The origin of fibre charge in chemical pulp

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Abstract

Chemical components in wood contain multiple anionic groups, including carboxyl groups and hydroxyl groups. During kraft cooking and bleaching, such structures are also formed, degraded or modified by the action of reactions both deliberate and unwanted. It has previously been found by Laine that anionic groups with pKa values of 3.3 and 5.5 can explain the observed anionic charge on chemical fibres, corresponding to carboxylic acids on hemicelluloses as well as oxidized lignin structures, respectively. It has further been found that most of the fibre charge can be accounted for through the contribution from methylglucuronic acids as well as hexenuronic acids. This study aimed to provide additional information regarding the charge component unaffiliated with either of the aforementioned uronic acids by studying kraft pulps procured from an industrial kraft mill corresponding to unit operations through a fibreline using the $OD_{Hot}(EOP)D_1D_2$ bleaching sequence. Each sample had its total charge determined by means of conductometric titration, its content of methylglucuronic acid determined by means of methanalysis followed by GC, and its content of hexenuronic acids determined by means of the HUT-method for the determination of hexenuronic acids, followed by either UV absorbance measurements or calculations based on the reduction in kappa number during the selective acid hydrolysis. The lignin content was determined by means of kappa number analysis as well as by calculations based on the kappa number after selective acid hydrolysis, which was assumed to be characteristic of the kappa number addition from the lignin content of the samples.

The hexenuronic acid content was successfully determined according to the HUT-method. A difference in content was observed when results for the unbleached and oxygen delignified samples that was obtained from UV measurements were compared with the observed difference in kappa number prior and after selective acid hydrolysis for said samples. In both cases, the results based on the difference in kappa number was higher.

No correlation between remaining charge and lignin content could be made. It was instead observed that individual bleaching steps had binary effects on each of the analysed components of the fibre charge. A significant increase in charge unaffiliated with methylglucuronic acid or hexenuronic acid was observed during the EOP step, indicating an oxidation of chemical structures in the pulp: this effect could not be correlated to lignin content.
Sammanfattning

Kemisk massa kan ses som ett kompositmaterial bestående av cellulosa, hemi-
cellulosa och lignin. Dessa beståndsdelar, liksom separata lågmolekylära för-
enningar, innehåller anjoniska kemiska grupper som bidrar till att ge träfibrer
en anjonisk laddning. Ytterligare sådana grupper kan bildas under reaktioner
vid kokning och blekning, tillika kan sådana grupper modifieras eller brytas
ner. Laine har tidigare visat att fiberladdningen kan förklaras genom två skil-
da kategorier av kemiska grupper med pKa värdet på 3,3 samt 5,5, vilka
kan kopplas till karboxylsyragrupper på hemicellulosor respektive till lignin.
Man har därtill funnit att stora delar av fiberladdningen kan förklaras genom
tillskott från de två uronsyrorna methylglukuronsyra och hexenuronsyra.

Denna studie syftar till att undersöka det laddningstillskott som inte kan län-
kas till någon av dessa två uronsyror. Detta har gjorts genom att studera
kemiska massor från industrin, tagna från de olika stegen i en bleksekvens
av typen $OD_{Hot}(EOP)D_1D_2$. Massornas totalladdning mättes medelst kon-
duktometrisk titrering, emedan methylglukuronsyrhalten mättes via methano-
lysis följt av GC och hexenuronsyrhalten mättes via selektiv syrahydrolys per
HUT-metoden följt av UV-karakterisering respektive beräkningar baserade på
differensen i kappa tal före och efter sagda hydrolys. Ligninhalten i samtli-
ga prov mättes via kappatsmätningar samt genom beräkningar baserade på
ekappalets efter selektiv syrahydrolys, vilket anses vara kappatsbidraget från
ligninföreningarna.

Hexenuronsyrahlen mätta medelst UV-karakterisering respektive kap-
patsdifferens jämfördes mot varandra och fanns ge olika resultat för de oblek-
ta och syrgasdelignifierade massorna. I båge fallen gav mätningen baserade
på kappatsdifferens högre utslag.

Ingen korrelation mellan kvarvarande laddning - totalladdning minus tillskot-
tet från uronsyrorna - och ligninhalt kunde observeras. Istället observerades
binära effekter för varje uppmätt komponent under vardera blekningssteg.
Under EOP-steget observerades ett tillskott till den kvarvarande laddningen,
vilket skulle kunna förklaras genom oxidation av trästrukturer. Dock kan ej
heller detta relateras till ligninhalten i proverna.
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1 Introduction

1.1 Natural wood and the pulp material

1.1.1 Natural wood

Natural wood is composed of wood cells. Fibres are wood cells that provide structural support [1]. The cell walls of fibres are a composite material, consisting of a multitude of biopolymers including cellulose, hemicellulose and lignin. Cellulose forms the “skeleton” of the composite, with chains of glucose units linked together by means of β-1,4-glycosidic bonds [2, 3, 4, 5]. These chains associate into layers by means of intermolecular hydrogen bonding. These layers further associate by means of hydrophobic interaction and van der Waal forces, forming elementary crystallites, which, when combined with amorphous segments, form elementary fibrils. Bundles of such elementary fibrils form the core of microfibrils, which are covered by amorphous cellulose and surrounded by hemicelluloses [6, 7, 5]. The hemicelluloses in question form covalent connections between separate microfibrils, as well as forming covalent bonds with lignin structures [8]. Networks of microfibrils build up the various layers of the plant cell wall, including the primary wall, the secondary cell walls and the tertiary cell wall. Each of these layers has a different composition and morphology [9, 10]. Figure 1 illustrates the hierarchical structure of plants, as well as the chemical structure of cellulose. Figure 2, figure 3 and figure 4 illustrate common hemicelluloses as well as the monolignols of lignin, respectively [11].
Figure 1: Structure and morphology of plant cells. Adapted from the Office of Biological and Environmental Research of the U.S. Department of Energy Office of Science. [http://genomicscience.energy.gov]
Figure 2: Illustration of xylan structures, arabinoglucuronoxylan being present in softwood and glucuronoxylan being present in hardwood.
Figure 3: Illustration of glucomannan structures, glucomannan being present in both softwood and hardwood. Part of the softwood glucomannan is rich in galactose substituents.

Figure 4: The three common monolignols found in lignin structures.
1.1.2 Kraft pulping

In order to use native wood as a material, it must first be modified in a process called pulping. There are two primary categories of pulping: mechanical pulping and chemical pulping. In chemical pulping, of which the kraft process is the most common, wood fibres are liberated from each other by degrading and dissolving lignin. These liberated fibres then constitute a pulp material that can be used in paper making as well as in the making of other paper based products [12, 13].

Figure 5: Dried chemical eucalyptus pulp, procured by means of the kraft process.

1.1.3 Bleaching chemical pulp from the Kraft process

After kraft pulping, the pulp material is coloured by chromophoric structures that are formed during the pulping process. These chromophores originate in the lignin that is not degraded during pulping, called “residual lignin” [14]. Bleaching involves reducing colour either by further degrading lignin or by specifically degrading the coloured chromophores [15]. Lignin-preserving bleaching will improve yield, but residual lignin also contain structures that can react with light and oxygen in order to form new chromophores in a process called “post-yellowing” [16, 17], making lignin degrading bleaching required for certain applications. Even in bleached chemical pulp, however, post-yellowing can occur through a similar, thermally induced process. This process is believed to originate in the degradation of hexenuronic acid into furoic acids.
Finally, bleaching also aims to remove extractives and rests of bark that are undesirable in the finished product [15]. Because no single economically feasible bleaching process has the ability to eliminate all of the various substances of interest, so called “bleaching sequences” consisting of various bleaching “steps” are used. For kraft pulps, the first step of such a sequence is generally an oxygen delignification. This is a lignin degrading step that significantly reduces the residual lignin content. This is followed by steps that further reduce the lignin content, while also attacking chromophores and non-lignin substances. The final step of the sequence is chosen to also affect the chemical environment in the pulp to inhibit post yellowing [12, 21].

Figure 6: Dried chemical eucalyptus pulp, procured by means of the kraft process and bleached according to a bleaching sequence consisting of an oxygen delignification, followed by a chlorine dioxide step at elevated temperature, followed by an alkaline extraction enforced by oxygen and hydrogen peroxide, followed by two final chlorine dioxide bleaching steps.

1.2 The nature of fibre charges

Wood components contain multiple chemical groups that, after dissociating, form anionic groups. These include carboxyl groups and hydroxyl groups [22]. When countered by free cations in the electrolyte, these groups form an electrical double layer: cations, including hydronium ions, agglomerate on the anionically charged surface as a “Helmholtz” layer, after which a “diffuse layer”
follows, structured as per the Debye-Hückel theory [23, 24, 25]. The Debye-Hückel theory predicts that a system can lower its free energy by maximising the distance between ions of opposing charge, leading to a system where ions of a given charge are surrounded by ions of the opposing charge. This minimizes coulombic repulsion, while also generating a shielding effect, further lowering the free energy of the system [26]. The composition of the double layer is illustrated in figure 7. The differences in ionic concentration between the Helmholtz layer and the diffuse layer results in a potential difference, measured in $[\text{V}]$ [24]. However, although charge is usually measured as a potential $[\text{V}]$ in the field of electrochemistry, fibre charge is usually measured as the amount of anionic groups in the fibre, normalized by weight [µmol/g].

![Diagram of the electrical double layer](image)

**Figure 7:** The electrical double layer.

Fibre charge directly affects the hydrophilicity of the fibre, and thus the fibres ability to absorb moisture, its ability to swell (which also influences the tensile strength of papers made from such fibres [27]) as well as the degree with which
water spreads out on the surface of a sheet composed of such fibres. Whether these are desirable properties or not depends on the application of the product: a tissue or absorbent would certainly benefit from increased moisture uptake, whereas paper sheets are commonly treated to reduce their hydrophilicity, in order to minimize ink spreading [28, 29, 22, 30].

Fibre charge also influences the interaction with other charged chemicals. The counter ions bound to the dissociated acids can be replaced with polyelectrolytes, for instance, allowing for physical absorption of a variety of different compounds [22]. Fibre charge can also act to modify the properties of individual component substances, thereby altering the material indirectly. For instance, for a given polymer a higher amount of charged groups will yield a lower glass transition temperature for the polymer in question. This is utilized in chemithermomechanical pulping (a variant of mechanical pulping): by adding sulphuric acid groups to the lignin structure, lignin particles are made more charged, which acts to lower its glass transition temperature. Sulphur is thus used as a softener in regards to lignin, thereby reducing the mechanical energy needed to separate fibres in this process [22].

1.3 The origin of fibre charges

In natural wood, fibre charges are primarily associated with hemicelluloses (figure 2 and figure 3), phenolic lignin (figure 4), pectins (figure 8) and extractives (non-polymeric wood structures). During the conversion of wood into chemical pulp, however, cooking and bleaching steps act to modify these structures, either deliberately or through side reactions. Thus, charged groups are removed, converted or formed.

![Figure 8: Pectin, a component of natural wood.](image)
1.3.1 Reactions during kraft pulping

In kraft pulping, lignin is degraded through the action of hydroxide ions and hydrosulphide ions according to the reactions seen in figure 9 and figure 10 below [31]. Note the formation of new phenolic lignin as these structures are degraded. Also note, however, that these groups are then made soluble and removed from the pulp, resulting in a decrease in lignin amount [32].

![Figure 9: Hydroxide ions degrade non-phenolic lignin.](image1)

![Figure 10: Hydrosulphide ions act to degrade phenolic lignin. R denotes either a hydrogen or a carbohydrate molecule.](image2)
In the pulp and paper field, “selectivity” refers to the degree with which a given process degrades polysaccharides in relation to its ability to degrade lignin: a high selectivity indicates that the process can efficiently degrade lignin with minimal polysaccharide losses. In kraft pulping, the alkaline nature of the process results in the degradation of polysaccharides by means of multiple side reactions as seen in figures 11 through 13 [33]. Figure 11 illustrates the “peeling” of a carbohydrate, using xylose in this specific example. Through peeling, polysaccharides are degraded monomer by monomer at the reducing end. The peeling reaction competes with various “stopping” reactions, one example being the arabinose elimination on xylan illustrated in figure 12. This reaction prevents peeling while also increasing fibre charge through the formation of a carboxylic acid group. Another stopping reaction is the β-hydroxycarbonyl elimination on glucose. This reaction acts on glucose rather than xylose, with the O-Ara in figure 12 substituted for a hydroxyl group. Finally, at higher temperatures polysaccharides can degrade through alkaline hydrolysis, as seen in figure 13. Alkaline hydrolysis will split the polysaccharide chain in two, creating a new end-group at which peeling can occur [33, 34].

Figure 11: Peeling of xylose.
Figure 12: Arabinose elimination in arabinoglucuronoxylan.
Figure 13: Alkaline hydrolysis of glucose.
Pectin is especially susceptible to hydrolysis. As can be seen in figure 14, pectins contain multiple carboxylic acid groups that contribute significantly to the fibre charge in native wood. This contribution is, however, completely absent in chemical pulp [35]. By means of the reaction shown in figure 14 almost all pectin structures are degraded during kraft cooking [36].

![Figure 14: Degradation of pectin by β-elimination.](image)

In addition to these reactions, the substituents on hemicellulose structures can be modified in alkaline media. In native wood, xylan is substituted with methylglucuronic acid groups, as seen previously in figure 2. The methylglucuronic acid groups contribute to the fibre charge by means of their carboxylic acid groups. During kraft cooking, most of these methylglucuronic acid substituents are converted into hexenuronic acid structures, by means of the reaction shown in figure 15, although part of these structures are then further degraded during the cook [37]. Since the carboxylic acid group is preserved during this conversion, hexenuronic acid also contributes to the fibre charge. Its chemical properties, however, differ significantly from its predecessor. Some of these properties have been discussed previously in section 1.1.3.

![Figure 15: Hexenuronic acid is a by-product of the kraft cook that induces yellowing and contributes to the kappa number measurement. It is formed from methylglucuronic acid in alkaline media.](image)
1.3.2 Reactions during bleaching

The bleaching sequence used in this work is \( OD_{Hot}(EOP)D_1D_2 \), referring to an oxygen delignification followed by an acidic chlorine dioxide step at elevated temperature, followed by an alkaline extraction enforced by a combination of oxygen and hydrogen peroxide. This is then followed by two chlorine dioxide steps. This bleaching sequence would be an example of an ECF (elementary chlorine free) bleaching sequence, referring to the fact that elementary chlorine (\( Cl_2 \)) is not used in the process. Elementary chlorine has electrophilic properties, allowing it to efficiently degrade lignin as well as hexenuronic acids and chromophoric structures, but it also forms large amounts of adsorbable organohalogen structures. Its use has thus declined in the western world due to environmental reasons [14].

Oxygen delignification (\( O \)) is a bleaching step that carries out the bulk of delignification in the bleaching of chemical kraft pulp. Although it lacks selectivity due to the action of hydroxyl radicals, it is the cheapest of the bleaching processes, and oxygen of required purity can often be generated on site. Oxygen is a biradical, allowing it to oxidise phenolic lignin according to the scheme shown in figure 16 [38]. This increases charge, while also allowing such structures to be dissolved and removed.
Chlorine has the ability to exist in multiple oxidation numbers and thus has the ability to form multiple compounds. One possible compound, in which chlorine exists in the +IV state, is the chlorine dioxide radical ($\text{Cl}_2\text{O}_4^-$). This compound is unstable, and must be generated on site by one of multiple possible methods. As a radical, chlorine dioxide has the ability to oxidise phenolic lignin structures much like oxygen. One possible reaction is shown in figure 17, resulting in the generation of a carboxylic acid group [38]. Chlorine dioxide is also susceptible to various degradation processes which form other chlorine compounds, as well as chlororadicals. The former allows chlorine dioxide to oxidise structures other than phenolic lignin, while the latter is an unwanted side reaction which reduces selectivity and harms cellulose. Chlorine dioxide, being a radical itself, can act as a radical scavenger, limiting the damage done by the formation of such radicals. The degradation reactions are affected by the pH of the solution. In the $D_{\text{Hot}}$ step, also called the $D_0$ step or the $D^*$ step, bleaching is performed at an elevated temperature and a pH of 2, whereas latter chlorine dioxide steps are performed at pH values between 3.5 to 5. The conditions of the $D_{\text{Hot}}$ step allows part of the chlorine to form other compounds that act more like elementary chlorine. This allows
for efficient removal of hexenuronic acids, as well as other unwanted non-lignin structures [21].

Figure 17: Oxidation of lignin by chlorine dioxide.
Acidic bleaching steps such as the chlorine dioxide step are followed by alkaline extraction ($E$). During alkaline extraction, the oxidised structures generated during acidic steps are deprotonated through the action of hydroxide ions, making the structures more soluble and allowing their removal. Alkaline extraction at high pH values is not selective, due to the deprotonation of acidic groups on hemicelluloses, allowing for the loss of such structures [38].

Peroxide ($P$) is a lignin preserving bleaching step where peroxide is allowed to form the nucleophilic $\text{HOO}^-$ structure under alkaline conditions, which then acts to degrade coloured quinone lignin structures. By increasing the temperature, the same bleaching step can be used to also degrade residual lignin. For kraft pulp, the coloured nature of the residual lignin makes the latter process necessary. Peroxide steps are usually preceded by a chemical treatment with the purpose of lowering the metal ion content in the pulp. This is due to the fact that such ions can catalyse a Fenton reaction where hydroxyl radicals are formed. These radicals, like the chlororadicals discussed above, lower the selectivity towards lignin [38].

The combined ($EOP$) step refers to an alkaline extraction which is enforced by oxygen and small amounts of hydrogen peroxide. In normal peroxide bleaching steps, it is common to remove metal ions in a prior treatment in order to avoid formation of radicals. These treatments are, however, not used before the combined ($EOP$) step. Instead, the hydroxyl radicals are allowed to form and are then used to convert non-phenolic lignin compounds into phenolic compounds, thereby activating lignin for latter bleaching steps at the cost of a lower selectivity [21].

### 1.3.3 Previous work: Fibre charge in fully bleached chemical pulp

The processes discussed in sections 1.3.1 and 1.3.2 will yield fully bleached chemical pulp, a material with physical and electrical properties that are both very different from those in native wood. The fibre charge of native wood as well as bleached mechanical and chemical pulp was investigated by Sjöström [39]. He concluded that fibre charge in pulp had its origin in ionised carboxyl and sulphonic acid groups. Of the carboxyl groups, the uronic acids were concluded to be the main carriers of charge. A later study by Laine et al. [40] used potentiometric titration and computer models to identify two chemical groups with pKa values 3.3 and 5.5, respectively, as the origin of fibre charge in bleached chemical pulp. The former of these was suggested to be linked to uronic acids, as previously predicted by Sjöström, while the latter was
suggested to be linked to phenolic lignin. A later study by Buchert et al. [37] investigated the xylan structure in bleached chemical pulp, using enzymatic peeling and proton NMR. They were able to conclude that hexenuronic acid is degraded during pulping, as well as during ozone bleaching and chlorine dioxide bleaching. Methylglucuronic acid is degraded into hexenuronic acid during cooking, but is stable during oxygen and chlorine-based bleaching steps. This was confirmed by Fardim et al. [41]. Laine [42] was able to measure the content of lignin carboxylic acids in unbleached softwood kraft to be about 20% of the total amount of acids, which was reduced to about 13% for fully bleached pulp. A later study by Buchert et al. [43] identified the content of lignin carboxylic acids in unbleached kraft pulp to be 32% of the total amount of acids.

In a study by Sevastyanova et al. [44], the efficiency of the final D stage of various bleaching histories were compared. It was suggested that the contribution to fibre charge from oxidised lignin can be determined by subtracting the contribution to the total charge associated with the hexenuronic acids and the methylglucuronic acids. This statement would be in agreement with the study by Laine. The statement was questioned, however, due to the low lignin content present in those samples. Another explanation could be that the remaining charge is associated with oxidised cellulose structures. Sevastyanova et al. found that an increase in total fibre charge had a negative effect on the final brightness and viscosity during the final bleaching stages. As such, identifying the chemical nature of the groups that contribute to fibre charge could allow for improvements to the bleaching methodology.

1.4 Experimental theory

1.4.1 Total charge: Conductometric titration

Conductometric titration, originally developed by Katz [45], is a method that allows measurement of the total amount of charged groups in pulp. The method utilizes the principles that the conductance of a liquid sample is proportional to its ionic strength and that the counter ions to charged groups has a negligible effect on the ionic strength, assuming equal valency of these counter ions. It thus follows that if a pulp sample suspended in an acidic environment is titrated with sodium hydroxide, three different regions will be observed regarding the conductance: First, free hydronium ions in the solution will be neutralised, thus lowering the ionic strength and resulting in a
linear decrease of conductance. When all free hydronium ions are neutralised, hydrogen ions bound to the hydroxyl groups will be replaced by sodium counter ions and neutralised. Since the sodium ions are of equal valency to the hydrogen ions, this replacement will not affect the conductance of the sample. Once all such counter ions has been replaced, addition of sodium hydroxide will only act to increase the ionic strength of the sample, with a linear increase of conductance as a result. The second region, which corresponds to an exchange of counter ions regarding the charged groups, will thus be indicative of the amount of charged groups in the sample.

1.4.2 Methylglucuronic acid content: Methanolysis followed by Gas Chromatography

The content of methylglucuronic acids was determined according to the methanolysis-GC method developed by Li and Gellerstedt [46]. Because the linkage between the xylan chain and the methylglucuronic substituent is stronger than the β-1,4-linkage between the xylose molecules in the main chain, strong conditions are required in order to properly isolate the compound. In the method by Li and Gellerstedt, these conditions are satisfied using a 2.6M methanolic-HCl solution. However, the conditions necessary in order to isolate the compound also induces degradation of the hydrolysed methylglucuronic acids, meaning that it is not possible to quantify all the groups in a given sample, since some groups will either remain unhydrolysed or will already have suffered from degradation. This is solved by using a reference xylan compound with a known content of methylglucuronic acids for the quantification.

1.4.3 Hexenuronic acid content: KTH-method followed by HPLC; HUT-method followed by UV and kappa number determination

Unlike methylglucuronic acids, hexenuronic acids readily undergo acid hydrolysis. However, hydrolysed hexenuronic acid groups further degrade into furoic acids [18]. As a result, methods for determining the content of hexenuronic acids need to be more gentle than the methods used to determine the content of methylglucuronic acids. The hexenuronic acid content is measured by one of three distinct methods, named after the universities and the research institute where they were developed. These are referred to as the HUT (Helsinki University of Technology), VTT (VTT Technical Research Centre
of Finland) and KTH (Royal Institute of Technology) methods, respectively. In the HUT method, hexenuronic acid is treated with a mild acid hydrolysis, which selectively converts the hexenuronic acid groups into furan carboxylic acids [47], which are then measured by either UV-spectroscopy or by means of chromatography. In the VTT method, an enzymatic hydrolysis is used: the enzymatic cocktail taking the specific analysis into account. The enzymes reduce the hemicelluloses into monosaccharides, whereupon HPAEC can be used to characterise the different components (this also provides data on other uronic acids as well as various polysaccharides) [48]. Finally, the KTH method uses mercuric acetate to perform a selective hydrolysis of the hexenuronic acid groups, which are then measured by HPLC [49]. The KTH method has been shown to give slightly higher results than the other methods, meaning that the HUT and VTT methods are not as efficient in their hydrolysis of the hexenuronic acids.

1.4.4 Kappa number determination

In the kappa number method, standardised according to ISO 302:2004, pulp samples are treated with a solution of 20 mM potassium permanganate for a duration of 10 min, after which the reaction is stopped through the addition of potassium iodide. The remaining potassium iodide is then titrated with sodium thiosulphate in order to determine the final concentration of potassium iodide, and thus, the final concentration of permanganate. One can then calculate the volume of 20 mM permanganate which was added to the solution, which when normalised by the o.d. weight of the sample, is defined as the “permanganate number”. The permanganate, being a strong oxidising agent, will continuously react with the sample according to first degree kinetics. It is therefore necessary to define the kappa number as valid only for certain pre-set conditions. These are traditionally set to a reaction time of 10 min, a temperature of 25 °C and a 50% permanganate consumption. Due to the difficulties of adjusting the latter two values, two correction factors are used, corresponding to temperature and consumption, respectively. The kappa number thus becomes the permanganate number adjusted according to these correction factors:

\[
Kappa = \left( \frac{V_{CP}[ml]}{m_{pulp} \ [g]} \right) \times 10^{0.00093(V_{CP}[ml]−50)} \times (1 + 0.013 \ (25 - T [°C])) \left[ \frac{ml}{g} \right]
\]  

(1)

25
where $V_{CP}$ is the volume of consumed permanganate; $m_{pulp}$ is the weight of bone dry pulp and $T$ is the temperature of the suspension.

### 1.4.5 Calculated lignin determination

According to the work of Li [50], 10µmol of hexenuronic acids will correspond to 0.86 kappa number units, while 11.6 equivalents of permanganate are required in order to fully oxidise the average C9 lignin structure found in chemical pulp. This was determined not to vary with wood species. Li was also able to determine the molecular weight of various C9 lignin structures. Using this data, it is possible to determine the lignin content corresponding to a given kappa number once the interfering hexenuronic acid groups have been removed. It is also possible to determine the content of hexenuronic acids in charge equivalents once their contribution to the kappa number have been found.

### 1.5 Purpose and hypothesis

The purpose of the present study concerns the nature of charged groups in bleached chemical eucalyptus grandis pulps that do not stem from hexenuronic acids or methylglucuronic acids. As such, pulp samples corresponding to different stages of a $OD_{Hot}(EOP)D_1D_2$ bleaching sequence, including a sample of unbleached pulp, will have their total amount of charged groups determined by conductometric titration. The methylglucuronic acid content will be determined using acid methanolysis followed by GC. The hexenuronic acid content will be determined by selective acid hydrolysis followed by UV as well as kappa number measurements. The kappa number will be used to determine the reduction in kappa number during hydrolysis, which will be used to calculate the content of hexenuronic acid groups. The two values for the hexenuronic acid content will be compared.

It is hypothesised that oxidised lignin structures will contribute linearly to the total charge of the chemical pulp samples. The charge remaining after subtracting the contribution from hexenuronic acids and methylglucuronic acids from the total amount of charged groups will be correlated to the lignin content of the samples, determined by means of kappa number analysis after selective acid hydrolysis. If this correlation is non-linear, the hypothesis is falsified. Falsifying the hypothesis would mean that the remaining charge cannot be solely linked to lignin. This would not disprove the theory of lignin
contributing to fibre charge, but would indicate that other compounds must be taken into consideration as well.

2 Experimental

2.1 Material

Eucalyptus kraft pulps corresponding to the sections of the $OD_{Hot} (EOP) D_1 D_2$ bleaching sequence, including an unbleached sample, were acquired from an industrial kraft mill. The samples were not procured simultaneously, nor from a single occasion. As such, variations in composition between the pulp samples are possible. All pulp samples were washed and then dried at a temperature of 40 °C. Pulp samples were then stored in black plastic bags at room temperature. Commercial chemicals of analytic or purum quality was used in all methods and analyses.

2.2 Method

Dry content was measured with a Mettler PM460 IR-scale from DeltaRange. All weights were measured using either a Mettler PJ scale, a AG204 DeltaRange scale or a Precisa XB620M scale. In the two latter cases, a Zerostat anti-static instrument was also used to eliminate static electricity.

Samples corresponding to 25 o.d. gram were washed for 30min in 2l of distilled water, after which they were filtrated and dried.

Samples were dried using either a Termaks laboratory drying oven or a Heraeus D-6450 Hanau oven.

The washing steps of the conductometric titration were performed using 500 ml beakers, 38X8mm Octagonal PTFE magnets from Fisher Scientific, a SB 162-3 hotplate stirrer from Stuart, a 2l Büchner flask, a Büchner funnel and Munktell qualitative filter papers. The titration also used a ThermoOrion model 150 conductivity meter, a IKA RET magnetic stirrer and a 200 µl - 2 ml Rainin pipet lite micropipette. Stock solutions of sodium hydroxide, hydrochloric acid and sodium chloride were prepared from Analytical reagent grade sodium hydroxide pastilles from Fischer Scientific, Analytical reagent...
grade sodium chloride from Fisher Scientific and pro analysi 37% hydrochloric acid from Merck, respectively.

The Methanolic-HCl solution for the determination of methylglucuronic acid content was made using HPLC grade methanol from Fisher Scientific, as well as (≥ 99%) Acetyl chloride from Fluka Analytical. These were mixed using a glass tube placed in an ice bath as well as a 50 ml beaker and a 200 µl - 2 ml Rainin pipet lite micropipette. Ice was procured from a Porkka KL31 ice maker. The samples were placed in 10 ml sealed crimp-top glass vials, and heated in a Stuart SBH200D/3 block heater. They were dried with a nitrogen flow using a Stuart SBHCONC/1 sample concentrator. Acetylation was performed using purum quality (>98%) Acetic anhydride from Fluka Analytical and purum quality (>98%) Pyridine from Fluka Analytical. The samples were analysed using a Hewlett Packard HP6890 Series GC System using the 'OpenLAB CDS, Chemstation Edition for GC Systems. Rev. C01.04[35]' software from Agilent Technologies. A 30 m, 0.32 mmID, 0.25 µm Rtx-5MS fused silica capillary column was used. (>99%) meso-Erythritol from Sigma Life Science was used as an internal standard, and (>99%) SigmaUltra D-(+)-Xylose from Sigma Life Science was used as an external reference.

The selective acid hydrolysis was performed in 500 ml round bottle flasks, connected to a coil condenser and heated using a Fisherbrand heating mantle with controller. The hydrolysis also used a buffer solution prepared from (>98%) ultrapure formic acid from Aristar and sodium formiate from Riedel-de Haen Ag Seelze-Hannover as well as 20 KEBOLabAB boiling stones per sample. The filtration used the same materials as the washing steps in the conductometric titration. The UV analysis was performed using a Shimadzu UV-2550 UV-VIS spectrophotometer using the UVProbe version 2.34 software from Shimadzu Corporation. Hellma Präzisions-küvetten aus Quarzglas Suprasil cuvettes were used.

Kappa number measurements were automated using a Metrohm DMP titrino set-up using the Kappamatprogram ver 2.2.226B software from Kappa Electronics AB, Sweden.

2.3 Analysis

Conductometric titration was performed as per the original article by Katz [45], modified as follows: Samples of 3 g were washed twice for 45 min in 300 ml of 0.01M HCl, followed by a single washing step in 500 ml of deionized...
water for 20 min. The titration was performed with concentrations of 0.001M and 0.0002M for the hydrochloric acid and the sodium chloride, respectively. Triple tests were made on each of the six chemical pulp samples.

The content of methylglucuronic acids was determined according to the method of Li and Gellerstedt [46]. Triple tests were made on the D-Hot, EOP and D2 bleached kraft pulps. Double tests were made on the Unbleached, Oxygen delignified and D1 bleached samples.

The content of hexenuronic acids was determined according to the work of Vuorinen et al. [47], modified according to the work of Chakar et al. [51] in regards to the hydrolysis time, which was set to 3 hours for each sample. Also unlike the method of Vuorinen et al. [47], no nitrogen atmosphere was used. Samples were analysed according to their UV absorbance, using the molar absorption coefficient of 8700 \( \frac{L}{mol \cdot cm} \) for the peak at 245nm, as determined by Vuorinen et al. [47]. Samples were also analysed by measuring the kappa number before and after hydrolysis. The pulp samples were washed twice in deionised water as per the conductometric titration, as well as oven dried, prior to the kappa number analysis. The hydrolysis was performed once for each kraft pulp sample. After hydrolysis, single tests were made in regards to the UV analysis, while the kappa number analyses were performed as triple tests.

Kappa numbers were determined according to the ISO 302:2004 standard. Double tests were made in regards to the kappa analysis of the untreated kraft pulp samples.

### 2.4 Calculations

An estimated lignin content was determined by using the results presented in the doctoral thesis of Li [50]. The kappa number of samples treated in the HUT hydrolysis was taken as the kappa number component of lignin, and used in the following formula:

\[
Lignin\ content\ [%] = \frac{\Delta\kappa}{1000} \times \frac{N}{Eq_{C9}} \times M_{C9} \times 100\ [%] 
\]  

(2)
where \( N \) is the normality of the permanganate used in the analysis, \( E_{q_{C9}} \) is the equivalents of permanganate needed to fully oxidise the average C9 unit in lignin and \( M_{C9} \) is the molecular weight of the average C9 unit in the sample. \( N \) was 0.1 mol/l. \( E_{q_{C9}} \) was taken as 11.6 according to the work of Li [50]. \( M_{C9} \) was taken as \( 197 \text{ g mol}^{-1} \), the molecular weight of the average C9 unit in residual birch pulp, whose lignin structure is similar to that of eucalyptus, according to the work of Li [50].

All data acquired in the present study was analysed statistically by calculating averages as well as confidence intervals based on the inverse of the two-tailed student t distribution, as defined by the following formula [52]:

\[
I_{\mu} = (\bar{x} - t_{\alpha/2} (f) \, d, \, \bar{x} + t_{\alpha/2} (f) \, d)
\]

\[
d = s / \sqrt{n}; \, f = n - 1
\]

where \( I_{\mu} \) is a two point interval for \( \mu \), the true expected value; \( \bar{x} \) is the experimental average, \( t_{\alpha/2} (f) \) is the student t quantile, which is a function of the degree of freedom as well as the confidence level \( \alpha \); \( n \) is the number of samples for which the experimental average is calculated and \( s \) is the experimental standard deviation, defined as:

\[
s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}}
\]

where \( x_i \) refer to the individual experimental values, \( \bar{x} \) is the experimental average and \( n \) is the number of samples in the population.

A confidence level of 5% was used for all calculations. Tabulated values for the student t quantiles can be found on page 397 in Blom et al. [52].

3 Results and discussion

3.1 Determination of lignin content

Kappa numbers before and after selective acid hydrolysis, as determined by a Metrohm DMP titrino set-up are shown in table 1, figure 18 and figure 19. Also
presented is the calculated lignin content, which was determined according to the work of Li [50], as explained previously in section 1.4.5 and section 2.4. Confidence intervals were calculated by means of the two-tailed inverse of the student t distribution, see section 2.4.

Table 1: Kappa numbers before and after selective acid hydrolysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kappa number before hydrolysis</th>
<th>Confidence interval: Kappa number</th>
<th>Kappa number after hydrolysis</th>
<th>Confidence interval: Modified kappa number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>14.9</td>
<td>1.8</td>
<td>7.4</td>
<td>0.39</td>
</tr>
<tr>
<td>Oxygen delignified</td>
<td>11.7</td>
<td>-</td>
<td>5.0</td>
<td>0.08</td>
</tr>
<tr>
<td>D-Hot</td>
<td>2.2</td>
<td>0.3</td>
<td>1.2</td>
<td>0.03</td>
</tr>
<tr>
<td>EOP</td>
<td>1.9</td>
<td>1.2</td>
<td>0.9</td>
<td>0.06</td>
</tr>
<tr>
<td>D1</td>
<td>1.8</td>
<td>0.1</td>
<td>0.6</td>
<td>0.07</td>
</tr>
<tr>
<td>D2</td>
<td>0.7</td>
<td>0.7</td>
<td>0.4</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Table 2: Calculated lignin content, calculated from the kappa number after hydrolysis using equation 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated lignin content [%]</th>
<th>Confidence interval: Calculated lignin content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>1.26</td>
<td>0.152</td>
</tr>
<tr>
<td>Oxygen delignified</td>
<td>0.84</td>
<td>0.030</td>
</tr>
<tr>
<td>D-Hot</td>
<td>0.20</td>
<td>0.010</td>
</tr>
<tr>
<td>EOP</td>
<td>0.14</td>
<td>0.023</td>
</tr>
<tr>
<td>D1</td>
<td>0.10</td>
<td>0.025</td>
</tr>
<tr>
<td>D2</td>
<td>0.06</td>
<td>0.013</td>
</tr>
</tbody>
</table>
Figure 18: Kappa numbers before and after selective acid hydrolysis after unit operations through the fibreline.

Figure 19: Calculated lignin content after unit operations through the fibreline, calculated from the kappa number after hydrolysis using equation 2.

The kappa number before hydrolysis was seen to decrease from 14.9 for the unbleached sample, to 11.7 after oxygen delignification, 2.2 after the acidic chlorine dioxide step at elevated temperature, 1.9 after the alkaline extraction
enforced by a combination of oxygen and hydrogen peroxide and 1.8 and 0.7 after the two final chlorine dioxide bleaching steps. Taking the confidence interval into consideration, these results are all in perfect agreement with the results previously obtained by Sevastyanova et al. [44]. The accuracy of the present measurements was less than perfect, however, with an average coefficient of variation of 38.9%. Indeed, for the D2 sample, a strict reading of the data would allow one to draw the conclusion that there might not by any lignin in the sample at all, which contradicts the more accurate result that the lignin content is 0.06%. In comparison, the accuracy of the post-hydrolysis kappa numbers was excellent, with an average coefficient of variation of 6.29%. This difference is clearly a result of the fact that the kappa number analysis of the pulp before hydrolysis was performed as a double test whereas the post-hydrolysis kappa number was performed as a triple test, thereby reducing the standard deviation by a factor of $\sqrt{2}$ while also increasing the degree of freedom by one. It must be noted however, that the confidence interval for the post-hydrolysis kappa numbers presented here only take the deviation of the kappa number measurement into account. A full analysis of the method deviation should include this deviation as well as the deviation in the selective acid hydrolysis.

Performing the selective acid hydrolysis reduced the kappa number by almost 50% for unbleached pulp. This stands in agreement with the results previously obtained by Sevastyanova et al. [44], as well as the results from the article of Vuorinen et al. [47] that first presented the method. From these results the calculated lignin content was ascertained: The lignin content for the unbleached pulp was 1.2%, and descended to 0.06% at the end of the bleaching sequence. Since the calculated lignin content was proportional to the post-hydrolysis kappa number, its validity follows from the validity of those values. Likewise, the accuracy of the calculated lignin content was calculated from the standard deviation in the post-hydrolysis kappa numbers.

### 3.2 The origin of fibre charge in chemical pulp

The results from the conductometric titration, the methanolysis and the HUT-method for the determination of hexenuronic acids are summarised in table 3, figure 20 and figure 21. Confidence intervals were calculated by means of the two-tailed inverse of the student t distribution, see section 2.4.
Table 3: Total charge, methylglucuronic acid content and hexenuronic acid content after unit operations through the fibreline, as determined by conductometric titration, methanolysis and the HUT-method for the determination of hexenuronic acids analysed by means of UV absorbance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total charge [µmol/g]</th>
<th>Confidence interval: Total charge [µmol/g]</th>
<th>Methyl glucuronic acid content [µmol/g]</th>
<th>Confidence interval: Methyl glucuronic acid [µmol/g]</th>
<th>Hexenuronic acid content [µmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>127.7</td>
<td>5.8</td>
<td>48.4</td>
<td>4.3</td>
<td>72.8</td>
</tr>
<tr>
<td>Oxygen delignified</td>
<td>132.8</td>
<td>4.8</td>
<td>60.0</td>
<td>6.3</td>
<td>61.4</td>
</tr>
<tr>
<td>D-Hot</td>
<td>84.3</td>
<td>5.7</td>
<td>56.9</td>
<td>4.6</td>
<td>10.1</td>
</tr>
<tr>
<td>EOP</td>
<td>85.8</td>
<td>2.6</td>
<td>25.8</td>
<td>0.9</td>
<td>10.1</td>
</tr>
<tr>
<td>D1</td>
<td>74.7</td>
<td>9.4</td>
<td>28.2</td>
<td>0.2</td>
<td>10.6</td>
</tr>
<tr>
<td>D2</td>
<td>66.8</td>
<td>1.2</td>
<td>28.0</td>
<td>3.4</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Figure 20: Total charge, methylglucuronic acid content and hexenuronic acid content after unit operations through the fibreline, as determined by conductometric titration, methanolysis and the HUT-method for the determination of hexenuronic acids, presented separately.
Figure 21: Total charge and corresponding contributions to the total charge related to the methylglucuronic acid content as well as the hexenuronic acid content, as determined by conductometric titration, methanolysis and the HUT-method for the determination of hexenuronic acids.

Total charge showed a downward trend as the bleaching sequence continues. The total amount of charged groups in the unbleached sample was determined to be 127.7 µmol/g, which agrees well with a previous study on eucalyptus kraft pulp, where the total amount of charged groups was determined to be 116.0 µmol/g, also using conductometric titration [53]. The total amount of charged groups increased to 132.8 µmol/g after oxygen delignification. Oxygen delignification also resulted in a decrease in hexenuronic acid content, from 72.8 µmol/g to 61.4 µmol/g, as well as an increase in methylglucuronic acid content, from 48.4 µmol/g to 60.0 µmol/g. A similar increase in total charge was previously reported by Laine [42]. Laine’s results, however, showed an increase in hexenuronic acid content while predicting a decrease in methylglucuronic acid content. Laine’s results also have support in the work of Buchert et al. [37], who showed methylglucuronic acids to be stable under oxygen delignification. It therefore seems likely that the measured content of methylglucuronic acids in the present study, as well as the content of hexenuronic acids in either or both of the bleaching steps could differ from the true values. Indeed, while it can be shown that the coefficient of variation related to the methylglucuronic acid is 7.3% the deviation related to these two bleaching steps in particular are such that the difference in results are close to being statistically insignificant.
Total charge was reduced by 48.5 μmol/g during the hot acidic chlorine dioxide bleaching step. This reduction can be seen to be completely attributed to the degradation of hexenuronic acid, the content of which was reduced by 51.3 μmol/g. Although this result implied the formation of new oxidised groups, the difference was minor and not statistically significant. The content of methylglucuronic acid was also reduced, but this reduction was also minor and statistically insignificant. The degradation of hexenuronic acid seen in these results is unsurprising, since the degradation of hexenuronic acid is one of the main goals of this bleaching step [21]. A similar reduction in total charge was seen in the study by Laine [42]. Laine’s study also showed an efficient degradation of hexenuronic acids during this bleaching step. The stability of the methylglucuronic acid content further agrees with the study by Buchert et al. [37].

The stability of methylglucuronic acid during chlorine dioxide bleaching as predicted by Buchert et al. [37] can be further seen in the two final chlorine dioxide bleaching steps. The final step also saw a decrease in hexenuronic acid content, as seen in the hot acidic chlorine bleaching step and predicted by Laine [42]. This reduction in hexenuronic acid content was not seen, however, in the D1 step, which could be explained by industrial process parameters. The total amount of charged groups decreased linearly across the EOP, D1 and D2 bleaching steps, from 85.8 μmol/g, through 74.7 μmol/g into 66.8 μmol/g. The charged groups not associated with uronic acids, however, only decreased during the D1 step, from 49.9 μmol/g to 35.8 μmol/g. The D2 step did not affect the remaining charge to any statistically significant degree.

During the alkaline extraction enforced by oxygen and hydrogen peroxide the total charge was increased by 1.5 μmol/g, a statistically insignificant effect. No difference could be observed for the content of hexenuronic acids. The content of methylglucuronic acids, however, was seen to decrease by 31.1 μmol/g. Furthermore, since the total amount of charged groups was unchanged, this reduction must be balanced by an equal oxidation of other structures in the pulp. Although neither the study by Laine [42], or Buchert et al. [37], investigates the EOP step specifically, it is seen in the study by Laine that hexenuronic acids are stable during normal alkaline extraction while it is shown in the study by Buchert et al. that the methylglucuronic acid content is stable during both oxygen and hydrogen peroxide bleaching stages. Hexenuronic acid has further been shown to be stable to oxygen and hydrogen peroxide in a later study by Vuorinen et al. [47]. The reduction in methylglucuronic acids could, however, be linked to hemicellulose losses during alkaline extraction, as discussed in section 1.3.2. Specifically, the extraction of hemicelluloses
from eucalyptus grandis was recently investigated by Vena et al. [54] and it was shown that native eucalyptus grandis xylan structures are soluble under alkaline conditions, especially at high temperatures.

The observed oxidation of non-uronic acid structures could be related to a conversion of non-phenolic lignin into phenolic lignin, as explained in section 1.3.2 allowing an oxidation of lignin. This would agree with the suggestion of Sevastyanova et al [44], and oxidation of lignin by the action of peroxide has been reported previously in chemithermomechanical pulp [55]. This disagrees, however, with the results seen in the final chlorine dioxide stages as well as with the calculated lignin content: As seen in figure 19, the lignin content is almost cut in half during the D2 bleaching step. In contrast, the charged groups that are not related to uronic acids are stable during the same step, as discussed above. If the oxidation during the EOP step was related to an oxidation of lignin, this would not be the case. Further, were the remaining charge in the D2 step solely related to oxidised lignin, this would mean that each C9 group would have to contribute with 12 equivalents of charge, which is obviously impossible. In section 1.5 it was proposed that the remaining charge should be correlated with the lignin content of the samples, and that a linear relationship would give support to a direct correlation between oxidised lignin and remaining charge. Since this was not observed, and the observed data instead contradicts such a statement, the hypothesis presented in section 1.5 is falsified.

The observed reduction of methylglucuronic acid content coupled with an increase of anionic groups not related to uronic acids in the EOP step was observed in a previous study on alkaline peroxide bleaching on chemithermomechanical pulp by Li et al. [56]. In this study, the authors explained this to be due to the deesterification of LCC bonds between lignin and hemicelluloses, as originally explained by Obst [8], and further investigated by Sundberg et al. [57], the idea being that the deesterification of uronic acids linked to lignin will result in novel carboxylic acid groups. Although the initial lignin content in the EOP step of the present study is low, it is still four times larger than the lignin content at the end of the bleaching sequence. Also, once liberated, these groups would not be susceptible to lignin degradation. As such, this theory could explain the increase in oxidised structures, but confirming this would require further investigation.
3.3 Determination of hexenuronic acid by means of selective acid hydrolysis

In addition to characterising the hexenuronic acid content by measuring the absorbance at 245nm, as per the work of Vuorinen et al. [47], the hexenuronic acid content was also determined according to the method of Chakar et al. [51]. The results of these studies are presented in table 4 and illustrated in figure 22. Confidence intervals were calculated by means of the two-tailed inverse of the student t distribution, see section 2.4.

Table 4: Hexenuronic acid content after unit operations through the fibreline, as determined by the decrease in kappa number during selective acid hydrolysis as well as by characterisation through UV absorbance measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV based determination of hexenuronic acid content [µmol/g]</th>
<th>Kappa based determination of hexenuronic acid content [µmol/g]</th>
<th>Confidence interval: Kappa measurements [µmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unbleached</td>
<td>72.8</td>
<td>88.8</td>
<td>6.7</td>
</tr>
<tr>
<td>Oxygen delignified</td>
<td>61.4</td>
<td>80.3</td>
<td>0.9</td>
</tr>
<tr>
<td>D-Hot</td>
<td>10.1</td>
<td>12.0</td>
<td>0.9</td>
</tr>
<tr>
<td>EOP</td>
<td>10.1</td>
<td>12.6</td>
<td>3.4</td>
</tr>
<tr>
<td>D1</td>
<td>10.6</td>
<td>14.0</td>
<td>0.8</td>
</tr>
<tr>
<td>D2</td>
<td>2.6</td>
<td>4.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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Figure 22: Hexenuronic acid content after unit operations through the fibreline, as determined by the decrease in kappa number during selective acid hydrolysis as well as by characterisation through UV absorbance measurements.

The validity and accuracy of the results as determined by UV characterisation has been discussed above in section 3.2, while the validity and accuracy of the method based on the difference in kappa number measurements follow from the respective validities and accuracies of the pre- and post-hydrolysis kappa number measurements, as discussed in section 3.1.

For the unbleached and oxygen delignified samples, a statistically significant difference was observed for the two methods: For the unbleached pulp, this difference was 16 µmol/g, while the difference was 18.9 µmol/g for the oxygen delignified sample. The differences between the other samples were minor, in the order of 1-4 µmol/g, and statistically insignificant for the EOP and D2 samples. Further, since the UV characterisation was performed as single tests, a confidence interval for those measurements could not be made. It is therefore entirely possible that the differences between the two methods for the D-Hot and D1 samples also would have proved to be statistically insignificant. In the referenced study by Chakar et al. [51], samples of unbleached US hardwood kraft pulps were treated with a selective acid hydrolysis and subjected to kappa number measurements as well as having the hexenuronic acid content determined by means of UV spectroscopy. The authors note that the results of these studies were in agreement with each other, which
contradicts the results obtained in this study. Further, it is obvious that the values obtained in the present study from the difference in kappa numbers is too large: The sum of the methylglucuronic acid content and the hexenuronic acid content as determined by difference in kappa number exceeded the total amount of charged groups for the samples in question. As such, the selective acid hydrolysis seems to have degraded other structures in the pulp samples. Given that the unbleached and oxygen delignified samples had a higher lignin content than the latter samples, see table 1, the observed difference between the UV measurements and the kappa number difference measurements could be due to delignification. A minor delignification is indeed discussed in the original article by Vuorinen et al. [47], which specifies that the removal of 10 \( \mu \text{mol/g} \) of hexenuronic acids resulted in the dissolution of 380 mg TOC/kg (Total organic carbon) of additional structures, half of which was determined to be neutral carbohydrates.

4 Conclusions

No correlation between lignin content and charge remaining after accounting for the contribution from hexenuronic acids and methylglucuronic acids was found. Instead, it was found that each bleaching step had binary effects on the measured charge components, including remaining charge. Oxygen delignification was found to have minor effects on each of the measured components. The D-Hot step was found to degrade hexenuronic acid, with a corresponding decrease of total charge but not to affect the methylglucuronic acid content. The EOP step was found to degrade methylglucuronic acids, while leaving hexenuronic acids unaffected. No difference in total charge was observed between the D-Hot and EOP steps, meaning that a non-measured component must have been oxidized: this effect could not be correlated to the lignin content. Negligible effects for each component was observed for the D1 step, while the D2 step efficiently degraded hexenuronic acids.

The hexenuronic acid content was successfully determined according to the HUT-method. A difference in content was observed when results obtained from UV measurements were compared with the observed difference in kappa number prior and after selective acid hydrolysis. This difference was 16 \( \mu \text{mol/g} \) for the unbleached sample and 18.9 \( \mu \text{mol/g} \) for the oxygen delignified sample.
References


[41] P. Fardim, B. Holmbom, Critical comparison and validation of methods for determination of anionic groups in pulp fibres, Nordic Pulp & ...17 (3).


