

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

On the Oxidation of Kraft Pulp

Formation of Carbonyl Groups During Acidic Hydrogen Peroxide Oxidation

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2020

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Cover: Reaction vessel for oxidation of pulp.

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Abstract

A shift from fossil based to bio based raw material is necessary if the needs of a growing population are to be fulfilled sustainably. Today, the packaging industry is heavily dependent on products originating from fossil feedstocks. Lignocellulosic biomass is a well-used material for packaging as its constituents may be used to produce strong and flexible materials. The hydrophilic structure of the cellulose, however, makes utilization of pure cellulose materials in wet or moist conditions difficult since the hydrogen bonds, that are keeping the structure together, are easily disrupted by water. Through the use of additives and mechanical treatments the wet-strength of paper may be slightly increased. An alternative to these techniques is chemical modification of the cellulose itself. By introducing carbonyl groups to the cellulose structure via oxidation, covalent cross-links, i.e. hemiacetals, can form. These cross-links are not interrupted as easily as hydrogen bonds. Traditional methods for introducing carbonyl groups are, however, limited by environmental or economical constraints that prevent them from being suitable for industrial applications.

Oxidative chemistry is typically utilized in the production of bleached qualities of chemical pulp. These processes are optimized to minimize effects on the carbohydrate structures, as this would lead to yield loss or undesirable effects, such as yellowing of the pulp. Altering the conditions in a bleaching stage to favour the introduction of carbonyl groups would allow a carbonyl-rich pulp, with inherent wet-strength, to be produced on a large scale using the existing infrastructure of pulp mills.

The main aim of this work has been to evaluate the oxidation of bleached softwood and hardwood kraft pulp using a common bleaching agent: hydrogen peroxide. Process conditions, such as pH and temperature, have been varied and their influence on the formation of oxidized functionalities and the degradation of the carbohydrates has been analysed. It was found that a pH of 4 greatly increased the formation of carbonyl groups, compared to the traditional alkaline conditions of a hydrogen peroxide stage. Sheets produced from the oxidized pulp showed a significantly enhanced durability at aqueous conditions and were also found to withstand mild stirring in water while exhibiting only limited swelling.

Keywords: Hydrogen peroxide, cellulose oxidation, wet-strength, bleaching.

List of Publications and Presentations

The thesis is based on the following papers:

Paper I. **Modification of softwood kraft pulp fibres using hydrogen peroxide at acidic conditions**

Axel Martinsson, Merima Hasani, Antje Potthast, Hans Theliander
Cellulose, 2020, 27, 7191-7202.

Paper II. **Hardwood kraft pulp fibre oxidation using acidic hydrogen peroxide**

Axel Martinsson, Merima Hasani, Hans Theliander
Submitted manuscript

Part of the work has been presented by the author at:

The 7th AvanCell Conference (oral presentation)

Gothenburg, Sweden, 9-10 October 2019

Contribution Report

The author's contribution to the papers presented in this thesis:

- Paper I: Main author. Responsible for evaluation of results and preparation of the manuscript. Carried out the all of the experimental work with the exception of the fluorescence labelling and GPC measurements, which were carried out at BOKU, and the total organic carbon analysis, carried out at Södra Innovation.
- Paper II: Main author. Responsible for evaluation of results and preparation of the manuscript. Carried out all of the experimental work.

Contents

1	Introduction.....	1
1.1	Objectives.....	2
2	Theory.....	3
2.1	Wood Structure	3
2.2	Wood Composition	4
2.2.1	Cellulose	4
2.2.2	Hemicellulose	4
2.2.3	Lignin.....	5
2.3	Pulping and Bleaching	5
2.4	Oxidation of Holocellulose	7
2.4.1	Oxidizable Sites	7
2.4.2	Oxidation of Carbohydrates Using Hydrogen Peroxide	7
3	Materials and Methods.....	9
3.1	Materials.....	9
3.2	Oxidation of Kraft Pulp.....	9
3.3	Cold Caustic Extraction of Hardwood Pulp.....	9
3.4	Quantification of Carbonyl Groups.....	9
3.4.1	Hydroxylamine Hydrochloride Titration	9
3.4.2	Quantification of Carbonyl Groups Through Fluorescence Labelling	10
3.4.3	Quantification of Aldehyde Groups.....	10
3.5	Quantification of Carboxyl Groups.....	10
3.6	Analysis of Carbohydrate Degradation	11
3.6.1	Gel Permeation Chromatography	11
3.6.2	Intrinsic Viscosity Measurement	11
3.7	Compositional Analysis	11
3.8	Fibre Image Analysis	12
3.9	Wet Durability Test.....	12
4	Results and Discussion	13
4.1	Results of Unbuffered Oxidations of Softwood Pulp	13

4.2	Oxidation of Softwood and Hardwood Pulps at Constant pH	17
4.3	Results of the Oxidation of CCE Hardwood Pulps at Constant pH.....	19
4.4	Material Properties of Oxidized Pulps	21
4.4.1	Fibre Image Analysis	21
4.4.2	Wet Durability	22
5	Conclusions.....	25
6	Future Work.....	27
7	Acknowledgements.....	29
8	Bibliography	31

1 Introduction

An increasing world population means that a number of challenges need to be addressed in the very near future. In 2019, there were approximately 7.7 billion people, with the expectation of reaching 10.9 billion by the end of the century (United Nations, 2019). Historically, many markets have relied on an increase in the production of fossil-based materials. However, in order to deal with issues related to the use of fossil-based materials, e.g. the release of CO₂, the possibility of using renewable resources, such as biomass, must be further examined. Today, the worldwide production of paper and paperboard is roughly 425 million tonnes and increasing steadily. Segments such as graphical paper have decreased due to the increased digitalization of society, but the production of both packaging and tissue paper is on the rise (Berg and Lingqvist, 2019). Globally, the packaging market has grown rapidly: fuelled by increasing E-commerce and changing consumer behaviours, it has recently seen an annual growth of 3 % (McKinsey & Company, 2019). The packaging industry is, however, partly reliant on fossil-based materials, mainly in the form of flexible and rigid plastics (Interpack Alliance, 2016), which needs to be addressed in order to fulfil the increasing demand in a sustainable fashion.

Cellulose has been investigated thoroughly as a potential replacement for fossil-based materials such as packaging materials (Wang *et al.*, 2018; Su *et al.*, 2018). Alongside it being the most abundant polymer on Earth, the strength and flexibility of cellulose make it suitable for several paper and textile applications. Its hydrophilic nature, however, makes it difficult to utilize cellulose-based materials on the surfaces of products that are subjected to aqueous conditions for extended lengths of time. Water may interrupt the inter-fibre hydrogen bonds that keep the paper materials together and, when wetted, the material can lose in excess of 90 % of its original strength (Dunlop-Jones, 1991). This figure can be improved marginally by mechanical treatments such as wet-pressing and refining, although wet-strength agents are typically added to further increase the wet-strength of paper materials. Wet-strength agents, such as polyamide or epoxide-based agents, are nevertheless linked to emissions of adsorbable organic halides (AOX) and may also cause problems with the re-pulping of broke or recycling of the final product (Bates, Beijer and Podd 1999; Espy and Geist, 1993). An alternative to using wet-strength agents is chemical modification of the cellulose itself. The introduction of carbonyl groups allows the material to form covalent cross-links, hemiacetals, that are not as easily interrupted as hydrogen bonds (Chen *et al.*, 2002). The most commonly used methods for introducing carbonyl groups in cellulose are periodate oxidation, which forms a 2,3-dialdehydecellulose (Kim *et al.*, 2000) and TEMPO oxidation, which results in a C6-aldehyde cellulose (Saito and Isogai, 2005). Both methods, however, have serious impediments that prevent them from being suitable for the large-scale production of carbonyl cellulose: sodium periodate is environmentally harmful and TEMPO oxidation suffers from economic drawbacks (Serra *et al.*, 2017).

The bleaching agents used in the production of bleached qualities of kraft pulp include oxidizers such as chlorine dioxide, hydrogen peroxide and ozone. These processes are optimized to dissolve residual lignin or react with chromophoric groups, while minimizing reactions with the carbohydrate chains. As hemicelluloses and cellulose are contributing to the majority of the strength of the pulp, extensive degradation reactions with these polymers could lead to loss in strength, as well as yield loss (Reeve, 1996). If the conditions for the bleaching could be altered in such a way that the formation of carbonyl groups in carbohydrates could be favoured, then large quantities of pulp with inherent wet-strength could be produced using the existing infrastructure of a kraft pulp mill. Hydrogen peroxide could be a good candidate, since it is a commonly used bleaching agent often employed in the final bleaching stage of high brightness pulps. One benefit of using hydrogen peroxide is that the main decomposition products are water and oxygen, which would be suitable for both elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching sequences. Hydrogen peroxide is typically utilized at alkaline pH, where the bleaching effect is achieved through the decomposition of hydrogen peroxide into the hydroperoxy ion (Gullichsen, 1999). It may also form radicals, mainly hydroxyl radicals, capable of oxidizing the C2 and C3 hydroxyls into ketones (Gierer, 1997). If this reaction could be optimized, whilst minimizing the degradation of the carbohydrates, a green and economic route for the production of carbonyl rich cellulose could be achieved.

1.1 Objectives

The main objective of this work was to investigate the introduction of carbonyl groups in kraft pulp using a commonly used bleaching agent, namely hydrogen peroxide. An understanding of the mechanisms involved in hydrogen peroxide oxidation at different conditions could potentially be utilized in the development of a large-scale production of fibres with an enhanced carbonyl content.

The study has involved investigations of the influence of oxidation conditions on the formation of oxidized functionalities, the degradation of carbohydrates and the properties of the material used. Softwood and hardwood kraft pulps were used as raw materials in order to gain understanding of the differences in oxidation caused by variations in their chemical composition and structure.

2 Theory

2.1 Wood Structure

The properties of wood, and the resulting products thereof, can differ drastically depending on the source. Wood is typically divided into soft and hardwood, where the former is sourced from gymnosperms and the latter from angiosperms. The wood itself is comprised of a highly ordered structure of cells; it is the longitudinal direction of the tree where cells of high aspect ratio are found. These cells are responsible for the main mechanical support of the tree. In softwood, these cells are fibre tracheids while in hardwood, they are a mixture of tracheids and libriform cells. In general, softwood fibres are greater in length than those of hardwood. The mean fibre length of Norway spruce is 3.5 mm whereas in birch, it is 1.3 mm, where the fibre tracheids are slightly shorter than the libriform cells. Other cell types, with the purpose of storing and transporting nutrients and fluid, are present in the radial direction of the tree. Softwood has an overall simpler structure than hardwood: fibre tracheids compose 89-95 % of the wood volume of softwood whereas tracheid and libriform cells form 37-65 % of hardwood (Retulainen, Niskanen and Nilsen, 1998).

Wood fibres need to be liberated from their matrix, Figure 1, before they can be utilized. This can be done by either mechanical or chemical procedures. In chemical pulping, this is done by dissolving the lignin-rich middle lamella, which effectively adheres the fibres together. The cell wall of the fibres is stiff and comprised of two main layers of cellulose microfibrils in a lignin/hemicellulose matrix, Figure 1. The thin primary cell wall has a random cellulose fibril orientation whereas the secondary cell wall consists of multiple layers with differing microfibril orientation, which contributes to the mechanical properties of the fibre.

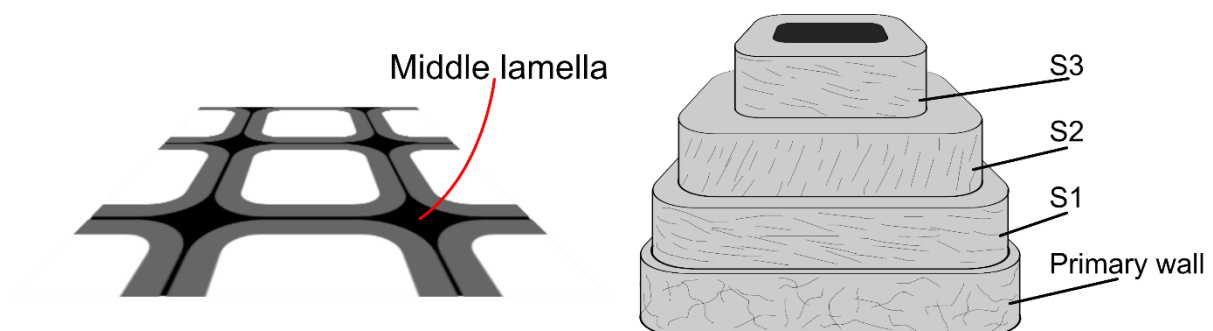


Figure 1. Matrix of fibres and the lignin-rich middle lamella holding them together (left). The layers of the primary and secondary cell walls of a wood fibre (right).

2.2 Wood Composition

2.2.1 Cellulose

Approximately 40-50 % of wood is comprised of cellulose, which is a linear homopolymer consisting of D-glucopyranose units linked by $\beta(1\rightarrow4)$ glycosidic bonds (French, 2017). In native wood, cellulose may have a degree of polymerisation (DP) of about 10 000 – 15 000. After being subjected to pulping and bleaching, however, the DP may be reduced to 2 000-4 000 due to the degradation reactions occurring during these processes (Sixta, 2006). The two ends of cellulose show different chemical properties. The end with a free C1 hydroxyl can open into the aldehyde form shown in Figure 2, and has reducing properties. The opposing end, on the other hand, has a free C4 hydroxyl group and does not show any reducing properties (Klemm *et al.*, 2004).

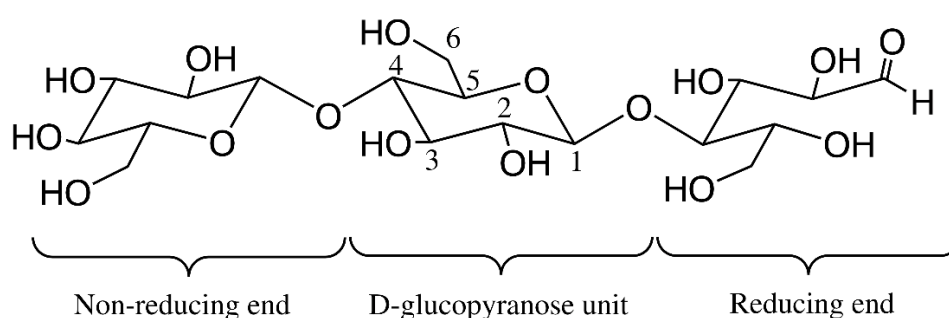


Figure 2. Structure of non-reducing end and reducing end of cellulose.

Cellulose can form stiff chains through the formation of intramolecular hydrogen bonds (Figure 3) that, in turn, are ordered in sheets held together by hydrogen bonds between the C6 and C3-hydroxyl groups on neighbouring chains. These sheets are further ordered in layers, held together through van der Waals bonds and hydrophobic interactions, thereby forming cellulose microfibrils. In wood pulp, microfibrils are often found in aggregates larger than those present in native wood. This is due to the pulping process removing lignin and hemicellulose, which increases the contact surface between microfibrils. The aggregates thus formed are often referred to as macrofibrils (Henriksson and Lennholm, 2009).

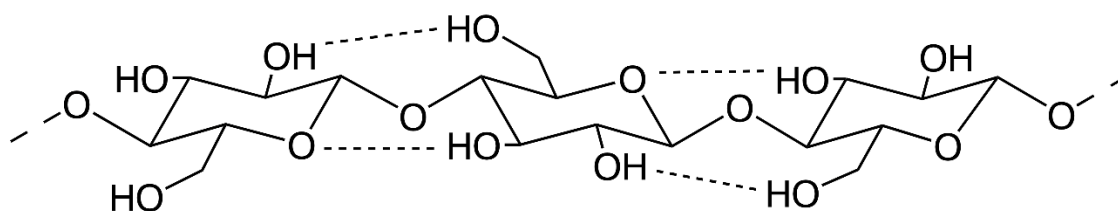


Figure 3. Intramolecular hydrogen bonding in the cellulose chain.

2.2.2 Hemicellulose

Together with cellulose, wood is also comprised of another group of carbohydrates, known as hemicelluloses. These are heteropolymers of much shorter length than cellulose, with a maximum DP of roughly 200 (Teleman, 2009). The hemicelluloses are mainly hexoses, such

as: D-galactose, D-mannose and D-glucose, and pentoses: D-xylose and L-arabinose. Hydroxyl groups are substituted along the linear backbone of the hemicelluloses.

The main function of hemicelluloses is to add flexibility to the cell wall through interactions with cellulose and lignin (Mikkonen 2013; Terrett and Dupree, 2019). The most abundant hemicelluloses found in wood are xylans and mannans. Xylans consist of $\beta(1\rightarrow4)$ -linked D-xylose units, with side groups along the chain. Hardwood xylan (glucuronoxylan) and softwood xylan (arabinoglucuronoxylan) differ in a few ways, one being acidity: softwood xylan has a higher substitution of 4-O-methyl-D-glucuronic acid side groups. Softwood xylan has L-arabinose side groups, whereas hardwood xylan has acetyl side groups. Mannans have a backbone comprised of $\beta(1\rightarrow4)$ -linked D-glucose and D-mannose with differing ratios, depending on the source and partially acetylated D-mannose units. In the case of softwood (galacto)glucomannan, a fraction of the D-mannose units is branched with D-galactose units, which is not found in hardwood.

2.2.3 Lignin

Roughly 15-35 % of softwood and 20 % of hardwood is comprised of lignin (Henriksson, 2009). This not only contributes to the strength of the fibres but also provides the wood with hydrophobic and antimicrobial properties. The structure of lignin is completely unordered: it forms a random 3D-network where the monomers, i.e. monolignols, are connected through different carbon-carbon or ether bonds (mainly β -O-4). Lignin is mainly derived from three different monolignols: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol, see Figure 4. Its composition of lignin units (derived from monolignols) varies, depending on the source of the raw material. Hardwood lignin (syringyl-guacyl lignin) consists of sinapyl and coniferyl alcohol, whereas softwood lignin (guaiacyl lignin) consists of coniferyl alcohol and has only trace amounts of p-coumaryl alcohol.

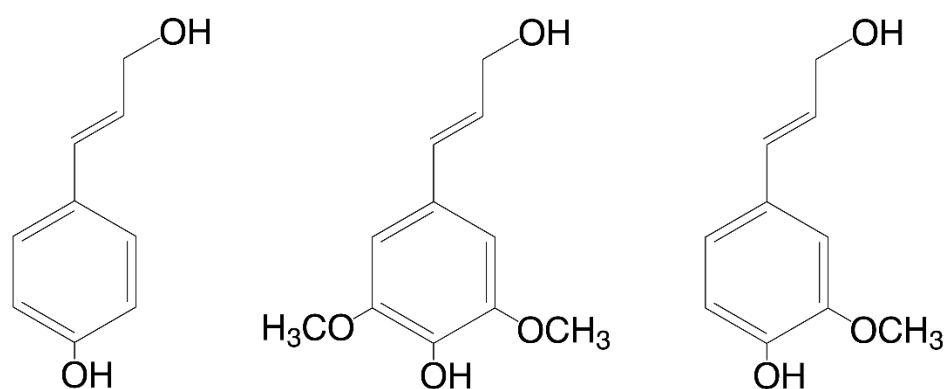


Figure 4. The main monolignols in lignin. From left: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol.

2.3 Pulping and Bleaching

The fibres in wood are accessed by first being liberated from the fibre matrix. In mechanical pulping, this is achieved through thermal and mechanical treatments, whereas in chemical

pulping the lignin that holds the fibres together is solubilized using chemical treatment alone. The dominating chemical pulping technology currently employed is kraft pulping, which utilizes a combination of hydroxide ions and hydrosulphide ions at temperatures between 150 and 170 °C to fragment and solubilize the lignin (Gellerstedt, 2009). However, this not only affects lignin but also solubilizes carbohydrates to some extent. During the initial phase of delignification, a significant amount of glucomannan is dissolved at temperatures between 100 and 130 °C. At slightly higher temperatures, above 140 °C, xylan will dissolve. This dissolution of hemicelluloses does, nevertheless, slow down during the later stages of the cook (Gullichsen, 1999). The alkaline conditions prevalent during pulping mean that methanol is eliminated from the 4-O-methyl-D-glucuronic acid side groups of xylan, and a hexenuronic acid group is formed (Teleman *et al.*, 1995). The stability of xylan in alkaline conditions may allow it to be adsorbed onto the surface of fibres later on via non-electrostatic attraction (Yllner and Enström, 1956).

With increasing alkalinity, the extent of the degradation of carbohydrates caused by peeling reactions, as well as by alkaline hydrolysis, increases in severity. Peeling reactions are initiated at the reducing end of the carbohydrates. The reducing end may undergo ring opening; in the presence of alkali, this may lead to β -elimination which, in turn, cleaves off the end group and forms a new reducing end. This peeling will continue until a stable metasaccharinic acid end group has been formed (Gellerstedt, 2009). The severity of the carbohydrate degradation increases during the residual delignification of the pulp, so it may be more favourable to remove residual lignin through bleaching operations instead.

A bleached pulp is necessary for products that require high brightness or high purity, such as printing paper and food board. Bleaching, which removes the chromophoric groups present in the residual lignin or the carbohydrate fraction, can be performed in two principle ways: through a lignin-preserving process, as is used for mechanical pulps, or a lignin-removing process, as is used for chemical pulps.

The bleaching efficiency of a single bleaching stage is reduced over time, so bleaching processes are typically performed in several stages. This increases selectivity and maximizes yield while minimizing degradation reactions with the carbohydrates; the resulting brightness is higher than what is achievable with a single stage. Bleaching has been performed historically using chlorine (Cl_2) or hypochlorite (OCl^-) but, for environmental reasons, these were gradually phased out during the 1980s and 1990s, and replaced by more environmentally friendly bleaching agents, such as chlorine dioxide (ClO_2), hydrogen peroxide (H_2O_2), oxygen (O_2) and ozone (O_3). Modern bleaching sequences are typically categorized as being elemental chlorine free (ECF), where no other chlorine-containing compounds other than chlorine dioxide are used, or being totally chlorine free (TCF).

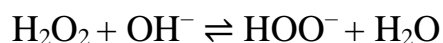
2.4 Oxidation of Holocellulose

2.4.1 Oxidizable Sites

The majority of bleaching agents currently in use are oxidizers, so carbohydrates are subjected to oxidative degradation to some degree. This can occur through a number of different reactions, with negative consequences: a loss of DP or brightness reversion can result from the introduction of oxidized functionalities. The main oxidation reactions occurring with cellulose can be classified as the oxidation of reducing end-groups, glycol-cleavage oxidation, primary hydroxyl oxidation, secondary hydroxyl oxidation or oxidation of anomeric carbon (Lai, 2001). Non-ideal process conditions (e.g. excessive temperature and/or pH), impurities (e.g. metal ions) or extensive bleaching to low contents of lignin can all result in increased oxidation of the carbohydrate fractions. It is therefore important to maintain process conditions such as temperature and pH, as well as using pre-treatments to reduce the content of metal ions, in order to minimize yield loss, prevent the undesired introduction of oxidized groups and decrease chemical consumption.

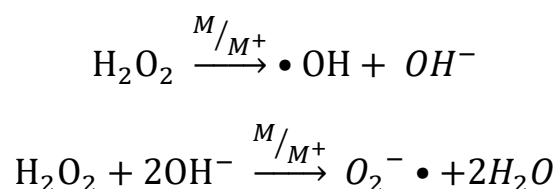
2.4.2 Oxidation of Carbohydrates Using Hydrogen Peroxide

Hydrogen peroxide bleaching is typically performed at alkaline pH, with a final pH between 10.5 and 11.5. The bleaching power of hydrogen peroxide is mainly attributed to the hydroperoxy ion, produced from the decomposition of hydrogen peroxide at alkaline conditions according to Reaction 1.



Reaction 1. Disassociation of hydrogen peroxide into the hydroperoxy ion at alkaline conditions.

In the presence of transition metals such as iron, manganese and copper, however, hydrogen peroxide decomposes rapidly, causing hydroxyl and superoxide anion radicals to form (Reaction 2), and results in a lowering of the DP of the carbohydrates, and an increased consumption of chemicals (Hjerdeet *et al.*, 1994; Lachenal, 1996). Hydrogen peroxide bleaching is therefore often preceded by a pre-treatment in order to reduce the amount of transition metals. This is performed either by an acid wash or a chelating treatment using diethylenetriaminepentaacetic acid (DTPA) or ethylenediaminetetraacetic acid (EDTA).



Reaction 2. Transition metal-catalysed decomposition of hydrogen peroxide into hydroxide and superoxide radicals.

The aforementioned hydroperoxy ion is not associated with severe degradation and oxidation of the carbohydrate structure. However, the hydroperoxy ion may also further oxidize carbonyl groups if they are present either on the primary or secondary hydroxyl groups, and thereby form carboxyl groups. In the case of a 2,3-diketo cellulose, this would effectively break the glycol bond and open up the ring structure, Figure 5 (Gierer, 1986).

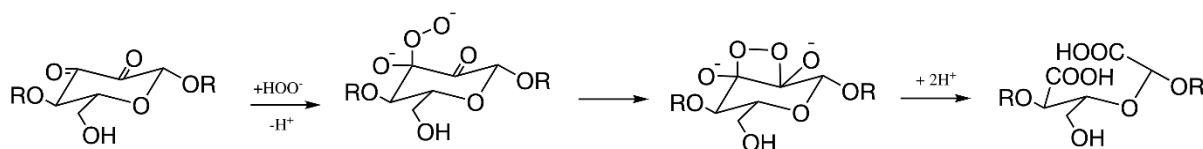


Figure 5. Glycol cleavage of a 2,3-diketocellulose by the hydroperoxy ion.

Hydroxyl radicals mainly react with the carbohydrate structure in two ways: through oxidation of the secondary hydroxyl groups, forming a ketone (Gierer, 1997), or oxidation of the anomeric carbon, causing chain cleavage. Computational analysis by Guay *et al.* suggests that the third step in the formation of a ketone (Figure 6), i.e. the leaving of a superoxide radical, is not favourable energetically at alkaline pH. However, Kishimoto and Nakatsubo (1998) showed that, during ozone bleaching at acidic pH, the formation of carbonyl groups was caused mainly by radicals, i.e. it is possible that ketone could form during oxidation with hydrogen peroxide at acidic pH. Oxidation of the anomeric carbon is initiated in a similar fashion to the oxidation of the secondary carbonyl groups. The hydrogen abstraction of C1 is followed by a homolytic or hydrolytic fragmentation, effectively cleaving the cellulose chain at the point of the anomeric carbon (Fredricks, Lindgren and Theander, 1971; Gierer, 1990), Figure 6. The work of Guay *et al.* and Kishimoto and Nakatsubo suggests that acidic pH should be favourable for producing a ketone-rich cellulose, although extensive fragmentation due to oxidation of the anomeric carbon may result in severe loss of strength in the fibre.

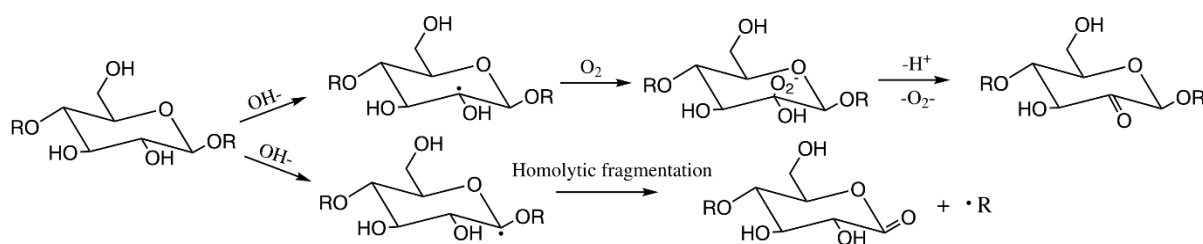


Figure 6. Oxidation mechanism of the oxidation of C2 or C1 initiated by the hydroxyl radical.

3 Materials and Methods

3.1 Materials

Two different pulps were subjected to oxidation using hydrogen peroxide: a softwood kraft pulp provided by Södra Cell Värö and a hardwood kraft pulp provided by Södra Cell Mönsterås. All reagents were purchased from Sigma-Aldrich and used as received.

3.2 Oxidation of Kraft Pulp

The raw material was oxidized using hydrogen peroxide in a jacketed glass reactor equipped with baffles and a condenser. The reactor was stirred with a pitched-blade impeller at 1000 rpm. The pulp consistency used in the experiments was 2.5 % and the initial concentration of hydrogen peroxide was 5 % (wt% of the liquid fraction). The temperature range studied was 65 – 85 °C and the residence times varied between 30 and 90 minutes. A circulating heater with external temperature control was used to heat the reactor.

Once the desired reaction time had elapsed, the reaction was quenched by adding 500 ml of cold, deionized water. The suspension was filtered and the filtrate recirculated once, followed by washing with 1000 ml of deionized water, after which the filter cake was placed in 500 ml of deionized water for 10 minutes. Finally, the suspension was filtered again, and the filtrate recirculated once, followed by washing with an additional portion of 1000 ml of deionized water, adjusted to pH 3.5 using sulphuric acid to minimize the impact of β -alkoxy elimination.

3.3 Cold Caustic Extraction of Hardwood Pulp

Cold caustic extraction (CCE) of xylan was performed in order to study the influence of xylan on the oxidation of hardwood pulp; the method is based on the procedure of Janzon, Saake and Puls (2008). A pulp consistency of 5 % and sodium hydroxide concentration of 10 wt% were used. The suspension was stirred continuously using a pitched-blade impeller at room temperature for 1 hour, after which the suspension was filtered and the filtrate recirculated once. The pulp was then washed using a three-stage procedure, starting with washing with a 2 % sodium hydroxide (aq) solution, followed by washing with 5 % acetic acid (aq) and, finally, washing with 2 000 ml of hot, deionized water.

3.4 Quantification of Carbonyl Groups

3.4.1 Hydroxylamine Hydrochloride Titration

Hydroxylamine hydrochloride was used to quantify the carbonyl groups by applying a method based on that of Zhao and Heindel (1990). A 500 mg (O.D. weight) sample of never-dried pulp was dispersed in 100 ml of deionized water, adjusted to pH 4 using hydrochloric acid. The suspension was left for 10 minutes, after which it was filtered and the filtrate recirculated once. The filter cake was then washed with 500 ml of deionized water adjusted to pH 4 and transferred to a beaker containing 25 ml of 0.25 M hydroxylamine hydrochloride (aq), adjusted

to pH 4. The reaction was left for 2 hours at room temperature with constant mixing. The suspension was thereafter filtered and the filtrate titrated back using 0.01 M NaOH (aq). The filter cake was placed in an oven at 105 °C for 24 hours and used to determine the exact weight of the sample. The number of carbonyl groups was then quantified from the amount of titrant needed to titrate the sample back to pH 4 and the weight of the dried sample. All analyses were performed in duplicate.

3.4.2 Quantification of Carbonyl Groups Through Fluorescence Labelling

The carbonyl groups were quantified by labelling with carbazole-9-carbonyl-oxy-amine (CCOA), performed according to the procedure of Röhrling *et al.* (2002). The samples were then dissolved in N,N-dimethylacetamide/lithium chloride (9%) (DMAc/LiCl) after solvent exchange at room temperature. The analysis of the labelled samples was performed with a gel permeation chromatograph (GPC) coupled with a multi-angle laser light scattering (MALLS) and fluorescence refractive index (RI) detection system, which yields the oxidized groups relative to the molecular weight distribution of the sample. The fluorescence labelling and subsequent GPC analysis were performed by Dr. Sonja Schiesser at BOKU in Vienna, Austria.

3.4.3 Quantification of Aldehyde Groups

Sodium chlorite oxidation of the pulps was performed to determine the number of aldehydes present in the samples. It was followed by measuring their carboxyl content, with any increase in this being attributed to aldehydes. The oxidation procedure was performed according to Saito and Isogai (2004). Deionized water was added to a 2 g sample of pulp to create a slurry of 10 % consistency, which was added to a mixture comprised of 1.81 g of sodium chlorite, 20 ml of 5 M acetic acid (aq) and 57 ml of deionized water. The pH was adjusted to 4.5 using a 50 % sodium hydroxide (aq) solution and placed on a shaking table for 48 h, after which the pulp was filtered and the filtrate recirculated, before being washed with 2 L of deionized water.

3.5 Quantification of Carboxyl Groups

The number of carboxyl groups was quantified using a method based on the procedure of Barbosa *et al.* (2013) using potentiometric titration. A never-dried sample of 500 mg (O.D. weight) was placed in a beaker containing 60 ml of 0.1 M HCl (aq) and dispersed well to ensure protonation of the carboxylic groups. After 2 hours at room temperature, the sample was filtered and the filtrate recirculated once, followed by washing with deionized water until a neutral filtrate was obtained. The pulp sample was transferred to a beaker containing 50 ml of 0.5 M NaCl (aq) and titrated using 0.02 M NaOH in 0.5 M NaCl (aq). The suspension was then filtered; the filtrate was washed with one portion of deionized water, followed by another portion of deionized water, before being placed in an oven at 105 °C to determine the mass of the sample. The number of carboxyl groups were calculated from the volume of titrant at the equivalence point and the mass of the oven dried sample. All analyses were performed in duplicate.

3.6 Analysis of Carbohydrate Degradation

3.6.1 Gel Permeation Chromatography

The GPC system was comprised of a TSP FL2000 fluorescence detector for monitoring of the carbonyl label, a MALLS detector (Wyatt Dawn DSP, Wyatt Inc., Santa Barbara, USA) with a diode laser ($\lambda = 488$ nm) and an RI detector (Shodex RI-71). Four serial GPC columns, PL gel-mixed ALS, 20 μm and 7.5 \times 300 mm (Agilent, Waldbronn, Germany) were used as the stationary phase. A degasser (Dionex DG-2410), autosampler (HP 1100), pulse damper pump (Kontron pump 420) and column oven (Gynkoteck STH 585) were also utilized.

3.6.2 Intrinsic Viscosity Measurement

The intrinsic viscosity of the pulps dissolved in bis(ethylenediamine)copper(II) hydroxide (CED) solution was used to evaluate the extent of carbohydrate degradation, and performed according to SCAN C 15:62. A portion of air-dried pulp was dispersed in 25 ml of deionized water, followed by the addition of 25 ml of 1 M CED solution. The sample was allowed to dissolve for 30 min in a water bath set to 25 °C, followed by intrinsic viscosity measurement made in a capillary viscosimeter. Elution times were calculated as an average of three measurements; all samples were analysed in duplicate. Prior to the intrinsic viscosity measurements, the pulp was reduced using 5 % sodium borohydride at 4 % consistency and room temperature for 24 hours. This was performed to prevent degradation by any carbonyl groups that may have been introduced from occurring.

Conversion from intrinsic viscosity (cm^3/g) to viscosity average weight (kDa) was performed using the Mark-Houwink-Sakurada equation, using the parameters calculated by Kes and Christensen (2013).

3.7 Compositional Analysis

The composition of the pulps was analysed by subjecting 200 mg of oven-dried pulp to complete acid hydrolysis with 72 % sulphuric acid, using a method based on that of Theander and Westerlund (1986). Following acid hydrolysis, the sample was filtered and the insoluble material was considered to be Klason lignin. The filtrate was used to determine the amount of acid soluble lignin (ASL) and the content of carbohydrates. ASL was determined using an Analytik Jena Specord 150 UV spectrometer at wavelength of 205 nm, with an absorptivity constant of 110 $\text{dm}^3/\text{g cm}$. The monomeric sugars were analysed with a Dionex ICS-5000 equipped with CarboPac PA1 columns using NaOH/NaAC (aq) and NaOH (aq) as eluents. An electrochemical detector was used for detection and Chromeleon 7, Vers. 7.1.3.24.25 was used as software.

3.8 Fibre Image Analysis

Dimensional fibre analysis was performed using a Kajaani FS300 fibre image analyser. A 50 mg (oven dried weight) sample of never-dried pulp was added to 2 L of deionized water and defibrillated for 30 000 revs in a standard pulp disintegrator. Approx. 30 ml of the suspension was subsequently transferred to a beaker for analysis.

3.9 Wet Durability Test

The durability of the different pulps in deionized water was tested using a simple test for identifying potential changes in wet-strength due to the introduction of carbonyl groups. Sheets were produced by adding a known amount of never-dried pulp to 2 L of water and disintegrating for 30 000 revs in a standard pulp disintegrator. The suspension was then filtered through a Büchner funnel to create a sheet that was allowed to dry at room temperature, from which a 3x3 cm square was thereafter cut. This was placed in a beaker containing deionized water and a stir bar and allowed to swell whilst being observed over time, after which it was stirred at 200 rpm for 60 seconds and its disintegration witnessed.

4 Results and Discussion

4.1 Results of Unbuffered Oxidations of Softwood Pulp

Initial studies were aimed at finding conditions favourable for the formation of carbonyl groups when oxidizing softwood kraft pulp with hydrogen peroxide in unbuffered solutions. The starting pH of the reaction was adjusted using either sulphuric acid or sodium hydroxide to achieve an acidic or alkaline starting pH (pH 4 or pH 10).

Without any added buffer system, the pH varied during the course of the oxidation process due either to the formation of hydroxyl groups from the decomposition of the hydrogen peroxide or the organic acids formed during cellulose hydrolysis (Wen *et al.* 2019), Figure 7. For the oxidations carried out at acidic pH, a gradual lowering of the pH was noted after the first 30 minutes which resulted in a final pH of 5.2, whereas those starting with an alkaline pH showed a gradual increase in pH which resulted in a final value of 12. This difference in the pH change between the acidic and alkaline oxidations suggests that the oxidation mechanism that takes place differs in the two cases.

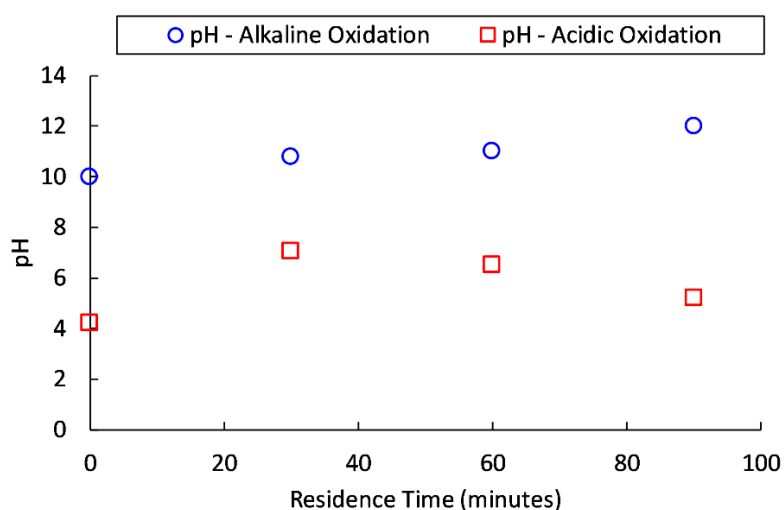


Figure 7. Change in pH during the oxidation experiments with acidic and alkaline starting pH.

The samples were analysed for the formation of oxidized functionalities and degradation. From the results of the quantification of carbonyl groups using the hydroxylamine hydrochloride method, Figure 8, it can be observed that, at acidic conditions, significantly more carbonyl groups were introduced compared to oxidation at alkaline conditions, which does not seem to increase the carbonyl content at all. The number of carboxyl groups, however, remains stable throughout oxidation in both cases, Figure 9. This may be explained either by the increased solubility of fractions with carboxylic functionalities, which would dissolve during oxidation or be washed away during the subsequent washing sequence, or the fact that the oxidation of carbonyl groups into carboxyl is not extensive. The alkaline conditions seem to result in a more rapid degradation of carbohydrates compared to the acidic, Figure 10, as measured by capillary

viscosimetry (used to assess changes in the molecular weight of the oxidized samples). At reaction times below 60 minutes, acidic oxidation results in a higher viscosity than alkaline oxidation: for the final 30 minutes, however, degradation at alkaline conditions seems to level off, whereas it continues to decrease during acidic conditions, suggesting that the two cases may have differing reaction mechanisms.

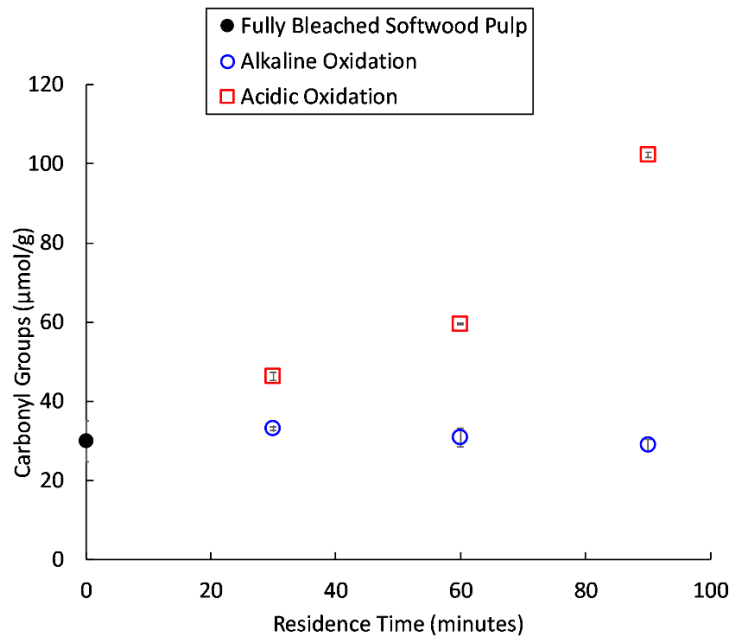


Figure 8. Total number of carbonyl groups in pulps oxidized in acidic or alkaline conditions, measured using the hydroxylamine hydrochloride method.

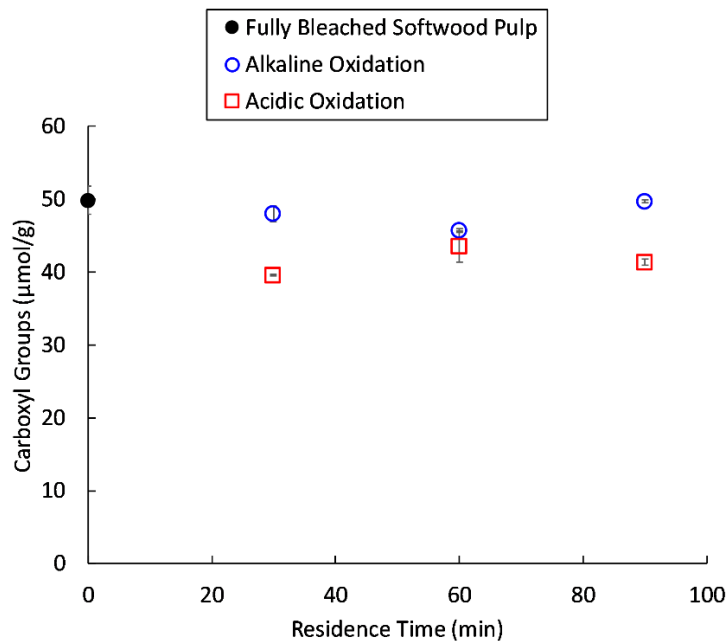


Figure 9. Number of carboxyl groups in pulps oxidized in acidic and alkaline conditions, measured using potentiometric titration.

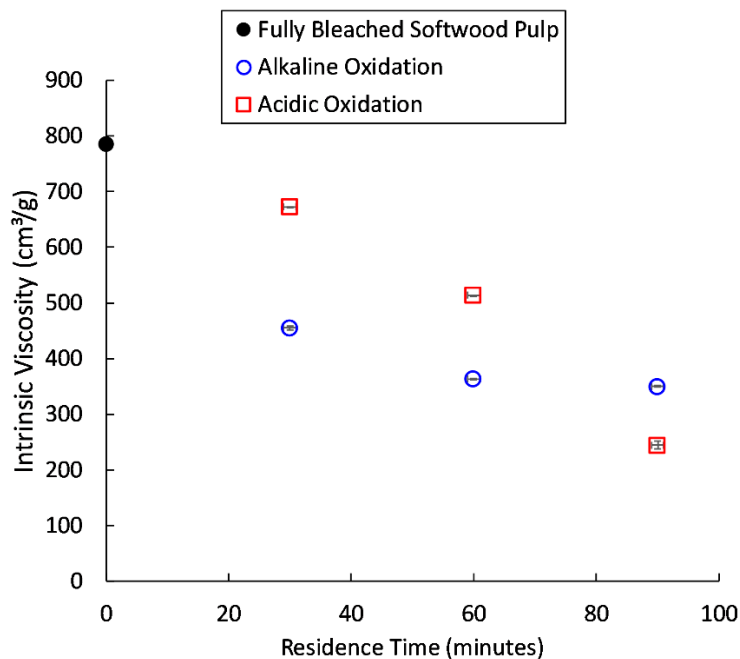


Figure 10. Intrinsic viscosity of pulps oxidized in acidic or alkaline conditions, measured using capillary viscosimetry.

The results obtained using the hydroxylamine hydrochloride method and capillary viscosimetry were verified using CCOA labelling of the carbonyls introduced, with a subsequent GPC measurement using UV detection, Figure 11. Intrinsic viscosity values were converted to viscosity average molecular weight to enable a better comparison to be made with the results obtained from the GPC. No comparison could be made for the reference pulp and acidic oxidation for 30 minutes because the DMAc-LiCl used for dissolution of the samples for GPC analysis suffers from poor dissolution of softwood pulps of larger molecular weight. Comparisons made for both the carbonyl groups and molecular weights show similar trends, suggesting that capillary viscosimetry and the hydroxylamine hydrochloride method can be used to quantify oxidation and degradation, although the latter seems to overestimate the number of carbonyl groups slightly. Since the method uses the change in pH after reaction with the hydroxylamine hydrochloride solution to quantify the number of carbonyl groups, acidic functionalities in the cellulose could potentially contribute to the consumption of the alkaline titrant, thereby leading to a slight overestimation. In the case of molecular weight, the absolute values for the two methods are expected to differ: the viscosity average molecular weight (M_v) and the weight average molecular weight (M_w) are not directly comparable, in terms of absolute values. The trends for the two methods seem nevertheless to correlate well.

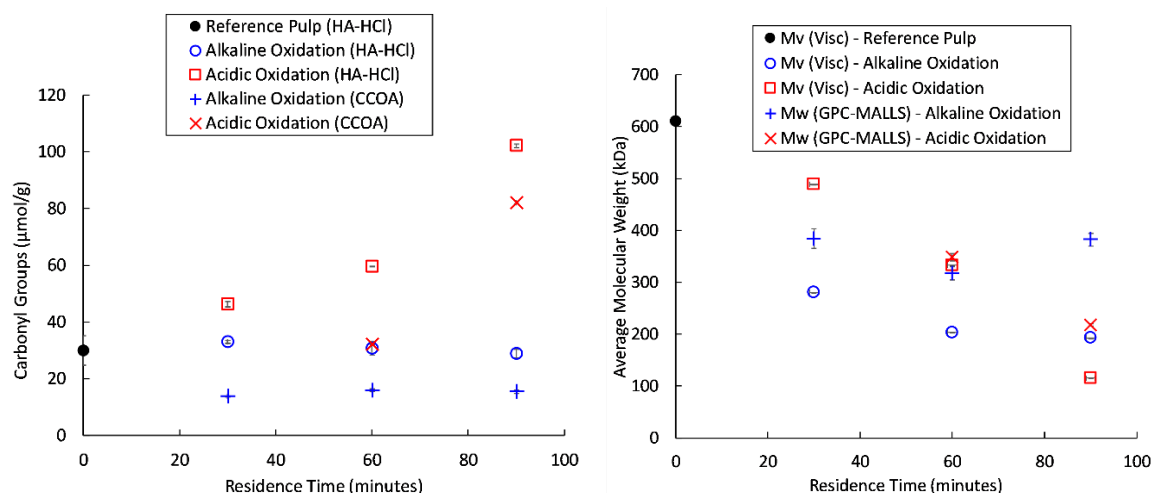


Figure 11. Comparisons between the hydroxylamine hydrochloride method (HA-HCl) and CCOA labelling (left) and capillary viscosity and GPC-MALLS (right).

Compositional analyses of the samples were carried out to investigate the effect of the oxidation on the various carbohydrate fractions as well as the lignin content, the results of which are reported in Table 1.

Table 1. Compositional analysis of pulps oxidized in acidic and alkaline conditions.

	Cellulose (%)	Galacto-glucomannan (%)	Xylan (%)	ASL (%)	Klason (%)	SUM (%)	Not detected (%)
Bleached Kraft Pulp	70.7	7.44	8.23	0.77	0.00	87.2	12.8
Acidic Oxidation, 30 minutes	70.9	5.96	8.12	0.64	1.65	87.3	12.7
Acidic Oxidation, 60 minutes	70.9	5.16	7.95	0.70	1.40	86.2	13.8
Acidic Oxidation, 90 minutes	70.1	5.22	8.03	0.69	1.50	85.6	14.4
Alkaline Oxidation, 30 minutes	69.9	6.43	8.49	0.66	1.70	87.2	12.8
Alkaline Oxidation, 60 minutes	69.5	5.58	8.28	0.65	1.50	85.5	14.5
Alkaline Oxidation, 90 minutes	69.6	5.97	8.25	0.67	1.40	85.9	14.1

The main trends observed in the compositional analysis of the oxidized samples were a reduced amount of galactoglucomannan for both the acidic and alkaline oxidations and a slight reduction in xylan for the acidic oxidations, suggesting that these may be targeted by the

oxidation. An increase in both Klason lignin and non-detected material could also be seen in the oxidized samples, and can probably be explained by the formation of humins/pseudo-lignins. These are fragments of hydrolysed and/or oxidized carbohydrates that will not be detected as carbohydrates by the compositional analysis, ending up instead as either Klason lignin or non-detected material: this could also explain the reduction in hemicelluloses (Li, Henriksson and Gellerstedt, 2005; Sannigrahi and Ragauskas, 2008; van Zandvoort et al. 2013).

4.2 Oxidation of Softwood and Hardwood Pulps at Constant pH

The large variation in pH detected in the initial experiments, Figure 7, meant that a buffer was required so that oxidation at a specific pH could be evaluated. The sodium acetate/acetic acid buffer was found to be a good option for further studies not only due to its buffering range but also since it was found not to affect the actual oxidation.

Comparing the oxidation of softwood and hardwood pulps at pH 4 (Figure 12), the trends seem similar at 65 °C and 75 °C. At 85 °C, however, oxidation was found to introduce significantly more carbonyl groups in the softwood pulps. The carbonyl measurement of the hardwood reference may be underestimated and, judging from the trends of the different oxidation temperatures, would be expected to be in the range of 40 to 50 $\mu\text{mol/g}$. One explanation here is that this could be due to hornification, which could possibly be reversed by the mechanical treatment to which the sample is subjected during oxidation. The three 30-minute oxidations of hardwood pulp seem to have a similar value, indicating that few carbonyls are introduced at this point.

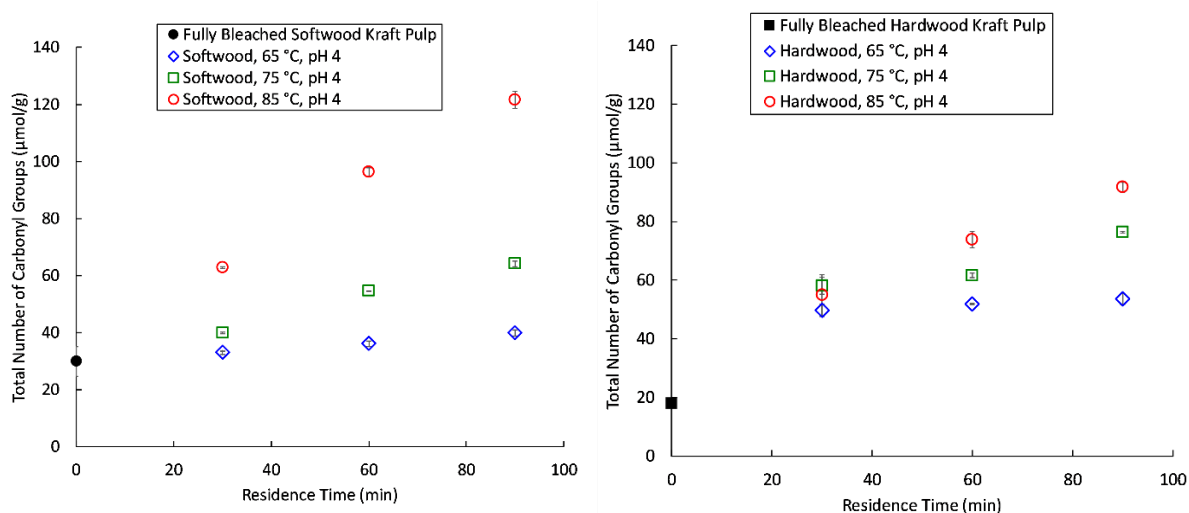


Figure 12. Carbonyl content of softwood and hardwood kraft pulps oxidized at varying temperatures.

Similar to the experiments carried out in the absence of a buffer, the oxidations do not seem to impact the carboxyl content to any significant extent with the exception of oxidation of hardwood pulp at 85 °C, where a slight decrease can be noted (Figure 13). Once again, this could be due to the dissolution of smaller fragments with carboxyl groups being introduced and/or there being limited oxidation of the carbonyl groups formed.

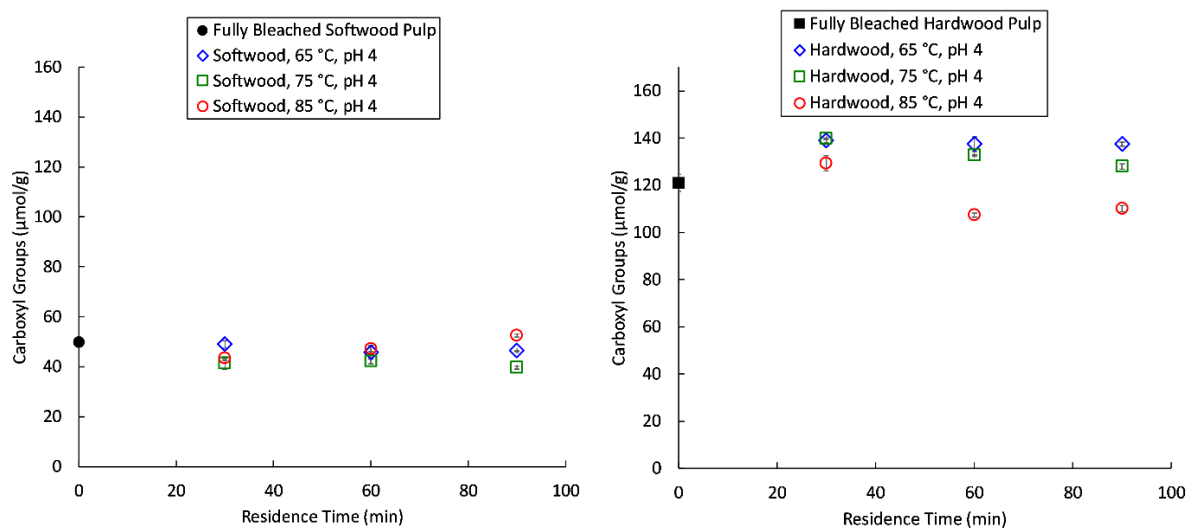


Figure 13. Carboxyl content of softwood and hardwood kraft pulps oxidized at varying temperatures.

Comparing the change in the intrinsic viscosity of oxidized softwood and hardwood pulps shows similar trends, with the carbohydrate degradation appearing to be of similar severity, Figure 14.

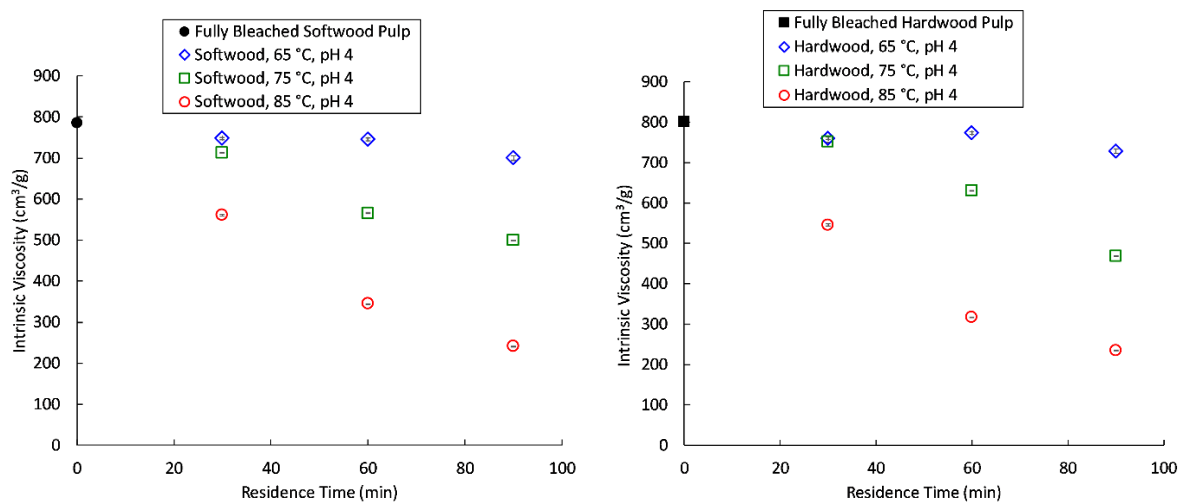


Figure 14. Intrinsic viscosity of softwood and hardwood pulps oxidized at varying temperatures.

In Paper II, the extent of the formation of aldehyde groups in hardwood pulp was studied using further oxidation of the introduced aldehydes with sodium chlorite. The number of aldehyde groups can be quantified by measuring the carboxyl content prior to and post sodium chlorite oxidation, since sodium chlorite selectively oxidizes aldehyde groups into carboxyl groups. No increase in carboxyl content was found, however, for the pulps oxidized at 75 °C or 85 °C,

except for residence times exceeding 60 minutes at 85 °C (Figure 15). In all other cases, a small decrease was found, which is likely due to the experimental error of the measurements of carboxyl content. Further experiments at temperatures above 85 °C and residence times longer than 90 minutes are therefore necessary to evaluate whether or not the formation of aldehyde is more pronounced at these conditions.

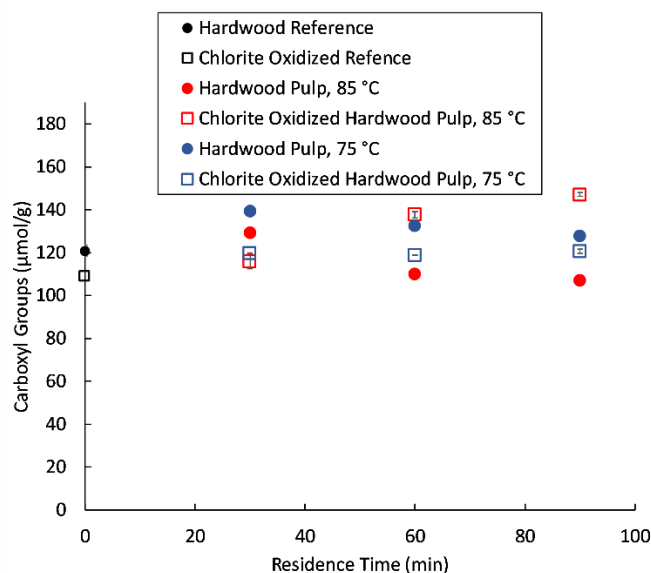


Figure 15. Differences in carboxyl content before and after sodium chlorite oxidation.

4.3 Results of the Oxidation of CCE Hardwood Pulps at Constant pH

A compositional analysis of the hardwood oxidized at 85 °C was carried out; it was found that oxidation reduces the detectable xylan content of the pulp significantly whereas the glucose content remains stable, Table 2, thereby indicating that the oxidation of xylan is favoured. One possible explanation for this could be that the location of xylan is on the surface of the fibre, due either to adsorption/precipitation during pulping or to its natural distribution in the cell wall (Danielsson, 2007; Hutterer *et al.*, 2017; Sjöberg *et al.*, 2005).

Table 2. Composition of hardwood pulp oxidized at 85 °C, pH4.

	Reference	30 min	60 min	90 min	90 min Blank
Glu.	69.1	69.0	70.2	71.0	69.5
Xyl.	19.4	19.0	17.7	16.3	19.5
Man.	0.08	0.40	0.40	0.31	0.18
Klason	0.32	0.20	0.10	0.15	0.12
ASL	0.93	1.01	0.91	0.95	0.90
Undetected	10.17	10.39	10.69	11.29	9.80

The influence the xylan present in hardwood pulp has on oxidation was evaluated further by performing a cold caustic extraction (CCE) on the hardwood pulp in order to reduce its content

of xylan. Compared to the reference hardwood pulp, 88 % of the xylan was removed during the CCE, Table 1, and even more was removed during the course of oxidation. A comparison of the relationship between glucose and xylose in the samples shows that the xylan content is clearly lowered when oxidizing hardwood pulp whereas it remains more or less constant during the oxidation of CCE pulp, Figure 16. This indicates that glucose and xylose units are oxidized to the same extent in the CCE pulp.

Table 3. Composition of oxidized and unoxidized CCE pulp.

	CCE Reference	30 min	60 min	90 min
Glu	81.4	85.60	86.10	85.90
Xyl	2.39	2.27	2.08	1.73
Man	0.50	0.51	0.49	0.46
Klason	0.50	0.08	0.10	0.07
ASL	0.55	0.61	0.73	0.91
Undetected	14.66	10.93	10.50	10.93

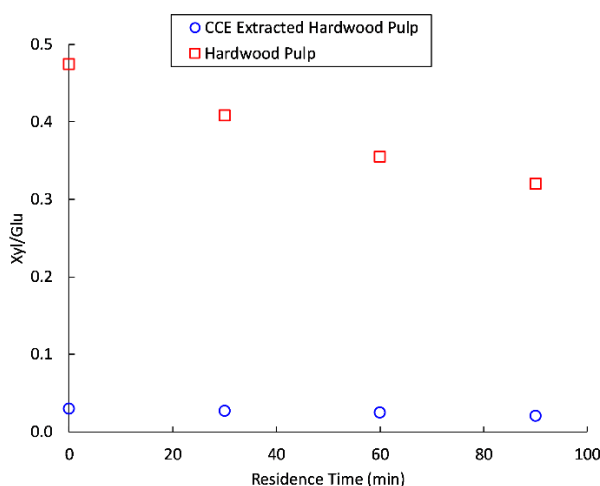


Figure 16. Relationship between the xylose and glucose contents of hardwood pulp and CCE hardwood pulp.

In Figure 17, which compares the carbonyl content and intrinsic viscosity of oxidized pulps with and without CCE, it can be seen that the pulp subjected to CCE has a more rapid oxidation and severe degradation. The oxidized CCE pulp shows a larger loss in viscosity after 30 minutes than hardwood pulp oxidized for 60 minutes. The CCE hardwood reference also has a higher intrinsic viscosity than the regular hardwood pulp, which can be explained by the removal of low molecular xylan that contributes to a lowering of the average intrinsic viscosity. The more rapid degradation of the CCE pulp may be explained by the cellulose being oxidized to a greater extent without the presence of xylan covering the cellulose surface, which could lead to a more severe loss in viscosity. The removal of xylan from the CCE pulp would also lead to the formation of additional pores, and thereby an increase in the accessible surface area

in the never-dried state. It is likely that this also explains the more rapid introduction of carbonyl groups to the CCE treated pulp (Dou and Tang, 2017). On the other hand, the degradation effect seems to be more pronounced than the increased introduction of carbonyl groups to the pulp at residence times below 60 minutes, when the carbonyl content is similar for the two pulps but the intrinsic viscosity of the CCE pulp is significantly lower.

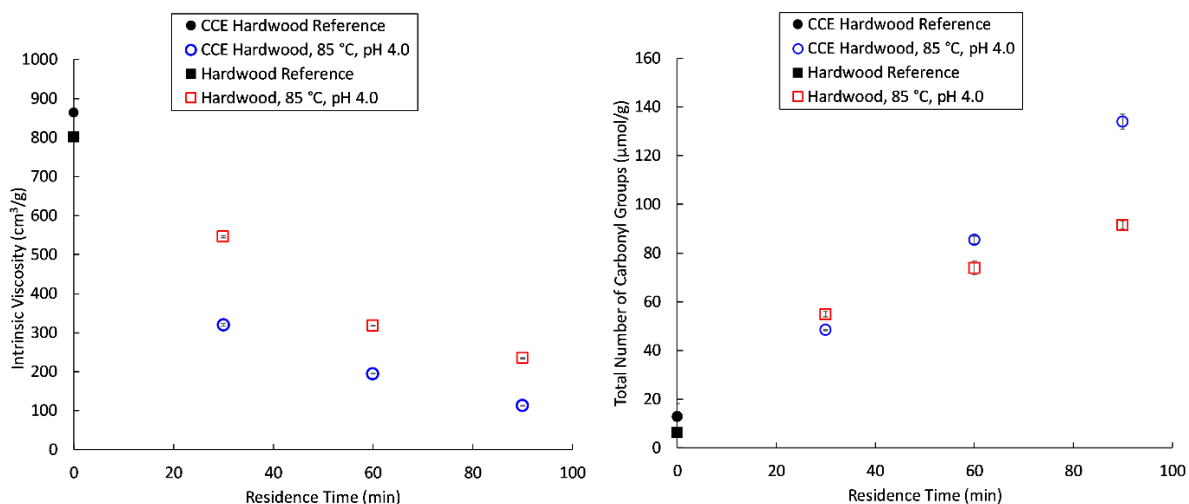


Figure 17. Intrinsic viscosity and carbonyl content of oxidized hardwood pulps with and without CCE.

4.4 Material Properties of Oxidized Pulps

4.4.1 Fibre Image Analysis

A fibre image analysis was carried out to investigate whether or not oxidation affected the fibre dimensions. The extensive formation of carbonyl groups in the fibre wall, for example, could potentially affect the swelling of the fibre, and thereby its width. The results reported in Figure 18, however, indicate that oxidation affects neither the length nor the width distribution to any significant extent. Although no change was found after oxidation for either the softwood or hardwood pulp, a fraction of shorter length fibres was removed during CCE.

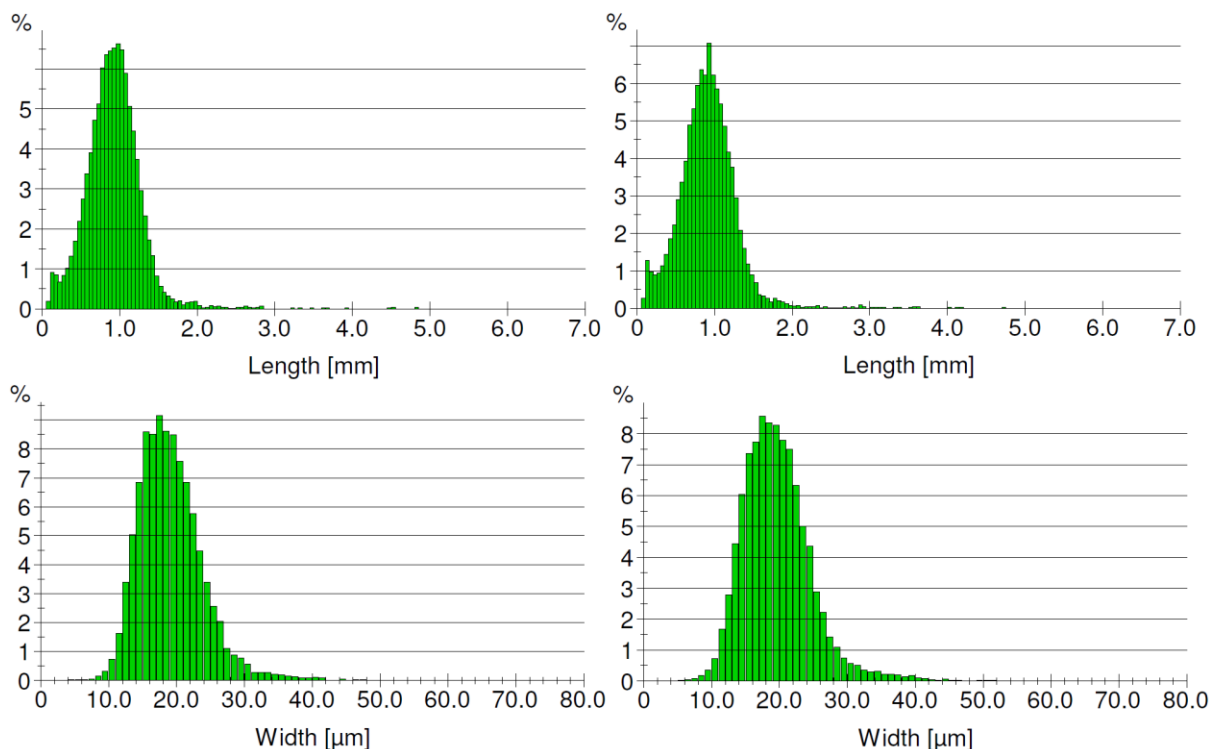


Figure 18. Top left: Fibre length distribution of hardwood pulp oxidized for 90 minutes at 85 °C. Top right: Fibre length distribution of the fully bleached hardwood pulp. Bottom left: Width distribution of hardwood pulp oxidized for 90 minutes at 85 °C. Bottom right: Width distribution of the fully bleached hardwood pulp.

4.4.2 Wet Durability

A simple wet durability test was performed to test the cross-linking effect that occurs when carbonyl-rich pulp is being dried. Sheets were produced from the reference pulp and a pulp oxidized for 90 minutes at 85 °C and, once dried, a 3x3 cm square cut from each sheet was placed in a beaker of water. After being left to soak for ten minutes, the oxidized samples could withstand mild stirring without disintegrating, something neither of the reference pulps were capable of. The sheets produced from oxidized pulp were found to swell to a lesser extent, thus indicating interfibrillar cross-linking. Figure 19 shows the results obtained from the wet durability tests carried out on unoxidized and oxidized softwood pulp. No difference in wet durability was found when oxidized softwood and hardwood pulps are compared. The sheets of oxidized CCE pulp were found to partially withstand mild stirring, although they were noticeably less dense and loose fibres were observed after stirring. A possible explanation for this could be increased hornification due to the collapse of pores in the extracted fibres. This enhanced hornification leads to less flexible fibres that could have a limited ability to form cross-links, leading to the durability of the final sheet in water being reduced.

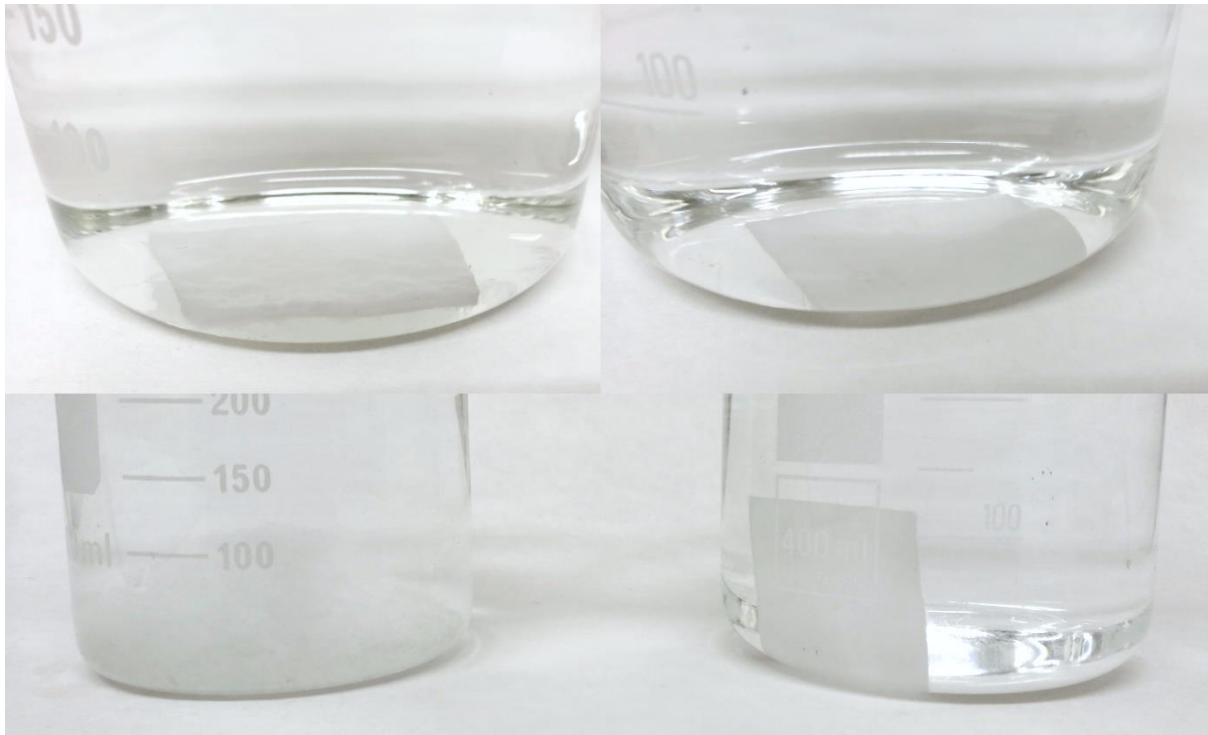


Figure 19. Top left: Sheet from the reference softwood pulp after swelling in water. Top right: Sheet from softwood pulp oxidized for 90 minutes at 85 °C after swelling in water. Bottom left: Sheet from the reference softwood pulp after stirring at 120 rpm for 60 seconds. Bottom right: Sheet from softwood pulp oxidized for 90 minutes at 85 °C after stirring at 120 rpm for 60 seconds.

5 Conclusions

In this work it has been shown that acidic conditions can increase the formation of carbonyl groups significantly when softwood and hardwood pulps are oxidized with hydrogen peroxide, in contrast to alkaline conditions. Compositional analyses of the oxidized pulps show that hemicelluloses are affected significantly by oxidation; it is especially pronounced in the case of hardwood pulp, and is likely due to the high amount of xylan present on the surface of the cell walls being oxidized.

At temperatures below 85 °C the carbonyl groups formed are probably mostly ketones, as was found when the aldehydes were quantified through further oxidation with sodium chlorite.

The pulps oxidized at acidic conditions show increased durability in water, which is presumably due to the formation of cross-links, i.e. hemiacetals, between the fibres.

6 Future Work

Extensive investigations of the material properties of the oxidized materials are necessary in order to evaluate the manner in which the introduction of carbonyl groups affects both the end product and the processability of the pulp. This will doubtlessly embrace, among other things, wet and dry-strength tests, freeness and yellowing measurements after heating or exposure to UV-light.

Furthermore, the effects of re-pulping on the aforementioned properties should be investigated to appraise potential changes during the re-pulping of broke or recycling of the final product.

Processability and scale-up potential would also require studying. Could oxidation be performed at medium consistency and using hydrogen peroxide at lower concentrations?

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8 Bibliography

- Barbosa, L. C., Maltha, C. R., Demuner, A. J., Casal, C. M., Reis, E. L., & Colodette, J. L. (2013). A Rapid Method for Quantification of Carboxyl Groups in Cellulose Pulp. *BioResources*, 1043-1054. doi:10.15376/BIORES.8.1.1043-1054
- Bates, R., Beijer, P., & Podd, B. (1999). Wet Strengthening of Paper. In L. Neimo (Ed.), *Papermaking Chemistry* (pp. 289-302). Helsinki: Fapet Oy.
- Berg, P., & Lingqvist, O. (2019). *Pulp, Paper, and Packaging in the next decade: Transformational change*. McKinsey & Company.
- Chen, N., Hu, S., & Pelton, R. (2002). Mechanisms of Aldehyde-Containing Paper Wet-Strength Resins. *Industrial & Engineering Chemistry Research*, 5366-5371. doi:10.1021/ie020355m
- Danielsson, S. (2007). Xylan Reactions in Kraft Cooking (Doctoral Thesis). Stockholm: Royal Institute of Technology.
- Dou, X., & Tang, Y. (2017). The Influence of Cold Caustic Extraction on the Purity, Accessibility and Reactivity of Dissolving-Grade Pulp. *Sustainable Chemistry*, 11462-11468. doi:10.1002/slct.201701551
- Dunlop-Jones, N. (1991). Wet-Strength Chemistry. In J. C. Roberts (Ed.), *Paper Chemistry* (pp. 76-96). New York: Chapman and Hall.
- Espy, H. E., & Geist, G. W. (1993). Persulfates as repulping reagents for neutral/alkaline wet-strength broke. *TAPPI Journal*, 139-142.
- Fredricks, P. S., Lindgren, B. O., & Theander, O. (1971). Chlorine Oxidation of Cellulose. *Svensk Papperstidning*, 597-603.
- Gellerstedt, G. (2009). Chemistry of Chemical Pulping. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper Chemistry and Technology* (Vol. 2). Berlin: de Gruyter. Retrieved from <https://app.knovel.com/hotlink/toc/id:kpPPCTPC03/pulp-paper-chemistry/pulp-paper-chemistry>
- Gierer, J. (1986). Chemistry of Delignification* Part 2: Reactions of lignins during bleaching. *Wood Science and Technology*, 1-33.
- Gierer, J. (1990). Basic Principles of Bleaching Part 2: Anionic Processes. *Holzforschung*, 395-400.

- Gierer, J. (1997). Formation and Involvement of Superoxide ($O_2^{\bullet-}/HO_2^{\bullet}$) and Hydroxyl (OH^{\bullet}) Radicals in TCF Bleaching Processes: A Review. *Holzforschung*, 34-46. doi:10.1515/hfsg.1997.51.1.34
- Guay, D. F., Cole, B. J., Fort, R. C., Hausman, M. C., Genco, J. m., Elder, T. J., & Overly, K. R. (2001). Mechanisms of Oxidative Degradation of Carbohydrates During Oxygen Delignification. II. Reaction of Photochemically Generated Hydroxyl Radicals with Mehtyl β -Cellobioside. *Journal of Wood Chemistry and Technology*, 67-79. doi:10.1081/WCT-100102655
- Gullichsen, J. (1999). Fiber Line Operations. In J. Gullichsen, & C.-J. Fogelholm (Eds.), *Chemical Pulping* (pp. A19-A243). Helsinki: Papet Oy.
- Henriksson, G. (2009). Lignin. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper Chemistry and Technology* (Vol. 1). Berlin: de Gruyter. Retrieved from <https://app.knovel.com/hotlink/toc/id:kpPPCTPC03/pulp-paper-chemistry/pulp-paper-chemistry>
- Henriksson, G., & Lennholm, H. (2009). Cellulose and Carbohydrate Chemistry. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper Chemistry and Technology* (Vol. 1). Berlin: de Gruyter. Retrieved from <https://app.knovel.com/hotlink/toc/id:kpPPCTPC03/pulp-paper-chemistry/pulp-paper-chemistry>
- Hjerde, T., Kristiansen, T. S., Stokke, B. T., Smidsrød, O., & Christensen, B. E. (1994). Conformation Dependent Depolymerisation Kinetics of Polysaccharides Studied by Viscosity Measurements. *Carbohydrate Polymers*, 265-275. doi:10.1016/0144-8617(94)90070-1
- Hutterer, C., Fackler, K., Schild, G., Ibl, V., & Potthast, A. (2017). Xylan Localization on Pulp and Viscose Fiber Surfaces. *Bioresources*, 5632-5648. doi:10.15376/BIORES.12.3.5632-5648
- Interpack Alliance. (2016). *Emerging Packaging Markets*. Düsseldorf: Interpack alliance.
- Janzon, R., Saake, B., & Puls, J. (2008). Upgrading of paper-grade pulps to dissolving pulps by netren extraction: properties of nitren extracted xylans in comparison to NaOH and KOH extracted xylans. *Cellulose*, 15:161-175. doi:10.1007/s10570-007-9154-8
- Kes, M., & Christensen, B. E. (2013). A Re-investigation of the Mark-Houwink-Sakurada Parameters for Cellulose in Cues: A Study on Size-exclusion Chromatography Combined with Multi-angle Light Scattering and Viscometry. *Journal of Chromatography*, 32-37. doi:10.1016/j.chroma.2013.01.038

- Kim, U.-J., Kuga, S., Wada, M., Okano, T., & Kondo, T. (2000). Periodate Oxidation of Crystalline Cellulose. *Biomacromolecules*, 488-492. doi:10.1021/bm0000337
- Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (n.d.). General Considerations on Structure and Reactivity of Cellulose: Section 2.1-2.14. In D. Klemm, B. Philipp, T. Heinze, U. Heinze, & W. Wagenknecht (Eds.), *Comprehensive Cellulose Chemistry*. doi:doi.org/10.1002/3527601929.ch2a
- Lachenal, D. (1996). Hydrogen Peroxide as a Delignifying Agent. In C. W. Dence, & D. W. Reeve (Eds.), *Pulp Bleaching - Principles and Practice* (pp. 347-361). Atlanta: TAPPI Press.
- Lai, Y.-Z. (2001). Chemical Degradation. In D. N.-S. Hon, & N. Shiraishi, *Wood and Cellulosic Chemistry* (pp. 443-512). New York: Marcel Dekker.
- Li, J., Henriksson, G., & Gellerstedt, G. (2005). CarboHydrate Reactions During High-Temperature Steam Treatment of Aspen Wood. *Applied Biochemistry and Biotechnology*, 175-186. doi:10.1385/ABAB:125:3:175
- McKinsey & Company. (2019). *No Ordinary Disruption - Winning with new models in packaging*. McKinsey & Company.
- Mikkonen, K. S. (2013). Recent Studies on Hemicellulose-Based Blends, Composites and Nanocomposites. In T. S, V. P, & M. A, *Advances in Natural Polymers. Advanced Structured Materials, vol 18* (pp. 313-336). Berlin: Springer. doi:10.1007/978-3-642-20940-6_9
- Reeve, D. W. (1996). Introduction to the Principles and Practice of Pulp Bleaching. In D. W. Carlton, & D. W. Reeve (Eds.), *Pulp Bleaching - Principles and Practice* (pp. 3-24). Atlanta: TAPPI Press.
- Retulainen, E., Niskanen, K., & Nilsen, N. (1998). Fibers and bonds. In K. Niskanen (Ed.), *Paper Physics* (pp. 55-87). Helsinki: Fapet oy.
- Saito, T., & Isogai, A. (2005). A novel method to improve wet strength of paper. *Tappi Journal*, 4(3), 3-8.
- Sannigrahi, P., & Ragauskas, A. J. (2008). Effects of Two-Stage Dilute Acid Pretreatment on the Structure and Composition of Lignin and Cellulose in Loblolly Pine. *BioEnergy Research*, 205-214. doi:10.1007/s12155-008-9021-y
- Serra, A., González, I., Oliver-Ortega, H., Tarrès, Q., Delgado-Aguilar, M., & Mutjé, P. (2017). Reducing the Amount of Catalyst in TEMPO-Oxidized Cellulose Nanofibers: Effect on Properties and Cost. *Polymers*, 557-570. doi:10.3390/polym9110557

- Sixta, H. (2006). Pulp Properties and Applications. In H. Sixta (Ed.), *Handbook of Pulp* (pp. 1009-1068). Weinheim: Wiley-VCH. doi:10.1002/9783527619887
- Sjöberg, J., Potthast, A., Rosenau, T., Kosma, P., & Sixta, H. (2005). Cross-sectional analysis of the polysaccharide composition in cellulosic fiber materials by enzymatic peeling/high-performance capillary zone electrophoresis. *Biomacromolecules*, 3146-3151. doi:10.1021/bm050471j
- Su, Y., Yang, B., Liu, J., Sun, B., Cao, C., Zou, X., . . . He, Z. (2018). Prospects for Replacement of Some Plastics in Packaging with Lignocellulose Materials: A Brief Review. *Bioresources*, 4550-4576. doi:10.15376/BIORES.13.2.SU
- Teleman, A. (2009). Hemicelluloses and Pectins. In M. Ek, G. Gellerstedt, & G. Henriksson (Eds.), *Pulp and Paper Chemistry and Technology* (Vol. 1). Berlin: de Gruyter. Retrieved from <https://app.knovel.com/hotlink/toc/id:kpPPCTWCW5/pulp-paper-chemistry/pulp-paper-chemistry>
- Teleman, A., Harjunpää, V., Tenkanen, M., Buchert, J., Hausalo, T., Drakenberg, T., & Vuorinen, T. (1995). Characterization of β -deoxy-beta-L-threo-hex-4-enopyranosyluronic acid attached to xylan in pine kraft pulp and pulping liquor by ¹H and ¹³C NMR spectroscopy. *Carbohydrate Research*, 55-71. doi:10.1016/0008-6215(95)96873-m
- Terrett, O. M., & Dupree, P. (2019). Covalent interactions between lignin and hemicelluloses in plant secondary cell walls. *Current Opinion in Biotechnology*, 97-104. doi:10.1016/j.copbio.2018.10.010
- Theander, O., & Westerlund, E. (1986). Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber. *Journal of Agricultural and Food Chemistry*, 330-336. doi:10.1021/jf00068a045
- United Nations. (2019). *World Population Prospects 2019*. New York: United Nations.
- van Zandvoort, I., Wang, Y., Rasrendra, C. B., van Eck, E. R., Bruijmimcx, P. C., Heeres, H. J., & Weckhuysen, B. M. (2013). Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions. *ChemSusChem*, 1745-1758. doi:10.1002/cssc.201300332
- Wang, J., Gardner, D. J., Stark, N. M., Bousfield, D. W., Tajvidi, M., & Cai, Z. (2018). Moisture and Oxygen Barrier Properties of Cellulose Nanomaterial-based Films. *ACS Sustainable Chemistry & Engineering*, 49-70. doi:10.1021/acssuschemeng.7b03523
- Wen, J., Yin, Y., Peng, X., & Zhang, S. (2018). Using H₂O₂ to selectively oxidize recyclable cellulose yarn with high carboxyl content. *Cellulose*. doi:10.1007/s10570-018-2217-1

- Yllner, S., & Enström, B. (1956). Studies of the adsorption of xylan on cellulose fibers during the sulphate cook. Part 1. *Svensk Papperstidning*, 229-232.
- Yllner, S., & Enström, B. (1957). Studies of the adsorption of xylan on cellulose fibers during the sulphate cook. Part 2. *Svensk Papperstidning*, 549-554.
- Zhao, H., & Heindel, N. D. (1990). Determination of degree of substitution of formyl groups in polyaldehyde dextran by the hydroxylamine hydrochloride method. *Pharmaceutical research*, 8(3). doi:10.1023/A:1015866104055

