

Fiber Surface and Paper Technical Properties of *Eucalyptus globulus* and *Eucalyptus nitens* Pulps after Modified Cooking and Bleaching

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The SuperBatch™(SB), CompactCooking™(CC), and Lo-Solids™ (LS) modified cooking methods were evaluated relative to the cell wall surface and paper technical properties of bleached *Eucalyptus globulus* and *Eucalyptus nitens*. *E. globulus* pulps presented higher screened yield and brightness than *E. nitens*, which needed higher H-factor to reach a kappa number target. Independently of the cooking method or species, all the samples consumed similar amounts of ClO₂ to reach a brightness of 90% ISO. *E. nitens* pulps showed lower carbohydrates and higher extractives content on the fiber surface, regardless of the cooking method. *E. nitens* presented slightly higher surface charge of the bleached pulps. Surface charges of CC and LS pulps were higher independently of cooked *Eucalyptus* species. Water retention value (WRV) for *E. nitens* pulps were higher than for *E. globulus*. No differences were observed in refinability of different cooking methods, however *E. nitens* pulps showed higher tensile and lower bulk compared to *E. globulus*. *E. nitens* presented a thinner fiber cell wall than *E. globulus*. This seems to be more relevant for paper technical properties and WRV than fiber charge or surface composition. No correlation between surface composition, fiber surface properties, and paper technical properties among the cooking methods could be determined.

Keywords: Pulping; Bleaching; Modified cooking method; *Eucalyptus globulus*; *Eucalyptus nitens*; Kraft cooking; XPS; Fiber surface; Fiber charge; Fiber cell wall thickness; Paper technical properties

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INTRODUCTION

In conventional kraft cooking, wood chips and white liquor are charged into a digester at the same time; then both materials are heated under pressure until the desired degree of delignification is achieved. Alkali concentration is very high at the beginning of the cooking but low at the end. This may cause carbohydrate degradation during cooking, resulting in an inefficient delignification rate (Antes and Joutsimo 2015a). Based on these observations, higher selectivity during cooking is needed. The Royal Institute of Technology (KTH) and the Swedish Pulp and Paper Research Institute (STFI) developed a more selective kraft process by introducing several modifications to the conventional kraft process (Carnö and Hartler 1976; Nordén and Teder 1979; Teder and Olm 1981; Johansson *et al.* 1984). Thereby, the conditions for modified cooking were developed and can be summarized as: (1) a leveled-out alkali concentration, (2) a high concentration of hydrogen sulfide ions, especially at the beginning of the bulk phase, (3) low concentrations of dissolved lignin and sodium ions, especially at the end of cooking, and (4) a lower cooking temperature. These modifications allowed pulp producers to extend

cooking to lower kappa levels without significant loss of pulp strength or yield. Several new pulping technologies for continuous and batch systems have been developed since the implementation of this modified kraft process, including rapid displacement heating (RDH), black liquor impregnation (BLI), modified continuous cooking (MCC), extended modified continuous cooking (EMCC), and isothermal cooking (ITC). The most recent developments have resulted in Lo-Solids™ (LS) and CompactCooking™ (CC) modified continuous cooking technologies, which are currently the two primary continuous kraft cooking systems. SuperBatch™ (SB) has been used as a modified batch digester system (Antes and Joutsimo 2015a).

The general main cooking features for each method can be summarized as:

- **SB:** Reuse of heat in the subsequent batches. Modified cooking chemistry (alkali profiling and low content of dissolved matters). Efficient use of residual and fresh cooking chemicals.
- **CC:** Low temperature during the impregnation stage. Maintain high liquor to wood ratio and high sulfidity in the impregnation phase of the cook.
- **LS:** Minimizes the quantity and concentration of dissolved solids in the bulk and residual delignification phases

Evaluation of how these methods complied with the four rules of modified cooking (Hartler 1978) are presented in Table 1:

Table 1. The Four Rules of Modified Cooking Related to Cooking Methods

| Rules of Modified Cooking | SB | CC | LS |
|--------------------------------------------------------------------------------------------------------|----|----|----|
| (1) Leveled out OH- | ✓ | | |
| (2) High concentration of SH- ions, especially at the beginning of the bulk phase | ✓ | ✓ | |
| (3) Low concentrations of dissolved lignin and sodium ions, especially at the end of the cooking stage | | | ✓ |
| (4) Low cooking temperature | | ✓ | |

The composition of extractives is dependent on the wood species, and the amount is generally much lower than that of carbohydrates and lignin. However, relatively high amounts of extractives can be found in heartwood and knots in softwoods (Willför *et al.* 2003). The process used for kraft pulp manufacturing significantly affects the amount and distribution of extractives, which influence the interactions of fibers in the bleaching and papermaking processes (Fardim *et al.* 2005). Thus, the fiber surface extractives are high in pulp (Ohno *et al.* 1992). Extractives are deposited onto fiber surfaces during chemical pulping and bleaching (Laine *et al.* 1994; Kleen *et al.* 2002). Surface extractives are believed to affect both pulp and paper strength in refining and wetting properties, important parameters which influence product performance (Shen *et al.* 1998; Fardim and Durán 2001; Widsten *et al.* 2001; Kokkonen *et al.* 2002). According to Laine *et al.* (1996), surface layers of the fibers, whether originating from wood fibers (remnants of middle lamella) or formed during cooking (reprecipitated), retards the bleachability of kraft pulps. There are some indications that the poor dissolution of surface lignin in the early stages of bleaching is due to a low amount of free phenolic lignin units or too high an amount of condensed structures, or that the outer cell wall layers contain substantial

amounts of lignin-carbohydrate complexes (Laine *et al.* 1996). Surface lignin also plays a significant role with respect to brightness development during bleaching. A tentative conclusion was proposed by Laine *et al.* (1994) and Laine *et al.* (1996) that the surface lignin is more colored than the residual lignin in the other regions of the fibers.

Fiber Charge and Fiber Surface

Wood pulp fibers carry charges when suspended in water due to the presence of acidic groups in hemicellulose and lignin. The amount of charge present is a function of pulping, bleaching, or other processing methods used, the pH, and the electrolyte concentration in the surrounding water. The fiber charge is an important parameter to consider during papermaking, because many of the interactions between soluble and particulate fractions of papermaking furnishes are charge induced.

The surface charge density of the fibers has also been reported to be a contributing factor in obtaining tensile strength in certain grades of paper sheets (Ampulski 1985; Engstrand *et al.* 1991). Studies have shown that the specific surface area of never-dried pulp fibers can be more than 100 m² per gram (Stone *et al.* 1966). The surfaces of fibers formed by chemical processes tend to have higher free energy when compared to fibers that were separated from each other by mechanical means (Backström *et al.* 1999).

According to Bhardwaj *et al.* (2004), the effects of fiber charge on retention of additives at the wet end of paper machines are the main subject in many studies. When one considers charge density of the fibers, it is also a major factor in formulation of hydrogen bonding between fibers. It is important to consider that the fiber charge is related not only to the carboxylic groups of the carbohydrate but also on the phenolic groups of lignin in the fibers. The methods used to produce pulp directly affect the degradation and formation of carboxylic groups and have significant effects on the electro kinetic properties of fibers (Lindström and Carlsson 1982; Laine *et al.* 1994). It has been reported by Zhang *et al.* (1994) that pulp properties such as hydrophilicity (wettability) and fiber swelling also are influenced by fiber surface charge.

Work by Sanders and Schaefer (1995) suggests that the measurements of fiber charge are important for optimization of stock preparation prior to the sheet formation stage. According to Wågberg *et al.* (1989), polyelectrolyte titration, which determines the amount of a charged polymer that is adsorbed on the fiber surface, has proved to be a popular method for the control of the wet end chemistry.

In the production of bleached kraft pulp, a significant part of the extractives is removed from the pulp during cooking and washing. However, a certain amount of extractives always remains in the brownstock pulp and is carried over to the bleaching plant. The bleaching chemicals react with extractives, oxidizing and thus modifying them (Björklund-Jansson *et al.* 1995). The extent of the reaction depends on the accessibility of the extractives and on the oxidation potential of the bleaching agent used.

According to Fardim *et al.* (2005), analyses of surface extractives are regularly carried out by x-ray photoelectron spectroscopy (XPS) and more recently with time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS has been used for the estimation of surface coverage of extractives, while ToF-SIMS has been used for assess the detailed surface composition in addition to surface distribution. Also according to Fardim *et al.* (2005), applications of atomic force microscopy (AFM) for characterization of fiber surfaces are relatively recent compared to XPS.

Refining

Pulp consists of cellulose fibers that come from wood and non-wood plants, and it is the major raw material in papermaking (Gharehkhani *et al.* 2015). Kraft fibers are usually refined by one or more passes between the rotor and stator of a typical refiner. During refining, mechanical and hydraulic forces are employed to change the fibre characteristics, and this affects both the morphological structure of fibres and the macroscopic properties of paper (Mou *et al.* 2013). Bunches of fibers within the suspension become squeezed and sheared between the working surfaces of the refiner (Hubbe *et al.* 2007). Though it is well known that the strength of paper can be substantially improved by refining, subsequent loss in inter-fiber bonding potential can also be much larger when (kraft) fibers are refined, before they are dried and recycled (Stürmer and Göttching 1979; Peng *et al.* 1994). The effect of refining on chemical pulps has been reported by several authors (Retulainen 1997; Robinson 1980; Hiltunen 2003; Paulapuro 2000). The aim of refining is to reach certain paper strength property such as tensile breaking length with a minimum impact in other strength properties such as tear. Drainability of the pulps measured as Schopper Riegler ($^{\circ}$ SR) and water retention value (WRV) are affected during refining. Water Retention Value is often used to measure fiber swelling is the water retention value (Maloney 2000). In the WRV test, a pulp pad is centrifuged under conditions that are assumed to remove the water between the fibers. Generally the water removal from the pulp suspension is more difficult as the refining energy increases.

Refinability is also affected by cooking parameters. Hanna *et al.* (1998) have presented evidence that pulping with lower alkalinity results in pulps of higher hemicellulose content which leads to less energy requirement during refining. Colodette *et al.* (2002) concluded that lower temperature and/or residual alkali during pulping favored pulp refining. According Wan Rosli *et al.* (2009), active alkali and the cooking temperature have the most significant impacts on the dissolution of wood components and therefore the strength properties of the pulps are also significantly influenced by these two factors.

This publication is part of a series of publication that evaluates the effect of modified cooking methods in the fiber chemical composition, cell wall structure, fiber surface, and morphology and paper technical properties. The objective of this present work was to evaluate how and whether selected modified cooking methods (SB, CC, and LS) affect fiber surface composition, and, if this change occurs, how it will impact drainability as $^{\circ}$ SR and WRV, fiber cell wall thickness and technical properties of the paper like tensile index, Scott bond, and bulk under refining.

EXPERIMENTAL

Raw Material

The brown pulp used in this work was produced from fresh chips of *E. globulus* and *E. nitens*. The chip classification prior to cooking followed the standard SCAN CM:40-01 (2001). The wood raw material basic density and age were chosen according to the average data for *Eucalyptus* harvesting for pulp production from central Chile (Region VIII – Bio-Bio). The wood basic density expected would have very similar

levels: $500 \pm 20 \text{ kg/m}^3$. The *E. globulus* sample was 12 years old, and the *E. nitens* sample was 15 years old. The basic density of the wood samples were 523 kg/m^3 and 507 kg/m^3 , respectively. To measure the basic density, the TAPPI T 258 om 11 (2011) standard method was used.

Cooking Experiments

All the cooking experiments were performed at the VTT Technical Research Centre of Finland. The laboratory digestion for modified cooking was performed in a forced circulation digester with a volume of 30 L. Heating of the digester was carried out by water jacket heating. The digester used to generate black liquor, which was used as the displacement liquor and wash liquor in LS modified cooking, was produced with the corresponding raw material. The cooking equipment used was a set of 15 L rotating batch digesters. The heating of the batch digester was controlled electronically by electric heating of the digester jacket. The cooking experiments for liquor generation were carried out at $160 \text{ }^\circ\text{C}$ and with a constant alkali charge of 17% Effective Alkali (EA) as NaOH. The sulfidity of white liquor used in all cooking methods was 35%. For all the modified cookings, the kappa number target was 17 ± 0.5 . The cooking procedures for all modified cooking methods are described in Table 2 and more details about the cooking conditions can be found in Antes and Joutsimo (2015a)

Table 2. Main Features Used in SuperBatch™(SB), CompactCooking™(CC) and Lo-Solids™(LS) Cooking Methods

| Phase/Modified Cooking Type | SB | CC | LS |
|-----------------------------------------------------------|----------------------------|--------|---------|
| Impregnation Zone | | | |
| Temperature (°C) | 90 | 115 | 105 |
| Liquor to wood ratio | 5:1 | 6:1 | 4:1 |
| Alkali charge WL* + BL** as EA (%) | 5 | 6.3 | 10.5 |
| Process time: <i>E. globulus</i> / <i>E. nitens</i> (min) | 40/40 | 60/60 | 45/45 |
| Cooking Zone I | | | |
| Temperature (°C) | 148 (HBL*** fill) | 141 | 135 |
| Liquor to wood ratio | 4.25:1 (HBL fill) | 6:1 | 4:1 |
| Alkali charge as EA (%) | 5 (HBL fill) | 7 | 7.2 |
| Process time: <i>E. globulus</i> / <i>E. nitens</i> (min) | 60/60 | 90/100 | 20/20 |
| Cooking Zone II | | | |
| Temperature (°C) | 152 (cooking circulation) | 141 | 148 |
| Liquor to wood ratio | 5:1 (cooking circulation) | 3.8:1 | 4:1 |
| Alkali charge as EA (%) | 10.6 (cooking circulation) | 0.0 | 0.0 |
| Process time: <i>E. globulus</i> / <i>E. nitens</i> (min) | 34/40 | 90/100 | 100/100 |
| Washing Zone | | | |
| Temperature (°C) | 80 | NA | 90 |
| Washing Liquor to wood ratio | 5:1 | NA | 4:1 |
| Alkali charge as EA (%) or g/L (NaOH) | 2.2% | NA | 5.0 g/L |
| Process time <i>E. globulus</i> / <i>E. nitens</i> (min) | 90/90 | 60/60 | 40/40 |
| Total alkali charge for all cooking process | | | |
| Total alkali charge in the cook as EA (NaOH) (%) | 22.8 | 21.0 | 21.9 |

NA = Not applicable, WL* = White Liquor, BL** = Black Liquor, HBL***

Bleaching Experiments

The unbleached pulps were bleached at VTT in Finland using the bleaching sequence of 5 stages: D₀E₁D₁E₂D₂. The main bleaching agent used in this experiment was Chlorine dioxide (ClO₂) in D stages. Every experiment was repeated two times, and the results presented are the averages. The bleaching conditions were performed and explained in detail as follows:

D-stages

D-stages were performed in 18 L air bath reactors. Preheated pulp was added to the reactor first and, after that, water with acid or alkali (for pH adjustment). After the mixing pH was measured, chlorine dioxide was charged into the reactor, and the cover was closed immediately.

Pulp was first mixed for 4.5 min by rotating the reaction vessel (30 rpm/min). During the reaction, the reactor was rotated periodically (stopped for 70 s, change in the direction of rotation, rotation for 30 s). After the reaction, final pH was measured from the pulp at the reaction temperature. The residual chlorine content of the bleaching filtrate was determined. The pulp was diluted and washed in a standard way.

Alkaline extraction stage

The alkaline extraction stage (E) was performed in a Teflon coated 40 L reactor as follows: the pulp and most of the water were heated to the reaction temperature in a microwave oven and placed into the reactor. Alkali with additional water was charged, the pulp slurry was mixed for 1 min at 300 rpm, and the pH was measured. During the reaction, the pulp slurry was mixed every 20 min for 12 s at 300 rpm. After the reaction, final pH was measured from the pulp at the reaction temperature. The pulp was diluted and washed following the procedure below.

Pulp washing

Pulp washing between bleaching stages was a standard laboratory procedure: pulp was diluted to 5% concentration with deionized water, which was at the same temperature as the preceding bleaching stage. After dewatering, the pulp was washed 2 times with cold deionized water with an amount of water equivalent to 10 times the mass of oven dry pulp amount.

The homogenization of pulp was done by hand. Sheets (10 g abs. dry pulp) for brightness and kappa number measurement were formed after the bleaching stages by adjusting the pH to 4.5 with SO₂ before sheet forming.

Pulp testing methods

Pulp testing methods were performed according to the following standards: kappa number ISO 302 (2004):04, dry content of pulp ISO 638 (2008), intrinsic viscosity ISO 5351 (2010), and brightness from split sheet surface ISO 2470-1 (2009). The bleaching conditions are presented in Table 3. The bleaching agent chlorine dioxide (ClO₂) is present as active chlorine. It is a common unit oxidant; one weight unit of chlorine dioxide is equal to 2.63 weight units of active chlorine. The kappa factor applied for this experiment in D₀ was 0.20.

Acetone Extractives

Extractives were measured according to the SCAN standard CM 49 (2003). This standard method is utilized for the determination of non-volatile lipophilic matter in wood chips and pulp samples through gravimetric analysis. The method entails solid-liquid extractions with acetone in a Soxhlet extractor for at least 16 or 24 cycles for pulp and wood, respectively.

Table 3. Main Bleaching Conditions

| Parameters/Bleaching conditions of different cooking methods | | <i>E. globulus</i> | | | <i>E. nitens</i> | | |
|--------------------------------------------------------------|----------------------------------------------------|--------------------|------|------|------------------|------|------|
| | | SB | CC | LS | SB | CC | LS |
| D₀ Consistency 10% 60 °C, 60 min | ClO ₂ charge (%), as active chlorine | 3.30 | 3.40 | 3.40 | 3.40 | 3.30 | 3.33 |
| | H ₂ SO ₄ charge, (%) | 0.50 | 0.54 | 0.54 | 0.56 | 0.54 | 0.54 |
| E₁ Consistency 10% 70 °C, 60 min | NaOH charge, (%) | 1.36 | 1.35 | 1.38 | 1.36 | 1.32 | 1.33 |
| D₁ Consistency 10% 70 °C, 120 min | ClO ₂ charge (%), as active chlorine | 1.15 | 1.20 | 1.12 | 1.06 | 1.12 | 1.19 |
| | NaOH charge, % | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 | 0.10 |
| E₂ Consistency 10% 70 °C, 60 min | NaOH charge, (%) | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 | 0.80 |
| D₂ Consistency 10% 70 °C, 180 min | ClO ₂ charge (%), as active chlorine | 0.20 | 0.20 | 0.21 | 0.30 | 0.23 | 0.21 |
| | H ₂ SO ₄ charge, (%) | 0.09 | 0.10 | 0.11 | 0.09 | 0.10 | 0.11 |

Fiber Charge

The accessibility of the charges in the fibers was evaluated by the adsorption of poly (dimethyldiallylammonium) chloride (poly-DMDAAC). The poly-DMDAAC has a distribution of three different molar masses ($3 \times 10^4 < M_w < 5 \times 10^4$, $1 \times 10^5 < M_w < 3 \times 10^5$, and $M_w > 3 \times 10^5$ g/mole) and a charge density of 6.19×10^{-3} eq/g. Determinations of polyelectrolyte adsorption and pulp pretreatments were done using the method described by Wågberg *et al.* (1985). The titration was performed in two ways: directly from the fiber suspension (which gives the charge density of the suspension) and then after fiber removal from the suspension. Although many methods have been developed for fibre charge measurement, titrations using a cationic polymer of high molecular weight are normally used to measure the charge on the fibre's surface (Wågberg *et al.* 1989).

Surface Chemical Composition

The composition of fiber surfaces were measured at Aalto University, Finland, using XPS with the equipment AXIS 165 (KRATOS Analytical, USA) according to the following methodology. A piece less than 1 cm² was cut and secured onto the steel sample holder with a metal clip. A laboratory specified fresh reference sample of 100% cellulose was measured with each sample batch, in order to monitor the instrument and

ultra-high vacuum (UHV) conditions during all the experiments. Each batch was pre-evacuated in the instrument preparation chamber overnight before analysis. During the measurements, samples were exposed to minimal radiation dose, using a low-power setting and localized monochromated Al K α X-ray irradiation. No sample deterioration was detected during the experiment.

Recorded runs for each sample were:

- 3 x low-resolution wide spectrum (0 - 1100 eV, elemental composition),
- 3 x high-resolution regions of carbon and oxygen main peaks (C 1s and O 1s),
- Area of analysis less than 1 mm², and
- Analysis depth of 2 to 10 nm, depending on the element and material studied (samples were measured from at least three locations).

Each recording was manually optimized for an intense, non-charged signal. The samples were charge-neutralized during data acquisition with slow thermal electrons (a Kratos patent). The binding energies in the HiRes data, shifted due to charging, were energy corrected using the aliphatic C-C carbon component of the C 1s spectra at 285.0 eV (Beamson and Briggs 1993)

The data analysis and calculations of surface lignin, extractives, and hydrocarbons are described in the results section:

- Low-resolution spectra: 0 to 1100 eV, 1 eV step, 80 eV PE, mg lens, slot;
- High-resolution C 1s and O 1s region, 0.1 eV step, 20 eV PE, mg lens, slot.

Refining and Testing of the Pulps

The pulps were refined in a Voith Sulzer LR1 lab-refiner at VTT-Finland. The refining parameters used in this trial were: fillings 2/3-1.46-40D (hardwood fillings), refining consistency 4%, and the specific edge load (SEL) was 0.4 J/m. The refining energy levels used were 0, 40, 80, and 120 kWh/ton. The standards used to evaluate the refining results were: pulps reparation of laboratory sheets for physical testing ISO 5269-1 (2005), determination of pulps and board tensile Part 3: Constant rate of elongation method (100 mm/min) ISO 1924-3 (2005), drainability part 1: Schopper-Riegler (°SR) method ISO 5267-1 (1999), and thickness and apparent bulk density or apparent sheet density ISO 534 (1988). The water retention value (WRV) was measured in never-dried pulp according to ISO 23714 (2007). Internal bond strength (Scott type), used test method TAPPI/ANSI T 569 om-14 (2014)

Fiber Wall Thickness

The fiber morphology was measured in VTT Finland. Fiber wall thickness were measured with a light microscope and semi-automatic image analysis from wet longitudinal fiber parameters (water/glycerol). Around 500 fibers were analyzed for each sample.

RESULTS AND DISCUSSION

Cooking

In Table 4 a summary of the cooking results is presented, including H-Factor, kappa number, total yield, rejects, screen yield, brightness, and intrinsic viscosity. The Standard Deviation (SD) of the measurements are presented as well.

Table 4. Summary Results of Different Cooking Methods

| Raw Material/ Cooking Results | H factor /SD | Kappa number/S D | Total yield (%)/SD | Rejects (%)/SD | Screened yield (%)/SD | Bright- ness (%)/SD | Intrinsic Viscosity (mL/g) |
|-------------------------------------|-----------------|------------------------|-----------------------|-------------------|-----------------------------|---------------------------|----------------------------------|
| SB | | | | | | | |
| <i>E. globulus</i> | 300/5.12 | 16.50/0.46 | 58.76/0.44 | 1.62/0.80 | 57.14/0.70 | 41.50/0.14 | 1590 |
| <i>E. nitens</i> | 315/3.98 | 17/0.32 | 57.89/0.40 | 1.33/0.40 | 56.56/0.45 | 39.36/0.06 | 1620 |
| CC | | | | | | | |
| <i>E. globulus</i> | 239/4.47 | 17/0.12 | 58.59/0.51 | 1.88/0.33 | 56.71/0.34 | 41.57/0.26 | 1660 |
| <i>E. nitens</i> | 262/5.20 | 16.5/0.10 | 57.22/0.23 | 1.13/0.13 | 56.09/0.22 | 40.33/0.10 | 1650 |
| LS | | | | | | | |
| <i>E. globulus</i> | 244/5.23 | 17/0.51 | 58.66/0.46 | 1.71/0.56 | 56.95/0.40 | 41.51/0.33 | 1600 |
| <i>E. nitens</i> | 273/4.78 | 16.5/0.14 | 56.84/0.37 | 1.19/0.21 | 55.65/0.38 | 39.84/0.17 | 1625 |

SB technology required higher H-factor to reach the desired kappa number (17 ± 0.5) than other modified cooking methods, independently of the raw material used in the experiments. Pulps of *E. nitens* were less bright regardless of cooking method; by contrast, *E. globulus* presented a higher amount of rejects and screened yield. The intrinsic viscosity for unbleached pulp is about the same range for all the modified cooking methods.

Bleaching

The pulps were bleached to target brightness 90 ± 0.5 using the sequence $D_0E_1D_1E_2D_2$ described above. The general results are presented in Table 5.

Table 5. Bleaching Chemical Consumption of Different Cooking Methods

| Chemical consumption in bleaching of different modified cooking methods | | <i>E. globulus</i> | | | <i>E. nitens</i> | | |
|----------------------------------------------------------------------------------|-------------------------|--------------------|------|------|------------------|------|------|
| | | SB | CC | LS | SB | CC | LS |
| Total Chemical Consumption for Brightness ISO % 90 (interpolated) | | | | | | | |
| NaOH | % | 2.26 | 2.25 | 2.28 | 2.26 | 2.22 | 2.23 |
| H ₂ SO ₄ | % | 0.59 | 0.64 | 0.65 | 0.65 | 0.64 | 0.65 |
| ClO ₂ | % as active chlorine | 4.68 | 4.79 | 4.77 | 4.77 | 4.63 | 4.70 |
| ClO ₂ | % ClO ₂ | 1.78 | 1.82 | 1.81 | 1.81 | 1.76 | 1.79 |

All pulp needed the same level chlorine dioxide consumption to reach ISO 90% Brightness; similar results were seen for sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) used for pH adjustments.

Surface Composition and Acetone Extractives

Cellulosic fibers carry a negative charge when suspended in water due to the presence of ionisable acidic groups in the hemicellulose and lignin (Banavath *et al.* 2011). Figure 1 shows fiber surface composition in both unbleached and bleached fibers.

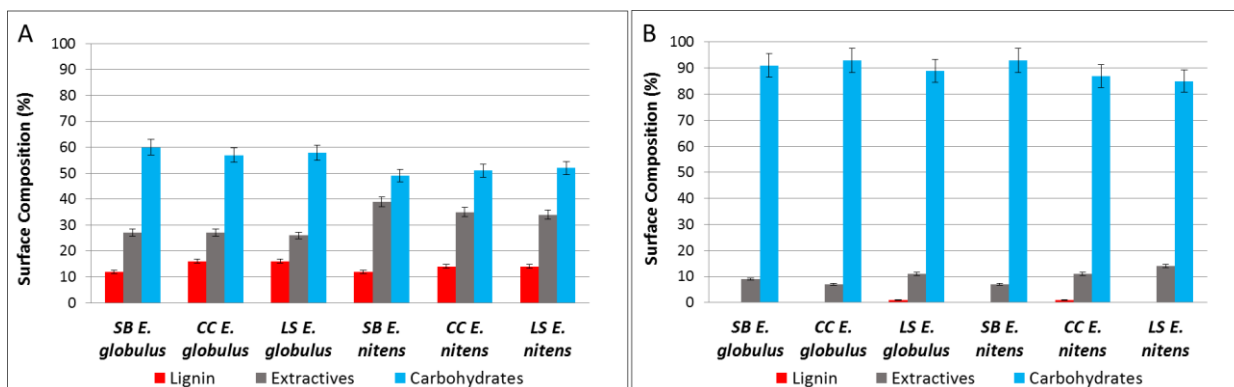


Fig. 1. The fiber surface composition of SB, CC, and LS cooked samples. (A) Unbleached and (B) bleached *E. globulus* and *E. nitens* fibers. The error bars present the 95% confidence interval of the mean of the measurement.

Figure 1 presents the amounts of lignin, extractives, and carbohydrates on the fiber surface of unbleached and bleached pulps. With the exception of LS and CC for *E. globulus* unbleached pulps, the amounts of lignin on the fiber surfaces were at the same level. The small difference in the amount of lignin on the fiber's surface can be attributed to the error of the method. The amounts of extractives found *E. nitens* surface were higher than *E. globulus*, independently of the cooking method. In bleached pulps, the proportion of extractives was slightly higher for *E. nitens* with the exception of the SB modified cooking method. On the other hand, fibers of *E. globulus* presented higher carbohydrate surface composition than *E. nitens*, independently of the modified cooking method. This tendency was not observed in bleached pulps where the proportion of carbohydrates is very similar among the species and modified cooking method. In Fig. 2, the total amounts of extractives in the pulp are presented.

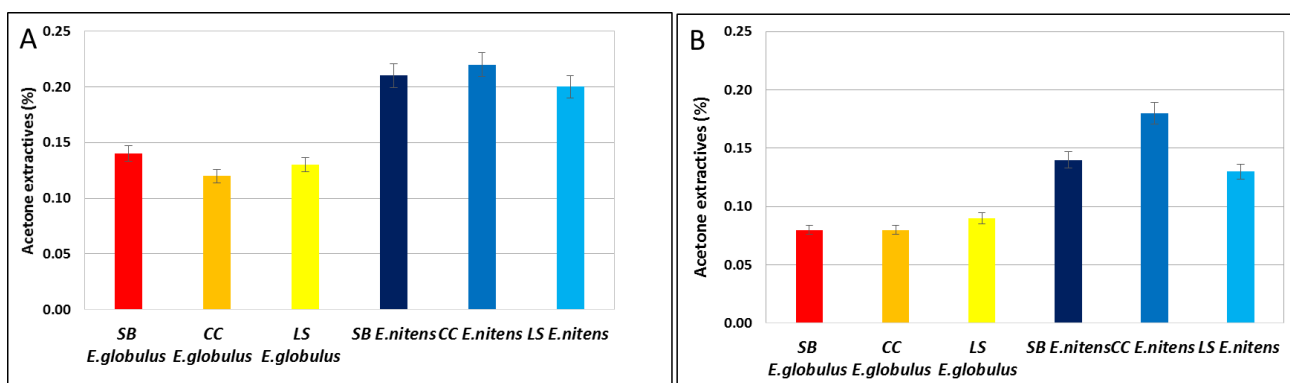


Fig. 2. Acetone extractives in the pulps produced by SB, CC, and LS modified cooking methods. (A) Unbleached, and (B) bleached *E. globulus* and *E. nitens* fibers. The error bars present the 95% confidence interval of the mean of the measurement.

From Fig. 2, it can be seen that the amounts of the extractives found in the unbleached and bleached pulps of *E. nitens* were higher compared to *E. globulus* pulps. This result is in accordance with the literature; according to Ohon *et al.* (1992), the surface coverage of extractives is much higher than the amount percent in pulp. After bleaching with exception of extractives the fiber surface presented the same amount of

carbohydrate on the surface, independently of which modified cooking method was employed.

Fiber Total Charge and Superficial Charge

The charge of fibers is a complex function of the chemical composition, state of ionization of the acid groups, and the nature and amount of additional substances adsorbed on the fiber's surface. The population of ionisable groups depends on the origin of the fibers and on chemical treatments such as pulping and bleaching (Bhardwaj *et al.* 2007). The total charges of the unbleached and bleached fibers are presented in Fig. 3.

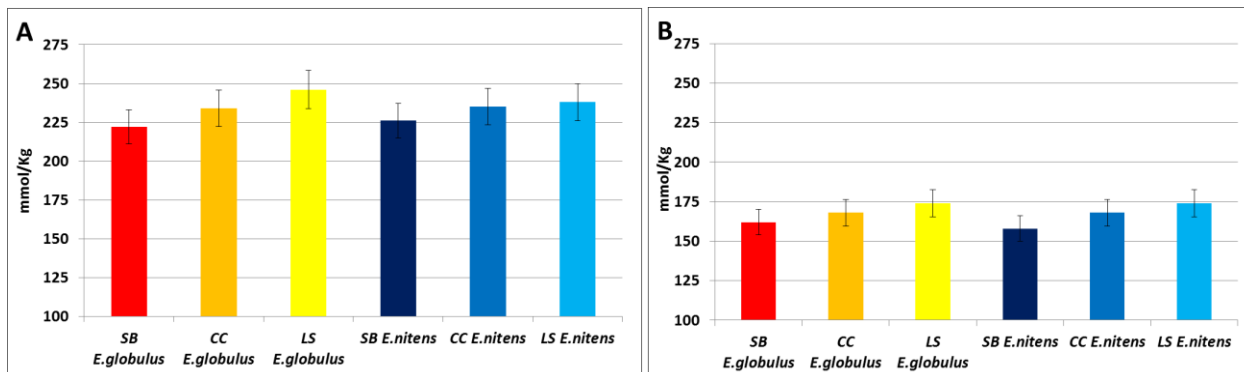


Fig. 3. Fiber total charge of SB, CC, and LS cooked samples. (A) Unbleached, and (B) bleached *E. globulus* and *E. nitens* fibers. The error bars present the 95% confidence interval of the mean of the measurement.

Figure 3 shows that there were basically no statistically significant differences in the fiber total charge independent of the cooking method or wood species used in the unbleached and bleached pulps. Banavath *et al.* (2011) concluded that the total charge depended mainly on the chemical composition of the fiber but not on the physical change in the fiber. The higher proportion of carbohydrate in unbleached fibers of *E. globulus* might explain the tendency of a higher total charge than in *E. nitens*, even though they are not statistically different. One possible explanation of the higher surface charge of the bleached LS pulps could be the lower amount of extractives on the fiber surface compared to other bleached pulp. The surface charges of the fibers are presented in Fig. 4.

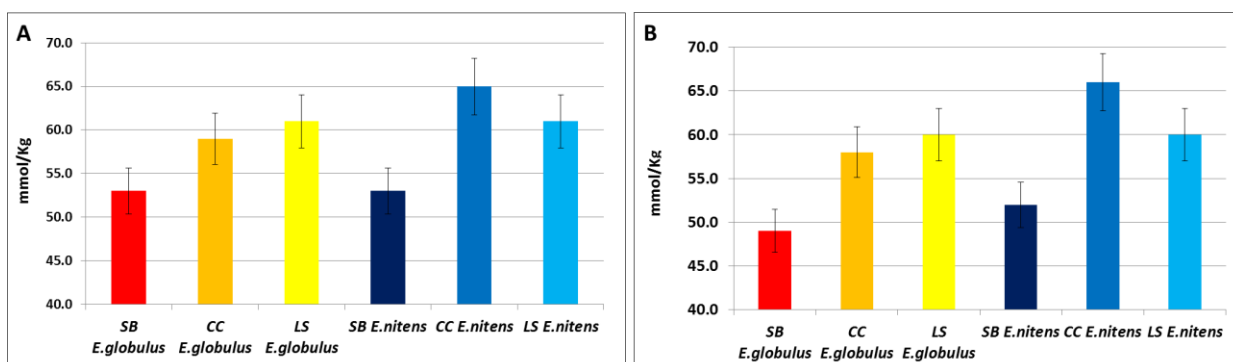


Fig. 4. Fiber surface charge of SB, CC, and LS cooked samples. (A) Unbleached, and (B) bleached *E. globulus* and *E. nitens* fibers. The error bars present the 95% confidence interval of the mean of the measurement.

Figure 4 shows the surface charge of *E. globulus* and *E. nitens* unbleached and bleached fibers. From Fig. 4 it can also be seen that the highest surface charges were generated by CC modified cooking in the case of bleached *E. nitens* pulp. More studies have to be conducted to understand this effect because it was found only in bleached fibers. Similar values have been reported in the literature for *Eucalyptus* sp. (Bhardwaj *et al.* 2007). The WRV values of the pulps are shown in Fig. 5.

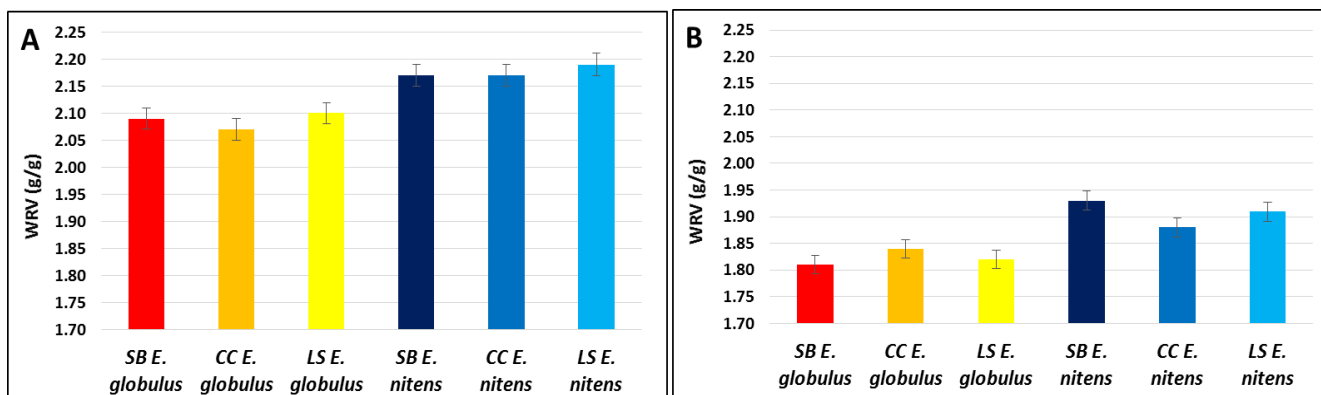


Fig. 5. The water retention values of SB, CC, and LS cooked unbleached and bleached samples. (A) *E. globulus*, and (B) *E. nitens* pulps. The error bars present the standard deviation of the measurements.

The WRV values (Fig. 5) clearly show that *E. nitens* had significantly higher WRV values compared to the *E. globulus* fibers. Antes and Joutsimo (2015b) reported that *E. nitens* has higher hemicellulose content compared to *E. globulus* in bleached and unbleached pulps, which can explain the differences since higher amounts of hemicellulose absorb and retain more water in the cell wall.

Refining of Chemical Pulps

Cellulosic fibers for papermaking are normally subjected to a mechanical treatment usually known as beating or refining. This treatment results in structural changes of the treated fibers, including fiber shortening and internal/external fibrillation (Page 1989). In Fig. 6, the °SR and tensile index are presented as a function of refining energy of the SB, CC, and LS bleached *E. globulus* and *E. nitens* pulps.

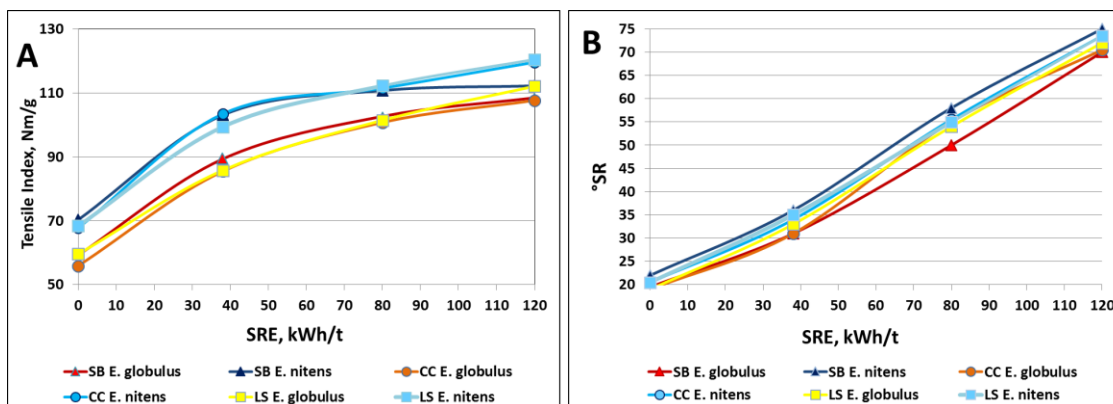


Fig. 6. SR and tensile index as a function of refining energy of the SB, CC, and LS after fully bleached pulps. (A) °SR, and (B) tensile index of *E. globulus* and *E. nitens* pulps.

E. nitens pulps showed slightly faster °SR development compared to *E. globulus* pulps, and the tensile index development is significantly faster for *E. nitens* pulps compared to *E. globulus* pulps. One explanation for higher tensile index of the *E. nitens* pulps could be higher bonding ability, however as shown in Fig. 7, Scott Bond as function of °SR are very similar for both species. Therefore the explanation may lay in the differences in segment activation, already proposed by Giertz (1964). According to Vainio and Paulapuro (2007), activation is one of the relevant properties of fibers within a network. It occurs during drying, when lateral shrinkage of fibers is transmitted to axial shrinkage of the neighboring fibers at bonded areas. The same authors also concluded that the lower cell wall shrinkage could also explain the lower fiber segment activation, *i.e.*, lower tensile index of the pulp sheet made of *E. globulus* fibers. It is important to notice that the differences in tensile strength cannot be explained by the surface properties as Fig. 4 demonstrated. In Fig. 7, A) Bulk and B) Scott Bond are presented as a function of °SR.

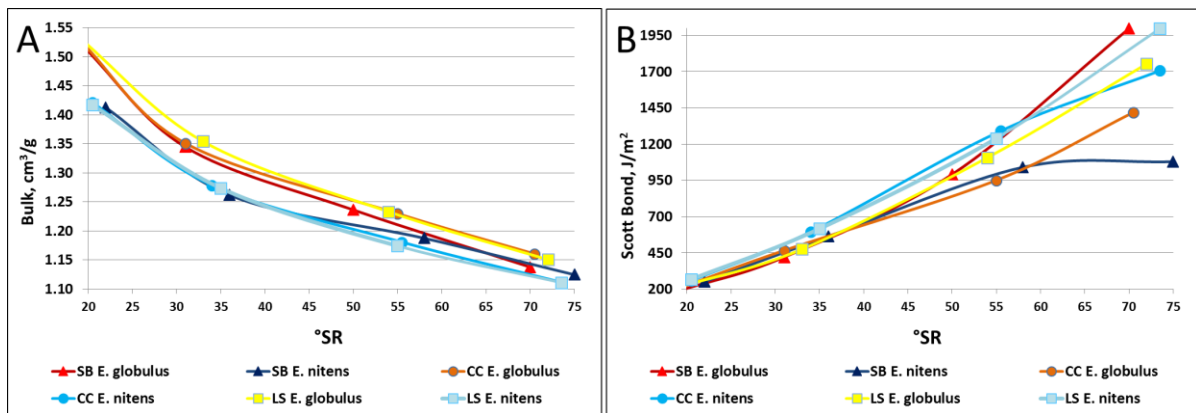


Fig. 7. A) Bulk and B) Scott Bond as a function of °SR of the SB, CC, and LS fully bleached pulps of *E. globulus* and *E. nitens* fibers.

The higher bulk presented by *E. globulus* fibers could be addressed to lower WRV of the *E. globulus* fibers compared to *E. nitens* already presented in the Fig. 5. Basically, this lower water holding capacity of the cell wall means lower cell wall shrinkage, *i.e.*, higher bulk of the pulp sheet (Joutsimo and Asikainen 2013). It has been reported by Paavilainen (1993), that fibers with low fiber wall thickness influence tensile strength and density of hand sheets positively. Figure 8 shows differences in cell wall thickness of bleached pulp of both species in all modified cooking methods studied in this work.

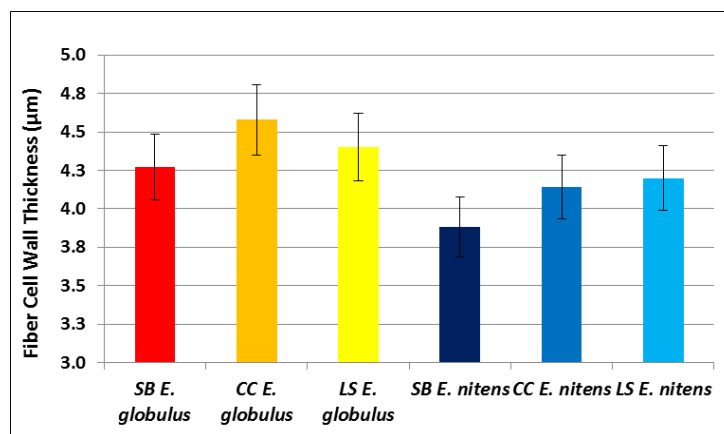


Fig. 8. Fiber cell wall thickness of SB, CC, and LS fully bleached *E. globulus* and *E. nitens* pulps. The error bars present the 95% confidence interval of the mean of the measurement.

The thickness of the fibre wall has an important bearing on most paper properties, with thick-walled fibres forming bulky sheets of low tensile but with a high tearing strength (Wardrop 1969). The fiber network structure of paper depends on the collapsibility, conformability, and flexibility of wet fibres (Pulkkinen *et al.* 2008).

Even though no significant statistical differences were found among bleached pulps submitted to different modified cooking methods, there was a tendency that *E. globulus* pulp presents thicker fiber walls than *E. nitens* pulps. This would explain the higher bulk of *E. globulus*. It has been reported by Pulkkinen *et al.* (2010) that increase of fiber cell wall thickness decreases WRV of the fibers. This also suggests fiber cell wall thickness contributes significantly more than fiber charge or surface composition for WRV, bulk, and tensile index of the pulp sheet.

CONCLUSIONS

1. At the kappa number target (17 ± 0.5), *E. globulus* pulps presented higher screen yield and brightness than *E. nitens*, which needed higher H-factor to reach the desired kappa number. Independently of the cooking method or species, all the samples consumed a similar amount of ClO_2 to reach 90% ISO brightness.
2. *E. nitens* pulps had lower carbohydrate surface areas and higher extractives content on their surfaces on unbleached pulps, independently of cooking method. The highest amount of extractives were also found in *E. nitens* pulps, unbleached and bleached.
3. *E. globulus* presented a tendency towards higher total charge than *E. nitens*, but the difference was not statistically significant. On the other hand, *E. nitens* pulps showed slightly higher surface charges when the CC modified cooking method was employed.
4. The cooking method did not have an effect on refinability of the pulps. However, *E. nitens* showed higher tensile strength and lower bulk compared to *E. globulus* pulps.
5. No correlation between surface composition, fiber surface properties, and paper technical properties could be determined.

6. Even though there was not a statistical difference among fiber cell wall thickness, there was a tendency that *E. nitens* had thinner cell walls and therefore it showed lower bulk and higher tensile index.
7. Fiber cell wall thickness contributes significantly more than fiber charge or surface composition for WRV, bulk, and tensile index of the pulp sheet, independently of modified cooking method.

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REFERENCES CITED

- Ampulski, R. S. (1985). "The influence of fiber surface charge on tensile strength," Proc. Tappi Papermakers Conference, Denver, USA, April 15-17, pp. 9-16.
- Antes, R., and Joutsimo, O. (2015a). "Effect of modified cooking on chemical composition of pulps from *Eucalyptus globulus* and *Eucalyptus nitens*," *BioResources*. 10(1), 210-216.
- Antes, R., and Joutsimo, O. (2015b). "Effect of modified cooking on bleachability of *Eucalyptus globulus* and *Eucalyptus nitens*," *BioResources* 10(1), 597-612.
- Backström, M., Fellers, C., and Htun, M. (1999). "Influence of kappa number and surface energy on paper-to-paper friction," *Nordic Pulp Paper Res. J.* 14(3), 204-208.
- Banavath, H. N., Bhardwaj, N. K., Ray, A. K. (2011). A comparative study of the effect of refining on charge of various pulps. *BioResources* 102 (6), p.4544-4551
- Beamson, G., and Briggs D. (1993). "High resolution XPS of organic polymers: The Scienta ESCA 300 database" The Scienta ESCA 300 database. G. Beamson and D. Briggs, 280 pp., John Wiley & Sons, Chichester, ISBN 0471 935921
- Björklund-Jansson, M., Wormald, P., and Dahlman, O. (1995). "Reactions of wood extractives during ECF and TCF bleaching of kraft pulp," *Pulp Pap. Can.* 96, T134-T137.
- Bhardwaj, N. K., Tuan, D. D., Hoang, V., and Nguyen, K. L. (2004). "Determination of fiber charge components of Lo-Solids unbleached kraft pulps," *Journal of Colloid and Interface Science* 274(2), 543-549.
- Bhardwaj, N. K., Hoang, V., and Nguyen, K. L. (2007). "A comparative study of the effect of refining on physical and electrokinetic properties of various cellulosic fibers," *Bioresource Technology* 98(8), 1647-1654. DOI:10.1016/j.biortech.2006.05.040
- Carnö, B., and Hartler, N. (1976). "Kraft pulping to low kappa numbers," *Report B 382*, Swedish Pulp and Paper Research Institute, STFI, Stockholm, Sweden.
- Engstrand, P., Sjögren, B., Ölander, K., and Htun, M. (1991). "Significance of carboxylic groups for the physical properties of mechanical pulp fibers," *Appita 6th International Symposium on Wood & Pulping Chemistry Proceedings*, Melbourne, Vol. 1, pp. 75-79.

- Fardim, P., Gustafsson, J., Schoultz, S. V., Peltonen, J., and Holmbom, B. (2005). "Extractives on fiber surfaces investigated by XPS, ToF-SIMS and AFM," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 255(1-3), 91-103
- Fardim, P., and Durán, N. (2001). "Surface chemical composition and mechanical properties of *Eucalyptus grandis* kraft pulp investigated by XPS and PCA," Proceedings of the 11th International Symposium on Wood and Pulping Chemistry, ATIP, Nice, 11-14 June, p. 305.
- Gharehkhani, S., Sadeghinezhada, E., Kazi, S. N., Yarmanda, H., Badarudina, A., Safaei, M. R., and Zubir, M. N. M. (2015). "Basic effects of pulp refining on fiber properties—A review," *Carbohydrate Polymers* 115, 785-803.
- Giertz, H. W. (1964). "Contribution to the theory of tensile strength," EUCEPA/ European TAPPI Conference on Beating, Venice, Italy, September 1964. Proceedings, EUCEPA, pp. 39-47
- Hanna, R. J., Fisher, J. J., Krotm, M. J., Goyal, G. C., Packwood, R. E., and Ragauskas, A. J. (1998). "Differences in bleaching and refining response of displacement batch hardwood and softwood caused by pulping conditions and structure of residual lignin," International Pulp Bleaching Conference, Helsinki, Finland, TAPPI Press, Atlanta, pp. 323-328.
- Hartler, N. (1978). "Extended delignification in kraft cooking - A new concept," *Svensk Papperstidn.* 81(15), 483-484
- Hiltunen, E. (2003). "On the beating of reinforcement pulp," Doctoral Thesis. Laboratory of Paper Technology, Reports Series A16. Helsinki University of Technology, Espoo. 132 p.
- Hubbe, M. A., Venditti, R. A., and Rojas, O. J. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* 2(4) 739-788.
- ISO 5269-1 (2005). "Pulps - Preparation of laboratory sheets for physical testing - Part 1: Conventional sheet-former method," *International Organization for Standardization*, Geneva, Switzerland.
- ISO 1924-3 (2005). "Pulps and board - Determination of tensile properties - Part 3: Constant rate of elongation method (100 mm/min)," *International Organization for Standardization*, Geneva, Switzerland.
- ISO 5267-1 (1999). "Pulps - Determination of drainability — Part 1: Schopper-Riegler method," *International Organization for Standardization*, Geneva, Switzerland.
- ISO 534 (1988). "Paper and board - Determination of thickness and apparent bulk density or apparent sheet density," *International Organization for Standardization*, Geneva, Switzerland.
- ISO 23714 (2007). "Pulps — Determination of water retention value (WRV)," *International Organization for Standardization*, Geneva, Switzerland
- Johansson, B., J. Mjöberg, Sandström, P., and Teder, A. (1984). "Modified continuous kraft pulping – now a reality," *Svensk Papperstidn.* 87(10), 30-35.
- Joutsimo, O. P., and Asikainen, S. (2013). "Effect of fiber wall pore structure on pulp sheet density of softwood kraft pulp fibers," *BioResources* 8(2), 2719-2737.
- Kleen, M., Sjöberg, J., Dahlman, O., Johansson, L. S., Koljonen, K., and Stenius, P. (2002). "The effect of ECF and TCF bleaching on the chemical composition of soda anthraquinone and kraft pulp surfaces," *Nord. Pulp Pap. Res. J.* 17(3), 357-367. DOI: 10.3183/NPPRJ-2002-17-03-p357-363

- Kokkonen, P., Korpela, A., Sundberg, A., and Holmbom, B. (2002). "Effects of different types of lipophilic extractives on paper properties," *Nord. PulpPap. Res. J.* 17(4), 382-386. DOI: 10.3183/NPPRJ-2002-17-04-p382-386
- Laine, J., Lovgren, L., Stenius, P., and Sjöberg, S. (1994). "Potentiometric titration of unbleached kraft cellulose fibre surfaces," *Colloids Surf. A Physicochem. Eng. Aspects* 88(2-3), 277-287. DOI:10.1016/0927-7757(94)02834-6
- Laine, J., Stenius, P., Carlsson, G., and Ström, G. (1994). "Surface characterization of unbleached kraft pulps by means of ESCA," *Cellulose* 1(2), 145-160. DOI: 10.1007/BF00819664
- Laine, J., Stenius, P., Carlsson, G., and Ström, G. (1996). "The effect of ECF and TCF bleaching on the surface chemical composition of kraft pulp as determined by ESCA," *Nord. Pulp Pap. Res. J.* 11(3), 201-210. DOI: 10.3183/NPPRJ-1996-11-03-p201-210
- Lindström, T., and Carlsson, G. (1982). "The effect of chemical environment on fiber swelling," *Svensk Papperstidning* 85 (3), R14-20.
- Maloney, T. C. (2000). "On the pore structure and dewatering properties of the pulp fiber cell wall," Helsinki University of Technology, Dissertation, Acta Polytechnica Scandinavia, Chemical Technology Series No. 275, 52p.
- Mou, H., Iamazaki, E., Zhan, H., Orblin, E., and Fardim, P. (2013). "Advanced studies on the topochemistry of softwood fibres in low-consistency refining as analyzed by FE-SEM, XPS, and ToF-SIMS," *BioResources* 8(2), 2325-2336.
- Nordén, S., and Teder, A. (1979). "Modified kraft processes for softwood bleached-grade pulp," *Tappi* 62(7), 49-51.
- Ohno, N., Sawatari, A., and Yoshimoto, I. (1992). "Studies on distribution of extractives in pulp fibers by means of ESCA," *Jpn. Tappi J.* 46(10), 1295-1312.
- Paulapuro, H. (2000). *Papermaking. Part 1, Stock Preparation and Wet End*, Papermaking Science and Technol. Ser., No. 8, Fapet Oy, Helsinki.
- Page, D. H. (1989). "The beating of chemical pulps – The action and the effects," Transactions of 9th Fundamental Research Symposium, Fundamentals of papermaking. MEP, London, p. 1.
- Peng, Y. X., Valade, J. L., and Law, K. N. (1994). "Effects of recycling and blending of virgin fibers on paper properties," *China Pulp and Paper* 13(2), 3-9.
- Pulkkinen, I., Fiskari, J., and Alopaeus, V. (2008). "The use of fiber wall thickness data to predict handsheet properties of eucalypt pulp fibers," *O Papel* 69(10), 71-85.
- Pulkkinen, I., Fiskari, J., Alopaeus, V. (2010). New model for tensile strength and density of eucalyptus hand sheets – An activation parameter based on fiber distribution characteristics. *Holzforschung* 64, 201-209.
- Retulainen, E. (1997). "The Role of fiber bonding in paper properties," Laboratory of Paper Technology, Reports, Series A 7. Helsinki University of Technology, Espoo, 63 p
- Robinson, J. V. (1980). "Fiber bonding," in: Casey, J. P. (ed.): *Pulp and Paper. Chemistry and Chemical Technology*, Vol. II, 3rd ed. John Wiley & Sons, New York, pp. 915-963.
- Sanders, N. D., and Schaefer, J. H. (1995). "Comparing papermaking wet-end charge-measuring techniques in kraft and groundwood systems," *TAPPI* 78(11), 142-150.
- SCAN (2001). "Size distribution," SCAN-CM 40:01, Scandinavian Pulp, Paper and Board Testing Committee, Stockholm, Sweden.

- SCAN (2003). "Content of acetone-soluble matter," SCAN-CM 49:03. Scandinavian Pulp, Paper and Board Testing Committee, Stockholm.
- Shen, W., Parker, I. H., and Sheng, Y. J. (1998). "The effects of surface extractives and lignin on the surface energy of eucalypt kraft pulp fibres," *Adhes J. Sci. Technol.* 12(2), 161-174. DOI: 10.1163/156856198X00038
- Stone, J. E., Scallan, M. A., and Aberson, G. M. A. (1966). "The wall density of native cellulose fibers," *Pulp and Paper Magazine of Canada* 67(5), T263-T268.
- Stürmer, L., and Götttsching, L. (1979). "Physical properties of secondary fiber pulps under the influence of their previous history. Part 3: Influence of the paper manufacturing process," *Wochenbl. Papierfabr.* 107(3), 69-76.
- Teder, A., and Olm, J. (1981). "Extended delignification by combination of modified kraft pulping and oxygen bleaching," *Pap. Puu* 63(4a), 315-326.
- TAPPI T 258 om-11 (2011). "Basic density and moisture content of pulpwood," TAPPI Press, Atlanta, GA.
- TAPPI T 569 om-14 (2014). "Internal bond strength (Scott type)," TAPPI Press, Atlanta, GA.
- Vainio, A., and Paulapuro, H. (2007). "Interfiber bonding and fiber segment activation in paper," *BioResources* 2(3), 442-458.
- Wan Rosli, W. D., Mazlan, I., and Law K. N. (2009). "Effects of kraft pulping variables on the pulp and paper properties of *Acacia mangium* kraft pulp," *Cellulose Chem. Technol.* 43(1-3), 9-15.
- Wardrop, A. B. (1969). "Fibre morphology and papermaking," *Tappi J.* 52(3), 396-408.
- Widsten, P., Laine, J. E., Qvintus-Leino, P., and Tuominen, S. (2001). "Influence of carbohydrate physical state on pulping and bleaching chemistry," *J. Wood Chem. Technol.* 21(3), 227-245. DOI: 10.1081/WCT-100105373
- Willför, S., Hemming, J., Reunanen, M., and Holmbom, B. (2003). "Phenolic and lipophilic extractives in Scots pine knots and stemwood," *Holzforschung* 57, 359-372. DOI: 10.1515/HF.2003.054
- Wågberg, L., Winter, L., and Lindström, T. (1985). "Determination of ion-exchanged capacity of carboxymethylated cellulose fibers using colloid and conductometric titrations. Papermaking Raw Materials: Their interaction with the production processes and their effect on paper properties," Fundamental Research Symposium, Oxford, September, V. Punton. (ed.), Vol. 2, Mechanical Engineering Publ. Ltd. London, pp. 917-923.
- Wågberg, L., Odberg, L., and Glad-Nordmark, G. (1989). "Charge determination of porous substrates by polyelectrolyte adsorption. Part 1. Carboxymethylated, bleached cellulosic fibers," *Nordic Pulp Pap. Res. J.* 4(2), 71-76. DOI: 10.3183/NPPRJ-1989-04-02-p071-076
- Zhang, Y., Sjogren, B., Engstrand, P. and Htun, M. (1994). "Determination of charged groups in mechanical pulp fibres and their influence on pulp properties," *J. Wood Chem. Technol.* 14(1), 83-102. DOI: 10.1080/02773819408003087

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