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KRAFT PULP BLEACHING PRETREATMENTS

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Abstract

Wood-based chemical pulp is an environmentally sustainable raw material for several conventional and possible future applications as it is biobased and biodegradable raw material. For paper and board there is an existing recycling process. These benefits provide it with a competitive advantage over fossil-based raw materials. Modern pulp mills are considered as multiproduct biorefineries utilizing the process side streams in a variety of products. Pulp raw material can also be used in textiles and composite materials. By-products can be used to produce biogas and chemicals.

Bleaching aims at increasing the brightness and purity of pulp by removing residual lignin in a process consisting of multiple stages, in which different chemicals are added to the pulp. Besides lignin, also hexenuronic acid (HexA), which is formed from xylan during cooking consumes bleaching chemicals such as chlorine dioxide. Enhancing HexA removal and delignification in a pretreatment preceding the bleaching sequence can influence the consumption of chlorine-based chemicals.

The aim of this thesis was to study bleaching pretreatments that would enable using less chlorine-based chemicals in the bleaching sequence. Oxygen delignified softwood and hardwood pulps from Finnish mills were treated with different chemicals such as peracids and sulfite. The pretreatment stages were carried out for 120 minutes at 90 °C and excluding one test point at pH 3. In some test points the effects of an activator were studied.

Paper property measurements with softwood pulp showed slight effect of acid treatments on tear and tensile properties, which was also in line with the viscosity drop seen. In both pulp pretreatments, Caro's acid pretreatment with and without an addition of silica molybdate resulted in significant reduction in kappa number. Hardwood results indicated that addition of silica molybdate would have a preserving effect on carbohydrates. Using Caro's acid in a pretreatment for both HW and SW kraft pulp bleaching showed chlorine consumption savings potential. This would reduce chlorine emissions in process water effluents and further have a positive effect on environmental impact.

Keywords Pretreatment, Chemical pulp, Bleaching, HexA, Lignin, Delignification

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Tiivistelmä

Sellu on kestävä ja ympäristöystävällisen lopputuotteen näkökulmasta lupaava materiaali biopohjaisuutensa ja -hajoavuutensa ansiosta. Paperille ja kartongille on olemassa kierrätysprosessi. Sellulla on näistä syistä kilpailuetu fossiilipohjaisiin tuotteisiin nähden. Nykyaikaiset sellutehtaat rakennetaan ja ajatellaan sivuvirtoja hyödyntävinä biotuotetehtaina. Perinteisten kartongin ja paperin lisäksi biotuotetehtaiden selluraaka-ainetta voidaan käyttää tekstiili- ja komposiittituotteissa. Sivuvirtoja hyödynnetään esimerkiksi kemikaalien ja biokaasun valmistamisessa.

Valkaisun tärkeimpiä tavoitteita ovat vaaleuden ja puhtauden nostaminen jäännösligniiniä poistamalla. Tavoite saavutetaan usein moniosaisella valkaisu prosessilla, jossa hyödynnetään erilaisia kemikaaleja. Ligniinin ohella sellunkeitossa xylaanista muodostuva heksenuronihappo (HexA) kuluttaa valkaisu kemikaaleja, kuten klooridioksidia. Delignifioinnin ja HexAn poiston tehostamisella ennen valkaisu sekvenssiä voidaan vaikuttaa kloorikemikaalien kulutukseen valkaisussa.

Tässä työssä tutkittiin valkaisun esikäsittelyitä, valkaisussa käytettävien kloorikemikaalien vähentämiseksi ja ympäristöystävällisemmän valkaisun mahdollistamiseksi. Erilaisten kemikaalien kuten perhappojen ja sulfiitin vaikutusta happivalkaistuihin havu- ja lehtipuuselluihin tutkittiin yhtä koepistettä lukuunottamatta happamissa esikäsittelyissä, joiden kesto oli 120 minuuttia ja lämpötila 90 °C. Myös aktivaattorien vaikutusta osaan käsittelyistä tutkittiin.

Havumassalle tehtyjen paperi ominaisuusmittausten pohjalta nähtiin happamilla käsittelyillä olevan vaikutusta repäisy- ja veto-ominaisuuksiin, mikä korreloi käsittelyiden aiheuttaman viskositeettihäviön kanssa. Sekä havu- että lehtipuumassojen esikäsittelyissä huomattiin caronhapon vaikutus kappalukuun sekä silikamolybdaattilisäyksellä että ilman. Lehtipuutuloksten perusteella silikamolybdaatti-lisäys suojaa hiilihydraatteja käsittelyltä. Caronhappoesikäsittely kummallekin massalle osoitti mahdollisuuden vähentää kloorikemikaalien käyttöä valkaisussa vaikuttaen kloorijäämien määrään poistovesissä. Tällä olisi positiivinen ympäristövaikutus

Avainsanat esikäsittely, kemiallinen massa, valkaisu, HexA, ligniini, delignifikaatio

Foreword

This thesis project has given me insight to a whole new field of study and taught me more about life and myself than I could have guessed when I started. For this opportunity I want to give my heartfelt thanks to my advisors Anna-Stiina Jääskeläinen and Leif Robertsén. Thank you for the support and great conversations along the way.

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Symbols and Abbreviations

%ISO	ISO Brightness value as %
°C	The degree Celsius
AcOH	Acetic acid
A-stage	Acid hydrolysis stage, in bleaching
D	Chlorine dioxide, ClO ₂ , in bleaching
D ₀	First chlorine dioxide stage, in bleaching
D ₁	Second chlorine dioxide stage, in bleaching
DTPA	Diethylenetriamonepentacetic acid
PAA	Peracetic acid, CH ₃ COOOH
dPAA	Distilled peracetic acid
E	Alkaline extraction stage with sodium hydrogen, in bleaching
ECF	Elemental chlorine free
EDTA	Ethylenediaminetetraacetic acid
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulfuric acid
H ₂ SO ₅	Caro's acid
HexA	Hexenuronic acid
HW	Hardwood
ISO	International organization for Standardization
NaOH	Sodium hydroxide
O	Oxygen stage, O ₂ , in bleaching
P	Hydrogen Peroxide stage, in bleaching
P	Primary wall, wood cell wall construction
Q	Chelation, in bleaching
rpm	revolutions per minute
SiMo	Silicone molybdate
S	Secondary wall, wood cell wall construction
S1	First sublayer of secondary wall, wood cell wall
S2	Second sublayer of secondary wall, wood cell wall
S3	Third sublayer of secondary wall, wood cell wall

SW	Softwood
TCF	Totally chlorine free
TEF	Totally effluent free
UV	Ultraviolet
UVR	Ultraviolet resonance Raman
UVRRS	Ultraviolet resonance Raman spectroscopy
VTT	Valtion teknillinen tutkimuskeskus
WRV	Water retention value
X	Enzyme treatment stage, in bleaching
XRF	X-ray fluorescence spectrometry
Z	Ozone stage, O ₃ , in bleaching

1 Introduction

From a sustainability perspective, chemical pulp from wood is one of the most promising raw materials for future material applications. It is composed of cellulosic fibers that are inherently fully biobased and biodegradable. Furthermore, there is an existing recycling process for paper and board to reuse pulp fibers. Compared to plastics and other materials of fossil origin, chemical pulp has significant advantages in these respects.

Wood pulping is the established technology for producing cellulosic pulp for paper, board, textiles, biocomposites and numerous other applications. Modern pulp mills can be described as multiproduct biorefineries as the process side streams can be used to produce several by-products, such as tall oil, turpentine, biogas, sulfuric acid and lignin (Jordan, 2017). In addition, modern pulp mills produce surplus energy and electricity that can be fed into the grid and the mill can be operated without any fossil energy sources.

In the 1970s the pulp industry had a significant impact on environment. However, since then less harmful and remarkably lower emissions have been achieved even though production volume has also increased significantly (Metsäteollisuus, 2017). Especially, the quality of effluents has changed for the better, due to the recirculation of the process waters and minimizing the use of chlorine in the processes, which enables the reduction of chlorinated hydrocarbons. At its current state the kraft cooking process can be performed without wastewater, hence water emissions are more of an issue of the bleaching stage of the process.

The main objective of pulp bleaching is to enhance brightness and purity of pulp by means of further lignin removal. This target is usually achieved through multiple process stages and via utilization of different chemicals and their chemistries to remove the residual lignin present in pulp after the majority of the wood lignin has been removed during cooking. (Knowpulp, 2019) Purity of bleached pulp is one of the most important properties quality wise, especially as the applications such as textiles and pharmaceuticals applications for bleached pulp become ever more demanding.

The main goal of this thesis is to study bleaching pretreatments that could be used to

decrease the demand of chlorine-containing chemicals during the bleaching sequence, thus permitting more sustainable bleaching. The scope is limited to pretreatments between oxygen delignification and the bleaching sequence. The experimental part was performed for both hardwood and softwood kraft pulps, even though many hardwood fiberlines have a hot acid hydrolysis stage (A-stage) preceding bleaching. Improving A-stage could be one possible way to meet the target of finding pretreatments that enable more sustainable bleaching.

Both softwood and hardwood kraft pulp bleaching processes include a storage tank between oxygen delignification and bleaching. In the hardwood fiberline, this tank is where the A-stage is commonly carried out. Therefore, the possibility for implementation of a pretreatment stage to a softwood process exists. In addition, as extractives from wood can cause problems and disturb both bleaching and papermaking processes, extractive content of some pretreated and bleached hardwood pulps was also measured. Since the final pulp properties need to be as good as with today's bleaching process, the effect of the pretreatments on the final pulp properties was studied after a conventional DED-bleaching sequence.

2 Wood structure and composition

This chapter will concentrate on the part of the composition of wood that affects bleaching and further the bleaching pretreatment process before bleaching sequence, in which lignin and hemicelluloses play a significant role. In improving the pretreatment for bleaching of oxygen delignified softwood and hardwood pulps, one critical improvement would be to increase the delignification occurring before the bleaching sequence. However, this should be done without compromising the strength properties of the pulp. Fibers as the main strength contributing compound in wood will also be described shortly.

2.1 Hardwood and softwood cells and their structure

While all wood cells and their cell walls are composed of the same structural elements, the proportions of the elements vary depending on wood species. Table 1 (adapted from Sixta, 2006) below gives an overview on the composition of softwood and hardwood.

Table 1. Chemical composition of hardwood and softwood (adapted from Sixta, 2006)

	Content of compound (%)	
	in softwood species	in hardwood species
Cellulose	33-44	38-51
Hemicelluloses	25-32	15-35
Lignin	25-32	16-25
Extractives	1-5	1-8

In the wood cell wall structure, cellulose acts as a framework substance. Apart from cellulose, other carbohydrates function as the matrix substances. In addition, lignin is incrustrated in the microcapillary regions of the cell walls. (Sixta, 2006)

Fiber cell wall is a multilayered structure, where micro- and macrofibrils constructed of cellulose play a significant role as the construction units. The chemical composition and the orientation of the substances differs regarding of the part of the cell wall. This causes a concentric arrangement of the individual cell wall layers. (Fengel and Wegener, 1989) Between adjacent cells is a layer called middle lamella, keeping the cells together. The cell wall layers from the middle lamella towards the cell are: primary wall (P) and secondary wall (S), from which the latter can be seen to compose of two or three different layers (S1, S2 and S3). P layer is thin, consisting of microfibrils arranged in no particular order in a pectin and hemicellulose matrix. (Sixta, 2006) Of the thin middle lamella, lignin amounts up to 70-80% (Fardim, 2011). Nevertheless, the highest proportion of total lignin (70-80%) is in the secondary wall, even though the amount of lignin amounts to only about 20 % of total components of the S layer. (Fardim, 2011; Sjöström 1992)

The second sublayer of secondary wall (S2) amounts to the thickest portion of the cell wall, concurrently contributing substantially to the bulk of the cell wall and the physical and mechanical properties of the fiber. The microfibrils in the S2 are arranged mostly in parallel, representing the thickest portion (2-5 μm). Contrarily to the S2, the other two sublayers are narrow and consist more of helically arranged microfibrils. Furthermore, the third sublayer, when distinguishable, comprises the interface with the cytoplasm in living cell or the cell lumen in dead cells. (Sixta, 2006)

In addition to the main structural compounds in wood, there are also extractives and inorganic substances present, which make up a small percentage of the composition,

while significantly affecting biomass processing i.e. pulping and bleaching in paper making. Usually there are more extractives in hardwoods than in softwoods as can be observed from Table 1 above. (Sixta, 2006)

2.2 Chemical components of wood

The main structural compounds cellulose, hemicelluloses and lignin are described in this chapter. In wood there are also other substances present, which comprise a small percentage of all components but are significant regarding processing and refining of wooden material. Therefore, extractives and inorganic substances are presented at the end of this subchapter.

2.2.1 Cellulose

Cellulose, a linear polymer consisting of anhydroglucose units, comprising the most significant amount of wood, is the most abundant renewable resource available worldwide. In wood, cellulose is incorporated in a form of microfibrils into a matrix consisting of all the chemical compound in the structure, i.e. hemicelluloses, lignin, extractives and inorganics. (Sixta, 2006) The molecular structure of cellulose is illustrated in Figure 1.

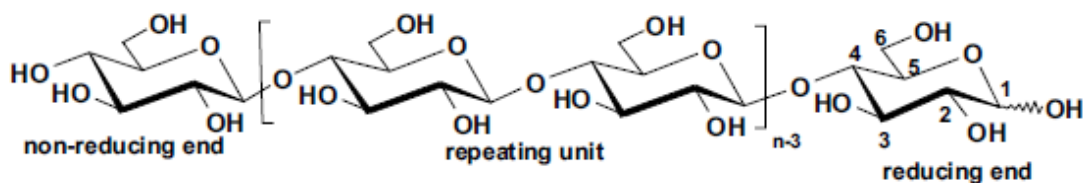


Figure 1. The molecular structure of cellulose (Sixta, 2006).

Cellulose has a complex supramolecular organization in the wood cell wall structure, with a high amount of hydrogen bonds occurring both intra- and intermolecularly. The intermolecular hydrogen bonds and their accessibility affect most properties of cellulose and cause the high tendency of cellulose to organize into crystallites. Pulping and bleaching chemistries introduce a considerable number of different functionalities, such as carboxyl and carbonyl groups to the structure. (Sixta, 2006)

2.2.2 Hemicelluloses

The structure of hemicelluloses is branched, and the chains compared to cellulose significantly shorter. (Fengel and Wegener, 1989) Hemicelluloses are the cell wall components that contain highest proportion of accessible hydroxyl groups. This is due to their generally amorphous nature. Thus, hemicelluloses are substantially more reactive and less thermally stable than cellulose or lignin. (Hill, 2006) Furthermore, hemicelluloses count as an important fiber-to-fiber bonding agent in paper making process (Mahoney, 2000).

Hemicelluloses are closely associated with cellulose in the cell wall structure (Hill, 2006) being partly oriented at the same direction (Jääskeläinen and Sundqvist, 2007). Hemicelluloses are known to act as interfacial coupling agent between cellulose microfibrils and lignin matrix (Hill, 2006). In addition, hemicelluloses are covalently bonded with lignin which increases the difficulty of delignification without loss of hemicelluloses. (Jääskeläinen and Sundqvist, 2007)

Hemicelluloses are commonly found in higher proportions in hardwoods than in softwoods (Hill, 2006). Generally, hemicelluloses are composed of anhydro-sugar units, which can be divided into four groups according to the structure (Table 2). A high proportion of hardwood hemicelluloses are xylose units, whilst mannose units amount to a high proportion of softwood. Compared to softwoods, hardwoods have more acetyl groups but less galactose units. (Sixta, 2006)

Table 2. The sugar units in hemiselluloses.

Subdivision	Sugar units
Pentoses	xylose and arabinose
Hexoses	glucose and mannose
Hexuronic acids	glucuronic acid
Deoxyhexoses	rhamnose

The primary hemicellulose component in hardwood species, amounting up to 30-35 % is glucuronoxylan, also referred to as xylan. (Sjöström, 1992, Sixta 2006). 4-O-methylglucuronic acid groups are linked in no particular sequence to the xylose units in xylan chains, as illustrated in Figure 2 (Sixta, 2006). Some of the xylose units in

hardwoods are also substituted by O-acetyl groups. In addition, small amounts of rhamnose and galacturonic acid have been identified in hardwood xylans. (Sixta, 2006)

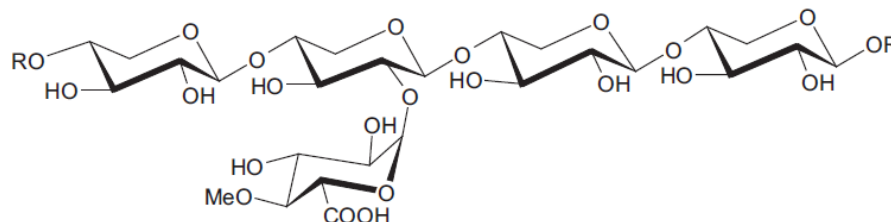


Figure 2. Hardwood xylan (Sixta, 2006).

As glucuronoxylans are related to hexenuronic acid formation and further to the consumption of electrophilic bleaching agents (Sixta, 2006), galactoglucomannan won't be highlighted in this section, despite being the main hemicellulose of softwood species, amounting up to 20%. Glucuronoxylans and their impact on bleaching will be discussed more in detail in Section 3.

Where xylans are present in higher amounts in hardwoods, the amount of the softwood xylans vary from 10 to 15% (Sjöström, 1992). Softwood xylans, arabinoglucuronoxylans, compared to hardwood xylans have arabinose units linked to the xylan backbone by glycosidic bonds, resulting structure seen in Figure 3. (Sixta, 2006)

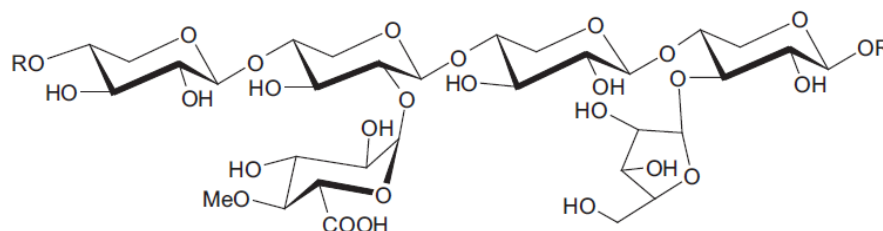


Figure 3. Softwood xylan (Sixta, 2006).

2.2.3 Lignin

Lignin is a characteristic structural component of woody plants, having its typical location in the vascular tissues. Amount of lignin in wood cell wall varies depending on wood species and between different parts of the tree. (Fengel and Wegener, 1989) In general, hardwoods contain less lignin than softwoods (Table 1) (Sixta, 2006). Lignin contributes to the density and strength properties of wood cell walls. Additionally, the swelling characteristics of wood cell walls are mostly influenced by lignin. (Fengel and Wegener, 1989)

Distinctly differing from the carbohydrates, lignin is an aromatic polymer comprising of phenylpropane units linked randomly in the structure, which is due to various oxidative coupling reactions containing biosynthesis process. The reactivity of lignin is affected by the functional groups, which are for example methoxyl groups, phenolic hydroxyl groups and some terminal aldehyde groups in the side chains. Linkages formed to neighboring phenylpropane units cause most phenolic hydroxyl groups to be occupied (Fardim, 2011, Sjöström 1992).

The structure and heterogeneity make lignin a difficult polymer. In addition, it is challenging to extract lignin from wood cell wall structure as it is so strongly bonded with the polysaccharides (Jääskeläinen and Sundqvist, 2007). Chemical pulping process aims to as complete lignin removal as possible, to liberate the fibers, without too high impact on carbohydrates (Sjöström, 1992).

2.2.4 Extractives

Besides its main structural components, wood also contains a number of other compounds some of which are extractable and hence called extractives. Some of them, such as terpenes, waxes and phenols, can be extracted from wood using organic solvents, while others are water-soluble. (Fengel and Wegener, 1989; Mahoney, 2000; Sixta, 2006) Composition of extractives varies between wood species, but also between different individuals within the same species depending on growth conditions (Fardim, 2011). Extractives, however, amount to only a small percentage (1-8%) in the wood composition (Fengel and Wegener, 1989; Mahoney, 2000; Sixta, 2006).

About 2-5% of wood material in the species from temperate zones is soluble in organic solvents. However, depending on the part of the tree even higher concentrations of extractives may be present. (Fengel and Wegener, 1989) Usually the highest amounts can be found in the resin canals and the ray parenchyma cells of wood, whereas ML, intercellular and cell walls of tracheids and libriform fibers usually contain lower amounts of extractives. (Sixta, 2006)

Extractives can be considered a valuable side stream in chemical pulping, as they can be utilized as raw material for organic chemicals. For example, in alkaline pulping the high extractive content of southern pine results in considerable amounts of by-product, such as crude turpentine and raw tall oil. (Fardim, 2011)

Terpenes are a group that consists of pure hydrocarbons, while terpenoids have functional groups such as hydroxyl group, carbon oxygen double bond or carboxyl acid group. Fats and waxes are defined as glycerol containing esters of fatty acids and esters of fatty acids with higher alcohols. The content of fats and waxes are usually in range of 0.3-0.4% and 0.08-0.09% respectively (dry wood), as determined for *picea abies* and *pinus sylvestris*. Furthermore, over 20 different fatty acids have been found in various softwood species. (Fengel and Wegener, 1989)

In coniferous species degradation of unsaturated compounds such as fats and fatty acids occurs during the growing season which has its effect on the production of pulp as pitch problems, or possibly, yellowing of the pulp (Sixta, 2006). Today, a significant part of extractives that are soluble in organic solvents can be removed during the production of bleached kraft pulps (Fardim, 2011; Jansson et al. 1995). Extractive content of pulp usually decreases due to solubilization during kraft cooking. However, some extractives remaining after cooking, especially unsaturated fatty acids, react with bleaching chemicals. (Dence and Reeve, 1996) Besides the kraft cooking stage, the oxygen-alkali delignification stages have an impact on the extractive content of pulp as well as washing of corresponding pulps.

Although, a large part of wood extractives can be removed, some of them are still present in bleaching and consuming bleaching chemicals to some extent. Thus, being harmful to the process. The remaining extractives form sticky deposits on the process equipment and spots in pulp and are quality wise harmful. Therefore, bleaching resulting in minimum extractive content is favorable. (Fardim, 2011; Jansson et al. 1995) Extractives may also influence pulp strength and later processing stages such as drying, gluing and finishing (Sixta, 2006).

2.2.5 Inorganics

The wood species from the temperate zones comprise only a small percentage of inorganics. The growing environment (i.e. soil, climate, site) together with the part of the tree have a significant influence on the minerals content and composition of minerals. Some of the cations of inorganics (e.g. aluminum (Al), zinc (Zn), copper (Cu) and nickel (Ni)) are present in concentrations of less than 50 ppm, whereas, oxalates, carbonates and glucuronates are the form in which most of the following minerals are in wood:

calcium (Ca), potassium (K), magnesium (Mg), iron (Fe) and sodium (Na). (Sixta, 2006)

Chromophore formation can be initiated by metal ions bound to the unbleached pulp, which is associated with complex formation. The contribution of certain metal ions such as manganese (Mn), Cu, Fe, Mg and Al to the color of a pulp will be of increasing importance with the increasing closure of the water cycle in the washing and bleaching areas. (Sixta, 2006)

3 Chemical pulping and bleaching

This chapter concentrates on kraft pulping and bleaching processes (Figure 4). From the perspective of kraft pulping most important process steps, chemicals, reactions regarding lignin and carbohydrates as well as the differences considering hardwood and softwood cooking are described. The effect of oxygen delignification on bleaching is shortly presented in Subchapter 3.2. Section 3.3 concentrates on the target of bleaching and the chemicals that are used in bleaching.

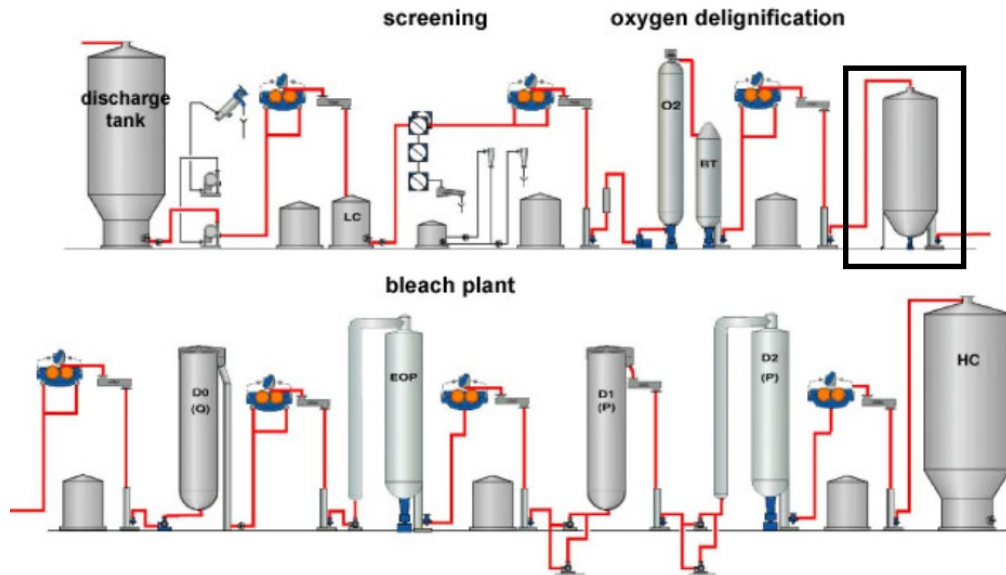


Figure 4. Fiberline. (Knowpulp, 2019)

3.1 Kraft pulping

Kraft pulping aims at separation of lignin from cellulosic wood compounds, to liberate the fibers, enabling value-added pulp product manufacturing (Chakar and Ragauskas, 2004).

In kraft process wood chips are cooked at high temperature (150-170 °C) in a pressurized digester (Fardim, 2011) with strongly alkaline liquor, so called white liquor (pH ~ 14 (Fardim, 2011)). The pH during the process is usually above 12 and duration varies between 0.5-3 h (Biermann, 1996). The chemicals affecting active alkali are sodium hydroxide (NaOH) and sodium sulfide (Na₂S). (Chakar and Ragauskas, 2004) The primary active compounds reacting with lignin are hydroxide (HO⁻) and hydrosulfide (HS⁻) anions. (Chakar and Ragauskas, 2004; Fardim, 2011)

Temperature is maintained throughout the cook until wanted delignification level is reached. After cook, pulp is washed and screened. Counter-current washing system is used to recover spent liquor. In addition, heat and volatile compounds are recovered from the process. Before further processing, pulp is stored at medium (10-15%) consistency. (Fardim, 2011)

Kraft process has low demand on wood species and quality i.e. amount of extractives and the condition or purity (decay and bark) of wood, which gives the process a great advantage. Other advantages include relatively short duration and recovery of the chemicals together with established benefits from utilization of by-products and produced heat. Although, kraft pulping is the most common commercial pulping process, its disadvantages are investment costs and unbleached pulp darkness. (Fengel and Wegener, 1989)

Hardwood fibers are usually shorter than softwood fibers, in addition to which hardwood and softwood pulps differ from each other in their composition. However, composition of wood varies also to some extent between species and trees. Process conditions in pulping and the wood species affect both the chemical composition and the properties of the pulp obtained in the process. Thus, the origin of the wood influences the yield, properties and performance of the pulp in the following process steps. (Fengel and Wegener, 1989)

Lignin reactions during kraft pulping process can be divided into degradation and dissolution, which removes lignin from the wood matrix, and condensation reactions. The first is the preferred as it leads to the liberation of fibers (Chakar and Ragauskas, 2004; Fardim, 2011)

Hemicellulose dissolves more readily than cellulose, due to both lower crystallinity and

degree of polymerization compared to cellulose (Fardim, 2011). Losses of cellulose, however, occur as well during alkaline cooking by peeling reaction as described by Sjöström (1992). In addition, at dissolution of the residual lignin phase, which occurs after about 90% of all lignin has been dissolved, degradation of cellulose is at its highest (Gullichsen and Fogelholm, 1999).

At the initial stage of delignification, acidic compounds such as acetic acid and uronic acid are liberated from wood polysaccharides. The acids require a significant amount of alkali for their neutralization. This alkali results up to 10 % of the total alkali consumption. However, alkali consumed in neutralizing lignin degradation products can account for up to 25-30% of the alkali consumption. (Sjöström, 1992)

Kraft pulping process converts a great extent of the 4-O-methylglucuronic acid groups of xylans to 4-deoxy-4-hexenuronic acid groups, hexenuronic acid (HexA) (Figure 5). (Henricson, 1997; Vuorinen et al., 1996; Vuorinen et al. 1999) The substitution of xylan with 4-O-methylglucuronic acid is higher in softwoods than in hardwoods. However, as there is usually higher amount of xylan in hardwoods, the HexA level in hardwood kraft pulps is higher. (Sixta, 2006)

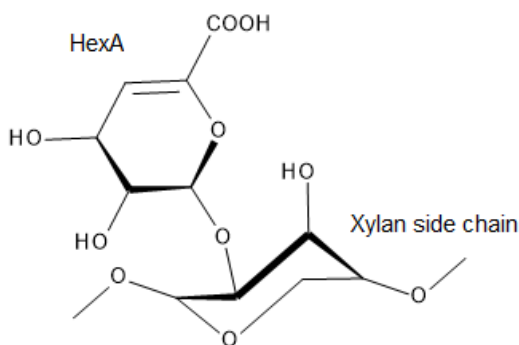


Figure 5. Model of HexA on a xylan side chain (adapted from Sixta, 2006, p. 884)

Partial degradation of carbohydrates cannot be avoided during kraft cooking, in addition to dissolution of lignin. This results in a yield decrease and strength loss. In softwood processing, however, higher alkali concentrations are commonly required to obtain similar degree of delignification as for hardwoods. (Fengel and Wegener, 1989) Softwood kraft pulps having lower yields is a result of high dissolution of glucomannan as well as the higher relative amount of lignin removed, due to higher initial lignin content. (Gullichsen and Fogelholm, 1999)

Besides the reactions of lignin and carbohydrates discussed above, kraft cooking involves chromophore formation. While some chromophoric structures naturally exist in wood, most of the chromophore formation occurs through oxidation reactions of lignin. (Fardim, 2011) Chromophores are discussed in more detail in Section 3.3.1.

3.2 Oxygen delignification

Oxygen delignification is a common lignin removal stage before bleaching, as oxygen delignification stage provides chemical cost savings and yield retention compared to chlorine dioxide bleaching. In addition, oxygen delignification improves the process from the environmental perspective, since less lignin needs to be removed in bleaching. However, there are also drawbacks, costs from investments and lignin selectivity. (van Heiningen et al., 2008) The alkaline conditions support the solubilization of the lignin via carboxylates. Figure 6 illustrates reaction pathways. (Suess, 2010)

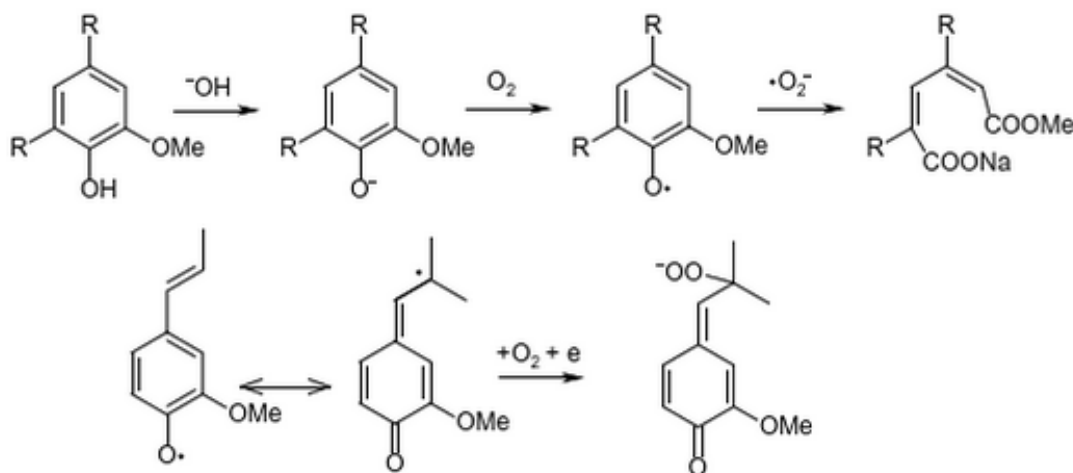


Figure 6. Reaction pathways of carboxylate generation from lignin in alkaline condition (Suess, 2010).

The radical oxygen reacts with phenol hydroxyl group stealing hydrogen or abstracts an electron from phenolate anions. The radical generated, phenoxy or quinone methine, reacts further with oxygen forming peroxy radical. (Suess, 2010)

At the first delignification stage both oxygen and alkali additions cause a sharp viscosity drop rather early, indicating cellulose depolymerization during oxygen delignification. This prevents prolonging of the stage to achieve low lignin contents. Residual lignin content of unbleached pulp is usually decreased only up to 50% from pulp when oxygen and

alkali are used with magnesium salts present. If a higher percentage of lignin removal is desired and delignification carried out using oxygen and alkali, cellulose depolymerization will happen concurrently, affecting strength yield. (Sjöström, 1992)

3.3 Kraft pulp bleaching

Some lignin remains in pulp after cooking and oxygen delignification. Further lignin removal in these stages will cause loss in pulp yield together with fiber properties as discussed previously. In bleaching pulp is treated with more selective chemicals to break lignin into smaller compounds that are water- or alkali-soluble to cause minimum effect on carbohydrates. Thus, multiple steps are required to keep the effect on pulp fibers at a minimum level. (Knowpulp, 2019) Consequently in bleaching different sequences comprising of varying stages with different chemistries are utilized to produce pulp with low lignin content and high brightness. Following sections will further discuss the chemicals and stages used in bleaching sequences as well as the targets of bleaching. The properties of bleached pulps are discussed in the chapter 5.

HexA can interact with reducing groups derived from carbohydrates and lignins causing brightness reversion. (Knowpulp, 2019) Electrophilic bleaching agents react with the double bond in HexA structure (Figure 5) (Sixta, 2006). In addition to bleaching chemical consumption, HexA causes additional undesirable effects; brightness reversion and binding metal ions to itself causing process problems. (Vuorinen et al., 1996)

HexA has an important role in the bleaching of kraft pulp. Since both consume chlorine, ozone and peracetic acid (PAA), these chemicals can be used to remove HexA from pulp, however, peroxide and oxygen cannot be used. (Henricson, 1997) Vuorinen et al. (1996) studied a mild selective hydrolysis to be used to avoid undesirable effects of HexA. It was discovered with optimized treatment conditions that undesirable changes in yield and strength properties could be avoided. (Vuorinen et al. 1996) Pretreatments to enhance bleaching including hot acid hydrolysis stage are discussed in more detail in chapter 4.

3.3.1 Target of bleaching

Chromophores in the pulp affect its brightness properties. These light-absorbing components in unbleached pulps are mainly functional groups obtained from residual

lignin degradation or modification. (Sjöström, 1992; Fengel and Wegener, 1989) Hexa-derived chromophoric compound structures have been studied and identified by Rosenau et al. (2017). In bleaching, the principal aim of increasing brightness can be achieved by affecting chromophoric groups. This can be done using lignin-removing bleaching, which aims to delignification, causing loss of substance (Sjöström, 1992; Fengel and Wegener, 1989). Supplementary to lignin removal the substance loss may include other compounds (Fengel and Wegener, 1989). HexA removal for hardwood pulps is carried out in the A-stage, which is discussed in more detail in Section 4.1. Extractives and ash compounds as well as particles such as shives and bark specks may be removed to a certain extent. Thus, bleaching has additional relevance from pulp purification perspective. (Fengel and Wegener, 1989)

For the properties of the pulp to be desirable considering the end use application the length of the fiber should not be changed. In bleaching fiber length is usually not influenced, while, however, linear density is likely to be reduced. Linear density reduction results in more fibers in unit weight. This has its effect further on properties such as tear strength, refinability (improved), brightness stability and durability of absorptivity (Knowpulp, 2019) Changes in the pulp properties are dependent on the used bleaching sequences as well as on the used chemicals. The following parameters influencing the different processes, however, are equally important in all bleaching sequences: chemical charge, bleaching consistency, time and temperature. (Fengel and Wegener, 1989)

3.3.2 Bleaching chemicals

Chemical pulp bleaching is performed in sequences, in which different chemicals are applied. Sometimes multiple stages are run at the same time or after one another without washing between stages. Commonly known bleaching stages and the chemicals used in them are presented in . Environmental concerns related to chlorinated organic compounds formed during chlorine bleaching have led to development of totally chlorine free (TCF-), which is carried out without chlorine-containing chemicals, and elemental chlorine free (ECF-) sequences, in which only chlorine is not used allowing for example chlorine dioxide (Fardim, 2011).

Table 3 below. Environmental concerns related to chlorinated organic compounds formed during chlorine bleaching have led to development of totally chlorine free (TCF-), which

is carried out without chlorine-containing chemicals, and elemental chlorine free (ECF-) sequences, in which only chlorine is not used allowing for example chlorine dioxide (Fardim, 2011).

Table 3. Commonly used bleaching stages and the chemicals used in them. ¹(Sixta, 2006)

Oxidant	Abbreviation	Active chemistry	Reaction sites in lignin and carbohydrate structures
Chlorine dioxide	D	ClO ₂	lignin free phenolic hydroxyl groups, double bonds, HexA ¹
Oxygen	O	O ₂	lignin free phenolic hydroxyl groups, double bonds ¹
Hydrogen peroxide	P	H ₂ O ₂	carbonyl groups, conj. double bonds ¹
Ozone	Z	O ₃	olefinic and aromatic (lignin), HexA ¹
Peracetic acid	PAA	CH ₃ COOOH	aromatic lignin units ¹ , HexA
Alkaline extraction	E	NaOH	swelling of fiber wall structure, dissolving of chlorinated lignin
Enzyme treatment	X	Xylanase	improved accessibility for conventional bleaching agents, breaking lignin-xylan
Chelation	Q	EDTA ^a , DTPA ^b	Deactivates metals

^a Ethylenediaminetetraacetic acid

^b Diethylenetriamonepentacetic acid

Some combinations used in bleaching processes are D(EOP)DP, D(EOP)D and D(EOP)DD. Generation of chlorine dioxide for industrial applications is carried out by reduction of sodium chlorate. Chlorine is in the form of a free radical, as having an unpaired electron, thus having limited stability. (Suess, 2010) The advantage of chlorine dioxide is a selective oxidation of chromophoric structures without strength property losses. Chlorine dioxide charge, which is usually dependent on the kappa number of the pulp entering the stage, is expressed as active chlorine. (Sixta, 2006)

The first D-stage (D₀), usually carried out at medium consistency, is in most important applications placed after the oxygen delignification stage, functioning as a delignification stage removing significant amount of residual lignin. (Fardim, 2011) D₀-stage efficiency

is mainly dependent on temperature, time, pH and on the existence of an oxygen delignification stage prior to the stage. As a temperature sensitive chemical, chlorine dioxide is consumed at a faster rate at elevated temperatures. A final pH for D₀-stage as presented in Table 4 has been seen most preferable, promoting delignification. Low pH increases the concentration of chlorine formed during lignin and chlorine dioxide reactions. As chlorine also can contribute to the delignification, lower final pH is advantageous. (Fardim, 2011)

Table 4. Commonly used conditions in the most important stages considering this thesis. (Fardim, 2011; Knowpulp, 2019)

Stage	pH	Temperature, °C	Time, min
D₀	2-4	40-60	30-80
E	10.5-11	55-90	30-120
A	3-3.5	90-110	60-180
PAA	4-6	50-80	30-150

During bleaching, chlorine dioxide reduction from +4 valence to -1 occurs via different steps involving several inorganic oxychlorine species (Tarvo, 2010), chlorite ion and hypochlorous acid being the primary reduction products (Dence and Reeve, 1996). As chlorite does not contribute to delignification, chloride dioxide may lose its delignification potential, if chlorate and chlorite formation during D-stage is significant. However, chlorine dioxide reactions and the bleaching efficiency are highly dependent on the pH profile of the stage. At acidic conditions chlorite is oxidized and regenerated into chlorine dioxide, increasing the bleaching efficiency. (Lehtimaa, 2002; Sixta, 2006)

The aim of the E-stage is to remove lignin, which has been made soluble during the preceding oxidizing stage as well as reactivate the pulp to further oxidizing stages (Dence and Reeve, 1996). Alkaline extraction stage using only sodium hydroxide (E), is a relatively simple stage compared to alkaline stages that are carried out with hydrogen peroxide (EP) and/or oxygen (EO) (EOP). Targeted final pH of the extraction stage is above 10, resulting in efficient lignin removal. E-stage is usually run at medium consistency. Both temperature and time are important parameters. The most significant lignin removal occurs during the first 30 minutes, Nevertheless, the slow solubilization of lignin for the next 30 to 60 minutes is equally important, as it will affect the kappa number of the pulp and further decrease the chemical consumption at the following bleaching

stages. Some typical conditions for E-stage are listed in Table 4. (Fardim, 2011)

Chemicals such as chlorine dioxide, peroxyacetic acid and ozone are commonly used in acidic bleaching treatments. Delignification is initially driven by reactions, in which sites of high electron densities are attacked by an electrophile after which nucleophilic reactions take place. The primary reactions between chlorine and lignin include electrophilic substitution, electrophilic side-chain displacement, oxidative cleavage of aryl-alkyl ether linkages and oxidation of displaced side chain structures, oxidative decomposition of aromatic rings. (Fengel and Wegener, 1989).

4 Pretreatments to enhance bleaching

Pretreatment in which delignification and HexA removal are improved preceding bleaching sequence would be beneficial for bleaching chemical consumption. At many mills hot acid hydrolysis stage (A-stage) for hardwood is carried out in the storage tank preceding bleaching (black box in Figure 4). A-stage has been seen effective as a prebleaching stage, which improves bleaching efficiency, usually carried out using sulfuric acid with hardwood pulps (Knowpulp, 2019).

The lack of selectivity towards lignin without compromising carbohydrates has been limiting the use of oxygen in delignification. (Sjöström, 1992) In addition, hydrogen peroxide treatment in certain conditions in order to decrease residual lignin has been found inefficient. Yet, acidic, electrophilic reactions carried out utilizing oxidizing chemicals such as peracids or ozone have been found effective. (Jones, 1999)

Adding chemicals in A-stage could be one way to improve both delignification and HexA removal. The improvement could be implemented without significant changes in the existing process. In this chapter above mentioned treatments will be discussed. Sulfite addition to pretreatment is discussed as one delignification improving alternative.

4.1 Hot acid hydrolysis as a pretreatment for hardwood pulp bleaching

Acid hydrolysis (A-stage) is one of the bleaching stages and carried out at medium consistency. The aim of A-stage is to remove hexenuronic acids (HexA) that especially

hardwood pulps contain in considerable proportions after pulping process. Typically, this treatment is carried out at high temperature. (Know pulp, 2019) Sulfuric acid is commonly used in A-stage (Fardim, 2019). The typical conditions used in A-stage are presented in Table 4.

Equal to lignin HexA contributes to bleaching chemical (chlorine dioxide, ozone, hydrogen peroxide) consumption when present. Thus, a treatment stage before actual bleaching sequence to remove HexA can help decreasing chemical consumption and therefore create financial benefit and less need of bleaching chemicals. Treatment with acidic conditions and at high temperature (80-100°C) can be carried out in the storage tank before bleaching which saves mills from additional investment expenses. In connection with HexA removal, A-stage is preventing of generation of oxalate sediment which may cause problems later in the process when accumulating, especially in washers. (Knowpulp, 2019)

4.2 Peroxide and peracid treatments

Hydrogen peroxide treatment in order to decrease residual lignin from pulp at alkaline conditions has been seen inefficient, whereas acidic, electrophilic reactions carried out utilizing oxidizing chemicals such as peracids or ozone have been found effective. However, using ozone as an oxidizing agent can be challenging for example from the investment point of view. The most common peracids are peroxymonosulfuric acid (Caro's acid, H_2SO_5) and peracetic acid. (Jones, 1999)

Electrophilic reactions usually occur when peroxy acids are used. The oxygen atoms of peroxy acids are transferred to substrate nucleophiles in the electrophilic oxygen transfer, which is the most characteristic reaction of peroxy acids. Electrophilic oxygen transfer reaction is illustrated in Figure 7. (Ando, 1992)

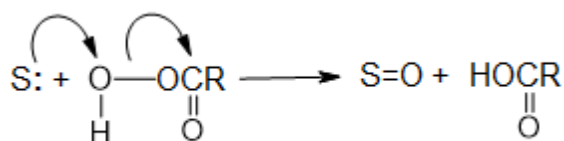
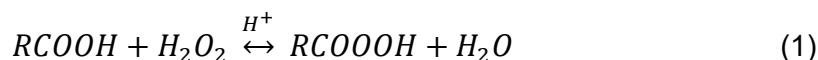


Figure 7. Electrophilic oxygen transfer to the substrate (S) nucleophile (adapted Ando, 1992).

Peracids preparation is done via reacting hydrogen peroxide and carboxylic acid. The

reaction is acid-catalyzed equilibrium and the reaction is shown in the equation (1) below: (Ando, 1992)



Peracetic acid is preferably used as a distilled product (dPAA) for economical reasons. Even though it is unstable, transportation and storing is possible when carried out at cooled conditions. Peracetic acid has lower sensitivity towards transition metals compared to hydrogen peroxide, which is an advantage. However, compared to chlorine dioxide the delignification efficiency of peracetic acid is lower. Recommended bleaching conditions are listed below. (Fardim, 2011) The conditions suitable for peracetic acid bleaching are similar to those of A-stage (Table 4).

Peracetic acid is known to be selective towards lignin and can be used in acidic solution for delignification. In acidic conditions, both peracetic acid and hydrogen peroxide have the hydroxonium ion as the reactive species. Hence, the main reaction mechanisms (Figure 8) are alike for both chemicals. Hydroxy radicals may also be partly involved as reactive agents. (Fengel and Wegener, 1989)

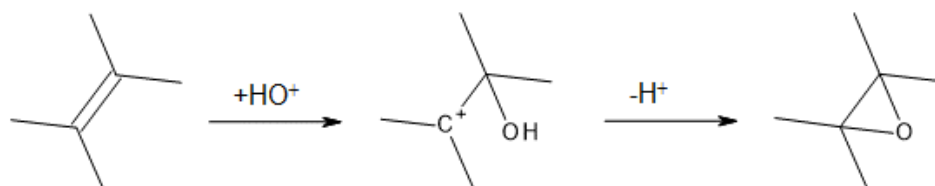


Figure 8. Principal reactions of lignin units with hydroxonium ions (adapted from Fengel and Wegener (original according Gierer), 1989).

Electrophilic nature of peracids enables them to oxidize both phenolic and non-phenolic lignin structures, but also attacking HexA groups. In the electrophilic reactions with lignin, displacement of protons or alkyl side groups leads to hydroxylation of the aromatic ring, whereas the other electrophilic reactions result in formation of o-quinones through demethoxylation and dealkoxylation. Electrophilic HexA attacks might involve intermediates that can be oxidized to formic acid and carbon dioxide through reactions consuming 6 equivalents of peracids. Heikkilä et al. (1996) studied the electrophilic and nucleophilic reactions of lignin and HexA with peracetic acid. The nucleophilic secondary reactions were found to favorably compete with primary electrophilic addition and lignin reactions. (Heikkilä et al. 1998)

4.3 Sulfite treatment

Sulfonation of lignin has two important factors affecting lignin: softening of the lignin and rendering its nature more hydrophilic, thus improving the removal of lignin from the fibers (Ingruber, 1983). In sulfonation hydrophilic sulfonic acid groups are generated in the hydrophobic lignin polymer (Sjöström, 1992).

Rallming and Yuan-Zong (2009) studied oxygen delignified kraft pulp residual lignin using sulfite treatment. Oxygen delignified kraft pulp residual lignin from Norway spruce showed increased reactivity. Higher ratio of lignin sulfonation to the phenolic hydroxyl group content was a response to sulfite treatment at pH 7.5. The conditions used in the treatment attributed the sulfonation to the phenolic lignin components as well as to some extent to the sulfonation of etherified structures. (Rallming and Yuan-Zong, 2009)

Various studies concerning lignin sulfonation and dissolution during acidic sulfite pulping have been carried out. It has been found that the process leads to extensive delignification. (Gellerstedt, 1976) Gellerstedt and Gierer (1971) studied the lignin reactions during acidic sulfite pulping with model compounds, which were both of phenolic and non-phenolic in nature. As a result, acidic reactions of lignin showed considerable sulfonation of benzylic carbon atom in both aforementioned model compound units. (Gellerstedt and Gierer, 1971)

Hydrolysis of HexA forms aldehydes, which might further affect delignification as they react with lignin through condensation reactions. Sulfite is a strong nucleophile and could react with the aldehydes and was therefore selected in the pretreatment studies in the experimental part as it might have effect on these condensation reactions.

The effect of sulfonation of lignin preceding bleaching under acidic conditions is unclear. However, as the oxygen delignified pulps, affected already significantly in the oxygen delignification stage, treated with bisulfite under acidic conditions, it has been discussed, that sulfonation of lignin might not occur. Thus, affecting dissolution. Considering HexA reactions with sulfite at $\text{pH} < 7$, the reactions could be mostly condensation reactions between aldehydes and phenols, whereas, the condensation of lignin could possibly be prevented with the presence of sulfite under the corresponding conditions. In addition, there could also be drawbacks or unseen reactions occurring, depending also on the pulp. (Vuorinen, 2019)

5 Properties of bleached pulps

Chemical composition of pulp affects further processing and properties e.g. yield, strength, color of pulp. As important properties of bleached pulp brightness, cellulose chain length, lignin content and purity, will be discussed in this chapter.

5.1 Brightness and brightness stability

One main aim of bleaching is to increase brightness by chemically lowering chromophore concentration without compromising strength properties. Decreased chromophore concentration increases the reflectance of blue light of the substance, as chromophores absorb the type of light causing the brown color of paper or pulp sheet. Hence are bleached pulp products less brown in color than unbleached ones. (Dence and Reeve, 1996)

Brightness can be used as a characterization of the color of pulp measured at 457 nm wavelength. For brightness determination several different methods and standards exists. Brightness gain is the increase in brightness that is obtained during bleaching. (Fengel and Wegener, 1989)

Brightness reversion refers to how bleached pulp tends to darken over time and is originated from the chemical structure of pulp (Dence and Reeve, 1996). In addition to heat-induced color changes and darkening, light exposure can accelerate aging and therefore also cause brightness reversion of pulp. Light exposure is not an indispensable condition for yellowing of pulp, however, and whether yellowing happens in dark or in light, it is accelerated by the presence of oxygen. Yet, humidity variations have a more pronounced effect on the yellowing of pulp in lightless conditions. (Sjöström, 1992)

Besides lignin, also carbohydrates and extractives contribute to the yellowing (Sjöström, 1992). The heat-induced yellowing of TCF- and ECF-bleached pulps is commonly connected with chromophores. The formation of chromophores is in association with reactions occurring in the presence of thermally less stable polysaccharide components, which are formed in pulp via partial oxidation of hemicelluloses and in some cases also by cellulose degradation. (Beyer et al., 2006)

5.2 Cellulose chain length

The average length of cellulose molecules can be determined to give an indication of the extent of cellulose degradation during certain treatment. Viscosity measurement is usually used to illustrate the cellulose chain length or the polymerization degree. For the determination the viscosity of a solution, in which cellulose is dissolved, is measured. The viscosity of the solution describes the cellulose average chain length; hence it is a good indicator of the potential on strength of the of pulp sheet, but not being directly proportional to pulp strength. (Dence and Reeve, 1996)

5.3 Lignin content

Lignin content in pulp is most commonly measured by determining the kappa number of pulp. Kappa number measurement is based on potassium permanganate oxidizing certain pulp structures under selected conditions (Dence and Reeve, 1996), which is a measure of the permanganate demand of the pulp, also known as a kappa number measurement. Besides oxidizing lignin aromatic structure, permanganate as a strong oxidizing compound reacts also with other double bonds in pulp. Thus, the contribution of HexA to the kappa number of pulps has also been identified. (Sixta, 2006)

In industrial processes kraft pulp kappa numbers after cooks are usually 15-20 for hardwood and 25-30 for softwood. (Fardim, 2011; Sixta, 2006) After oxygen delignification kappa numbers of hardwood and softwood pulps are 10-13 and 11-18, respectively. Furthermore, the kappa number for both pulps after D₀E are usually reduced to 3-5. (Fardim, 2011)

5.4 Extractives content and purity

From the perspective of manufacture of a high quality and added-value cellulose products, purity is an important property of pulp (Sixta, 2006).

Today, a significant part of extractives can be removed during the production of bleached kraft pulps with modern operations. Besides the kraft cooking stage, the oxygen-alkali delignification stages have an impact on extractive content of pulp as well as washing of corresponding pulps. Even though, a large part of wood extractives can be removed, some of them are still present in the bleaching and consuming bleaching chemicals to

some extent. The remaining extractives form sticky deposits on the process equipment and pulp and are quality wise harmful. Therefore, bleaching resulting in minimum extractive content is favorable. (Fardim, 2011; Jansson et al. 1995)

6 Experimental

This work was carried out to investigate bleaching pretreatments which would enable decreasing use of chlorine chemicals during bleaching sequence, making it more sustainable. Another target was being able to reach a competitive combination of pretreatment and bleaching, for producing pulp with desirable level of brightness and strength properties.

The raw materials in this study were oxygen delignified softwood and hardwood pulps. These pulps were used to study the effect of pretreatment with different chemicals. Different bleaching pretreatments were carried out to study the effect of different chemicals on oxygen delignified pulp. The experimental part of this thesis was completed in three treatment phases, that were of different scales. The first phase was to carry out pretreatments using different chemicals in a small scale in plastic bags (50 g, dry pulp). Second phase was carried out using 100 g (dry) of pulp for selected pretreatment, after which pulp was bleached using DED-sequence.

After these two smaller scale phases, two softwood pretreatments were chosen in addition to a reference and up-scaled to about 1.5 kg batch treatment (dry) after which DED-sequence was carried out similarly to the second phase. From these pulps, the effect of the pilot-scale treatment on refinability was studied. From the last phase tests laboratory sheets were prepared and the paper sheet properties were measured to study the effect of the treatment on the strength properties.

As different chemicals were used and the experiments were carried out at elevated temperatures, both chemical and working safety were considered and discussed to identify hazards and evaluate possible risks throughout the experimental work. Also, for the pilot scale operations risk assessment was carried out with all individuals participating that experimental phase.

6.1 Materials

More detailed description of both birch and softwood pulps is given in Section 6.1.1. Chemicals used in experimental part are presented in Section 6.1.2.

6.1.1 Pulps

Both the hardwood pulp and the softwood pulp were from Finnish pulp mills. **The hardwood (HW) pulp** (kappa number 10.6, HexA content 51.3 mmol/kg, viscosity 960 mL/g, brightness 54.8%) was taken after oxygen delignification stage from a birch fiberline. Before pretreatments and bleaching, the HW pulp was centrifuged and homogenized with a mixer at the consistency of 29.8%. **The softwood (SW) pulp** (kappa number 9.2, HexA content 32.0 mmol/kg, viscosity 780 mL/g, brightness 44.9%) used was also taken after oxygen delignification stage and homogenized with a mixer at the consistency of 21.5%.

6.1.2 Chemicals

Hydrogen peroxide (H_2O_2) (49.5%, Kemira) and urea peroxide (> 97%, VWR) were used in pretreatments. Concentrated PAA solution Kemirox DP (Kemira) (PAA > 39-41%, AcOH < 4%, H_2O_2 < 2%) was used in the dPAA-pretreatments. Sodium bisulfite (Kemira) was used in sulfite pretreatments. Caro's acid (H_2SO_5) was prepared using sulfuric acid (95%, Kemira) and hydrogen peroxide (49.5%, Kemira). The preparation of Caro's acid was carried out in ice bath using magnetic stirrer. The amount of sulfuric acid used was based on the amount needed to adjust the pH of the pulp (HW or SW) to the target level. Hydrogen peroxide (chemical charge 5 kg/t) was then added slowly to the acid. Caro's acid was prepared at least 30 minutes before addition to the pulp. Silica molybdate (SiMo) (10%, Kemira) was used in hydrogen peroxide, dPAA and Caro's acid pretreatments as an activator. In addition, acetone was used in dPAA and Caro's acid pretreatment test points as an activator and added to the pulp prior chemical addition. Chlorine dioxide solution (Industrial made) was used in both D-bleaching stages. Sulfuric acid (H_2SO_4) solution (Merck) was used to adjust the pH of the pretreatment so that it could be carried out in acidic conditions. Sodium hydroxide (NaOH , Merck) was used in pH control and in E-stage of the DED-bleaching sequence.

More specific information regarding combinations of chemicals and chemical charges in

different test points in both small and large laboratory scale pretreatments and bleaching stages can be found in APPENDICES I-II.

6.2 Methods

Pulp consistency used in the pretreatments was 10 %, and temperature and time used were 90°C and 2 hours, respectively. Initial pH used was 3 except for one test point carried out with dPAA and acetone, which was done at pH 7. SW pulp reference sample in large laboratory and pilot scale pretreatments was prepared without addition of any chemical. As A-stage is already commonly used in mills for hardwood, it was used as a reference for HW pulp pretreatments. Chemical charges and specified parameters and conditions used in each pretreatment can be found in APPENDIX I.

For pretreatments and bleaching stages in laboratory scale water baths (Julabo TW20) and pH meter (Schott) were used. Pulp washing was carried out in a Büchner funnel with a ratio of 20 times deionized water to the amount of pulp (2x20) at corresponding treatment temperature.

The active chlorine content of chlorine dioxide solutions, used in D-stages, were determined by iodometric titration. Titration was carried out with sodium thiosulfate after acidification and addition of potassium iodide. The concentration of sodium bisulfite solution (Kemira), used in sulfite pretreatments, was determined by titration using iodine solution and sodium acetate as a buffer in titration with sodium thiosulfate solution with starch as an indicator. In addition, concentrations of H₂O₂ and peroxy acid of both dPAA and Caro' acid solution were determined using two-phase titrations first of which was carried out to determine H₂O₂ with cerium sulfate solution and ferroin indicator. The latter titration was carried out to determine the concentration of peroxy acid by released iodine titration with sodium thiosulfate solution using starch as an indicator. Determined residual chemical amounts are presented in APPENDICES IV-V. All residual chemical determination methods carried out after pretreatments and bleaching stages are described in Section 6.2.4.

Lorentzen and Wettre pulp disintegrator was used to carry out laboratory wet disintegration according to ISO 5263-1. Laboratory hand sheet preparations and drying for determination of brightness and CIE color coordinates were carried out according to modified standard ISO 3688. More specific description can be found in the Section 6.2.5.

6.2.1 Pretreatments in small laboratory scale

Pretreatments in small laboratory scale were carried out at medium consistency using 50 g (dry) of pulp and different chemicals. The pretreatments were carried out in plastic bags (PE, Thickness 0.05 mm) in 90°C water bath for 2 hours. Chemical charges differed depending on the chemical in use. The chemical charges used as well as other pretreatment parameters can be found in APPENDIX I.

6.2.2 Pretreatment and final bleaching in large laboratory scale

Pretreatments in large laboratory scale for HW pulp were carried out for following pretreatments from smaller laboratory scale: A-stage, dPAA with acetone, Caro's acid with SiMo and larger charge (6 kg/t) of sulfite. The chemical charges and other parameters of the pretreatments can be found in APPENDIX I.

In D₀-stage the chlorine dioxide charge was determined according to lowest kappa number that was measured from the samples pretreated in the small laboratory scale. Sheets for brightness measurements were prepared at the same day of bleaching and the brightness was measured the day after as described earlier. After the D₀ stage, E-stage was carried out. Kappa number of the pulp was measured after the E-stage. For the second D-stage, D₁, the chlorine dioxide charge was determined according to lowest kappa number from the E-stage similarly to D₀. Sheets for brightness measurements were also prepared at the same day. Chemical charges and bleaching conditions are presented in APPENDIX II.

6.2.3 Pretreatment and final bleaching in pilot scale

Pilot scale pretreatments and bleaching sequences were carried out in the NORPPA reactor at VTT Bioruukki. Following pretreatments were carried out: Reference, A-stage and Caro's acid. As reference SW pulp was treated with similar conditions compared to the other two treatments (120 min, 90 °C), however, pH was not adjusted. The mixing was 100 rpm for 30 seconds in intervals for 15 minutes. More specific parameters for pretreatments and DED-bleaching are listed in APPENDIX I-II.

After pretreatments and bleaching, pulps were refined for sheet preparation and laboratory sheet measurements. Refining was carried out with multiple refining energies

for each sample to create refining series. Water retention value (WRV) and Schopper-Riegler (SR) number measurements were carried out to analyze pulp properties. From laboratory sheets grammage, density, thickness as well as tear and tensile strengths were measured.

6.2.4 Chemical and spectroscopic analyses

Nonpolar bonds with symmetrical charge distribution have the most intense Raman scattering, which is produced when the polarization of chemical bond is changed. UV resonance Raman spectroscopy (UVRRS) provides information on the structure of residual lignin and may also be used to gather information on the vibrational energy levels in the sample constituents. The method precision also enables analyzing residual lignin of fully bleached pulps. (Saariaho, 2004)

UVRRS measurements were carried out using UV Raman spectrometer (Renishaw 1000 UV Raman, Leica DMLM microscope with objective 40, Innova 90C FreD frequency-doubled argon ion laser) with laser wavelength of 244 nm for the measurements. For the baseline adjustments the software Grams/32 was used. For the measurements the center was set at 1332.0 cm^{-1} shift, detector time to 30 seconds, accum. to 3, laser power 10 mW and from the software set to 25 %. For UVRR results three (3) measurements from each sample were carried out.

Extractive content of the second laboratory scale bleached HW pulps were analyzed at Åbo Akademi according to Willför et al. (2003). Residual peroxide determination was based on titration of released iodine. Titration was carried out by titration of filtrate from the pretreatment in which iodine solution was added using $\text{Na}_2\text{S}_2\text{O}_3$ with starch as an indicator. The residual chemicals peroxide and Caro's acid from Caro's acid pretreatments were determined using two-phase titrations first of which was carried out to determine peroxide with cerium sulfate and ferroin indicator and the latter to determine residual peroxy acid by released iodine titration with sodium thiosulfate using starch as an indicator. Residual sulfite determination was carried out using iodine solution and sodium acetate as a buffer in titration with sodium thiosulfate solution with starch as an indicator. Residual PAA was measured using RQFlex 10 reflectometer (Merck). Residual alkali and chlorine determinations from the bleaching sequence were carried out also by titrations. Residual alkali was determined with hydrochloric acid using phenolphthalein as

an indicator. Residual chlorine titration was carried out similarly to the active chlorine determination titration of chlorine dioxide described in the Section 6.2.

HexA content was determined from selected smaller laboratory scale HW pulp and SW pulp samples. The HexA content determination was carried out according to method based on Helsinki University of Technology (HUT)-method: Selective acid hydrolysis, determination by UV-spectroscopy (Tenkanen et al., 1999).

X-ray fluorescence spectrometry (XRF) -analysis (Panalytical, Axios 2.4 kW) was carried out for HW pulp and SW pulp before laboratory treatments to determine metals from the pulps. For sample preparation 2.5 g of oven dried sample was weight and grinded in 10 second cycles until sample was fully grinded, after which 5 g of licowax and 1 g of grinded sample was used to make a pellet by pressing.

6.2.5 Pulp and paper properties

Brightness of the small and the large laboratory scale samples was measured from laboratory sheets of about 80 g/m² grammage, which were prepared using KCL sheet former (Lorentzen and Wettre), pressed for 5 minutes using 4 bar pressure (Sheet press, Lorentzen and Wettre), and dried with drum drier (Lorentzen and Wettre). Otherwise the brightness measurements were carried out according to ISO 3688.

Kappa number was analyzed according to ISO 302:1981. with a modification that the determination was carried out at ¾ scale (75 ml KMnO₄ (Oy FF-Chemicals Ab)). Determination of kappa number of HexA was carried out using UVRR method and the amount of HexA determined via acid hydrolysis. The method is specified in APPENDIX VIII. Viscosity was measured from selected small-scale laboratory pretreatment samples, and the measurements were carried out according to the standard ISO 5351.

In pilot scale pretreatments and bleaching, kappa number of each sample was determined after pretreatments and E-stages according to ISO 302:2015. Brightness was measured according to the standard (ISO 2470) after all pilot scale pretreatment and bleaching stages from split sheets. Viscosity was measured from totally bleached pulps following ISO 5351. Residual chlorine dioxide was also determined via titration after both D-stages.

After bleaching samples were refined at Kemira R&D Center. Refining was carried out using Voith LRF refiner equipped with conical plates (3-0.5-30) and each fully bleached pulp was refined using four specific refining energy (SRE) targets, which were 0, 60, 120 and 180 kWh/t. SR number and WRV measurements, to analyze pulp properties from pilot scale fully bleached samples, were carried out according to ISO 5267 and modified ISO 23714. Latter standard was modified by using deionized water instead of standard water and preparing of four replica samples from same sample pad.

From the refined pilot-scale samples, the paper property measurements, performed to laboratory sheets (ISO 5269), were carried out according to following standards: density and grammage (ISO 534), tensile and tear strength (ISO 5270). In tear strength tests four replica samples were tested, one test piece consisting of four sheet pieces.

7 Results and discussion

All the results from the experimental part are gathered and discussed in this chapter. Hardwood and softwood pretreatment and bleaching results are presented separately in the Sections 7.1 and 7.2. In addition, in softwood results also pilot scale and refining results as well as pulp and paper properties are presented.

The results from XRF-analysis presenting the metals content of the initial HW and SW pulps are presented in Table 5 below.

Table 5. Results of metals content (ppm) analysis by XRF of HW and SW pulps.

Sample	Ca	Cu	Fe	Mg	Mn	Na	S
HW pulp	1100	1	59	790	49	4900	1400
SW pulp	670	<1	6,3	200	23	6600	2200

The most critical metals from peroxide and dPAA treatment point, Mn and Fe are considerably higher for HW pulp than for the SW pulp, however in general, the metal contents are on a normal level.

7.1 Hardwood pulp bleaching pretreatments

In this chapter results from HW pulp laboratory pretreatments and bleaching sequences are presented. The results from the small laboratory scale in which only pretreatments were carried out are presented and discussed in subchapter 7.1.1. From the small laboratory scale pretreatments, reference A-stage and five other pretreatments were scaled up in large laboratory scale and then bleached with DED-sequence. The results from the large laboratory scale are presented in Subsection 7.1.2.

7.1.1 Small laboratory scale pretreatments

HW pulp small laboratory scale pretreatments were carried out using various different chemicals. The effects of peroxide, peroxy acids as well as sulfite pretreatments on the brightness and kappa number were studied. A-stage was carried out as reference.

Acetone together with Caro's acid has been showing effective *in situ* dimethyl dioxirane forming reactions, having a selective delignification effect (Dence and Reeve, 1996). Dioxiranes which are cyclic peroxides have a strong electrophilic nature, capable of transferring oxygen onto aromatic and unsaturated structures (Suchy and Argyropoulos, 2001). Thus, addition of acetone to dPAA and Caro's acid was carried out to study its effect to the treatments as an activator.

The brightness results are presented in Figure 9. The kappa number results from which kappa of HexA and lignin can be distinguished as the differently patterned sections of the kappa number column can be seen in Figure 10. Viscosity was measured from SW pulp, A-stage, dPAA with acetone, Caro's acid, Caro's acid with SiMo and higher chemical charge sulfite pretreated pulps. Viscosity results for aforementioned test points are presented in Figure 11.

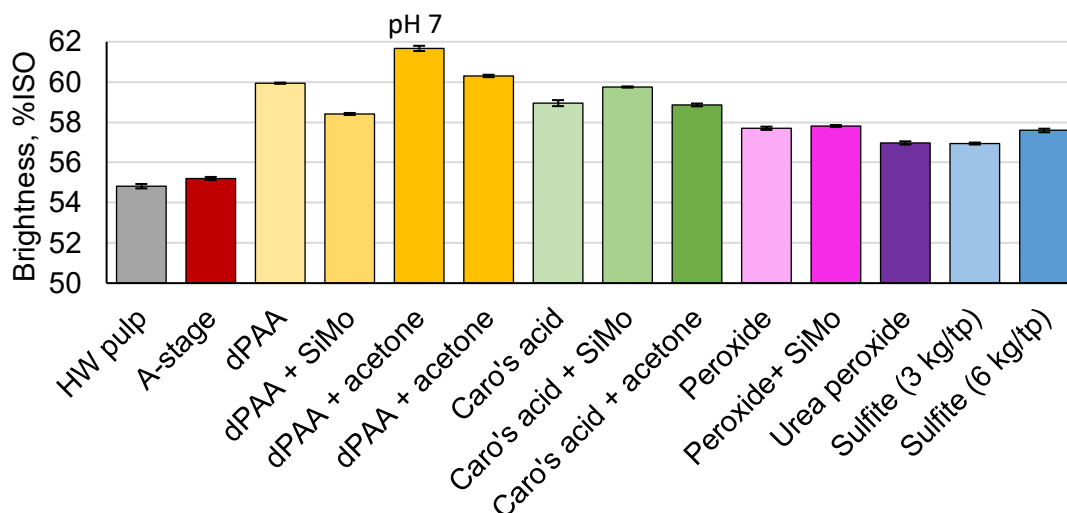


Figure 9. Brightness results from HW pulp small laboratory scale pretreatments.

All small laboratory scale pretreatments for HW pulp increased brightness compared to untreated and reference A-stage brightness results (Figure 9). Pretreatment carried out with dPAA and acetone (without pH adjustment) was measured with highest brightness value. Also, dPAA and acidic dPAA with acetone resulted in the highest brightness values Caro's acid with SiMo being on the same level. Peroxide, urea peroxide and both sulfite tests points resulted in only maximum of two unit raise from the brightness value of the reference.

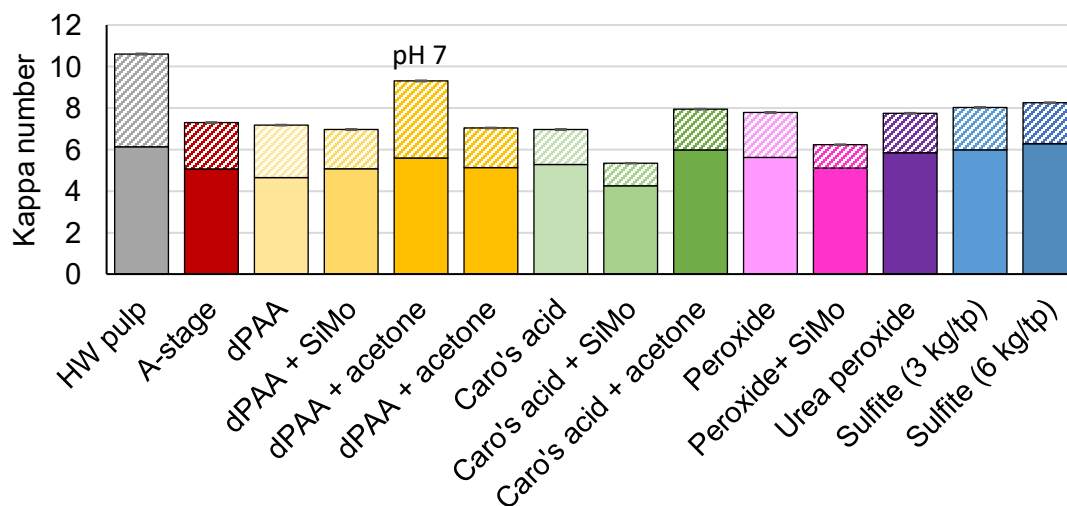


Figure 10. Kappa number results from HW pulp small laboratory scale pretreatments separated to kappa of HexA (pattern fill) and lignin (solid fill).

Urea peroxide and both sulfite test points reached similar kappa number level, that was about one unit higher than reference A-stage pretreatment. A-stage kappa number

reduction was mostly due to HexA reduction. Acetone addition to dPAA at pH 7 seemed to prevent kappa number reduction, more specifically the kappa number of HexA was significantly higher.

Caro's acid with SiMo was only test point reaching kappa number under 6, while the test point carried out using peroxide and SiMo was the only other pretreatment achieving kappa number that was lower than that of reference. Caro's acid pretreatment with and without SiMo addition reduced both lignin and HexA kappa number, however, with SiMo addition HexA removal was enhanced. Similar behavior can be observed from peroxide results, which indicates that SiMo activates peroxide in both Caro's acid and peroxide pretreatments. Similar effect of SiMo with dPaa can also be seen. Acetone addition to Caro's acid seems to prevent delignification and HexA removal.

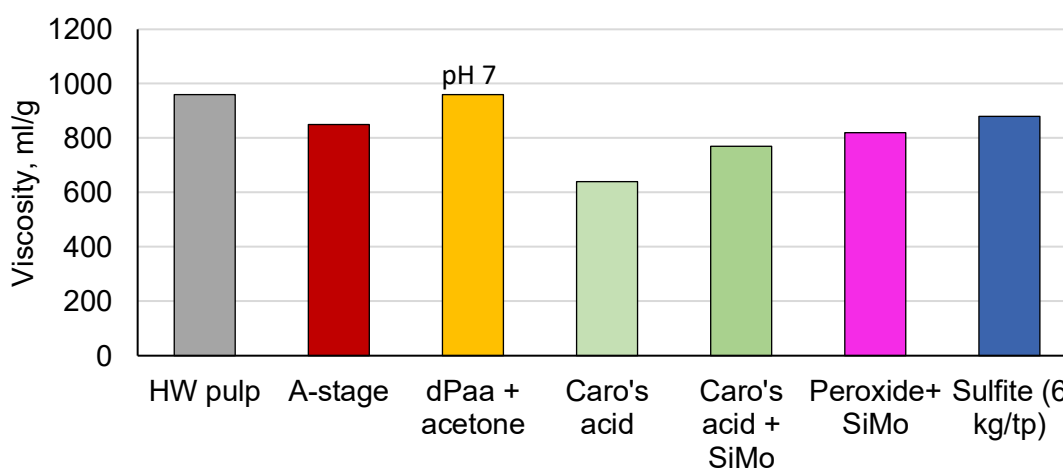


Figure 11. Viscosity values of selected HW pulp samples after small laboratory scale pretreatments.

Caro's acid resulted in most notable decrease in viscosity, even though, the HexA and lignin removal was more significant with SiMo addition. Similar behavior can be observed with peroxide with SiMo addition. Thus, indicating increased selectivity of Caro's acid or peroxide towards lignin and HexA, and further enabling to perform pretreatment with increased ability to preserve carbohydrates.

7.1.2 Large laboratory scale pretreatments and bleaching

In addition to the reference A-stage following pretreatments from previous experimental phase were selected: dPAA with acetone, Caro's acid with SiMo and larger charge (6

kg/t) of sulfite. Caro's acid showed promising results in the first pretreatments, hence selected to be further studied. Sulfite and dPAA pretreatments were selected in order to see the effect of the treatments after bleaching stage.

Results from the large laboratory scale pretreatment and bleaching are presented and discussed in this chapter. Brightness (Figure 12), kappa number (Figure 13), UV Raman spectroscopy (APPENDIX VI) and extractive content (Figure 14) measurements were performed on the samples from these treatments.

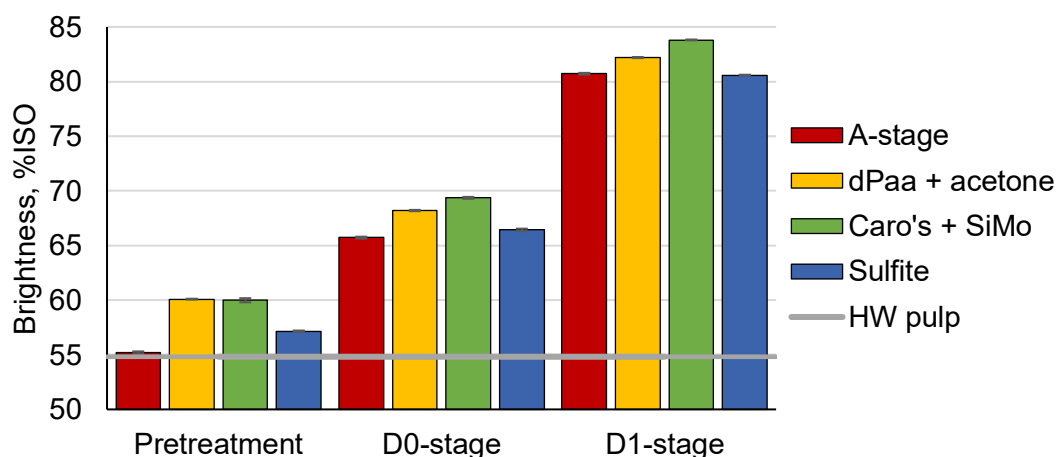


Figure 12. Birch kraft pulp ISO-brightness results for pretreatments, after D_0 and D_1 - phases of the large laboratory scale.

In large laboratory scale sample pretreatment carried out using dPaa with acetone and Caro's acid with SiMo had similar level in brightness, however, Caro's acid with SiMo reached the highest brightness value after final bleaching. Compared to A-stage, the final brightness of Caro's acid with SiMo test point was about 4 units higher.

The brightness of totally bleached samples did not reach the full brightness (>88 %ISO). However, full brightness was not targeted, while the difference in brightness and the constant bleaching chemical charge, thus comparative treatments, were more of an importance on this work. In addition, considering the chemical charges of chlorine chemicals (as active chlorine) used in this study, which was 11 kg/t in both D-stages, can be considered low.

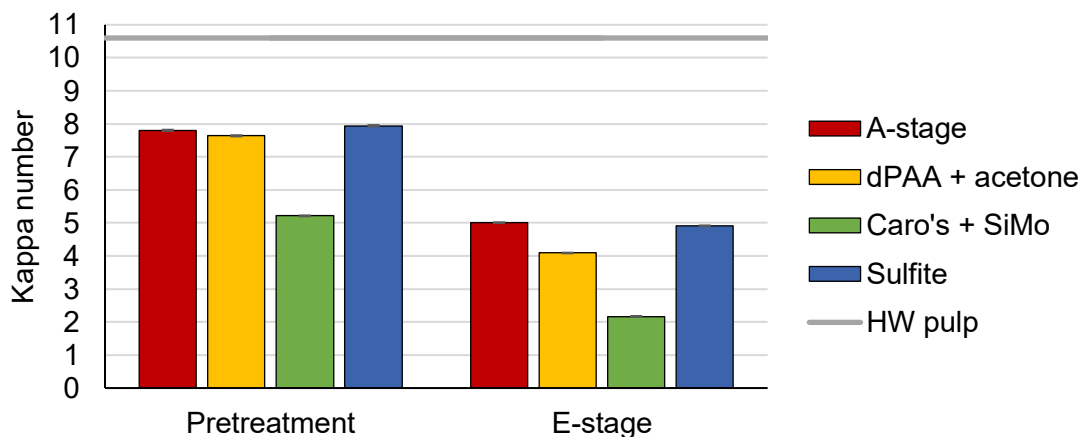


Figure 13. Measured kappa numbers after pretreatments and E-stage for HW pulp in the large laboratory scale.

Kappa number results after pretreatment correspond to the kappa number values from the same stage in large laboratory scale. Results after E-stage can be observed to be in line with the pretreatments results – differences between the samples have similar trend. Caro's acid with SiMo addition resulted in significantly lower kappa number compared to other samples.

Chlorine dioxide charge, as discussed previously depends usually on the kappa number of the pulp entering the stage. Based on the kappa number level difference between the Caro's acid pretreatment with SiMo addition and the reference there is chlorine consumption savings potential.

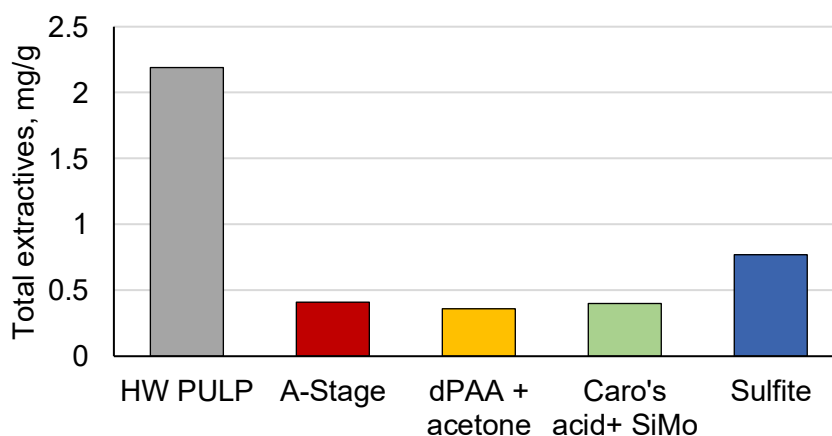


Figure 14. Total extractive content of totally bleached samples.

Apart from sulfite pretreatment, the other results from selected pretreatment samples for extractive studies did not notably differ from each other. The extractive content of the

sulfite treatment is most probably a measurement error. The extractive content is considerably lower than that seen for industrial pulps (UPM-Kymmene Corporation, 2019a and 2019b) and that is due to the intense washing done for the laboratory pulp compared to industrial pulps.

7.2 Softwood pulp bleaching pretreatments

In this chapter results from SW pulp laboratory scale pretreatments and bleaching stages are presented. In addition to small and large laboratory scale results which are presented in subchapters 7.2.1 and 7.2.2. results from pilot scale pretreatments and DED-bleaching are presented and discussed in the subchapter 7.2.3. Refining and pulp properties as well as paper properties of the pilot scale fully bleached pulps are presented in Sections 7.2.4 and 7.2.5 respectively.

7.2.1 Small laboratory scale bleaching pretreatments

SW pulp small laboratory scale pretreatments were carried out using selected pretreatments from the HW pulp pretreatments. The effects of peroxy acids as well as sulfite pretreatments on the brightness (Figure 15) and kappa number (Figure 16) were studied. In addition, viscosities were measured from the samples excluding dPAA samples, and the results are presented in Figure 17. All results from measurements for pretreated softwood kraft pulps carried out are summarized in APPENDIX IV, excluding UVRR spectra which are presented in APPENDIX VI.

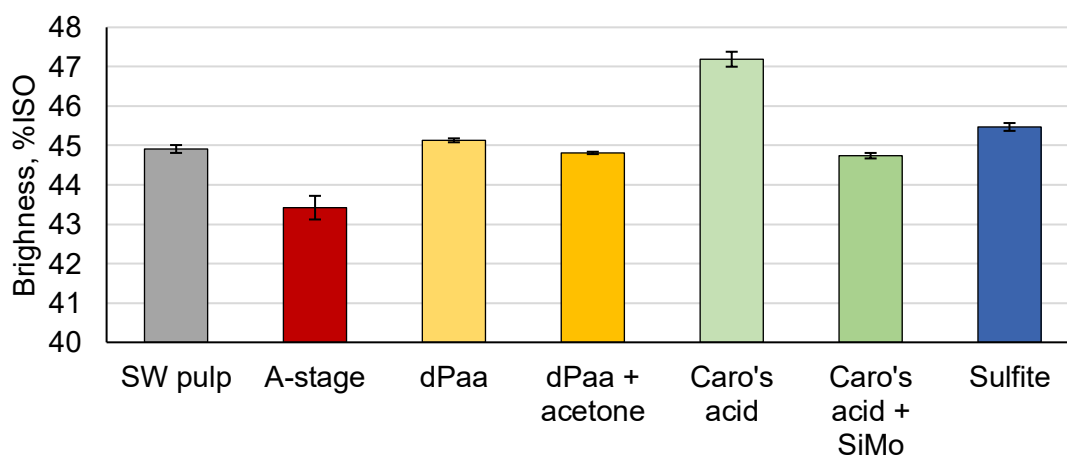


Figure 15. SW brightness results for small laboratory scale pretreatments.

The brightness result of A-stage was notably lower than that of the initial SW pulp. The

highest brightness result, that was about two units higher than that of the other treatments, was achieved with Caro's acid test point. Other treatments did not show significant differences in brightness.

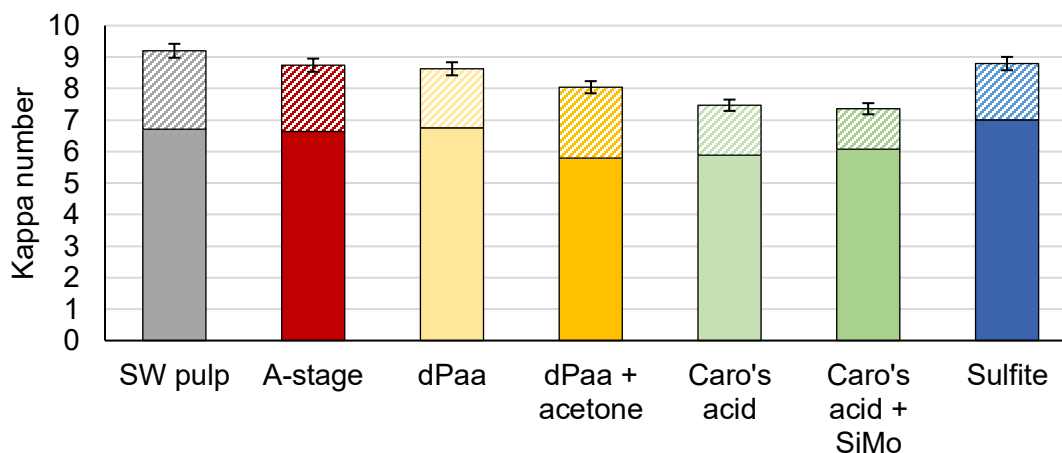


Figure 16. SW pulp kappa number results for small laboratory scale pretreatments separated to kappa of HexA (patterned fill) and lignin (solid fill).

Kappa number of HexA in relation to kappa of lignin is smaller in SW pulp compared to HW pulp. This is in concordance with the lower initial glucuronoxytan amount in softwoods, and thus with the lower HexA amount in softwood pulp.

DPAA pretreatment with acetone as well as both Caro's acid test points resulted in lowest kappa numbers. However, Caro's acid pretreatments showed more notable decrease in kappa number of HexA. The other pretreatments, A-stage, dPAA and sulfite, did not have a particular difference in the kappa number. Simo addition to Caro's acid seemed to slightly improve HexA removal similarly to HW pulp.

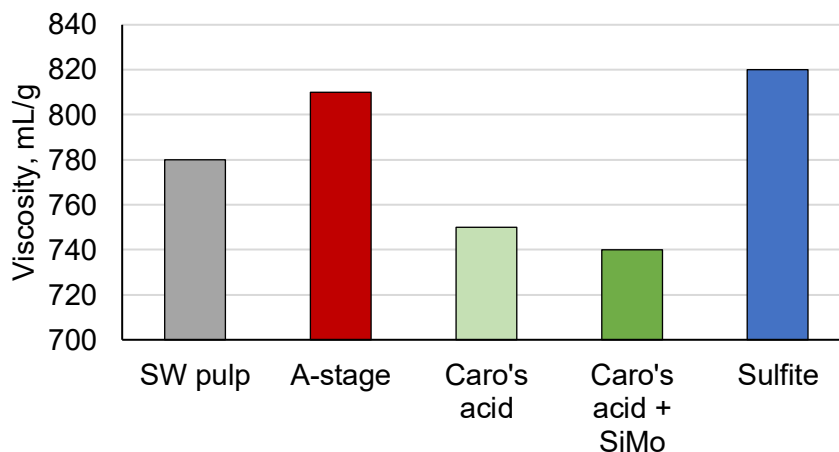


Figure 17. Viscosity results of selected SW pulp smaller laboratory scale pretreatment samples.

Caro's acid treatments can be seen to have a significant effect on the viscosity of the pulp. Both sulfite pretreatment and A-stage seem to have higher viscosity than SW pulp, however, there is no explanation for that sort of behavior, thus more likely reason would be an error occurred in the measurement of the initial SW pulp viscosity.

7.2.2 Large laboratory scale pretreatments and bleaching

The selection of experiments to be carried out in the large laboratory scale pretreatments and bleaching was based on the results from the small laboratory scale experiments. The treatments chosen were A-stage and both Caro's acid pretreatments in addition to the reference, which was carried out without pH adjustment.

Caro's acid test points showed promising results in the small laboratory scale decreasing kappa number. They did, however, cause a significant drop in viscosity. Due to aforementioned reasons, both test points were selected to the second phase studies, in order to see the further impact on the SW pulp after bleaching sequence. The charge of bleaching chemicals was the same for all experiments and based on the kappa number achieved with Caro's acid pretreatment (APPENDIX II). The Brightness (Figure 18) results from the large laboratory scale are presented below.

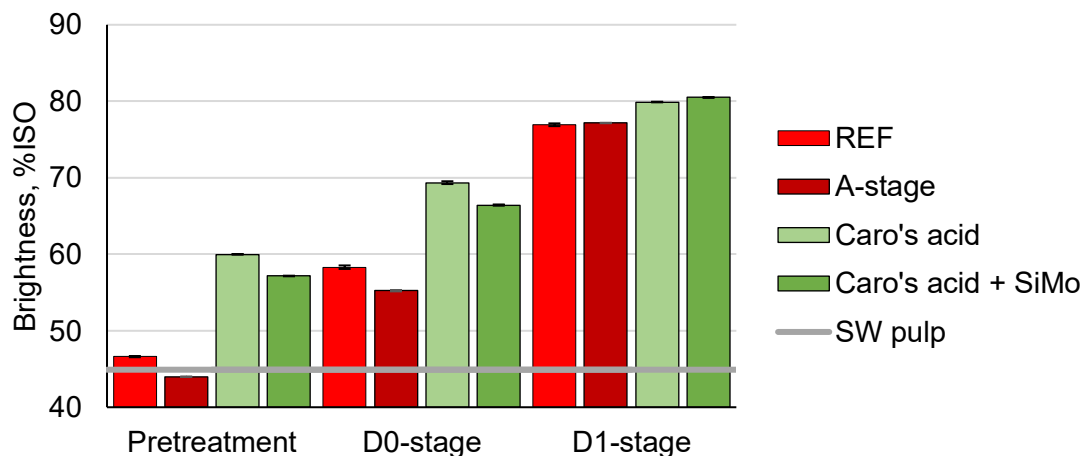


Figure 18. SW pulp ISO brightness results for pretreatments, after D₀- and D₁-stages of the large laboratory scale.

The advantage in brightness that was achieved with Caro's acid pretreatment compared to the one where also SiMo was used as an activator was present also after D₀-stage. However, after final bleaching stage the difference leveled out as can be seen in the Figure 18. The difference in brightness value that was achieved with both Caro's acid test points in comparison to the reference and A-stage leveled out also after the last chlorine dioxide bleaching stage.

In larger scale laboratory pretreatments kappa number determination was carried out after pretreatment and E-stage. The results can be seen in Figure 19.

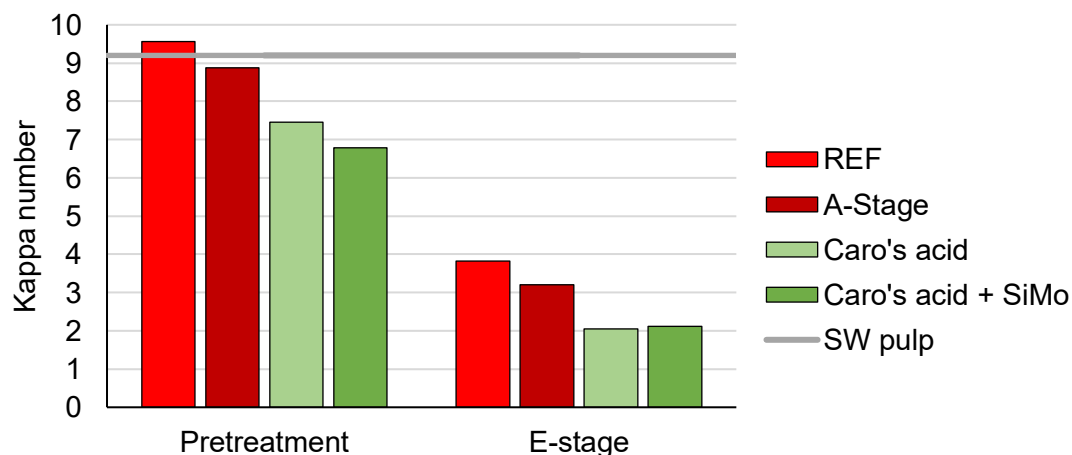


Figure 19. Measured kappa numbers after pretreatments and E-stage for softwood kraft pulp in the large laboratory scale.

Both Caro's acid test points resulted in kappa number that was about two units lower than

the one of the references. In the kappa number determination of the Caro's acid samples after E-stage, the permanganate consumption exceeded the threshold value (consumption between 30-70% of the 0-sample consumption) set by the standard (ISO 302:1981). Thus, the weighed amount of the sample should have been higher. However, at this kappa number level, the amount of pulp sample needed for this determination would have resulted in poor disintegration, homogenization and mixing during determination. Which would further also result in error as well as impaired repeatability. So, the error from the deviation from the standard was considered to be small and thus used in this work. Based on the kappa number level reduction compared to reference, using Caro's acid in a pretreatment for SW kraft pulp bleaching offers chlorine consumption savings potential.

7.2.3 Pilot scale bleaching pretreatments and bleaching

Two pretreatments, A-stage and Caro's acid, were carried out in the pilot scale in addition to reference. Reference sample was treated at the same consistency, temperature and time as the other two, however, the pH was not adjusted. The parameters are presented in APPENDIX I. After pretreatments the samples were bleached using DED-bleaching sequence, using the same charge of active chemicals as in the large laboratory scale. Brightness, kappa number and viscosity results are presented in figures below (Figure 20-Figure 22).

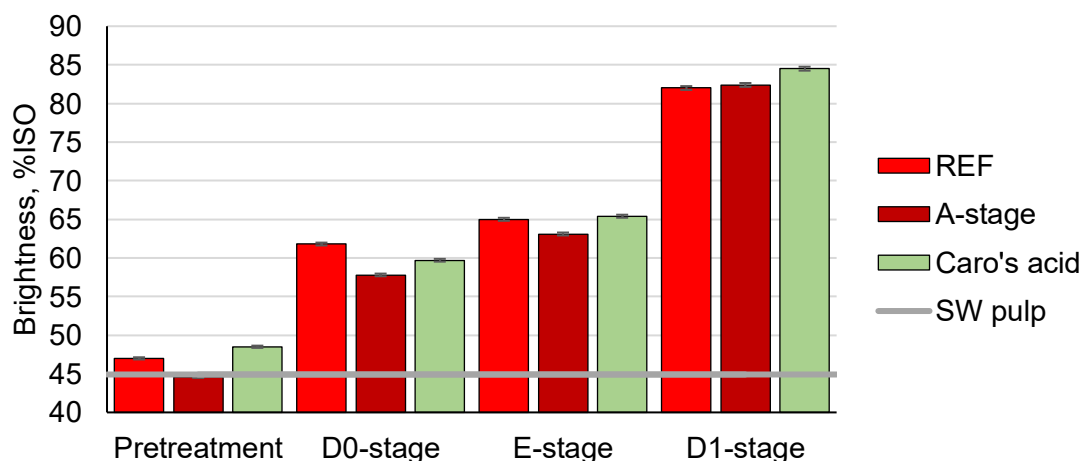


Figure 20. Brightness results from pilot scale experiments after pretreatment and bleaching stage.

The final brightness results from the pilot scale measurements (Figure 20) are in line with

the results from the large laboratory scale. Similarly to the large laboratory scale, the difference in the brightness value of Caro's acid was higher after the D₁-stage than that of the other two samples. In addition, the brightness difference between A-stage pretreated and reference pulp leveled out in the final bleaching.

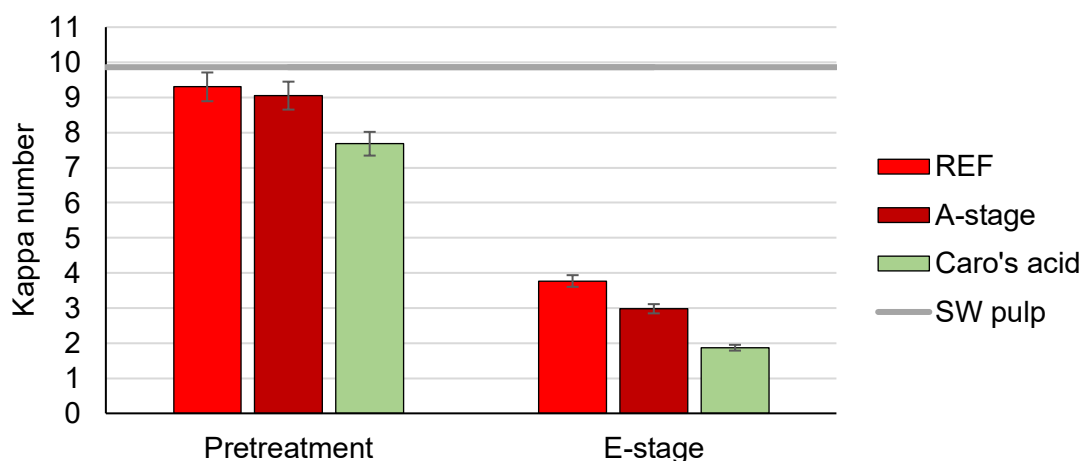


Figure 21. Kappa number results from pilot scale experiments after pretreatments and bleaching E-stages.

The trend in kappa number decrease is in line with the previous large laboratory scale experiments, as can be seen in Figure 21. Caro's acid shows a significant decrease in kappa number between pretreatment and E-stage. Furthermore, after E-stage the pulp treated with Caro's acid has the lowest kappa number. Thus, as with HW pulp large laboratory scale results, it can be said that kraft pulp pretreated with Caro's acid has potential for chlorine-containing chemical consumption savings in bleaching.

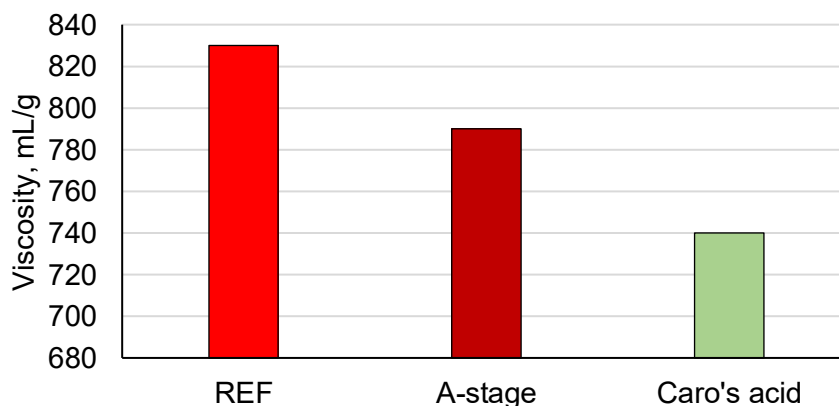


Figure 22. Viscosity results for the pilot scale totally bleached samples.

Viscosity of Caro's acid pretreated and DED-bleached pulp can be seen to be significantly decreased. Also, A-stage has affected the viscosity of the pulp.

7.2.4 Refining and pulp properties

WRV measures the ability of the fiber to retain water and is related to the extent of fiber fibrillation. It is widely used in the pulp and paper industry to measure this characteristic. In addition, WRV can be used as a reliable characterization method for fibrillation extent of micro and nanofibrils. (Gu et al., 2018) Mechanical stress, when directed to the fiber, causes delamination. Delamination in the presence of water leads to swelling due to internal fibrillation, increasing fiber flexibility. (Hartman, 1984) This affects the WRV, which is thus increased by beating or refining (Hartman, 1984; Roffael and Kraft, 2012) In addition, external fibrillation occurs increasing external surface area (Hartman, 1984).

After pretreatments and DED-bleaching pilot scale, pulps were refined using four different specific refining energies. WRV and SR values from each pilot scale pulp as a function of SRE used in refining are presented in Figure 23 and Figure 24 below.

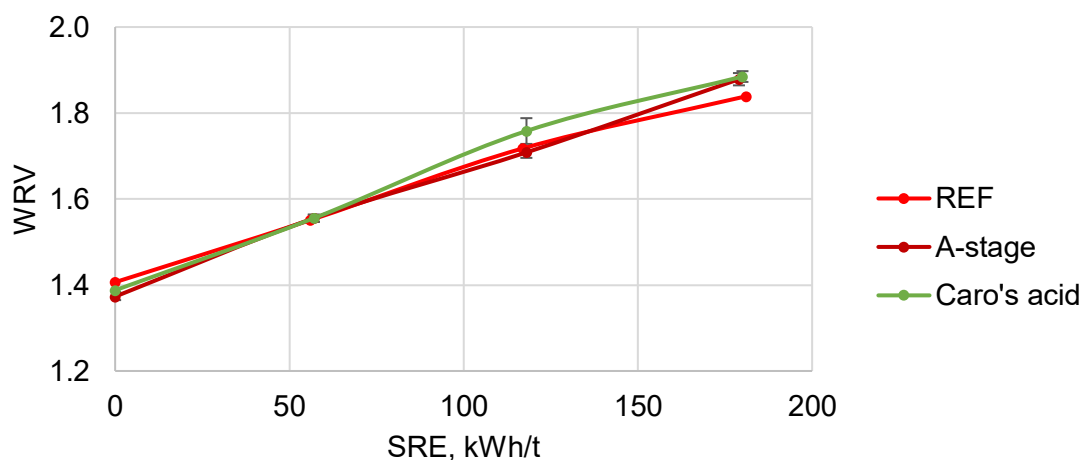


Figure 23. WRV results from refined fully bleached pilot scale pulps.

The WRV results of the fully bleached and refined pulps do not differ greatly from each other, indicating that dewatering properties had not been altered with the pretreatments.

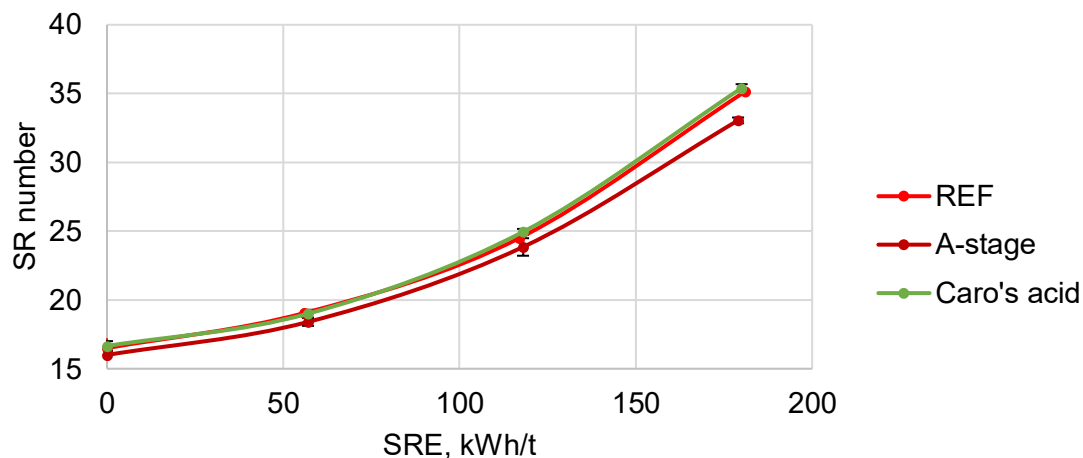


Figure 24. SR number results from refined pilot scale pulps.

Also, the SR number results from the refined pulps are on the same level, supporting the observations from the WRV measurements, that the pretreatments had no effect on the dewatering properties.

7.2.5 Paper properties

Tear and tensile indexes were determined from sheets prepared from the pulps from all of the refining points. Measurements were carried out to study the influence of the studied pretreatments on paper properties.

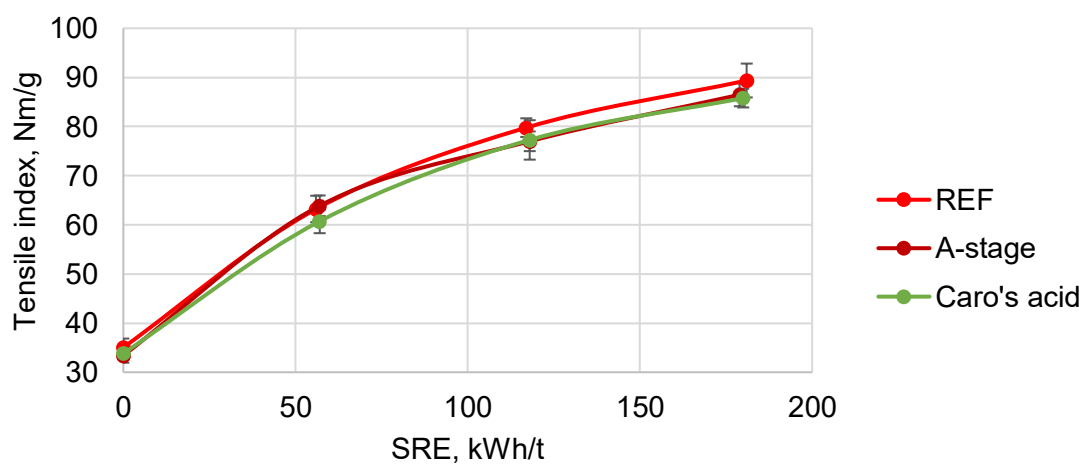


Figure 25. Tensile index as a function of refining energy.

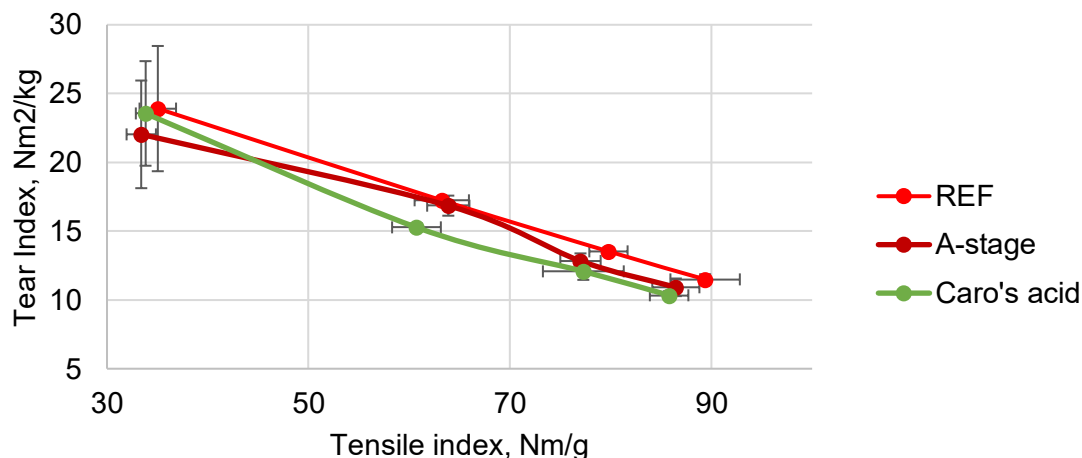


Figure 26. Tear index as a function of tensile index.

From Figure 25 it can be seen that Caro's acid pretreated pulp and also A-stage pretreated pulp, require more energy input to reach the same tensile index as reference at higher tensile indexes. Furthermore, the acidic pretreatments also result in lower tear index at certain tensile than reference pulp. This is in correlation with the decrease seen in the viscosity with Caro's acid treatment. Thus, it can be concluded that the acidic pretreatments have a small effect on the studied strength properties.

8 Conclusions

The aim of this thesis was to study possibilities to enhance bleaching of softwood and hardwood kraft pulps, enabling decrease in chlorine-containing chemical consumption. Experimental part of the work was carried out studying different pretreatments preceding conventional DED-bleaching sequence. Evaluation of the pretreatments was based on the brightness level, kappa number and with some test point viscosity, as the properties have certain requirements considering the industrial processes and end use applications.

In hardwood pulp pretreatments, Caro's acid with SiMo addition was seen to affect the reactions occurring with both lignin and hexenuronic acid and concluded in an increase in the HexA removal. The results also indicate that addition of SiMo would result in preserving carbohydrates. Extractives content after selected pretreatments resulted in lower amounts of what typical of industrial pulps, however affected most likely by more intense washing.

Caro's acid pretreatments were detected to have significant effect on kappa number of softwood pulp, however, having decreasing effect on the viscosity. At the same time brightness was increased. The results from refining considering WRV and SR number were similar with all pulps (reference, A-stage and Caro's acid pretreated), which indicates that dewatering properties were not affected. There was slight effect of acidic pretreatments observed on tear and tensile properties, which was in line with the drop in viscosity that was seen.

With both hardwood and softwood pulps silica molybdate (SiMo) was observed to have an activating effect on hydrogen peroxide to reduce kappa number. Based on the kappa number level reduction compared to reference, using Caro's acid in a pretreatment for both HW and SW kraft pulp bleaching has chlorine consumption savings potential. This would reduce chlorine emissions in process water effluents and further have a positive effect on environmental impact.

This thesis focused on studying pretreatments carried out using different chemicals and showed some promising results without optimization of the pretreatments. More suitable parameters and focus on the optimization of each pretreatment, especially of those with improved HexA removal or delignification would further give information on the magnitude of the more specific saving or substitution possibilities.

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APPENDIX I (1/2)

Pretreatment parameters

Table 1. Conditions for all laboratory scale pretreatments.

Consistency (%)	10
Temperature (°C)	90
Time (min)	120

Table 2. Other parameters for HW pulp small laboratory scale pretreatments.

Sample	Chemical charge, H ₂ SO ₄ , kg/tp	Pretreatment chemical charge kg/tp	Activator charge, kg/tp	pH, initial	pH, end
A-stage	14			3.0	2.8
dPAA	13	3		3.1	3.0
dPAA + SiMo	13	3	0.3	3.1	3.0
dPAA + acetone (pH 7)		3	0.3	7.2	6.8
dPAA + acetone	13	3	0.3	3.3	3.0
Caro's acid		14 + 5 (act. H ₂ O ₂)		3.1	2.8
Caro's acid + SiMo		14 + 5 (act. H ₂ O ₂)	0.3	3.0	2.9
Caro's acid + acetone		14 + 5 (act. H ₂ O ₂)	0.3	3.5	3.2
H ₂ O ₂	14	5 (act. H ₂ O ₂)		3.0	2.9
H ₂ O ₂ + SiMo	14	5 (act. H ₂ O ₂)	0.3	3.1	3.0
Urea peroxide	14	5 (act. H ₂ O ₂)		3.0	3.0
Sulfite (3 kg/tp)	14	3		3.0	3.0
Sulfite (6 kg/tp)	14	6		3.1	3.0

Table 3. Other parameters for HW pulp large laboratory scale pretreatments.

Sample	Chemical charge, H ₂ SO ₄ , kg/tp	Pretreatment chemical charge kg/tp	Activator charge, kg/tp	pH, initial	pH, end
A-stage	14			3.0	2.8
dPAA + acetone	14	3	0.3	3.3	2.9
Caro's acid + SiMo		14 + 5 (act. H ₂ O ₂)	0.3	3.0	2.8
Sulfite (6 kg/tp)	14	6		3.0	2.9

Table 4. Other parameters for SW pulp small laboratory scale pretreatments.

Sample	Chemical charge, H ₂ SO ₄ , kg/tp	Pretreatment chemical charge kg/tp	Activator charge, kg/tp	pH, initial	pH, end
A-stage	23	-		3.0	3.0
dPAA	23	3		3.1	3.1
dPAA + acetone	23	3	0.3	3.2	3.2
Caro's acid		23 + 5 (act. H ₂ O ₂)		3.4	3.2
Caro's acid + SiMo		23 + 5 (act. H ₂ O ₂)	0.3	3.4	3.1
Sulfite	25	6		3.2	3.2

APPENDIX I (2/2)

Table 5. Other parameters for SW pulp small laboratory scale pretreatments.

Sample	Chemical charge, H ₂ SO ₄ , kg/tp	Pretreatment chemical charge kg/tp	Activator charge, kg/tp	pH, initial	pH, end
REF					
A-stage	23	-		3.2	3.2
Caro's acid		23 + 5 (act. H ₂ O ₂)		3.4	3.2
Caro's acid + SiMo		23 + 5 (act. H ₂ O ₂)	0.3	3.4	3.1

Table 6. Other parameters for pilot scale pretreatments.

Sample	Chemical charge, H ₂ SO ₄ , kg/tp	Pretreatment chemical charge kg/tp	Activator charge, kg/tp	pH, initial	pH, end
REF				10.2	10.1
A-stage	23			3.1	3.1
Caro's acid		23 + 5 (act. H ₂ O ₂)		3.1	3.0

APPENDIX II (1/2)

Bleaching conditions

Table 7. Conditions for HW pulp DED-bleaching in large laboratory scale.

		REF	A-stage	Caro's acid	Sulfite
D0	Consistency (%)	10	10	10	10
	Temperature (°C)	70	70	70	70
	Time (min)	30	30	30	30
	pH, initial	2.7	2.8	2.7	2.8
	pH, end	2.6	2.7	2.6	2.5
	ClO ₂ charge, (act. Cl, kg/tp)	11	11	11	11
E	Consistency (%)	10	10	10	10
	Temperature (°C)	70	70	70	70
	Time (min)	60	30	30	30
	pH, initial	11.1	11.1	11.2	11.2
	pH, end	11.0	11.0	11.1	11.1
	NaOH charge, (kg/tp)	10	10	10	10
D1	Consistency (%)	10	10	10	10
	Temperature (°C)	75	75	75	75
	Time (min)	120	120	120	120
	pH, initial	4.1	4.2	4.1	4.2
	pH, end	3.9	3.9	3.5	3.9
	ClO ₂ charge, (act Cl, kg/tp)	11	11	11	11

Table 8. Conditions for SW pulp DED-bleaching in large laboratory scale.

		REF	A-stage	Caro's acid	Caro's acid + SiMo
D0	Consistency (%)	10	10	10	10
	Temperature (°C)	70	70	70	70
	Time (min)	30	30	30	30
	pH, initial	2.7	2.7	2.8	2.7
	pH, end	2.4	2.6	2.5	2.5
	ClO ₂ charge, (act. Cl, kg/tp)	15	15	15	15
E	Consistency (%)	10	10	10	10
	Temperature (°C)	70	70	70	70
	Time (min)	60	30	30	30
	pH, initial	11.2	11.2	11.2	11.2
	pH, end	11.2	11.1	11.2	11.1
	NaOH charge, (kg/tp)	10	10	10	10
D1	Consistency (%)	10	10	10	10
	Temperature (°C)	75	75	75	75
	Time (min)	120	120	120	120
	pH, initial	4.1	4.1	3.8	4.0
	pH, end	3.1	3.1	3.0	3.1
	ClO ₂ charge, (act Cl, kg/tp)	11	11	11	11

APPENDIX II (2/2)

Table 9. Conditions for DED-bleaching in pilot-scale.

		REF	A-stage	Caro's acid
D0	Consistency (%)	10	10	10
	Temperature (°C)	70	70	70
	Time (min)	30	30	30
	pH, initial (before ClO ₂ add.)	3.4	4.3	3.8
	pH, end	2.1	1.9	1.9
	ClO ₂ charge, (act Cl, kg/tp)	15	15	15
E	Consistency (%)	10	10	10
	Temperature (°C)	70	70	70
	Time (min)	60	30	30
	pH, initial	10.9	10.8	10.8
	pH, end	10.8	10.7	10.8
	NaOH charge, (kg/tp)	10	15	15
D1	Consistency (%)	10	10	10
	Temperature (°C)	75	75	75
	Time (min)	120	120	120
	pH, initial (before ClO ₂ add.)	8.1	8.2	8.3
	pH, end	2.5	2.5	2.4
	ClO ₂ charge, (act Cl, kg/tp)	11	11	11

APPENDIX III

Refining conditions

Table 10. Refining conditions for pilot scale fully bleached reference pulp.

Refining conditions	1	2	3	4
Refining time (s)	0.00	3:49	3:18	3:04
Mass of suspension (g)	2072	1964	1938	1985
Sample mass (g)	83	79	78	79
Mass of residue (g)	1212	113	1056	976
Feed pressure (bar)	0.6	0.6	0.6	0.6
Total output (kW)	2.223	2.632	2.819	2.851
Refining output (kW)	0	1.069	1.255	1.288
Specific work (kWh/t)	0	138	275	413
SRE (kWh/t)	0	56	117	179

Table 11. Refining conditions for pilot scale A-stage pretreated and fully bleached pulp.

Refining conditions	1	2	3	4
Refining time (s)	0:00	3:58	3:26	3:12
Mass of suspension (g)	2071	1945	2028	2012
Sample mass (g)	83	78	81	80
Mass of residue (g)	1258	1180	1099	1019
Feed pressure (bar)	0.5	0.6	0.6	0.6
Total output (kW)	2.271	2.688	2.9	2.891
Refining output (kW)	0	1.088	1.26	1.291
Specific work (kWh/t)	0	141	280	420
SRE (kWh/t)	0	57	118	181

Table 12. Refining conditions for pilot scale Caros' acid pretreated and fully bleached pulp.

Refining conditions	1	2	3	4
Refining time (s)	0.00	4.00	3:28	3:14
Mass of suspension (g)	1997	1988	2017	1986
Sample mass (g)	80	80	81	79
Mass of residue (g)	1274	1195	1114	1034
Feed pressure (bar)	0.7	0.6	0.6	0.6
Total output (kW)	2.3	2.7	2.9	2.9
Refining output (kW)	0.0	1.1	1.3	1.3
Specific work (kWh/t)	0	140	279	418
SRE (kWh/t)	0	57	118	180

APPENDIX IV (1/2)

Pretreatment results

Table 13. HW pulp and SW pulp results.

Sample	Brightness, %ISO	Kappa number	Viscosity, mL/g	HexA, mmol/kg	Total Extractives, mg/g
HW pulp	54.8	10.6	960	51.3	2.19
SW pulp	44.9	9.2	780	32.0	

Table 14. HW pulp small laboratory scale pretreatment results.

Sample	Brightness, %ISO	Kappa number	Viscosity, mL/g	HexA, mmol/kg	Residual chemical, kg/tp
A-stage	55.2	7.3	850	28.4	
dPAA	59.9	7.2		27.9	0.00
dPAA + SiMo	58.4	7.0	960		0.00
dPAA + acetone (pH 7)	61.7	9.3			0.01
dPAA + acetone (pH 3)	60.3	9.7			0.00
Caro's acid	59.0	7.0	640	20.6	0.05/0.14
Caro's acid + SiMo	59.8	5.3	770	11.2	0.02/0.30
Caro's acid + acetone	58.9	7.9			0.02/0.22
H2O2	57.7	7.8		24.7	2.29
H2O2 + SiMo	57.8	6.2	820	12.3	0.00
Urea peroxide	57.0	7.7			2.57
Sulfite (3 kg/tp)	56.9	8.0			0.92
Sulfite (6 kg/tp)	57.6	8.3	880		1.15

Table 15. HW pulp large laboratory scale pretreatment results.

Sample	Brightness, %ISO	Kappa number	Residual chemical, kg/tp
A-stage	55.2	7.3	
dPAA + acetone	61.7	9.3	0.01
Caro's acid + SiMo	59.8	5.3	0.14/0.01
Sulfite	57.6	8.3	0.97

Table 16. SW pulp small laboratory scale pretreatment results.

Sample	Brightness, %ISO	Kappa number	Viscosity, mL/g	HexA, mmol/kg	Residual chemical, kg/tp
A-stage	43.4	8.7	810	23.1	
dPAA	45.1	8.6			0.00
dPAA + Acetone	44.8	8.0			0.00
Caro's acid	47.2	7.5	750	14.7	0.31/0.14
Caro's + SiMo	44.7	7.4	740	19.1	0.24/0.02
Sulfite	45.5	8.8	820		1.47

Table 17. SW pulp large laboratory scale pretreatment results.

Sample	Brightness, %ISO	Kappa number	Residual chemical, kg/tp
REF	46.6	9.6	
A-stage	44.0	8.9	
Caro's acid	47.8	7.5	0.33/0.14
Caro's acid + SiMo	45.2	6.8	0.22/0.02

APPENDIX IV (2/2)

Table 18. Pilot scale pretreatment results.

Sample	Brightness, %ISO	Kappa number
REF	47.0	9.3
A-stage	44.6	9.1
Caro's acid	48.5	7.7

APPENDIX V

Bleaching results

Table 19. HW pulp large laboratory scale bleaching results.

Sample	Brightness, %ISO	Kappa number	Residual ClO, kg/tp	Total extractives, mg/g
A-stage	65.7 ^a /80.7 ^c	5.0 ^b	0.00 ^{a, c}	2.19
dPAA + acetone	68.2 ^a /82.2 ^c	4.1 ^b	0.00 ^{a, c}	0.41
Caro's acid + SiMo	69.4 ^a /83.8 ^c	2.2 ^b	0.00 ^{a, c}	0.36
Sulfite	66.4 ^a /80.6 ^c	4.9 ^b	0.00 ^{a, c}	0.77

a after D0

b after E

c after D1

Table 20. SW pulp large laboratory scale bleaching results.

Sample	Brightness, %ISO	Kappa number	Residual ClO, kg/tp
REF	58.3 ^a /76.9 ^c	3.8 ^b	0.00 ^{a, c}
A-stage	55.2 ^a /77.2 ^c	3.2 ^b	0.00 ^{a, c}
Caro's acid	58.4 ^a /79.0 ^c	2.1 ^b	0.00 ^{a, c}
Caro's acid + SiMo	58.0 ^a /80.5 ^c	2.1 ^b	0.00 ^{a, c}

a after D0

b after E

c after D1

Table 21. Pilot scale pretreatment results.

Sample	Brightness, %ISO	Kappa number	Residual Chemical, %	Yield, %
REF	55.2 ^a /77.2 ^c	3.8 ^b	0.00 ^{a, c}	92.0 ^c
A-stage	58.4 ^a /79.0 ^c	3.2 ^b	0.00 ^{a, c}	95.0 ^c
Caro's acid	58.0 ^a /80.5 ^c	2.1 ^b	0.00 ^a / 0.01 ^c	96.1 ^c

a after D0

b after E

c after D1

APPENDIX VI (1/5)

UVVR spectra

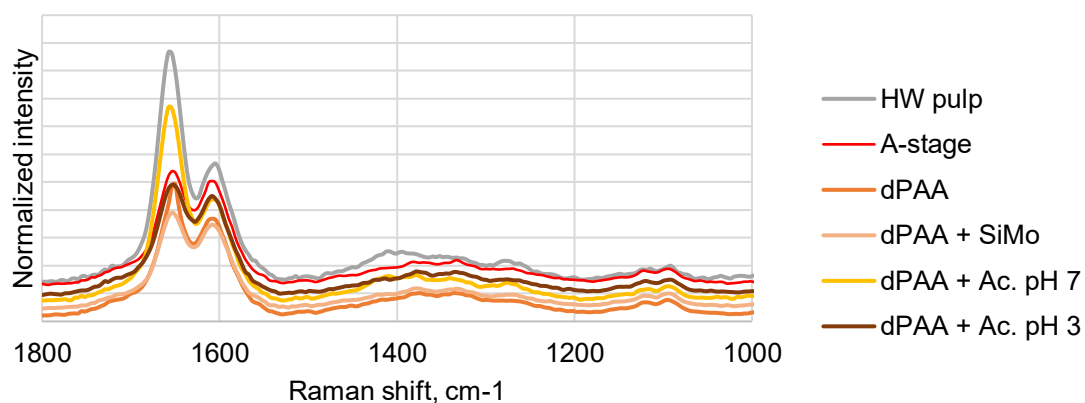


Figure 27. dPAA UVVR bands from small laboratory scale HW pretreatments.

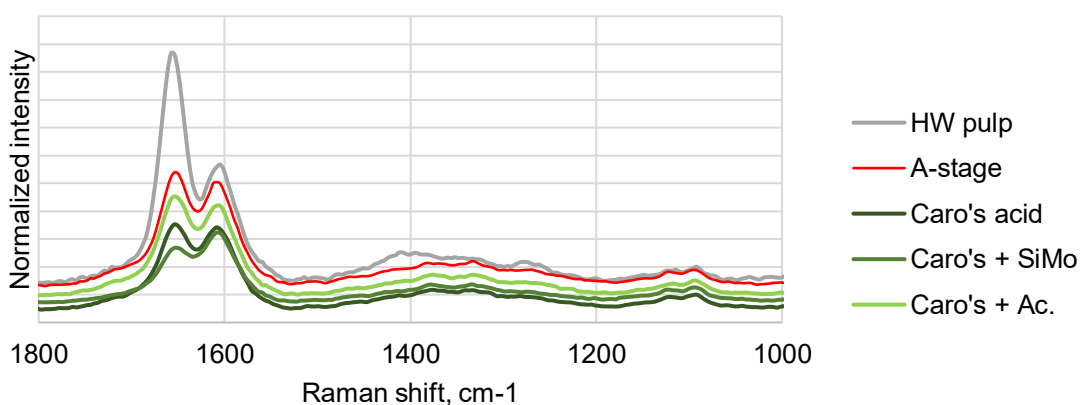


Figure 28. Caro's acid UVVR bands from small laboratory scale HW pretreatment.

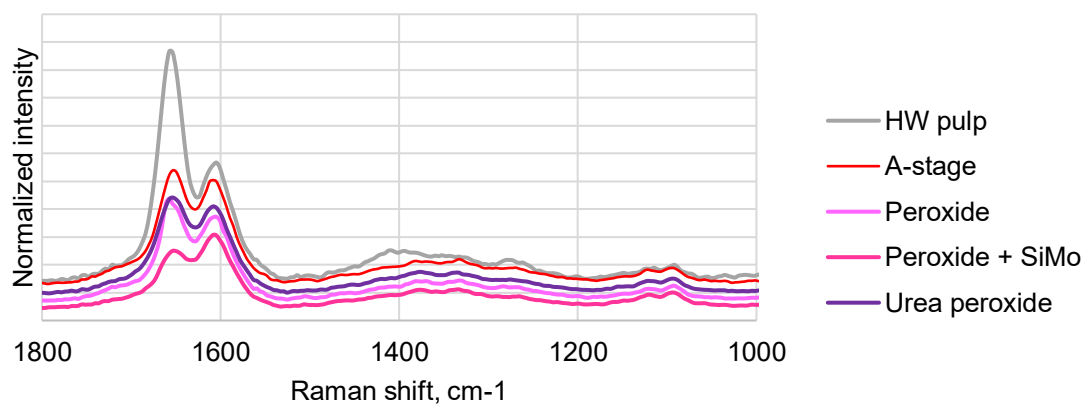


Figure 29. Peroxide and urea peroxide UVVR bands from small laboratory scale HW pretreatments.

APPENDIX VI (2/5)

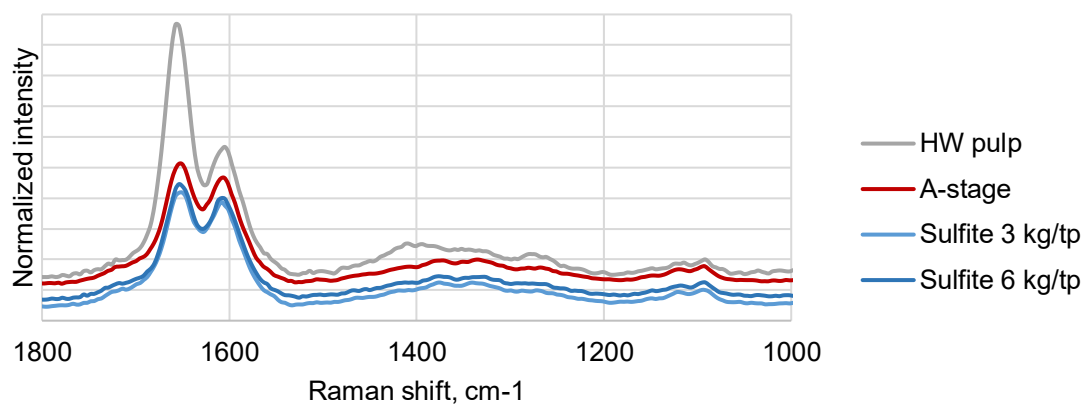


Figure 30. Sulfite UVVR bands from small laboratory scale pretreatments.

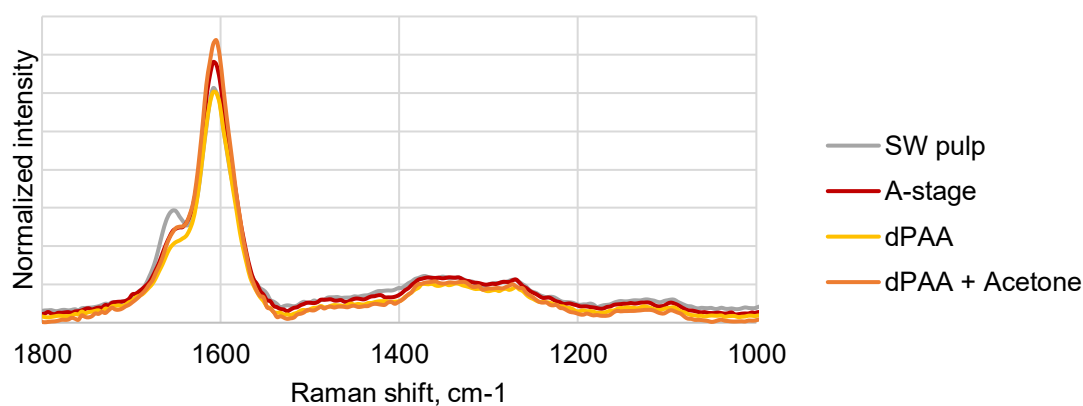


Figure 31. dPAA UVVR bands from small laboratory scale SW pretreatments.

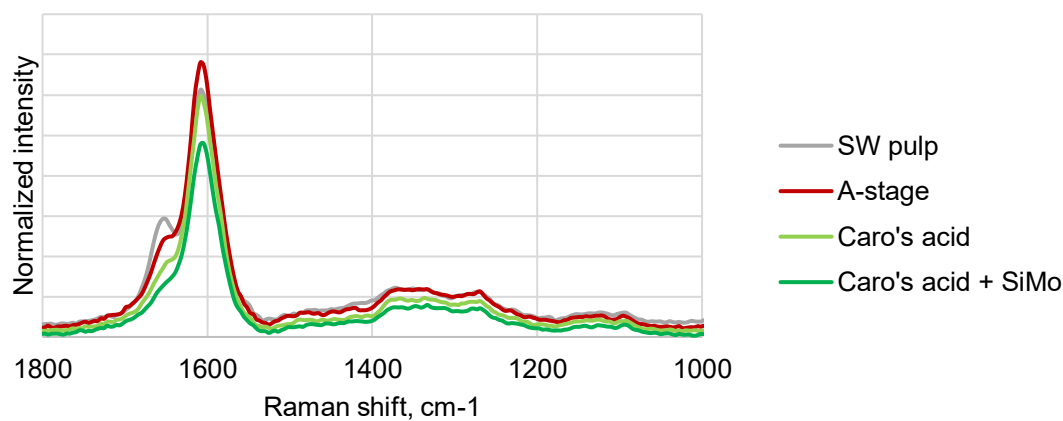


Figure 32. Caro's acid UVVR bands from small laboratory scale SW pretreatments.

APPENDIX VI (3/5)

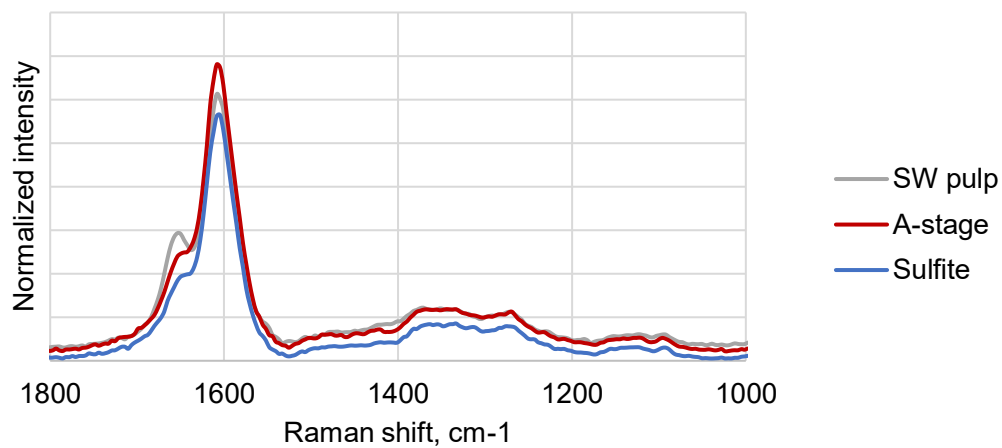


Figure 33. Sulfite UVVR bands from small laboratory scale SW pretreatments.

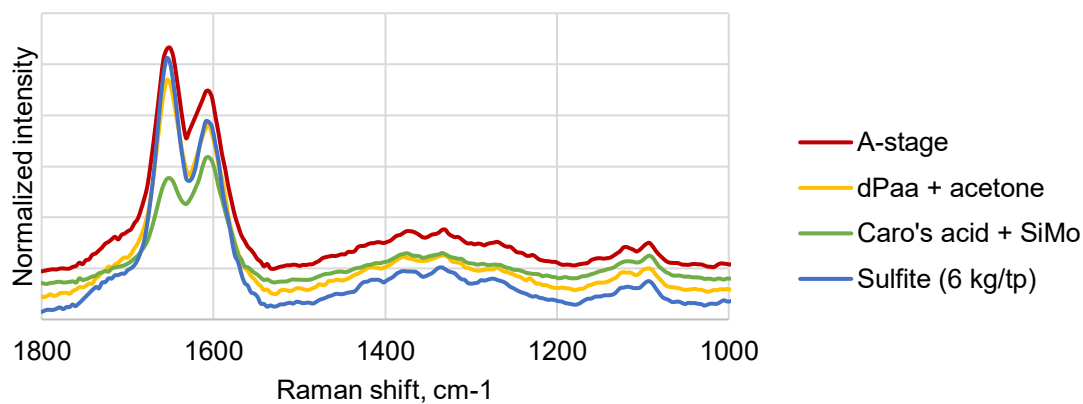


Figure 34. UVVR bands from HW pulp large laboratory scale pretreatments.

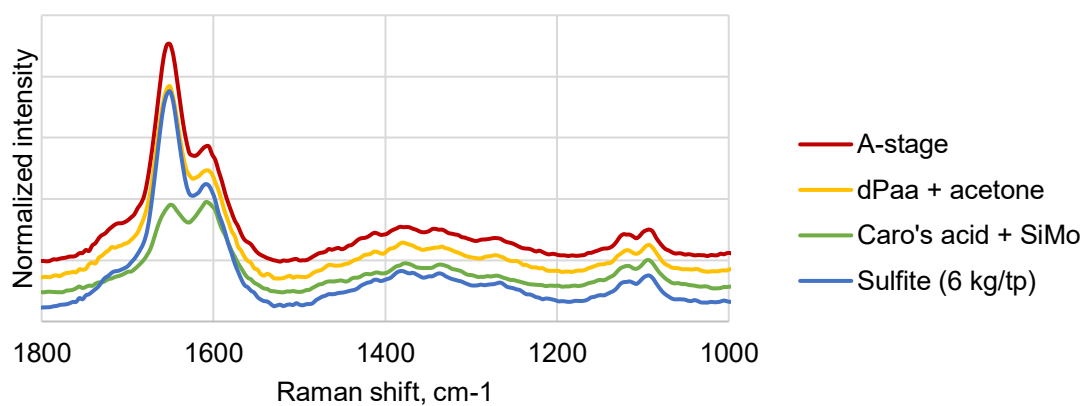


Figure 35. UVVR bands from HW pulp large laboratory scale D0-stages.

APPENDIX VI (4/5)

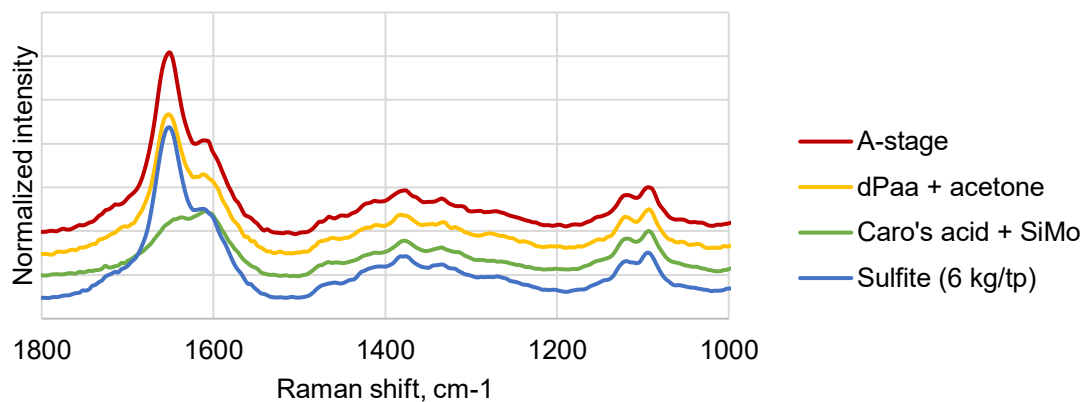


Figure 36. UVVR bands from HW pulp large laboratory scale D1-stages.

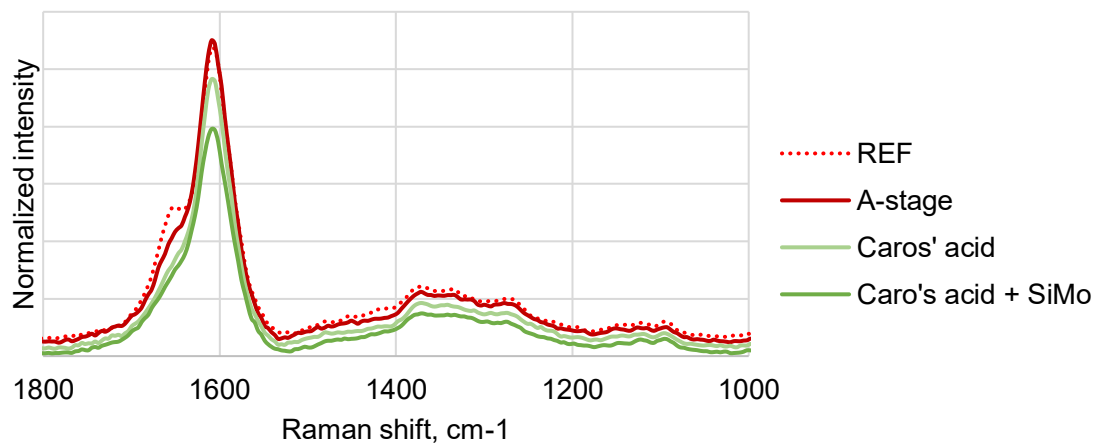


Figure 37. UVVR bands from SW pulp large laboratory scale pretreatments.

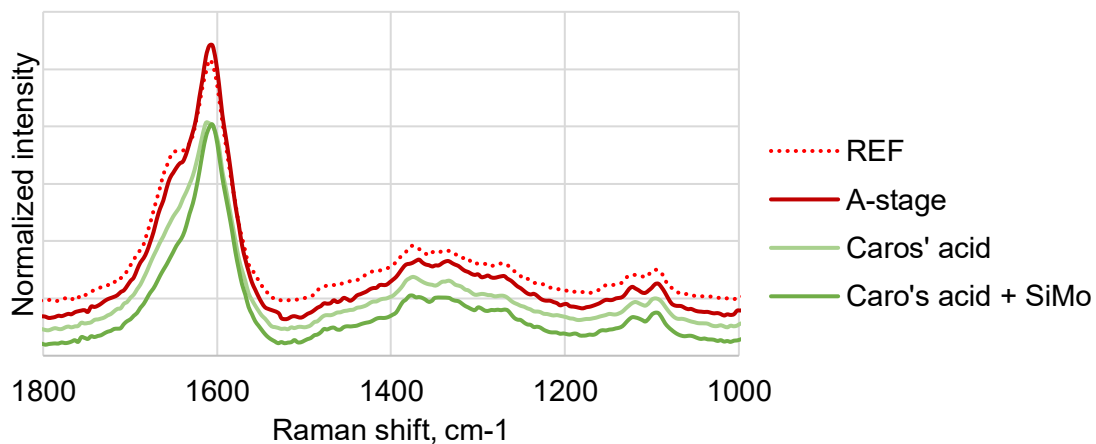


Figure 38. UVVR bands from SW pulp large laboratory scale D0-stages.

APPENDIX VI (5/5)

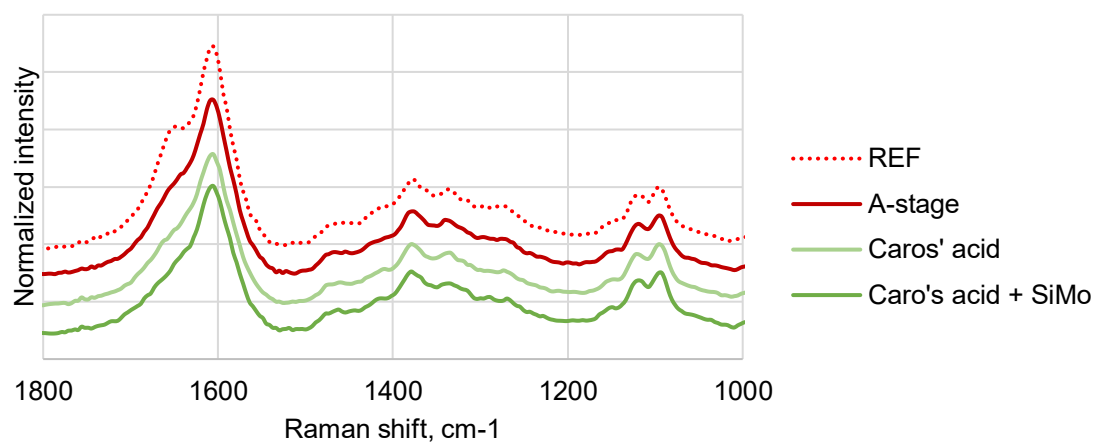


Figure 39. UVVR bands from SW pulp large laboratory scale D1-stages.

APPENDIX VII

HexA content determination by selective acid hydrolysis

Taulukko 1. Determination of HexA content of selected pulps from small laboratory scale HW and SW pretreatments.

Treatment	Weighed mass, g (as is)	Dry matter content, %	Weighed, dry	A 245nm	A 480nm	DA	HexA, mmol/kg
HW pulp	6.251	30.9	1.933	0.866	0.003	0.863	51.3
HW A-stage	7.660	26.3	2.018	0.508	0.009	0.499	28.4
dPAA	8.541	23.3	1.991	0.495	0.012	0.483	27.9
Caro's acid	8.740	24.4	2.130	0.384	0.003	0.381	20.6
Caro's acid + SiMo	7.138	28.2	2.016	0.208	0.012	0.196	11.2
Peroxide	10.250	20.1	2.064	0.449	0.005	0.444	24.7
Peroxide + SiMo	8.487	25.3	2.149	0.236	0.006	0.230	12.3
SW pulp	8.185	21.8	1.783	0.736	0.240	0.496	32.0
SW A-stage	7.223	26.2	1.893	0.384	0.003	0.381	23.1
Caro's acid	7.270	26.2	1.903	0.249	0.006	0.243	14.7
Caro's acid + SiMo	7.201	26.0	1.875	0.317	0.006	0.311	19.1

APPENDIX VIII (1/2)

Determination of kappa number of HexA

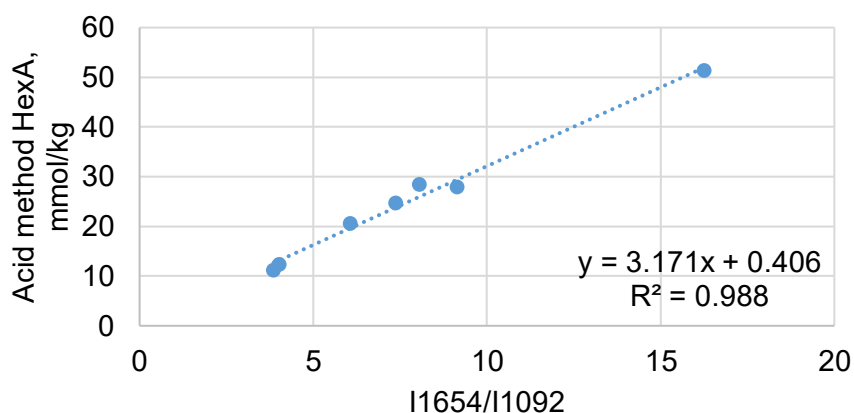


Figure 1. Correlation between the HexA content of the HW pulp measured using acid method and the relative band height at 1654 cm^{-1} .

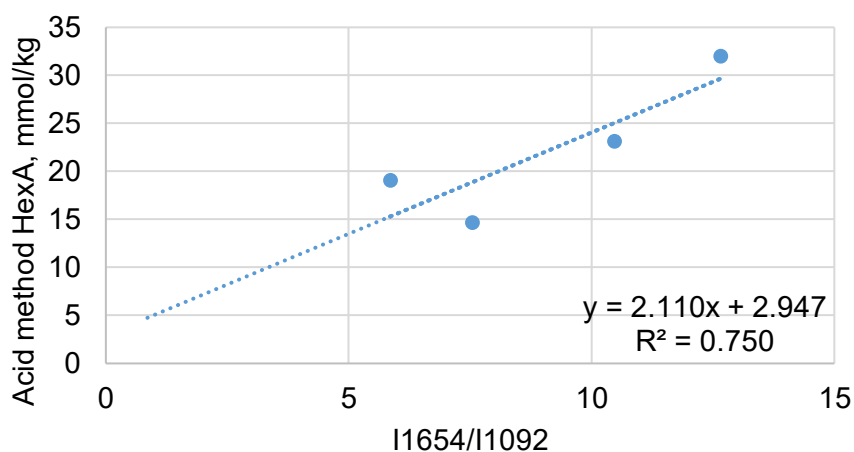


Figure 2. Correlation between the HexA content of the SW pulp measured using acid method and the relative band height at 1654 cm^{-1} .

Slope and intersect were determined from figures above (Figure 1 and Figure 2, APPENDIX VIII). HexA amount in mmol/kg was calculated from the HexA and cellulose band intensity relationship (I1654/I1092) which was determined based on UVRR measurement results (APPENDIX VI) as shown below in eq. 1 (APPENDIX VIII):

APPENDIX VIII (2/2)

$$\text{HexA amount} = a \times \frac{I_{1654}}{I_{1092}} + b \times \frac{\text{mmol}}{\text{kg}} \quad (1)$$

,where

a = slope from the correlation between HexA content measured using acid method and relative band height at 1654 cm^{-1}

$\frac{I_{1654}}{I_{1092}}$ = HexA and cellulose UVRR band ratio

b = intersect from the correlation between HexA content measured using acid method and relative band height at 1654 cm^{-1}

10 mmol of HexA present in 1 kg of pulp corresponds to kappa number of 0.84 (Li and Gellerstedt, 1997). Therefore, the kappa number of HexA can be then determined according to the eq. 2 (APPENDIX VIII):

$$\kappa_{\text{HexA}} = \frac{\text{HexA amount}}{10 \frac{\text{mmol}}{\text{kg}}} \times 0.84 \quad (2)$$

where,

κ_{HexA} = kappa number of HexA

The kappa number of HexA for small laboratory scale A-stage pretreated HW pulp was determined as follows according to the equations above (1 and 2):

$$\text{HexA amount} = 2.1099 \times 12.653 + 2.947 \frac{\text{mmol}}{\text{kg}} = 29.6 \frac{\text{mmol}}{\text{kg}}$$

$$\kappa_{\text{HexA}} = 29.6 \frac{\text{mmol}}{\text{kg}} * 0.084 = 2.549 \approx 2.5$$

All small laboratory scale HW pulp kappa of HexA result were determined similarly relating to the UVRRS results and HexA determination by acid methods using slope and intersect from Figure 1 (APPENDIX VII). SW pulp results were determined similarly to HW pulp using slope and intersect from Figure 2 (APPENDIX VII).

APPENDIX IX

Pulp and paper property results

Table 22. WRV and SR number results

Sample	SRE (kWh/t)	WRV	St. dev	SR number,	St. dev
REF	0	1.41	0.00	16.5	0.7
	56	1.55	0.01	19.1	0.1
	117	1.72	0.01	24.5	0.3
	179	1.84	0.00	35.2	0.4
A-stage	0	1.37	0.01	16.0	0.0
	57	1.56	0.01	18.4	0.3
	118	1.71	0.01	23.9	0.6
	181	1.88	0.01	33.1	0.2
Caro's acid	0	1.39	0.00	16.7	0.4
	57	1.56	0.01	19.0	0.3
	118	1.76	0.03	25.0	0.2
	180	1.88	0.01	35.4	0.3

Table 23. Results from grammage, thickness measurements as well as density and bulk results.

Sample	SRE (kWh/t)	Grammage, g/m ²	St. dev.	Thickness, μ m	St. dev.	Density, g/cm ³	Bulk, cm ³ /g
REF	0	62.9	1.3	105.8	2.3	0.6	1.7
	56	63.9	0.7	98.4	1.9	0.6	1.5
	117	64.3	0.7	94.6	1.7	0.7	1.5
	179	64.9	1.5	91.8	2.7	0.7	1.4
A-stage	0	64.4	2.1	107.9	2.7	0.6	1.7
	57	63.5	2.4	100.1	2.3	0.6	1.6
	118	63.4	1.1	93.5	3.0	0.7	1.5
	181	62.8	0.9	90.9	1.6	0.7	1.4
Caro's acid	0	64.1	1.2	108.2	3.6	0.6	1.7
	57	59.0	2.0	91.6	3.7	0.6	1.6
	118	65.3	2.3	95.6	3.1	0.7	1.5
	180	64.5	1.3	91.4	1.7	0.7	1.4

Table 24. Tensile and tear properties of pilots scale refined pulps.

Sample	SRE (kWh/t)	Tensile strength, kN/m	St. dev.	Tensile index, Nm/g	St. dev.	Tear Strength, mN	St. dev.	Tear Index, Nm ² /kg	St. dev.
REF	0	2.2	0.1	35.0	1.8	1503	286	23.9	4.6
	56	4.0	0.2	63.2	2.7	1101	17	17.2	0.3
	117	5.1	0.1	79.8	1.9	870	19	13.5	0.3
	179	5.8	0.2	89.4	3.4	746	24	11.5	0.4
A-stage	0	2.1	0.1	33.4	1.5	1418	252	22.0	3.9
	57	4.1	0.1	63.9	2.1	1070	46	16.9	0.7
	118	4.9	0.1	77.0	2.0	814	35	12.8	0.6
	181	5.4	0.1	86.5	2.3	686	40	10.9	0.6
Caro's acid	0	2.2	0.1	33.8	1.0	1511	244	23.6	3.8
	57	3.6	0.1	60.7	2.4	901	19	15.3	0.3
	118	5.0	0.3	77.3	4.0	789	40	12.1	0.6
	180	5.5	0.1	85.8	1.9	667	19	10.3	0.3