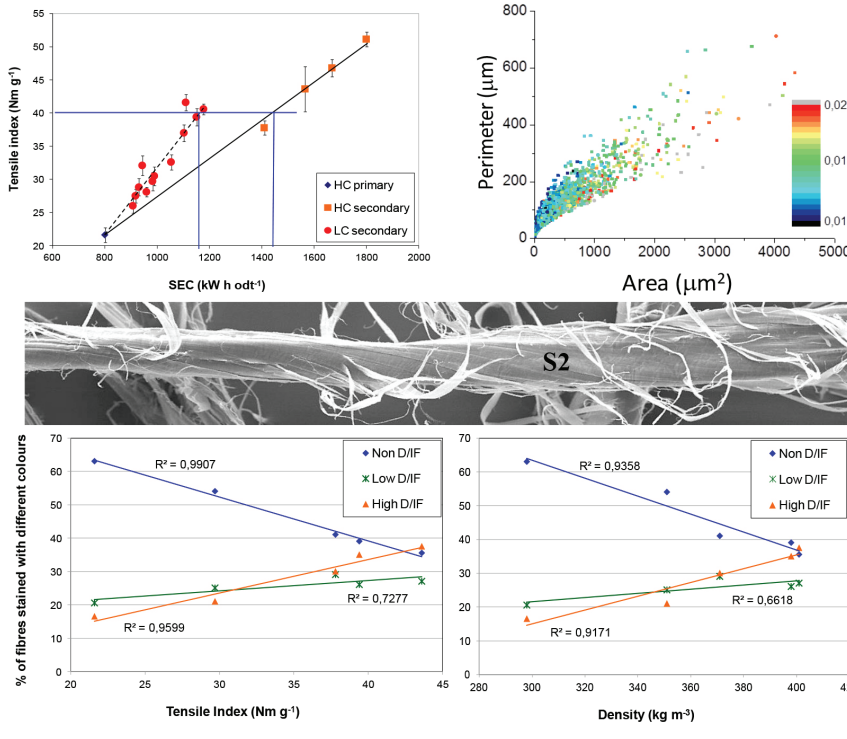
# CRUW Mechanical Pulping

## High- and low-consistency refining of TMP using mixed softwoods

**Dinesh Fernando, Jonas Hafrén,** *SLU;* **Dmitri Gorski,** *University of British Columbia;* **Geoffrey Daniel,** *SLU*




**Intern rapport nr 12** (begränsad spridning)

**CRUW**
**Centre for Research on Ultrastructure of Wood fibres**
**Centrum för forskning om Vedfiberns Ultrastruktur**
**Sveriges lantbruksuniversitet**
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**Uppsala 2013**

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# Contents

## Background

One of the critical issues facing the mechanical pulping (MP) industry nowadays is the accelerating electrical energy costs. Therefore, many research efforts have been dedicated to finding better process solutions. One of the new innovations evolved in this process is Advanced Thermo-Mechanical Pulp (ATMP) refining that consists of unit operations with the objective of separating the defibration and fibre development phases into subsequent process stages with the addition of chemicals. It has been proven to reduce the refining energy demand (ca 40%) while preserving and/or improving the quality of final product (Sabourin et al. 2003).

In addition, low-consistency (LC) refining has also been shown in recent years as an energy-effective approach to increase tensile index (Eriksen and Hammar 2007) although it has long been used in chemical pulp fibre development processing and also applied as reject- and post-refining during MP. Further reduction in energy during MP has been demonstrated by combining the ATMP concept as a primary-stage refining with secondary LC stages (Gorski et al. 2012; Sabourin et al. 2011).

In order to obtain fundamental understanding of process and product property relationships in MP, it is necessary to have a better knowledge of the development of fibre properties at the cell wall level during processing. In particular, changes in fibre structure (both internal and external micro-ultrastructure), fibre fibrillation, fibre/surface development and also the development of fines are of great interest.

One major goal of the CRUW Mechanical Pulping project is to support development of more energy efficient mechanical pulping processes by increasing knowledge on the ultrastructural changes of pulp fibres during pulping. Thus LC refining of mechanical pulps is a very relevant field of study for CRUW who could contribute with ultrastructural competence for understanding more clearly and explaining phenomena during both LC- and HC refining. These studies should provide knowledge for improvement and optimization of the concept of LC refining in MP and even for new avenues for improving products.

The CRUW project had a successful cooperation for the above theme with Dmitri Gorski, (post-doctoral fellow at University of British Columbia, Mech. Eng. Dept. & Pulp and Paper Centre, Vancouver, Canada) who conducted experimental pilot scale trials for comparing secondary HC and secondary LC refining of first stage ATMP pulps using mixed softwoods. The principle objective of the study was to achieve a tensile index of 40 Nm/g (common target of newsprint mills) with low energy input and compare pulp properties (e.g. density, freeness, light scattering coefficient, tear index, tensile energy absorption (TEA), and length weighted average fibre length) of the HC- and LC refined pulps at this tensile index. The

selected pulps from the trials were made available for CRUW to conduct more advanced studies on the pulp fibres and fines and this report presents abbreviated results from these works.

# Summary

In this pilot trial, the anticipated objectives were achieved by a reduction in total energy of approximately 300 kWh/odt (20%) to produce mechanical pulp (MP) having a target tensile index of 40 Nm/g by utilizing two stages of optimized LC refining compared to second stage HC refining. Here, LC refining required only 1150 kWh/odt whereas HC refining consumed a total of ca 1450 kWh/odt (*Figure 1*).

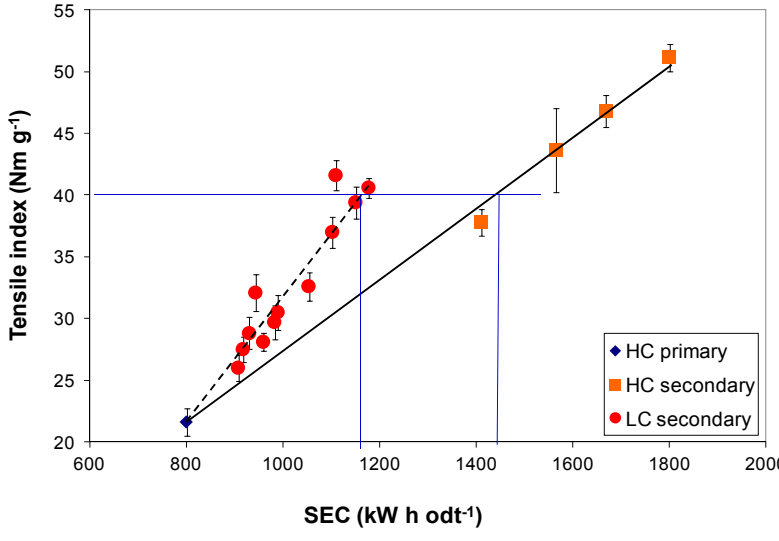


*Figure 1. Development of the tensile index of handsheets produced from LC and HC refined pulps.*

Compared at this tensile index, paper produced from the LC refined pulps had a similar light scattering coefficient (ca 59 $m^2/kg$) and density (398 $kg/m^3$) but lower in TEA (ca 12 $J/m^2$), tear index (2 $mNm^2/kg$) and average fibre length (0.4 mm) compared to the HC refined pulps (*Appendix 1)*. Pressure filtration measurements suggested that the differences in fibre length distributions between HC and LC refined pulps should not however cause differences in paper machine dewatering but require confirmation in full-scale trials (Gorski et al. 2012).

The development of fibre properties (e.g. fibre length) proceeded in a different manner in HC and LC refining even when compared at similar handsheet properties such as tensile index and light scattering (Gorski et al. 2012).

In order to understand of how different property profiles of HC- and LC-refined fibres are able to produce paper with similar final optical and strength properties, in-depth studies at the fibre level were carried out during the present work. The

aim was to contribute to a better understanding of fundamental mechanisms governing fibre property development in LC- and HC-refined pulps at the cell wall micro/ultrastructural level.

Internal fibre development (i.e. delamination/internal fibrillation (D/IF)) were evaluated and statistically analyzed using Fernando and Daniel's (2010) method of Simons´ staining. Results indicated that both the energy input and consistency (HC/LC systems) significantly enhanced wall D/IF of pulp fibres (*Figure 2*).

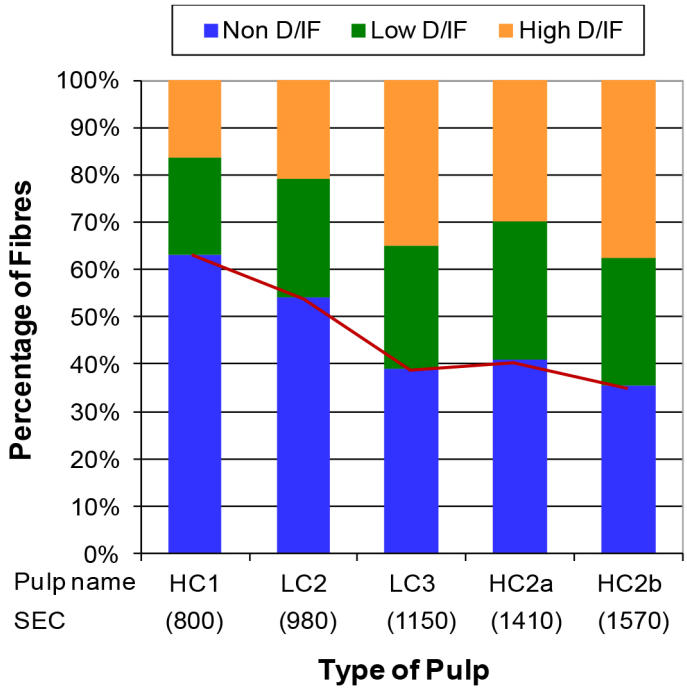


*Figure 2. Percentage of the three major groups of fibres, representing different levels in the degree of wall delamination/internal fibrillation (D/IF), following Simons' staining. SEC: specific energy consumption.*

Statistical evaluation of internal fibre development showed the fibre populations of LC- and HC-refined pulps to have a similar degree of fibre wall D/IF despite having large differences in refining energy input (420 kWh/odt less energy for LC3 compared to HC2b). This confirmed that D/IF was promoted more energy-efficiently in LC compared to HC refining and thereby provides a fundamental basis for the energy-efficiency associated with LC refining (*Appendix 2*).

SEM investigations revealed that the character of external fibrillation and surface ultrastructure of the pulp fibres produced during the two processes were very

different. LC refining appeared to promote the development of thin "hair-like" threads of S2 ribbons from fibre surfaces, sometimes along the whole fibre length, in addition to efficient D/IF development. Broad sheet- and lamellar-types of external fibrillation with high bonding potential originating from the S2 layer (typical for HC refining) were rarely observed in the investigated LC-refined pulps. Mechanisms of fibre development during LC and HC refining are proposed and the differing mechanisms between the two processes appear to govern most of the physical and optical properties of the investigated pulps (Fernando et al. 2012).

Morphological characteristics concerning the ultrastructure of fine particles produced during the two processes corroborated well with results obtained on external fibrillation and surface ultrastructure of fibres (*see Appendix 2*). The quality of the fines generated during HC and LC refining differed between the two processes regarding morphology. High strength properties of HC-refined pulps were partly explained by their type of fines particles characterized by long ribbon fibrils from the secondary S2 cell wall layer. Much broader sheet-like fibrils and lamellar-sheets were common in the fines producing carpet forming structures in the fibre network of paper due to their greater bonding potential.

In contrast, LC refining generated mainly long string/thread-like very narrow fibrils as fines that lacked the much broader sheet-like and lamellar fibril sheets. These thin long fibrils are reported as excellent light scatters in a pulp and thus were a primary reason for the exhibited greater light scattering property which was almost as high as that shown by the high energy HC pulps. In addition, flake-like particles were commonly observed in 2$^{nd}$ stage LC compared to third stage LC refining and were more pronounced with the greatest proportion in primary stage HC pulps.

A newly developed automated fluorescence microscopy method with image-based analysis applied for studying fines produced from the two processes showed quantitative differences in the morphological properties between the fines. About 40% of the fine particles were smaller than 10 $\mu m^2$ in cross section but contributed <2% of the bulk, whereas about 20% of the total number of fines having a cross section area over 100 $\mu m^2$ contributed to over 80% of the total bulk of fines material. LC refining was shown to produce small fibril-like fines at lower SEC levels than HC refining.

The results reported in the present sub-project of the CRUW provides important aspects for understanding LC and HC refining processes concerning property development and energy-efficiency that can help lead to new opportunities for energy-efficient MP.

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# Appendices

### APPENDIX 1. PILOT SCALE HIGH AND LOW CONSISTENCY REFINING OF MECHANICAL PULPS

*Dmitri Gorski, Post-doctoral Fellow at University of British Columbia, Mech. Eng. Dept. & Pulp and Paper Centre, Vancouver, Canada. (Now at; REINERTSEN AS, Sandslimarka 35, 5254, Bergen, Norway.)*

## Background

Reduction in the electrical energy demand in mechanical pulping has become a critical issue primarily due to constantly increasing electricity cost. New process solutions have been developed to address the issue. One process solution is the Advanced Thermo-mechanical Pulp (ATMP) refining process that was commercially introduced in 2010 (Hill et al. 2010).

Another way of reducing the electrical energy demand is by utilising low-consistency (LC) refining after first stage high-consistency (HC) refining. Replacing second stage HC refiner with LC refining has been reported to reduce the overall energy demand to reach a tensile index of 40 Nm/g by 300 kWh/odt for Norway spruce (Hammer et al. 1997). Pilot scale ATMP studies demonstrate a 100-200 kWh/odt reduction in the total refining energy, when compared at a similar tensile index of 40 Nm/g, by replacing the second stage HC refiner with multiple stages of LC refining; the total refining energy being less than 1000 kWh/odt (Sabourin 2007). At the same tensile index, the LC-refined pulps has a similar freeness and light scattering coefficient, however both tear and average fibre length were lower compared to the HC-refined pulps. Hammer et al. (2009), using Norway spruce as raw material, reports approximately 15% reduction in refining energy at equal tensile index where second stage HC refining is substituted with LC refining. The LC-refined pulps are shown to reduce fibre length compared to the HC-refined pulps corroborating results from previous work.

In this study, refining of first stage ATMP using HC second stage refiner was compared to two-stage LC refining. Each of the LC refining stages was optimized with focus on the development of pulp properties. The target was to achieve a tensile index of 40 Nm/g (common target of newsprint mills), and compare other pulp properties of the HC- and LC refined pulps at this tensile index. Pulp properties evaluated included freeness, light scattering coefficient, density, tear index, tensile energy absorption (TEA), stretch and length weighted average fibre length.

## Experimental

Pilot scale trials were performed using mixed softwood chips obtained from a Canadian TMP mill during the study. The raw material consisted of approximately 80% Lodgepole pine with the rest 20% from Sitka spruce and Western Balsam Fir from interior British Columbia. The ATMP concept was utilized for primary refining as described in the literature (Hill et al., 2010; Gorski et al. 2011). HC refining was conducted at the Andritz pilot plant in Springfield, OH, USA. Chips were pre-heated and defibrated using mechanical pre-treatment consisting of a MSD Impressafiner (40 kWh/odt energy input) and a Fiberizer (220 kWh/odt). The fiberized material was primary stage refined at RTS™ conditions (Sabourin et al. 1997) with an energy input of 530 kWh/odt. Sodium bisulphite (3.1% on oven-dry fibre basis, which decreased the pH of the pulp from 5.5-6.0 to 4.7) was added at the refiner inlet via the refiner dilution water.

A part of the primary stage pulp was further refined using an atmospheric HC double disc refiner at four different energy inputs (610-1000 kWh/odt). LC refining of the primary stage ATMP pulp was conducted in two optimized stages at the pilot plant located in the Pulp and Paper Centre, University of British Columbia, Vancouver, Canada. The pulp was disintegrated in water at 60ºC for 4 hours prior to refining at low consistency (3.0-3.4%) using a 14" Aikawa LC pilot refiner equipped with 0.41 m (16") overhung segments and driven by a 110 kW variable frequency motor. Refining conditions were varied by closing the gap of the refiner while the throughput was kept constant. This provided specific energy inputs of 70-180 kWh/odt in the first LC stage and 70-240 kWh/odt in the second LC stage. FineBar (AFT) segments were used in the refiner (BEL= 5.59 km, groove depth 4.8 mm, groove width 2.4 mm, bar width 1 mm, bar angle 15º).

Laboratory testing of pulp and sheets was conducted according to TAPPI standards at the UBC Pulp and Paper Centre laboratory: Bauer McNett fractionation - T233; Handsheets (approximately 60 g/m$^2$) preparation from hot disintegrated pulp - T205; Strength properties of the handsheets - T220; Light scattering - T425; Optical fibre characterization - FQA (Fibre Quality Analyzer) and Fibre Vision. The standard deviation of the results was calculated where possible and plotted as error bars.

## Results and discussion

Specific energy consumption (SEC) in LC refining was varied by adjusting the refiner gap. The relationships between the refiner plate gap and the net motor power is shown in *Figure 1*. As expected, smaller gap led to higher net power since the friction between the refiner segments and the pulp suspension between them increased. The relationship appears to be linear up to the point where the plate gap became small enough (<0.05 mm) for the fibre pad to collapse.

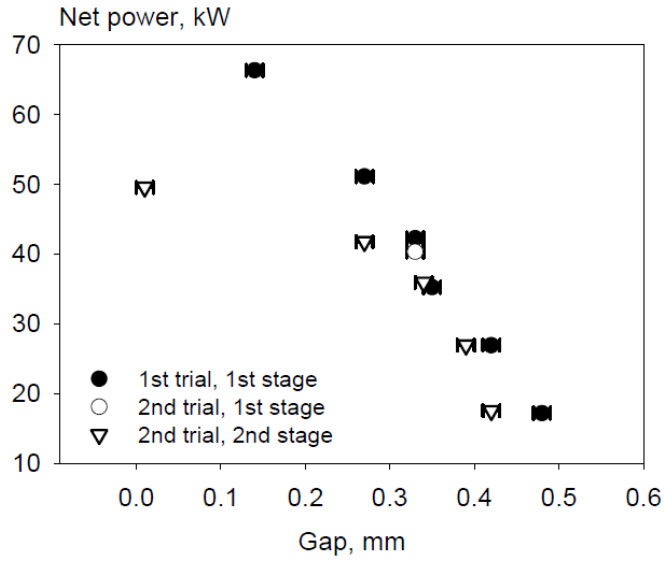


*Figure 1. Net refiner motor power at different LC refiner gaps in both refining stages.*

Process conditions such as refining intensities (expressed as Specific Edge Load, SEL), SEC and gaps for the LC refining trials are presented in *Table 1*. Since the energy input in refining was adjusted by closing in the gap, the intensity was higher for the pulps with higher SEC. A SEL of 0.38 J/m gave the best property development in the first trial, while a SEL of 0.24 J/m gave the greatest property development in the second trial.

*Table 1. SEL, SEC (gross) and gap in LC trials*

| **1st stage LC (first trial)** | | | **2nd stage LC (second trial)** | | |
|---|---|---|---|---|---|
| **SEC kWh/odt** | **SEL J/m** | **Gap mm** | **SEC kWh/odt** | **SEL J/m** | **Gap mm** |
| 104 | 0.15 | 0.48 | 120 | 0.16 | 0.42 |
| 117 | 0.24 | 0.42 | 127 | 0.24 | 0.39 |
| 130 | 0.31 | 0.35 | 168 | 0.32 | 0.34 |
| 143 | 0.38 | 0.33 | 195 | 0.37 | 0.27 |
| 159 | 0.46 | 0.27 | 240 | 0.45 | 0.01 |
| 189 | 0.59 | 0.14 | n/a | n/a | n/a |

The results indicate that the optimum LC refining intensity varies for different feed pulps. Optimum SEL intensity decreased with decreasing feed pulp freeness which is in agreement with previous work (Sabourin 2007).

## OPTIMISATION OF LC REFINING

Six different gap settings were used in the first series to determine the point of maximum tensile index development. In the second series, 5 different gap settings were used. *Figure 2* shows the development of paper tensile index in the first and second refining stages. Some first stage trial points were repeated in the second trial and the results (repeatability) appeared to be satisfactory.

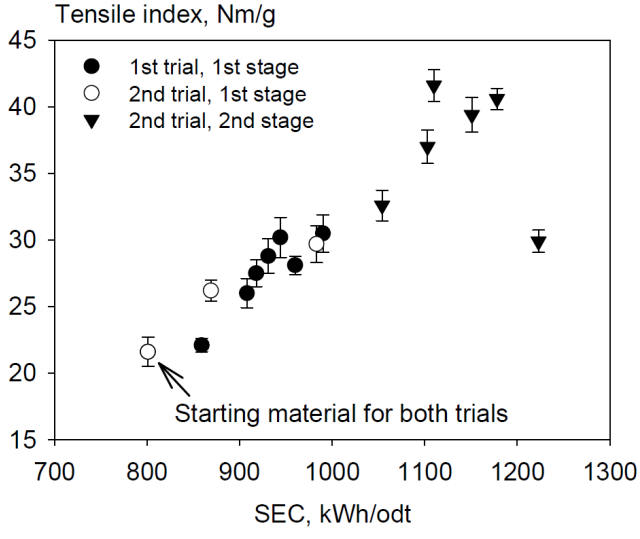


*Figure 2. Development of the tensile index of handsheets produced from pulp refined in one and two LC stages.*

In the first stage the tensile index development reached a maximum increase at a gross specific energy of 143 kWh/odt. The tensile index increased from 22 to 30 Nm/g, at a freeness of 205 CSF. The development of the maximum tensile index was achieved with a gross specific energy of 127 kWh/odt at a freeness of 132 CSF. The optimum gap size for maximum tensile index development was 0.33 mm in the first stage and 0.39 mm in the second stage.

The gross specific energy required to increase the tensile index by 1 Nm/g was approximately 18 kWh/odt in the first LC stage and 11 kWh/odt in the second stage; the SEL was 0.38 and 0.24 J/m respectively. Both pilot and mill data show a similar 17 kWh/odt per unit of tensile using SEL's of 0.5 and 0.6 J/m respectively (Sabourin 2007). The differences in tensile strength development and energy

efficiency between this study and the values reported in the literature depend on the different refining conditions and feed pulp, both influenced by species mix and refining degree before the LC refining.

### COMPARISON OF PULP PROPERTY DEVELOPMENT IN LC AND HC REFINING

Two stages of optimised LC- after primary HC refining in the ATMP process decreased the overall energy demand by 300 kWh/odt (20%) compared to HC refining at a tensile index of 40 Nm/g. *Figure 3* shows that specific energy demand was decreased by more than 300 kWh/odt when LC-refining was utilized. If the energy required for the first refining stage is not taken into consideration, refining at low consistency requires only approximately half of the energy input required to reach the tensile index of 40 Nm/g using high-consistency refining.

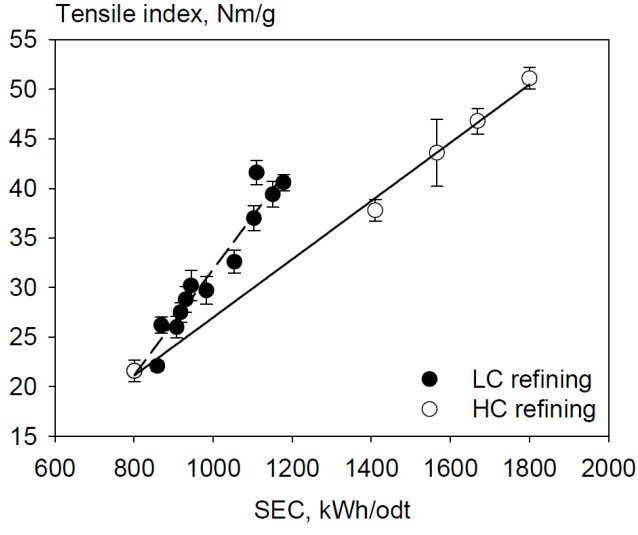


*Figure 3. Tensile index of handsheets produced from LC and HC refined pulp.*

*Figures 4-8* illustrate the development of light scattering coefficient, density, tensile energy absorption (TEA), tear index and average fibre length as a function of the tensile index development of handsheets. The intention was to compare these properties at a target tensile index of 40 Nm/g for both the HC- and LC pulps, particularly when the SEC was reduced with LC refining.

Development of both the light scattering coefficient and apparent sheet density appears to be very similar for LC and HC refining (*Figures 4 and 5*). This contradicts previous results where no light scattering development was reported for LC-refined pulps (Andersson and Sandberg 2011).

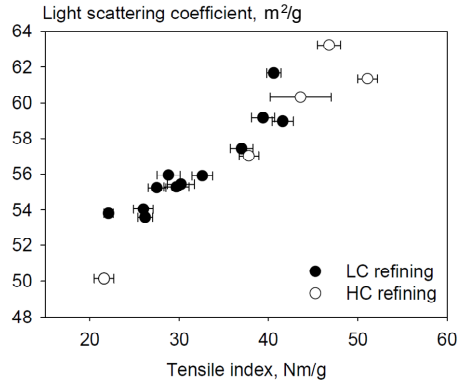


*Figure 4. Relationship between light scattering coefficient and tensile index of handsheets.*

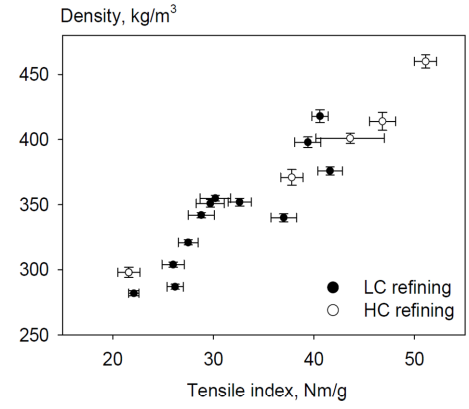


*Figure 5. Relationship between apparent density of paper and tensile index.*

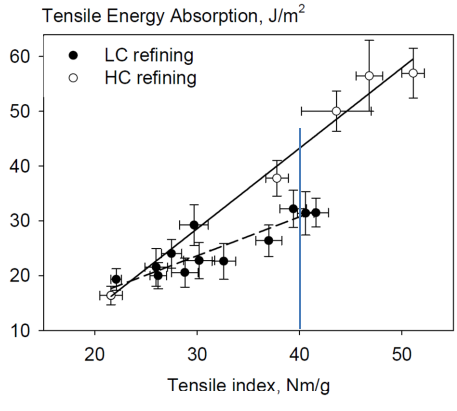


*Figure 6. Relationship between tensile energy absorption and tensile index of handsheets.*

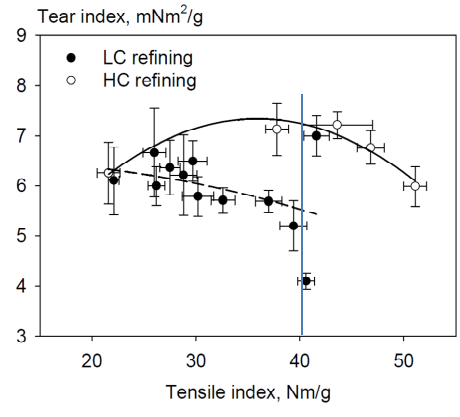


*Figure 7. Relationship between tear index and tensile index of handsheets.*

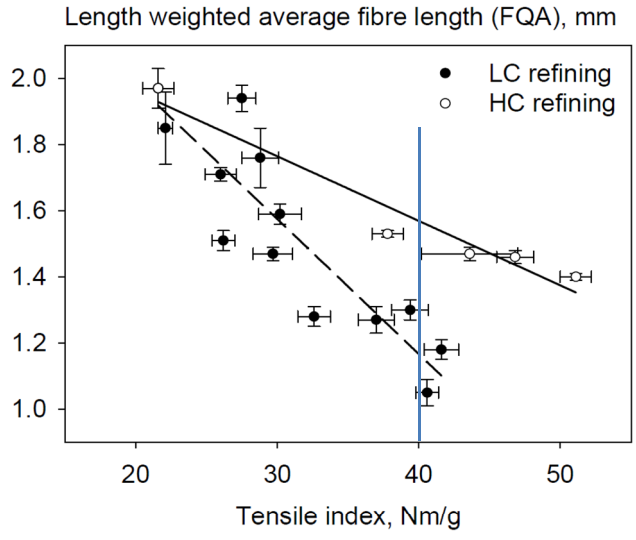


*Figure 8. Relationship between average fibre length (l.w.) and tensile index of handsheets.*

The TEA, tear index, and length weighted average fibre length all showed lower values for the LC refined pulp compared at equivalent tensile with the HC refined pulps (*Figures 6-8* respectively). Fibre length reduction is a known characteristic of LC refining. The shorter fibre length results in a decreased tear index. The reason for the lower TEA with LC refining remains unknown and is subject for further study (see *Appendix 2*).

The pulps produced from the HC- and LC processes demonstrated similar drainage and tensile strength properties; however the LC pulps had a lower average fibre length. This suggests a fundamental difference in fibre development between these two processes. The results from the trial indicated that HC- and LC refining produces pulp fibres, presumably with different property profiles, that are able to produce paper with similar final optical and strength properties. The mechanisms leading to these are to a large extent unknown including the basis of energy efficiency associated with LC refining observed during the trial. The studies reported in *Appendices 2-4* were therefore focused primarily on understanding the fundamentals behind the property development including the mechanisms of fibre development occurring during the two processes.

## Conclusions

- It is possible to produce high-quality mechanical pulp suitable for printing papers (tensile index 40 Nm/g and light scattering 59 $m^2$/kg) using the ATMP process with a single HC refining stage followed by two-stage LC refining.

- The HC refining required a total of approximately 1450 kWh/odt, whereas HC refining followed by the two optimised LC refining stages required a total of 1150 kWh/odt, approximately 300 kWh/odt less.

- The Light scattering coefficient and apparent density of the sheets developed similarly for both HC and LC refining.

- The tear index, length weighted average fibre length, stretch and TEA were lower for the LC-refined pulp.

## Acknowledgements

The author would like to express his gratitude to the staff of UBC Pulp and Paper Centre (George Soong and Christine Seville) and especially Dr. Antti Luukkonen. Dr. Jens Heymer (AFT), Professor James Olson (UBC PPC) and Marc Sabourin (Andritz, USA) are acknowledged for their advice and support during the LC refining trials. Dmitri Gorski would also like to acknowledge the financial support of Gålöstiftelsen, Hans Werthén Fonden and Jansons Legat who all contributed to his post-doc at the University of British Columbia.

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## APPENDIX 2. ULTRA/MICRO-MORPHOLOGICAL CHARACTERIZATION OF FIBRE CELL WALLS DURING HC AND LC REFINING OF MIXED SOFTWOODS; EXPLORATION OF THEIR FIBRE DEVELOPMENT MECHANISMS

*Dinesh Fernando and Geoffrey Daniel, SLU Uppsala.*

# Background

Low consistency (LC) refining of mechanical pulp (MP) has long been utilized in thermomechanical pulp (TMP) refining processes with emphasis on both reject and post refining. In recent years, LC refining has also gained increased interest as a means of reducing electrical energy input in TMP refining while maintaining or improving pulp quality compared with high consistency (HC) refining (Sabourin 2007; Gorski et al. 2012). HC- and LC refining develop pulp fibres with different property profiles (e.g. fibre fraction distribution, cross-sectional dimension, surface area etc) that are able to produce paper with similar final optical and strength properties (Gorski et al. 2012). The mechanisms behind these phenomena are to a large extent unknown.

Characterization of MP fibres at the cell wall level is an invaluable step in papermaking science. It provides the basic knowledge required to maximize the papermaking potential of wood and pulp fibres along their way to final paper products with required quality. This requires a better understanding of fibre development concerning both the internal (e.g. delamination/internal fibrillation (D/IF)) and external (e.g. external fibrillation) micro/ultrastructure of pulp fibres during refining processes. The latter two fibre characteristics (i.e. D/IF and external fibrillation), which can presumably be tailored depending on the processes and/or treatments wood fibres undergo, play a key role in governing final pulp and paper products (Kang & Paulapauro 2006; Fernando et al. 2011). For example, fibre wall D/IF is considered a requisite pulp fibre characteristic that essentially makes stiff wood fibres flexible, a basic fibre property that governs most pulp and paper physical (e.g. strength) and optical properties and also contributes to improved paper formation (Abitz and Luner 1989; Paavilainen 1993; Fernando et al. 2011, 2012).

Characterization of fibre development during LC and HC refining processes was therefore carried out in this study aimed at improving the understanding of how different property profiles of HC- and LC-refined fibres are able to produce paper with similar final optical and strength properties. The purpose was to contribute to a better understanding of the fundamental mechanisms governing property development in LC- and HC-refined pulps at the micro- and ultrastructural level of fibre cell walls. An improved understanding of fibre property development and the

fundamental mechanisms governing this development during LC refining should promote new opportunities for energy-efficiency in MP and tailor-made products.

## Experimental

### PULPS CHOSEN FOR FIBRE CHARACTERIZATION

Five never-dried pulp samples from a wide range of pulps produced during the trial were chosen for characterization of fibre properties (*Figure 1*). The choice was made based on specific energy consumption (SEC) and the properties of handsheets made from the refined pulps for representing extreme levels and/or similar properties (*Figure 1 and cf. Table 1*). It is known that paper with similar physical properties can be produced from LC-refined pulps at significantly lower energy input compared to HC-refined pulps (Gorski et al. 2012). In this study, investigation of HC- and LC-refined fibre properties at the cell wall micro/ultrastructural level were therefore performed with emphasis given on pulps that gave similar handsheet properties.

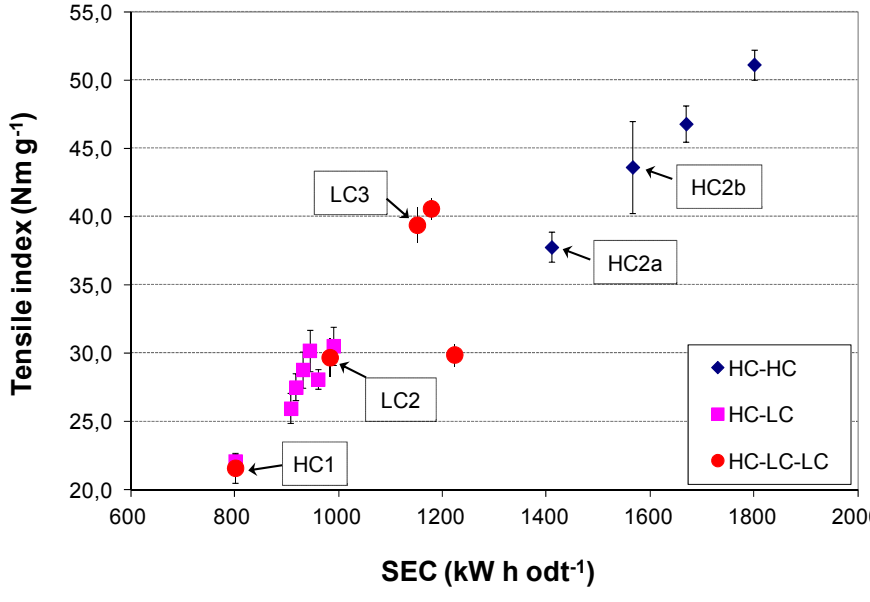


*Figure 1. Tensile index development during HC- and LC refining as a function of SEC. The pulps chosen for the study are labelled inside squares.*

*Table 1. Abbreviations and important data of the pulps investigated. Specific energy consumption (SEC); tensile index (TI); density; tensile energy absorption (TEA); Canadian standard freeness (CSF); light scattering coefficient (LS)*

| Pulp Name | Position (Stage) | SEC (kW h $odt^{-1}$) | Basic properties | | | | |
|---|---|---|---|---|---|---|---|
| | | | TI (N m $g^{-1}$) | Density (kg $m^{-3}$) | TEA (J $m^{-2}$) | CSF (ml) | LS ($m^2$ $kg^{-1}$) |
| HC1 | 1st HC | 800 | 21.6 | 298 | 16.4 | 487 | 50.1 |
| HC2a | 2nd HC | 1410 | 37.8 | 371 | 37.8 | 170 | 57.0 |
| HC2b | 2nd HC | 1570 | 43.6 | 401 | 50.0 | 117 | 60.3 |
| LC2 | 2nd LC | 980 | 29.7 | 351 | 29.2 | 238 | 55.3 |
| LC3 | 3rd LC | 1150 | 39.4 | 398 | 32.2 | 110 | 59.2 |

## SIMON'S STAINING

The development of fibre wall D/IF of the selected pulps was evaluated and assessed using Fernando and Daniel's (2010) method of Simon's staining (SS). Staining was performed on ca 1g of pulp from each of the five samples and then immediately examined and analyzed using light microscopy (LM) as described previously (Fernando and Daniel 2010).

Data obtained on degree of D/IF of pulp fibres were summarized graphically providing an overview of internal fibre development (IFD) for the two processes and further analyzed statistically for differences in degree of D/IF development between the pulps. Ordinal Logistic Regression (OLR) test was performed on the categorical data of colour reaction to SS and the analysis done using SAS computer software (SAS/STAT, version 9.3 for Windows XP-Pro platform, SAS Institute Inc., Cary, NC, USA).

## SCANNING ELECTRON MICROSCOPY (SEM)

Characterization of fibre surface ultrastructure and external fibrillation of pulp fibres was performed with SEM. Approximately 2g of wet samples from each of the five TMP samples were dehydrated separately using a series of increasing ethanol and then acetone concentrations as described previously (Fernando and Daniel 2008). Samples were then critical point dried using an Agar E3000 critical point dryer with $CO_2$ as the drying agent and coated with gold using an Emitech K550X sputter device. Observations were made using a Philips XL 30 ESEM operated at 10 kV and images recorded digitally.

# Results and Discussions

## CHARACTERIZATION AND QUANTITATIVE ASSESSMENT OF INTERNAL FIBRE DEVELOPMENT

The response of individual fibres to SS differed with fibres stained in varying colour intensities from blue to yellow/orange depending on the severity of fibre wall D/IF as reported previously (Blanchette et al. 1992; Fernando and Daniel 2010; Fernando et al. 2011). This indicated a diverse distribution of individual fibre development within a given pulp. This is expected as the starting wood raw material is substantially heterogeneous with varying inherent fibre properties like cell wall thickness, stiffness, latewood/earlywood ratio, presence of reaction wood and other properties. This heterogeneous raw material is subjected to mechanical pulp processing which is stochastic in nature. Wood fibres are thus treated and developed differently based on refining conditions and treatments during processing (e.g. SEC, temperature, intensity etc), changing both the chemical and morphological structure of the native fibre wall (Claudia-da-Silva 1983; Fernando 2007; Daniel et al. 2009). Refining conditions are shown to have a direct influence on the degree of IFD. For example, an increase in SEC or refining intensity enhances the proportion of treated fibres with a high degree of D/IF thereby improving the overall IFD of a pulp (Fernando et al. 2012).

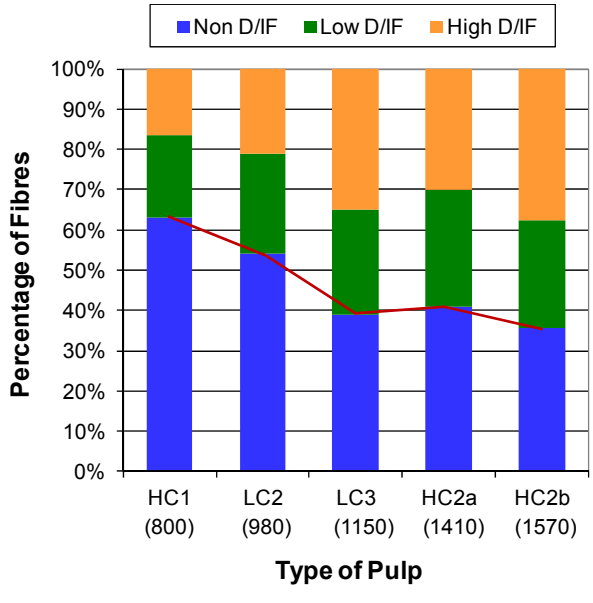


*Figure 2. Percentage of the three major groups of fibres in each pulp sample investigated representing different levels in the degree of wall D/IF obtained using the SS method. The number within parenthesis located below the x-axis labels represents specific energy consumption (SEC) level of the respective pulp.*

An overview of the results from the SS study is shown in *Figure 2*. The five S-FPs were simplified into three major groups "non D/IF", "low D/IF" and "high D/IF" as described in the method for ease of understanding (*Figure 2*). An initial assessment of fibre development in HC and LC pulps was obtained with the information from these preliminary results.

As expected, increasing the energy input in refining (SEC) significantly reduced the percentage of untreated fibre population resulting in enhanced fibre development (red line, *Figure 2*). The difference was pronounced when comparing the initial primary stage pulp (HC1) with any of the secondary pulps irrespective of refining consistency (e.g. HC1 vs LC2). The primary pulp with lowest refining energy input (HC1, 800 kW h $odt^{-1}$) consisted of approximately 63% untreated stiff fibres and only 16% fibres with high degree of D/IF. In contrast, pulp HC2b with the highest refining energy input (1570 kW h $odt^{-1}$) was the most developed at the fibre wall level. It was dominated by a treated fibre population (~65%) with the majority of fibres from the high D/IF group (~38%) that represents the most flexible fibre population as previously described by Fernando et al. 2011. The preliminary data also indicated that pulps LC3 and HC2b appeared to have more or less similar fibre populations concerning the degree of D/IF (61% and 65 % treated fibre population respectively). This suggests that LC refining was more energy-efficient for inducing wall D/IF and thereby generating flexible fibres compared to HC-refining in this trial, as the refining energy input in LC3 was 420 kW h $odt^{-1}$ lower than HC2b.

### STATISTICAL ANALYSIS FOR THE DEGREE OF D/IF

Detailed statistical analyses was performed using data from all five S-FPs from the investigated pulps to obtain an accurate evaluation of the significance of the input factors (i.e. refining energy and consistency) and further information related to HC and LC fibre development. A summary of results from the analysis of the degree of fibre wall D/IF for the five pulps using the OLR test is presented in *Table 2*. OLR was carried out to determine (A) overall significance in the degree of D/IF among all pulps; (B) the effect of the two refining conditions (i.e. (Bi) refining energy input and (Bii) refining consistency); and (C) the impact of the different refining conditions on morphological changes (i.e. D/IF) in the different pulps by analyzing two at a time.

*Table 2. Logistic regression statistics for type 3 analysis of ordinal logistic regression test for significant differences among HC and LC refined pulps on the degree of fibre wall D/IF*

| Source | DF | $\chi^2$ | Pr > $\chi^2$ |
|---|---|---|---|
| **Pulps**[A] | 4 | 53.18 | <.0001 |
| **Energy**[Bi] | 1 | 41.39 | <.0001 |
| **HC/LC sytem**[Bii] | 1 | 15.66 | <.0001 |
| **HC1 vs LC2**[Ci] | 1 | 3.94 | 0.0472 |
| **LC2 vs LC3**[Cii] | 1 | 8.43 | 0.0037 |
| **LC3 vs HC2a**[Ciii] | 1 | 0.04 | 0.8461 |
| **HC2a vs HC2b**[Civ] | 1 | 2.36 | 0.1241 |
| **LC3 vs HC2b**[Cv] | 1 | 1.50 | 0.2213 |

[A]Overall significance; [B]two refining conditions ([Bi]energy- and [Bii]HC/LC system effect); [C]comparing two pulps for differences in overall degree of D/IF of their fibres.

The five pulps differed greatly to each other concerning the degree of wall D/IF at 0.01% significance level (A, $p$ <0.0001; *Table 2*). This was due to both the increasing SEC, which is in line with previous results (Fernando et al. 2011, 2012) and changing the refining conditions (HC/LC). Statistical evidence for this was provided when analysing the two variables separately. Results indicated that both the energy input (Bi; p <0.0001) and the LC/HC refining conditions (Bii; $p$ <0.0001) had a very high significant influence on enhancing fibre wall D/IF making wood fibres more flexible.

Further statistical analysis on pulps pair-wise raised novel information related to internal fibre development during LC and HC refining. There was a difference at the 5% significance level in the development of fibre wall D/IF between primary HC and secondary LC pulps (i.e. HC1 vs LC2; Ci, $p$ = 0.0472). There was also a significant difference between the pulps from the two LC refining stages (with only 170 kW h $odt^{-1}$ difference in SEC) at 1% significant level (LC2 vs LC3; Cii, $p$ = 0.0037). The interaction of increasing energy input and the low consistency seemed to cause accelerated internal fibre development in LC refining which was reflected in pulp LC3 containing a greater percentage of treated fibres (*Figure 2*). It should be noted that the interaction effect could not be statistically estimated since not all combinations of energy and consistency were available in the data (i.e. the combination high energy input and LC was missing due to practical limitations of the refining system). Furthermore, statistical analysis indicated that the fibre populations of the two pulps generated in the third LC (LC3) and second HC stage (HC2b) had very similar degrees of D/IF (LC3 vs HC2b; Cv, $p$ =

0.02213). This finding thus gave statistical evidence that LC refining with lower SEC could be used to produce pulps with a similar degree of IFD as the pulps from HC refining with higher SEC, thus confirming the improved energy efficiency of LC refining.

### FIBRE SURFACE ULTRASTRUCTURE OF LC- AND HC REFINED TMPS

SEM studies revealed differences in fibre surface ultrastructure especially between the primary HC1 pulps (*Figure 3a*) and secondary HC2b pulp with high energy input (*Figure 3b*). The majority of the pulp fibres in HC1 (SEC of 800 kW h $odt^{-1}$) had the S1 secondary wall as their outer surface layer (*Figures 3a and 4a*). It was most often fibrillated into typical flake-like fibrils (*arrows in Figure 4a*), sometimes with remaining parts of the compound middle lamella (CML; *Figures 3a and 4a*). In addition, most of the HC1 fibres retained their native geometrical shape of wood fibres which is indicative of intrinsic stiffness. Contrary, almost all the fibres in the HC2b pulp (SEC of 1560 kW h $odt^{-1}$) displayed an exposed cellulose-rich S2 layer with typical ribbon-type fibrillation and the fibres exhibited greater collapsibility/conformability (*Figure 3b*). The collapse of these fibres was most likely attributable to their thinner walls which resulted from the removal of the major part of fibre wall materials down to the inner secondary wall layers as shown in *Figure 3b*.

Most of the fibres from the LC2 and LC3 pulps also exhibited an exposed S2 layer, often with typical ribbon-like fibrils projecting from the fibre surface (*Figures 3c, d*). Both LC-refined pulps appeared morphologically similar although the LC2 pulp with lower energy input had more fibres covered with outer S1 wall material, indicating an inferior peeling effect compared to the LC3 pulp produced with higher energy input.

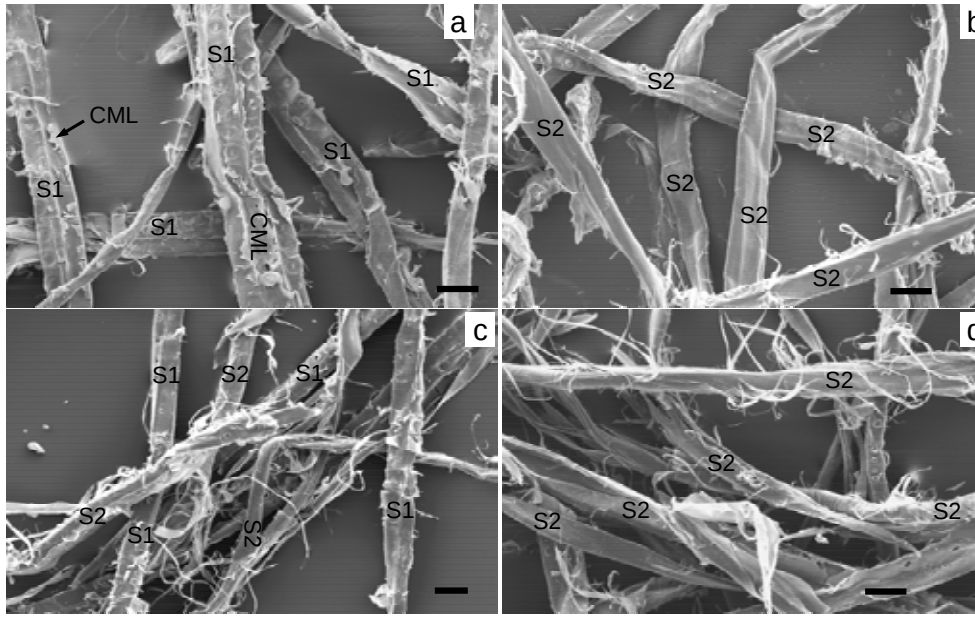


*Figure 3a-d. SEM micrographs of HC- and LC refined TMP fibres showing their surface morphological ultrastructural characteristics: (a) HC1 fibres exhibiting the secondary S1 layer of the fibre wall as their outer surface layer. Note the retention of native geometrical shape of wood fibres; b) almost all the fibres of HC2b possess the S2 as the fibre outer wall layer with ribbon-type fibrillation or sometimes with clear outer surfaces. Note improved collapsing of the never-dried fibres losing their square-like geometrical form; c) LC refining at lower energy (LC2) generated more fibres with S1 as the outer layer while some showed an S2 secondary layer; d) majority of LC3 fibres had the S2 layer exposed most often with hair-like fibrils protruding from the surface. Bars: a-d; 40 µm.*

Detailed SEM investigations revealed additional information related to fibre development mechanisms in HC and LC refining. Severe fibre splitting was already initiated during the ATMP refining process in the first stage pulp (*arrows in Figure 4b*). However, extensive peeling of the fibre wall down to the inner secondary wall layers was observed only at higher SEC.

The development of fibre surface morphology was found to vary strongly between the HC and LC refining systems. HC refining with higher energy input generated various types of characteristic S2 fibrillation (*Figure 4c*) (e.g. ribbon-type fibrils) ranging from thin thread-like- (*arrows in Figure 4d*) to broad sheet-like fibrils (*Figure 4e, f*) and lamellar sheets (*Figure 4g, h*) peeling from the fibre surfaces. Particularly, the latter two types of much broader morphologically important external fibrillation were common on fibres in the HC2b pulp although they were also observed infrequently in the HC2a pulp produced with lower energy input.

The relative bonded area (RBA) of these broad sheet-like fibrils and lamellar sheets are greater and acquire high bonding potentials. They are thus excellent binders in a pulp.

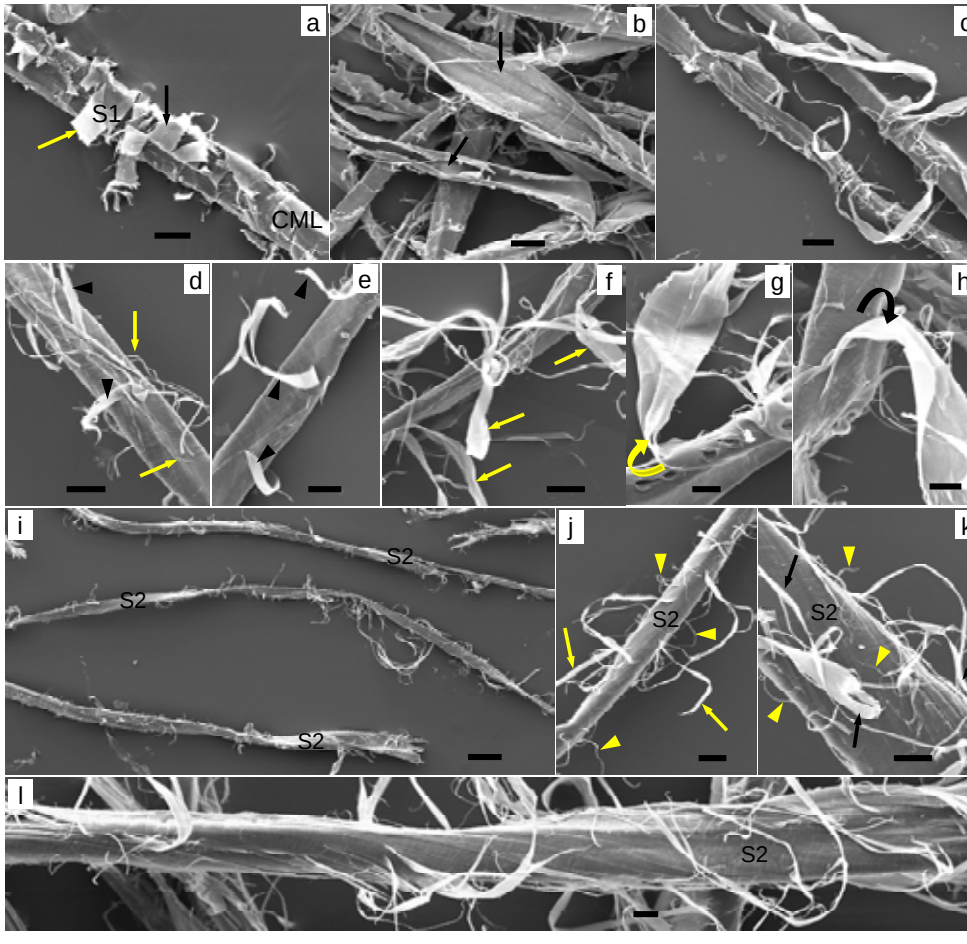


*Figure 4a-l. SEM micrographs detailing surface ultrastructure/external fibrillation of HC/LC refined fibres: (a) HC1 fibre giving rugged appearance due to typical bricks-like structures (arrows) from fibrillated outer S1 surface layer. Note the presence of parts of the remaining compound middle lamella (CML) and retention of the square-like native fibre form; (b) some HC1 fibres were opened exposing the cell lumen due to deep splitting of the wall along the fibre (arrows); (c) typical ribbon-type S2 fibrillation of HC2b fibres with varying morphological features reflecting native hierarchical structure of the fibre wall as illustrated in d-h; (d) thin thread/string-like ribbons most likely representing the smallest macrofibrils (arrows); (e) wide band-like ribbons formed by aggregates of smaller numbers of macrofibrils (arrowheads in d and e); (f) much broader sheet-like ribbons (arrows); (g, h) broad carpet forming lamellae sheet peeling from the thick S2 layer (curved arrow). The*

*RBA of these lamellae is large and thus are excellent binders; (i) hair-like structures of ribbons from the S2 surface layer developed along the fibres (pulp LC3) during LC refining; (j, k) hair-like ribbons were either thin thread/string-like fibrils presumably representing single or small macrofibrils (arrowheads) or slightly wide band-like ribbon fibrils (arrows) from the exposed S2 layer; (l) LC3 pulp fibre illustrating distinct S2 external fibrillation along the fibre so that they appear as "hairs" projecting from the surface. This seemed to be a characteristic of external fibrillation in LC refining. Bars: a,d-f,j, 20 µm; b,c, 40 µm; g,h,k-l, 10 µm; i, 100 µm.*

LC refining promoted a different kind of action leading to distinct fibre development mechanism where fibre surfaces were most often developed into thin hair-like threads, sometimes along the whole fibre length (*Figure 4i, l, m*). Broad sheet- and lamellae types of external fibrillation were rarely observed in the LC pulps and the major hair-like surface wall structures were thread-like (i.e. similar to single macrofibrils; *arrowheads in Figure 4j, k*) or very thin ribbon-like fibrils originating from the S2 layer *(arrows in Figure 4j, k*). In mechanical pulp refining, micro-cracks are developed along naturally occurring weak zones in the lamellae of the already exposed S2 layer, i.e. between single macrofibrils or aggregates of various sizes of macrofibrils within a lamellae (Fernando and Daniel 2004). LC refining appears to enhance the development of micro-cracks predominantly between smaller aggregates of macrofibrils. The resulting ribbons of thin threads were thereby easily peeled off from the surface by the action of shearing forces inside the refiner.

It was earlier reported that the external fibrillation in LC refining was lower than that developed in HC refining compared at equal tensile index of handsheets (Gorski et al. 2012). This study also indicated that there were distinct morphological differences in external fibrillation promoted between HC and LC refining.

### IMPACT OF THE CHARACTER OF FIBRE DEVELOPMENT ON FINAL PRODUCT QUALITY

The relationship of the three major D/IF groups to the tensile strength was established in earlier work (Fernando et al. 2011). The present study also supported those findings with very similar results (Figure 5a). A very strong positive correlation ($r2 = 0.96$) to tensile index of handsheets was exhibited by pulp fibres possessing high D/IF, whereas untreated non D/IF fibres had the same correlation coefficient ($r2 = 0.99$) but in the negative direction indicating an inverse correlation with strength. Fibres with low D/IF showed a positive trend with lower strength gain. Furthermore, the three groups of fibres were correlated to density of the handsheets with exactly the same strength and directions as they had with tensile strength (Figure 5b). The results thus emphasize the direct influence of the relative proportions of the two groups high- and low D/IF in a given pulp, which

contain desirable flexible fibres, for the development of strength and density. It can thus be concluded that the higher the amount of high D/IF fibres in a given pulp the better the properties of tensile strength and density of the pulp.

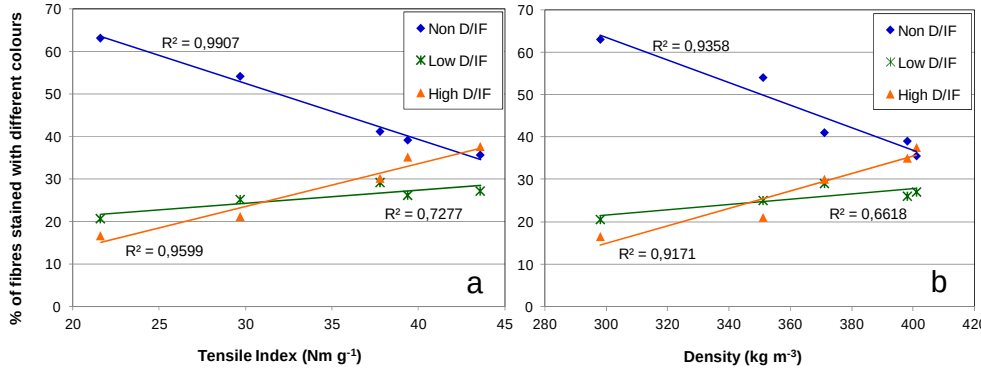


*Figure 5a-b. Linear correlation of the three major groups of sub-fibre populations present in each pulp to the tensile index (a) and apparent density (b) of their handsheets. The non- and high D/IF groups had extremely strong but opposite correlation (note their $R^2$ values) with the properties reflecting the direct influence of the degree of fibre wall delamination/internal fibrillation (D/IF) to property development of a given pulp.*

Accordingly, the significant differences in the degree of D/IF among the five pulps provide the fundamental basis behind the development of varying tensile strength, freeness and density of the pulps. Elevated D/IF in LC3 and HC2b pulps made them highly flexible and thereby improved the collapsibility and conformability of the pulp which accounts for enhanced fibre-fibre bonding and better densification of the sheet (Heikkurinen et al. 1991; Paavilainen 1993).

In addition, the surface ultrastructural characteristics of each pulp also contributed substantially for most of the physical and optical properties of their respective handsheets. For example, the exposed S2 layer and greater S2 fibrillation with long ribbon-like cellulose fibrils, particularly the broad sheet-like and lamellae fibrils exhibited by pulp HC2b are known to be key characters for giving good bonding ability of the pulp. These characteristics promote sheet density, tensile index and Scott Bond strength (Kang and Paulapuro 2006) and thereby explained the higher tensile index and density of HCb2 and LC3 pulps. In contrast, the inferior external fibrillation reflected by the lignin-rich S1 surface layer with flake-like short S1 fibrils of poor bonding potential (which in turn indicated very low peeling action) was partly responsible for obstructing the development of density and strength properties in HC1 and LC2 (Fernando et al. 2011, 2012). A considerably larger proportion of their untreated stiff fibres (63% and 54% respectively, Figure 2a) also collectively contributed to the observed lower quality.

Light scattering was shown to be on the same level for LC- and HC-refined pulps compared at equal tensile index (Gorski et al. 2012). Braaten (2000) describes RBA of external fibrils as the determining factor for both strength and optical properties of a paper sheet and the important role of thread-like and narrow ribbon-shaped fibrils for a higher light scattering property. Consequently, the morphological character of external fibrillation found in LC3 pulps was presumably the principle reason for its equally high light scattering ability. The RBA of the hair-like narrow long ribbons is very low and significantly influences the light scattering coefficient of the pulp (Braaten 1997, 2000).

## Conclusions

The increasing SEC and the pulp consistency of the refiners (i.e. HC and LC) significantly influence the degree of fibre wall D/IF developed during TMP refining. The internal fibre development during secondary HC and LC refining was similar when compared at similar handsheet tensile index although the refining energy input for the latter was 420 kW h $odt^{-1}$ less. The study confirmed that fibre wall D/IF is promoted more energy-efficiently in LC- compared to HC refining. Ultrastructural characterization of the pulp fibre surfaces revealed significant differences in external fibre development between the two processes. LC refining appeared to induce a distinct action that promotes fibre surfaces to develop into thin hair-like threads of S2 ribbons, sometimes along the whole fibre length. Broad sheet- and lamellar-types of external fibrillation with high bonding potential originating from the S2 layer, that were typical for HC refining, were rarely observed in the investigated LC-refined pulps. It is therefore proposed that there exists differing mechanisms of fibre development at the cell wall level in HC and LC refining that appear to govern most of the physical and optical properties of the investigated pulps.

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## APPENDIX 3. ULTRASTRUCTURAL CHARACTERISTICS OF FINES FRACTION PRODUCED DURING HC AND LC REFINING OF MECHANICAL PULPS USING MIXED SOFTWOODS

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# Background

When addressing the issue of reducing energy consumption in mechanical pulping (MP), (i.e. the primary objective of the main project; *Appendices 1-4*), it is of prime important to focus research not only on process property relationships but also on basic studies for understanding fundamental mechanisms at fibre level including particle development. One approach is to characterize how the properties of the particles (i.e. fines) develop and/or change during the refining process. Fines fraction can occupy up to ca 40% of MPs, for instance in printing papers, which indicate their greater importance for the final product.

It has been known for a long time the importance of fines in MP with research work goes back to the 1930s when Brecht and coworkers first published groundbreaking studies on fines (Holl and Brecht 1939; Brecht and Klemm 1953; Honkasalo et al. 1983). Since then several attempts have been made to characterize the properties of fines particularly with emphasis on the amounts of particles, divided primarily into “flake-like” and “fibrillar-like”, produced during processing. It is also common knowledge that the fines play a significant role in determining the properties of pulp and paper and the influence of both the contents and the type (i.e. quality) of fines particles (Mohlin 1980; Corson 1989; Lukko et al. 1997; Rundlöf 1995). However, properties of fines fraction concerning morphological ultrastructural aspects are hardly investigated in these works.

The present study was therefore carried out for ultrastructural characterization of mechanical pulp fines produced during high-consistency (HC) and low-consistency (LC) trials aimed at reducing electrical energy demand (*see Appendix 01*) using scanning electron microscopy (SEM). Fines materials consist of a wide range of morphologically different particles primarily generated from wood fibre cell walls (e.g. broken fibre parts, pits, parts of primary and secondary cell walls) in additions to other cellular origins of micro-meter range like parenchyma cells. Studies on ultrastructural characteristics of these cellular constituents in a MP should provide fundamental understanding of how wood fibres behave and response during pulping processes and thereby elucidate fibre development mechanisms leading to improved understanding of process property relationships.

## Experimental

Five pulps investigated during fibre characterization (*Appendix 2*) were also used in the present study (i.e. HC1, HC2a, HC2b, LC2 and LC3) for analyzing their fines fraction using electron microscopy (EM). Details of processes, process conditions and physical and optical properties of these pulps are found in *Appendix 1*.

### SCANNING ELECTRON MICROSCOPY (SEM)

Morphological ultrastructural characteristics of fines (Bauer-McNett fraction mesh >200) from the five pulps were analyzed with SEM. Ca 20 ml of fines suspension from each pulp sample was pipetted and all fines particles collected by filtering. Each fines sample was then dehydrated separately, as described by Fernando and Daniel (2008). Samples were dried in an Agar E3000 critical point dryer (Agar Scientific Ltd, Stansted, UK) with carbon dioxide as the drying agent, and subsequently coated with gold using an Emitech K550X sputter device (Quorum Technologies Ltd, Ashford, Kent, UK). Observations were made in a Philips XL 30 ESEM (FEI Company, Eindhoven, Netherlands), operated at 10 kV with images recorded digitally

## Results and Discussions

Since particles in the fine fraction are around or below 76 µm in size, careful handling and sample preparation were adopted in order not to lose constituents and preserve their native morphology. SEM investigations (*Figures 1-4*) provided information on the ultrastructural characteristics of fine fraction of each pulp and corroborated well with results obtained on the respective fibre fraction (*see Appendix 2*).

As expected the fine fraction of the low energy primary HC pulp consisted primarily of flake-like particles (*Figure 1a, b*). They were mainly from the fibre outer surface of S1 layer which is rich in lignin. In addition, wall fragments from compound middle lamella (CML), cut fibre ends, short fibre fragments and broken/unbroken ray cells also contributed to the flake category (*Figure 1b*). The observations were in good agreements with the results from a previous study on the fibre fraction of the same pulps (*Appendix 2*). Majority of fibres from the primary HC pulps are reported to exhibit S1 as their outer surface layer which is often fibrillated into short flake-like fibrils. This indicates that during the initial phase of the low energy primary refining process, only the outermost layers of the fibre wall (e.g. very thin outermost CML and the outer lamellae of the adjacent S1layer) were loosen and fibrillated into typical bricks-like particles/fibrils. They were then sequentially separated out from the fibre surface at the later stages of primary refining forming a pulp with a fines fraction dominated by flakes.

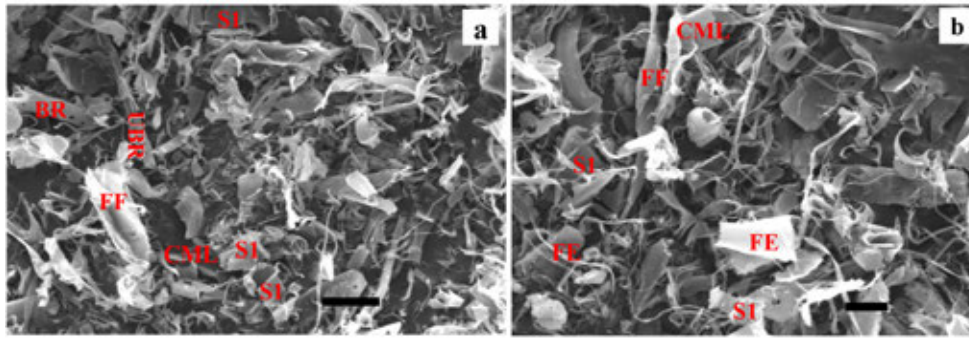


*Figure 1a-b. SEM micrographs showing constituent particles of the fine fraction of the pulp HC1. Primary refining with low energy generated particles only from outer fibre wall in addition to broken/cut fibres that led to dominating flake-like particles. BP= broken parenchyma; CML= compound middle lamella; FE= cut fibre ends; FF= fibre fragments. Bars: a, 40 µm; b, 20 µm.*

There were considerable differences in the fines fraction of the two pulps; low energy 3rd LC (LC3) and high energy HC (HC2b) regarding the morphological ultrastructure of their fines particles. A wide variation in the fine morphology, in particular long ribbon-type fibrils, existed within the fine fraction of HC pulps (*Figure 2a-d*). The characteristic ribbon fibrils from the S2 secondary wall layer made up the greatest part of its fine fraction (*Figure 2a*) while flake-like particles from the CML, secondary S1 layer and short fibre fragments, cut fibre ends and broken/unbroken parenchyma cells contributed the rest (*Figure 2b*). The various types of morphologically dissimilar ribbon fibrils in the fines represent different hierarchical levels in the ultrastructure of the native S2 secondary wall layer ranging from the smallest microfibrils (*arrows in Figure 2c, d*) to aggregates of various sizes of macrofibrils (*arrowheads in Figure 6c*) and the widest lamellae sheets of S2 (*LS; Figure 2d*). Particularly, broad band-like fibrils (*BFb; Figure 2c, d*) and lamellae sheets, which are the carpet forming particles in a pulp, were commonly observed in the fines (*Figure 2c, d*) corroborating the results obtained on the pulp fibres (*Appendix 2*). The work discusses the external fibrillation mechanism of HC pulp fibres where typical S2 fibrillation by peeling, such as thin thread- to broad sheet-like ribbons and lamellae sheets, is the key fibrillation phenomena for the pulp. These diverse long ribbon fibrils originating from the outermost lamellae of the thick S2 layer at early stages of secondary refining were gradually peeled off from the fibre surfaces during the latter part of the process due to high energy refining action and collected in the fines of the pulp.

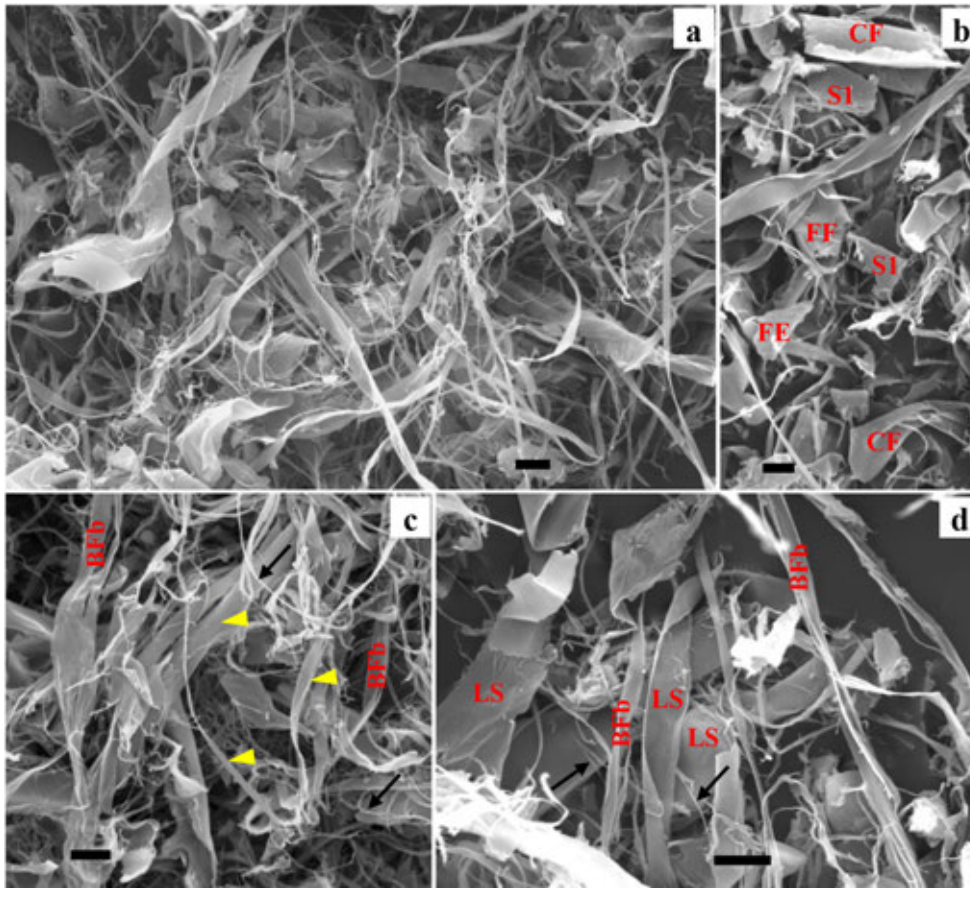


*Figure 2a-d. Fines fraction of HC2b pulp dominated by morphologically different various types of ribbon fibrils from the S2 fibre wall layer: (a) general appearance of fines rich in long ribbons ranging from string-like to broad fibrils; (b) flake-like particles were also observed though in significantly lesser amounts; (c) string/thread-like fibrils (arrows) of presumably smallest macrofibrils (MaF) and broad ribbons in varying size widths (arrowheads) reflecting different types of aggregates of MaFs within a S2 lamellae; (d) much broader sheet-like fibrils and lamellar-sheets. BFb=Band-like fibril; FE=Fibre end; FF=fibre fragments; LS=lamellar-sheet. Bars: a-d, 10 µm.*

The high bonding potential of broader fibrils (i.e. sheet-like fibrils and lamellae sheets) are said to reinforce bonding and densification of the sheet. They possess a high relative bonded area (RBA) which is a determining feature of a fine particle for improved strength properties of a paper.

However, fines from the 3rd LC (LC3) were marked by thin long ribbons and string-like threads of ribbons (ca 0.06-0.3 µm width) from S2 (*Figure 3a-d*). In

addition, flake-like particles (*Figure 3b*) and very rarely broad sheet-like fibrils were also observed within the fines. Fernando et al. (2012) explored the mechanisms of external fibrillation of LC fibres, which differs from HC pulps, where "hair-like" threads and strings of ribbons are its characteristic features. Consequently, the present investigation on the morphological ultrastructure of fines in LC pulps added further evidence for the proposed mechanisms of fibre development and also the hypothesis concerning refining mechanisms in LC process. Presumably the hair-like threads of ribbons were initially developed on the outermost lamellae of the thick S2 layer of the fibre wall. They were then completely peeled from the fibre surfaces during refining and accumulated in the fine fraction. The significance of their contribution (in proportion) to the LC fines fraction was marked by their appearance as lumps of long strings (*arrows in Figure 3c*) that could have presumably developed during their aggregation and drying.

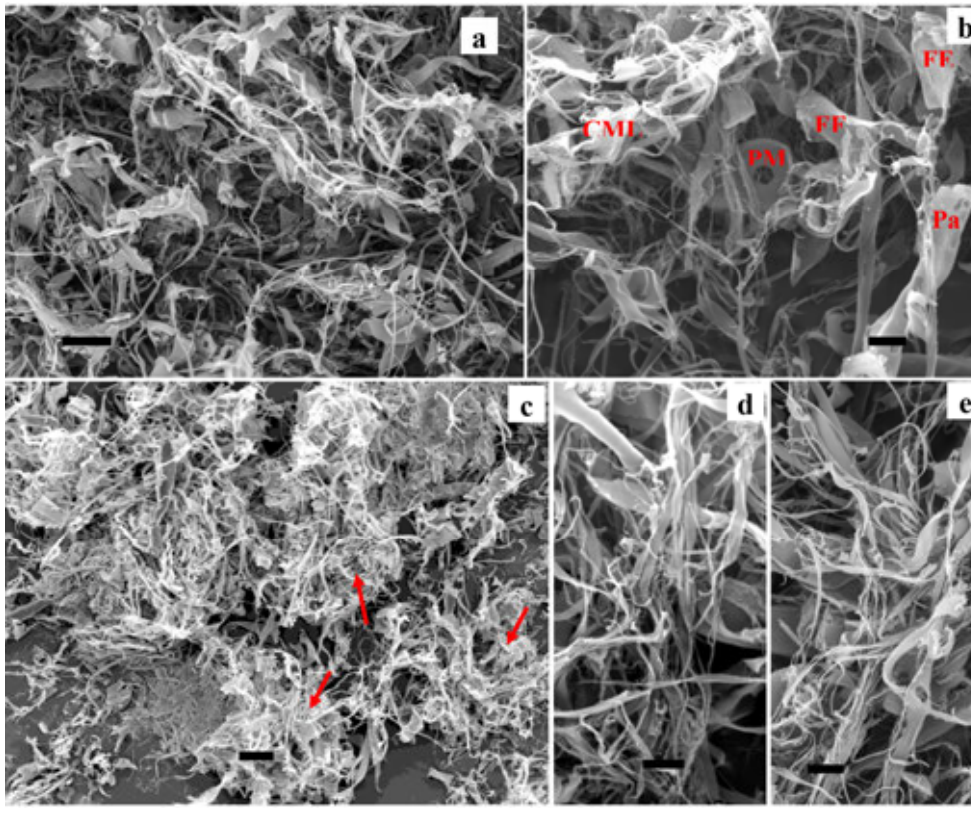


*Figure 3a-e. SEM micrographs of LC-refined pulp fines (LC3 fines) showing the distinct character of its fines particles: (a) general appearance indicating greater proportion of narrow band-like or string-like long fibrils; (b) contribution of flake-like particles from*

*broken fibre fragments and parenchyma cells, pit-membranes and compound middle lamella etc that were most prominent in LC2 pulps; (c) high content of strings of long ribbon fibrils adhered together giving an appearance of lumps (arrows) scattered within the LC3 fine fraction when observed at low magnification; (d, e) high magnification views from a fine fraction illustrating the size (width) of thread/strings of fibrils that were under the half micro-meter range. CML=compound middle lamella; FE=broken fibre ends; FF= fibre fragments; Pa=parenchyma cell; PM=pit-membrane. Bars: a, 30 µm; b, e, 10 µm; c, 50 µm; d, 5 µm.*

The RBA of these narrow ribbon fibrils is very low particularly for the thread- and string-like ribbons and are thus known to primarily contribute to the light scattering of a pulp (Braaten 1997; 2000). The size widths of these long fibrillar fines were under the wavelength of light (*ca 0.06-0.4 µm; Figure 3d, e*) indicating their excellent scattering ability. In addition, it seems that they effectively create new ancillary scattering sites in the fibre network of a sheet in the micrometer range (*Figure 4a-c*). This was achieved by enhancing the number of optically active micro-pores that are reported solely responsible for boosting the optically available surface area within a sheet structure as indicated by Rundlöf (1995). Therefore, due to the nature of their specific morphology (e.g. poor bondability as a consequence of very low RBA; Braaten 2000), these fibrillar fines (*e.g. structural scattering sites 1-7 in Figure 4b,c*) appeared to induce the formation of such pores that leads to establish the required porous structure within the sheet. This enhanced the greater ability of the sheet to scatter light. The diameter of most of these pores was in the range above half the wavelength of light as illustrated in the *Figure 4b, c* (optically active pores named a-g in the Figures were between 0.27-0.6 µm Φ) and each of the Figures represents a part in the micrometer scale within the fine fraction of the LC pulp.

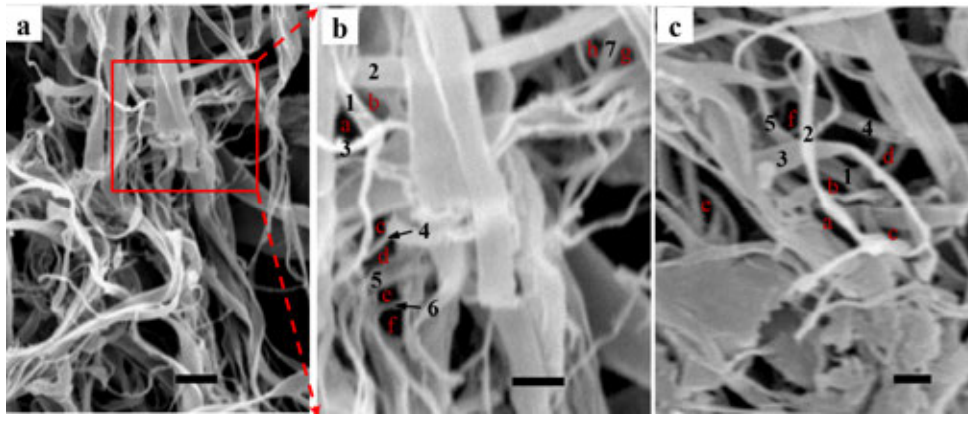


*Figure 4a-c. High magnification views of few regions in the micro-meter range within a sample of LC3 fines that illustrate its greater scattering ability due to structural sites*

*within fines: (a) specific morphological features of narrow string-like fibrils providing excellent scattering sites within the network formed by these particles; (b, c) details of the development of scattering sites within a micro-meter scale area marked by red square in a is shown in b and c was a area (similar to b) taken from another region of the sample. Numbers 1-7 (in b and c) are narrow band-like and string-like fibrils and widths of these particles were less than the wavelength of light and thus acquire excellent scattering power. Letters a-h represent adjacent optically available surface areas created by these fine particles. These micro-pores provide additional scattering sites as they were optically active pores in the network. Bars: a, 2 µm; b-c, 1 µm.*

Accordingly, thin narrow band- and thread-like ribbons with high content in a fine fraction of LC pulp should significantly contribute to its light scattering coefficient which is almost as high as that of high energy HC pulps.

Fines from secondary LC-refined pulp (LC2) appeared morphologically similar to primary HC pulps although there were thread-like fibrillar fines in lesser quantities. High SEC secondary HC pulps showed fines that resembled those of the 3$^{rd}$ HC fines and thus the fines of the two pulps are not included here.

The present findings on ultrastructural aspects of fines morphology in the fines fraction of HC and LC pulps thus strongly support the hypotheses proposed earlier by Fernando et al. (2012) on the refining mechanisms between HC and LC refiners in this trial and the resulting fibre development mechanisms.

## Conclusions

Morphological characteristics concerning the ultrastructure of the fines fraction of LC-refined pulps significantly differed to that of HC-refined pulps. HC refining generated a wide range of morphologically different long ribbon fibrils which dominated the fines fraction. The characteristic fibrillar fines from the S2 secondary wall layer produced during HC refining consisted of a range from thin thread/string-like smallest microfibrils to aggregates of various sizes of macrofibrils and the widest sheet-like fibrils and lamellae sheets of S2. In contrast, LC refining generated mainly string/thread-like very narrow long fibrils as fines that lack the much broader sheet-like and lamellar sheets fibrils. In addition, flake-like particles were commonly observed in 2$^{nd}$ stage LC compared to third stage LC refining and they were more pronounced with a greatest proportion in the primary stage HC pulps. The morphological characteristics of the fines from the two processes explain, at least partly, some of the physical and optical properties of their pulps. The present results provide further evidence and thereby strongly support the hypothesis on the differing refining and fibre development mechanisms proposed earlier for the HC- and LC processes.

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## APPENDIX 4. IMAGE-BASED AUTOMATED ANALYSIS OF HIGH-YIELD PULP FINES USING HIGH-THROUGHPUT FLUORESCENCE MICROSCOPY

*Jonas Hafrén, SLU, Uppsala, Florian Salomons, KI, Stockholm*

## Summary

We have developed a new high-throughput image-based method using an automated fluorescence microscope combined with image analysis for studies in small particles. The automated microscopic method was applied to fines isolated from 5 different pulps, produced using high- and low consistency refining, in order to analyze the effect of pulping consistency on the morphology of fines. In all samples a large number of small fine particles were found; about 40% of the fines particle were smaller than 10 $\mu m^2$ in cross section but contributed only to <2% of the bulk, whereas about 20% of the total number of fines having a cross section area over 100 $\mu m^2$ contributed to over 80% of the total bulk of fines material. Low consistency refining produced small fibril-like fines at lower SEC levels than high consistency refining, possibly contributing to the known beneficial tensile index-SEC ratio shown by LC refining.

## Introduction

When analyzing the morphology of wood pulp constituents, such as fibers and fines, the size- and structural heterogeneities are major obstacles for obtaining quantitative and relevant information on the pulp's structural properties. Whole fibers may be measured in millimeters and fines in micrometers. This is one reason why methods for high-throughput analysis for wood fibers may give good quantitative data on fibers, but is less efficient on fines that may differ in size from fibers by three orders-of-magnitude. Since fines can contribute to about one third of the dry weight of some high-yield pulps and are known to affect many pulp and paper properties (e.g. strength and optics), more qualitative and quantitative information of the structure of fines is of interest. Therefore, microscopy-based methods for imaging fines have been developed and successfully applied in analyses of fine particles (Luukko et al. 1997).

In this study a new high-throughput image-based analysis of mechanical pulp fines has been developed. The fluorescence-microscopic method allows for automated image acquisition and morphological analyses (segmentation, classification, measurement, statistics and computational infrastructure) of large amount of fines without need for extraneous stains, and with additional information on lignin content analyzed by autofluorescence.

## Experimental

Fines were produced from mixed softwood chips, supplied from the interior of British Columbia, Canada and consisted of approximately 80% Lodgepole pine, and the remainder of Sitka spruce and some Western balsam fir. Fines from five samples were analyzed. Starting material, high consistency refined (1'st HC, SEC 801 kWh/odmt) pulp, was further refined in two additional steps using either low consistency (LC) or HC refining (low LC, 983 kWh; high LC, 1151 kWh; 2'nd HC, 1419 kWh and 3'rd HC, 1566 kWh).

The pulps were fractionated and fines from Bauer-McNett fraction mesh >200 used for the analyses. The fines were suspended in water and a droplet (~ 50 μl) of the suspension was added into each well of a multi-well plate. The plate was inserted in an ImageXpress Micro cellular imaging system from MolecularDevices (Sunnyvale, CA, U.S.). The imageXpress microscope allows for high-throughput automated and consecutive image acquisition of several wells of several multi-well plates. Between 4-6 wells were used for each sample, in each run, and from each well between 25 to 100 wide-field fluorescence images were automatically collected at excitation wavelength 352-402 nm and emission λ= 417-477nm (i.e blue). Enough images were collected to ensure > 5000 separate fine particles were identified in each sample. All raw image data were collected as tiff file format and thereafter analyzed using an image processing and analyses software, Cell profiler (www.cellprofiler.org; Carpenter et al. 2006; Lamprecht et al. 2007). In Cellprofiler a designated "pipeline" was created for wood-pulp fines that allowed for automated segmentation, identification and analysis of the fines based on their intrinsic autofluoresence. The outdata were collected in excel files as tables of for example surface area, perimeter, length, width, form factor and fluorescence properties for each fine particle.

## Results and discussion

High magnification image of an object may give excellent qualitative and highly resolved spatial information. But, in order to obtain quantitative data it is necessary to analyze many objects; however, to collect images of a large amount of objects using high magnification imaging techniques can be tedious due to the labour-intense sample preparation, image- acquisition and analysis. However, new microscopic methods that combine robotic sample preparation and automated image-acquisition and analysis has opened up new possibilities for high-throughput microscopy-based screening. Using a new high-throughput fluorescence microscopy-based analysis, a large amount of fine particles have been analyzed for number, size and lignin content. In *Figure 1*, the projected 2-D surface areas (as shown in the microscope) of individual fine-particles are plotted against their perimeters. There was an apparent and relative higher number of

smaller particles and the relative number of particles trailed off with size. Also, the fluorescence properties showed that the relative amount of lignin per fine particle increased with size.

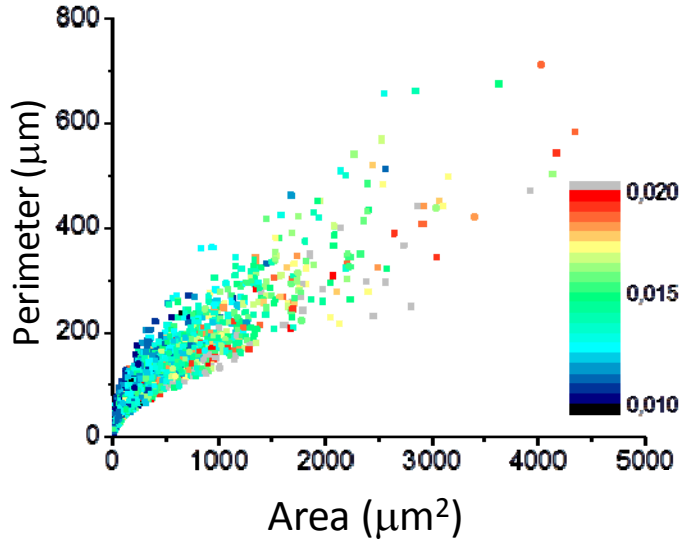


*Figure 1. Fines from 1'st HC refining, color bar = mean autofluorescence of fine particle; (black ≤0.01, grey ≥0.02).*

In order to facilitate comparisons between samples we divided the fines into subgroups based on surface area. In *Figure 2*, the fine fractions were divided in 5 subgroups. *Figure 2a* shows the frequency distribution in percent of number of separate fine particles in each subgroup. There are no apparent trends between the first stage HC starting material and additional HC or LC refining. In *Figure 2b*, the percentage of surface area the fines in the subgroups occupy of the total material is shown. The large number of smaller fine particles (up to 10 $\mu m^2$), shown in *Figure 2a*, is in *Figure 2b* shown to contribute very little to the total bulk of the fine matter, whereas the larger fine objects >1024 $\mu m^2$ are relatively few in numbers. The distribution of the lignocellulosic autofluorescence in *Figure 2c* show the same trend as *Figure 2b*, but all samples showed a relative increased lignin presence in the larger fine fraction (>1021 $\mu m^2$), presumably due to fragments of heavy lignified ray tracheids and broken fiber ends. The Form factor [=(4*π*(Area/Perimeter$^2$)] in *Figure 2c* show that the larger the fine particle the less round (circle = Form factor 1) with all samples showing the same trend.

The secondary and tertiary refining stages seemed to have shifted the distributions of size and fluorescence towards to the smaller subgroups of the fines, with LC fines closer to the starting material than HC. HC pulps have higher SEC and it is

plausible that more intense refining produces smaller fine particles. It is possible that very small fine particles may attach to a single fiber surface, or fill gaps in the fiber network, rather than bridge an inter-fiber gap. It has been proposed that fines may bridge, fill or block inter-fiber networks. Depending on size and shape, the fines may add more to sheet density and strength properties (fibrillar fines) or light scattering (flake-like fines). For these LC and HC pulps, the total amounts of fines were similar for both HC and LC.

Fernando et al. (2012) showed that the character of the surface fibrillation is very different between HC and LC fibers compared at equal tensile index of handsheets. LC refining appeared to induce development of thin hair-like threads of S2 ribbons, sometimes along the whole fiber length. Indeed, by analyzing the automated-microscopy data as scatter plots of perimeter versus area, differences in the amount of small fine-particles with large perimeters could be detected. Since high-bonding fines like fibrils and "ribbons" have: a) larger perimeters than flake-like fines, and b) smaller surface area than larger fiber ends or ray tracheids; therefore, we analyzed the relative abundance of small fines with large perimeter. In scatter plots of the fines from the starting material (*Figure 1*) a gated area (area $\leq 200\ \mu m^2$, perimeter $\geq 20\ \mu m$) was selected. Then, the relative number of fines within the gated area was calculated for all samples (i.e. fines with lower area, higher perimeter). Relative to the starting material low 2'nd HC showed a +2.4% increase; high 2'nd HC +8.6%, 2'nd LC +0.3% and 3'rd LC +10.9% relative to the starting material, indicating that LC refining promotes the generation of high inter-fiber bonding fines at lower SEC levels than HC refining.

## Conclusions

The newly developed high-throughput image-based analysis, using an automated fluorescence microscope combined with image analysis, was shown able to analyze a large number of fines (>5000 per sample) and show quantitative differences in morphological properties between fines from low and high consistency refined samples. From the results obtained in this and other studies it seems low consistency refining introduce several effects on the pulp that differ from HC-refining, which combined may explain the differences between HC and LC pulping.

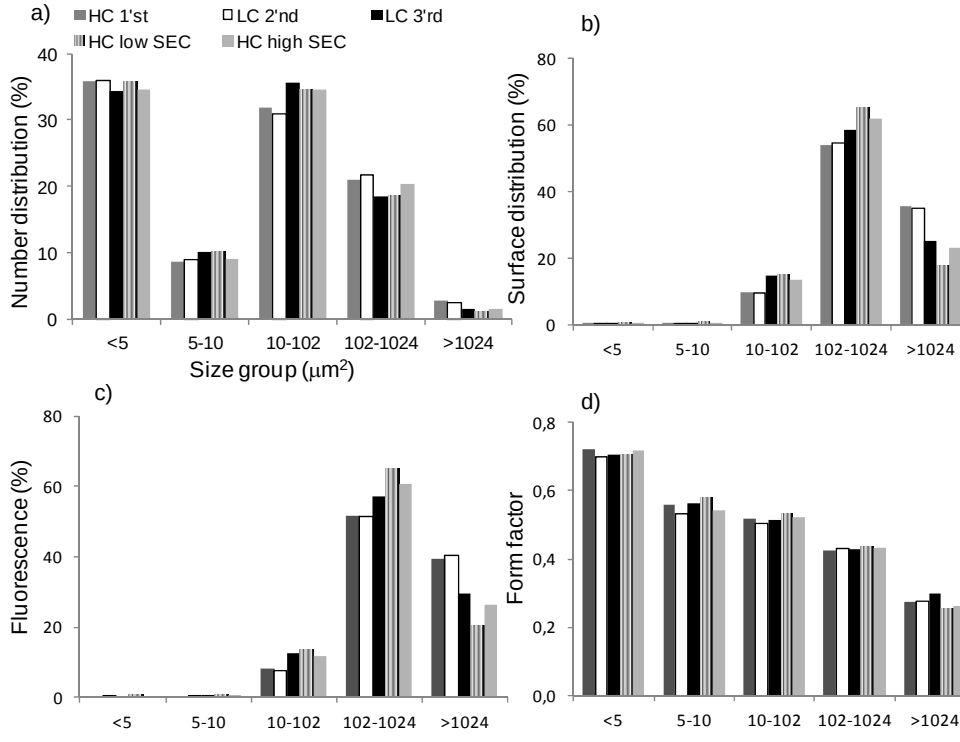


*Figure 2. a) Distribution of numbers of fine particles in the size groups, b) surface distribution, c) fluorescence distribution and d) average Form factor within each sub-group.*

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***Collaborative Research on the Ultrastructure of Wood Fibres (CRUW)***

CRUW represents a collaborative research program between the Swedish Forest Industries Akzo Nobel, 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"*.

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