fibres respectively).

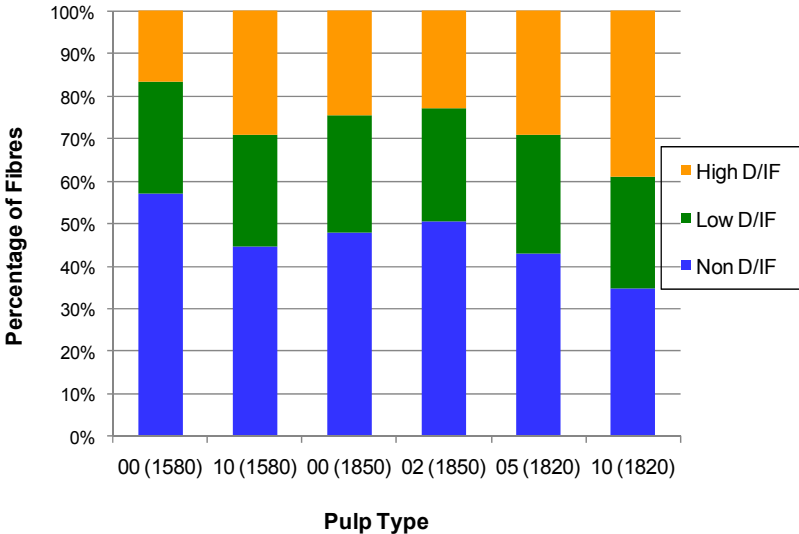


Figure 2. Percentages of fibres in the three major groups of each sulfonated TMP sample representing different levels of D/IF revealed using the SS method.

Statistical analysis (*Table 2*) provided evidence for the information gained from the preliminary results described above:

- a) There were highly significant differences among all the pulps analyzed on the degree of D/IF (p value - < 0.0001);
- b) Both the energy and sulphite pre-treatment had a very high significant influence on the fibre wall D/IF (p values – 0.0039 and 0.0033 respectively);
- c) Fibre development in the pulp produced from the highest energy input after sulfonating chips with highest dosage was much greater than in the pulp produced under lowest energy input without sulfonation of chips (p value – < 0.0001);
- d) Even with the same energy input, high dosage of sulfite treatment significantly elevated the degree of D/IF compared to that in the corresponding pulp produced from chips without sulfonation (p value – 0.0032);
- e) However, there was no significant difference concerning the degree of D/IF between the pulps 00(1850) and 10(1580) (p value - 0.3647) indicating the existence of similar fibre behaviour for the two pulps.

Table 2. LR statistics for type 3 analysis of ordinal logistic regression test for significant differences in the degree of D/IF of pulps from sulfonated and/or unsulfonated TMPs

| Source | DF | Chi-Square | Pr > ChiSq |
|---------------------------|----|------------|------------|
| Pulps | 5 | 34.87 | < .0001 |
| Energy effect | 2 | 11.10 | 0.0039 |
| Chip pre-treatment effect | 3 | 13.71 | 0.0033 |
| 00(1580) vs 10(1580) | 1 | 8.70 | 0.0032 |
| 10(1820) vs 00(1580) | 1 | 13.02 | < .0001 |
| 00(1850) vs 02(1850) | 1 | 0.28 | 0.5949 |
| 05(1820) vs 10(1820) | 1 | 4.60 | 0.0319 |
| 00(1850) vs 10(1820) | 1 | 12.05 | 0.0005 |
| 00(1580) vs 00(1850) | 1 | 4.44 | 0.0351 |
| 10(1580) vs 10(1820) | 1 | 6.45 | 0.0111 |
| 00(1850) vs 10(1580) | 1 | 0.82 | 0.3647 |

Results thus suggest that similar fibre development at the fibre cell wall level can be gained using low energy input on the chips pre-treated with 10 kg sulphite dosage as for untreated chips refined to highest SEC indicating an energy-efficient process with the former system.

Conclusions

Sulphite chip pre-treatment exerted an impact at the fibre wall level during TMP refining that was visualized and revealed using Fernando and Daniel's method of SS. Statistical analysis indicated that both the energy input and chip pre-treatment significantly induced wall D/IF of pulp fibres. Furthermore, it was shown that fibre development of pulp 10(1580) (with lowest SEC) gained via improved wall D/IF was almost similar to that of pulp 00(1850) (with highest SEC). This indicates that an energy efficient refining can be obtained with 10 kg/BDT sulfite pre-treatment prior to refining that can produce the most flexible fibres.

References

- Fernando, D., Daniel, G. (2010) Characterization of spruce thermomechanical pulps (TMP) at the fiber cell wall level: a method for quantitative assessment of pulp fiber development using Simons' stain. *Tappi J.* 9:47-55.
- Fernando, D., Muhic', D., Engstrand, P., Daniel, G. (2011) Fundamental understanding of pulp property development during different TMP refining conditions using the application of new Simons' stain method and fibre surface ultrastructure. *Holzforschung* 65, 777-786.
- Koljonen, T., Heikkurinen, A. (1995) Delamination of stiff fibres. In: *International Mechanical Pulping Conference*, Ottawa, Canada. pp. 79-84.
- Simons, F.L. (1950) A stain for use in microscopy of beaten fibers. *Tappi J.* 33(7): p. 312-314.

APPENDIX 4. OPTICAL PROPERTIES OF LOW-SULFITE PRE-TREATED TMP

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Summary

Wood chips impregnated with alkaline Na_2SO_3 were refined at two specific energy (SEC) levels. The obtained pulps were analyzed using standard optical tests, and spectral imaging. At low sulfite dosage (0.24 wt.-%) pulps displayed reduced light absorption and higher brightness, with a clear dose-response effect with more sulfite. This refining process resulted in an increase of the red edge fluorescence of sulfonated long fibre surfaces. Spectral imaging showed capable to capture minute changes of the lignocellulosic optical properties, and allowed visualization of a sub-population of fibres with different fluorescence wavelength distributions.

Introduction

The wood fibre can be considered as a heterogeneous lignocellulosic biocomposite of polysaccharides (cellulose, hemicelluloses and pectins) and lignin. Many industrial wood processes target lignin since it affects the flexibility, bonding and colour of the wood fibres; also resistance to temperature, irradiation, chemical and biological degradation can be correlated to lignin. Many of these properties are related to the aromatic chemical structure of lignin since larger aromatic structures are more rigid and the π - π transitions in large conjugated systems are responsible for the absorption of visible light; thereby directly affecting mechanical and optical properties of lignocellulose. Part of these π - π transitions are also autofluorescent which affects the optical properties of wood fibres. The fluorescence can be utilized to obtain information about the aromatic lignin structures. The fluorescence intensity and spectral shape of lignin are sensitive to chemical modifications like e.g. alkaline sulfite treatment in high yield pulp production.

There have been pilot studies showing that potential energy savings and improved pulp properties can be obtained in TMP production by pre-treating the wood chips with sulfite prior to high intensity refining (Hill et al. 2010). Therefore, in this study TMP has been produced at full industrial mill scale with addition of low amounts sulfite to the wood chips prior to defibration. Since newsprint is commonly produced from TMP and the optical properties are vital parameters for the process and paper quality, we have in this study focused on probing the pulps

for refining- and sulfonation effects on light properties, which in turn depends on chromophores and lignocellulose physio-chemistry.

Fluorescence spectroscopic analysis has previously been performed on wood and fibres in bleaching and yellowing studies of mechanical pulp and on Kraft pulp. In high-yield pulping most wood constituents are retained in the pulp and is therefore heterogeneous, and contains fibres and fine material derived from different wood cell types, of different shapes and surfaces, with different properties. Conventional bulk spectroscopic analysis do not account for these heterogeneities. Therefore, in this study the pulps were spectroscopically investigated with spatial resolution on a sub-fibre level. This was achieved by combining autofluorescence spectral detection with two-photon excitation fluorescence microscopy (Denk *et al.* 1990); the scanning of the two-photon microscope is synchronized with the spectral acquisition of a CCD camera (Hafrén *et al.* 2011).

Experimental

PULPING

The wood pulps were produced from Norway spruce wood chips, at Holmen Paper's pulp mill (at Braviken). Sodium bisulfite and sodium hydroxide NaOH were added to the process water used for the impregnation and then added to the wood chips in the impregnator vessel. The dosage of sodium bisulfite was adjusted by the chip feed from the Impressafiner and the NaOH concentration was adjusted in the process water to keep pH ~9 in the impregnation solution. The wood chips were left 10-15 min before being fed to a double disc refiner (from Metso), operating at 1500 rpm, about 150 °C and 4.5 bar. Pulp samples were collected directly from the blow line after refining.

TESTS OF THE PULP AND PAPER SAMPLES

The samples were tested for physical properties as pulps, or as handsheets produced using rapid Köthen (ISO standard, 2004). The analyses were performed according to respective standardized test method in triplicates, consistency (ISO standard, 4119:1995), Canadian standard freeness (ISO standard, 5267-2:2001) and optical properties (ISO standard, 2470-2:2008).

NON-LINEAR SPECTRAL IMAGING

Both wood chips and pulp samples were stored frozen and were thawed just prior to analyses, in a never dried state. The pulp samples for autofluorescence spectral imaging were fractionated for size, and Bauer-McNett fractions mesh 16-30 was used representing the long fibre fraction. The nonlinear spectral imaging microscope is home built and optimized for high detection sensitivity over a broad

wavelength range (Palero et al. 2007). The obtained spectra were corrected for the wavelength-dependent sensitivity of the system. To visualize the three-dimensional (i.e., x and y dimensions and wavelength channel) images, they were transformed into RGB images. Here, the RGB color represents the 'real' colour of the autofluorescence. Furthermore, for regions of interest the average autofluorescence spectrum were extracted. For additional information on the spectral imaging, see CRUW Mechanical pulping internal report nr. 1 (Ander *et al.* 2010).

Results and Discussion

OPTICAL EFFECTS OF LOW SULFONATION

Two specific energy consumption (SEC) levels were targeted for pulp production, a lower energy input level around 1750 kWh per ton pulp and a higher around 2050 kWh per ton dry weight pulp, in order to isolate any energy input derived effects from the effect of the sulfite pretreatments. In *Figure 1a*, handsheets made from the pulps were analyzed for brightness (diffuse blue reflectance factor). High pulp brightness directly from the refiner is often desirable since it may reduce the amount chemicals needed in subsequent pulp bleaching steps. Brightness is measured at $\lambda=457$ nm, according to specifications by the standard test method. In *Figure 1b*, the reflectance intensities over a broad wavelength range (420-700 nm) are shown for the high SEC samples (0-1.21 wt.-% sulfite). In both *Figure 1a* and *b*, a clear dose-response effect was shown, even when a low amount of sulfite (0.24%) added to the wood chips a significant increase in brightness was obtained. The relative increased brightness effect was similar at both high and low SEC levels, with the more sulfite added to the pulps the higher brightness was obtained. Therefore, we isolated the four extreme pulp samples and in subsequent analyses focused on the effects of 0 and 1.21% sulfite, at high and low SEC levels.

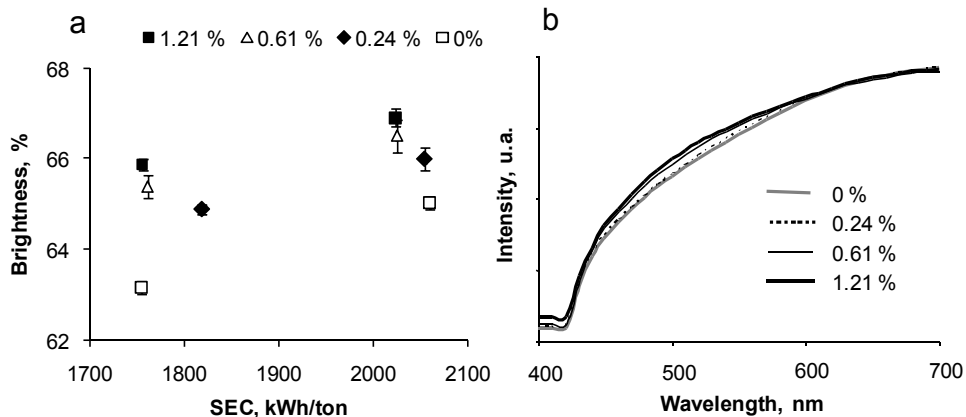


Figure 1. Effect of sulfonation with different amount added sulfite (wt.-%) and specific energy consumption levels (SEC) on brightness (a) and diffuse reflection intensity measured over 420-700 nm (b). Analyzed handsheets made from pulps produced at high level SEC and with different amount added sulfite. Data points and error bars represent mean values \pm standard deviation (a) and curves show means of triplicates (b).

BRIGHTNESS AND FLUORESCENCE OF LIGNOCELLULOSE

In Figure 2 the reflection intensities over the wavelengths 420-700 nm are shown for the four samples analyzed. Both SEC and sulfonation affected the intensity distribution, moreover, high SEC and sulfonation showed the highest reflection intensity over 450-650 nm, and low SEC and no added sulfite showed the lowest reflection intensity. At higher wavelength numbers the differences between samples are smaller. The perceived brightness of paper containing natural fluorophores (or added fluorescent whitening agents) has two components, reflected light and fluorescence. Lignocellulose interacts more with UV and visible light than with near infrared, thus the fluorescent component in diffuse reflectance measurements is more prominent in visible light than in near-IR. In order to study the lignocellulose fluorescent properties in more detail and with spatial resolution we also employed spectral imaging.

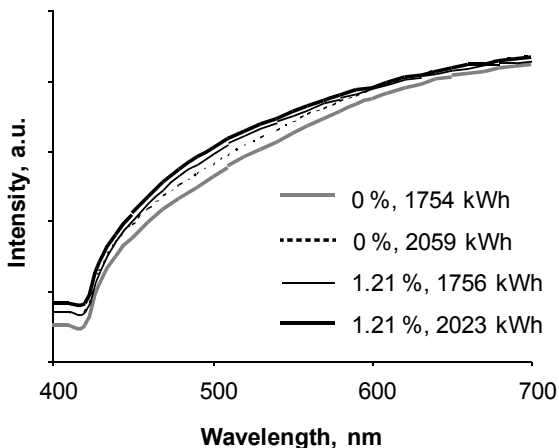


Figure 2. Effect of sulfonation (0 and 1.21 wt.-% added sulfite) and specific energy consumption (SEC, kWh/ton) on diffuse reflection intensity over 420-700 nm (means of triplicates). Analyzed handsheets made from pulps produced at different SEC and with different amount added sulfite.

SPECTRAL IMAGING OF PULP FIBRES

Size fractionated pulp samples were used for spectral imaging. We used mesh fraction 16-30, which represented about 13-14% of the pulp material and is enriched in whole long fibres, but even so, the fibre fractions are not homogeneous and always contains a certain amount of odd size objects and fine material. However, one of the advantages of the spectral imaging technique is that it allows for direct visualization of the sample's features and spatially optimized sampling on microscopic level for the autofluorescence spectral analyses. Thus, in the images of fibres we could easily identify and analyze specifically "fine material free" regions of interest, in order to specifically obtain spectra of real fibres. The respective sample spectrum, containing the sum of all spectra from all pixels in the image, or region of interest, was used for comparing spectra between different samples containing seemingly similar fibres.

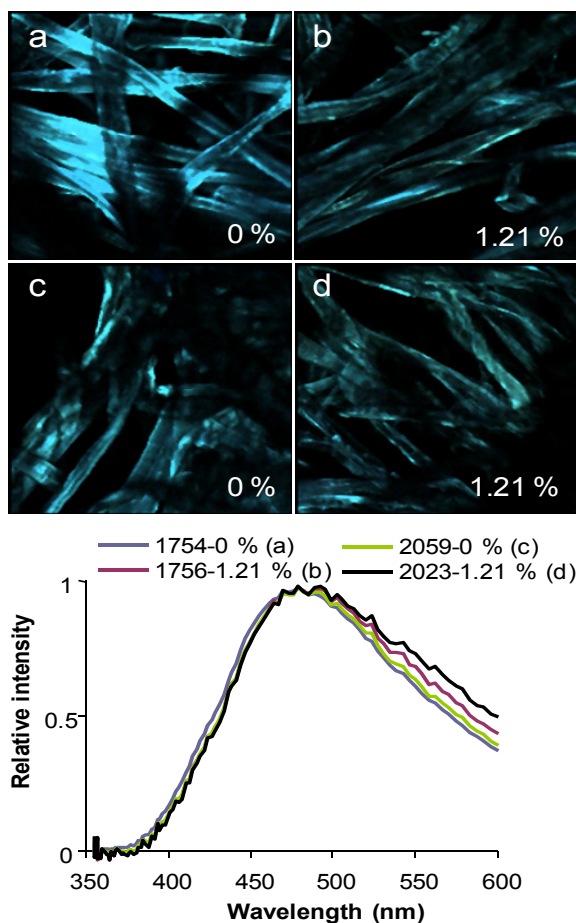


Figure 3. Representative autofluorescence spectral images of fibres at low specific energy consumption levels, 1754 kWh (a) and 1756 kWh (b), and high energy input 2059 kWh (c) and 2023 kWh (d) with 0 % and 1.21 wt.-% sulfite added (image size $75 \times 75 \mu\text{m}$, at excitation 760 nm). The spectra below show the normalized averaged sum wavelength distributions of all pixels from respective sample image above (a-d).

For all four samples the pulp fibre fluorescence showed similar emission maxima in Figure 3, but the two sulfonated pulps showed relatively more fluorescence over longer wavelengths ($>500 \text{ nm}$), with the higher SEC pulp showing the strongest effect. Of the five fluorophore components, as designated by Donaldson et al. (2010), a relatively increase of components IV ($\lambda_{\text{max}}=500 \text{ nm}$) and V ($\lambda_{\text{max}}=535 \text{ nm}$) may result in a redshifted spectrum. Also, elongation of the π -electron system, by e.g. chemical rearrangements extending conjugated structures, typically results in red shifted emission spectra (Valeur 2002). Alternatively, the red shift may result from physical rearrangements in the lignocellulose nano-environment facilitating

energy transfers between fluorophores. Moreover, the lignocellulose composition is spatial- and chemical heterogeneous throughout the cell wall layers- and middle lamella of the wood fibre. The more a fibre is refined, the more material is broken- or shredded off from the fibre surface, thereby, new fibre surfaces may be exposed. Thus, the fibre surface depends on where in the wood matrix the fiber separation occurred, and on level of fibre refining.

FIBRE SUB-POPULATION AUTOFLUORESCENCE

While investigating pulp samples for fibres to analyze we noticed that the spectral images revealed that two distinctly optically different fibre populations existed in the pulps, both in sulfonated and non-sulfonated pulp samples. The majority of the pulp fibres were bluish under two-photon microscopic analyses at excitation $\lambda=760$ nm, but some fibres were clearly greener

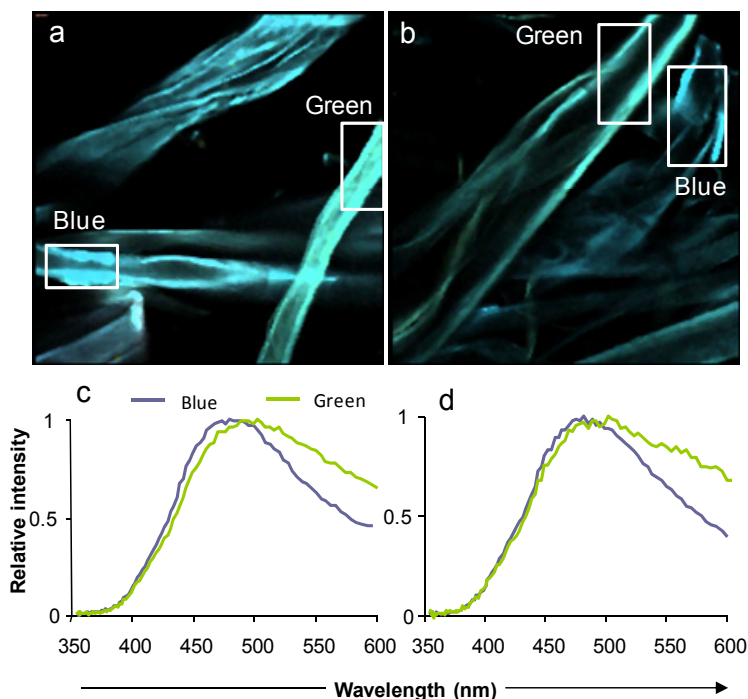


Figure 4. Autofluorescence spectral images of (a) unsulfonated low energy input pulp fibres (1421 kWh/ton and 0 wt.-% sulfite) and (b) sulfonated high energy input fibre sample (1693 kWh/ton and 1.21 wt.-% added sulfite), at excitation 760 nm (image size $75 \times 75 \mu\text{m}$). In the images, fibre sections have been marked by rectangular boxes labeled blue and green, respectively, and the normalized averaged sum wavelength distributions of all pixels within these regions of interest are shown in the spectra below. The spectra in (c) show the wavelength distributions from image (a), and the spectra in (d) represent image (b).

In *Figure 4a* and *b*, micrographs of non-sulfonated fibres produced at low SEC and sulfonated fibres produced at high SEC are shown and the regions of interest marks blue- and green fibres, respectively, in both samples. The wavelength distributions for the regions of interest are shown in *Figure 4c* and *d*. In both samples, the greener fibres have red-shifted emission maxima and wider peaks on the red side, and from the spectral images it is clear the colors are uniform within the respective fibre indicating the fibres are distinctively and wholly different from the bluish fibres. Perhaps these are process induced pulp heterogeneities since heat induces red-shifts of wood fluorescence, or the greener fibres may be derive from compression wood, which has shown higher concentration of red edge fluorescence components (Donaldson *et al.* 2010). It is worth mentioning the green fibre population was identified by spatially resolved analysis, since a conventional bulk spectroscopic analysis may not account for these heterogeneities on the individual fibre level. This may have implications for interpreting results from optical analyses in wood high-yield paper.

Conclusions

With little addition of sodium bisulfite to wood chips prior to refining, we obtained wood pulps showing improved optical properties, e.g. higher brightness. Also, clear dose-response effects were shown for both higher and lower SEC levels, with larger whiteness effects at high SEC level. The photochemical effects of sulfonation, as revealed by diffuse reflectance intensities and spectral imaging of pulp at high and low SEC levels showed complex results on lignocellulosic autofluorescence. Compared to wood, both wood chips and the pulp fibres showed a clear blue-shifted fluorescence maxima (Ander *et al.* 2010), which is significant for shortened conjugated system, i.e. the chipping and Impressafiner pretreatment induced a slight degradation of the lignocellulosic matrix that can be measured by optical means such as spectral imaging. However, refining relatively increased the red edge fluorescence of the sulfonated whole long fibre fraction with a similar effect heat has on lignin fluorescence of wood.

References

- Ander, P., Bardage, S., Daniel, G., Fernando, D., Hafrén, J., Muhic, D., Salmén, L. (2010). Ed. Sandström, P. Mechanical Pulping 1. Effect of different refining pressures and energy using spruce TMP pulps from Braviken. Intern rapport nr 1. CRUW, Centrum för forskning om vedfibers ultrastruktur, Sveriges Lantbruksuniversitet, Inst. för Skogens Produkter, Uppsala 2010.
- Denk, W., Strickler, J.H. and Webb, W.W. (1990). Two-photon laser scanning fluorescence microscopy. *Science* 248, 73.
- Donaldson, L., Radotić, K., Kalauzi, A., Djikanović, D. and Jeremić, M. (2010). Quantification of compression wood severity in tracheids of *Pinus radiata* D. Don using confocal

- fluorescence imaging and spectral deconvolution. *J. Struct. Biol.* 169, 106.
- Hafrén, J., Muhić, D., Gerritsen, H.C. and Bader, A.N. (2011). Two-photon autofluorescence spectral imaging applied to probe process-effects in thermomechanical pulp refining. *Nord Pulp Paper Res J.* 26, 372-379.
- Hill, J., Sabourin, M., Johansson, L., Mörseburg, K., Axelsson, P, Aichinger, J. P. Braeuer, J.P and Gorski, D. (2010). Combining selective bleaching chemistries and ATMP technologies for low energy mechanical pulping at higher brightness. *Proc. 7th Int. Sem. Fund. Mech. Pulp Res.* Nanjing, China, June 21-23, 2010, p. 170.
- Palero, J.A., de Bruijn, H.S., van der Ploeg-van den Heuvel, A., Sterenberg, H.J.C.M. and Gerritsen, H.C. (2007): Spectrally-resolved multiphoton imaging of in vivo and excised mouse skin tissues. *Biophys. J.* 93, 992.
- Valeur, B. (2002): *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, Germany.

APPENDIX 5. TESTING OF SULPHITE TREATED TMP PULPS WITH THE HCL METHOD

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Background

Out of 18 TMP pulps produced in mill trials at Holmen Braviken, six were tested with the HCl method. The pulps had been refined in an impressafiner at different sulphite concentrations and refining energies. In this part of the project, the purpose was to analyse for dislocations and other weak points using the HCl method.

EXPERIMENTAL

HCL Method

Six of the pulps given in *Table 1*, were Bauer McNett separated and the 30 mesh fraction used. The pulps were tested both before and after delignification in H₂O₂/conc. acetic acid (1:1) at 60 °C for 50 hours. After delignification the fibres were washed with 1M phosphate buffer at pH 7 until the washing water had neutral pH. The different pulps were tested by the HCl method in duplicates using 120 mg fibres (as dry-weight) as reported earlier (Ander *et al.* 2008; 2010; Heinemann and Ander 2011). Length weighted fiber lengths and other dimensions were determined using the FibreMaster at StoraEnso in Karlstad (Anders Moberg). Calculation: **Cleavage per fibre: $(L_0 / L) - 1$** reflecting dislocations and other weak points. L₀ = original fibre lengths in mm and L = fibre lengths after HCl treatment.

Table 1. Fibre lengths and cleavage per fibre of six sulphite treated TMP pulps(30 mesh) before and after HCl treatment

| Sulphite TMP SEC/sulphite)* | SEC/Sulphite** | Control LWFL (mm) L ₀ | HCl LWFL (mm) L | Cleavage / fibre |
|--------------------------------|----------------|-------------------------------------|--------------------|------------------|
| 1. 1580/00 | 1579/0 | 0.95 | 0.53 | 0.79 |
| 2. 1580/10 | 1580/10.15 | 0.94 | 0.56 | 0.68 |
| 3. 1820/05 | 1822/5.05 | 0.79 | 0.49 | 0.61 |
| 4. 1820/10 | 1821/10.15 | 0.84 | 0.49 | 0.71 |
| 5. 1850/00 | 1853/0 | 0.86 | 0.52 | 0.65 |
| 6. 1850/02 | 1849/1.99 | 0.86 | 0.49 | 0.755 |

* wished values **measured values: SEC kWh/ton; sulphite kg/t

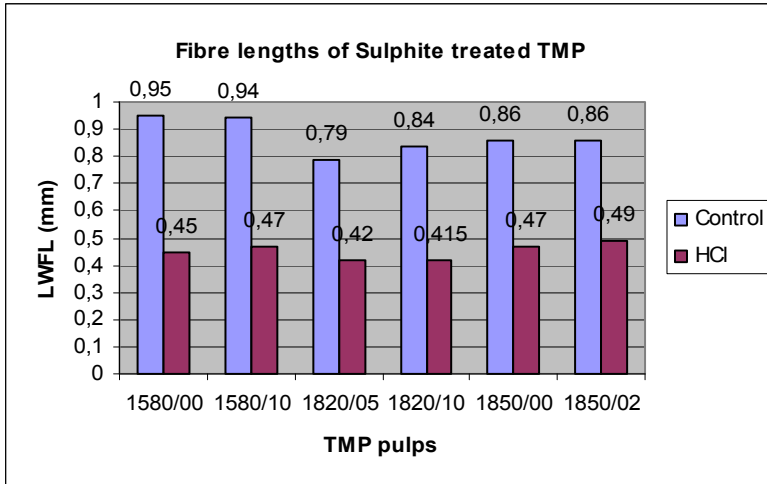


Figure 1. LWFL (mm) for six sulphite treated TMP 30 mesh pulps before and after HCl treatment.

Table 2. Fibre lengths and Cleavage per fibre for six sulphite treated delignified TMP pulps before and after HCl treatment

| Sulphite TMP SEC/sulphite* | SEC / Sulphite** | Control LWFL (mm) L ₀ | HCl LWFL (mm) L | Cleavage / fibre |
|-------------------------------|---------------------|-------------------------------------|--------------------|------------------|
| 1. 1580/00 | 1579/0 | 0.81 | 0.19 | 3.26 |
| 2. 1580/10 | 1580/10.15 | 0.78 | 0.18 | 3.33 |
| 3. 1820/05 | 1822/5.05 | 0.84 | 0.17 | 3.94 |
| 4. 1820/10 | 1821/10.15 | 0.69 | 0.16 | 3.31 |
| 5. 1850/00 | 1853/0 | 0.70 | 0.17 | 3.12 |
| 6. 1850/02 | 1849/1.99 | 0.73 | 0.17 | 3.29 |

*wished values **measured values: SEC kWh/ton; sulphite kg/t

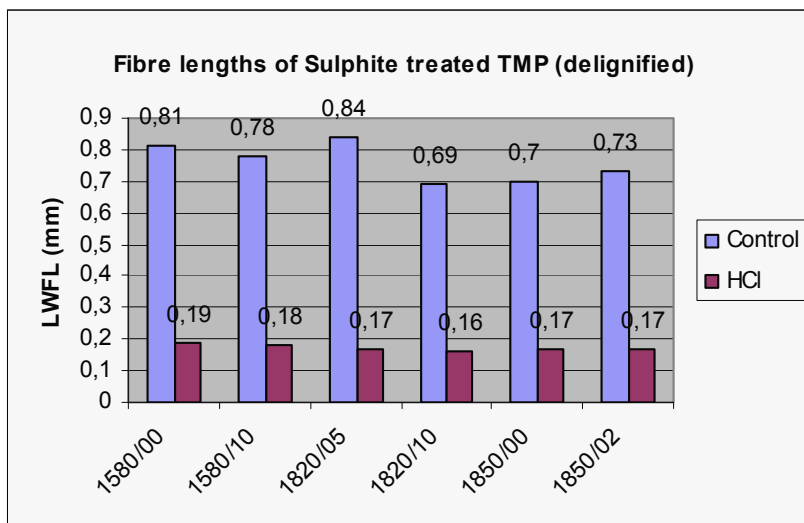


Figure 2. LWFL (mm) for six sulphite treated and delignified TMP 30 mesh pulps before and after HCl treatment.

Results

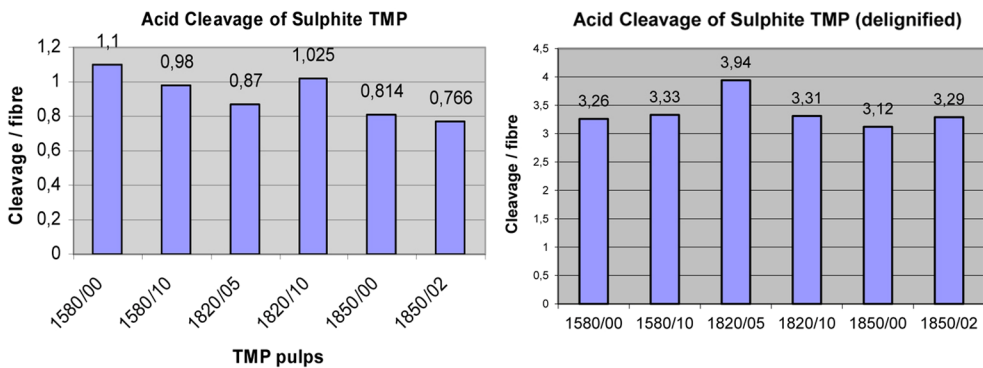
Fibre lengths are shown in *Tables 1* and *2* and in *Figures 1* and *2*. There were only small effects of sulphite on the original pulps, except for a small positive effect on pulp 1820. After HCl treatment there were only small differences in fibre length (0.49-0.56 mm). Delignification decreased fibre length by about 0.1 mm, except for 1820/05 which increased slightly from 0.79 to 0.84. The last three pulps in the series (red in *Table 2*) were slightly smaller (0.7 mm long) than the first three pulps (blue in *Table 2*) which were about 0.8 mm. Acid treatment of the delignified pulps strongly decreased fibre length to 0.16-0.19 mm compared with 0.49-0.56 mm from the beginning. This strongly indicate that lignin and to some extent also hemicellulose are protecting the fibres against acid attack. This effect has been reported previously (Ander *et al.* 2007).

It is interesting to note that HCl treatment and delignification gave almost the same fibre length for all six pulps regardless of energy input or sulphite treatment. This may indicate that impressafiner refining gives unrestricted (unselective) penetration of the small acid molecule into the cell wall structure, in contrast to that with kraft pulps differently treated or cooked.

Calculation of cleavage per fibre using original fibre lengths L_0 and the fibre lengths after HCl treatment (L) gave some unexpected results seen in *Figures 3*

and 4. In *Figure 3*, the fibres 1850/00 and 1850/02 with highest energy input, had the lowest cleavage per fibre 0.814 and 0.766, respectively. After delignification, the fibres had a cleavage number of 3.1-3.3, except for pulp 1820/05 which was strongly cleaved having 3.94 cleavages per fibre. No explanation for this strong cleavage can be given. Delignification increased cleavage by 3-4 times (*Figs 3 and 4*), as also suggested by decreased fibre lengths after delignification and HCl treatment.

In general, it is hard to see any significant trend for the effect of sulphite on these TMP fibres. Furthermore, increased energy input did not give stronger fibre cleavage after HCl treatment. The HCl method may not be suitable for these impressafiner pulps. However, the results should be compared with strength properties of the pulps.



Figures 3, 4. Cleavage per fibre of six sulphite treated TMP pulps before and after HCl treatment, with and without laboratory delignification.

References

- Ander, P., Bardage, S., Fernando, D., Hafrén, J., Daniel, G., Hammar, L-Å, Hedenberg, Ö., Hornatowska, J., Salmén, L. (2007). Mechanical Pulps II Differences between *Pinus sylvestris*, *Pinus contorta* and *Picea abies* for mechanical pulp: Changes in fiber properties and morphological organization during industrial processing. Internal report nr 11. WURC, SLU, Inst f. Skogens Produkter, Uppsala.
- Ander, P., Hildén, L. and Daniel, G. (2008). Cleavage of softwood kraft pulp fibres by HCl and Cellulases. *Bioresources* 3(2), 477-490.
- Ander, P., Bardage, S., Daniel, G., Fernando, D., F., Hafrén, J., Muhic', D., Salmén, L. (2010). Ed. Sandström, P. Mechanical Pulping 1. Effect of different refining pressures and energy using spruce TMP pulps from Braviken. Intern rapport nr 1. CRUW, Centrum för forskning om vedfiberns ultrastruktur, Sveriges Lantbruksuniversitet, Inst för Skogens Produkter, Uppsala 2010.
- Heinemann, S. and Ander, P. (2011). Standard pulp and paper tests. In: *Fine Structure of*

Papermaking Fibres, COST Action E54 Characterisation of the fine structure and properties of papermaking fibres using new technologies. *Eds:* Ander P., Bauer W., Heinemann S., Kallio P., Passas R. and Treimanis A. Swedish University of Agricultural Sciences. ISBN 978-91-576-9007-4, p. 211-232.

Collaborative Research on the Ultrastructure of Wood Fibres (CRUW)

CRUW represents a collaborative research program between the Swedish Forest Industries Eka Chemicals, Holmen, Smurfit Kappa Packaging, SCA, Stora Enso, Södra, SLU, Innventia, KTH and Mid Sweden University. The program is directed towards energy efficient processes for mechanical pulping and retention of the full fibre potential in chemical pulping. It is believed that research ideas based on insight into fibre ultrastructure can provide openings for breakthroughs in the applied area. The program forms part of the VINNOVA and Industry *”Branschforskningsprogram för skogs- och träindustrin”*.