THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Oxidation of Kraft Pulp Fibres

Hydrogen Peroxide Oxidation under Acidic Conditions and its Influence on the Properties of Pulp

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Department of Chemistry and Chemical Engineering
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Abstract

An increase in the use of bio-based products, combined with a decrease in the use of fossil-based products, is important for fulfilling the demands of a growing population in a sustainable manner. Moreover, reducing the usage of single-use plastics is vital in combating the plastic pollution that is afflicting our environment. A partial solution to these problems is to replace plastic products with products based on cellulose fibres. Their hydrophilic nature, however, makes utilization of fibre-based materials difficult under wet or moist conditions: the hydrogen bonds that contribute to the majority of the material's strength are broken in wet conditions. The wet strength can be increased through the addition of wet strength agents or mechanical treatments or, alternatively, the carbohydrate fraction of the fibres may be modified to improve their wet strength. One such modification is to introduce carbonyl groups in the carbohydrate fraction through oxidation, which would improve the wet strength by forming inter-fibre hemiacetal bonds. Methods often used on a laboratory scale to introduce carbonyl groups in the carbohydrate structure may, however, have economical or environmental drawbacks. In a kraft pulp mill producing bleached pulps, oxidative chemistry is typically utilized in the bleaching step in which the processes are optimized to remove residual lignin and chromophoric groups. Optimizing the oxidation operation to introduce carbonyl groups to the carbohydrate structure has the potential of producing a kraft pulp with inherent wet strength using the existing infrastructure of the mill, e.g., in the final bleaching step.

The main aim of this work was to investigate the feasibility of using a common bleaching agent, namely hydrogen peroxide, to introduce carbonyl groups into the carbohydrate fraction of kraft pulp. It was found that oxidations carried out under mildly acidic conditions (pH 4, 85 °C) could increase the carbonyl content by a factor of about 4 at a residence time of 90 minutes. Also, the content of transition metal ions in the liquid phase requires to be controlled, which is important in industrial applications where the liquid fraction is recirculated. Oxidation was found to be successful in increasing the wet-web tensile strength (+ 6-23%) and wet tensile strength (+ 134-242%), with a slight reduction (– 4-11%) occurring in the dry tensile strength.

Keywords: Hydrogen peroxide, kraft pulp, oxidation, wet strength, carbonyl groups

List of Publications

Paper I	**Modification of softwood kraft pulp fibres using hydrogen peroxide at acidic conditions** Axel Martinsson, Merima Hasani, Antje Potthast and Hans Theliander *Cellulose,* 2020, 27, 7191-7202.
Paper II	**Hardwood kraft pulp fibre oxidation using acidic hydrogen peroxide** Axel Martinsson, Merima Hasani and Hans Theliander *Nordic Pulp & Paper Research Journal*, 2021, 36(1), 166-176.
Paper III	**The influence of transition metal ions on the oxidation of kraft pulp using hydrogen peroxide under mildly acidic conditions** Axel Martinsson, Merima Hasani and Hans Theliander *(Submitted Manuscript)*
Paper IV	**Physical properties of kraft pulp oxidized by hydrogen peroxide under mildly acidic conditions** Axel Martinsson, Merima Hasani and Hans Theliander *(Submitted Manuscript)*

Contribution Report

Paper I	Main author. Performed the experimental work, apart from fluorescence labelling, subsequent GPC-MALLS analysis and TOC analysis. Wrote the paper and evaluated the results with the support of the co-authors.
Paper II	Main author. Performed the experimental work. Wrote the paper and evaluated the results with the support of the co-authors.
Paper III	Main author. Performed the experimental work, apart from ICP-MS analysis which was carried out by Dr. Stellan Holgersson. Interpreted the results and wrote the paper with the support of the co-authors.
Paper IV	Main author. Performed the experimental work partly together with Charlotte Merup at Södra Innovation. Wrote the paper and evaluated the results with the support of the co-authors.

Results related to this work have also been presented at the following conferences:

Influence of pH on Oxidation of Cellulose Using Hydrogen Peroxide
Axel Martinsson, Merima Hasani and Hans Theliander
15th European Workshop on Lignocellulosics and Pulp,
Aveiro, Portugal, June 2018.
(Poster)

Investigation of Cellulose Oxidation Through Bleaching
Axel Martinsson, Merima Hasani and Hans Theliander
7th AvanCell Conference,
Gothenburg, Sweden, October 2019.
(Oral Presentation)

Oxidation of Kraft Pulp Using Hydrogen Peroxide at Acidic Conditions
Axel Martinsson, Merima Hasani and Hans Theliander
7th International Polysaccharide Conference,
Nantes, France, October 2021.
(Poster)

Södra, Nya Initiativ i Befintliga Processer
Sven Hermansson, Axel Martinsson
Ekmandagarna,
Stockholm, Sweden, January 2022.
(Oral Presentation)

Contents

1 Introduction

The on-going work of reducing the use and dependence on fossil-based resources and replacing these with bio-based resources is important in order to fulfil the needs of a growing population, with an increasing standard of living, in a sustainable manner. The transition to bio-based products is a significant step in reaching the goals of carbon neutrality by 2050, according to the European Green Deal (European Commission, 2019). In addition, fossil-based products such as single-use plastics are also targeted due to the plastic pollution currently afflicting the world: a ban was placed on marketing of single-use plastics, such as drinking straws and cutlery, within the European Union after July 3rd, 2021 (European Commission, 2021). A possible solution in achieving carbon-neutral products and also combating plastic pollution is to replace plastics with products based on cellulose fibres.

The replacement of plastics with cellulose-based materials has attracted significant interest in recent years (Su *et al.*, 2018; Wang *et al.*, 2018). Wood fibres in particular are of interest due to their strength and flexibility, which makes them ideal for many applications, such as packaging. The hydrophilic nature of cellulose fibres is, however, a drawback. The durability of a fibre-web is reduced when wetted: the fibres swell and inter-fibre hydrogen bonds are hydrolysed by the water, resulting in a loss of more than 90% of the web's initial strength (Dunlop-Jones, 1991). The strength can be partially retained either through mechanical treatments prior to the formation of the fibre product or by the addition of additives, known as wet strength agents, during the production process (Bates *et al.*, 1999).

Wet strength is achieved via two main mechanisms: by preventing the fibres from wetting, which protects the inter-fibre bonds, and through the formation of new, covalent bonds (Andersson and Wågberg, 2009). Wetting and subsequent swelling can be prevented by using methods such as internal sizing, where hydrophobic agents are added to resist wetting (Lindström, 2009). Wet strength can also be achieved via mechanical methods such as hot-pressing where, in the presence of lignin, the contact area is increased and covalent bonds between lignin and hemicellulose increase thereafter (Joelsson, 2021). However, the most common way of achieving wet strength is through the addition of wet strength agents, such as wet strength resins. The use of wet strength resins results in a permanent wet strength, since the resins cure and form a network around the fibres; they may even react with hydroxyl or carboxyl groups present in the fibre and thereby create covalent bonds. Finally, resins may also enter the pore structure of the fibres and cause the pores to close up. This will, at the very least, partially hinder water/water vapour from being transported into the structure which, in turn, will reduce swelling of the fibres (Fellers and Norman, 1998). These types of wet strength agents do nevertheless have some drawbacks: the manufacture of polyamide and epoxide-based resins may, for example, be linked to emissions of adsorbable organic halides (AOX) (Bates *et al*., 1999). The recycling of broke or used paper products in which wet strength resins are present becomes complicated, as harsh alkaline or oxidative treatment is then required (Yang and Luettgen, 2020).

Wet strength agents that can achieve a temporary wet strength can be produced from bio-based resources, such as oxidized starches or cellulose. The carbonyl functionalities of the oxidized carbohydrates may form hemiacetal bonds with hydroxyl groups on the fibres and thereby result in a temporary wet strength, because the hemiacetal bonds are not broken as easily as hydrogen bonds. Oxidized carbohydrates with a high carbonyl content may be formed using oxidizers such as sodium metaperiodate (Kim *et al*, 2000) and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (Jaschinski *et al.,* 1999; Saito and Isogai, 2005). Oxidation of cellulose with sodium metaperiodate results in a C2-C3 dialdehyde, whereas TEMPO-oxidation may yield C6 aldehydes. These oxidizers suffer, however, from certain drawbacks: sodium metaperiodate is harmful to the environmental and TEMPO is expensive, making it unsuitable for large-scale production (Serra *et al*., 2017).

A modern kraft pulp mill producing bleached pulp generally uses oxidizers such as chlorine dioxide, hydrogen peroxide and ozone. The bleaching operations are optimized in order to remove chromophoric groups and residual lignin while minimizing reactions with the carbohydrate fraction, as this would lead to degradation and thereby yield loss. However, altering the process conditions could allow the bleaching agents to be used to oxidize the carbohydrate fraction and thereby create a carbonyl rich pulp with inherent wet strength. One candidate for such an oxidation is hydrogen peroxide: it is rather non-specific and known to produce several reactive species, which may be beneficial where reactions with carbohydrates are of interest. The main decomposition products of hydrogen peroxide oxidation are water and oxygen, making hydrogen peroxide an environmentally friendly option. Hydrogen peroxide is used when bleaching pulps at alkaline pH, where the main bleaching effect is derived from the hydroperoxide ion. However, hydroxyl radicals are also known to form, for example, from reactions with transition metal ions (Wuorimaa, 2006) and are capable of oxidizing the C2 and C3 hydroxyl groups of cellulose into ketones (Gierer, 1997). Optimizing this reaction, while minimizing the effects of carbohydrate degradation, would provide a basis for the potential development of a large-scale production of carbonyl rich pulp.

1.1 Objectives

The main objectives of this work were to investigate the possibility of introducing carbonyl groups into the carbohydrate fraction of fully-bleached kraft pulps using a common bleaching agent, namely hydrogen peroxide, and to study the effects of the oxidation on the composition of the pulp and the properties of the fibres. The effects of the hydrogen peroxide charge and the recirculation of oxidant were investigated in order to approach industrial conditions.

Both softwood and hardwood pulps were studied in order to investigate potential differences in the oxidation and its effect on the different compositions of the pulps. A study of the key physical properties, such as wet and dry tensile strength, wet web tensile strength and water retention value, was carried out to investigate the influence that the oxidation had on the properties of the sheet produced.

2 From Wood to Kraft Pulp

2.1 The Structure of Wood

The properties of products based on wood fibre depend largely on the type of wood used. The cells of gymnosperms and angiosperms, softwood and hardwood, have different compositions and their fibre morphology is quite dissimilar. Tracheids, the main type of fibre in softwood (89-95% of wood volume) (Retulainen *et al.*, 1998), have a high aspect ratio and are aligned in the longitudinal direction of the tree. In the radial direction, there are ray cells, which have the purpose of storing and transporting nutrients. Hardwoods, on the other hand, have a more complex structure: the mechanical strength comes from fibre tracheids and libriform cells, the volume of which is about 37-65% (Retulainen *et al.*, 1998). The fibre morphology of softwood and hardwood tracheids also differs, e.g. the former have an average length of 3.1-3.4 mm (Swedish softwood species) whereas that of the latter is 0.4-1.3 mm (Swedish hardwood species) (Daniel, 2009).

The fibres are organized in a matrix in the wood according to Figure 1, where the lignin-rich middle lamella that surrounds the fibres acts as a glue between them. The fibres themselves are comprised of multiple layers consisting of cellulose microfibrils within a hemicellulose and lignin matrix. The thin primary wall is comprised of cellulose microfibrils of random orientation, whereas the secondary layer consists of 2-3 layers of directionally-oriented cellulose microfibrils, Figure 1.

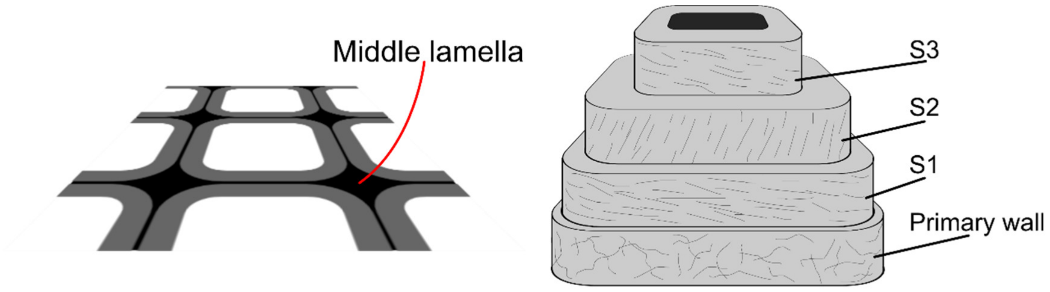

Figure 1. Matrix of fibres showing the location of the middle lamella (left). Structure of the cell wall of a wood fibre (right).

2.2 The Composition of Wood

2.2.1 Cellulose

The main component of the cell wall of a wood fibre is cellulose, which is a linear homopolymer comprised of D-glucopyranose units linked by β(1→4) glycosidic bonds. Native cellulose may have a degree of polymerisation as high as 15000 (Henriksson and Lennholm, 2009). The structure of the cellulose chain gives rise to intra-chain hydrogen bonding, according to Figure 2, and result in a very rigid and strong structure.

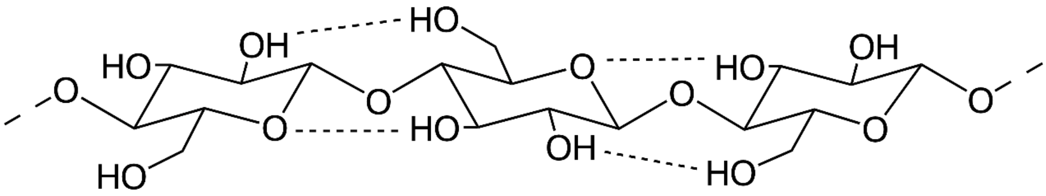

Figure 2. Intra-chain hydrogen bonding in a cellulose chain.

The two ends of the cellulose chain exhibit contrasting properties. The end with a free C1 hydroxyl group can open into an aldehyde form, as shown in Figure 3: its aldehyde functionality means it has reducing properties and is therefore labelled the reducing end. The opposite end, on the other hand, has a free C4 hydroxyl group and has no such properties (Klemm *et al.*, 1998).

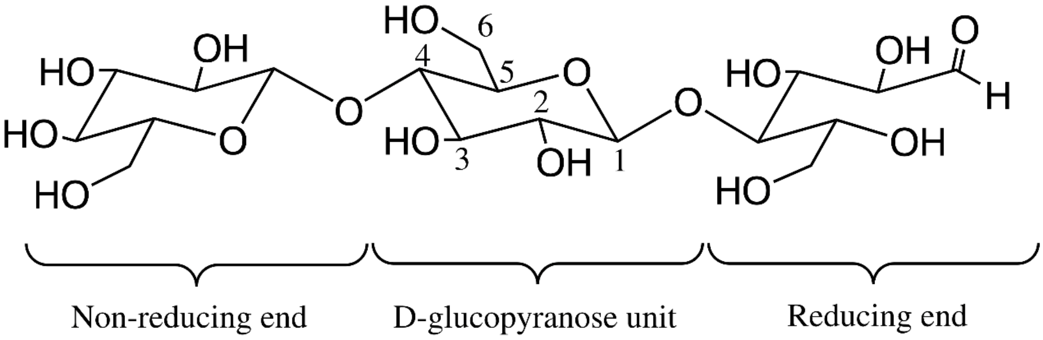

Figure 3. A cellulose chain comprised of a non-reducing end, a D-glucopyranose unit and a reducing end.

The cellulose chains are ordered further in sheets, where the individual chains are linked through additional hydrogen bonding. These sheets are, in turn, stacked into fibrillar elements held together mainly by van der Waals forces (Henriksson and Lennholm, 2009).

2.2.2 Hemicellulose

Hemicellulose and cellulose are both polysaccharides. Hemicelluloses are, however, generally heteropolymers consisting of varying pentoses (such as arabinose and xylose) and hexoses (such as galactose, glucose and mannose). In addition, hydroxyl groups on the backbone of both are substituted, and small side chains and side groups are present along the chain. In contrast to cellulose, hemicelluloses have a relative short chain length with a DP that is normally below 200 (Teleman, 2009). Hemicelluloses are found in the cell wall, in the matrix between the cellulose fibrils and lignin, and are believed to contribute to the mechanical properties of the cell wall (Terrett and Dupree, 2019).

Hemicelluloses are generally amorphous, with the consequence that they usually react rapidly with, for example, cooking chemicals. The hemicelluloses most prevalent in wood are mannans and xylans, the structures and amounts of which differ depending on whether the source is hardwood or softwood. On average, hardwood contains more hemicelluloses (30-35% of weight) than softwood (25-30% of weight). An example of a structural difference in the hemicelluloses present in the two types of wood is that both hardwood and softwood xylan consists of a $\beta(1\rightarrow4)$ linked xylose units, however, softwood xylan has a higher degree of substitution of 4-O-methyl-D-Glucuronic acid side groups. Moreover, softwood xylan also has arabinose side groups whilst hardwood xylan has acetyl side groups.

2.2.3 Lignin

Lignin consists of a random 3D-network of monomers, monolignlos (see Figure 4), linked together through a variety of carbon-carbon and ether bonds. The concentration of the various monolignols and the amount of lignin present vary, depending on the type of wood. The lignin content is roughly 15-35% of softwood and 20% of hardwood (Henriksson, 2009). Although the highest concentration of lignin is found in the middle lamella, where it effectively glues the fibres together, the majority is located within the fibre wall. Lignin also contributes to the strength of wood as well as providing hydrophobic and antimicrobial properties.

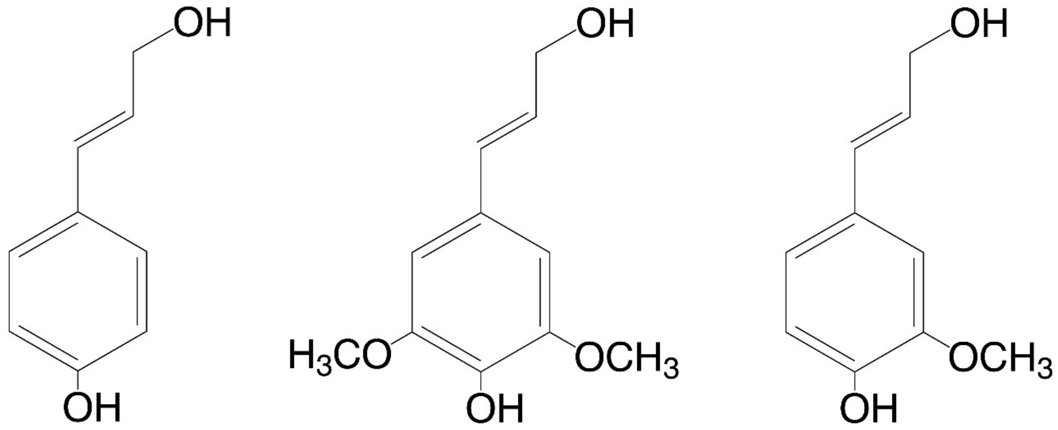

Figure 4. Molecular structure of the main monolignols. Left to right: p-coumaryl alcohol, sinapyl alcohol and coniferyl alcohol.

2.3 Pulping and Bleaching

Pulping is carried out in order to liberate the fibres from the wood matrix. This can be achieved through mechanical or chemical treatments, or a combination of both. Mechanical treatments rely on the heat produced and the mechanical shear forces to separate the fibres from each other whilst in chemical pulping, the lignin is solubilized using cooking chemicals and the fibres are thereby liberated. In contrast to mechanical pulping, chemical pulping removes lignin from the pulp, with the consequence that the yield of unbleached chemical pulps is between 45-56% (Brännvall, 2009) but that of mechanical pulps may reach 97-98% (Sundholm, 1999).

The pulping process utilized most commonly worldwide is the kraft process, which utilizes a cooking liquor comprised of hydrosulphide and hydroxide ions at temperatures ranging from 140 to 170 °C. At these conditions, however, it is not only lignin that is affected: hemicelluloses are also solubilized, to some extent, during the cook. Glucomannan undergoes degradation at temperatures as low as around 90-120 °C and is solubilized; a noticeable solubilization of xylan starts at around 120 °C, with rapid dissolution above 140 °C (Wigell *et al*, 2007). Such dissolution of hemicelluloses does, nevertheless, retard during the later stages of the cook. As xylan resists further degradation in the alkaline solution, part of the xylan may later be adsorbed onto the fibre surface through non-electrostatic attractions, such as van der Waals forces (Yllner and Enström, 1956). The degradation reactions of carbohydrates become increasingly severe at longer cooking times, higher temperatures and with increasing alkalinity. Degradation reactions originating from the reducing end of the carbohydrate chains, known as peeling reactions, cause an end-wise degradation where the end group is cleaved off, thereby forming a new reducing end. This will continue until a stable, metasaccharinic acid end group is formed (Gellerstedt, 2009). Additionally, degradation reactions such as alkaline hydrolysis may also contribute to the degradation of carbohydrates through chain scissioning, which also produces a new reducing end group and, as a consequence, secondary peeling will occur. These reactions mean that it is often more favourable to remove residual lignin through operations known as bleaching, where the selectivity is higher than for the later stages of the kraft cook.

It is necessary to bleach a pulp if it is to be used in products that require a high level of purity, such as board for packaging food, or in products that require a high degree of brightness, such as printing paper. Removing the lignin fractions in the pulp or the chromophoric groups present in the carbohydrate gives a brighter pulp. The bleaching process is often categorized as being either lignin preserving or lignin removing. The former is applied to mechanical pulps, which are not delignified during pulping, and the latter is typically applied to chemical pulps to remove the lignin that remains after the cook. Bleaching is usually performed in several stages, using a variety of different bleaching agents, in order for the process to be efficient and to minimize carbohydrate reactions. This increases the selectivity that is possible, thereby reducing carbohydrate degradation.

2.3.1 Hydrogen Peroxide Bleaching

Chlorine-based bleaching agents of historical importance, such as chlorine and hypochlorite, were finally phased out during the 80s and 90s for environmental reasons, which allowed more environmentally friendly bleaching agents, such chlorine dioxide, ozone and hydrogen peroxide, to take their place. Hydrogen peroxide is a commonly-used bleaching agent in modern bleaching sequences, in both elemental chlorine free (ECF) and totally chlorine free (TCF) sequences, and has the advantage of being able to bleach residual lignin efficiently (Suhr *et al.*, 2015).

Hydrogen peroxide is normally used either as an alkaline peroxide stage (P), as the final stage of a sequence, or an alkaline extraction stage, reinforced with oxygen and hydrogen peroxide (EOP), usually in-between chlorine dioxide stages for bleaching chemical pulps or to reinforce an oxygen stage (OP) (Suhr *et al.*, 2015). The decomposition of hydrogen peroxide is catalysed by transition metal ions such as iron, manganese and copper, so a chelating (Q) or acid wash (A) stage usually precedes the peroxide stage in order to minimize both the consumption of hydrogen peroxide and the formation of unwanted hydroxyl radicals. A P-stage is commonly carried out at a temperature of 90 °C and a pH of 10.5-11.5, with residence times of up to 4 hours (Germgård, 2009). At these conditions, the main bleaching potential of the hydrogen peroxide is attributed to the hydroperoxide ion, formed from the disassociation of hydrogen peroxide at alkaline conditions according to Reaction 1.

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^- \qquad (1)$$

The presence of transition metal ions would lead to the formation of radicals according to Reactions 2 and 3 (Lachenal, 1996). A high concentration of transition metal ions would lead not only to an increase in the consumption of hydrogen peroxide but also a reduction in bleaching efficiency: the radicals formed are not as efficient as the hydroperoxide ion resulting from the disassociation of hydrogen peroxide.

$$H_2O_2 + M^{n+} \rightarrow \; M^{(n+1)+} \bullet OH + \; OH^- \tag{2}$$

$$HOO^- + \; M^{(n+1)+} \rightarrow M^{n+} + \; \bullet O_2{}^- + \; H^+ \tag{3}$$

2.4 Oxidation of Holocellulose Using Hydrogen Peroxide

The oxidation of holocellulose may occur via several reaction paths. It is classified as either the oxidation of reducing-end groups, hydroxyl oxidation, glycol-cleavage oxidation or oxidation of the anomeric carbon (Lai, 2001). The oxidation of carbohydrate structures by hydrogen peroxide under alkaline conditions is associated mainly with the hydroxyl radical, which may form through, for example, the decomposition, catalysed by transition metal ions, as mentioned previously. The most prominent effect of hydroxyl radicals under these conditions is the formation of carbonyl groups, mainly C2 or C3 ketones, according to the reaction illustrated in Figure 5 (Gierer, 1997). Under acidic oxygenated conditions, an attack on the C2 position may also cause depolymerisation, as shown in Figure 6 (Chirat and Lachenal, 1997). However, subjecting cellulose to oxidation catalysed by transition metal ions under acidic conditions, using hydrogen peroxide, has been investigated; the results showed an increase in the contents of both carbonyl and carboxyl (Hellström *et al.*, 2014).

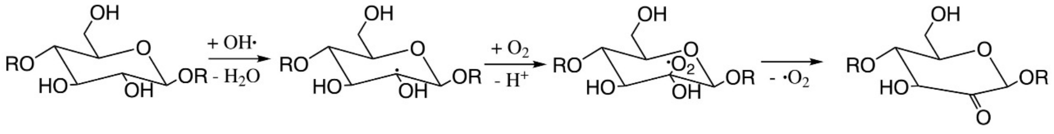

Figure 5. Introduction of a C2 ketone caused by a hydroxyl radical attack.

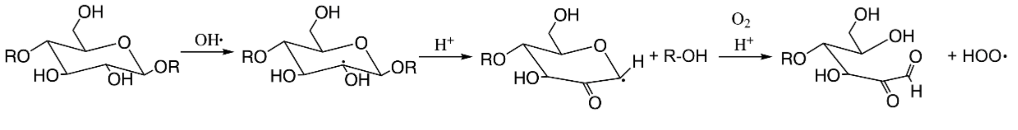

Figure 6. Depolymerisation of cellulose caused by an attack at the C2 position.

The hydroperoxide ion is not usually associated with the degradation of carbohydrates. In the presence of 2-3 diketo structures, however, the hydroperoxide ion is capable of glycol cleavage oxidation thereby producing a dicarboxyl, see Figure 7 (Gierer, 1986).

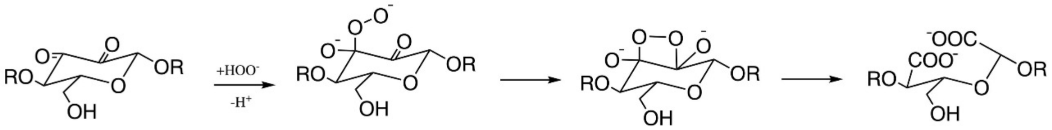

Figure 7. Reaction for the glycol cleavage of 2,3-diketocellulose by the hydroperoxide ion.

2.5 Wet Strength

The strength of a paper in the dry state is a result of several factors, including the properties of the fibres (strength, length, stiffness, etc.), specific bond strength (SBS) and relative bonded area (RBA) (Lindström *et al.*, 2005). It is also strongly dependent on the moisture content of the fibre structure, from which it can be assumed that hydrogen bonding plays a key role in the development of strength in a dry sheet. Cellulose fibres are hygroscopic, which means that the moisture content and temperature of the surrounding air also play important roles. Two main principles are employed for maintaining strength at increasingly moist conditions: the protection of inter-fibre bonds and the formation of covalent inter-fibre bonds (Andreasson and Wågberg, 2009). Strategies that can be deployed to achieve wet strength include the addition of wet strength resins, such as urea formaldehyde resins, melamine formaldehyde resins or polyamide-epichlorohydrin resins. Alternatively, the addition of oxidized carbohydrates (such as dialdehyde starch) or the oxidation of the carbohydrate structure of the pulp itself may be utilized (Jaschinski *et* al.,1999; Saito and Isogai, 2005). The aldehyde groups in the oxidized carbohydrates are hydrated into the diol form, which may then react further with the hydroxyl group on the fibre, forming a hemiacetal, or continue to react into an acetal (Lindström *et al.*, 2005).

The use of the above-mentioned resins leads to the paper having a permanent wet strength as the resins cure. This also means, however, that such fibre materials face a number of problems when being recycled because they must first undergo harsh, alkaline or oxidative treatments (Yang and Luettgen, 2020). Oxidized carbohydrates, on the other hand, result in a temporary wet strength as the hemiacetal bonds that are formed may undergo hydrolysis after extended (>2 h) soaking or alkaline conditions (Espy, 1995).

In addition to the strength of a dried paper sheet subjected to water, the strength of the wet fibre web during the formation of the paper is also of interest: this property influences, for example, the runnability of pulp on a paper machine (Lindqvist, 2013). The strength of a wet fibre web at dry contents between 30 and 50% is believed to be dominated by entanglement friction and capillary forces, whereas hydrogen bonding becomes increasingly important at dry contents above 50% (van de Ven, 2008).

3 Quantification of the Oxidation of Kraft Pulp

Reliable quantification methods are of the utmost importance in studies of the oxidation of kraft pulp. Analysis of the oxidized functionalities in pulp is nevertheless faced with several challenges. The morphological structure of the fibres and the cell wall layers complicate the transport of reagents that are necessary for indirect measurement methods where the oxidized functionalities are modified in order to be quantified. Further on in the process, i.e. during delignification, the cellulose structure is partly aggregated due to microfibril coalescence, which impairs its overall accessibility (Pönni, 2014). Finally, the limited solubility of the material aggravates quantification in a dissolved state. The quantification of oxidized functionalities is therefore complicated, especially at low degrees of oxidation (Potthast *et al.*, 2006). In addition, the reactivity of the carbonyl groups themselves further complicates such analysis because these groups may exist as masked forms, e.g. hydrated forms, hemiacetals or hemialdals (Kim *et al.*, 2000). Several different methods were evaluated and tested for the quantification of oxidized functionalities in the studies that led to the articles discussed in this thesis. Although not all of them were used in published studies, the methods that were evaluated are nevertheless described and discussed hereafter.

3.1 Quantification of Carbonyl Groups

3.1.1 Copper Number

The reducing properties of cellulose have long been used in the identification of carbonyl functionalities (Clifford and Fargher, 1922). The copper number is defined as the number of grams of metallic copper, in the form of copper(I) oxide, that can be reduced from a copper(II) sulphate solution by 100 g of pulp fibres, according to TAPPI T430.

The copper number may be interpreted as a measurement of the content of carbonyl groups in oxidized carbohydrates, lignin or sugars, all of which possess reducing properties (SCAN-C 22:66, TAPPI T430 om-94). The copper number has been found to have a linear correlation with the carbonyl content of pulp, as measured with fluorescence labelling. Knowledge of the underlying mechanism involved in the reduction of copper is, however, poor (Röhrling *et al.,* 2002b). Ultimately, the copper number cannot be interpreted as a quantification of carbonyl groups because they are not alone in exhibiting reducing properties in pulp.

In the procedure (TAPPI T430 om-94) a boiling mixture, containing a carbonate-bicarbonate solution and a solution of copper sulphate, is added to a sample of dried and finely ground fibres. The resulting suspension is heated for an extended time by means of an oil bath, after which it is filtered and washed thoroughly. This washed pulp is added to a phosphomolybdic acid solution and mixed, before being filtered and washed once again. The filtrate is titrated using potassium permanganate, from which the copper number can be calculated. A simplification of this method has been evaluated by Chai *et al.* (2007) whereby the consumption of copper sulphate is instead measured spectrophotometrically, thus eliminating the time-consuming washing steps and titration.

3.1.2 Oxime Method

The number of carbonyl groups may be quantified through reaction with hydroxylamine hydrochloride, which forms an oxime upon reaction with carbonyl groups and results in the release of hydrochloric acid at a ratio of 1 mol of hydrochloric acid per mol of carbonyl groups (Nypelö *et al.*, 2021). A pulp suspension and a hydroxylamine hydrochloride solution are both adjusted to a set pH, mixed and allowed to react. This results in a lowering of the pH due to the release of hydrochloric acid, and the number of carbonyl groups can be calculated from titration with sodium hydroxide back to the initial pH. Alternatively, the oxime method may be carried out in a buffer, at a fixed pH. The nitrogen content of the sample can be analysed thereafter through atomic absorption spectroscopy, thus yielding the number of oximes formed (Kim *et al.*, 2000). The former alternative is the one utilized in the studies related to this thesis, and is based on the procedure of Zhao and Heindel (1991). The oxime method is one of the more commonly used methods for quantifying carbonyl groups. However, hydroxylamine hydrochloride is suspected of causing cancer according to the European Chemicals Agency, and should therefore be used with caution (European Chemicals Agency, 2021).

3.1.3 Fluorescence Labelling with CCOA

Carbazole-9-carboxylic acid [2-(2-aminooxyethoxy)ethoxy]amide (CCOA) can be utilised as a fluorescence marker for carbonyl groups. The fluorescence labelled sample is dissolved in N-N-dimethylacetamide/lithium chloride (DMAc/LiCl) and analysed with gel permeation chromatography, using DMAc/LiCl as eluents and fluorescence, multiangle laser light scattering (MALLS) and refractive index (RI) detection (Röhrling *et al.,* 2002a; Röhrling *et al.,* 2002b; Potthast *et al.,* 2003). One major benefit of this method is that profiles of carbonyl groups can be obtained by overlaying the degree of oxidation with the molecular weight distribution, something that is not possible to achieve with the other methods described here. It allows changes caused by oxidation to be evaluated more precisely.

3.1.4 Fourier Transform Infrared Spectrometry (FTIR)

Fourier transform infrared spectrometry using attenuated total reflectance measurements has been employed to analyse changes in chemical structure following oxidation with sodium metaperiodate (Kim *et al.,* 2000; López Durán *et al*., 2016). Two bands, around 880 cm^{-1} and 1740 cm^{-1}, are usually assigned as the signal for the carbonyl group and the hemiacetals or hydrated forms (Kim *et al.,* 2000). In the studies of Kim *et al.* (2000) the band at 1740 cm^{-1} forms a distinct peak once a degree of oxidation of 12% has been reached, whereas the more diffuse hemiacetal band start to appear at degrees of oxidation exceeding 20%. Identification of changes in the chemical structure of pulp with acceptable precision may therefore only be possible at relatively high degrees of oxidation. Furthermore, obtaining quantitative data requires the results obtained from FTIR analysis to be correlated to those from another method, e.g. the oxime method (Simon *et al*., 2022) or fluorescence labelling with GPC analysis.

3.1.5 Sodium Chlorite Oxidation

Sodium chlorite oxidation at pH 4-5 may be used to quantify aldehyde groups (Davidson and Nevell, 1955; Saito and Isogai 2004). Sodium chlorite selectively oxidises aldehyde groups into carboxyl groups, so the amount of aldehyde groups can be quantified through measurement of the number of carboxyl groups pre and post sodium chlorite oxidation. The method may also be employed to differentiate between ketones and aldehydes. Measurements of carbonyl groups made using the oxime method or CCOA labelling, for example, give results for both aldehydes and ketones; the difference between the measurements of the aldehyde group using sodium chlorite and the carbonyl group should therefore yield the number of ketones.

3.2 Quantification of Carboxyl Groups

3.2.1 Conductometric Titration

The number of acidic groups present in pulps can be determined through conductometric titration for example, according to SCAN-CM 65:02 (2002). Prior to titration the acidic groups are converted to the proton-form through treatment with hydrochloric acid, after which the pulp is washed thoroughly with deionised water. It is then titrated with sodium hydroxide in a weak sodium chloride solution, with the conductivity being recorded after each addition. Three distinct phases can be observed during titration, as shown in Figure 8. For pulps containing sulphonic acid groups, such as sulphite pulp or chemi-thermomechanical pulp (CTMP), the first phase is the titration of these strong acidic groups. In kraft pulps, the first phase is the neutralisation of protons liberated by the addition of sodium chloride. The second, near horizontal, phase is from the neutralisation of carboxylic groups, where the conductivity remains basically unchanged due to the added sodium ions mainly entering the fibre wall (Katz *et al.*, 1984). The third and final phase is an increase in conductivity resulting from the accumulation of sodium ions in the solution. The total content of acidic groups can be calculated from the amount of titrant consumed at the intersection between the second and third phases and the mass of the oven-dried sample.

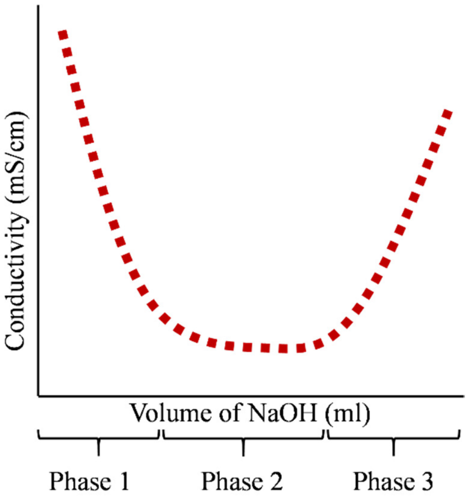

Figure 8. Schematic illustration of a conductivity titration graph showing the three phases.

3.2.2 Potentiometric Titration

Potentiometric titration, like conductometric titration, may also be employed to quantify acidic groups (Räsänen *et al.*, 2001; Fras *et al.*, 2005). However, contrary to conductometric titration, no differentiation between strong and weak acidic groups can be made due to insufficient separation of the dissociation constant of the two (Katz *et al.*, 1984). The pulp sample is converted into its protonated form by treating it with hydrochloric acid before being washed thoroughly and placed in a sodium chloride solution in order to control the ionic strength. The sample is then titrated using dilute sodium hydroxide in sodium chloride (Barbosa *et al.*, 2013); the total number of acidic groups is calculated from the amount of titrant used at the equivalence point and the mass of the oven-dried sample.

3.2.3 Methylene Blue Adsorption

The adsorption of methylene blue dye on cellulosic substrates has long been used to detect the presence of acidic groups in cellulose (Clibbens and Geake, 1926). The conditions for this adsorption, in terms of pH, anion content and concentration of methylene blue, are critical in obtaining accurate results, as investigated by Davidson (1948). Davidson also examined adsorption by hydroxyl groups which, at higher concentrations of methylene blue, is significant. Adsorption by hydroxyl groups is negligible for oxidized celluloses with a high carboxyl content but for unmodified cotton cellulose, for example, it may contribute partially to the overall adsorption of methylene blue (Davidson, 1948). Fardim *et al.* (2002) concluded that adsorption of methylene blue gave results similar to those obtained from conductometric titrations.

A sample of dried pulp is placed in a solution containing methylene blue in a barbital or phosphate buffer at pH 7.8. The size of the sample is adjusted to achieve a 50% adsorption of the methylene blue available. The suspension is covered and left in the dark for a time ranging between 1 and 20 hours, after which it is filtered; the filtrate is then analysed using UV-visible spectroscopy at 664 nm. The absorbance is correlated to the concentration of methylene blue using a standard curve; the content of anionic group is calculated from the mass of the oven-dry sample and the amount of methylene blue consumed (Fardim *et al.*, 2002; Wernersson Brodin and Theliander, 2012).

3.3 Discussion

Ideally, all methods for quantifying oxidized functionalities should be conducted on samples in the dissolved state as this would eliminate potential issues related to the morphological structure of the fibre and the accessibility of the oxidized groups. This is often difficult, due not only to the limited solubility of the material but also to the potential degradation that can occur during the dissolution process in some solvents.

The quantification of carbonyl groups was, of course, of the utmost importance to this work, which had the overall aim of introducing carbonyl groups to the carbohydrate fraction of kraft pulp. In the initial experiments, the copper number method was evaluated due to its long and relatively common use in the industry. Its main drawback is, however, that it does not quantify the number of carbonyl groups directly: rather, it is an index of the overall reducing power of the pulp, expressed by the weight of reduced copper. This makes it difficult to compare the results with those obtained by other methods. Although FT-IR spectroscopy was used to investigate dried pulp samples, the low degree of oxidation of the samples meant that no usable data could be secured, so the oxime method was evaluated instead. In the first study, the results from the oxime methods were compared to GPC (gel permeation chromatography) measurements of the CCOA-labelled samples; the similar trends and absolute values that were obtained indicated that the accessibility of the carbonyl groups did not pose a problem for the oxime method. Furthermore, the requirement that the sample must be dissolved in DMAC-LiCl is a drawback of the fluorescence labelling method because softwood kraft pulps of high degrees of polymerisation are difficult to dissolve in this system (Sjöholm *et al.*, 1997). Taking all these factors into consideration, the decision was taken to employ the oxime method for measuring carbonyl groups in further studies.

The use of sodium chlorite oxidation for differentiating between aldehyde and ketone groups was utilised in the second paper. However, this method relies on making measurements of carboxyl and carbonyl groups using two methods: using potentiometric or conductometric titration both before and after sodium chlorite oxidation, and using the oxime method or any other suitable carbonyl measurement. This may lead to less reliable absolute values, since results are used from two methods that are based on different principles: the trends obtained could still be utilised, nonetheless.

Acidic groups were quantified initially by methylene blue adsorption. The method does, however, suffer from drawbacks such as the possible influence of hydroxyl groups on the results when analysing pulps with lower contents of acidic groups, and the light sensitivity of methylene blue. Potentiometric titration was therefore chosen as the method for quantifying acidic groups, but this was later replaced in favour of conductometric titration due to it being an accepted industry standard.

The most sensitive methods currently available for analysing oxidized functionalities are fluorescence labelling methods. Analysis is carried out in a dissolved state, thereby eliminating issues related to the accessibility of oxidized functionalities. Fluorescence labelling is also capable of yielding carbonyl profiles as a function of the molecular weight distribution, which is not possible using any of the other analytical methods mentioned previously. On the other hand, the method is time-consuming and labour-intensive, making it more suitable for research rather than industrial purposes. The best method available for measuring carbonyl groups in samples in which complete dissolution is impossible is therefore the oxime method: despite being time-consuming, it provides an accurate measure of the number of carbonyl groups present. Conductometric titration is likely the best option for carboxyl groups, as it may provide more information than potentiometric titration.

4 Materials and Methods

4.1 Oxidation of Kraft Pulp

4.1.1 Materials

Different batches of fully-bleached, ECF softwood kraft pulp were used in Papers I, III and IV, and one fully-bleached, TCF hardwood kraft pulp was used in Paper II. Glacial acetic acid and sodium acetate were used in the preparation of the buffers in which the oxidation process was carried out. Hydrogen peroxide was added in the form of 30% hydrogen peroxide. Iron(II) acetate, copper(II) acetate monohydrate and manganese(II) acetate tetrahydrate were used to simulate elevated concentrations of the metal ions. All chemicals were purchased from Sigma/Merck and were used as received.

4.1.2 Equipment

The oxidation procedures were carried out in a 500 ml jacketed glass reactor (100 mm in diameter) equipped with a condenser and fitted with baffles. A pitched blade impeller (50 mm in diameter) was used to stir (1000 rpm) the suspension whilst a circulating heating bath with external temperature regulation was used to maintain a constant temperature.

4.1.3 Experimental Conditions

In Paper I, a hydrogen peroxide charge of 200% was used in unbuffered oxidations and oxidations at a constant pH of 4: a pH that was employed in all further investigations. The reaction temperatures investigated were between 65 and 85°C. The same experimental conditions were investigated in Paper II for the oxidation of hardwood pulp. In Paper III, a reaction temperature of 85°C was used and hydrogen peroxide charges of 10, 50 and 200% were investigated. A hydrogen peroxide charge of 50% was used for the further investigation of the effect of recirculation and the elevated concentrations of metal ions. A reaction temperature of 85°C and hydrogen peroxide charges of 50 and 200% were used in Paper IV.

4.1.4 Methodology

Fully bleached kraft pulp was oxidized at a solid to liquid ratio of 1:40. The buffered oxidations were carried out in a 0.1 M acetate buffer at pH 4 with varying charges of hydrogen peroxide (10% to 200% on pulp basis). Once the desired residence time was reached, the reaction was stopped by adding the suspension to 500 ml of cold, deionised water. The suspension was filtered and the filtrate recirculated once, followed by washing with 1000 ml of deionised water. The pulp was then added to 500 ml of deionised water and left for 10 minutes, after which the suspension was filtered and the filtrate recirculated once. Finally, the pulp was washed with an additional 1000 ml of deionised water, the pH of which had been adjusted to 3.5 with sulphuric acid.

In experiments investigating the influence of recirculation, the suspension was filtered immediately after oxidation and the filtrate recirculated once. The filtrate was then weighed and a new batch of pulp was oxidized using the same liquid phase. The mass of the second batch was adjusted in order to maintain the same solid to liquid ratio, as some of the filtrate was lost when separating the pulp. Both batches had the same residence time.

4.2 Cold Caustic Extraction of Xylan

A cold caustic extraction of xylan was carried out according to the procedure described by Janzon *et al.* (2008), using a pulp consistency of 5% and a sodium hydroxide concentration of 10%. The extraction was carried out at room temperature under continuous stirring for 1 hour, after which the suspension was filtrated and the filtrate recirculated once. A three-stage washing sequence was then executed in the order 2% sodium hydroxide (aq.), 5% acetic acid and, finally, hot deionized water.

4.3 Hydrogen Peroxide Titration

The concentration of hydrogen peroxide in the liquid fraction of the oxidation was measured using iodometric titration. A sample of 2 ml, taken from the liquid fraction during the oxidation process, was added to a beaker containing 10 ml of 10% potassium iodide (aq), 10 ml of 20% sulphuric acid (aq), 30 ml of deionised water and three drops of saturated ammonium molybdate. The resulting solution was titrated using 0.1 M sodium thiosulphate (aq), with a starch solution being used as indicator.

4.4 Quantification of Carbonyl Groups

4.4.1 Quantification of Carbonyl Groups Using the Oxime Method

The total number of carbonyl groups was measured using a method based on the study by Zhao and Heindel (1991). A sample of never-dried pulp corresponding to 0.5 g of oven-dry pulp was added to a beaker containing 100 ml of deionised water adjusted to pH 4 and dispersed thoroughly. The suspension was filtered after 10 minutes had passed and the pulp washed with 100 ml of deionised water adjusted to pH 4. The pulp was transferred to a beaker, into which 25 ml of 0.25 M hydroxylamine hydrochloride (aq.) was added, and then placed on a shaking table for 2 hours. The suspension was thereafter filtered and the filtrate was titrated back to pH 4 using 0.01 M sodium hydroxide (aq.) The pulp fraction was washed using deionised water and transferred to an oven at 105 °C; the oven-dry mass of the sample was measured 24 hours later. The total number of carbonyl groups could then be calculated from the volume of titrant required to titrate back to pH 4 and the oven-dry mass of the pulp. All analyses were carried out in duplicate.

4.4.2 Quantification of Carbonyl Groups Using CCOA-labelling

CCOA labelling of carbonyl groups was performed as described by Röhrling *et al.* (2002a). After labelling the samples, dissolution in DMAc/LiCl 9% (w/v) was achieved after a solvent exchange at room temperature. Cellulose analysis was performed with a GPC coupled with MALLS, RI and fluorescence detection, which yields the molecular weight distribution (MWD) in addition to the profiles of the carbonyl groups relative to the MWD.

The GPC system was comprised of a TSP FL2000 fluorescence detector for monitoring the label, a MALLS detector (Wyatt Dawn DSP, Wyatt Inc., Santa Barbara, USA) with a diode laser (λ = 488 nm) and a RI detector (Shodex RI-71). Four serial GPC columns, PL gel-mixed ALS, 20 µm and 7.5 x 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 (Gynotek STH 585) also formed parts of the system.

The operating conditions of the GPC were as follows: 1.00 mL/min flow rate, 100 µL injection volume, 45 min run time, λex = 290 nm and λem = 340 nm for fluorescence detection of the CCOA label. DMAc/LiCl (0.9% w/v) was used as the eluent after filtering through a 0.02 µm filter. The data was evaluated using standard Chromeleon, Astra 4.73 and GRAMS/32 software.

4.5 Quantification of Carboxyl Groups

4.5.1 Potentiometric Titration of Carboxyl Groups

The number of carboxyl groups was quantified using a method based on the work of Barbosa *et al.* (2013). A sample of never-dried pulp corresponding to an oven-dry weight of 500 mg was placed in a beaker containing 60 ml of 0.1 M hydrochloric acid (aq.) and dispersed thoroughly. When 2 hours had lapsed, the suspension was filtered and the filtrate recirculated once, after which the sample was washed with deionised water until the filtrate was neutral. The pulp was then transferred to a 100 ml beaker containing 50 ml of 0.5 M sodium chloride (aq.) and titrated using 0.02 M sodium hydroxide (aq.) in 0.5 M sodium chloride (aq.). Following titration, the suspension was filtered and the sample of pulp washed before being transferred to an oven set to 105 °C and left for 24 hours. The carboxyl content was calculated from the oven-dry mass of the sample and the volume of titrant at the equivalence point. All analyses were performed in duplicate.

4.5.2 Conductometric Titration of Carboxyl Groups

The content of carboxyl groups was measured according to the SCAN-CM 65:02 (1962) standard. 1 g (oven-dry weight) of a never-dried pulp was protonated using 0.1 M hydrochloric acid (aq.) at a consistency of 1% for 15 minutes. The suspension thus produced was filtered and the filtrate recirculated once, after which the pulp was washed thoroughly using deionised water until the conductivity of the filtrate was below 5 µS. The pulp was then transferred to a beaker containing 490 ml of deionised water and 10 ml of 0.05 M sodium chloride (aq.). The suspension was titrated using 0.05 M sodium hydroxide (aq.) in additions of 0.1 ml made 30 seconds apart before being filtered and the resulting pulp washed. The pulp was transferred to an oven at 105 °C for 24 hours, after which its oven-dry weight was measured. Using the amount of sodium hydroxide consumed after the second phase of the titration and the oven-dry mass of the sample, the carboxyl content could be calculated. All analyses were carried out in duplicate.

4.6 Analysis of Carbohydrate Degradation

4.6.1 Gel Permeation Chromatography

The MWD of the pulp was analysed according to the procedure described in Section 4.4.2.

4.6.2 Intrinsic Viscosity Measurements

Measurements of the intrinsic viscosity of pulp dissolved in bis(ethylenediamine)copper(II) hydroxide solution (CED) (aq.) were made according to the SCAN-C 15:62 standard (1962). A sample of air-dried pulp of known dry content and weight was dispersed in 25 ml of deionised water before 25 ml of CED (aq.) was added. After being shaken thoroughly, the sample was conditioned in a water bath at 25

°C for 30 minutes prior to measurement in a capillary viscosimeter. The elution times were measured in triplicate; the average elution time and the concentration of the pulp allowed the intrinsic viscosity to be calculated. The analyses were carried out in duplicate.

4.7 Compositional Analysis of Kraft Pulp

The composition of the pulp samples was determined using the method used by Jedvert *et al.* (2012), which is based on the study of Theander and Westerlund (1986). A 200 mg oven-dry sample of pulp was placed in a 150 ml beaker and subjected to 3 ml of 72% sulphuric acid (aq.), followed by evacuation for 15 minutes. The sample was put in a 30 °C water bath for 1 hour and stirred every twenty minutes. 84 g of deionised water was then added before it was placed in an autoclave at 125 °C for 1 hour. The sample was filtered and the resulting filter cake washed with a small amount of warm deionised water. The filter cake was dried at 105 °C for 24 h and its weight was considered as Klason lignin. The filtrate was diluted with deionised water and filtered using a 0.2 μm filter before being analysed in a Dionex ICS-500 equipped with CarboPac PA1 columns, using NaOH/NaAc (aq) and NaOH (aq) as eluents. Detection was carried out using an electrochemical detector, with Chromeleon 7 Version 7.1.3.2425 as the software. When converting monomeric sugars in the softwood samples into carbohydrates, the molar ratio between mannose and glucose in galactoglucomannan was assumed to be 3.5:1 (Meier, 1958).

4.8 Mass spectrometry of Liquid Phase

Inductively coupled plasma mass spectrometry (ICP-MS) analysis was carried out on the liquid phase from the oxidation of softwood pulp at acidic conditions in order to quantify the amounts of iron, manganese and copper that leach out from the pulp into the liquid phase. A 1 ml sample was diluted to 5 ml using 0.5 M nitric acid (Merck Suprapur) containing an internal standard of 2 ppm scandium and indium. External standards of 0, 2, 20 and 200 ppb were prepared from 10 ppm standards (VHG Labs, CPA Chem.) by dilution, using the same nitric acid. A 1 ml blank solution was added to each standard to compensate for any effects the sample matrix may have. The samples were analysed using a Thermo iCAP Q, ICP-MS. Five replicates were made, from which the concentration was calculated.

4.9 Physical Testing of Kraft Pulp

4.9.1 Sheet Forming

Sheets (160x160 mm) of grammage 370 g/m^2 were produced in order to simulate the drying of an airborne web dryer in a pulp mill producing market pulp. The sheets were produced using a Finnish type hand-sheet former (Lorentzen & Wettre, Sweden), after which the wet sheets were stacked with 3 blotters and an ebonite plate between each sheet. The whole stack was then pressed for 10 minutes at 50 bar after which the blotters were replaced and the pressing procedure repeated. After the second pressing, the sheets were transferred to a drying cupboard, set to 90 °C and 50% relative humidity, for 1 hour. These pulp sheets were used to produce the stock for measuring the water retention value (WRV), Schopper-Riegler, as well as for producing laboratory sheets, see Figure 9.

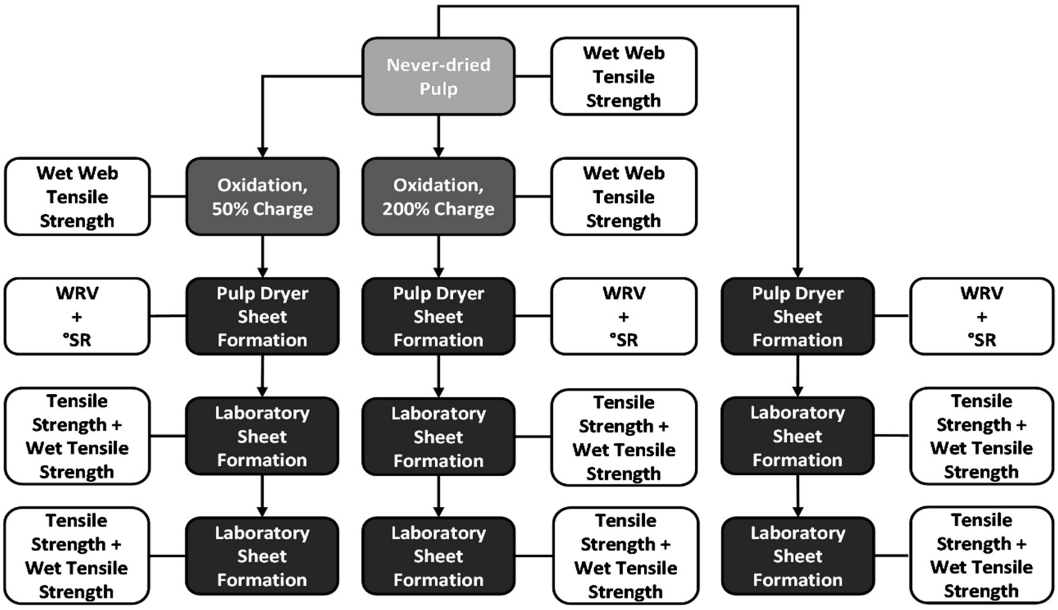

Figure 9. Schematic description of the sheet forming procedure and analyses.

Laboratory sheets, with a target grammage of 60 g/m^2, were produced according to the ISO 5269-1:2005 standard (2005); the pulps were not subjected to beating. The pulp dryer sheets produced previously were defibrillated by a standard pulp disintegrator for 30 000 revolutions, after which the suspension was transferred to a stirred tank and diluted to a concentration corresponding to a grammage of 60 g/m^2. Sheets were formed from the stock using a Finnish type hand-sheet former (Lorentzen & Wettre, Sweden) and the moist sheets were placed between blotters and ebonite plates before being stacked up in a pile. The pile was pressed at 4 bar for 5 minutes; the blotters were then replaced and it was pressed once more at 4 bar for 2 minutes. After the pressing procedure was complete, the sheets were transferred to a conditioned room and air-dried on ebonite plates for 24 hours.

4.9.2 Tensile Strength

The tensile strength of the laboratory sheets was tested according to the ISO 1924-3:2011 (2011) standard. The sheets were cut into strips 15 mm wide before being tested in a Lorentzen & Wettre horizontal tensile tester, run at a separation speed of 100 mm/min. A total of 10 strips were tested for each data point.

4.9.3 Wet Tensile Strength

The wet tensile strength of the laboratory sheets was tested according to the ISO 12625-5:2017 (2017) standard. The sheets were cut into 50 mm wide strips that were tested in a Lorentzen & Wettre horizontal tensile tester, using a soaking time of 15 seconds and a separation speed of 50 mm/min. A total of 10 strips were tested for each data point.

4.9.4 Wet Web Tensile Strength

A stock corresponding to 60 g/m^2 dry sheet grammage was prepared after which sheets were made, using a sheet former, according to ISO 5269-1:2005 (2005). A blotter was used to transfer the moist sheets from the sheet former to a stack that was comprised of a press felt, a plastic sheet, 2 blotters, a moist sheet (on a blotter), 3 blotters, a plastic sheet and a press felt. The stack was pressed at 4 bar for a set amount of time. The pressing time was changed in order to vary the dry content of the sheet: the times investigated were 3, 5 and 8 minutes. Immediately after pressing, the sheet was removed from the stack and placed between two plastic sheets; whilst between these two sheets, 3 strips of width 50 mm were cut and their tensile strength tested using a Lorentzen & Wettre horizontal tensile tester. A total of 9 strips were tested for each pressing time. All of the pieces of the sheet were collected directly after testing, and their moist weight noted, before being placed in an oven at 105 °C for 24 hours. The dry content at the time of testing was then calculated.

4.9.5 Water Retention Value

The WRV was measured according to the ISO 23714:2015 (2015) standard, although a centrifugation time of 15 instead of 30 minutes was employed. A stock with a concentration of 2 g/L was prepared and a test-pad formed by dewatering it through a glass-fibre filter. The test-pad was placed in a test-pad holding unit and transferred to a centrifuge, where it was centrifuged for 15 minutes at 3000 g. Its moist weight was measured before the sample was transferred to an oven at 105 °C for 24 hours. The WRV could be calculated from the moist weight after centrifugation and the oven-dry weight.

4.9.6 Schopper-Riegler

The drainability of the pulp was evaluated using the Schopper-Riegler (SR) method, according to the ISO 5267-1:1999 (2000) standard. A sample of 1000 ml was taken from a stock with a concentration of 2 g/L and poured into the drainage chamber of a Schopper-Riegler apparatus. The SR number is provided by the volume of water drained.

4.10 Fibre Image Analysis of Kraft Pulp Fibres

A sample of never-dried pulp was dispersed thoroughly in deionised water at a concentration of approximately 50 mg/L. The suspension was analysed using a Kajaani FS300 Fiber Analyzer.

4.11 Oxidation of Kraft Pulp at Elevated Concentrations of Metal Ions

Figure 10 is a schematic illustration of the calculation model used to investigate the accumulation of transition metal ions in a closed system that recirculates the liquid fraction after the oxidation of pulp employing hydrogen peroxide under acidic conditions. It was assumed that all the metal ions (copper, iron and manganese) present in the pulp would end up in the liquid fraction. The low pH results in the protonation of carboxyl groups and also prevents insoluble hydroxide salts from forming on the fibres (Eriksson and Gren, 1996). Additionally, a high temperature leads to a reduction in the bonding strength between the metal ions and the fibres (Eriksson and Gren, 1996). Taking all these factors into consideration, sorption to the fibres was assumed to be negligible.

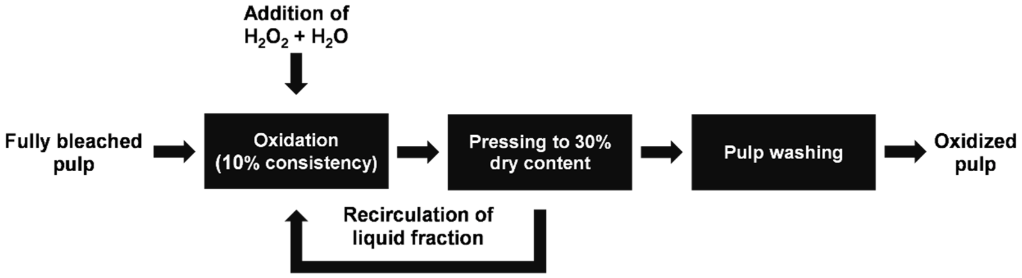

Figure 10. Schematic illustration of the model used for calculation of elevated transition metal ion concentrations. Hydrogen peroxide and water are assumed to be added in order to maintain a constant hydrogen peroxide concentrations and consistency.

5 Results and Discussion

5.1 Introduction of Carbonyl Groups to Softwood and Hardwood Kraft Pulps

5.1.1 Results of the Unbuffered Oxidation of Softwood Kraft Pulp

The aim of the study in Paper I was to investigate the conditions favourable for the formation of carbonyl groups in the carbohydrate fractions of kraft pulp and the implications of the oxidizing treatment on some key properties of the fibres, e.g., chemical composition, degree of polymerisation and content of oxidized functionalities.

Initially, an oxidation carried out at acidic pH was compared to one at alkaline pH: the later conditions that are similar to those employed in the industrial bleaching of kraft pulp, which uses hydrogen peroxide. The starting pH of the alkaline oxidation was adjusted to pH 10 and that of the acidic oxidation was adjusted to pH 4. No buffer was used, so a change in pH could be observed that was due either to the formation of hydroxide ions from the decomposition of the hydrogen peroxide or the formation of organic acids from cellulose hydrolysis (Wen *et al.*, 2018). The pH of the alkaline oxidation was found to increase gradually, resulting in a final pH of about 12 after 90 minutes of oxidation at 85 °C. At the same temperature and residence time, the acidic oxidation resulted in a final pH of 5.2, as shown in Figure 11. The differences in pH observed over time between the two cases suggest that the alkaline and acidic oxidations may have different overall oxidation mechanisms. For example, the equilibrium of the dissociation of hydrogen peroxide into the hydroperoxide ion, Reaction 1, will favour the formation of hydroperoxide ions at alkaline pH, thereby giving different reaction constituents.

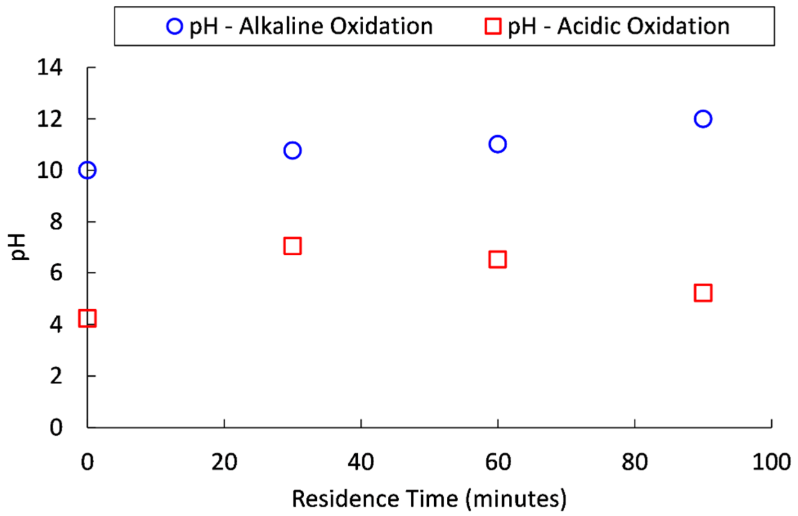

Figure 11.Change in pH over time during the oxidation of softwood pulp under alkaline and acidic conditions.

The oxidized pulp was analysed for carbonyl content using both the oxime method and fluorescence labelling with subsequent GPC analysis. In Figure 12 it can be observed that the acidic conditions enhance the introduction of carbonyl groups significantly: this is in contrast to the alkaline conditions, where the carbonyl content was unchanged. The trends resulting from the two analyses are in good agreement, even though the oxime method gives a higher absolute value. As the oxime method is based on the titration of the acid released during the reaction, the higher content of carbonyl groups observed could be caused by acidic functionalities other than the hydrochloric acid produced from the oxime reaction. The degradation of the carbohydrates, assessed by average molecular mass, was determined by GPC as well as indirectly via intrinsic viscosity measurements. It should be noted that GPC measurements could not be carried out for the reference pulp or the pulp oxidized at acidic conditions for 30 minutes due to incomplete dissolution in the DMAc/LiCl. Nevertheless, as seen in Figure 13, both methods show that alkaline conditions result in a more rapid degradation at short residence times than acidic conditions. At longer residence times, however, acidic conditions result in a lower average molecular weight, which is possibly due to the introduction of carbonyl groups during acidic oxidation: these carbonyl groups could be weak points that cause further degradation. Although the two methods produce similar trends regarding average molecular weight, the absolute values differ. One obvious reason for this is that the viscosity average molecular weight (Mv) is based on a method and theory that differ from the weight average molecular weight (Mw). The carboxyl content, seen in Figure 14, appears more or less unchanged for both the alkaline and acidic conditions. This may be explained by a low formation of C6 aldehydes that could, in turn, be oxidized further into carboxyl groups. It is nevertheless more likely that the predominant oxidation is the formation of C2 or C3 ketones. Another possible explanation is that the introduction of carboxyl groups leads to the increased solubility of the shorter carbohydrate fractions. This would mean that the oxidized carbohydrates either dissolve during oxidation and/or are washed away during the subsequent washing sequence and are thus not detected in the pulp fraction.

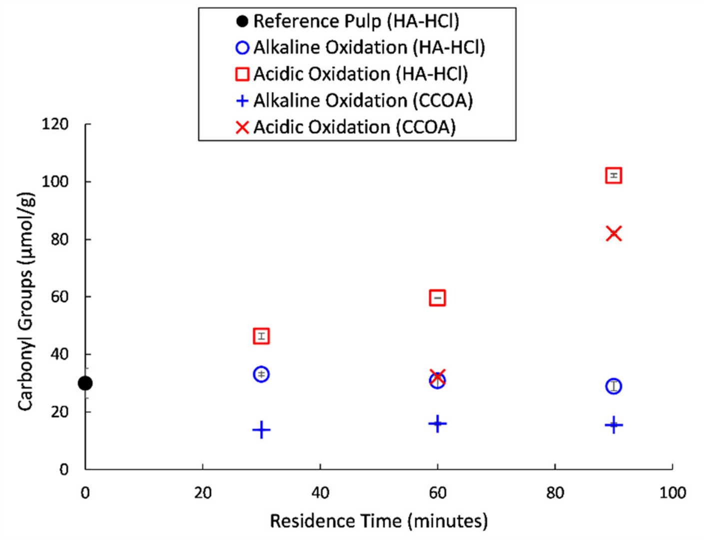

Figure 12. Total number of carbonyl groups as measured by either CCOA labelling with subsequent GPC analysis or the oxime method using hydroxylamine hydrochloride (HA-HCl)

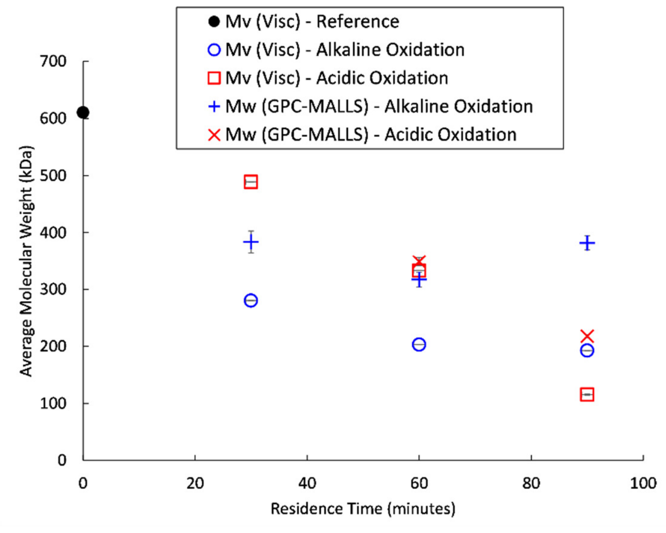

Figure 13. Carbohydrate degradation in pulp oxidized under acidic or alkaline conditions, as measured by either intrinsic viscosity or GPC.

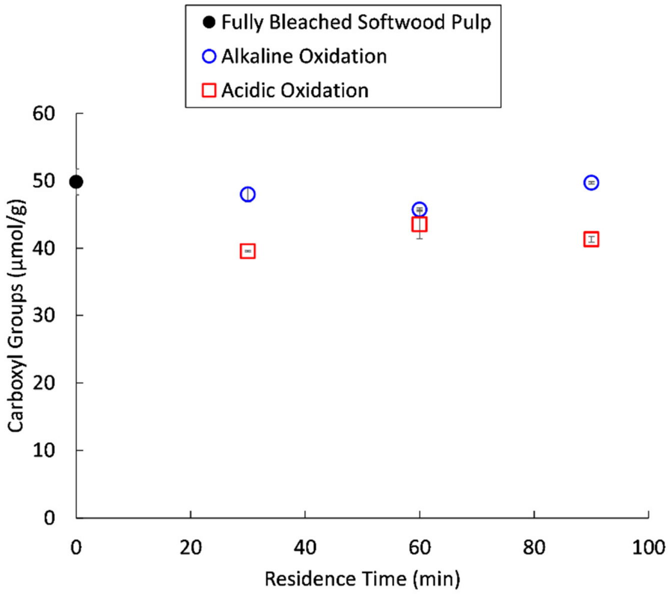

Figure 14. Carboxyl content of softwood pulp oxidized under acidic or alkaline conditions, measured using potentiometric titration.

CCOA labelling and GPC analysis were able to provide additional data regarding the oxidation and degradation of the carbohydrates. It is obvious, from the molecular weight data obtained from the GPC and the total carbonyl content given in Table 1, that the number of carbonyl groups increased more than the theoretical number of reducing end groups. This implies that the majority of the increase in carbonyl content is due to the introduction of carbonyl groups along the chains of the carbohydrates, rather than reducing ends formed as a consequence of chain scission.

Table 1. Number average molecular weight (Mn), weight average molecular weight (Mw), Z average molecular weight (Mz), dispersity, reducing end groups (Reg) and total number of carbonyl groups (C=O), measured using GPC. Bleached softwood kraft pulp and the acidc oxidation at 30 minutes are within paranthesis, as these are a result of partial dissolution.

	Mn (kDa)	**Mw (kDa)**	**Mz (kDa)**	**Dispersity (Mw/Mn)**	**Reg (µmol/g)**	**C=O (µmol/g)**
Bleached Kraft Pulp	(24.0)	(311)	(893)	(12.8)	(41.3)	(6.90)
Acidic oxidation 30 minutes	(28.0)	(308)	(886)	(11.1)	(36.5)	(16.9)
Acidic oxidation 60 minutes	43.2	349	1230	8.09	23.3	32.3
Acidic oxidation 90 minutes	33.6	218	858	6.48	29.8	82.1
Alkaline oxidation 30 minutes	41.8	384	1440	9.41	24.7	13.8
Alkaline oxidation 60 minutes	42.8	317	1250	7.40	23.4	15.9
Alkaline oxidation 90 minutes	52.4	382	1560	7.34	19.2	15.5

By using the data from the GPC analysis of the CCOA labelled samples it was also possible to obtain a carbonyl profile as a function of the molecular weight distribution, Figure 15. A clear difference between the acidic and alkaline conditions can be noted.

Introduction of carbonyl groups can be observed throughout the molecular weight distribution for the pulp oxidized at acidic conditions. The majority of the carbonyl groups are however, found in the low molecular weight fractions. No conclusion regarding if the oxidation affects the hemicellulose fraction or cellulose can be drawn from this information though as softwood hemicelluloses will elute over the entire size distribution, as opposed to hardwood pulp which show a population of low molecular weight xylan (Sjöholm, 1999).

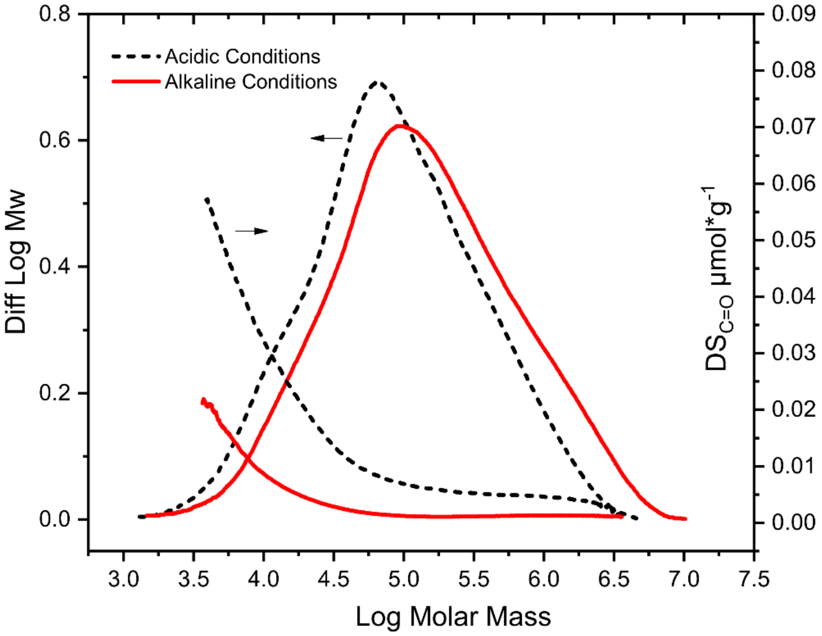

Figure 15. Carbonyl profile as a function of the molecular weight distribution for pulps oxidized under either acidic or alkaline conditions for 90 minutes.

A compositional analysis of the reference pulp and the oxidized pulps was carried out in order to study changes caused by the oxidation that were detectable, by analysing the monomeric sugars; the results are shown in Table 2. The main finding of the compositional analysis was the reduction in the galactoglucomannan content in the pulps oxidized under both acidic and alkaline conditions. In addition, a slight reduction in the xylan content of the pulps oxidized under acidic conditions was seen: this suggests that xylan may be oxidized because the method does not detect oxidized monomeric units. An increase in both Klason lignin and non-detected material was observed, which is probably caused 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: instead, they remain undetected or end up in the Klason lignin fraction (Li *et al.,*2005; Sannigrahi and Ragauskas, 2008; van Zandvoort *et al.,* 2013).

Table 2. Compositional analysis of the reference pulp and pulps subjected to acidic or alkaline oxidation. The composition is a sum of holocellulose, acid soluble lignin (ASL) and Klason lignin.

	Cellulose (%)	**Galacto-glucomannan (%)**	**Xylan (%)**	**ASL (%)**	**Klason Lignin (%)**	**SUM (%)**	**Undetected (%)**
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

5.1.2 Results of Kraft Pulp oxidation at constant pH

A large change in pH was observed during the oxidation of pulp using an acidic or alkaline starting pH. An evaluation of a suitable buffer system for the process was then necessary in order to evaluate the formation of carbonyl groups at a specific pH, so two buffers were evaluated: phosphate- and an acetate-based one, Table 3. Although they could not be evaluated at identical pH levels, as the pH-intervals of the two buffers have no overlap, a clear difference could nevertheless be noticed between them. The phosphate buffer resulted in a lower carbonyl content than the acetate buffer, with the latter having a carbonyl content close to that achieved in the unbuffered oxidation at the same conditions. The reason for the carbonyl content being lower in the phosphate-buffered oxidation may be that phosphate acts as a stabilizing agent for the hydrogen peroxide, which results in the oxidizing power being reduced (Aggarwal *et al.,* 1991; Kakarla and Watts, 1997).

Table 3. Carbonyl content and viscosity average molecular weight (Mv) after oxidation at 85°C using a 200% hydrogen peroxide charge (on pulp basis) for 90 minutes.

Sample	Carbonyl Content (μmol/g)	Mv (kDa)
Phosphate buffer, pH 5.8	66.4	240
Acetate Buffer, pH 5.6	91.2	111
Acetate Buffer, pH 4.0	115	91.5

The acetate buffer was evaluated further due to the possibility of peracetic acid being formed, which could potentially influence the oxidation. A series of oxidations, with a charge of peracetic acid identical to that of the hydrogen peroxide (200% on pulp basis) used previously, were carried out in an acetate buffer at pH 4, Figure 16. Compared to the reference starting material, peracetic acid was not found to cause an increase in the carbonyl content. The acetate buffer could therefore be assumed to be a suitable choice of buffer for the oxidation of pulp using hydrogen peroxide at acidic pH.

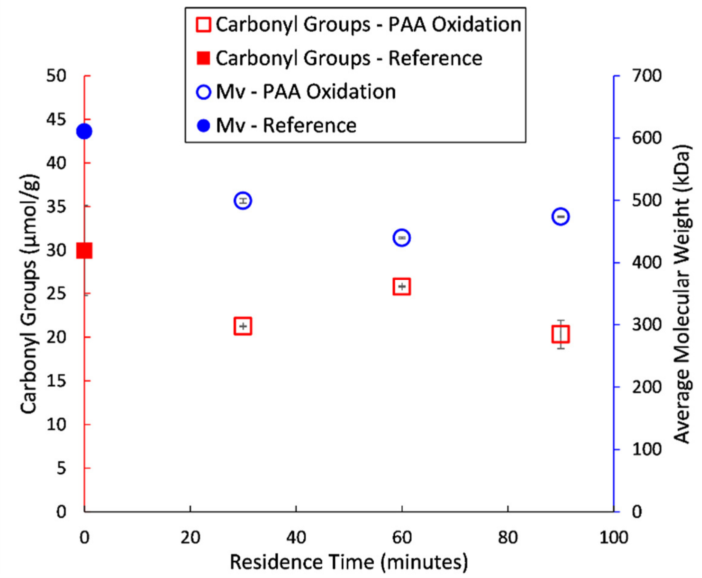

Figure 16. The effect on the carbonyl content and carbohydrate degradation of softwood kraft pulp oxidized with peracetic acid (PAA), as measured by the intrinsic viscosity average molecular weight (Mv).

The acetate buffer was utilised in all further experiments at constant pH, starting with the evaluation of the influence of the reaction temperature on the oxidation of softwood and hardwood pulps under acidic conditions. Three temperatures were investigated: 65, 75 and 85 °C, and the resulting carbonyl content, carboxyl content and intrinsic viscosity were analysed, Figure 17-19. After oxidation, the softwood pulp had a higher carbonyl content than the hardwood pulp. The starting material for the hardwood pulp oxidation has a lower carbonyl content than expected, Figure 17. Based on the linear trend of the oxidation of softwood, and the similar carbonyl content in the 30-minute oxidations of hardwood pulp, it is expected that the carbonyl content of the starting material should be in the range of 40 – 50 µmol/g. The reason for the starting material having a lower carbonyl content may be hornification, which could be partially reversed by the treatment that the pulp is subjected to during oxidation. Likewise, the carboxyl content of the starting material for the hardwood oxidation is also slightly lower than expected. Similar to previous results obtained for the carboxyl content of oxidized pulps, no apparent change can be seen for the oxidized softwood pulps at any of the temperatures investigated, Figure 18. For the hardwood pulp, on the other hand, a slight decrease can be noted at 75 °C and above, which could be explained by the solubilisation of, for example, oxidized xylan. The resulting intrinsic viscosities of the oxidized pulps, Figure 19, show very similar behaviours for both softwood and hardwood pulp oxidation, suggesting a similar degradation of carbohydrates.

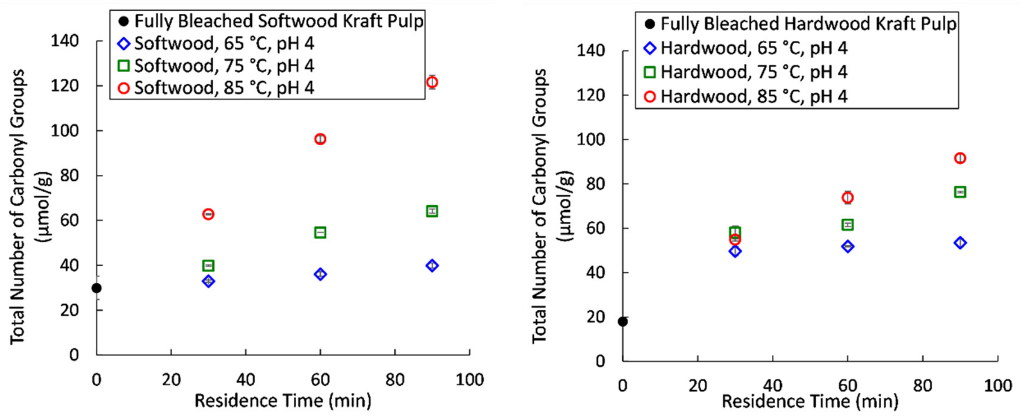

Figure 17. Content of carbonyl groups in softwood (left) and hardwood (right) pulps after oxidation with hydrogen peroxide, measured by the oxime method.

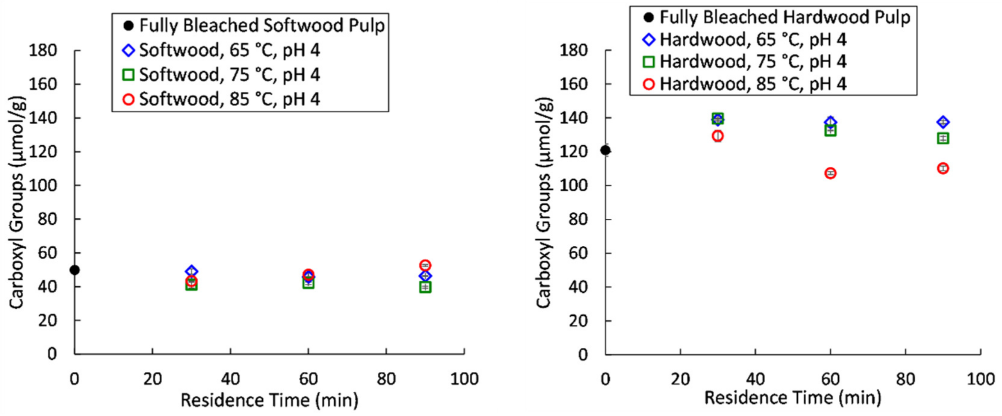

Figure 18. Content of carboxyl groups in softwood (left) and hardwood (right) pulps after oxidation with hydrogen peroxide, measured by potentiometric titration.

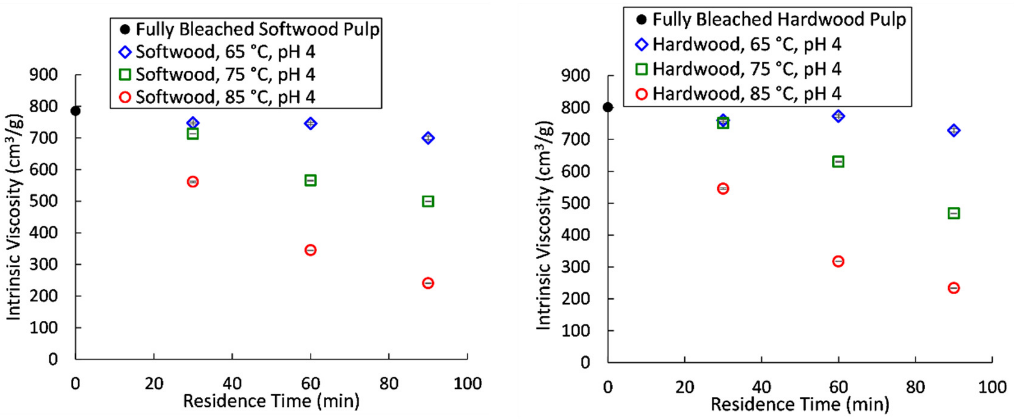

Figure 19. Degradation of carbohydrates in softwood (left) and hardwood (right) pulps after oxidation with hydrogen peroxide, measured as intrinsic viscosity.

As shown previously for the unbuffered oxidation of softwood kraft pulp, oxidation causes a change in the composition of the pulp that results in a reduction of galactoglucomannan and xylan, Table 2. Similarly, a compositional analysis of the hardwood kraft pulp oxidized at 85° C and pH 4 was made, Table 4. As well as the oxidations at 30, 60 and 90 minutes, a 90-minute blank run, without the addition of hydrogen peroxide, was carried out in order to evaluate the influence of the acidic conditions alone on the pulp. The acidic conditions were not found to influence the composition at the temperature investigated, compared to the reference pulp. The oxidized pulp, on the other hand, showed a gradual decrease in xylose with increasing residence time, probably due to the oxidation of xylan resulting in hydrolysis products that are not being detected as monomeric sugars by the method. This would also explain the gradual increase in undetected material with increasing residence time.

Table 4. Compositional analysis of hardwood pulp oxidized at 85 °C, pH 4, reported as monomeric sugar units (glucose, xylose and mannose), Klason lignin and acid soluble lignin (ASL).

	Reference	**30 min**	**60 min**	**90 min**	**90 min blank run**
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 (%)	10.2	10.4	10.7	11.3	9.8

The way in which the xylan content affects the oxidation of cellulose in hardwood kraft pulp was investigated by performing a cold caustic extraction (CCE) of xylan. The great availability of xylan close to, or on, the fibre surface as the result of either precipitation during pulping (Danielsson, 2007; Hutterer *et al.*, 2017) or the natural distribution of xylan in the cell wall (Sjöberg *et al.*, 2005) means that xylan is highly affected by the oxidation process. Once the easily available xylan is removed, for example through cold caustic extraction, it is probable that cellulose surfaces are exposed, and that the oxidation thereby affects the cellulose to a larger extent than with xylan present. A comparison of the composition of the CCE reference in Table 5 with the same pulp prior to the cold caustic extraction (Table 4) shows a reduction of around 88% in the amount of xylose. The amount of xylose is reduced further with increasing residence time. However, a maximum reduction of about 0.6 percentage points is observed, compared to the 3 percentage points of reduction observed on the non-extracted pulp. Comparing the ratio of glucose and xylose in the cases given in Table 4 and Table 5 allows the graph presented in Figure 20 to be obtained.

Table 5. Compositional analysis of cold caustic extracted, fully-bleached hardwood kraft pulp and oxidations thereof.

	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 (%)	14.7	10.9	10.5	10.9

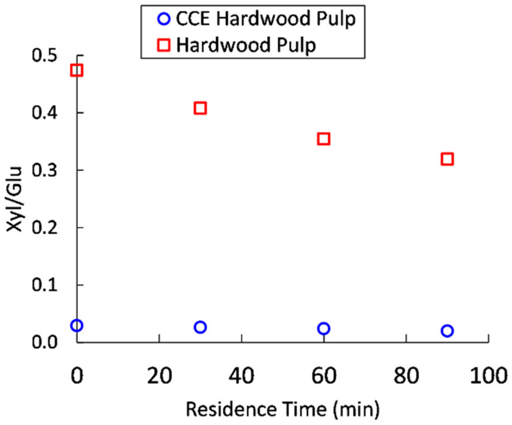

Figure 20. The ratio of xylose/glucose in hardwood kraft pulp and cold caustic extracted (CCE) hardwood kraft pulp during oxidation.

The effect of CCE on the carbonyl content and intrinsic viscosity is illustrated in Figure 21. It is obvious that oxidation of the CCE pulp resulted in a larger introduction of carbonyl groups and a more severe degradation of the carbohydrates, compared to that of the unextracted pulp. The greater increase in carbonyl content observed for the CCE pulp may be explained by the exposure of cellulose surfaces after the removal of xylan, or increased porosity caused by the removal of xylan, both of which result in a larger surface area being accessible in the never-dried state (Dou and Tang, 2017). It can be noted that, initially, the CCE pulp has a higher viscosity due to the extraction removing low molecular weight xylan and thereby increasing the average molecular weight. Furthermore, it was found that the oxidation of CCE pulp leads to a more severe degradation than that of hardwood kraft pulp, in which the xylan remains: a similar viscosity can be observed (317 cm^3/g and 320 cm^3/g) when the hardwood kraft pulp oxidized for 60 minutes is compared with the CCE pulp oxidized for 30 minutes. The carbonyl content of the CCE pulp at this point is, however, much lower than for the oxidized hardwood pulp (48 µmol/g compared to 74 µmol/g).

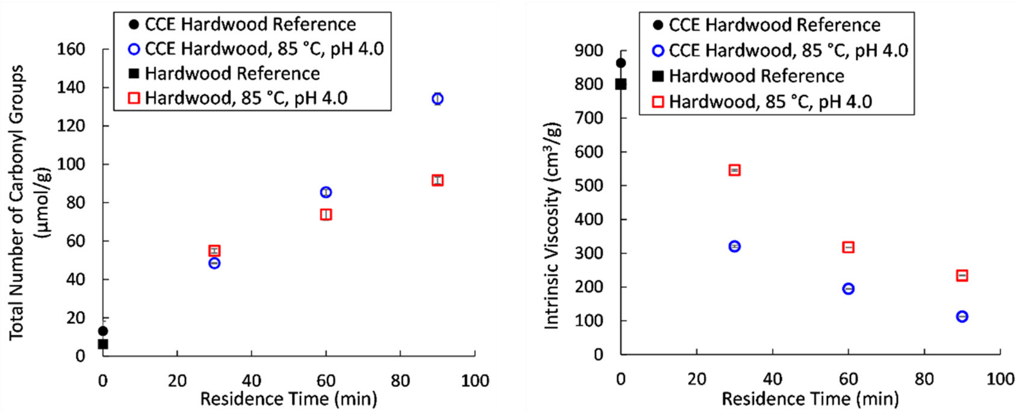

Figure 21. Comparison of the oxidation of hardwood kraft pulps and cold caustic extracted (CCE) hardwood kraft pulps as measured by intrinsic viscosity. Left: carbonyl content. Right: carbohydrate degradation.

5.2 Influence of the Concentration of Hydrogen Peroxide on the Oxidation of Softwood Kraft Pulp

In the studies presented above, a high hydrogen peroxide charge was used to investigate the influence of factors such as reaction temperatures. A natural next step was to investigate the influence of the concentration of hydrogen peroxide in order to approach industrial conditions. Lower charges, of 10% and 50% hydrogen peroxide (on pulp), were used initially, resulting in the carbonyl contents and intrinsic viscosities presented in Figure 22. At a charge of 10% and a residence time of 120 minutes, no apparent change in either carbonyl content or intrinsic viscosity could be observed, making additional data points using shorter residence times unnecessary. A slight increase in carbonyl content could be observed at 50% charge and a full time series was therefore carried out. However, it is obvious that the carbonyl content of the 50% charge series is much lower when compared to a charge of 200%. As the 200% series was obtained from an earlier study (Figure 17), using a different softwood kraft pulp as starting material, an additional data point using a residence time of 90 minutes was carried out to investigate whether any major differences could be detected. A slightly lower carbonyl content was in fact obtained, but it is still a large difference compared to the charge of 50%. Similarly, the new starting material had a slightly lower carbonyl content than the one in the previous study. The reasons why a high (>10%) hydrogen peroxide charge is required are not yet fully understood: one could be the stability of hydrogen peroxide at acidic conditions due to the equilibrium of the dissociation reaction of hydrogen peroxide, as discussed previously, according to Reaction 1 (Section 5.1.1) (Schumb, 1949). Another could be the relatively low temperature, compared to industrial hydrogen peroxide bleaching at alkaline conditions, which has temperatures around 90 °C, even though temperatures as high as 110 °C may be employed for pressurised stages (Germgård, 2009). Temperature dependence in alkaline and acidic conditions might, however, differ.

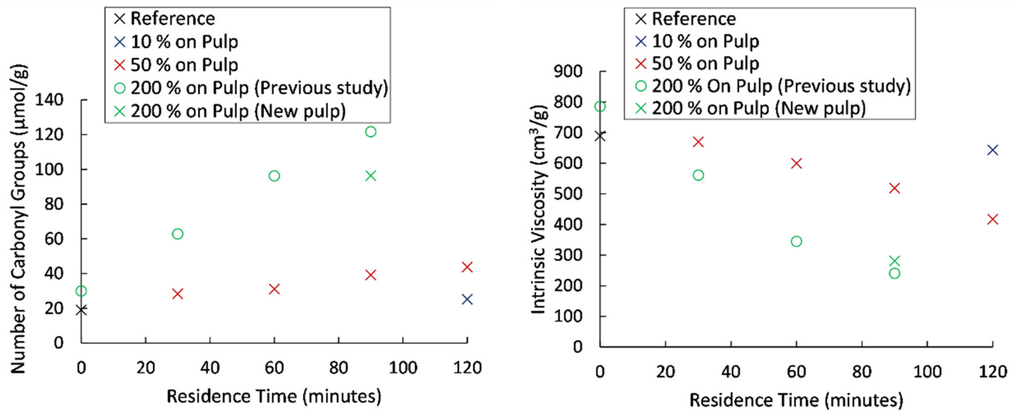

Figure 22. Carbonyl content (left) and intrinsic viscosity (right) of pulps oxidized with hydrogen peroxide charges (on pulp basis) of 10%, 50% and 200%, resp. An additional data point was carried out for 200% as the 200% series was from a previous study, utilizing a different softwood kraft pulp as starting material.

5.3 Influence of Transition Metal Ions on the Oxidation of Softwood Kraft Pulp

It is obvious that a high concentration of hydrogen peroxide is required, so the oxidation liquid must be recirculated in an industrial case. In order to study the effects of recirculation, a hydrogen peroxide charge of 50% was used in experiments on softwood kraft pulp in which the liquid phase was recirculated and a second batch was oxidized for the same residence time as the first batch. The resulting carbonyl content, intrinsic viscosity and total content of acidic groups are found in Figure 23. The second batch shows a consistently higher carbonyl content and a lower intrinsic viscosity, and the total content of acidic groups remains unchanged, the later similar to the studies presented previously. The stable content of acidic groups indicates that neither the formation of aldehydes (from either the oxidation of primary hydroxyl groups or the reducing ends from chain cleavage) nor the oxidation of aldehydes are substantial. Compared to Batch 1, the higher carbonyl content and lower intrinsic viscosity of Batch 2 indicate a more substantial oxidation.

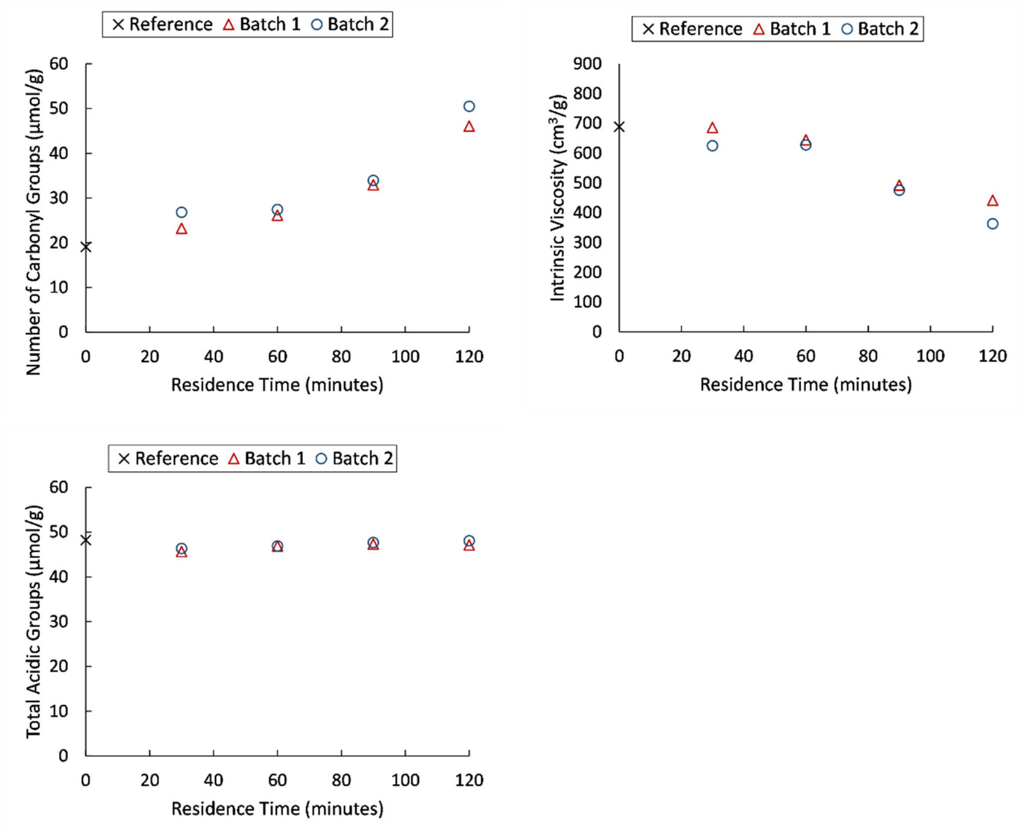

Figure 23. Carbonyl content (top left), intrinsic viscosity (top right) and total content of acidic groups (bottom left) for pulps oxidized with a 50% hydrogen peroxide charge at 85 °C. Batch 2 was oxidized using the same liquid phase as Batch 1.

One possible explanation for the more substantial oxidation is that it may be due to the accumulation of transition metal ions in the liquid phase, which could lead to an increased formation of radical species (Bryant and Edwards, 1994). Acidic conditions favour the desorption of transition metal ions, so the concentrations of these ions are likely to be higher during the oxidation of the second batch than of the first. An ICP-MS analysis of the liquid phase was therefore carried out and the results summarized in Table 6; as expected, the concentrations of transition metal ions are consistently higher in the second batch. In this case, it is the manganese content in particular that has increased, although elevated concentrations of copper and iron can be observed at longer residence times. One irregularity that was discovered was the high concentration of copper in the second batch oxidized at 30 minutes: this might be due to impurities in the pulp, or the experimental setup. This anomaly may explain the larger difference in carbonyl content and intrinsic viscosity of the two 30-minute oxidations seen in Figure 23. The elevated concentrations of the metal ions did not only impact the oxidation but also the consumption of hydrogen peroxide, as shown in Table 7.

Table 6. Concentrations of copper, iron and manganese in the liquid phase during oxidation. Concentrations of copper below 7 ppm and iron below 3 ppm are below the detection limit of the instrument.

Residence Time	Batch number	Cu [ppb]	Fe [ppb]	Mn [ppb]
30	1	<7	<3	129±7
	2	30±7	<3	257±8
60	1	<7	<3	136±7
	2	<7	<3	273±8
90	1	<7	7±3	139±7
	2	10±7	49±3	291±8
120	1	12±2	57±6	208±4
	2	29±2	118±7	401±8

Table 7. Concentration of hydrogen peroxide after the oxidation of Batch 1 and Batch 2 for 90 minutes at 85 °C.

Number of Oxidations	H_2O_2 (g/L)
0	13.4
1	12.9
2	11.7

The model developed to describe accumulation of transition metal ions, described in Section 4.11, was used to estimate the accumulative increase of copper, iron and manganese when recirculating the oxidation liquid. The input data for the desorption of the metal content used the results obtained for the first batch oxidized at 120 minutes, as given in Table 6; the result of these calculations is shown in Figure 24. Based on the concentrations of the metal ions acquired after 10 recirculations (Figure 24), a series of oxidation experiments at elevated metal ion concentrations were carried out in order to simulate a scenario with very high concentrations of metal ions.

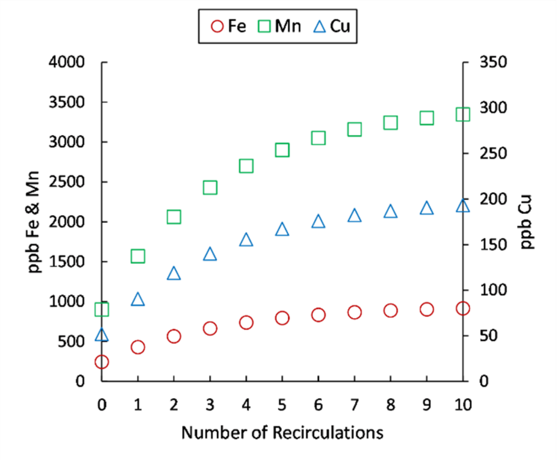

Figure 24. Increase in the concentration of metal ions after repeated recirculation. The initial concentrations are based on the concentrations obtained for the first batch after 120 min of oxidation. The model used to achieve the resulting increase is described in Section 0.

The oxidation experiments in which transition metal ions were added resulted in the rapid oxidation shown in Figure 25, where the content of carbonyls is seen to reach a maximum after 60 minutes. Similarly, residence times exceeding 60 minutes only result in a minor reduction in intrinsic viscosity compared to one of 60 minutes. An increase in the total content of acidic groups is observed for the pulp oxidized with the addition of transition metal ions, an increase of acidic groups has not been observed previously in our studies. This may indicate different oxidation mechanisms to those in action at low concentrations of transition metal ions, possibly due to the large amount of hydroxyl radicals formed during the experiments carried out at elevated concentrations of transition metal ions.

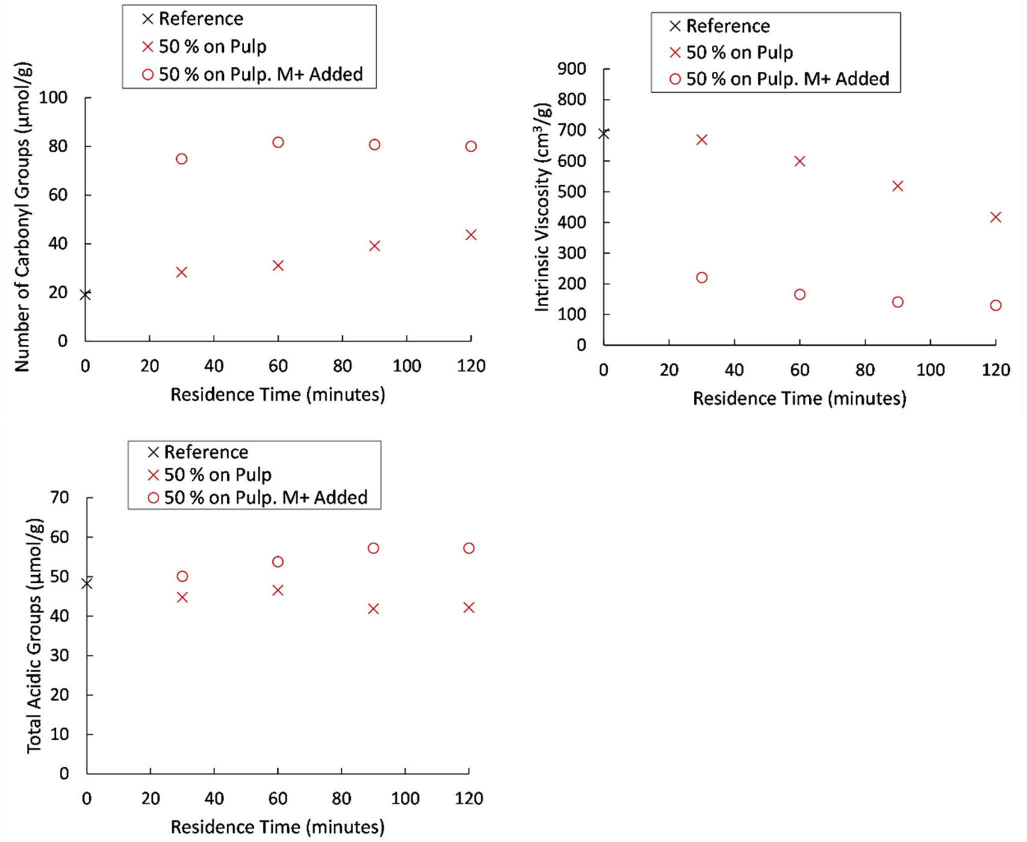

Figure 25. Carbonyl content, intrinsic viscosity and total content of acidic groups of pulps oxidized at 85^0 C with the addition of transition metal ions, compared to oxidation without the addition of transition metal ions at the same conditions.

The very low concentrations of hydrogen peroxide is a plausible reason as to why no increase in carbonyl content was observed after 60 minutes, see Figure 26. After 120 minutes, the concentration of hydrogen peroxide approaches values similar to a 10% hydrogen peroxide charge (2.5 g/L), where no changes in the carbonyl content or intrinsic viscosity were found, Figure 22. The experiments conducted at elevated concentrations of transition metal ions thereby demonstrate the necessity of controlling the content of metal ions in the pulp prior to oxidation, otherwise the results will be a large consumption of hydrogen peroxide accompanied by severe degradation of the pulp.

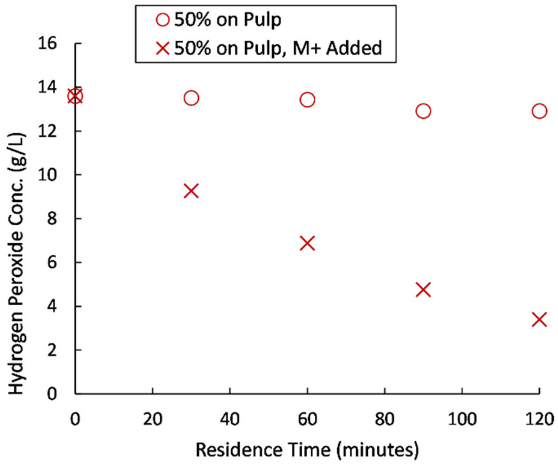

Figure 26. Concentration of hydrogen peroxide in the liquid phase during oxidation, with and without the addition of transition metal ions.

5.4 Physical Testing of Sheets Produced from Oxidized Pulps

The physical properties of two oxidized softwood pulps were tested and compared to those of the unoxidized pulp. The oxidation conditions, along with the resulting carbonyl content, intrinsic viscosity and total content of acidic groups, are presented in Table 8.

Table 8. The oxidation conditions, carbonyl content, intrinsic viscosity and total content of acidic groups of the reference pulp and the two oxidized pulps tested.

	Residence Time (min)	Temperature (°C)	pH	H_2O_2 Charge on Pulp (%)	Total Number of Carbonyl Groups (µmol/g)	Intrinsic Viscosity (cm^3/g)	Total Acidic Group Content (µmol/g)
Reference	-	-	-	-	8.88	800	35.9
Low Oxidation	90	85	4	50	28.1	560	32.8
High Oxidation	90	85	4	200	66.4	308	36.3

A fibre analysis was carried out to verify whether oxidation had affected the dimensions of the fibres or the content of fines, as both factors affect the physical properties to be tested later on. However, the oxidation was not found to affect either of them, see Table 9.

Table 9. Fibre analysis of the never-dried reference pulp and the two oxidized pulps.

	Reference	50% H_2O_2 Charge	200% H_2O_2 Charge
Fibre length (l)(mm)	2.41	2.35	2.39
Fibre width (l) (µm)	30.3	30.4	30.2
Fines (l) (%)	4.66	4.85	4.73

A compositional analysis of the fibres was also carried out in order to reveal any changes that might have occurred to the composition of carbohydrates. As in the studies presented previously, oxidation resulted mainly in a decrease in the amount of hemicelluloses, see Table 10. This is, as mentioned earlier, likely due to the oxidation of hemicelluloses or to the partial dissolution of these fractions.

Table 10. The compositional analysis of the pulps, with carbohydrates given as monomeric sugars and lignin as Klason lignin and acid soluble lignin (ASL).

	Reference	**50% Charge**	**200% Charge**
Arabinose (%)	0.46	0.45	0.42
Galactose (%)	0.16	0.15	0.13
Glucose (%)	82.4	81.6	82.7
Xylose (%)	6.44	6.24	5.96
Mannose (%)	5.51	4.90	4.95
Klason (%)	0.70	0.70	1.00
ASL (%)	0.54	0.52	0.57
Total (%)	96.2	94.5	95.7
Undetected (%)	3.82	5.50	4.30

The pulps were tested for Schopper-Riegler and water retention value. The differences in Schopper-Riegler were within the experimental errors but, for the water retention value, a slight decrease could be observed with increasing oxidation, Figure 27. This could potentially be a result of the removal of hemicelluloses which, in turn, would lead to increased hornification (Oksanen *et al.*, 1997). Another possible explanation could be the formation of hemiacetal crosslinks within the fibre wall due to the formation of carbonyl groups: these could cause a reduced swelling and thereby reduce the water retention value.

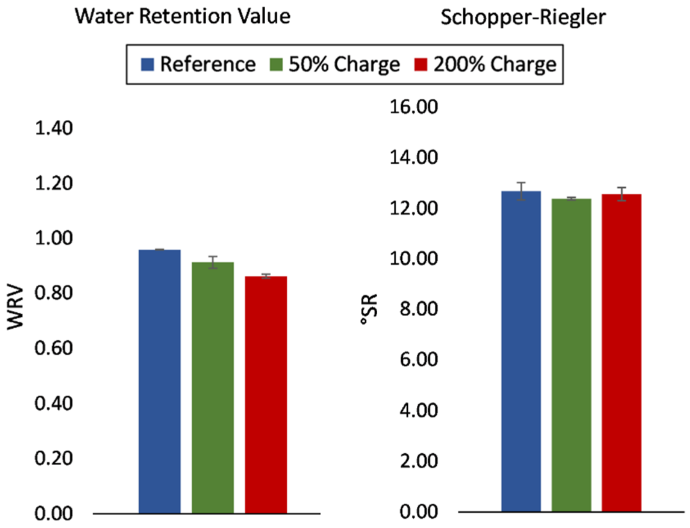

Figure 27. Measurements of the water retention value and Schopper-Riegler of the reference and oxidized pulps.

The runnability of the pulp in a paper machine was investigated using a wet web tensile strength test. The never-dried pulps were first formed into sheets that were subjected to increasing pressing times to provide them with different dry contents; the results of the test are shown in Figure 28. An interesting finding is the lower dry content of the oxidized pulps at the same pressing time, the only exception to which is the pressing time of 3 minutes: the pulp oxidized with a charge of 50% hydrogen peroxide has a higher dry content than the reference pulp. In addition, it can be seen that the oxidized pulps have a consistently higher tensile index than the reference pulp despite the lower dry content. At dry contents below 50% the strength of a paper web depends mainly on inter-fibre capillary forces and the friction of entanglement; the strength of a paper web increases with increasing dry content (van de Ven, 2008; Lindqvist 2013). The fact that the oxidized pulps exhibit a higher tensile index at lower dry contents, i.e. below 50%, suggests that another phenomenon causes the increase in tensile index. A plausible explanation here is the formation of hemiacetal bonds between fibres, which has been proven to form even in the wet state (Erlandsson *et al*., 2018). It is also likely that bonds between fibres would result in a stiffer network of fibres, which also may explain the lower dry content of the oxidized pulps.

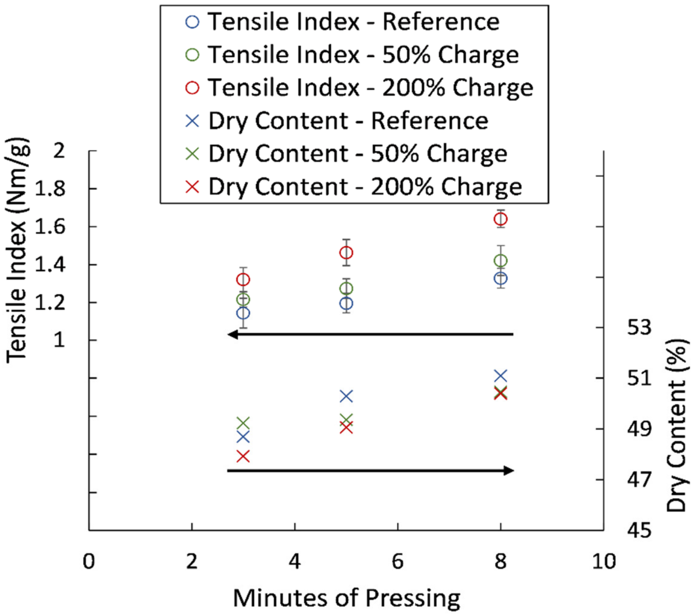

Figure 28. Results of the wet web tensile test applied to the reference and two oxidized pulps. The tensile index and dry content are given as a function of the pressing time.

New laboratory sheets were tested for tensile and wet tensile strengths, as were sheets produced from recycled laboratory sheets. This was done to investigate if the increase in wet strength (possibly due to hemiacetal bonds) could be maintained after the sheets were recycled via defibrillation. The sheets produced from oxidized pulps were easily defibrillated and, from ocular inspection, there were no signs of aggregation after defibrillation in water. This is a major advantage because it would facilitate the recycling of broke or potential products.

Oxidation of the pulps resulted in a minor decrease in tensile strength: about 4% for the 50% hydrogen peroxide charge and about 11% for the 200% charge, see Figure 29. As the fibre analysis did not show any changes in the dimensions of the fibres or content of fines, a possible reason for this decrease may be the increased hornification of the oxidized samples, which was indicated by the water retention value. Increased hornification will lead to a reduction in tensile strength due to a decrease in the relative bonded area (RBA) (Nazhad, 2005; Hubbe *et al.*, 2007). Furthermore, the degradation of carbohydrates that was shown by the intrinsic viscosity measurements could potentially contribute to the reduction in tensile strength by decreasing the strength of the individual fibres: in this case, it is not unlikely to be a combination of a reduced RBA and weaker individual fibres. Recycling the sheets seems to cause a reduction in the tensile strength of the reference pulp, whereas the oxidized pulps appear to remain more or less unchanged within the standard deviation for this measurement. The wet tensile strength was significantly increased for the oxidized pulps compared to the reference, the probable cause of which is the formation of inter-fibre hemiacetals. It is interesting that the enhanced wet tensile strength was found to be maintained at least to some degree even after the laboratory sheets were recycled. The reduction in wet tensile strength after recycling may be explained by the same phenomena as for the reduction in dry tensile strength, namely an increase in hornification and a decrease in the relative bonded area, which cause a reduction in the number of inter-fibre bonds, including probable hemiacetals bonds.

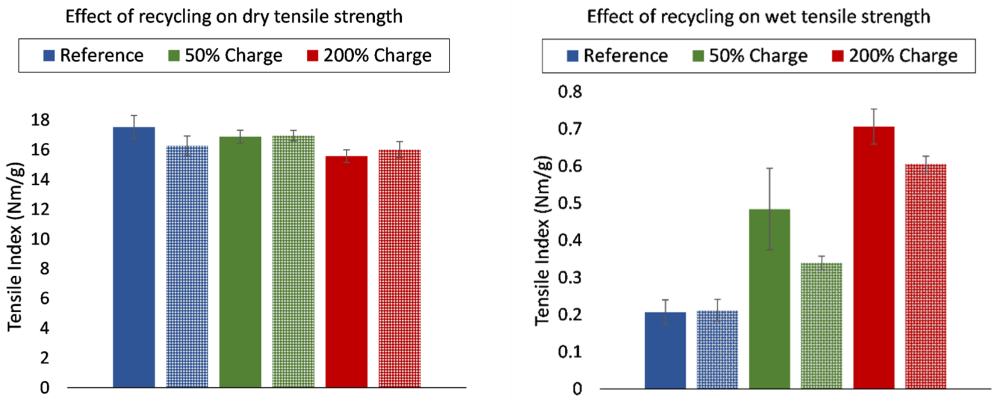

Figure 29. Effect of recycling on the dry and wet tensile strengths of the reference and oxidized pulps. The patterned bars are sheets made from recycled laboratory sheets.

5.5 Discussion

All of the studies presented show that the carbonyl content of kraft pulp can be increased through oxidation with hydrogen peroxide if acidic conditions are used. Only two pH levels were investigated for the acetate buffer: 5.6 and 4, with the latter yielding the highest carbonyl content. A lower pH could potentially be used to achieve an even higher carbonyl content using the same buffer system, as the acetate buffer may be utilized at as low pH as 3.6. However, if the pH is lowered, acid hydrolysis of the carbohydrates may start to affect the oxidation, which requires further investigation. It should be added that acid hydrolysis was not found to have a measurable effect at pH 4.

The necessity of a high charge of hydrogen peroxide is not fully understood: but as mentioned previously, acidic conditions will stabilize the hydrogen peroxide which is likely to be contributing to this. Temperatures over 85 °C would also need investigating if further insight is to be gained into this dependence on the hydrogen peroxide charge. It is interesting to note that the consumption of hydrogen peroxide was found to be low, see Figure 26, unless a high concentration of transition metal ions were present. One important factor that should be kept in mind here is the solid-to-liquid ratio: low consistency was used in this study, which means that a lower concentration was obtained than would have been for an oxidation at medium consistency with the same hydrogen peroxide charge. It is therefore likely that lower charges are required if oxidation is to be carried out at medium consistency.

Recirculation of the liquid phase is a prerequisite in the financial aspect of reaching a high concentration of hydrogen peroxide: pre-treatment of the pulp is therefore necessary to minimise the concentration of transition metal ions in the reactor.

The physical testing of the oxidized pulps highlighted some important features of the material. Most importantly, the benefits, in terms of wet tensile strength and wet web tensile strength, could be observed even for the lower degree of oxidation (28 μmol/g). Moreover, the decrease in tensile strength of the oxidized pulps is not as severe as was expected from the intrinsic viscosity measurements. Oxidation may, however, have a greater negative impact on the strength of individual fibres. The Schopper-Riegler measurements showed no differences between the reference and oxidized pulps, which means that dewatering and web formation should not be affected. A sufficiently high turbulence and shear in, for example, pumps would probably be needed to avoid the formation of stable flocks caused by hemiacetal formation. The pressing procedure carried out during the wet web tensile strength measurements showed a lower dry content for the oxidized pulps, indicating that additional pressing may be required to obtain similar dry contents as for an unoxidized pulp in an industrial situation. An alternative would be to increase the capacity of the dryer, which, however, would lead to higher operating costs. The enhanced wet web tensile strength indicates that the hemiacetals form already in the wet state, during the pressing procedure. This means that the benefits of oxidized pulps, in terms of wet strength, may be utilized not only in the end-product but also during production, as this could enhance their runnability in a paper-machine.

6 Conclusions

The studies presented in this thesis have shown that acidic conditions can be utilized in the oxidation of kraft pulp to favour the formation of carbonyl groups. Compared to alkaline conditions, a significant increase in the number of carbonyl groups is observed, accompanied by a degradation of the carbohydrate fraction. Compositional analysis of the pulp shows that oxidation causes a reduction in the amount of hemicelluloses present, suggesting that they are oxidized to a large extent.

A high charge of hydrogen peroxide is necessary in order to achieve a substantial formation of carbonyl groups at the temperatures investigated.

The accumulation of transition metal ions caused by recirculation of the liquid phase will influence the oxidation process, resulting in an increased formation of carbonyl groups and severe degradation. A high concentration of transition metal ions will also lead to an increase in the consumption of hydrogen peroxide and, possibly, a different composition of oxidized functionalities. This is shown by the increase in carboxyl groups, indicating that the high concentration of transition metal ions may result in an oxidation mechanism different to that in action at low concentrations.

Sheets formed from the oxidized pulps exhibited an increase in wet tensile strength at the expense of a slight reduction in dry tensile strength: this enhanced wet tensile strength was found to be partially preserved after the sheets were recycled.

An increase in wet web tensile strength suggests that the formation of hemiacetals occurs already in the wet state, even at dry contents below 50%, and therefore has the potential of being utilised to enhance the runnability of paper machines.

7 Outlook

Several questions related to the oxidation of kraft fibres under acidic conditions remain to be answered in order for the process to be fully understood and its potential evaluated. Firstly, the dependence on hydrogen peroxide charge requires further examination. This includes investigating medium consistency oxidation, as this would also affect the resulting hydrogen peroxide concentration. Secondly, the material balance of the process needs to be evaluated. It is inevitable that the severe degradation is linked to a loss in yield, which necessitates investigation. Another process-related question that requires further scrutiny is the temperature dependence of the oxidation. Temperatures above 85 °C were not, however, employed here: hydrogen peroxide is more stable under acidic than alkaline conditions, so it is possible that temperatures higher than those investigated in this study are necessary for acidic oxidations in order to achieve optimal oxidation.

It would also be of interest to investigate the oxidized pulp further, for example, the distribution of carbonyl groups in the fibre. Does oxidation affect mainly the fibre surface or is the entire cross-section of the fibre wall impacted? Studies of the mechanism, reactive species and the location of the carbonyl groups would also be of considerable interest.

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