Properties of highly hydrated softwood kraft fibers

Huaicheng Wang
Abstract
Chemical modification of pulp can improve pulp quality. Mercerization as a method to modify natural fiber has a history of two hundred years, and the mechanism of mercerization is a simple transformation from cellulose I to cellulose II. Mercerized pulp has been profoundly investigated. The target of this thesis was to understand whether mercerization and PFI-refining can improve the properties of softwood kraft pulp. First, softwood kraft pulp was treated with NaOH(15wt%) to produce highly hydrated softwood kraft fibers. Then, PFI-refining was introduced to improve the pulp property. Afterward, the modified pulp was made into handsheets. The original pulp and modified pulp were analyzed by different devices to demonstrate fiber properties and their chemical components. DSC tests and WRV were performed to explore the swelling property and thermoporometry. Various sheet strength tests are applied to study bonding potential and strength properties. Our results verified that mercerization (15wt% NaOH) can turn cellulose I into cellulose II, improve the swelling of the pulp, and increase the volume of micropores while decreasing the strength properties. Moreover, PFI-refining does not influence thermoporometry but can boost the tensile strength of the sheet made from both kraft pulp and mercerized pulp.

Keywords  Mercerization, PFI-refining, Cellulose II, Thermoporometry, Handsheets, Tensile strength
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Preface

First of all, I would like to express my gratitude to my thesis supervisor Professor Thaddeus Maloney, and my thesis advisors Antti Koistinen and Dr. Eero Hiltunen. Thank you for your guidance and for giving me the chance to finish my thesis work. It is my pleasure to work with them.

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Last, I am grateful to my friends and family who have kindly provided me with assistance and companionship. Especially, Fengyang Wang, my roommate, helped me a lot in both study and daily life. There are also some of my friends who have given me lots of companionships online even though they are in China and Japan.

Otaniemi, July 2022
Huaicheng Wang
## Symbols and abbreviations

### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
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<tr>
<td>HPEAC</td>
<td>High-performance anion exchange chromatography</td>
</tr>
<tr>
<td>NDBSW</td>
<td>Never-dried bleached softwood kraft pulp</td>
</tr>
<tr>
<td>NFW</td>
<td>Non-freezing water</td>
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<tr>
<td>WRV</td>
<td>Water retention value</td>
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1. Introduction

1.1 Background
The improvement of the quality of paper products has been a complication to be tackled by researchers and the industry. The quality of paper products can be improved by modifying their raw material: pulp. Pulps commonly used today comprise chemical pulp and mechanical pulp. Some modified pulps with better properties have the potential to replace them, such as hydrated pulp, which refers to pulp fibers that are highly swollen (mercerized) with concentrated sodium hydroxide. Under suitable conditions, sodium will intercalate the cellulose sheets to form a cellulose hydrate and swell individual fibrils and parent fibers. It is expected that such fibers can have high bonding and strength properties, leading to the property change in the paper product. Budtova et al. (2016) reviewed the dissolution of cellulose in NaOH/water solvent, revealing that swelling and mercerization are strongly connected to the dissolution. In recent years, there are a lot of research on mercerized pulp. Eronen et al. (2009) analyzed cellulose supramolecular structure after alkaline treatment using Raman spectroscopy and AFM and discovered that the NaOH concentration considerably influences how much pulp turns from cellulose I to cellulose II. Mercerization also changes the pulp at the molecular level. Wada et al. (2010) explained how hydrated cellulose II works at the molecular level. Specifically, the wet mercerized pulp has a larger unit cell and can hold more water molecules in its structure. Additionally, PFI-refining was adopted as a mechanical method to improve pulp properties. PFI mill, which is a high-energy, very low-intensity refining device, can beat the fiber to increase density and better the bonding between fibers (Kerekes, 2005). Since the effect of PFI-refining on mercerized pulp remains unclear, PFI-refining will be applied in the experiment to find the answer.

1.2 Target & hypothesis
The target of this master’s thesis is to understand the bonding potential and other properties of highly hydrated kraft pulp. The bonding potential can be demonstrated by measuring the tensile strength of sheets made from the pulp. The swelling of the pulp can be determined by water retention value and thermoporometry (pore size distribution, and pore volume)

The hypotheses were that
1. Compared with original kraft pulp, mercerization can improve the swelling of pulp fibers and the tensile strength of sheets made from the pulp.
2. PFI-refining can enhance the swelling and tensile strength of mercerized pulp, just like the kraft pulp, while the degree of improvement may vary.
2. Literature review

2.1 Hardwood & Softwood
Wood is the main resource for the papermaking industry and it can be divided into softwood and hardwood according to their structure and density. Hardwood which comes from angiosperm (broad-leaved) trees has vessels, which look like pores through the microscope. While softwoods which come from gymnosperm (coniferous) trees do not have vessel cells since softwoods have tracheids to transport water (Donaldson, Nanayakkara, and Harrington, 2017). Figure 1 exhibits the structure of hardwood and softwood.

Figure 1. Structure of softwood and hardwood. (a) The structure of softwood consists of earlywood tracheids, latewood tracheids, and uniseriate rays. (b) The structure of hardwood consists of vessels, libriform fibers, and multiseriate rays. (Reiterer, Sinn and Stanzl-Tschegg, 2002)
Figure 2. The hierarchical and porous structure of wood (a) The hierarchical structure of wood (b) Composition in cross-section and the longitudinal direction (Chen et al., 2020)

Wood has a hierarchical porous structure, with hollow channels oriented longitudinally. Individual wood cells have three layers of secondary walls (S1, S2, and S3) surrounding the internal lumen (that is, the void space in the center of the cell) (Chen et al., 2020). Figure 2 illustrates the hierarchical and porous structure of wood.

The three principal components that make up the stiff cell wall of wood are cellulose, hemicelluloses, and lignin (Marchessault, 1994). Cellulose is the main component of the plant cell wall and polysaccharide with a repeating unit of glucose. It will be introduced in detail in Chapter 2.3. Hemicellulose is a polysaccharide or carbohydrate composed of several different types of monosaccharides with side chains. The building units of hemicellulose are hexoses (D-glucose, D-mannose, and D-galactose), pentoses (D-xylose...
Larabinose, and -arabinose), or deoxyhexoses (L-rhamnose or 6-deoxy-L-mannose and rare L-fucose or 6-deoxy-galactose). Small amounts of certain uronic acids (4-OMethyl-D-glucuronic acid, Dgalacturonicacid, and Dglucuronicacid) are also present. Figure 3 illustrates the structure of the two most common hemicelluloses found in softwood, galactoglucomannan, and arabinogluconoxylan (Impola, 2016). The principal hemicellulose of softwoods is galactoglucomannan, with about 20%-25% of woody material (Riitonen et al., 2013). Lignin is one of the components making up the cell wall of plants and has the effect of connecting cells. Lignin is a polyphenol compound containing many negatively charged groups. Figure 4 exhibits an idealized structure of lignin from a softwood (Glazer and Nikaido, 1995).

Figure 3. Structure of the two most common hemicelluloses found in softwood (Impola, 2016)
The cellulose microfibrils contained in the lignin and hemicellulose matrix have both crystalline and amorphous microfibril regions, as demonstrated in cross-section and longitudinal images of the wood cell wall. Different chemical compositions contribute to different properties that ultimately influence wood properties (Pereira, Graça, and Rodrigues, 2004). The chemical compositions of softwoods and hardwoods are listed in Table 1. The fiber length of softwood is around 3mm, leading to better strength properties. Softwood generally has more hemicellulose and lignin. Meanwhile, the fiber length of hardwood is about 0.5–1.5 mm, which is smaller than that of softwood(2-4mm), bringing better optical properties and surface properties to paper products of these fibers. Hardwood is mainly for chemical pulps, comprising eucalyptus, acacia, birch, and aspen. Softwood can be the raw material of both chemical pulps and mechanical pulps, such as spruce and pine (Scott et al., 2002). Softwood pulp is an excellent raw material for papermaking and is frequently adopted in the production of text paper.
printing paper, and other technical, and industrial papers. The key is to choose the right raw material for the end use. Softwood is unsuitable for some applications where hardwood properties are more desired.

<table>
<thead>
<tr>
<th>Chemical Composition (wt%)</th>
<th>Softwood</th>
<th>Hardwood</th>
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<tbody>
<tr>
<td>Cellulose</td>
<td>40–44</td>
<td>40–44</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>30–32</td>
<td>15–35</td>
</tr>
<tr>
<td>Lignin</td>
<td>25–32</td>
<td>18–25</td>
</tr>
<tr>
<td>Extractives</td>
<td>5</td>
<td>2</td>
</tr>
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Table 1. General compositions of softwoods and hardwoods (Ahmad et al., 2020)

2.2 Kraft pulping

Pulp and papermaking is a technology with a long history. As early as 105 AD, Cai Lun in China invented the papermaking method with paper mulberry plant along with hemp rag and net scraps. The traditional steps of papermaking in ancient China consisted of harvesting, cooking, making sheets, packaging, and end-use (AbuBakr and Thompson, 2004).

Pulp is a fibrous substance made from plant fibers and obtained by different processing methods. It is the raw material for the papermaking industry. Several kinds of plant fiber can be made into pulp, such as bast fiber, seed fiber, and wood fiber (Bajpai, 2016). Wood fiber is the most used raw material among all materials, and most paper mills use the kraft pulping process (Biermann, 1996). The pulp made from the wood fiber is comprised of cellulose, lignin which binds the cellulose fiber together, and hemicellulose (Vázquez-Vuelvas et al., 2021). Untreated fibers in raw materials of pulp, such as wood and fiber crops, are too stiff and have weak bonds, making them unsuitable for paper production. The purpose of pulp production is to separate fibers from each other and modify the fibers to be suitable for paper production.

The pulp can be classified in many ways. For instance, it can be divided into mechanical pulp, chemical pulp, chemimechanical pulp, and several kinds of pulp according to the processing method. Pulp is prepared by separating fibers from their raw materials. In chemical pulping, chemicals and heat are employed to separate the fibers from each other by dissolving the lignin. In mechanical pulping, fibers are separated by physical pressure created by grinding or refining. Both methods are applied in chemimechanical pulping methods (Bajpai, 2016). Chemical pulp and mechanical pulp have their advantages and disadvantages. Mechanical pulp has a higher yield, ranging from 90% to 98%, while the yield of chemical pulp is less than 50% (Biermann, 1996). However, the high yield of mechanical pulp indicates that
lignin still exists in the pulp and paper. Lignin in the paper can be easily modified by the air and sunshine. Consequently, paper made from mechanical pulp becomes yellow and brittle easily. Additionally, chemical pulp usually has longer fiber than mechanical pulp, and thus chemical pulp has better strength properties. However, the mechanical pulp has better smoothness, leading to better printability. Moreover, mechanical pulp does not use heat and chemicals, resulting in a lower cost and less pollution emitted into the water and air (Bajpai, 2016).

Kraft pulp or sulfate pulp is one of the most common chemical pulps. About 130 million tons of kraft pulp are annually produced all over the world (Bruijninckx 2015). It can generally be divided into two types: bleached and unbleached. Unbleached kraft pulp can be used to manufacture kraft paper, paper sacks, kraft liner boards, and general packaging paper and cardboard. Bleached kraft pulp can be utilized to make high-grade printing paper (Bajpai, 2018).

The goal of the kraft pulping process is to decompose and dissolve extractives, lignin, and some hemicelluloses. It is crucial to keep the hemicelluloses as much as possible in pulping process as hemicelluloses contribute to many paper properties (Hu, Fu, and Liu, 2013). One of the most imperative kraft pulping processes is that cut wood is treated with white liquor, a hot mixture of water, sodium hydroxide, and sodium sulfide. The effect of white liquor is to break the bonds between lignin and cellulose to separate cellulose. Besides, the pulping reactions (delignification) require 0.5–3 h at high temperatures (150–175°C) (Paulapuro et al., 2000). Both batch and continuous pressurized digesters are applied. Afterward, the left black liquor containing the dissolved lignin is usually burned in the recovery boiler. Compared with the other chemical pulping process, the effect of white liquor is not strong (Hintz, 2001). Therefore, fibers are strong, and the paper made from them has excellent strength properties, such as folding resistance and tensile strength.

The main function of the kraft cooking process is to remove the lignin and keep the hemicellulose. In the kraft pulping process, three lignin removal reactions occur: initial delignification, bulk delignification, and residual delignification. The initial delignification appears before the temperature reaching to 150°C. In this process, α-aryl and β-aryl ether bonds in phenolic units of lignin break, leading to a low rate of delignification. The cleavage mechanisms of these two bonds are presented in Figure 5. Nonetheless, carbohydrates degrade in this stage (Gustavsson et al., 1997; Paulapuro et al., 2000).
Most lignin is dissolved and degraded during the bulk delignification stage. It emerges when the temperature is above 150°C. The fracture of the non-phenol β-aryl ether bond occurs, and around 90% of lignin is removed (Sixta, 2006). The cleavage mechanism is illuminated in Figure 5. Meanwhile, the rate of carbohydrate degradation decreases (Paulapuro et al., 2000). In the residual delignification process, the carbon-carbon bond starts to break, the loss of carbohydrates appears, and the pulp yield and pulp quality decrease. Therefore, the time of the residual delignification process should be controlled to maintain the carbohydrates.

![Figure 5](image)

**Figure 5.** (a) The fracture of the phenol type α-aryl ethers in alkaline conditions (b) The cleavage of the phenol type β-aryl ethers (c) The fracture of the non-phenol type β-aryl ethers in alkaline conditions (Xu, Li, and Mu, 2016)

The main goal of controlling the parameters in the cooking process is to improve the selectivity of delignification. It can be determined by factors such as cooking time, cooking temperature, amount of alkali used, and sulfidity. The alkali concentration has a significant influence on the speed of delignification, pulp yield, and strength. Similarly, the degree of sulfidation noticeably impacts the cooking rate, pulp yield, and strength. Therefore, the composition and some other parameters of white liquor are essential factors in the control of the kraft pulping process. Additionally, some chemicals can
be added to improve the production process. For example, anthraquinone (AQ) can serve as a digester additive to increase the rate of the delignification reaction and the yield of carbohydrates (Hintz, 2001). The mechanism is that anthraquinone functions as a redox catalyst by oxidizing cellulose and reducing lignin (Aravamuthan, 2004).

2.3 Cellulose
Cellulose is the most abundant renewable organic resource on earth. It exists widely in higher plants, bacteria, animals, algae, and other organisms. In the 1980s, the annual global consumption of commercial cellulose provided by higher plant life was already around 150 million tons (MARCHESSAULT and SUNDARARAJAN, 1983). Since the production of cellulose must be much more today, cellulose has huge economic development value. From the 1950s to the 1960s, the development and research of cellulose resources were highly affected by the rise of synthetic polymer materials. In the early 1970s, this kind of renewable resource that had been neglected was paid attention to again due to the oil crisis in the world. Utilizing these abundant renewable resources is crucial to handle the energy difficulty in the future. Therefore, industry and academia all over the world attach great importance to the research and development of cellulose.

2.3.1 Molecular structure
Cellulose molecular structure is the basis for the researchers to clarify the properties of cellulose and propose new applications. Cellulose is a long, linear, biobased polymer with a repeating unit of anhydroglucose (AGU), and β-(1-4) glycosidic bonds connect repeating units to form long chains. Figure 6 exhibits the molecular structure of cellulose. The repeating unit has three hydroxyl groups. Specifically, the primary hydroxyl group is on C6, and the secondary hydroxy groups are on C2 and C3. It is responsible for the hydrogen bonds within and between molecules of cellulose, making it insoluble in neither water nor organic solvents. Hydroxyl groups at different ends of the cellulose chain exhibit different behaviors to gain or lose electrons. The hydroxyl group in the C1 end is reducing, while the C4 hydroxyl group is non-reducing (Klemm et al., 1998).

Figure 6. Molecular structure of celluloses repeating units with its reducing and non-reducing ends (French, 2017)
The average molecular mass is determined by the product of the DP and the repeating AGU molecular mass. The values of DP in cellulose samples vary widely with the species where the cellulose is from and pretreatment. In nature, the cellulose polymer chains are believed to have a DP of around 10000. These chains, which are linked by intermolecular hydrogen bonds and aggregated in lignocellulosic biomass into bundles, are commonly referred to as microfibrils. The smallest fibrils in these bundles are composed of 36 or 24 cellulose chains. Fernandes et al. determined if the number of chains in a microfibril is fixed, while they reported the existence of a 24-chain model in spruce cellulose (Fernandes et al., 2011).

### 2.3.2 Cellulose sources and forms

Cellulose is the most widely abundant polysaccharide in nature, accounting for more than 50% of the carbon content of various plants. Nature produces $10^{11}-10^{12}$ tons of cellulose every year (Klemm et al., 1998). With the continuous consumption of non-renewable resources, people have also shown great interest in natural polymers. It is also a critical chemical raw material at present. Cellulose is a major constituent of paper and pulp, as well as textiles made from cotton and other plant fibers (Bakri, Rahman, and Chowdhury, 2022). Cellulose exists in many aspects of people’s lives.

Cellulose is the main structural element of the cell wall of green plants. Cellulose in woody plants has been isolated for over a century, through a large-scale chemical process that dissolves lignin and hemicellulose during a combined chemical processing. In addition to plants, there are two other known sources of cellulose: bacteria (bacterial cellulose) and tunicates (animal cellulose) (Bakri, Rahman, and Chowdhury, 2022).

Studies on the supramolecular structure of native cellulose reveal that it is composed of crystalline and amorphous phases, cellulose chains are present in crystalline microfibril, and their surfaces are amorphous cellulose (Ruel, Nishiyama, and Joseleau, 2012). Amorphous cellulose regions have a low level of order and are easier to react with the penetrated reactants (Ciolacu, Ciolacu, and Popa, 2011). Cellulose has different crystal forms or allomorphs: cellulose I, II, III, and IV. Single, linear cellulose chains, with intramolecular hydrogen bonding, can form cellulose sheets. However, some evidence suggests that cellulose IV is considered a distorted form of cellulose I, rather than a genuine allomorph (Newman, 2008). Figure 7 illustrates different allomorphs and how they transfer.
Cellulose I is the naturally occurring form of cellulose, and cellulose chains form sheets connected by hydrogen bonds and van der Waals bonds. Hydrogen bonds work within the sheets, while van der Waals bonds work between the sheets (Klemm et al., 1998). Two forms of native crystalline cellulose exist, cellulose I\(\alpha\) and cellulose I\(\beta\). The difference lies in their morphology and source. Specifically, Cellulose I\(\alpha\) has a triclinic lattice with one chain per unit cell, and it is the predominant form of bacterial cellulose; cellulose I\(\beta\) has a monoclinic lattice with two chains per unit cell, and it is the main form of cellulose in higher plants (such as wood and cotton) and tunicate. However, in nature cellulose I\(\alpha\) and cellulose I\(\beta\) always coexist in the same microfibril, which is a fine fibril, on the inner surface of the primary cell wall (Rongpipi et al., 2019).

Cellulose II is the “Man-made” form of cellulose prepared by the concentrated sodium hydroxide solution treatment of Cellulose I or by dissolving the cellulose and then regeneration. After the alkali treatment, the fiber was swollen, and its diameter increased. Thus, cellulose II materials give a ‘silk-like’ texture, and cotton fabrics after mercerization (treated by NaOH solution) had better smoothness, luster, and mechanical properties. This is why they are applied in the textile industry. The distinctions between cellulose I and cellulose II at the molecular level are hydrogen bonding patterns and cellulose chain direction. Cellulose I chains are parrel, while cellulose II chain directions are anti-parrel. The antiparallel arrangement is thermodynamically more favorable than the parallel arrangement. Klemm et al. (1998) suggested that the hydrogen bonds between the macromolecular chains are broken up, contributing to relieving the internal stress stored in the fiber. Through stretching, the macromolecules are aligned again, new molecular bonds are established at new positions, and the intermolecular force is larger than that before swelling. The hydrogen bonds between the
oriented fibers are fixed, and the fibers are in a lower energy state, making them stable. Cellulose chains in parallel microfibrils intermingle and form new antiparallel crystals during the process.

Cellulose III is prepared by the treatment of cellulose I and cellulose II with diamine solution or liquid ammonia at -80 °C, resulting in cellulose III. Similar to their parent forms, cellulose III has parallel chains, while cellulose III presents antiparallel chains. They have the same unit cells. In Cellulose III, hydrogen bonding exists between the sheets and the molecules. The conversion of cellulose I and cellulose II to cellulose III is reversible, and cellulose III can revert to its parent form via hydrothermal treatment. The conversion from cellulose I to cellulose III dramatically decreases crystallinity and crystallite size, leading to the increase in accessibility and reactivity of cellulose III (Wada et al., 2004). As described before, cellulose IV is formed by cellulose III treated in a suitable liquid, like glycerol at a high temperature under tension (Newman, 2008).

Since cellulose IV is produced by the treatment of cellulose II or III in polar liquid at high temperature, it is called high-temperature cellulose and is the fourth crystal modification of cellulose. Generally, it is obtained by treating cellulose I, II, and III at high temperatures. Therefore, cellulose IV is also divided into cellulose IV1 and IV2 according to the different raw materials of the motif. The infrared spectrum of cellulose IV1 is similar to that of cellulose I. The infrared spectrum of cellulose IV2 is similar to that of cellulose II.

### 2.3.3 Swelling and dissolution

There is no clear boundary between the swelling and the dissolving of cellulose (le Moigne et al., 2007). The same system can work as a swelling agent or a dissolving agent per the properties of the cellulose and the operating conditions. The swelling and dissolution of cellulose fibers strongly depend on the quality of this system. The cellulose swelling process maintains the overall structure of cellulose as a part of particles, fibers, or film, while cellulose dissolution disperses cellulose in solution to form a single-phase system, destructing the supramolecular structure of cellulose (Li et al., 2018).

The reasons for dissolving cellulose are to prepare regenerated cellulose from dissolved cellulose, chemically modify cellulose in a homogeneous environment, and degrade cellulose more efficiently. Cellulose is neither soluble in water nor common organic solvents, such as alcohol, ether, acetone, and benzene. It is also not soluble in dilute alkaline solution. Therefore, it is relatively stable at room temperature because of the hydrogen bonding between cellulose molecules. Hydrogen bond does not automatically cause difficulty in solubility, and the hydrogen bonding between cellulose is stronger than that between water and the compound (Wohlert et al., 2022).
Some traditional methods of dissolving cellulose have a history of more than a hundred years. A strong NaOH solution can dissociate hydrogen bonds of cellulose to promote its dissolution (Zhang et al., 2010). Detailed information about this method will be discussed in the next chapter. Schweizer et al. reacted ammonia water with the copper hydroxide to form a blue solution. This solution has a strong ability to dissolve cellulose and is called Schweizer's reagent. Generally, it is the reaction of cellulose with a cuprammonium solution to form a complex compound, which can be dissolved in water (Sayyed, Deshmukh, and Pinjari, 2019).

Several kinds of strong acids can dissolve cellulose at high concentrations, such as concentrated sulfuric acid, trifluoroacetic acid, concentrated phosphoric acid, or ionic liquids (Chundawat and Agarwal, 2019). The hydroxyl groups of cellulose will be protonated. Phosphoric acid swollen cellulose (PASC) can serve as a cellulose substrate to assess the activity of cellulose-degrading enzymes. The process of cellulose dissolution in phosphoric acid involves the reaction between the hydroxyl groups in cellulose and phosphoric acid to form cellulose phosphate, as well as the formation of hydrogen bonding between hydroxyl groups and water molecules or hydrogen ions (Zhang et al., 2009).

Another well-known method is called ‘viscose’ (NaOH + CS₂). The pulp and NaOH solution are mixed at a certain temperature to produce alkaline cellulose. The degraded cellulose reacts with CS₂ to generate a cellulose xanthate, which can be dissolved in strong alkali to produce the corresponding viscose. A certain amount of sulfuric acid and sodium sulfate are pressed into the spinneret on the spinning machine after a series of aging, defoaming, and filtration; then, the dipping bath is adopted to solidify and stretch it for finally making viscose (Li et al., 2018). The H₂SO₄ in the solidification liquid promotes the formation of cellulose xanthate. Adding a certain amount of Na₂SO₄ can accelerate the inflow of salt with a higher concentration into the salt bath, and ZnSO₄ can exchange with sodium cellulose xanthate. When the viscose liquid is neutralized by sulfuric acid, its cellulose xanthate will form new cellulose through a hydrolysis reaction, and it will rapidly solidify with the traction and stretching during the period, resulting in a regenerated fiber, which is often referred to as viscose fiber (Huber et al., 2012). This traditional method of producing viscose requires the use of CS₂, which provokes severe pollution to the environment.

Some revealed that LiCl/DMAC solution can dissolve cellulose, and cellulose can be dissolved in LiCl/DMAC solution with a concentration of 9%. The principle of cellulose dissolution in this solution system is that the LiCl and DMAC undergo a complexation reaction, and then the hydrogen in the
cellulose hydroxyl group in the free state is combined with the alkaline chloride ion to form a hydrogen bond, which will destroy the original cellulose hydrogen bond and then dissolve cellulose (McCormick and Callais, 1987).

Ionic liquids (ILs) are considered a “green solvent”. The ionic liquid is a salt that melts below 100°C and is produced from non-toxic and harmless raw materials. The ability of ILs to dissolve cellulose was reported in 2002 (Swatloski et al., 2002). The anions can react with the hydroxyl groups in cellulose to dissolve the cellulose when the solution was heated to 100°C-110°C.

N-Methylmorpholine-N-oxide monohydrate (NMMO) can work as a solvent for cellulose to produce lyocell. The electron pair of the oxygen atom on the N-O bond in the NMMO molecule can generate a hydrogen bond with the hydrogen of the hydroxyl group close to it. Since the nitrogen-oxygen bond is a coordination bond, the oxygen atom has a higher electronegativity, and it has a stronger connection with the hydrogen atom. The ability of the nucleus to form hydrogen bonds is also ascribed to its strong electronegativity, and the hydrogen bonds formed by it have higher stability (Rosenau et al., 2001). The process of dissolving cellulose indicates destroying the hydrogen bonds formed between cellulose molecules and then producing Lyocell fibers by the “organic solvent dry jet wet spinning” (Fink et al., 2001).

Urea / NaOH / water systems can dissolve cellulose at low temperatures. 2-4 wt% urea can improve the solubility of cellulose in 6-8 wt% NaOH solution (Zhou and Zhang, 2000). Urea does not have a strong direct interaction with cellulose and NaOH. Urea can work through van der Waals forces and accumulate in the hydrophobic regions of cellulose to prevent the reaggregation of dissolved cellulose molecules. In this system, OH breaks the hydrogen bonding between celluloses, urea stabilizes the hydrophobic area of cellulose, and Na+ hydrations can stabilize the hydrophilic hydroxyl groups (Xiong et al., 2014).

2.4 Mercerization
2.4.1 History of mercerization
In 1844, John Mecer treated the cotton with 20-30% NaOH and did not apply tension. He found that the cotton had larger tensile strength and swelled. In 1890, Horace Lowe performed the mercerization on cotton with tension, revealing that the fabric had a silk-like luster since the mercerization had been applied in the textile industry (Holme and Blackburn, 2019). Now mercerizing is not only used in the textile field but also in other fields.
2.4.2 Mechanism of mercerization

Figure 8 illuminates how mercerization works. First, NaOH can enter the region of amorphous cellulose and crystal cellulose I. Sodium ions can combine water molecules and form sodium hydrates. Then, they break the hydrogen bonding among the cellulose. As the sodium hydrates enter in, Cellulose I combines with sodium ions to form the Na-cellulose, swelling the individual fibrils and the parent fiber. Afterward, the cellulose is washed with water to remove Na ion, so as to form cellulose II. Hence, cellulose I converts to cellulose II after the mercerization (A. Sayyed, Deshmukh, and Pinjari, 2019).

![Figure 8. Schematic representation of the mercerization process (A. Sayyed, Deshmukh, and Pinjari, 2019)](image)

The different concentrations of NaOH and the temperature influence the mercerization. NaOH concentrations below 5 wt%, and especially below 1 wt%, do not affect the structure of cellulose I. However, even 1 wt% NaOH can convert cellulose I to cellulose II when a low temperature (−17 °C) is applied (Duchemin, 2015). The effect of different NaOH concentrations and reaction times can vary a lot on the thermal and mechanical properties of fibers. The increasing NaOH concentration can contribute to the removal of other organic materials and impurities such as wax, ash contents, and cellulose. The reduction of these substances may enhance the tensile strength of the fiber. Nonetheless, high NaOH concentration and long immersion time can damage the fibers and affect their properties (Noori et al., 2021). Therefore, many factors can impact mercerization, including temperature, reaction time, and NaOH concentration.

2.4.3 Mercerized pulp
Mercerized pulp is treated with hot and diluted alkali. The surface structure, internal structure, fiber morphology, and fiber polymerization degree of mercerized pulp are significantly different from those of ordinary pulp. Mercerized pulp has some special properties, such as better tensile strength, porosity, and some other properties. Therefore, it is widely used in textiles, medicine, special paper manufacturing, the chemical industry, bioengineering, and other industries.

Liqun Wu et al. (2007) presented the fiber analysis results of different kinds of pulp treated with different concentrations of NaOH under different conditions. The fiber length and width of each pulp fiber did not exhibit any significant changes after the mercerization process. Compared with the cross-section of non-woven pulp, the average surface area of the mercerized pulp decreased, the twist angle increased, and the fibers were bent. There were the main changes in the twist angle of the bamboo and the separation of the pulp.

Mercerized pulp is broadly applied to the raw material of filter paper because it has a better porosity which is crucial for filtration efficiency. Nevertheless, low dispersion efficiency has always been challenging, and mechanical beating was considered to wrestle with this complication (Hao et al., 2014). Mercerization can also work as a method to improve the conversion of cellulose biomass into glucose because the enzymatic hydrolysis of cellulose II hydrate is faster than that of cellulose I (Wada et al., 2010). In addition, mercerization can make the TEMPO-catalyzed oxidation of pulp more effective for producing nanofibrillated cellulose (Pönni et al., 2014).
3. Material and methods

3.1 Materials
Never-dried bleached softwood kraft pulp (NDBSW) was obtained from a Finnish pulp manufacturer (dry matter content around 37%).

3.1.1 Alkali treatment of pulps
The treatments were executed at room temperature. Kraft pulp was alkali treated by preparing a solution with 10 w% kraft pulp and 25 w% sodium hydroxide solution. The NaOH concentration of the reacting solution was 15 wt%. After treatment, the pulp was pressed to remove most of the NaOH, diluted to the dry matter content of 3% with deionized water, and then neutralized with 1 M H$_2$SO$_4$. The final pH was 5.5. The pulp was washed with deionized water to remove the salt until the conductivity of the pulp suspension was less than 50 µS/cm. A Büchner funnel was utilized to filter the excess water. The dry matter content of the mercerized pulp was 11.25%.

3.1.2 PFI-refining
The fibers in NDBSW and alkali-treated pulp were separated from each other by disintegrator. Six samples of dry kraft pulp and alkali-treated pulp were weighed in an amount of 30 g. The cold disintegration follows ISO 5263-1. The diluted NDBSW and mercerized pulp were beaten by a PFI beating machine (model PFI-Mill 60, HAMJERN as) with 100, 200, 400, 800, and 1600 revolutions with the TAPPI T 248 method.

3.1.3 Hornification
The NDBSW and mercerized pulp were oven-dried at 105°C. The dried sample was rewet in deionized water.

3.1.4 Preparation of sheets
The 10% NDBSW and mercerized pulp with different refining revolutions were made into 80 g/m² hand sheets by Sheet Mold (model FI 101, Lorentzen & Wettre), wet pressed by a pneumatic sheet press machine (model SE 040, Lorentzen & Wettre), and dried by drum dryer (model FI 119, Lorentzen & Wettre) for two hours at 95°C-105°C according to the ISO 5269-1 method. The water used was deionized. After the preparation of hand sheets, the sheets were stored in a specific condition of 23°C and 50% humidity, according to ISO standard 187.

3.2 Methods
3.2.1 Raman spectroscopy
The dried NDBSW and alkali-treated pulp were analyzed using Renishaw in-Via™ Confocal Raman Microscope. The grating of the spectrogram used was
2400 grooves/mm. Besides, a 20X camera and green laser (wavelength 532nm) were used. The integration time for each spectrum was 0.5 s. The number of accumulations was 200. The crystallinities of cellulose I and cellulose II were calculated by the equations from Agarwal et al. (2010; 2021):

\[
\%\text{Cellulose I} = \frac{(I_{380} - I_{1096})}{0.0065} \\
\%\text{Cellulose II} = \frac{(I_{577} - I_{1096})}{0.0017}
\]

where \( I_{380} \) indicates the band intensity at 380 cm\(^{-1}\); \( I_{1096} \) denotes the band intensity at 1096 cm\(^{-1}\); \( I_{577} \) represents the band intensity at 577 cm\(^{-1}\).

### 3.2.2 Carbohydrate analysis

The NDBSW and mercerized pulp were air-dried and introduced into Wiley Mini Mill 475-A and ground into powder. The dry matter content was determined before sugar analysis. The pulp samples were diluted by a factor of 100, and SRS was diluted by a factor of 50. The carbohydrate compositions were determined with HPAEC (Dionex ICS-3000 Ion Chromatography System). The measurement method of carbohydrate analysis was followed by Sluiter et al. (2008). Carbohydrates composition was calculated by:

\[
\%R_{\text{sugar}} = \frac{\text{conc. detected by HPLC, mg/mL}}{\text{known conc. of sugar before hydrolysis, mg/mL}} \times 100
\]

\[
C_x = \frac{C_{\text{HPLC}} \times \text{dilution factor}}{\%R_{\text{sugar}}/100} \times 100
\]

\[
C_{\text{anhydro}} = C_x \times \text{Anhydro correction}
\]

\[
\%\text{Sugar extractive free} = \frac{C_{\text{anhydro}} \times V_{\text{filtrate}}}{\text{OWD}_{\text{sample}}} \times 100
\]

where \( \%R_{\text{sugar}} \) indicates the sugar recovery rate of each sugar; \( C_x \) refers to sugar concentration in mg/mL of sugar in the hydrolyzed; \( C_{\text{HPLC}} \) is conc. of sugar as determined by HPLC, mg/mL; \( C_{\text{anhydro}} \) signifies the concentration of the polymeric sugars; Anhydro correction is 0.88 (or 132/150) for C-5 sugars (xylose and arabinose) and 0.90 (or 162/180) for C-6 sugars (glucose, galactose, and mannose); \( \%\text{Sugar extractive free} \) stands for the sugar proportion of the extractive-free samples; \( V_{\text{filtrate}} \) is 86.73 ml, which is the volume of filtrate of the hydrolyzed sample; \( \text{OWD}_{\text{sample}} \) represents the oven-dried weight of the sample before hydrolysis.

### 3.2.3 Water retention value

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The water retention value (WRV) was measured following the modified SCAN-C 102 XE standard in the Thermo Scientific SL40FR centrifuge. Additionally, 1.54±0.1 g bone dry pulp samples whose dry matter content was 13-16% (±5%) were weighed to have a 1700 g/m² formed in a sample cup of the centrifuge. The samples were centrifuged with a 3000 g force for 15 min at 23 °C, weighed immediately, and dried at 105 °C until reaching constant weight. Afterward, the dry pulp was weighed. The samples used in this test were NDBSW and mercerized pulp refined with different revolutions, as well as the hornified NDBSW and mercerized pulp. WRV of the sample was calculated by

\[ W_{RV} = \frac{W_w - W_d}{W} \]

where \( W_w \) denotes the wet pulp weight, and \( W_d \) represents the dry pulp weight.

### 3.2.4 Fiber analysis

The pulp was analyzed using Valmet Fiber Image Analyser FS5 according to the instructions of device manufacturers. Fiber length, fiber width, fibrillation, kink, and curl were measured by the analyzer. The calibration program ran automatically before the measurements.

### 3.2.5 Thermoporometry measurements

Thermoporometry measurements were conducted on a Mettler Toledo DSC 3+. First, all bulk water was frozen by cooling the sample. Then, the temperature was increased, allowing bulk water and water inside the pores to be melted. Subsequently, the sample was cooled slowly, making all water in the pores frozen. Finally, all water was melted by heating the sample, and the curve was made automatically. DSC runs were repeated three times for each sample. The results of NFW(non-freezing water), pore diameter, and cumulative pore volume were obtained from the curves (DEODHAR and LUNER, 1980; Maloney, Paulapuro, and Stenius, 1998; Maloney, 2015).

\[ NFW = MC - \frac{\Delta H}{(\Delta H/W)} \]

where NFW denotes non-freezing water, g/g; MC represents moisture content, g liquid / g solids; \( \Delta H \) indicates melting heat from the experiment, mJ; \( \Delta H \) signifies specific heat of melting for normal water; W refers to the mass of the dry fiber, mg.

### 3.2.6 Simons’ Staining

The Simons’ Staining method was performed by applying a technique developed by Akhtar(1995). This Simons’ Staining dye consists of a 1% aqueous solution of Pontamine sky Blue 6BX and a 1% aqueous solution of Sun yellow mixed in a 1:1 ratio. Both refining and unrefined NDBSW and mercerized
pulp were flooded with the stain on the glass slide. Slides were heated at 60 °C until evaporation. A cover glass was placed over the fibers, which were then rinsed with distilled water to remove excess stain. Afterward, fibers were microscopically examined and immediately photographed by Leica DM750. The same process took place in the hornified NDBSW and hornified mercerized pulp.

3.2.7 Sheet properties test
The thickness, density, and bulk of the sheet were measured by Thickness Tester (model SE 250, Lorentzen & Wettre) and balanced according to ISO 534. Grammage was the ratio of sheet mass to sheet area under ISO 536.

Tensile properties of kraft pulp sheets were measured by Tensile Tester with Fracture Toughness (model SE 064, Lorentzen & Wettre). Considering that alkali-treated pulp sheets can break easily, their tensile properties were measured by a Tensile and Compression Testing Machine (model MTS 400, MTS System Norden) according to ISO 1924-3.

The internal bond strength of sheets was measured by Internal Bond Tester(model H411, Huygen Corporation) per Tappi T569. The zero span strength of sheets was measured by Zero Span Tester (model Z-Span 1000, Pulmac) following ISO 15361.
4. Results and discussion

4.1 Raman spectroscopy

The Raman spectra, in the region of 200–1500 cm\(^{-1}\) of NDBSW and mercerized pulp, are illustrated in Figure 9. As revealed by comparing the two curves, some peaks significantly change (900 and 1263 cm\(^{-1}\)), and some new peaks appear (353, 577, and 1463 cm\(^{-1}\)), owing to the mercerization. The peak at 380 cm\(^{-1}\) is observed at the NDBSW curve. It is related to cellulose I and can be used to calculate the amount of crystalline cellulose I. The reason why the peak at 380 cm\(^{-1}\) was used is that the Raman ratio plot for 380/1,096 in univariate analysis has better regression and sensitivity compared with WAXS analysis (Agarwal, Reiner, and Ralph, 2010). The peak at 577 cm\(^{-1}\) is displayed at the mercerized pulp curve and can be adopted to calculate the amount of crystalline cellulose II as the Raman ratio plot for 577/1,096 is sensitive to the detection of cellulose II (Agarwal et al., 2021).

**Figure 9.** Raman spectra, in the region 200–1500 cm\(^{-1}\), of NDBSW and mercerized pulp

The Raman spectra, in the region of 200-1500 cm\(^{-1}\) of NDBSW and mercerized pulp, are illustrated in Figure 9. As revealed by comparing the two curves, some peaks significantly change (900 and 1263 cm\(^{-1}\)), and some new peaks appear (353, 577, and 1463 cm\(^{-1}\)), owing to the mercerization. The peak at 380 cm\(^{-1}\) is observed at the NDBSW curve. It is related to cellulose I and can be used to calculate the amount of crystalline cellulose I. The reason why the peak at 380 cm\(^{-1}\) was used is that the Raman ratio plot for 380/1,096 in univariate analysis has better regression and sensitivity compared with WAXS analysis (Agarwal, Reiner, and Ralph, 2010). The peak at 577 cm\(^{-1}\) is displayed at the mercerized pulp curve and can be adopted to calculate the amount of crystalline cellulose II as the Raman ratio plot for 577/1,096 is sensitive to the detection of cellulose II (Agarwal et al., 2021).
The crystallinity of Cellulose I / II (%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>The crystallinity of Cellulose I / II (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBSW</td>
<td>Cellulose I, 13.0%</td>
</tr>
<tr>
<td>Mercerized pulp</td>
<td>Cellulose II, 50.3%</td>
</tr>
</tbody>
</table>

**Table 2. The crystallinity of Cellulose I/II**
The Raman intensity ratios $I_{380}/I_{1096}$ and $I_{577}/I_{1096}$ were linearly correlated with the amounts of cellulose I and cellulose II (Schenzel and Fischer, 2001; Agarwal, 2014). After the measurement of peak height and calculation (Agarwal et al., 2021; 2010), the crystallinity of Cellulose I in NDBSW was 13.0%, and the crystallinity of Cellulose II in mercerized pulp was 50.3%. However, the crystallinity of cellulose I was much smaller than that of Cellulose II ascribed to the lack of a calibration set.

At the molecular level, the complete transformation from cellulose I to cellulose II occurred during the mercerization process.

### 4.2 Carbohydrate analysis

<table>
<thead>
<tr>
<th>Components of pulp samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBSW</td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>Cellulose % on pulp</td>
</tr>
<tr>
<td>Xylan % on pulp</td>
</tr>
<tr>
<td>Glucomannan % on pulp</td>
</tr>
<tr>
<td>Arabinan % on pulp</td>
</tr>
<tr>
<td>RhamGal % on pulp</td>
</tr>
<tr>
<td>C5 % on pulp</td>
</tr>
<tr>
<td>C6 % on pulp</td>
</tr>
<tr>
<td>Hemicellulose on pulp</td>
</tr>
</tbody>
</table>

**Table 3. Components of pulp samples**
As demonstrated in Table 3, the mercerization decreased the amount of hemicellulose in the pulp from 19.06% to 9.23%.

Hydroxyl ions can destroy the hydrogen bond in the fiber. Sodium hydrates formed by sodium ions also contributed to this process since they can penetrate and split the inner fiber structure (Budtova and Navard, 2016). NaOH dissolves hemicelluloses. Compared with cellulose, hemicellulose has a lower degree of polymerization and a weaker hydrogen bonding capacity (Li et al., 2019). Therefore, hemicellulose was easier to lose.
The dissolved hemicelluloses were lost from the sample when the sample was diluted in its Na-cellulose form and washed away.

4.3 Fiber analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lc(n) [mm]</th>
<th>Lc(l) [mm]</th>
<th>Lc(w) [mm]</th>
<th>Fiber width [µm]</th>
<th>Fibrillation [%]</th>
<th>Kink [1/m]</th>
<th>Curl [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBSW 0 REV</td>
<td>0.70</td>
<td>1.74</td>
<td>2.42</td>
<td>28.29</td>
<td>0.07</td>
<td>4317.60</td>
<td>15.26</td>
</tr>
<tr>
<td>NDBSW 100 REV</td>
<td>0.69</td>
<td>1.73</td>
<td>2.40</td>
<td>28.18</td>
<td>0.08</td>
<td>3930.20</td>
<td>14.32</td>
</tr>
<tr>
<td>NDBSW 200 REV</td>
<td>0.66</td>
<td>1.70</td>
<td>2.40</td>
<td>28.08</td>
<td>0.09</td>
<td>3841.85</td>
<td>14.27</td>
</tr>
<tr>
<td>NDBSW 400 REV</td>
<td>0.69</td>
<td>1.77</td>
<td>2.48</td>
<td>28.04</td>
<td>0.09</td>
<td>3725.20</td>
<td>12.45</td>
</tr>
<tr>
<td>NDBSW 800 REV</td>
<td>0.68</td>
<td>1.70</td>
<td>2.39</td>
<td>28.32</td>
<td>0.11</td>
<td>3682.15</td>
<td>15.05</td>
</tr>
<tr>
<td>NDBSW 1600 REV</td>
<td>0.66</td>
<td>1.70</td>
<td>2.40</td>
<td>28.79</td>
<td>0.18</td>
<td>3615.10</td>
<td>15.07</td>
</tr>
<tr>
<td>Mercerized 0 REV</td>
<td>0.55</td>
<td>1.08</td>
<td>1.55</td>
<td>28.87</td>
<td>0.29</td>
<td>9177.80</td>
<td>36.70</td>
</tr>
<tr>
<td>Mercerized 100 REV</td>
<td>0.58</td>
<td>1.18</td>
<td>1.68</td>
<td>28.78</td>
<td>0.27</td>
<td>8788.90</td>
<td>35.37</td>
</tr>
<tr>
<td>Mercerized 200 REV</td>
<td>0.61</td>
<td>1.26</td>
<td>1.77</td>
<td>28.10</td>
<td>0.18</td>
<td>8267.50</td>
<td>34.02</td>
</tr>
<tr>
<td>Mercerized 400 REV</td>
<td>0.55</td>
<td>1.18</td>
<td>1.73</td>
<td>28.79</td>
<td>0.24</td>
<td>8433.50</td>
<td>33.50</td>
</tr>
<tr>
<td>Mercerized 800 REV</td>
<td>0.52</td>
<td>1.14</td>
<td>1.69</td>
<td>27.97</td>
<td>0.21</td>
<td>8374.50</td>
<td>34.18</td>
</tr>
<tr>
<td>Mercerized 1600 REV</td>
<td>0.60</td>
<td>1.31</td>
<td>1.85</td>
<td>27.27</td>
<td>0.14</td>
<td>7495.80</td>
<td>32.18</td>
</tr>
</tbody>
</table>

Table 4. Results of fiber analysis

Figure 10. Fiber length versus curling
The fiber width should be increased by mercerization since the fiber swelled and ended when NaOH was washed away (Motamedian, Halilovic, and Kulachenko, 2019). However, fiber width did not change a lot after mercerization and PFI-refining. The fiber lengths measured by the machine slightly decreased after mercerization. Figure 10 indicated that curling and fiber length had a linear correlation. Nonetheless, the fiber length measured by the machine was smaller than its contour length. The increased curl may lead to an error in the measurement of fiber length (Lund et al., 2012). After mercerization, apparent morphological change was not observed in the fiber (Halonen, Larsson, and Iversen, 2013). The PFI-refining (less than 1600 r) did not affect fiber length or fiber width.

Mercerization resulted in fibrillation (Zafeiropoulos, 2008). Hence, the fibrillation of mercerized pulp fiber was larger than that of NDBSW fiber. The fibrillation of NDBSW fiber increased with the increasing revolutions, but not the fibrillation of mercerized pulp. Since cellulose I fibers were easier to fibrillate than cellulose II fibers (Sharma et al., 2015), the increasing fibrillation of NDBSW was easier to observe.

The changes in the kink were similar to those of fiber curling. They both increased after mercerization. The high fiber deformations (fiber and curl) provoked high bulk, porosity, and tear strength (Sood et al., 2005). The PFI-refining (less than 1600 r) did not influence kink or curl.


4.4 WRV

Figure 11. The WRV of pulp samples

```
<table>
<thead>
<tr>
<th>Sample</th>
<th>WRV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hornified NDBSW</td>
<td>0.90±0.01</td>
</tr>
<tr>
<td>Hornified Mercerized</td>
<td>0.89±0.04</td>
</tr>
</tbody>
</table>
```

Table 4. The WRV of hornified pulp samples

WRV is a method to measure the ability of the fibers to take up the water and swell. According to Joutsimo and Asikainen’s research (2013), WRV was correlated with the amount of water in macropores larger than 200 nm.

Figure 11 implies that the WRV of mercerized pulp was slightly larger than the value of NDBSW before PFI-refining, and the small interior pores of the fibers and fibrils were expanded because of the alkaline treatment (Ji et al., 2018). However, the difference is insignificant since the excessive removal of hemicelluloses from the fiber structure decreased the WRV of the fibers (Dias et al., 2019). Additionally, mercerization introduced disordered cellulose at high NaOH concentrations, leading to lower total crystallinity, which results in high WRV (Halonen, Larsson, and Iversen, 2013). Under the influence of these factors, this difference is small.
Table 5 reveals that hornified NDBSW and mercerized pulp shared similar WRV results, and they were much smaller than the original pulp. The loss of ability to absorb water and swell resulted from the hornification. The effect of hornification was to decrease the pore volume of the fiber walls owing to an aggregation of the cellulose microfibril structure (Hult, Larsson, and Iversen, 2001; Salmén and Stevanic, 2018).

The WRV value became larger when higher PFI-refining revolutions were performed on the NDBSW. Refining equipment damaged the external, impermeable layers of cellulose fibers and then internal layers were available for water. Pulp fibers can absorb more water and swell after the PFI-refining (Gao et al., 2015). When the revolutions were beyond 800 r, WRV still increased but had a smaller slope. In other words, the depth beating fibrillation was less effective in creating a more water-accessible surface on the fiber (Gao et al., 2015).

However, the WRV value became smaller when higher PFI-refining revolutions were performed on the NDBSW. The beating of pulp fiber after alkali treatment decreased the WRV because the beating force made the water out of the fiber walls (Choi, Kim, and Cho, 2016). There is another hypothesis for explaining the decreasing WRV. Crosslinking happened after the mercerization: Hydroxyl groups of the cellulose became crosslinked causing cellulose fiber to bond, and the space between linked fibers became larger, so the water was more likely to lose.

Excessive NaOH (more than 10wt%) lessened the WRV of pulp due to the loss of hemicellulose since the hemicelluloses can bind water (Dias et al., 2019b). The removal of hemicellulose can be attributed to the washing in pretreatment and high pH in the alkaline treatment (Lund et al., 2012).
4.5 Thermoporometry measurements

![Graph showing NFW (Non-freezing water) measurements over refining revolutions.]

**Figure 12.** The NFW of pulp samples

NFW (Non-freezing water) is the water in fiber that does not freeze under any circumstances. Freezing water is calculated as the mass of water undergoing the phase transition. If this mass is smaller than the total mass of water in the sample, the mass difference is the amount of non-freezing water in the sample, that is, the volume of micropores in the fiber structure. Figure 12 demonstrates that the volume of NFW (micropores) of mercerized pulp increased by about 0.1 ml/g after mercerization and PFI-refining (less than 1600r) did not change the NFW.
Figure 13. The cumulative pore volume of pulp samples
Figure 14. The pore volume distributions of NDBSW samples with different PFI-refining revolutions
Figure 15. The pore volume distributions of mercerized pulp samples with different PFI-refining revolutions

<table>
<thead>
<tr>
<th>Name</th>
<th>Cumulative pore volume (ml/g)</th>
<th>Cumulative pore volume of micropores (&lt; 2 nm)</th>
<th>Cumulative pore volume of mesopores (2...50 nm)</th>
<th>Cumulative pore volume of macropores (&gt; 50 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBSW 0</td>
<td>0.934</td>
<td>0.23</td>
<td>0.67</td>
<td>0.04</td>
</tr>
<tr>
<td>NDBSW 100</td>
<td>1.055</td>
<td>0.27</td>
<td>0.75</td>
<td>0.03</td>
</tr>
<tr>
<td>NDBSW 200</td>
<td>1.202</td>
<td>0.28</td>
<td>0.89</td>
<td>0.03</td>
</tr>
<tr>
<td>Pulp Type</td>
<td>C1</td>
<td>C2</td>
<td>C3</td>
<td>C4</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>NDBSW 400</td>
<td>1.093</td>
<td>0.041</td>
<td>0.24</td>
<td>0.82</td>
</tr>
<tr>
<td>NDBSW 800</td>
<td>1.124</td>
<td>0.04</td>
<td>0.23</td>
<td>0.86</td>
</tr>
<tr>
<td>NDBSW 1600</td>
<td>1.078</td>
<td>0.101</td>
<td>0.17</td>
<td>0.88</td>
</tr>
<tr>
<td>Mercerized pulp 0</td>
<td>1.125</td>
<td>0.088</td>
<td>0.29</td>
<td>0.80</td>
</tr>
<tr>
<td>Mercerized pulp 100</td>
<td>1.138</td>
<td>0</td>
<td>0.34</td>
<td>0.77</td>
</tr>
<tr>
<td>Mercerized pulp 200</td>
<td>1.161</td>
<td>0.013</td>
<td>0.36</td>
<td>0.77</td>
</tr>
<tr>
<td>Mercerized pulp 400</td>
<td>1.179</td>
<td>0.095</td>
<td>0.33</td>
<td>0.82</td>
</tr>
<tr>
<td>Mercerized 800</td>
<td>1.160</td>
<td>0.052</td>
<td>0.32</td>
<td>0.81</td>
</tr>
<tr>
<td>Mercerized pulp 1600</td>
<td>1.118</td>
<td>0.039</td>
<td>0.30</td>
<td>0.79</td>
</tr>
</tbody>
</table>

**Table 5.** The analysis of cumulative pore volume distributions

The total pore volume of mercerized pulp is larger than that of NDBSW. The initial speculation is that the small interior pores of the fibers and fibrils were expanded by the alkaline treatment (Ji et al., 2018). PFI-refining should cause the fibrillation of pulp fibers and thus result in increased pore volume (Chen et al., 2013). However, the pore volume distributions exhibit similar results of NFW, and the volume difference between NDBSW and mercerized pulp is around 0.1 ml/g, according to Table 6, Figures 13, 14, and 15. The difference is exactly the amount of value difference of micropores.

As a result, the mercerization (15wt%) just increased the volume of micropores of pulp samples, and PFI refining (less than 1600 revolutions) did not affect the thermoporometry of pulp.
4.6 Simons’ Staining

Figure 16. Dyed fibers. (a) Unrefined NDBSW. (b) Refined NDBSW. (c) Unrefined mercerized pulp. (d) Refined mercerized pulp. (e) Hornified NDBSW. (f) Hornified mercerized pulp.

Simons’ Staining is a qualitative analysis rather than a quantitative analysis. It can estimate the accessibility of fiber surfaces fast. Yu et al. (1995) summarized that if the pores in the fiber cell wall are small, the small blue dye molecule can penetrate, while large high molecular weight yellow dye cannot, and the color of the fiber is blue. When the pores are large enough, the color of the fiber would be yellow since the high molecular weight yellow dye has a stronger affinity than blue dye. However, a different orange dye, sun yellow, is used in this experiment due to the unavailability of the yellow
dye Fast Orange 6RN. The molecular structure, chemical components, and molecular weight are unclear.

After mercerization, the cumulative pore volume of pulp increased owing to the swelling of the cell walls of fiber and the separation of the cell wall layers (Li and Liu, 2014). The hornification decreased the pore volume and size and had more micropores (Hult, Larsson, and Iversen, 2001). Therefore, an initial hypothesis is that the color of NDBSW fiber is blue, the color of mercerized pulp fiber is yellow, and the color of hornified pulp fiber is blue.

However, Figure 16 demonstrates that the color of NDBSW fiber is yellow, and the mercerized pulp fiber is blue. The color of hornified pulp samples is all blue. An initial conclusion can be made that the mercerized pulp fiber has more micropores and absorb more blue dye, enabling blue dye to exhibit a stronger affinity than large molecular weight yellow dye, just like the result in Table 6 that the mercerized pulp has more micropores. The probable reason why NDBSW fiber is yellow lies in that the NDBSW fibers also absorb both small low molecular weight yellow dye and blue dye, while yellow dye has a stronger affinity and the amount of blue dye is not enough. The hornified pulp has smaller pores than the original pulp, only blue dyes can penetrate, and its color is blue.

More experiments should be performed in the future. For example, the components of differing molecular sizes of yellow dye can be demonstrated by GPC (gel permeation chromatography). The yellow dye can be separated from high molecular weight and low molecular weight. They can be the variables in the experiment.

Additionally, the PFI- beating of less than 1600r did not change the effect of Simons’ staining. As reflected by comparing the microscopy images of the refined NDBSW pulp fiber and mercerized pulp fiber, more fines were observed in Figure 16 (b) than in Figure 16 (d). This suggests that cellulose I fibers were easier to fibrillate than cellulose II fibers.
### 4.7 Sheet properties

<table>
<thead>
<tr>
<th>sample</th>
<th>Thickness (mm)</th>
<th>Density (kg/m³)</th>
<th>Bulk (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDBSW 0 REV</td>
<td>0.19</td>
<td>480±36</td>
<td>2.09±0.17</td>
</tr>
<tr>
<td>NDBSW 100 REV</td>
<td>0.18</td>
<td>507±20</td>
<td>1.99±0.20</td>
</tr>
<tr>
<td>NDBSW 200 REV</td>
<td>0.18</td>
<td>529±20</td>
<td>1.89±0.08</td>
</tr>
<tr>
<td>NDBSW 400 REV</td>
<td>0.16</td>
<td>552±18</td>
<td>1.81±0.09</td>
</tr>
<tr>
<td>NDBSW 800 REV</td>
<td>0.15</td>
<td>591±17</td>
<td>1.70±0.17</td>
</tr>
<tr>
<td>NDBSW 1600 REV</td>
<td>0.14</td>
<td>635±15</td>
<td>1.60±0.28</td>
</tr>
<tr>
<td>Mercerized 0 REV</td>
<td>0.42</td>
<td>224±49</td>
<td>4.51±0.57</td>
</tr>
<tr>
<td>Mercerized 100 REV</td>
<td>0.43</td>
<td>233±54</td>
<td>4.31±0.28</td>
</tr>
<tr>
<td>Mercerized 200 REV</td>
<td>0.38</td>
<td>234±43</td>
<td>4.30±0.40</td>
</tr>
<tr>
<td>Mercerized 400 REV</td>
<td>0.37</td>
<td>233±40</td>
<td>4.34±0.53</td>
</tr>
<tr>
<td>Mercerized 800 REV</td>
<td>0.35</td>
<td>262±39</td>
<td>3.83±0.32</td>
</tr>
<tr>
<td>Mercerized 1600 REV</td>
<td>0.34</td>
<td>267±38</td>
<td>3.78±0.39</td>
</tr>
</tbody>
</table>

Table 6. Thickness, density & bulk of pulp samples

Figure 17. The zero-span strength of pulp samples

Zero-span strength can be adopted to estimate single-fiber strength and is impacted by interfiber bonding (Gurnagul and Page, 1989). Zero-span strength of NDBSW is larger than that of mercerized pulp (Figure 17). The concentrated NaOH solution can decrease the amount of hemicellulose and fibrils, make the cellulose transform, and curtail fiber strength (Ji et al., 2018). The changes in cellulose structure and removal of hemicellulose affect the single-fiber structure and thus single-fiber strength. Therefore, NDBSW
fibers have a larger zero-span strength than mercerized pulp fibers (Figure 17). Additionally, PFI-refining less than 1600r does not affect the zero-span strength.

![Graph showing density of pulp samples](image)

**Figure 18.** The density of pulp samples

The decreasing bulk and thickness and increasing density (Figure 18) can also attribute to the reduced fiber interspaces and internal fibrillation (Table 6). The fibers will have a greater swelling potential because water can penetrate the fiber wall following the new voids that have been introduced by the mechanical action of refining. One reason for sheet densification after beating is that this increase in swelling makes the fibers more compliant in the transverse direction and hence enhances fiber conformability during sheet production (Motamedian, Halilovic, and Kulachenko, 2019).
The internal bond strength of pulp samples

The internal bond strength is employed to measure the perpendicular tensile strength. The internal bond strength of NDBSW is much larger than that of mercerized pulp owing to the loss of hemicellulose (Figure 19). Hemicellulose leads to hydrogen bonding, and hydrogen bonding is a vital part of interfiber bonding. Moreover, interfiber bonding significantly contributes to internal bond strength (Ji et al., 2018). NaOH solution decreases the amount of hemicellulose and therefore the internal bond strength. During PFI-refining, the small fiber fines and fragments produced from beating filled the pores or interspaces among fibers. It boosted the amount of hydrogen bonding between fibers and then the internal bond strength of sheets (Gao et al., 2012).
Figure 20. The tensile strength of pulp samples

Figure 20 presents similar curves to Figure 19. The tensile strength of sheets was influenced by single-fiber fiber strength and internal fiber bonding. The sheet made from NDBSW has a much larger tensile strength than the sheet made from the mercerized pulp (Figure 20). The single fiber strength (Zero-span strength) of NDBSW is larger than that of mercerized fiber (Figure 17). After the treatment of high concentration NaOH (more than 4%) on kraft pulp fiber, the cellulose chains deteriorated because of penetration and swelling of NaOH, which was likely to reduce a specific bond strength between fibers (Lund, Sjöström and Brelid, 2012; Hasraf, Rahman and A. Majid, 2014). The specific bond strength could be induced by hemicellulose. The tensile strength results of dissolving pulp, which does not have hemicellulose, of Caglar (2019) suggested that hemicellulose did affect the tear index, while the effect was limited, around 10-30%. However, Figure 20 illustrates that the tensile strength of NDBSW and mercerized pulp has a more than ten times difference. Therefore, hemicellulose loss cannot explain all, and some more experiments should be performed.

The tensile strength of sheets made from both NDBSW and mercerized pulp increased when the beating revolution increased (Figure 20). After the mechanical beating, fibrillation took place on pulp fiber, and a greater degree of fibrillation led to an increase in the exposed surface area of microfibrils, so as to enhance the bonding strength (Sharma et al., 2015). Cellulose I fibers were easier to fibrillate than cellulose II fibers (Sharma et al., 2015), and the tensile strength of cellulose I fibers (NDBSW) increased more compared to
cellulose II fibers (mercerized pulp). Thus, the slope of the NDBSW curve was larger than that of mercerized pulp curve.
5. Conclusions

The aim of this thesis was to verify that mercerization and PFI-refining can improve swelling ability and sheet tensile strength. Therefore, never-dried bleached softwood kraft pulp (NDBSW) was mercerized in 15 wt% sodium hydroxide and refined using a PFI refiner. Raman spectroscopy and carbohydrate analysis were performed to determine the chemical composition of pulp samples. Besides, the swelling and thermoporometry of pulp samples were investigated through WRV, thermoporometry measurements, and Simons’ Staining. Afterward, handsheets were made from different pulp samples. Different strength ability tests were completed on handsheets to demonstrate the bonding potential of mercerized pulp.

Based on Raman analysis, Cellulose I in NDBSW was converted completely to cellulose II by mercerization with a 15wt% NaOH solution, and based on the carbohydrate analysis results mercerization reduced the amount of hemicellulose.

The WRV results suggested that mercerization (15wt%NaOH) can improve fiber swelling and porosity before mechanical beating. NDBSW can take up more water after PFI-refining, while mercerized pulp (15%wt NaOH treated) presented a smaller value with the increasing PFI-refining revolutions. PFI-refining enhanced the NDBSW swelling but lessened the mercerized pulp swelling.

Simons’ Staining and thermoporometry results all revealed that mercerized pulp had a larger pore volume and more micropores than NDBSW. However, PFI-refining did not affect the thermoporometry (pore size distribution, and pore volume). In other words, the first trial of this new Simons’ Staining recipe was successful.

PFI-refining reinforced the internal bond strength and tensile strength while not impacting the single fiber strength and fiber properties obtained from the fiber analyzer. Nonetheless, mercerization (15%) weakened the tensile strength and the internal bonding strength derived from lost hemicellulose and increased curling. Therefore, mercerization lessened the bonding potential and tensile strength, and PFI-refining can improve the tensile strength of pulp, and work better on kraft pulp compared with mercerized pulp.

In future experiments, a lower concentration of NaOH should be introduced, since 15wt% NaOH removed too much hemicellulose, leading to the lower tensile strength of sheets. Many researchers attributed the decreasing tensile strength to the loss of hemicellulose (Lund, Sjöström, and Brelid, 2012).
Nonetheless, it should not be the only reason. As mentioned, the dissolving pulp that had no hemicellulose did not significantly affect the tensile strength result compared with the original pulp. Thus, different concentrations of NaOH should be considered, and some other experiments should be performed to explain this phenomenon.
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