

Novel use of hydrogen peroxide to convert bleached kraft pulp into dissolving pulp and microfibrillated cellulose.

Andrea Estefania Vera Loor

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Nouvelle utilisation du peroxyde d'hydrogène pour convertir la pâte kraft blanchie en pâte à dissoudre et en cellulose microfibrillée.

Novel use of hydrogen peroxide to convert bleached kraft pulp into dissolving pulp and microfibrillated cellulose.

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NOVEL USE OF HYDROGEN PEROXIDE TO CONVERT BLEACHED KRAFT PULP INTO DISSOLVING PULP AND MICROFIBRILLATED CELLULOSE

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Introduction

The market of specialty cellulose (also called "dissolving pulps") for chemical or chemicalphysical applications is in expansion, more than 60% increase in 5 years, in order to replace petroleum-based polymers, plastics and textile fibers. Moreover, the production of microfibrillated cellulose (MFC) used as additives to reinforced bio-based materials is also expanding. However, current production processes are not always competitive. Classical dissolving pulps, obtained from the PHK process (Kraft Pre-Hydrolysis, i.e. acid pretreatment followed by alkaline Kraft pulping) or from the acid bisulfite cooking are not satisfactory: pulp from the PHK process requires major modifications in the existing Kraft facilities producing pulp for paper applications, and bisulfite pulp is highly polluting. Today the industrial production of MFC is also limited due the deconstruction step of the fiber wall of the cellulosic fiber which requires a lot of energy and a polluting chemical pre-treatment.

The PhD study aims at developing green industrial processes for the production of dissolving grade pulps and MFC from classical paper grade pulps by using hydrogen peroxide, a traditional environmentally friendly bleaching chemical. Unusual operating conditions and the use of coreagents will be attempted in order to favor the oxidation and the controlled depolymerization of polysaccharides as well as the weakening of the cellulosic fiber wall. The global objective of this work is to open new perspectives for the conception of lignocellulosic raw materials designed for industrial applications.

The first chapter presents a literature review which introduces the topic with relevant definitions about the substrates to be used, the conventional bleaching reagents and conditions in the industry, as well as a review of the on-going investigations. A focus is made on the key properties of dissolving pulps and MFC. In particular, an important property of a dissolving-grade pulp is its reactivity during the derivatization processes. The Fock test, reproducing the viscose process, is widely used for estimating the pulp reactivity. However, this test has shown significant drawbacks such as poor repeatability as well as the use of an expensive and toxic chemical, carbon disulfide (CS_2).

In the second chapter, a method has been proposed as an alternative to the Fock test: a standard derivatization reaction leading to full cellulose dissolution, where the dissolution rate was monitored by Dynamic Light Scattering (DLS), i.e. via particle size measurement. Cellulose heterogeneous carbanilation, carried out in DMSO used as solvent, was selected due to its

reproducibility and the fact that it should not affect the molar mass of the cellulosic sample. The proposed method not only allows to evaluate the dissolution behaviour and the substrate reactivity during carbanilation but also to further analyse it by high-performance size extrusion chromatography (HPSEC) to obtain the molecular weight distribution (MWD), and other interesting information. This study was conducted on six fully bleached cellulosic pulps from different origins: cotton linters, a sulfite dissolving pulp (softwood), and several bleached Kraft pulps (softwood and hardwood).

In chapters III and IV, unconventional oxidation processes based on the use of hydrogen peroxide have been investigated to design new dissolving grade pulp from fully bleached hardwood and softwood paper-grade pulp. Three systems have been studied:

- 1. the activation of hydrogen peroxide by copper species (copper II and a copperphenanthroline complex) to produce hydroxyl radicals with high oxidation potential,
- 2. the combination of caustic extraction with hydrogen peroxide oxidation to remove the hemicelluloses and in parallel to oxidize polysaccharides,
- 3. the oxidation by sodium periodate to create dialdehyde cellulose followed by a hydrogen peroxide oxidation to produce carboxyl functions.

Chapter III discusses the results obtained after the oxidation trials performed with different dosage of hydrogen peroxide with copper species (free copper II or copper-phenanthroline complex), and chapter IV presents the combination of hydrogen peroxide oxidation with the caustic extraction and with periodate oxidation. After oxidation, the pulps are fully characterized in order to understand the main modifications and the reactivity and solubility is evaluated trough the novel method developed in chapter II (substrate carbanilation monitored by DLS, followed by polymer analysis by HPSEC). Cellulose solubility in a water based system, i.e. NaOH:urea:water, was also evaluated.

As the investigated systems described above being degrading for cellulose and without strong removal of hemicelluloses, another way of valorisation is proposed in chapter V, i.e. the production of pre-oxidized pulps for the manufacture of microfibrillated cellulose (MFC), with the particularity of using the non-expensive chemicals commonly used in pulp mills for pulp bleaching. The most promising oxidative systems previously studied were applied as a chemical pre-treatment before cellulose mechanical fibrillation, to reduce the energy demand during the grinding step that produces the MFC. Two systems have been investigated, peroxide oxidation activated by a copper-complex, and the combination of periodate and peroxide. One hardwood

Kraft pulp has been selected. After oxidation and fibrillation, the resulting pulp mixture was fully characterized and nanopapers were prepared to evaluate their properties. The so-called "quality index", an index previously developed at LGP2, was also used to assess the relevance of the proposed oxidation systems for MFC applications.

The manuscript comprises also a chapter devoted to the description of the main material and methods used along the research work (Chapter VI), and finally a conclusion highlights the main results and the major insights for the upgrading of fully bleached paper-grade pulp into new added-value cellulosic products, i.e. dissolving grade pulps and MFC.

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I. Bibliography Review

The following bibliography review sets up the basics to understand what are cellulosic pulps, cellulosic derivatives, and how there are obtained conventionally. It also presents the current challenges for the conversion of paper grade pulps into value-added cellulosic products, i.e. dissolving pulps for textile applications, and microfibrillated cellulose. The lignocellulosic material chosen for the study is wood, which is introduced below in the Chapter.

I.1. Wood and its composition

The chemical composition of wood cannot be precisely defined for a given tree species or a given tree. It varies with the tree parts, type of wood, geographic location, climate and soil conditions. Data accumulated over the years have helped to define an average expected for the chemical composition of wood but cannot be used to identify individual species. In general terms, wood is chemically composed from about 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of metal ions (Na, K, Ca, Ma, Si). At macromolecular levels, it has two main components: lignin and carbohydrates. Both are complex, polymeric materials. Minor components such as organic extractives and inorganic minerals are also present. A complete analysis accounts for all the components.¹

	Softwoods	Hardwoods
Cellulose	40-44%	43-47%
Hemicellulose	25-29%	25-35%
Lignin	25-31%	16-24%

Table I-1. Main Constituents of wood species²

As shown in Table I-1, cellulose is the main constituent of wood with approximately >40% by weight of the dry substance in most substrates. The percentage of hemicelluloses is higher in Softwoods than in Hardwoods and at the same time, lignin content in hardwood is lower than softwood. Extractives is relatively low compared to other components (generally <5%).

I.1.1. Cellulose

Cellulose is the most abundant renewable polymer resource available worldwide³. Cellulose is a polysaccharide consisting in β -D-glucose units linked together by 1-4 glycosidic bonds, with an average viscosimetric degree of polymerization (DPv) that varies between 5,000 and 10,000 depending on the wood species. Cellulose is a linear polymer with a high tendency to form hydrogen bonds through hydroxyl groups, which in addition to its fibrous structure has a high tensile strength and is insoluble in most solvents⁴. The intermolecular H-bonds are responsible

for the majority of its properties such as stiffness⁵. The structure of the cellulose is presented in Figure I-1.



Figure I-1. Structure of Cellulose²

The very high *polarity* of cellulose fibres contrasts with the essentially hydrophobic character of most polymers⁶. Prevalence of hydroxyl groups in cellulose (three hydroxyl groups per monomer) allows a substantial intra-and interchain hydrogen bonding in the molecule (Figure I-2). The H-bonds, with the interactions originated from Van der Waals forces, encourage highly ordered arrangements of cellulose (crystalline regions), with some of disordered cellulose (amorphous regions). Regardless of the source, cellulose is generally highly crystalline, fibrous, with high molecular weight, and hydrophilic but insoluble in water and other common solvents. Yet, important properties are highly dependent on the source, such as DP, and crystallinity. i.e. cotton cellulose is more crystalline (~80%) when comparing it to wood cellulose (~50%)⁷.



Figure I-2. Intra and inter hydrogen bonding in cellulose⁷.

When treated in solid state with NaOH (mercerization), the primary wall of cellulose I can be converted into new allomorph, cellulose II, leading to the disappearance of the native microfibrillar morphology, as represented in Figure I-3. In this scenario, parallel-packed arrays of native cellulose (cellulose I) changes to antiparallel-packed fibrils of regenerated cellulose (cellulose II). For the case of other allomorphs, cellulose III (III_I and III_{II}), they can be prepared by dry liquid ammonia, starting from native or regenerated cellulose. Heating of cellulose III_I

and III_{II} produces cellulose IV (IV_I and IV_{II}). Conversions are never complete, which arises difficulties in the production of X-ray diffraction patterns. These modifications are irreversible.



Figure I-3. Conversion of cellulose I (left) to cellulose II (right) after mercerisation, according to Perez⁸.

I.1.2. Hemicelluloses

Hemicelluloses are carbohydrate polymers of relatively low molecular weight, with an average DP_v of 100-200 and are present in wood in a percentage of 25-35%, as indicated in Table I-1. Hemicelluloses are heterogeneous polysaccharides, consisting of ramified and linear assemblages of sugars: hexoses (mannose, galactose, glucose), and pentoses (xylose, arabinose). In addition, certain uronic acid units that result from the oxidation of the primary hydroxyl (-CH₂OH) of a hexose in acid function (-COOH) are present, such as glucuronic acid. The proportion of each of these compounds varies according to the wood specie. Considerable differences also exist in the hemicelluloses content and composition between the stem, branches, roots, and bark.

Softwoods are composed by mannose and galactose (called glucomannans), while hardwoods are composed by xylan. Both presented in Figure I-4. Due to their numerous branches, their low molecular weight, and the fact that they are amorphous and not crystalline, hemicelluloses are more reactive than cellulose.



Figure I-4. Molecular structures of xylan and glucomanan in hardwoods and softwoods².

I.1.3. Lignin

Lignin is the most complex polymer among naturally occurring high-molecular weight materials, and is the second most important substance after cellulose in wood and provides the tree with unique strength and elastic properties⁹. The structure of lignin is based on highly branched aromatic rings with many substituted groups, and consequently amorphous¹⁰; and the presence of complex carbon-to-carbon linkages between the units, makes it difficult to degrade the polymer to low-molecular fragments.

Lignin is derived from the radical polymerization of substituted phenyl propylene units. Softwood lignin precursor present more rapid oxidative cross-linking than hardwood lignin, which is desirable for high-yield cost-competitive carbonized derivatives¹¹. Softwood lignin is mainly composed of guaiacyl units, originated from its predominant precursor, trans-coniferyl alcohol; while hardwood lignin is composed of both guaiacyl, and syringyl units derived from trans-coniferyl, and trans-sinapyl alcohols respectively. Grass lignin contains p-hydroxylphenyl

unites derived from trans-coumaryl alcohol. In general, almost all plants contains guaiacyl, syringyl, and -hydroxyphenyl moieties¹². P-coumaryl, coniferyl, and sinapyl alcohols when incorporated into lignin, they are referred to as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, all presented in Figure I-5. Lignin compounds can be classified into two main groups: ether (C-O), and carbon-carbon (C-C) bonded lignins, which contains β -O-4, 5-5, β -5, 4-O-5, β -1, and β - β linkages, where β -O-4 is the most predominant¹³.



Figure I-5. The three precursors and resultant lignin structures.

In wood, lignin or native lignin, acts as a natural glue for fibres, and is also responsible for its yellow colour. The chromophores in lignin, responsible for the colour, mainly include quinoids, catechols, aromatic ketones, stilbenes, conjugated carbonyls with phenolics, and metal complexes. Additionally, there are some potential chromophores that can be produced upon oxidation, as leucochromophores, and some others derived from remnant carbohydrates¹⁴. Thus, lignin has to be removed in order to use wood cellulose for paper production or chemical cellulose for the manufacturing of cellulose derivatives, where the final colour is of importance.

Hydrogen bonding is recognized as one important linkage between cellulose and hemicelluloses as a result of the many suitable hydrogen bonding sites existing. Intramolecular hydrogen bonds also exist in cellulose and xylan. Linkages between lignin and polysaccharides are not hydrogen bonding, lignin is chemically linked to polysaccharides. In spruce wood, for example, a total of six lignin carbohydrate complexes (LCCs) have been identified, as glucomannan-lignin-xylan complex representing 48% of the lignin present in the wood, and xylan-lignin-glucomannan, 40% of the lignin¹⁵, Different interactions, such as the hydrogen bond network between

cellulose and hemicellulose, and covalent bonds between lignin-xylan and lignin-glucomannan, are present in woody biomass.

I.1.4. Others components

Apart of its major structural components, wood contains the so-called accessory compounds or extractives, and inorganic compounds. Extractives can be extracted with organic solvents or hot water. During pulping processes, the volatile fraction of the wood extractives is removed during pre-steaming and condenses from the relief condensates. The tall oil soap, from the non-volatile fraction, is removed during evaporation of the black liquor by skimming. The content and composition vary among the wood species, geographical site and season, and the absence of certain compounds causes yellowing of the pulp. The content of inorganic compounds is low (<5%) and they are entirely contained in the ash, the residue remaining after burning the organic matter. In Kraft pulping, high extractive contents of wood may result in a considerable reduction in pulp yield. The amount of extractives influences the refining of the pulp, the gluing and finishing of wood, as well as the drying behavior². Table I-2 lists the main extractives present in wood.

Volatile oils	Wood resins	Fats and waxes
Mainly softwoods	Mainly softwoods	<0,5%
Terpentines, monoterpenes,	Acidic diterpenes; resins of	Suberin
turpentine, tropolens	softwoods, basis of tall oil	
Tannins	Lignans	Carbohydrates
Hardwoods and softwoods	Hardwoods and softwoods	Typically food
Hydrolyzable tannins built	Optically active lignin dimer	reserves
upon glucose and gallic acid;	(controlled free radical	
condensed tannins,	coupling)	
flavonoid-based		

Table I-2. Main wood extractives²

I.1.5 Morphology of the fibre in wood

The wood cells are composed by cellulose, hemicelluloses and lignin, which are classified as framework, matrix, and encrusting materials respectively. Cellulose has mainly crystalline structure, while the hemicelluloses and lignin are amorphous. The following larger morphological unit, microfibrils with diameters of about 10-30 nm, are composed of aggregates covered by shorter hemicelluloses chains². Softwoods consist mainly of longitudinal fibres with a tubular structure of an average length of approximately 3.5 mm and a diameter of 30–35 μ m. For hardwoods, the length values are of approximately 1.1 mm, and 20-25 μ m of diameter¹⁶.



Figure I-6. Scheme of the cell wall layers and their composition².

Figure I-6 presents an illustration of the cell wall several layers and their chemical composition. Where ML refers to middle lamella, which functions as 'cementing' substance between cells: P to Primary wall, a loose aggregation of randomly arranged microfibrils; S to secondary walls, a compact region which contributes with most of the bulk cell material, as well to its physical and mechanical properties; and W, to warty layer².

I.2. Paper pulp

Pulping aims at separating cellulosic fibres to make pulp. There are two main technologies to produce paper pulp from wood: mechanical and chemical, which are presented below.

Mechanical pulping is the oldest pulping process, which can be performed with or without low quantity of chemicals. Compared to chemical pulps, lignin is not extracted but modified in order to become more plastic, and the fibre separation is enhanced by mechanical means. When performed without chemicals, the yield is of typically 90-98%, and are thus referred to as high-yield pulps¹⁷. As the separated fibres are partially damaged, mechanical pulps exhibit lower strength properties compared to chemical pulps, but are suitable for use in newsprint or other application with limited useful life. This process is usually limited to the long-fibred softwoods, and was used for many years, but its high energy requirements and excessive fibre damage have caused the largely replacement of the process.

Chemical pulping processes are dominant. Pulping is achieved by lignin removal from the lignocellulosic raw material, using chemicals and severe conditions (high temperature). During

pulping, most of the lignin is extracted, and hemicelluloses are partially depolymerised and removed. Softwoods give pulps with higher strength properties compared to hardwoods due to their longer fibres, but both species are used in the pulping industry.

Chemical pulping is carried out in water, in a digester, with the aim of damaging and dissolving lignin, the fibre binding agent, by the use of chemicals. Three chemical processes exist: soda, sulfite and Kraft pulping. Compared to mechanical pulping, chemical pulping generally produces higher pulp strength and paper quality, reuses chemicals and uses energy more efficiently¹⁷. However, they could present more pollution as chemicals are required. The conditions of sulfite pulping result in extensive hydrolysis of the carbohydrates, compared to Kraft pulping, and the final pulps typically have less strength potential than Kraft pulps in papermaking applications¹⁸.

I.2.1. Kraft pulping

The Kraft process is the most developed process in industry. It is mainly used for the production of packaging, and high strength papers and boards. It combines sodium hydroxide (NaOH) and sodium sulphur (NaS₂) as active delignifying chemicals, at temperatures in the range of 160-180°C, with a pH>12¹⁷. In parallel to delignification, cellulose and hemicelluloses are partially damaged but, in less extent, compared to the sulfite process. Despite the low fibre yield (45-50%)¹⁹, this process presents several advantages: it is able to process both hardwoods and softwoods, leads to pulps with high strength, the chemicals can be recovered, and the energy needed in the process is produced by burning the residual lignin²⁰. The main chemical reactions involved are described in the following paragraphs.

Cellulose is partially damaged to some extent in the Kraft process, mostly through the 'peeling' of its reducing end groups; but also because of alkaline hydrolysis, which strongly depolymerise the cellulose. The high yields in cellulose observed in the pulping processes lead to a successively increasing cellulose content up to high level in bleached pulp²⁰.

Reactions during the Kraft process

The dissolution of the lignin can be explained in three phases along the Kraft pulping: initial, bulk, and residual. *The initial phase* is characterised by the losses in carbohydrate fraction, where hemicelluloses undergo deacetylation and physical dissolution: peeling starts. The more important delignification occurs during *the bulk phase*, where both phenolic and nonphenolic β -O-4 ether bonds of lignin are cleaved, about 70% of lignin is removed. *The residual phase*

ends delignification and in parallel, lignin re-condensation as well chromophores formation occurs. The reactions occurring along the Kraft process are presented in Figure I-7. Yet, the lignin and chromophores present after the Kraft process contribute to the yellow colour of the final pulp, thus, bleaching sequences are required for bleached pulp applications.



Figure I-7. Delignification and respective reactions of wood components during Kraft pulping².

The main consumption of alkali takes place due to the rapid hydrolysis of acetyl groups in hemicelluloses; as well as primary peeling reactions of wood polysaccharides, where sugar units are lost one-by-one from the reducing end of the polysaccharide. During the heating period, *the initial phase* shown in Figure I-7, new reducing end groups are formed enabling secondary peeling. The peeling reactions are interrupted by competing stopping reactions, which convert the reducing end groups into stable carboxylic acid groups⁴. Under alkaline conditions, 4-O-methyl glucuronic acid contained both in softwood and hardwood xylans, is converted into hexenuronic acid (HexA) groups by elimination of methanol²¹; which are relatively stable, and contribute to the total amount of acidic groups in Kraft pulps. Moreover, cellulose is more resistant against alkali, compared to hemicelluloses, that degrade much more extensively²². In Figure I-8 presents the overall carbohydrate degradation reactions along the Kraft process: (1) Alkali-catalyzed hydrolysis; (2) stopping reactions of reducing end groups; (3) alkali-catalyzed peeling of reducing end groups; (4) formation and degradation of hexuronic acid groups (HexA).

As a consequence of peeling reactions and alkaline hydrolyses, the cellulose DP goes from 8000-10000 units down to 2000 units in Kraft pulp²³. Due to degradation and dissolution of polysaccharides in the black liquor, the carbohydrate yield loss in Kraft pulping is considerable and a major drawback of the process².



Figure I-8. Carbohydrate reactions in Kraft pulping²².

I.2.2. Bleaching sequences

To get white pulps for paper manufacture (or also for cellulose derivatives), bleaching processes are required²⁴. Bleaching is a chemical process applied to lignocellulosic materials to increase the brightness and its stability, as well as cleanliness, in the case of recycled fibres. It aims at removing and/or colour-strip residual lignin, which is the responsible of the colour.

Chlorinated compounds were the first oxidative chemicals used to bleach cellulosic pulps. During the 1990s, new regulations for the pulp and paper industry came forth due to the environmental issues related to high emissions of bio-accumulative and toxic chlorinated organic compounds in water bodies. As a result, elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching technologies were developed for pulp production as alternative to reduce the mentioned emissions²⁵. However, despite the significant reduction of adsorbable organic halides (AOX) emissions, TCF bleaching presents lower pulp strength and higher costs compared to ECF²⁶.

Regardless of the long discussion in the literature about the economic, environmental and technical aspects, ECF bleaching has become the dominant technology, representing 90-95%

in the production of bleached chemical pulp in the world. The main reasons to avoid TCF technologies include the poor efficiency of combined oxygen and hydrogen peroxide reactions resulting in high costs and low brightness stability; poor selectivity of ozone bleaching resulting in reduction of degree of polymerization of the cellulose; and technical issues and inefficiency during the early years of ozone bleaching technology development²⁷. Although the term ECF does not specify it, typically, chlorine dioxide is the principal bleaching agent for these processes.

The commonly used chemicals for bleaching include oxidants such as chlorine dioxide, oxygen, ozone, and hydrogen peroxide. Alkali is also applied with the use of sodium hydroxide to reinforce the lignin extraction after oxidation. The mentioned chemicals are dosed and mixed at determined pH and temperature conditions for a specified period of time. Bleaching chemicals are applied in sequences with intermediate washing steps, and its progress is monitored at the end of each stage by measuring lignin content, pulp brightness, and residual chemicals in the effluents. Table I-3 presents a summary of functions, advantages and disadvantages of the main bleaching processes.

Oxidant	Function	Advantages	Disadvantages
Chlorine Dioxide	Oxidises, decolorizes and solubilizes lignin	Achieves high brightness without loss of pulp strength; good bleaching Low cellulose depolymerisation	Must be made on-site; cost, some organochlorine formation, highly corrosive, no effluent recovery
Oxygen	Oxidises and solubilizes lignin	Effective for delignification Low chemical cost; provides chloride-free effluent for recovery	Requires significant capital equipment when used in large amounts; potential loss of pulp strength – cellulose DPv loss
Hydrogen Peroxide	Oxidises and decolorizes lignin	Easy to use; low capital cost, chlorine free chemical	High chemical cost; poor bleaching efficiency; can cause loss of pulp strength – cellulose DPv loss
Ozone	Oxidizes, decolorizes and solubilizes lignin	Effective for delignification; provides chloride-free effluent for recovery	Must be made on-site; costs; cellulose depolymerisation

Tabla	I_3	Advantages	and	dicadvantages	of	the	main	chamicals	hoau	in	blooching	stages24
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Alkali	Adjusts the pH to	Effective and economical	Darkens pulp, expensive
Sodium	alkaline		
hydroxide	conditions, and		
	for favours lignin		
	dissolution		

Each chemical presented in Table I-3 are represented by letters: D for chlorine Dioxide, ClO_2 ; O for oxygen, O₂; P for hydrogen peroxide, H₂O₂; Z for Ozone, O₃; E for sodium hydroxide extraction, NaOH. Typical bleaching sequences used in mills are: DED, D(EO)DED, ODED, OZ(EO)D. A diagram of a common bleaching sequence is presented in Figure I-9.



Figure I-9. Block diagram of chemical pulp bleaching (ODE₀D sequence)²⁴

The main characteristics of bleached paper-grade pulps are: brightness values higher than 85% ISO, the content of lignin represented by the Kappa number is lower than 1 for Kraft pulps (ECF and TCF), but in the case of TCF sulfite pulps, the value can increase up to 6.2; viscosity values range between 600-800 mL/g for Kraft pulps, and higher than 800 mL/g for sulfite pulps. For both Kraft and sulfite pulps, the alkali resistance values, represented as R18, are above 87%; regarding the carbohydrates content, glucose is above 70%, the rest of the fraction is mainly represented by mannose, galactose, xylose, and arabinose, and its proportion depends on the origin of the substrate².

Highlights about bleaching technologies

Because the colour of pulps is due to lignin, bleaching can be obtained either by delignification and/or by colour-stripping. O and D stages are mainly delignifying processes. Oxygen and chlorine dioxide react on lignin phenolic units, on the phenol functions to create muconic acids. This oxidized lignin is also partially depolymerized. All these reactions render lignin soluble in the bleaching medium. Then lignin is removed during washing steps placed between two bleaching stages. Parallel to delignification, cellulose may be also damaged. In the case of D stage, cellulose is preserved, which is the reason why chlorine dioxide is widely used in bleaching sequences. Most of the TCF sequences have implemented an ozone stage, as it is by far the most powerful chlorine-free oxidant available. The main drawbacks of this technology are not only cost-related, but also the extensive carbohydrate degradation, and increase in the carbonyl content, may lead to further depolymerization in the following alkaline stages, and could also decrease the brightness stability²⁸. O stage is often considered at the beginning of the bleaching sequence, but also used in TCF sequences combined with hydrogen peroxide or chelating stages²³.

The P stage could be used as a delignifying and/or a color-stripping agent, depending on the temperature applied during bleaching. The structures responsible for colour are polarizable groups (conjugated carbonyl groups, enones and quinones), able to react with hydrogen peroxide in alkaline medium by the action of the perhydroxyl anion (HOO⁻) at low temperature between 60 to 75°C. The reaction leads to selective oxidation into non-colored compounds²⁹. The destruction of these chromophores results in the whitening of the pulp, without lignin removal. At higher temperature, above 80°C, hydrogen peroxide is decomposed into highly reactive radicals, °OH, able to depolymerize the lignin, which is further removed by washing. In parallel cellulose is also attacked by these radicals leading to a partial cellulose depolymerization. The mentioned mechanisms of hydrogen peroxide will be further explained in Chapter III.

I.3. Dissolving pulps

I.3.1 Regenerated cellulose

Cellulosic fibres play an important role among raw materials for the textile industry. They are used for the production of apparel, household fabrics and various non-woven fabrics. The mentioned fabrics, such as non-woven, knitted fabrics, may be made of cellulose alone or in combination with other synthetic fibres. Cellulosic fibre-based textile products include feminine hygiene products, absorbent products, household wipes, babies' wipes and diapers, pillowcases, surgical dressings and shoe linings³⁰. There are two types of cellulose fibres sources: the natural ones mainly from cotton, which are only processed as much as needed to clean the fibres for use; and the manufactured ones, which come from processed pulps.

The key advantages of using natural cotton fibres compared to synthetic fibres are numerous. Cotton fibres are a renewable source, thus biodegradable; can be incinerated for energy recovery, have a lower specific weight which results in higher specific strength and stiffness; and are produced with low investment cost. Unfortunately, some of the listed disadvantages limit their application in the industrial level. Indeed, the availability and the quality of natural fibres as cotton strongly depends on variable factors: the weather; moisture absorption swells the fibre; a poor fire resistance; and its final price may fluctuate according to harvest or agricultural politics³¹.

For all these reasons, the textile industry is focusing on regenerated cellulose fibres. Regenerated cellulosic fibres are derived from cellulose which is obtained from cotton linter, wood, or bamboo. Regenerated cellulose is a class of materials manufactured by the conversion of natural cellulose to a soluble cellulosic derivative and subsequent regeneration, typically forming either a fibre (i.e. rayon) or a film (i.e. cellophane). After regeneration, the physical organization of the cellulose chains is re-organized leading, in the case of textile products, to a yarn with good strength properties. Rayon is a generic term for any regenerated cellulose fibre including viscose, modal, and lyocell (Lenzing AG).

In fact, there are two regeneration processes: derivatizing and non-derivatizing (direct dissolution) process. In the derivatizing process, cellulose is chemically modified to favour its dissolution, while in the non-derivatizing process, the cellulose is directly dissolved in the solvent without modification³². Figure I-10 presents a scheme with the classification of cellulose regeneration processes.



Figure I-10. Scheme with the current classification of cellulose regeneration processes

Rayon or viscose is one of the most common manufactured cellulose fibres in the textile industry. It can be produced out of wood pulp. This process will be further discussed in the following section.

I.3.2. Dissolving pulp production

Dissolving cellulose means to break the strong hydrogen bonds in between the cellulose chains and to replace them by interactions with a solvent or by derivatization of the cellulosic OH-groups³³.

By the end of 2014, the pre-hydrolysis Kraft process (PHK) represented 56% of the world dissolving pulp production, whereas the acidic sulfite (AS) process represented 45%. 88% PHK and 80% of AS dissolving pulps were used for viscose production³⁴. When using softwoods and hardwoods as raw materials, drastic conditions are needed in order to obtain a high-quality dissolving pulp as residual impurities can adversely affect its final properties².

The dissolution behaviour of the cellulosic substrates is defined for each pulping process. Cellulose is mostly preserved in sulfite pulps, whereas xylan is most stabilized in Kraft pulps due to its high resistance towards alkali. On the other hand, galactoglucomanan (GGM) is less degraded during sulfite pulping, which contributes to the higher yields of softwood sulfite pulps compared to Kraft pulps.

The sulfite process has been used to produce dissolving pulps for many decades². Sulfite pulping for paper production can be carried out under acidic, neutral or alkaline conditions. But for dissolving pulp production, only acidic conditions may be used. The main reason is the high cellulose purity required, and hemicelluloses are better removed at low pH. For paper production, the dominant interest is the fibre properties, whereas in the dissolving pulp production, the cellulose purity gains all the interest³⁵. A typical sulfite cooking process is performed on aqueous sulfur dioxide, and a base-calcium, sodium, magnesium, or ammonium, depending on the recovery system. The lignosulfonates generated in the liquor could be used as raw material for further chemical production¹⁹.

The sulfite process takes place at approximately 150 °C for 6 to 8 hours. After pulping, cellulose is purified by a hot alkaline treatment (HCE: Hot Caustic Extraction) or cold alkaline treatment (CCE: Cold Caustic Extraction). The extraction step can remove residual hemicelluloses by peeling mechanisms, without important decrease in the cellulose degree of polymerization. Following the extraction step, classical bleaching sequences are applied to remove the residual

lignin in order to reach the desired brightness. As the residual lignin is sulfonated (lignin molecule sufficiently hydrophilic to be dissolved in the cooking liquor²), it is also easier to be removed in pulp bleaching processes. Finally, the pulps are treated with sulfuric acid or hydrochloric acid aqueous solution to remove remaining mineral components. Drying conditions are important to control the reactivity of the cellulose, i.e. for acetate production, the drying temperature should be low at $65-70^{\circ}C^{36}$.

The PHK process is carried out in a combined process of acidic (prehydrolysis), where the hemicelluloses are extracted from the wood chips, followed by the Kraft pulping process, and finally by a multi-stage bleaching sequence to reach the desired purity of the dissolving pulp². The insertion of the prehydrolysis step prior to any alkaline pulping process leads to the production of high cellulose content pulp, which means less hemicelluloses content, thus less pentosan. Moreover, prehydrolysis could increase the lignin extraction during the subsequent steps in the alkaline pulping process, which in consequence could contribute to the reduction of ash content. The PHK process converts the hemicelluloses fraction of the initial wood pulp into a commercially valuable mixture of sugar oligomers and monomers³⁷. Hence, the aim of including a PHK step is to open up the cellulose fibres for further reactions and to decrease the hemicellulose (pentosan) and ash content³⁸.

The PHK process is carried out at high temperatures (160-180°C) and acidic pH (3-4) with water or steam alone, or diluted mineral acid. In the process, acetic acid is generated as the hemicelluloses are deacetylated. The acidic conditions hydrolyse the bonds between hemicelluloses and other components in the wood chips, which further degrades them to form oligosaccharides and monosaccharides. As the reaction continues, with the formation and dissolution of acids, the pH continues to decrease, leading to the dissolution of hemicelluloses³⁹. Yet, severe hydrolysis should be avoided since not only hemicelluloses but also cellulose can be affected, resulting in lower yield and brittle fibres. It can also increase the lignin condensation, resulting in higher Klason lignin⁴⁰.

I.3.2.1. The end products of dissolving pulps

Dissolving pulp is the main feedstock for manufacturing regenerated cellulose, and cellulose derivatives. The main products obtained from dissolving pulps are used in textiles, tires, coatings, paints, and tobacco products, as well as in food and pharmaceutical products⁴¹. A summary of these applications is shown below in Table I-4.

Manufacturing Process	Products	Applications		
Xanthation	Viscose	Textile, non-woven, tire cord, cellophane,		
		sausage skin, sponge, industry yarn, etc		
Acetylation	Acetates	Film, cigarette tow, plastic, acetate		
		yarn/fibre, etc.		
Nitration	Nitrates	Explosives, lacquers, celluloid, etc.		
Etherification	Ethers	Binder, glue, thicker, etc.		

Table I-4. End products of dissolving pulps

Dissolving pulps are characterized through the cellulose purity, the low content of hemicelluloses, and inorganic components, the brightness, the cellulose degree of polymerisation and the reactivity to derivatization processes and finally solubility. Depending on the application, the values expected vary, and are presented in Table I-5. In general, high cellulose content (R18), is required. Low dissolving pulp grades exhibits a cellulose content of approximately 90%, while medium and high grades have a cellulose content of 94 to 95% and greater than 96% respectively⁴¹. The low and medium grades are used for textile and cellophane production, while the high grades are mainly used for cellulose acetate and other specialty products.

Preferred Ap	plication	Viscose	Ether (HV)	Viscose	Acetate	Acetate
Raw Material		Hardwood	Softwood	Hardwood	Hardwood	Cotton
Cooking P	rocess	Sulfite	Sulfite	РНК	РНК	Linters
Brightness	%ISO	92.2	90.2	90.7	92.2	87.9
R18 content	%	93.4	95.2	97.9	98.2	99.0
Xylan	%	3.6	3.1	1.5	0.9	0.2
Carbonyl	µmol g-1	18.8	6.0	4.3	4.4	3.7
Carboxyl	µmol g-1	35.6	59.8	32.0	15.0	12.4
DPw		1790	4750	1400	2100	1250
DPn		277	450	460	650	700
PDI		6.5	10.6	3.0	3.2	1.8

Table I-5. Characteristics of dissolving pulps according to the pulp application²

Additionally, in Figure I-11 is presented two relevant characteristics monitored for the production of dissolving pulps, i.e. viscosity (mL/g), and purity (cellulose content, R18 %). This information was obtained from industrial partners of LGP2. It displays the key characteristics of some dissolving-pulp applications: acetate, textiles (green), MCC, cellulose, cellulose nitrates, and a bleached Kraft pulp.



Figure I-11. Viscosity (mL/g) vs hemicelluloses (%), for dissolving pulp applications. Information extracted from LGP2.

Regarding the chemical properties of dissolving pulps, it is essential to remove non-cellulosic carbohydrates, which constitute the major part of short-chain materials in a polymer. Hemicelluloses decrease the reactivity of pulp by blocking the hydroxyl groups⁴². During the first step of the viscose and etherification processes, steeping, the hemicelluloses are removed. The accumulation of hemicelluloses inhibits the mercerisation of cellulose during ageing and hemicelluloses react with carbon disulphide in xanthation, thus leading to a non-homogenous cellulose derivatization which further affects viscose filterability³⁴. When exceeding a certain hemicelluloses concentration level, the cellulosic yarn tenacity can be altered due to incorporation of low molecular-weight hemicelluloses; a good quality of viscose solution implies low content of non-cellulosic impurities which includes pentosans, certain inorganic substances, and resins. Hemicelluloses also contribute to discoloration of the resulting product, and particularly the xylans⁴³. For the case of acetate pulps, it is required high-purity with less than 1,5% hemicelluloses and no detectable residual lignin. When using the lower grade dissolving pulps (higher hemicelluloses content), the formation of hemicellulose acetates such as xylan acetate and glucomannan acetate results in industrial problems on filterability, turbidity (haze), and false viscosity 36 .

I.3.3. Regenerated cellulose processes

From many years, the viscose process, a derivatizing process, is the most dominant process for the production of regenerated cellulose fibres. Other processes such as Lyocell or Cupro (non-derivatizing processes) exist but are still rather limited. A comparison between the Lyocell process and the viscose process is presented in Figure I-12.

Process	Lyocell process/ fibers	Viscose process/ fibers		
Dissolution	NMMO direct dissolution Physical dissolution Without chemical reactions	NaOH /CS ₂ Mercerization/ xanthation Chemical reaction		
Spinning	Dry-jet wet spinning Direct dissolution to form highly viscous dopes Fibers are formed <i>via</i> a) an orifice spinneret in a dry form into an air gap, b) then in a coagulation bath. Irregular molecules arrangement to form crystallites laminas (Wendler <i>et al.</i> 2011; Ramamoorthy <i>et al.</i> 2014;).	Wet spinning Dopes with relatively low viscosity Fibers are formed using spinneret immersed in an aqueous bath containing sulfuric acid and additives. Stretching is done after the regeneration. The formed fibers are relatively amorphous, with low-tenacity (Wendler <i>et al.</i> 2011; Ramamoorthy <i>et al.</i> 2014).		
Environment	Environmentally friendly > 99% of the solvent recovered No harmful by-products formed High energy demand for solvent recycling	Heavy environmental loads CS ₂ (about 25-30%) not recovered (may also be converted to by-product) High demand for water		

Figure I-12. Comparison between Lyocell and Viscose process⁴⁴.

The Lyocell process uses the direct cellulose dissolution in the N-methyl morpholine-N-oxide (NMMO) solvent, making this process more environment-friendly, contrary to the viscose process, which requires a toxic chemical, CS₂. Moreover, more than 99% of NMMO solution can be recovered and reused in the process, and NMMO is biodegradable and does not produce harmful by-products⁴⁵. When comparing the properties of the final products of both processes, the average degree of polymerisation and the crystallinity of the lyocell fibres are higher, which leads to very high strength and Young modulus in comparison of viscose fibres. However, its overall production cost is still higher than viscose⁴⁴.

Briefly, the viscose process dissolves cellulose fibres into a spinnable solution using controlled and co-ordinated steps which later convert them into longer filaments. At the end of the process, these filaments are cut into staple fibres by maintaining the length, denier, cross-sectional shape, and other properties³². The conventional viscose process uses carbon disulphide (CS₂) to derivatize cellulose before regeneration. However, CS₂ is a toxic and harmful chemical, which is the main reason why the development of dissolving technology without the use of this chemical became of practical interest⁴⁴.

During the viscose process, the pulp is first steeped in an aqueous solution of sodium hydroxide to swell the fibres and convert the cellulose into alkali cellulose. After, the swollen mass is pressed to obtain a precise ratio of alkali to cellulose, which is then shredded to provide adequate surface area for uniform subsequent reactions. The alkali cellulose is aged to depolymerise the cellulose by oxidation to the desired degree of polymerisation prior to the reaction with carbon disulphide (CS_2) to form sodium cellulose xanthate. The xanthate is diluted

in sodium hydroxide to yield a viscose orange-coloured solution called viscose. The solution is then filtered, deaerated, and ripened to the desired point appropriate for spinning. The rayon filaments are formed when the solution is extruded through very small holes into a spin bath consisting of sulphuric acid, sodium sulphate, zinc sulphate and water. Coagulation of the filaments takes place immediately upon neutralizing and acidifying the xanthate to cellulose, which are key steps to achieve the desired tenacity and other properties. Finally, the filaments are washed, chemically treated (desulphurised) and bleached prior final wash. The filaments are collected continuously (yarns or tow) or as cut staple, prior drying and packaging⁴⁶.

The xanthation reaction, presented in Figure I-13, takes place on the hydroxyl groups of cellulose. It requires 32-34% of CS₂, which is significantly higher than the stoichiometric requirement (23,5% w/w of the cellulose) due to formation of byproducts⁴⁷. The excess is used to avoid difficulties downstream but it impacts raw material consumption as well as an overall environmental footprint. As CS₂ partly reacts with free NaOH in the alkali cellulose, the xanthation reaction also yields to the formation of by-products⁴⁸. Sodium trithiocarbonate, produced from the side reaction, gives to the viscose dope its characteristic orange colour. All the by-products consume sulphuric acid during the regeneration process.



Figure I-13. Main reactions of the viscose process: A, cellulose xanthation, and B, regeneration of cellulose.

The estimation of the dissolving ability is key when producing dissolving pulps. Yet, the more accepted way to represent it, is the Fock test, which is a time-consuming procedure, and requires the use the harmful chemical, CS_2 . The Fock test reproduces the viscose process, while
measuring the amount of regenerated cellulose (%) produced from dissolving pulp fibres³⁴. Several attempts have been investigated to find alternatives for the estimation of the dissolving ability and are further discussed in the following section.

To conclude this part, it has been revised that the production of dissolving pulp is polluting (viscose process) or costly (Lyocell process). Therefore, one of the challenges of the present PhD project, is producing dissolving pulps from unbleached Kraft pulp using classical chemical products for the pulp industry but by applying unconventional conditions. The main challenge is to remove hemicelluloses of paper-grade pulps, while reaching all the other desirable characteristics. Some research has been initiated at LGP2, which will be considered as base line to the development of the thesis. Interesting results found in the literature, included those from LGP2, are discussed in the section below.

I.3.4. Upgrading of bleached Kraft pulps into dissolving pulps

The increasing demand of cellulose derivatives had led to the conversion of several Kraft mills into dissolving pulp mills, generally by adding a pre-hydrolysis before Kraft pulping. However, this conversion represents high investment costs. Many studies for decreasing the cost of conversion have been performed in the late years⁴⁹.

As hemicelluloses are an important component for paper-pulp grades, they should be removed for dissolving pulp applications. The selective removal of hemicelluloses is a key issue. Systems using extraction with enzymes, Nitren, Cuen, NaOH, KOH, and many others can be found in literature. Some of them are described below.

Hemicelluloses removal from paper-grade pulps

Hemicelluloses are amorphous and very sensitive to alkaline solution, which results in the increase of the alkali viscosity. Moreover, the viscous alkali solution has difficulty to diffuse into cellulose microfibrils to react with cellulose, affecting directly the homogeneity of alkali cellulose; the large amount of short chains and reducing ends in hemicelluloses consumes part of the oxygen. As a consequence, the hemicelluloses prolong the pre-aging time required during the viscose process. The amorphous hemicelluloses have a negative influence on the xanthation process as they can react with carbon disulphide faster, compared to cellulose, leading to poor final dissolution of the cellulose xanthate. Finally, hemicellulose can also decrease the mechanical strength of final products⁵⁰.

To upgrade bleached Kraft paper-grade pulp into dissolving-grade pulps, enzymatic treatments have been proposed. Research has been performed in order to obtain higher reactivity, higher alpha-cellulose content (alpha cellulose has the highest degree of polymerization, and is the chief constituent of paper pulp and dissolving pulps; beta and gamma cellulose refers to hemicelluloses⁵¹), and desirable pulp viscosity. Combination of treatments have been proposed: EG-rich cellulase treatment followed by an alkaline peroxide stage⁵²; xylanase treatment followed by a cold alkaline extraction and a final endoglucanase treatment; and combinations of cold caustic treatment and acid-hot caustic treatment^{53,54,55}.

Cellulases are enzymes which can hydrolyse the 1,4- β -D-glycosidic bonds of the cellulose chain. For dissolving pulp, cellulase treatment improves the reactivity significantly, while controlling the molecular weight of the dissolving pulp⁵⁰.

Xylanase treatment is a promising alternative for removing hemicelluloses, as xylan accounts for a large proportion in the hemicelluloses, especially in hardwoods. However, the low accessibility of xylan inside the fibre wall causes that the efficiency of xylanase is not as high when treating isolated xylan. This accessibility can be boosted by improving the fibre morphological characteristics by mechanical refining, thus improving enzymatic xylan removal.

Still, the removal efficiency with only enzymatic treatments is limited. *Köpcke et al*⁵⁶, investigated the increase of accessibility and reactivity of bleached Kraft pulps using enzymatic treatments using commercial endoglucanase and xylanase. To reach properties close to the commercial dissolving-grade pulps, a combination of enzymatic treatment was used, as well as the introduction of an alkali extraction. Only the later combination allowed to reduce the hemicelluloses content to 2-4%, while achieving a commercial dissolving pulp-like reactivity of 65-70% (Fock test). However, the pulp viscosity was considerably affected⁵⁶.

For birch Kraft pulp, selective extraction of xylan resulted in a high purity pulp, with 95% of cellulose content, value not achieved when using NaOH and KOH extraction. For Eucalyptus Kraft pulp, extractions with Nitren and NaOH exhibited similar cellulose content, 97%. The highest cellulose content obtained for beech sulfite pulp was 97.5% when applying 10% NaOH charge. But, when using Nitren extraction, the beech sulfite pulp achieved only 96.5%, related to the inability of Nitren to remove mannans, present in the beech.

Studies on organosolv pulps have been also performed. For example, dissolving pulp properties were obtained when applying an additional oxidative stage after TCF bleaching of Acetosolv beech pulp. The more interesting results were observed when using treatments with peracetic acid or oxygen followed by hydrogen peroxide, obtaining a final brightness of 89% ISO, 604 mL.g⁻¹ viscosity, and 4.5% xylan content⁵⁷.

Another approach was to separate hemicelluloses from paper-grade Kraft pulp by means of ionic liquid/cosolvent systems, which is what the Ioncell process proposes. This process is considered as an environmental benign fractionation concept. The hemicelluloses content could be reduced from 16.6% to 2.4% while maintaining cellulose. The solvent used was 1-ethyl-3-methylimidazolium acetate (EMIM OAc), with stirring conditions of 3 hours at 60°C, and consistency of around 10.5%; as a comparison, a CCE with 2.5 M NaOH at room temperature with a liquid-to-solid ratio of 20 L/kg for 1 hour has been performed. The more favourable results were obtained with the EMIM OAc solvent, with a final pure cellulose, and fraction of hemicelluloses, without any depolymerisation, yield losses, or effect on the crystallinity^{58–60}. The use of this solvent should allow a simple integration into cellulose regeneration processes, such as Lyocell production for films or textile fibres. Nevertheless, the commercial realization of this technology strongly depends on the efficient solvent recovery⁶⁰.

At LGP2, related researches have been performed.

*Arnoul-Jarriault et al*⁵³. investigated the upgrading of softwood bleached Kraft pulp into dissolving pulps by cold caustic treatment and acid-hot caustic treatment. The study presented a comparison in between different NaOH concentrations, temperatures, and reaction times; and the effect on different pulp properties, such as the DPv, the sugar content, and the dissolving ability estimated by the Fock Test. 70% of hemicelluloses were successfully removed when using a modified CCE process carried out at 90-110°C. However, most of the cellulose was converted into cellulose II. An alternative was explored, an acid stage at high temperature (up to 150°C), followed by a hot caustic extraction at 110°C (A-HCE). Cellulose showed not to be degraded when using CCE but it was significantly affected when using A-HCE. Yet, no cellulose II was produced in A-HCE, which should lead to an improved reactivity, thus acceptable properties for viscose grades pulps⁵³.

*Golestani et al*⁵⁵. investigated the combination of a cold caustic extraction (CCE) with different enzymes for the removal of hemicelluloses. CCE was performed with 11% NaOH, 100g of pulp at 10% consistency. It was observed that CCE alone was more efficient on softwood than on

hardwood, as the xylan present in hardwood was much more difficult to remove. Final pulp DPv values slightly increased, suggesting the dissolution of carbohydrates of lower molecular weight (hemicelluloses), without any major effect on the cellulose fraction, which was confirmed with the molecular weight distribution (MWD) profiles. However, the more interesting results, regarding to the removal of hemicelluloses have been obtained when CCE treatment was applied after an enzymatic treatment: the percentage of hemicelluloses dropped from 13.7% to 6.2% in softwood pulps, and from 24.3% to 7% in hardwood pulps. In parallel of her work on hemicelluloses removal, Golestani investigated the NaOH:urea:water systems as a new dissolving pulp solvent. NaOH:urea:water with the ratio of 7:12:81wt% precooled to -12°C showed to be a proper solvent for cellulose dissolution. The dissolution behaviour of this system was linearly correlated with the degree of polymerization of each substrate, regardless of cellulosic substrate origin. The mentioned study considered hardwood and softwoods pulps produced by PHK, sulfite, and Kraft processes, as well as cotton linters.

Unconventional use of hydrogen peroxide

A proper viscosity is required for the different applications of dissolving pulps. i.e. a viscosity in a range of 400 mL/g is preferable for viscose applications, but 600 mL/g for acetates². Thus, a good control of the degradation of the cellulose in pulps is desirable. The research at LGP2 explores the usage of chemicals commonly found in mills to upgrade Kraft pulp into dissolving pulp. Hence, hydrogen peroxide, which is commonly used for bleaching stages, and because of its low environmental impact, became interesting for the present PhD study.

*Walger et al*⁶¹. studied the improvement of the efficacy of hydrogen peroxide in neutral and alkaline pH to colour-strip recovered fibres. The study included the use of the copper phenanthroline complex to activate the pulp oxidation with hydrogen peroxide. Copper (II)-Phenanthroline complexes, from now referred as Cu(Phen), have shown to activate hydrogen peroxide improving decolouration. Walger showed that the H₂O₂/Cu(Phen) system is a Fenton-like system, generating hydroxyl radicals. The intensity of the radical production depends on the pH of the reaction. However if bleaching is improved, cellulose is also partially damaged⁶¹. The same system has been investigated by *Vladut et al*⁶². for the activation of hydrogen peroxide to delignify softwood Kraft pulps. Again, the efficiency is strongly dependent on the pH of the medium, where pH>9 is needed for delignification, but pH>11 preferable to achieve the maximum delignification. It also noted that the addition of this complex allows P-stages to be performed under lower temperatures (50°C), with only 0.05% Cu(Phen) complex; obtaining a

delignification rate with more than tripled in 1 hour. As in the work of Walger, it was concluded that the main oxidant in this system is the hydroxyl radical.

The H₂O₂/Cu(Phen) system will be tested in the present study to upgrade paper grade pulp into dissolving pulps. Results will be presented in Chapter III.

I.4. Microfibrillated cellulose

Microfibrillated cellulose (MFC) refers to a cellulosic material, moderately degraded, with expanded high-volume and large surface area, obtained by a homogenisation process. MFC consists of aggregates of cellulose microfibrils, with fibre diameter in the range of 20-60 nm, and a length of several micrometres⁶³. Contrary to cellulose nanocrystals (CNC), MFC has both amorphous and crystalline parts presented in a web-like structure. Additionally, the high ratio of length and diameter (L/d) for MFC provides a low percolation threshold, and as MFC are highly entangled, it renders a good ability to form rigid network and gels⁶⁴.

I.4.1. The market for MFC

Biomaterials such as MFC has gained attention of researchers due to their biodegradability, good tensile strength and rigidity, low density, biocompatibility, and high availability. MFC have interesting properties such as mechanical reinforcement, binder, film-forming, bio-sourced plasticizer, and absorber of active molecules. Moreover MFC can be obtained from various sustainable raw materials (plants)⁶⁸. Applications goes from cements, inks, cosmetics, nanocomposites, films, fibres, coatings, papermaking, and much other applications in fields such as health, biomedicine, and electronics⁶⁹.

I.4.2. MFC production

Generally, the production of these materials consists of pre-treatment steps, which are followed by refining steps. The pre-treatments aim to purify and homogenize the material to ensure a more consistent reaction in the following treatments. In most cases, additional chemical or enzymatic treatments are performed in order to ease the control in the fragmentation of the cellulosic material during refining⁶⁹. In addition, several kinds of mechanical treatments can be used. A schematic of the production ways is represented in Figure I-14.



Figure I-14. Schematic diagram of MFC production⁷⁰.

Depending on the application, different characteristics become more relevant than others. For strength additive in paper and paperboard products, high mechanical properties are expected. MFC can used in papermaking applications to enhance: strength, barrier properties in food packaging, paper gloss, reduction of grammage, and to enable smart packaging (security papers)⁷¹. *Boufi et al*⁷², used modified or not nanofibrillated cellulose (CNF), and observed that several properties were enhanced, such as mechanical properties, water absorption, density, and barrier properties, in comparison to paper without any kind of CNF. The fibres seemed more packed thanks to the CNF acting like a binder in paper⁷².

For some applications, the cellulose fibril dispersions are expected almost transparent and highly viscous, and these characteristics can be reached by using the most common pretreatment, oxidation of cellulosic fibres with 2,2,6,6-tetramethylpiperine-1-oxyl (TEMPO). TEMPO-mediated oxidation certainly helps to reduce costs in mechanical treatments, it is a very expensive reactant whose price can easily surpass energy consumption. Therefore, TEMPO-mediated oxidation is not attractive to industrial manufacturing given the other alternatives⁶⁸; Indeed, a large amount of research is focused on finding alternatives. On the other hand, when referring to adhesive's applications, the transparency factor is not as relevant, and even MFC with lignin fractions, can be suitable. It has been observed that fibrillated sugar beet, and fibrillated NaOH pre-treated beech wood performance showed to be very promising with values up to 60% of the strength of standard industrial adhesives⁷³. Other potential MFC applications include barrier films, antimicrobial films, transparent films, biomedical implants, pharmaceuticals, drug delivery, fibres and textiles, templates for electronic components, separation membranes, batteries, supercapacitors, electroactive polymers, and many others⁷⁴.

Among chemical pre-treatment, TEMPO is the most recognised. It is known to weaken the fibre structure, thus decreasing the mechanical energy consumption by a factor of 100, in the following mechanical treatment. During TEMPO-mediated oxidation, primary hydroxyl groups of carbohydrates are converted into carboxyl groups in the presence of a primary oxidizing agent (sodium hypochlorite) and halogen salts (sodium bromide or sodium chloride) (Figure I-15). TEMPO catalyses this reaction. Attempts have been done in order to reduce the chemical usage, and therefore production costs⁶⁸. Even though, by reducing chemical usage the quality of the final product was not significantly affected, other parameters, such as energy demands should be considered when referring to industrial scaling.



Figure I-15. Possible routes for selective oxidation in the presence of nitroxyl radicals or periodates⁷⁵.

Another interesting treatment, already investigated, is the oxidation of carbohydrates by periodate ion. Periodate is known to produce dialdehyde cellulose (DAC). The aldehyde groups serve as reactive chemical anchors for further reactions, which could enhance chemical derivatisation of cellulose⁷⁶. Experimental research has been done in order to optimise the periodate oxidation in aqueous conditions, because applied on polysaccharides, periodate oxidation seems to depolymerise. The mechanisms of oxidation can be multiple, one possible route is presented in Figure I-15. As periodate is unstable and decomposes over time to form radicals, oxidations are generally performed in dark environment with the absence of oxygen, and using freshly prepared solutions. Remaining metals in the pulp should be removed as they can catalyse the formation of free radicals and can promote depolymerisation⁷⁶. After periodate oxidation it has been observed a decrease in cellulose crystallinity⁷⁷, almost linearly with the introduction of aldehyde groups; and the oxidation of high molecular weight areas in early stages of the reaction.

To conclude, micro and nanomaterials present very different properties than regular cellulose fibres obtained from mills, mainly due to their micro and nanoscale size, fibril morphology and large surface area. As shown in Figure I-14, MFC can be produced with a combination of steps, including chemical modifications. Thus, another challenge of the PhD thesis arises, and is to study the development of processes that favour the conversion of bleached Kraft pulp into MFC, with the mechanisms revised in the present thesis. Currently, in LGP2 there is investigation on going to convert Kraft pulps into MFC, with different methods and chemicals, with the intention to find alternatives to TEMPO oxidation. Details on the DAC production, as well as attempts to replace a chemical step to produce MFC are further presented in Chapter IV, and Chapter V respectively.

I.5. Conclusion

The upgrading of paper-grade pulp into dissolving-grade pulp, and microfibrillated cellulose with minor modifications of the available resources and technologies in the industry, is of main interest as the demand for cellulose-based materials increases.

Regarding the dissolving pulps, many authors investigated different systems in order to selectively remove hemicelluloses, while improving dissolving ability, obtaining a uniform cellulose molecular weight distribution (MWD), and avoiding significant effects on the cellulose degradation. To accomplish these objectives, a number of chemicals, or combination of treatments have been tested, such as NaOH, KOH, periodate oxidation, enzymes, ionic liquids, etc. But currently no industrial-scale solution has been found. On the other hand, the industrial production of MFC does not progress rapidly despite its high demand, due to the high energy required to deconstruct the fibre. Chemical and enzymatic treatments prior mechanical treatment have been proposed, but all of them with limitations. To this date no economical viable solution has been proposed.

The present PhD project attempts to develop processes for the production of dissolving grade pulps and MFC from classical paper grade pulps by using a traditional bleaching chemical, hydrogen peroxide, in unusual operating conditions. The process is to be design in order to favour the oxidation and controlled depolymerization of cellulose, as well as the weakening of the cellulosic fibre wall. One advantage is that hydrogen peroxide is an environmentally friendly chemical. Based on the work of Walger, done at LGP2, the $H_2O_2/$ Cu(Phen) oxidative system will be first investigated. The assumptions considered are: the strong depolymerisation effect of this system will first remove short chain carbohydrates, as hemicelluloses, and that the hydroxyl radicals generated during the reaction will favour the fibre weakening.

This literature review also highlights the estimation of the dissolving ability as a key parameter. Today, the reference method is the Fock test, which reproduces the viscose process at laboratory scale. The Fock test is a time-consuming procedure which requires a harmful chemical, CS₂. Some research has been done in order to find alternatives and more convenient ways to get estimation of this property. At LGP2, interesting findings have been observed when correlating the morphological properties of the fibres to their dissolving ability, or when observing dissolution behaviours in other systems. Before starting the study of the H₂O₂/Cu(Phen) oxidative system to upgrade paper pulp into dissolving pulp (chapter III, and IV) and MFC (Chapter V), the chapter II presents the development of an alternative method to the Fock test.

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II. Development of a new method to evaluate the dissolution ability of cellulosic pulps.

II.1. Introduction

The cellulose dissolution ability is a key property for dissolving grade pulps. Before studying new oxidative treatments to convert conventional Kraft paper grade pulp into dissolving pulp, methods to characterise the cellulose dissolution ability have been investigated.

As mentioned in Chapter I, the Fock Test is the recognized method for the characterization of commercial dissolving grade pulps. However, this method is time consuming and requires the usage of a harmful chemical, sodium disulfide (CS₂). This method reproduces the viscose production at lab-scale, which is the reason why it is mainly used to characterise pulps for viscose application. The dissolution ability can be also evaluated by gravimetry after cellulose dissolution in a suitable solvent, without cellulose derivatisation, where the undissolved fraction is weighted. Such methods have been already used at LGP2 to compare pulps but the result is dependent on the solvent used. In the present chapter, research was focused on an alternative method to evaluate the dissolution ability of cellulose: the derivatisation of cellulose into cellulose tricarbanilate (CTC), followed by the cellulose particle size measurement along the mentioned reaction. Cellulose derivatization into CTC is usually performed to carry out further analyses by Size Extrusion Chromatography (SEC) to obtain the cellulose molecular weight distribution (MWD). This method is well known and has been carefully studied, but never with a purpose of studying dissolution rate and ability. It has been observed that the dissolution time by this method depends on the pulp substrates used, and whether the substrate is grinded or not. Moisture has also an effect, and it is generally recommended to dry or lyophilise the pulp before dissolution. The purpose of studying carbanilation is to be able to combine the advantage of acquiring the MWD profile while monitoring the cellulose dissolving ability by Dynamic Light Scattering (DLS), in the same experiment.

In the present chapter, several commercial bleached pulps have been used to evaluate and compare three methods to characterise the dissolving ability. First, the tested pulps (Kraft pulps, sulfite pulps from softwood and hardwood, and cotton linters) will be presented, as well as the classical pulp characterisations. Later, the three methods will be presented (principle and procedure), and finally they will be applied on the commercial bleached pulps, and the results will be discussed in order to better understand their relevance.

II.2. Cellulosic substrates

The PhD project aims to valorise bleached Kraft pulps into dissolving pulps. For this reason, commercial bleached Kraft pulps from both softwood and hardwood have been selected. For comparison reasons, one commercial sulfite pulp (from softwood) has been also considered as part of the study, as well as a cotton linters pulp. The sulfite pulp is a dissolving grade pulp, so that it should exhibit a good dissolution ability. As for cotton linters, its behaviour is expected to differ from all the selected commercial pulps because of the absence of hemicelluloses.

II.2.1. Initial substrates

The six selected cellulosic substrates are listed below with their shortened code name used along the document in the discussions:

- CL, Bleached Cotton Linters pulp from Arjowiggins Co., France
- HW-K-1, Bleached Hardwood Kraft pulp from Fibre Excellence St Gaudens, France
- HW-K-2, Bleached Hardwood Kraft pulp from CELBI Co., Portugal
- SW-K-1, Bleached Softwood Kraft pulp from Botnia, Finland
- SW-K-2, Bleached Softwood Kraft pulp from Fibre Excellence Tarascon, France
- SW-S, Bleached Softwood Sulfite pulp from Rayonier Co., Tartas, France

II.2.2. Acid hydrolyses of cotton linters

In complement to the raw substrates, cotton linters have been submitted to acid hydrolyses to reach different values of cellulose DPv. The acid hydrolyses has been conducted at 10% consistency, at initial pH close to 2-2.5 using sulfuric acid (0.0003 mol H_2SO_4). The hydrolyses took place at 95°C during different reaction times, to achieve different values of cellulose DPv. The resulting pulps have been also characterized in terms of dissolving ability, and the discussion of results is presented in the last section of this chapter.

II.3. Three methods for cellulose dissolution ability

Two established methods have been used in the PhD, the Fock test, and a gravimetric method after direct cellulose dissolution in the system NaOH:urea:water. Subsequently, these methods have been compared with the new method under investigation developed in the present chapter, the monitoring of the cellulose particle size during cellulose carbanilation. The three mentioned methods are presented in the following section.

II.3.1 The Fock test

As mentioned in Chapter I, the Fock test is a widely accepted method to evaluate the dissolution ability of dissolving pulps, and it reproduces the viscose process. It is defined by the capacity of cellulose to react with CS_2 under defined conditions. The Fock reactivity estimates its processability in the viscose process and gives the measurement of the reacted cellulose (in percentage) during the xanthation reaction¹. The reactivity of pulp is an expression of the availability of functional groups, or reaction sites, for reaction with chemical agents or solvents.

The Fock test - protocol

The Fock test conditions have been slightly modified over the last years in order to optimise the usage of the pollutant CS_2 and to correct the high variations in repeatability. This study used the improved conditions presented by *Chao Tian et al*².

For xanthation and regeneration of cellulose, 0.5 g of pulp sample (oven-dried basis) was weighted and introduced in an Erlenmeyer flask with a stopper. 50 mL of 9% (w/w) aqueous NaOH solution was added, and the flask was maintained submerged in a water bath at room temperature with a magnetic stirrer for 10 min. Then, 3 mL of CS_2 were added and immediately the flask was closed with the stopper. The xanthation reaction took place for 3 h under stirring (250 rpm) in the water bath. When the time was up, distilled water was added to complete a total solution weight of 100 g (P₁). The solution was transferred into centrifugation tubes with stoppers and later centrifuged for 15 min at 3400 rpm to separate the dissolved cellulose from unreacted cellulose. 10 mL of the supernatant was weighted (P₂) and transferred into a 100 mL round bottom flask and neutralized with 3 mL of 20% (w/w) H₂SO₄ solution. The solution was regenerated in 20 hours. The amount of regenerated cellulose (dissolved cellulose during xanthation) was measured as follows: 20 mL of 68% (w/w) H₂SO₄ solution was added into the round bottom flask and stirred for 1 hour. Then, 10 mL of 1/6 M K₂Cr₂O₇ solution was added and the mixture was placed

under reflux for 1 hour where cellulose oxidation took place. After the mixture was cooled to room temperature, it was diluted into 100 mL with distilled water. 20 mL of this diluted solution were transferred into a 250 mL Erlenmeyer flask. 5 mL (v_1) of KI (0.1 M) was added, and the produced I₂ was titrated with Na₂S₂O₃ using starch to favour the observation of the colour change. The titration volume was recorded to obtain the percentage of cellulose that reacted with CS₂, according to the following equation:

Fock Reactivity (%) =
$$\frac{\left(c_1v_1 - \left(c_2v_2 * \frac{100}{20}\right) * \frac{1}{6} * M * \frac{1}{4} * \frac{P_1}{P_2}\right)}{m} * 100$$

Where, M is the molecular weight of anhydroglucose unit (AGU) (162 g/mol), *m* is the ovendried weight of the pulp sample (g), v_1 is the volume of 1/6 M K₂Cr₂O₇ added (0.01 L), c_1 is the concentration of K₂Cr₂O₇ solution (1/6 M), v_2 is the volume of consumed Na₂S₂O₃ (L), c_2 is the concentration of Na₂S₂O₃ solution (0.1 N), (100/20) means 20 mL diluted sample is taken out from 100 mL volumetric flask and titrated, (1/6) means each dichromate ion consumes six thiosulfate ions, (1/4) means each AGU unit consumes 4 dichromate ions, and P₁ stands for the real mass of the xanthation solution (100 g) and P₂ the mass taken from the supernatant after centrifugation (≈10.5 g).

II.3.2. Dissolution test in the NaOH:urea:water system

Many studies investigated the cellulose dissolution in aqueous NaOH. The advantage is to work in aqueous medium compared to organic solvent and soda is a rather cheap chemical, widely used in the pulp and paper industry. This could be an alternative to the polluting xanthate process³. *Isogai et al*³. worked on the optimisation of the cellulose dissolution in such system and found interesting conditions when the soda solution is prepared at 8-9% NaOH and when the dissolution is performed at -20°C. In this study, all the samples prepared from 2% w/w microcrystalline cellulose (very low DPv <200) were completely dissolved by this procedure. It was shown that the cellulose dissolution ability is not linked to the crystalline form of the cellulosic sample, nor to its molecular weight. *Egal et al*⁴. determined the limits of the cellulose solubility as 7-10% NaOH below 0°C. However, a clear drawback of this method is that dissolution is not complete for high molecular weight celluloses, which is the reason why it did not become a commercial process. Yet, a strong impact of temperature was also observed: lower temperatures probably favour stronger NaOH hydrates network, which prevents the cellulose chains from interacting with each other forming interchain hydrogen bonds⁴. This facilitates the cellulose dissolution.

Cellulose dissolution takes place if the cellulose and the solvent share affinity. Cellulose has a polar character, due to the presence of many OH groups with affinity for polar solutions. Cellulose dissolution proceeds by swelling, which is defined as a process where the solvent molecules penetrate the cellulose structure to significantly alter the volume and physical properties, while at the same time the solid, or semi-solid fractions remain practically unchanged. The complete dissolution is expected to destroy the supramolecular structure, resulting in a system where the polymer is to be molecularly dispersed⁵. The effect of alkali on cellulose fibres is mainly swelling, where the natural crystalline structure is relaxed, as shown in Figure II-1. However, aqueous NaOH alone does not exhibit a sufficient penetrating power to fully dissolved cellulose.



Figure II-1. Representation of the swelling process⁶.

Some studies reported that adding urea in the system strongly improved cellulose solubility^{7,8}. The role of urea was further investigated. It has been shown that it has no strong direct interaction with cellulose or NaOH; and it does not have much influence in the structural dynamics of water. Urea may accumulate in the hydrophobic region of cellulose via Van der Waal forces, thus improving the solubility and stability by preventing dissolved cellulose molecules from re-gathering⁹. The cellulose solubility has been shown to increase when the temperature was decreased and it also strongly depends on the cellulosic substrate molecular weight. The more interesting results were observed when the NaOH/urea aqueous solution was

pre-cooled to $-12,6^{\circ}C^{10}$. Concerning the stirring conditions, experiments suggested that larger stirring blade area, longer stirring time, and higher stirring rate could improve the saturated solubility value of cellulose (C_{max}) when the cellulose was not completely dissolved¹¹. A diagram of the dependence of the stirring time at 300 rpm is presented in Figure II-2.



Figure II-2. Dependence of C_{max} on the stirring time at 300 rpm at room temperature¹¹.

According to the considerations described by the authors, a NaOH/urea/water solution with the ratio 7:12:81% pre-cooled to -12°C could be a successful procedure to dissolve cellulose. A recent study carried out at LGP2 already demonstrated that the NaOH:urea:water system was able to dissolve various cellulosic substrates at 1 wt% concentration using temperature below 0°C. It was also shown that the solubility of cellulose is linearly correlated to the cellulosic substrate DPv, in the above described conditions.

In the present project, to better explain the dissolution behaviour of the selected cellulose samples, this method was evaluated. The protocol applied is detailed below.

Dissolution test in the NaOH:urea:water system - protocol

0.25 g (1 wt%) of cellulosic substrates were dispersed in 24.75 g pre-cooled (-12°C) solvent made of NaOH:urea:water with a ratio of 7:12:81 wt%. The liquid portion was pre-cooled in the system under agitation at 400 rpm for 15 min before adding the cellulose substrate. After the pre-cooling time, the bottle was opened and the sample transferred in with the help of a tweezer, very slowly and for exactly 5 min, while maintaining 400 rpm agitation. After the addition of the substrate, it was verified that there was no sample on the walls of the bottle. The system was closed and allowed to dissolve for 15 min. Afterwards, the solution was transferred

to centrifuge tubes and sent for centrifugation for 30 min at 4000 rpm. The supernatant was removed with a pipette and the undissolved fraction was washed with distilled water until reaching neutral pH (~600 mL). The pre-weighted crucible (pore No.2) used for washing, was then placed in the oven at 105°C for 24 h. Before measuring the final weight, the hot crucible was placed in a desiccator for 15 min. The cellulose solubility (Sa) in NaOH:urea:water solution was calculated as presented in the equation below, where w_0 is the weight of the sample and w_i the undissolved fraction.

$$S_a(\%) = \frac{w_0 - w_i}{w_0} * 100$$

II.3.3. An alternative method, cellulose derivatization

Previous studies have shown that cellulose can smoothly react with phenyl isocyanate in the presence of pyridine forming the cellulose tricarbanilate (CTC). Although the conversion needs a large excess of phenyl isocyanate only negligible cellulosic chain degradation occurs and almost no by-product is formed if suitable operating conditions are applied, especially at temperatures below 70-80°C. At the end of the reaction, the excess of phenyl isocyanate can be decomposed by addition of dry methanol¹²; and DMSO¹³ and THF can be used as cellulose tricarbanilate solvents. This derivatization is well known in SEC for the determination of cellulose molar weight distribution. As in the Fock test, cellulose is derivatized to make it soluble. However, the reaction employs less harmful products, and the cellulose dissolution is determined by a physical measurement, i.e. particle size evolution, and not by a chemical mean (titration). Compared to the dissolution in the NaOH:urea:water system, the cellulosic substrate is fully dissolved so that the particle size could be followed till total disappearance of cellulose particle in the solvent. The different steps of the proposed method are described in the following paragraphs.

Cellulose carbanilation

Cellulose carbanilation takes place by reaction of cellulose with phenyl isocyanate. This reaction is often carried out with the solvents dimethylsulfoxide (DMSO) or pyridine, and is widely used for the determination of parameters of cellulose by Size Exclusion Chromatography (SEC). The product of the reaction, cellulose tricarbanilates (CTC), are stable and can be stored for extended periods of time¹⁴. The reaction is presented in Figure II-3. It is relevant to mention that the presented reaction is one of the few reaction in which the cellulose

chains undergoes no degradation and goes to complete substitution¹⁵. Additionally, the solvent, reagent, and cellulose polarity increases cellulose swelling and reagent access¹⁶.



Figure II-3. Tricarbanilation of cellulose.

Cellulose carbanilation - Protocol

When producing dissolving pulps, there are key parameters that need special attention, as the dispersity of the molecular weight of the cellulose chains in the pulp. *Mortha et al*¹³ investigated the cellulose carbanilation to further analyse the MWD by SEC using two solvents, DMSO and pyridine. Slight cellulose degradation was observed in the former solvent, yet the latter one was less efficient in general and promoted molecular aggregation in THF, which affects the MWD measurements¹³. As observed in previous studies, it is important to mention that derivatization in DMSO should respect the maximum temperature of 70°C, to avoid cellulose degradation. The derivatisation set up used in this PhD project was carried out following the conditions in the mentioned publication with DMSO, and proceeded as follows.

250 mg of oven-dried grinded cellulosic substrates were weighted in a 250mL glass bottle with a screw cap and mixed with 25 mL of the reaction solvent (DMSO). Then it was left under stirring at 250 rpm overnight at room temperature. After 18 h, with continuous stirring, the temperature was raised to 70°C (approximately 1 hour) in the water system of the jacketed reactor under the fume hood. 5 mL of phenyl isocyanate (PhNCO) were added slowly under stirring for 5 min (t_0), followed by 20 mL of DMSO. The reaction proceeds for 48h.

The concentrations of PhNCO and alcoholic groups of cellulose (ROH) in 50 mL of solution are calculated by the following equations:

$$[PhNCO] = \frac{\left(5mL * 1.096 \frac{g}{mL} * \frac{1mol}{119.12g}\right) * 99\%_{purity}}{0.05L} = 0.91mol/l$$

$$[\mathbf{ROH}] = \frac{\left(0.25g_{OD} * \frac{1mol}{162g}\right) * 3}{0.05L} = 0.09mol/L$$

Thus, the stoichiometric ratio between PhNCO and ROH is:

$$\frac{[Ph - NCO]}{[ROH]} = \frac{0.91 mol/L}{0.09 mol/L} = 10.11$$

An optimisation of the PhNCO consumption was achieved in the protocol proposed in this thesis project, as the stoichiometric ratios in the protocols studied by *Mortha et al*¹³ were above 20, which represents a molar ratio of reagent on cellulosic OH. Several tests led to the optimisation of this molar ratio.

Particle size measurements by DLS

Particles in suspension undergo the Brownian motion caused by thermally induced collisions between the suspended particles and solvent molecules¹⁷. The smaller the particle size, the faster the Brownian motion.

When a beam of light encounters a solution containing molecules, it changes direction. This is called light scattering (LS). But, if the light disappears after the encounter, it is called light absorption. For both cases the transmitted intensity will decrease depending on the thickness of the material the light is passing through. When the attenuation of the light beam is due to absorption or due to scattering, the intensity can be estimated, as presented in Figure II-4, where I_0 is the intensity before the attenuation; α and τ are coefficients for absorption and turbidity, respectively¹⁸.



Figure II-4. Transmitted light is attenuated by either absorption (top) or by scattering (bottom)¹⁸.

In static light scattering (SLS), the measured intensity of the scattered light allows to obtain the average molecular weight of a macromolecule, as well as its radius of gyration¹⁹. In the case of dynamic light scattering (DLS), if the intensity fluctuations caused by the Brownian motion are analysed, one can derive the diffusion coefficient (D_{τ}), which is related to the hydrodynamic size of the macromolecules. The DLS technique is used for particle size analyses and size distribution in the micron and sub-micron region. However, it does present some limitations since the studied particles should be in the range of 1 nm-1000 nm and the volume of the analysed medium is typically 1 mL. Moreover, the sample solution must be completely transparent and should not absorb light in the wavelength used, the molecules in solution should have a refractive index different from the solvent and finally the solution should be thermodynamically stable, i.e. no reaction should take place. DLS is also referred to as Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering.

During the DLS analysis, the suspended particles are illuminated with a coherent monochromatic light source. Due to the Brownian motion of the suspended particles, the recorded scattered light intensity will fluctuate with time. The rate, at which the scattered signal changes, depends on the speed of particles, with large particles leading to slow fluctuations and small particles leading to fast fluctuations²⁰. The speed of the Brownian motion is defined by a property known as the translational diffusion coefficient and the size of a particle is calculated using the Stokes-Einstein equation below. The translational diffusion coefficient will depend not only on the size of the particle but also on the surface structure, as well as the concentration and type of ions in the medium.

$$d(H) = \frac{kT}{3\pi\eta D}$$

Where d(H) is the hydrodynamic diameter, D is the translational diffusion coefficient, k is Boltzmann's constant, **T** is the absolute temperature and η is viscosity. The hydrodynamic diameter measured by DLS refers to how a particle diffuses within a fluid, it is defined as 'the size of a hypothetical hard sphere that diffuses in the same fashion as that of the particle being measured'²¹. Figure II-5 shows examples of the diameter of a sphere measured by DLS, and Figure II-6 presents typical intensity fluctuations for large and small particles.



Figure II-5. Hydrodynamic diameter.

The DLS analyses the intensity fluctuations in the time domain. The average decay rate is estimated from the intensity autocorrelation function by means of the *cumulants* analysis method²⁰. The size distribution given by the software is a plot of the relative intensity of light scattered by particles in several size classes, and is known as an intensity size distribution. A sample with large particles will take longer time to decay, and a sample with small particles decays more rapidly as shown in Figure II-6.



Figure II-6. Schematic representation of fluctuations in intensity and the corresponding autocorrelation functions from suspensions of different size particles²².

Three mathematical algorithms are used to obtain the size distribution in the DLS software: the *Cumulants* method assumes that there is only one main population in the sample, and whose sizes respect a Gaussian distribution; the *Pade Laplace* method assumes that there is a discrete number of different sizes in the sample; and the *SBL* (Sparse Bayesian Learning) looks for a multimodal distribution and multi-disperse nanoparticle sizes²³. The method of cumulants is a standard technique used to analyse DLS data measured for polydisperse samples²⁴ and allows to obtain an intensity average of the diffusion coefficient of the particles²⁵. **Z-average** (average particle size), and **PDI** (Polydispersity Index) from the cumulants method are the only parameters recommended to be used by ISO 22412:2017 for particle size measurements²⁶.

However, the sedimentation of particles, depending on their density, sets a limit to the particle size with an upper limit much less than 10 μ m. Results obtained for homogeneous, monodisperse samples will exhibit less variability than results from polydisperse samples. Repeatability standard deviation for monodisperse materials with diameters between 50 nm and 200 nm should be below 2%, and 5% for reproducibility²⁷

As the thesis proposes the use of DLS for particle size measurements along the carbanilation reaction, more detail about the apparatus used, followed by the protocol, are described below.

DLS apparatus used

A typical DLS apparatus is composed of the following components: a laser that provides the light source, a sample holder where the light beam passes through, and some is scattered by the particles at different angles, a detector is used to measure the scattered light. The detector position will depend upon the particular DLS model, and the intensity of scattered light must be within a specific range to be measured. If there is too much light, it can become saturated. To control this, an attenuator is used to decrease the intensity of scattering. The opposite happens when the sample does not scatter much light, the attenuator allows more laser through to the sample. The appropriate attenuator position is determined by the software and covers a transmission range of 100% to 0.0003%, the intensity signal passes from the detector to a signal processing unit called correlator, which compares the intensities at successive time intervals to determine the rate of variation²⁸. This information is later passed to a computer where a software analyses the data. A diagram of the components is presented in Figure II-7.



Figure II-7. Components of a typical DLS apparatus.

The DLS input conditions remained very similar for all the selected cellulosic substrates. It was set at 25°C with 100% of the power, and the Dual Thickness Controller in position up. Other setting included values of 10 acquisitions with a maximum noise of 3 as well as the solvent properties such as DMSO refractive index of 1.4772 and the viscosity of 1.99 mPa/s.



Figure II-8. Diagram of the components of the VASCOTM DLS.

The VASCOTM particle size analyser contains a right-angle prism, where the sample is deposited on its superior side. On the collection side, the preferred scattering light upon a back-reflection angle of 135° , which is not refracted by the prism rear side. A diagram is presented in Figure II-8. The Dual Thickness Controller (DTC), is a mobile fused silica glass rod with two functions, to avoid any return of the transmitted laser light and to deal with the multi-scattering effect when the particle concentration is too high, by decreasing the sample layer down to a thin layer of about 100 µm. The light source used in this apparatus is from a diode laser emitting at 657 nm. The photo counting detector is used to efficiently detect low levels of light. The mentioned detector converts the incident light into electrons and uses them to generate pulses that go to the correlator. When using a photon counting module, the intensity is sampled in time interval Δt , leading to a digital intensity correlation, which is an accurate estimation of the instantaneous scattered intensity. The described apparatus has a measurement sensitivity for particle size ranged from 1 nm to 10 µm. The Software connected to the apparatus, and the one reporting results is called NanoQTM. The DLS equipment used for this project is presented in Figure II-9.



Figure II-9. DLS apparatus used for the present project. VASCOTM particle size analyser.

Particle size measurements by DLS - Protocol

For the particle size analysis, the carbanilation reaction should be stopped (with acetone). For that, 5 mL of DMSO and 1 mL of acetone were introduced into a 10 mL volumetric flask, and then 1 mL of the cellulosic substrate undergoing carbanilation and dissolution was sampled and added into the flask. After, the volumetric flask was completed with DMSO as solvent and the mixture was analysed. The sampling and analysis were repeated all along the carbanilation reaction to monitor the particle size of the cellulose substrate over the time. The repeatability of the described method was evaluated by triplicate analysis for the six cellulosic substrates.

1 mL of the diluted sample was poured on the holder and the cabin closed to start the measurement. When ready, the software presents a report with the particle size estimation from different methods: *statistic*, *Pade LaPlace*, and *Cumulants*, calculated by intensity, volume and number for each case. Yet, following the recommendations done by ISO 22412:2017, this project only considered the particle size value 'z' and PDI from the Cumulants method. The Intensity reporting section from the cumulants method is shown in Figure II-10.



Figure II-10. Information obtained by Cumulants method. NanoQTM Software.

At the end of the 48 h cellulose carbanilation, the remaining volume (50 mL - 1 mL * number of samples taken for DLS analyses) was carefully mixed with 16-18 mL of acetone to stop the

reaction. The medium was cooled down slowly under stirring. 1 mL of this solution was diluted in 10 mL of THF and later injected (only 100 μ L) in the SEC system for analyses.

SEC Analyses of the dissolved CTC

High performance size exclusion chromatography (HPSEC) is carried out on the tricarbanilate derivative of cellulose (derivatization is required to solubilise cellulose in the SEC compatible solvent). The system consists of a pump to push the solvent, an injection system to introduce the sample in the column, a column holding a gel phase, detectors to detect the components left in the column, and a software to control the instrument and display results. A scheme is presented in Figure II-11. The results depend on what remains in the column. If the polymer chains are much bigger than the pores of the stationary phase, they do not access the pores and consequently they are carried straight by the mobile phase. If they are smaller, they could enter the larger pores but not the smaller ones; and, if the polymer chains are very small, they could access any pores and potentially occupy all the stationary phase. As a result, short chain polymer can take longer time to exit the column, contrary to long chain polymer that did not enter the pores. Therefore, the way of elution strongly depends on the size of the pores²⁹. Briefly, molecules are only separated based on their hydrodynamic volume; long chain polymers are eluted first, whereas short chain polymers later, as they go through the pores.



Figure II-11. Scheme of SEC.

After the molecules are eluted by volume, they are analysed by detectors. Light scattering is an absolute detection technique that provides the weight average molecular mass (Mw) of the sample without the need for calibration with external standards. It is coupled with a concentration-sensitive detector such as refractive index (RI) detector. Following data treatments by a software, the molecular weight distribution can be plotted. It gives information of weight average molecular weight (Mw), number average molecular weight (Mn), viscosity

average molecular weight (Mv), and z average molecular weight (Mz)³⁰. It always comes in the following order:

$$Mn \le Mv \le Mw \le Mz$$

Coupled to viscosity measurements (viscosimeter sensor), it allows to estimate [η], the intrinsic viscosity and the hydrodynamic radius (*Rh*) of the polymer dissolved. The hydrodynamic radius represents the space occupied by a molecule in the solution. It changes based on the solvent as it is greatly influenced by the conformation of the molecule, and branching, as well as the interaction between the molecule and the solvent³¹. Polymer chains take various forms or conformations in solution and solid states depending on their primary structures and surroundings¹⁶. In cellulose, each anhydroglucose unit (AGU) ring adopts the ⁴C₁ chair conformation. This conformation ensures low Van der Waals and steric repulsion between the ring substituents and the glycosidic bonds. It is the most stable conformation, and as a consequence, the thermodynamically preferred one³².

The equipment used for the SEC analyses was the Viskotek TDAmax system (VE 2001 GPC Solvent/Sample module, TDA 302 Triple array detector, UV detector model 2501 with deuterium lamp). The triple detector array employs refractive index, viscosimeter, and light scattering. The MWD profiles were obtained using the software OmniSEC 4.5 (Viscotek Co.). Some of the parameters studied include peak integration limits (based on RI signal), and MW versus elution volume fit, both influenced by polydispersity index (PD) and MW calculations¹³. For the SEC analyses, the concentration of the final sample is needed to be used by the software, and it was calculated as follows:

$$\frac{0.25g}{162^{g}/mol} = 0.001543 \ mol$$

Where 0.25 g refers to the initial cellulosic sample used for the derivatization reaction, and 162 g/mol is the molar mass of AGU unit. When 8 sample were taken along the derivatization reaction, 42 mL (out of 50 mL) were left for the subsequent step, the stopping of the reaction and further analyses in SEC. Thus,

$$0.001543 * \frac{42}{50} = 0.001296 \ mol$$

To stop the reaction, 18 mL of acetone were added to the remaining volume. The amount of cellulose in the left volume was estimated, considering 60 mL as the final volume:

$$\frac{250 \text{ mg cellulose}}{50 \text{ mL DMSO}} = 5 \frac{\text{mg}}{\text{mL}} * 42 \text{ mL} = 210 \text{ mg cellulose}$$
$$\frac{210 \text{ mg cellulose}}{60 \text{ mL solution}} = 3.5 \frac{\text{mg}}{\text{mL}}$$

To inject the sample in the SEC system, it was diluted 10 times in tetrahydrofuran (THF), thus:

$$\frac{3.5^{mg}/_{mL}}{10 \,mL \,solution \,THF} = 0.35^{mg}/_{mL}$$

Finally, conversion is required after carbanilation, where 162 g is the weight of one AGU and 519 g is the weight of one derivatised AGU after tricarbanilation.

$$0.35^{mg}/_{mL} * \frac{519 g}{162 g} = 1.1213^{mg}/_{mL}$$

II.4. Comparison of the dissolution ability methods

To explain the different cellulosic substrates dissolving behaviours obtained through the three tested methods, all the substrates have been characterized. Detail of the methods used for the estimation of the cellulose degree of polymerization (DPv), brightness (%ISO), alkali resistance (R18) for cellulose content, as well as the crystallinity index, are presented in Chapter VI.

II.4.1. Characterisation of the cellulosic substrates

Intrinsic viscosity, as well as the cellulose DPv in CUED are presented in Figure II-12.



Figure II-12. DPv and intrinsic viscosity values of the reference cellulosic substrates.

The intrinsic viscosity $[\eta]$ is a measure of the polymer's ability to increase the viscosity of a solvent³³. DPv and IV values are presented together as for some experiments the degree of polymerization is considered for the discussion, and for some others, intrinsic viscosity. The highest values were observed for SW-S (sulfite pulp for dissolving application), followed by SW-K-1 (Kraft pulp for paper application), and CL; while the lowest value was observed for the sample HW-K-2. Some pulps are already in the lower range of IV acceptable for dissolving pulp grade (450-500 mL/g, for viscose applications³⁴). Therefore, attention should be focused on cellulose degradation during the oxidative treatments to be developed along the PhD work.

The brightness was measured accordingly to ISO 2470-1:2016. The highest value was observed for CL (90.2% ISO) and the rest of the samples were in the range of 85-88% ISO, as shown in Figure II-13. Despite the brightness values are not far away from the dissolving pulp target (>90% ISO, for viscose applications), increasing of few brightness points can become a difficult task, especially when working with pulps already bleached.





The crystallinity profiles of the reference cellulosic substrates were obtained by XRD analyses, and are displayed in Figure II-14. The crystallinity index was estimated by the Segal peak height method, which is explained in Chapter VI. Table II-1 shows the extracted maximum intensity values (I_{200}), found between the scattering angles $2\Theta=22^{\circ}$ and 23° ; as well as the minimum valued (I_{min}), typically between $2\Theta=18^{\circ}$ and 19° . With these values, the Crystallinity Index (CI) was calculated.



Figure II-14. Crystallinity profiles of the reference cellulosic substrates obtained by XRD analyses.

For all the wood pulps (SW-K-1, SW-K-2, SW-S, HW-K-1, HW-K-2) the diffractograms exhibited similar shapes. Nor the wood species or the pulp process differentiate the pulps. However, CL presents the highest CI value, i.e. 87,7%. The cellulose organisation is very different from the 5 other substrates (wood origin). For the six samples, cellulose 1 β structure was identified. Potential changes on the CI after the oxidation treatments will be monitored.

	I ₂₀₀	I _{min}	CI <i>,</i> %	
CL	77436	9492	87.7	
HW-K-1	45354	13063	71.2	
HW-K-2	65401	14637	77.6	
SW-K-1	55125	14517	73.7	
SW-K-2	56472	15032	73.4	
SW-S	61566	16384	73.4	

Table II-1. Crystallinity Index of the reference cellulosic substrates (Segal Method).

A key parameter for dissolving pulp is the cellulose content. For its estimation, two methods were considered. A rapid and simple method, the R18, ISO 699-1982 (alkali resistance in NaOH aqueous solution at 18%), and the sugar analyses carried out after complete cellulose hydrolysis and ionic chromatography analysis in HPLC, detailed in Chapter VI. R18 values represents the percentage of cellulose purity of the substrate. The results are presented in Figure II-15.



Figure II-15. Alkalinity Resistance, R18, of the reference cellulosic substrates.

As expected, the highest cellulose content was observed for CL. This substrate is very pure in terms of cellulose. The sulfite pulp is also rather pure, with more than 93% cellulose, as hemicelluloses have been largely removed during the pulping and purification processes. The lowest values were observed for SW-K, expected as the Kraft process, and classical bleaching sequences preserve a portion of hemicelluloses. Surprisingly, the two HW Kraft pulps do not contain a large proportion of hemicelluloses, around 10%.

Sugar analysis estimated by HPLC after acid hydrolysis are presented in Table II-2. CL results are not presented since the analysis revealed 100% presence of cellulose.

	HW-K-1	HW-K-2	SW-K-1	SW-K-2	SW-S
Cellulose, %	74	79	82	77	90
Hemicelluloses, %	26	21	18	23	10
Glucomannans, %	-	-	12	15	5
Xylans, %	26	21	6	8	5

Table II-2. Sugar analysis of the reference cellulosic substrates

As shown by the R18 test results in Figure II-15, the sugar analysis confirms that the sulfite pulp (SW-S) is very pure in terms of cellulose, which is not surprising since it is a dissolving-grade pulp, and it is used in this study for comparison with the paper-grade Kraft pulps. The sugar content of the Kraft pulps reveals that the cellulose content is between 74 and 82% depending on the substrate. Contrary to R18 results, HW-K-1 and HW-K-2 seem to contains more than 20% hemicelluloses. It is possible that in R18, the important presence of xylans may be have contributed to an error in the cellulose fraction, which is not the case for softwoods pulps, as they contain low amount of xylans, and the error decreases.

II.4.2. The alternative method, cellulose carbanilation

The dissolution of cellulose during the reaction was monitored by measuring the cellulose particle size using DLS by sampling of 1 mL, and diluting it 10 times in DMSO. The reaction was stopped with acetone. Several samples were taken during the 48 hours' time of reaction.

The first objective was to determine the most suitable dose of phenyl isocyanate for cellulose carbanilation. In previous studies carried out at LGP2, 250 mg of oven dried-grinded cellulosic substrates were treated with a volume of 10 mL phenyl isocyanate, which represents a large molar excess of reagent. In this PhD work, the excess was tested and the volumes of 2.5 mL, 5 mL, and 10 mL have been applied with softwood sulfite bleached pulp, representing a molar excess of 5, 10, and 20 respectively, as detailed in section II.2.3. As expected, the higher quantity of phenyl-isocyanate used, the faster the dissolution, as shown in Figure II-16. Very similar results were observed when using 5 mL and 10 mL of phenyl-isocyanate. However, when using 2.5 mL, it was observed the highest particle size after the first 24 h of the reaction, compared to 5 mL and 10 mL. In Figure II-17, one can observe the same tendency for cotton linters, where the slowest dissolution was achieved when using 2.5 mL, and similar behaviours when using 5 mL and 10 mL. Hence, it was selected a volume of 5 mL for the following experiments as it was possible to observe very similar dissolution behaviour, and at the same time reducing by half the dose of reactant used in the reference method, 10 mL.



Figure II-16. Dissolution of the SW-S pulp with different quantities of phenyl isocyanate.


Figure II-17. Dissolution of CL with different quantities of phenyl isocyanate.

As a summary, the following conditions were kept for the method: 250 mg of grinded cellulosic samples are placed to swell at room temperature, in agitation (250 rpm) with 25 mL DMSO overnight. After exactly 18 h, the temperature is raised up to 70°C (which approximately takes 1 hour), then 5 mL of phenyl isocyanate are added, representing the starting time of the reaction. The reaction volume is completed with 20 mL of DMSO. The total reaction volume is 50 mL.

Comparison of the dissolution ability of the cellulosic substrates

The repeatability was evaluated by triplicate. All the cellulosic substrates achieved a particle size under 100 nm in the first 8 h of the reaction and remained stable (approximately 50 nm particle size) for the next 40 hours of the experiment, as shown in Figure II-18.



Figure II-18. Average particle size of the cellulosic substrates undergoing carbanilation.

The main observations:

- During the first 2-3 hours, for all the substrates, the particle size was highly dispersed due to the heterogeneity of the initial particle population. Between 3 and 5 hours, different dissolution kinetics could be distinguished depending on the substrate nature. And after 8 hours, all the substrates achieved a particle size lower than 100 nm, whatever their origin.
- The SW-S (green curve) was rapidly dissolved. This is logical since this pulp is a dissolving-grade pulp. Surprisingly HW-K-1 presented a similar behaviour, even if it is paper-grade pulp.
- Cotton linters are the most resistant to dissolution.
- Hardwoods dissolved faster (3-4 h), followed by the softwoods (6-8 h).

Additionally, using the information of particle size obtained by DLS, it was possible to propose a *ranking of dissolution*. The ranking was obtained by calculating an average of the particle size values obtained along the reaction. The highest value obtained was for CL, which presented the highest particle sizes along the dissolution, and therefore, the slowest dissolution, as confirmed in Figure II-18. The lowest value obtained was for HW-K-1 which is thus considered the fastest to dissolve. The ranking remained the same, no matter if it was only considered data for the first 4h, or 8h of the reaction. The rank obtained is presented Table II-3, where CL was the slowest to dissolve, and HW-K-1 the fastest.

SAMPLE	4h	8h	
CL	331	251	
SW-K-1	247	201	
SW-K-2	230	187	
HW-K-2	143	123	
SW-S	123	97	
HW-K-1	109	92	

Table II-3. Average of the particle size values (nm) obtained by the DLS, for 4h and 8h of reaction.

MWD of the carbanilated cellulosic substrates

Table II-4 presents the most interesting information obtained from the SEC analyses.

SAMPLES	Rh (nm)	Mn	Mw	Mw/Mn	DPn*	DPw*	IV (mL/g)
CL	34	298971	720119	2.4	576	1388	481
HW-K-1	34	259500	756217	2.9	500	1457	419
HW-K-2	27	161883	647972	4.0	312	1249	271
SW-K-1	52	606272	2089123	3.4	1168	4025	637
SW-K-2	27	149563	524965	3.5	288	1011	319
SW-S	64	696477	2619716	3.8	1342	5048	891

Table II-4. Results obtained from the SEC analyses.

*To calculate DPn and DPw, Mn and Mw was calculated using the weight of cellulose tricarbanilate, 519 g/mol.

The hydrodynamic radius (Rh) presented values below 100 nm, similar to the DLS measurements, even though they were measured differently. The polydispersity index was obtained by Mw/Mn, and the values coincided with the dispersity observed in the MWD profiles shown in Figure II-20. The higher IV value was observed for the sulfite pulp, SW-S, followed by SW-K-1, and CL. These values globally correlate to the cellulose DPv in CUED shown in the correlation in Figure II.19. The less viscous solution was HW-K-2, as expected.



Figure II.19. DPv in CuED vs DPw SEC vs intrinsic viscosity.

Regarding the MWD profile, cotton linter (CL), with the slowest dissolution behaviour, exhibits one single signal attributed to cellulose and does not present aggregates. For Kraft pulps (HW-K-1, HW-K-2, SW-K-1 and SW-K-2), a bimodal profile is observed, with cellulose in the higher mass range and hemicelluloses in the lower mass region. Degraded cellulose can also potentially appear in the lower mass range, in the same region of hemicelluloses. The sulfite pulp, SW-S, presents no signal in the hemicelluloses mass range, as CL. Despite apparent good dissolution shown by DLS analysis, MWD profiles of some pulps revealed shoulders in the high mass range, which can be attributed to persistent aggregates, as shown for HW-K-1, SW-K-1 and SW-S. Aggregates are probably more numerous when the cellulose chains are long, meaning that, at molecular scale, some OH groups might remain underivatized.



Figure II-20. MWD of the selected cellulosic substrates after carbanilation.

Other interesting information that can be obtained by the SEC is the relation of Log Rh versus Log M. The value of the hydrodynamic radius is the radius of an equivalent sphere for the solvated polymer, which represents an estimation of the volume occupied by the polymer in solution. The Log Rh versus Log M curve represents the conformation of the substrates¹⁶. As presented in Figure II-21, all the derivatised cellulosic substrates presented similar conformation. No significant differences could be observed.



Figure II-21. Log Rh vs Log M curves of the reference cellulosic substrates after carbanilation.

The dissolution behaviour differences between are not explained by their degree of polymerization or by the wood specie. The main observations are that this novel method clearly discriminates cotton linter and the sulfite pulp, from Kraft pulps. With the proposed method, hardwood Kraft pulp dissolution is similar to the one observed for sulfite pulp.

Acid hydrolyses of cotton linters

To further investigate a possible correlation between the novel method and the cellulose degree of polymerization, cotton linters at various cellulose DPv have been analysed. The use of cotton linters is justified by the absence of hemicelluloses, where their possible effect on the dissolving ability is suppressed. Moreover, working on the same substrate will allow to examine if the dissolution effect is affected by the cellulose chain length. To achieve different values of cellulose DPv, acid hydrolyses were performed on CL at similar initial pH, same temperature, 95°C, but during different reaction times, as shown in Table II-5. The hydrolyses and characterisations were performed by duplicate.

SAMPLES	Final pH	DPv
CL-Ref	-	1005
CL-1h	2.6	797
CL-2h	2.3	748
CL-3h	2.1	681
CL-4h	2	613
CL-5h	2	580
CL-6h	2.2	567
CL-7h	2.1	533
CL-8h	2	478

No significant differences in terms of dissolution ability have been observed (Figure II-22). When a DPv of 580 was achieved, a slight improvement of the dissolution could be observed after 5 hours of dissolution. Yet, the reference sample with the highest DPv exhibited the fastest dissolution. As a conclusion, the apparent rate of dissolution did not show a correlation with the cellulose degree of polymerization. SEC analyses have been performed after the full carbanilation. As observed previously, IV and DP are correlated, and for both parameters, the longer the hydrolysis time, the lower the values. It was also noticed a decrease in Rh, and a more uniform MWD, indicated in the dispersity (Mw/Mn), compared to the reference. As expected, the CL MWD profile is displaced towards lower masses as cellulose depolymerisation proceeded. The CL dissolving behaviour during cellulose carbanilation is presented in Figure II-22. The values of DPv in CuED have been included in Table II-6 to confirm its correlation with the DPw obtained by SEC.





Figure II-22. Cellulose particle size observed by DLS of hydrolysed cotton linters.



Figure II-23. MWD profiles of the hydrolysed CL samples.

As observed previously, IV and DP are correlated, and for both parameters, the longer the hydrolysis time, the lower the values. It was also noticed a decrease in Rh, and a more uniform MWD, indicated in the dispersity (Mw/Mn), compared to the reference. As expected, the CL MWD profile is displaced towards lower masses as cellulose depolymerisation proceeded. The CL dissolving behaviour during cellulose carbanilation is presented in Figure II-22. The values of DPv in CuED have been included in Table II-6 to confirm its correlation with the DPw obtained by SEC.

Hydrolyses	REF	CL-1h	CL-3h	CL-5h	CL-8h
IV (mL/g)	481	332	291	262	240
Rh (nm)	34	32	29	27	24
Mw/Mn	2,4	1,7	1,7	1,8	1,8
DPw	1388	1347	1140	1029	897
DPv in CuED	1008	797	681	580	578

Table II-6. Information obtained by SEC for the hydrolysed-CL samples.

II.4.3. The Fock test

As discussed earlier in the chapter, the conditions of the Fock test have been slightly modified over the last years in order to optimise the use of the pollutant CS_2 and to correct the high variations in repeatability. The conditions used in this PhD are taken from the work of *Chao Tian et al*². The results are shown in Figure II-24, and were produced in duplicate.

Expecting a similar tendency as the results obtained in the carbanilation method, the samples in Figure II-24 were arranged from the slowest to dissolve (CL) to the fastest (HW-K-1 and

SW-S). However, the tendency observed in the Fock test was not the same, and the two methods did not correlate.



Figure II-24. Fock Reactivity (%) of the reference cellulosic substrates.

Surprisingly, the Fock test reactivity of the sulfite pulp (SW-S) is very low, less than 50% although this is a dissolving-grade pulp. The Fock reactivity should be higher (if not the highest), hence the obtained value is questioned. It can be concluded that cotton linters exhibited the lowest reactivity whereas no significant differences were observed between all the other wood substrates. The Fock test is not appropriate to distinguish Kraft from sulfite pulps.

II.4.4. NaOH:urea:water system

A third dissolution method was considered in the PhD study, the dissolution of cellulose in a cold NaOH:urea:water medium. Contrary to the two methods already discussed, no derivatization occurs, the dissolution is direct. In this case, the cellulosic substrates are not chemically modified, dissolution is due to the full solvation of the polymer chains after hydrogen bonds break up. The selected initial cellulosic substrates have been tested. The results are presented in Figure II-25.



Figure II-25. Solubility of the reference cellulosic substrates in the NaOH:urea:water system

For all the samples, the cellulose solubility was very low, less than 35%. A correlation between cellulose DPv and solubility was observed for the wood pulps, whatever the pulping process (sulfite or Kraft), or the wood specie: the lower the cellulose DPv value, the higher the cellulose solubility. A linear relation is observed (Figure II-25). Cotton linters, with DPv 1005, did not follow the same tendency, and reached 21% of solubility. SW-K-1, with a similar DPv value of 1086, reached a higher solubility, 26%, compared to CL. Two differences between cotton linters and the wood substrates may explain the behaviour: CL does not contain hemicelluloses, and exhibit a higher crystallinity, compared to the other substrates (Figure II-14). As soon as the substrates exhibits crystallinity of the similar magnitude, the solubility is affected mainly by the polymer chain length since the substrate accessibility is the same. To verify this latter assumption, hydrolysed cotton linters have been also submitted to dissolution in the NaOH:urea:water system. The results of degree of polymerization after the hydrolyses versus solubility are given in Figure II-26.



Figure II-26. Solubility of the hydrolysed-CL samples in the NaOH:urea:water system.

Similar to the results displayed in Figure II-25, the dissolution of the hydrolysed cotton linters was directly related to the degree of polymerization. The highest cellulose solubility, above 70%, was exhibited by the sample with the lowest DPv, 478 after 8 hours of hydrolysis. In the same context, the lowest solubility, 21%, belongs to the reference, with a DPv of 1005.

II.5. Conclusions

Dissolution ability of cellulosic substrates is a key parameter for dissolving grade pulps. In this chapter, three methods have been investigated.

The method widely used in literature is the Fock test, which reproduces the viscose process for textile applications of dissolving-grade pulps. In the test, the cellulosic substrate is derivatized, and the derivatization is affected by the presence of hemicelluloses. For this reason, paper-grade Kraft pulps are expected to exhibit poor dissolving ability, contrary to the sulfite pulps. However, when applied on the studied substrates, the Fock test revealed that it did not discriminate Kraft paper-grade pulps from dissolving-grade. As a consequence, the Fock test demonstrated to be not suitable for the characterization of the dissolving ability of pulps containing hemicelluloses, as those studied in this thesis. Moreover, the Fock reactivity of cotton was very low despite the absence of hemicelluloses, which is probably due to its high crystallinity, which may interfere with the derivatization.

A novel method to assess the dissolving ability of cellulosic substrates has been investigated: cellulose carbanilation, accompanied by the monitoring of particle size (by DLS) along the dissolution during the derivatisation reaction. It is an indirect dissolution method, as the Fock test, since it involves substrate derivatization to favour dissolution. The derivatisation agent is phenyl isocyanate whereas in the Fock test, it is carbon disulphide; and the solvents are DMSO and NaOH, respectively.

Monitoring the particle size during the cellulosic substrates carbanilation using DLS provides fast results, and enables to rank the cellulosic substrates by its dissolving behaviour. The discrimination of the selected substrates was possible: the sulfite pulp exhibited the fastest dissolving ability, whereas cotton linters were the most difficult to dissolve. The high crystallinity presented by CL is probably the reason for such behaviour. The proposed derivatization method also revealed that hardwood Kraft paper-grade pulps seemed easier to dissolve than softwood Kraft paper-grade pulps, without any correlation with the cellulose DPv, nor with hemicelluloses content. The different nature of hemicelluloses, mainly xylans in hardwood and glucomannans in softwood may be the reason, i.e. the derivatisation efficiency or disturbance may be linked to the hemicelluloses type.

An advantage of the proposed method is that, at the end of the derivatization reaction, the sample could be diluted in THF, to be later analysed by SEC for the obtention of MWD profiles, as well as for other additional information such as the Rh, IV, PDI.

Additionally, no correlation was found between the Fock test and the proposed method, but as discussed before, the Fock test did not show to be suitable for the characterization of hemicelluloses-containing pulps.

In order to better understand the dissolution behaviour of cellulosic pulps, a third method has been looked into: the direct dissolution of the substrates into NaOH:urea:water system without derivatisation. For this kind of dissolution, the intermolecular hydrogen bonds should be broken. Direct dissolution is expected to be more difficult compared to indirect dissolution (dissolution with a prior derivatisation), and was found strongly correlated to the cellulose DPv, i.e. the lower the DPv, the higher the cellulose solubility. In this system, the solvent diffuses between the molecular chains and the reaction starts from the end-groups of the polymer chain. If the chains are shorter, dissolution is faster. The presence of hemicelluloses did not seem to affect the dissolution behaviour of the substrate, and it may be dependent on the crystallinity (high crystallinity limits the solvent penetration).

After the investigation of dissolving methods, the next chapters will focus on the development of oxidative treatments to convert bleached Kraft pulp into dissolving pulps. To characterize the dissolving ability all along the proposed treatments, two methods will be used: the proposed method using carbanilation and the dissolution in NaOH:urea:water system, since they can give complementary information. The Fock test is abandoned since Kraft pulp dissolving ability could not be discriminated.

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III. Cellulose oxidation with H_2O_2 activated by Cu(Phen)

III.1. Introduction

Hydrogen peroxide is an environmentally friendly bleaching chemical largely used in the pulp and paper industry. Its usage is therefore controlled but remains limited to specific conditions, allowing lignin removal or colour-stripping (bleaching), without cellulose depolymerization. Previous studies conducted at LGP2 investigated the use of hydrogen peroxide in classical conditions or using additives to activate the bleaching effect^{1–4}. These studies showed that hydrogen peroxide can be activated by the addition of copper (Cu(II)) and/or by the copper(II)phenanthroline complex, improving delignification and/or bleaching while undergoing a strong cellulose depolymerization. The partial degradation of cellulose is not a problem for dissolving applications, when controlled. Moreover, if cellulose is degraded, hemicelluloses, which should be removed for dissolving pulp applications, may also be affected.

In this chapter, the reaction conditions of the conventional P-stage will be revisited, in order to control its effect on cellulose. The objective being to "tailor" the cellulose degradation according to the final application. Different operating conditions will be studied: pH variation (alkaline or acidic medium), as well the addition of additives Cu(II) or the Cu(II)-phenanthroline complex. The initial assumptions considered are:

- Using H₂O₂ in unconventional conditions will favour the hemicelluloses removal after depolymerization and will lead to the desired cellulose degradation,
- H₂O₂ oxidation carried in unconventional conditions will convert part of the hydroxyl groups of the anhydro-glucose unit of cellulose into carboxyl groups, favouring the dissolving ability of cellulose.

Prior to the discussion of the investigated conditions, a review on the classical hydrogen peroxide stage, and on the activation of hydrogen peroxide by Cu(II) and Cu(II)-phenanthroline is presented as an introduction of the chapter.

III.2. Hydrogen peroxide

Traditionally, chlorine dioxide is the chemical used for delignification, but it is also responsible for the formation of a variety of toxic chloro-organic compounds. Under the pressure of environmental demands, the use of non-chlorine containing chemicals has caught the attention of the paper industry². For this reason, other alternatives have been considered for delignification purposes.

Hydrogen peroxide is used as a bleaching agent for virgin wood chemical pulps since the 80's. Nowadays, due to its versatility, it is also used as reinforcement agent after oxygen delignification, and in alkaline extraction stages to avoid the yellowing induced by sodium hydroxide⁵. The P-stage is considered as a complementary stage in ECF sequence, to enhance the final brightness and brightness stability; and it is also a major bleaching stage in TCF bleaching sequences, for delignification. The P-stage can be performed alone or in combination with oxygen, the operation conditions of the P-stage are detailed in Table III-1:

	Pressure	Pulp	Temp.	Time	NaOH	рН	H ₂ O ₂
	(bars)	cons. (%)	(°C)	(min)	(%odp)		(%odp)
Classical	1	10-15	60-90	30-240	0.2-4	10-12	0.2-4
P-stage		10 13	00 50	30 2 10	0.2	10 12	0.2 1
(PO) or	3-8	10-35	80-120	30-180	0 2-4	10-12	0 2-4
(OP) stage		10 33			0.2 1	10 12	0.2 1

Table III-1. Operating conditions during P-stage⁶

However, hydrogen peroxide is easily decomposed. This decomposition is catalysed by metals or alkali and forms intermediate oxidative free radicals that can degrade cellulose. To avoid this, chelating agents (Q stage), and sodium silicate are used in industry. Yet, some remaining part of the metal ions in pulp are able to either oxidise or reduce H_2O_2 as shown in the reactions:

$$2H_2O_2 \to O_2 + 2H_2O$$
$$2Me^{n+} + H_2O_2 \to 2Me^{(n-1)^+} + O_2 + 2H^+$$
$$2Me^{(n-1)^+} + H_2O_2 + 2H^+ \to 2Me^{n+} + 2H_2O$$

....

Where Me is for metal, and Me^{n+} and $Me^{(n-1)+}$ are metal ions. Simultaneously, three possible radical species can be formed by a Fenton-like reaction: hydroxyl, hydroperoxyl or perhydroxyl, and superoxide. The classical Fenton system occurs with H_2O_2/Fe^{II} couple which forms hydroxyl radicals at acidic pH. In the following steps, hydrogen peroxide reacts with the hydroxyl ion (HO⁻) to produce the perhydroxyl anion (HOO⁻). The reactions derived from this system are detailed below:

$$\begin{aligned} H_2 O_2 + M e^{(n-1)^+} &\rightarrow H O^- + H O^\bullet + M e^{n+} (Fenton - like) \\ H_2 O_2 + H O^\bullet &\rightarrow H_2 O + H O O^\bullet \\ H O O^\bullet &\rightarrow O_2^{\bullet-} + H^+ \end{aligned}$$

Superoxide generation can also be formed at alkaline pH, induced by metals:

$$Me^{n+} + HOO^{-} + HO^{-} \rightarrow Me^{(n-1)^{+}} + O_2^{\bullet-} + H_2O^{\bullet-}$$

HO[•] is a strong electrophilic oxidant, able to react with lignin and other carbohydrates. O_2^{-} is a strong nucleophile, and a moderate reductant. Unlike O_2^{-} , HOO[•] is an oxidant. These species act as oxidants and are generated in alkaline medium, and occur typically in lignin-retaining bleaching and, in lignin-removal bleaching⁷. The mentioned ions are key compounds to understand the expected behaviour of H₂O₂ under the oxidation conditions studied in the present chapter.

III.2.1. Hydrogen Peroxide under alkaline conditions

Under alkaline conditions, superoxide radical anion (O_2^{\bullet}) can be generated, which can form hydroperoxyde anion (HOO⁻) that can further undergo a metal-catalysed disproportionation reaction forming hydroxyl radical (HO[•]). Most of these reactions are extremely quick but others can go very slowly⁸. The decomposition products lead to the introduction of hydrophilic carboxyl groups, the cleavage of bonds, and the dissolution of lignin. The reactions listed below proceed in oxygen delignification at temperatures of about 80-100°C:

$$0_{2}^{\bullet-} + H0^{\bullet} \to H0^{-} + 0_{2}$$

$$H00^{-} + H0^{\bullet} \to H0^{-} + 0_{2}^{\bullet-}$$

$$H0^{\bullet} + H0^{\bullet} \to H_{2}0_{2}$$

$$0_{2}^{\bullet-} + 0_{2}^{\bullet-} + H_{2}0 \to H0_{2}^{-} + 0_{2} + H0^{-}$$

$$0_{2}^{\bullet-} + H_{2}0_{2} \to H0^{-} + H0^{\bullet} + 0_{2}$$

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$$HOO^{-} + H_2O_2 \rightarrow HO^{\bullet} + O_2^{\bullet-} + H_2O$$

 $O_2^{\bullet-} + HO^{\bullet} + H_2O \rightarrow HOO^{-} + HO^{-}$

In alkaline conditions, HOO⁻ decomposes into hydroxyl radical (OH.), and superoxide radical anions (O2⁻). The hydroxyl radical (HO⁻) is a very reactive oxidizing species, capable of reacting with most organic compounds, typically by hydrogen abstraction⁹. The mechanisms suggested by *Gierer*¹⁰, and presented in Figure III-1, indicates that hydroxyl radicals degrade carbohydrates by attaching the C-2 position of the anhydroglycose units in the polysaccharide chains.



Figure III-1. Mechanism for oxidative cleavage of carbohydrates by hydroxyl radicals¹⁰.

Different studies performed by *Guay et al*¹¹, demonstrated that the formation of a ketone in the glycosidic unit allows for the cleavage of the glycosidic linkage by β -elimination. It was also demonstrated by the authors that hydroxyl radicals can simply cleave any randomly encountered glycosidic linkage in cellulose.

III.2.2. Activation of H₂O₂ by Copper phenanthroline

The addition of copper phenanthroline, in alkaline aqueous solution, promotes the formation of different complexes by self-assembly process, which depends on the concentration of OH⁻, and phenanthroline-to-copper molar ratio¹². Some of the formed species are presented in the reactions below.

$$Cu(Phen)^{2+} + H_2 0 \rightleftharpoons Cu(Phen)(OH)^+ + H^+$$
$$Cu(Phen)^{2+} + 2H_2 0 \rightleftharpoons Cu(Phen)(OH)_2 + 2H^+$$

$$2Cu(Phen)^{2+} + 2H_20 \rightleftharpoons [Cu(Phen)(OH)]_2^{2+} + 2H^+$$

Cu(Phen)complexes were first studied in biology, and it was observed that in the presence of H_2O_2 and a reductant, it could cleave DNA¹³; and later it was evidenced that they induced reactive oxygen species generation in the cells, thus damaging DNA and proteins⁶. The oxidative action of Cu(Phen)complexes in the presence of H_2O_2 has been the starting point of studies about oxidation of lignin compounds under alkaline conditions, and it was also evaluated for the decolorization of coloured cellulose fibres¹⁴. However, it was followed by a strong cellulose degradation, which may be explained as Cu(Phen) would activate H_2O_2 decomposition into highly oxidative radicals.



Figure III-2. Catalytic cycle proposed by Walger et al.

*Vladut et al*² proved that HO' generation during P stage is much more intense with Cu(Phen), when compared to a classical non-activated stage. The catalytic mechanism proposed by Walger et al⁶ is presented in Figure III-2, where the first step would be the reduction of Cu(II) to Cu(I) by reaction with the substrate. At alkaline pH, the substrate will refer to the dyed cellulose used in the mentioned study, whereas at neutral pH it would be H_2O_2 itself. As a consequence, the generated Cu(I) would react with H_2O_2 producing hydroxyl radicals, thus degrading the dye, and the cellulose, but not significantly affecting the physical properties of the pulp. The rate of hydroxyl radical production was also evaluated: in neutral medium, an intense and short-duration flow was produced as in the Fenton reaction; on the other hand, in alkaline medium the radical flow.

*Walger et al*⁶ showed that copper II alone, and also the copper II-phenanthroline complex, significantly improved the reactivity of H_2O_2 . The results are a better colour-stripping of dyed pulps, while cellulose is also more depolymerized. Similar results have been observed by Das

et al³. and Vladut et al². on chemical pulps: delignification was improved but cellulose DPv was affected. A detailed mechanistic study, carried by Walger et al. explained that copper II is the activating specie and phenanthroline only acts as a stabilizing agent to adjust the solubility, the stability and the redox potential of copper II. The activation of hydrogen peroxide is mainly due to the decomposition of H_2O_2 into hydroxyl radicals by the copper species and the extent of the activation is strongly dependent on the pH of the medium. Finally, this study concluded that the $H_2O_2/Cu(II)$ system is an interesting generator of hydroxyl radicals with adjustable flow. In the present chapter, this system will be investigated to oxidize lignin-free cellulosic pulps with the objective of producing dissolving grade pulps.

III.3. Oxidation trials with 2%H₂O₂

All the oxidation trials in the present chapter were carried out at high temperature to favour the formation of hydroxyl radicals. Final pH, chemical charge of H_2O_2 and NaOH have been varied.

III.3.1. Operating conditions of the H2O2-based oxidation systems

20g of oven dried pulp were weighted and later disintegrated using a Lhomargy apparatus for 1 min. The pulp was then concentrated by filtration and introduced in a polyethylene (PE) bag used as reactor. The total weight was completed up to 5% consistency (400 g of fibre suspension, considering the chemicals to be added). The pulp was preheated in a water bath at 95°C for 20 minutes, and the chemicals were added and mixed by hand in each step in the following order: Cu(Phen) or Cu₂SO₄, NaOH, and H₂O₂. The pH was measured before closing the PE bag, right before put it in the water bath for 1h to start the oxidation. After the reaction, the fibre suspension was filtered and the first effluent collected for pH measurement, and determination of H₂O₂ consumption. Finally, the pulp was washed with deionised water until neutral pH. 2 g of oven dried pulp were separated for brightness measurement, performed the same day of the oxidation. The remaining pulp was air dried for further measurements such as intrinsic viscosity, and functional group quantification.

The assumed reaction is the partial oxidation of the hydroxyl groups (-OH) of the cellulose into carbonyl (C=O) and / or carboxyl groups (COOH). The addition of such groups may enhance the dissolving ability of cellulose, but in parallel the oxidation may also depolymerise the cellulose chain.

The Cu(Phen) complex was prepared using CuSO₄·5H₂O and 1,10-phenanthroline, as done by *Walger et al*⁶. It was prepared in aqueous solution by dissolving phenanthroline and adding CuSO₄, using 2 moles of phenanthroline for 1 mole of CuSO₄. The complex is referred in the document as Cu(Phen).

III.3.2. Chemical preparation

For the oxidation trials, the reagents concentrations were calculated for 20 g (oven-dried) pulp.

NaOH

2% NaOH (0.4g NaOH out of 20 g pulp): 10 mL from a solution of 1 M NaOH were required.

0.2% NaOH (0.04 g NaOH out of 20 g pulp): 1 mL from a solution of 1 M NaOH was required.

H_2O_2

2% H₂O₂ (0.4g H₂O₂ out of 20g pulp): 1.03 mL was required from a 35% solution by weigh (density 1.11 g/mL). Titrations were performed prior the oxidation trials in order to confirm/correct the concentration of H₂O₂ solution.

Copper (II)

0.02% Cu(II) from CuSO₄· $5H_2O$ (0.004 g Cu(II) out of 20 g pulp) - A solution of 0.4 g Cu/L was prepared as follows:

$$0.4g Cu * \frac{1 \mod Cu}{63.4g Cu} * \frac{1 \mod CuSO_4 \cdot 5H_2O}{1 \mod Cu} * \frac{249.69 g CuSO_4 \cdot 5H_2O}{1 \mod CuSO_4 \cdot 5H_2O}$$

= 1.57 g CuSO_4 \cdot 5H_2O in 1 L

For each oxidation trial, 10 mL of the solution 0.4 g Cu/L were required:

$$\frac{0.004 \ g \ Cu}{0.4 \ g/L} * \frac{1000 \ mL}{1 \ L} = 10 \ mL \ of \ CuSO_4 \ Solution$$

Cu(*Phen*)

0.02% Cu(II) from Cu(Phen) (0.004g Cu(II) out of 20g pulp) – A solution containing 1 mol of CuSO₄.5H₂O and 2 moles of phenanthroline is prepared. In 1 L of solution, the quantity of CuSO₄·5H₂O, is the same (1.57 g) as it is expected the same concentration of Cu. The required quantity of phenanthroline for 1 L of solution was calculated as follows:

$$0.4 g Cu * \frac{1 mol Cu}{63.4 g Cu} * \frac{2 mol C_{12}H_8N_2}{1 mol Cu} * \frac{180.21 g C_{12}H_8N_2}{1 mol C_{12}H_8N_2}$$

= 2.27 g C_{12}H_8N_2 in 1 L

This quantity is mixed with 1.57 g of $CuSO_4 \cdot 5H_2O$ to obtain the Cu(Phen)solution. The quantity of the Cu(Phen)solution to be introduced per trial is 10 mL.

$$\frac{0.004 \ g \ Cu}{0.4 \ g/L} * \frac{1000 \ mL}{1L} = 10 \ mL \ of \ Cu(Phen)_2 \ Solution$$

III.4. Results and discussion

The screening of the more interesting conditions for cellulose oxidation with hydrogen peroxide has been carried out on Kraft pulps from hardwood and softwood. The cellulosic samples exhibiting the lowest intrinsic viscosity (IV) in CuED have been selected, SW-K-2, HW-K-2, with IV values of 563 and 496 mL/g, respectively. For comparison with a substrate without hemicelluloses, cotton linters (CL, IV of 695 mL/g) have also been included in the chapter.

Oxidation trials using H_2O_2 alone have been carried out, as well as trials with copper (II) activators, either Cu(II) from copper sulfate or from the Cu(Phen) complex. The pH of the oxidation reaction varied by the addition of different amounts of sodium hydroxide: 0, 0.2 or 2% NaOH, for a constant H_2O_2 charge (2%). Using these conditions, it was aimed to investigate the behaviour of the three H_2O_2 -based systems in acid, neutral and alkaline medium.

After oxidation, the pulps have been analysed, through intrinsic viscosity (IV), alkali resistance (R18), crystallinity, and brightness (%ISO). The final pH and the consumption of H_2O_2 were also monitored for the purpose of optimising the conditions for the oxidation. Finally, the dissolving ability of the pulp was assessed using the method proposed in Chapter II, derivatization of cellulose while measuring the particle size by DLS; as well as by the dissolution in NaOH:urea:water system. The chemical doses used for the oxidation trials are detailed in Table III-2. These conditions have been extracted from previous work done at LGP2 by E. Walger and S. Das.

Table III-2. Conditions using 2% H₂O₂ and 0.02% Cu or Cu(Phen) with different doses of NaOH.

Conditions	
0% NaOH	H_2O_2 alone
	H_2O_2 / Cu

	H_2O_2 / Cu(Phen)		
0.2% NaOH	H_2O_2 alone		
	H ₂ O ₂ / Cu		
	H_2O_2 / Cu(Phen)		
2% NaOH	H ₂ O ₂ alone		
	H_2O_2 / Cu		
	H_2O_2 / Cu(Phen)		

III.4.1. Cellulose oxidation using only H2O2





Figure III-3. Intrinsic viscosity (IV) in CuED and final pH after oxidations with 2% H₂O₂. (IV_{initial}: 563 ml/g for SW-K-2, 496 ml/g for HW-K-2, and 695 ml/g for CL).

In the initial trials only H₂O₂ were used with the combination of different doses of NaOH. It was observed similar tendencies for SW-K-2 and HW-K-2 but different for CL. For softwood and hardwood, while the final pH reached was below neutral, there was a significant reduction of the intrinsic viscosity (IV). But when the final pH was as high as 11, the IV reduction was much attenuated. It was observed that for CL, the higher the pH, the less affected the cellulose (with limited IV reduction) as presented in Figure III-3. This can be related to the type of fibre, due to the presence or absence of hemicelluloses, crystallinity, and accessibility. But they all obtained the highest intrinsic viscosity value when the oxidation was carried out at alkaline pH. When comparing softwood and hardwood, HW's intrinsic viscosity values decreased more than SW's, maybe as an indication of the better accessibility of reagents to cellulose in the nanostructure of the fibre wall.

The hydrogen peroxide consumption after the oxidation trials is presented in Figure III-4.



Figure III-4. H₂O₂ consumption, brightness (%ISO), and final pH after oxidations with 2% H₂O₂. (initial ISO brightness: 87.9% for SW-K-2, 87.9% for HW-K-2, and 90.2% for CL).

When using only different doses of NaOH, as presented in Figure III-4, it is observed that HW-K-2, SW-K-2, and CL behaved similarly: the H_2O_2 consumption increased when the final pH was higher. If we consider the intrinsic viscosity values higher than 400 mL/g, as for interesting dissolving applications, the acidic pH did not give interesting results, as well as not achieving total consumption of H_2O_2 . It is interesting to see that H_2O_2 consumption is not directly related to the decrease of IV. Indeed, the peroxide consumption is higher in alkaline medium despite a reduced bulk attack of cellulose, due to slower rate of HO[°] generation. In acidic medium, the bulk attack of cellulose is more important, but H_2O_2 consumption is less.

The role of copper as an activated specie is evaluated in the following section.

III.4.2. Cellulose oxidation by H2O2 activated by Cu(II)

2% H₂O₂ and 0,02% Cu were used in the following oxidation trials in combination with different doses of NaOH in order to evaluate the effect of different pH. Figure III-5, presents the final pH and intrinsic viscosity for the studied cellulosic substrates.



Figure III-5. Intrinsic viscosity (IV) in CuED and final pH after oxidations with 2% H₂O₂ and 0.02% Cu(II). (IV_{initial}: 563 ml/g for SW-K-2, 496 ml/g for HW-K-2, and 695 ml/g for CL).

For the case of HW-K-2, IV values were reduced significantly when the final pH was acidic. But, it was only reduced to 396 mL/g at alkaline pH, a similar behaviour as with H_2O_2 alone. Such behaviour was also observed for SW-K-2, as shown in Figure III-5, where the lowest IV value was reached with the lowest pH. Yet, CL behaved differently since degradation only took place at alkaline pH, going from its initial value of 695 mL/g, to 317 mL/g. Alkaline medium provided conditions for cellulose swelling and not too fast generation of radicals in the course of peroxide decomposition. This is because copper ions are hydroxylated in alkaline medium, which is not the case in acidic medium where the radicals flow is intense. At the same time, cellulose in CL is not protected by a hemicelluloses barrier around the microfibrils when it becomes more accessible by swelling.



In Figure III-6 it is observed that the presence of copper(II) enhanced the consumption of H_2O_2 , for all the cases and did not affect the brightness values (>80% ISO for all the cases).



To conclude, the addition of free copper (II) catalyses H_2O_2 decomposition, generating oxidising radicals whose aggressivity towards the substrate depend on the pH and the substrate accessibility. The effect of introducing copper as a complex, the copper-phenanthroline (Cu(Phen)), is presented below.

III.4.3. Cellulose oxidation by H2O2 activated by the Cu(Phen) complex

When using Cu(Phen) instead of CuSO₄, similar tendencies for the general cellulose degradation, reflected in the drop of IV, were observed in the Kraft pulps, and are presented in Figure III-7.



Figure III-7. Intrinsic viscosity (IV) and final pH after oxidations with 2% H₂O₂ and 0,02% Cu(Phen). (IV_{initial}: 563 ml/g for SW-K-2, 496 ml/g for HW-K-2, and 695 ml/g for CL).

With Cu(Phen), CuSO₄-H₂O₂ or H₂O₂ alone, for the Kraft pulps, the lowest cellulose degradation takes place at a higher final pH (2% NaOH). Contrary to CL, which achieved its highest IV value at pH closed to neutral (0.2% NaOH). Moreover, it is shown in Figure III-8 that similarly as with H₂O₂ alone, the complete H₂O₂ consumption is achieved at alkaline pH, but as for the CuSO₄-H₂O₂ system, it is also rather important at acidic pH, as a result of copper catalysis. The same behaviour was seen for the brightness (%ISO) values, lower at acidic pH. In general terms, at acidic pH, the intrinsic viscosity values decreased down to three times the initial values, the hydrogen peroxide decayed down to 20% consumption and the brightness %ISO was more affected compared with the other scenarios.



Figure III-8. H₂O₂ consumption, brightness (%ISO), and final pH after oxidations with 2% H₂O₂ and 0.02% Cu(Phen). (initial ISO brightness: 87.9% for SW-K-2, 87.9% for HW-K-2, and 90.2% for CL)

The addition of Cu(Phen)and CuSO₄, in comparison with the results without copper, made possible to observe the role of the hydroxyl radicals generated and their degree of penetration in the cellulose network, related to substrate accessibility. SW-K-2 was less degraded at acidic pH with free copper than with Cu(Phen). With free copper, the generation of radicals is so intense that diffusion inside the medium has no time to occur. Contrary to that, in HW-K-2, diffusion and reaction can take place at the same time and the bulk attack is more pronounced at acidic pH. With Cu(Phen), radical's generation is slowed down and diffusion can take place also in SW-K-2. These considerations on the reactivity of the different substrates submitted to the attack of hydroxyl radicals agree with the results of the carbanilation test in DMSO, which evaluated the dissolution ability of the substrates in an organic reaction with phenyl isocyanate, that required cellulose accessibility, as discussed in the previous chapter (see Figure II-18).

Comparison of the three H_2O_2 -based oxidation systems

In general terms, the discussed section above showed similar reactivities for HW-K-2 and SW-K-2, but significant differences with CL. In the latter, the cellulose structure is much more compact (high crystallinity) and hemicelluloses are absent. Cellulose swells in alkaline medium which allows better bulk penetration of reagents, under conditions promoting a regulated flow of radicals (by copper complexation, Cu(OH)₂ or Cu(Phen)). For CL, cellulose degradation takes place without the protection of an hemicelluloses barrier. The Kraft pulps are more accessible and thus reactive to the flow of radicals, despite the presence of an hemicelluloses barrier, especially in acidic medium. Finally, alkaline pH provides a better control of the radicals flow, which is almost inexistant in the absence of copper, leading to very little cellulose degradation and the highest brightness level.

III.4.4. Cellulose oxidation by H₂O₂/Cu(Phen) – towards optimisation

Additional tests were performed in order to determine the more interesting conditions to get a final pH close to neutral or slightly alkaline, and still reaching interesting final properties, with the aim of improving the dissolution ability of the studied substrates. For these tests, the concentrations of H_2O_2 and Cu(Phen)remained the same, 2% and 0.02% respectively, while the dose of soda was explored until reaching the desired final pH.



Figure III-9. Pulp IV and final pH after oxidations using 2% H₂O₂ and 0.02% Cu(Phen) with different NaOH doses. (IV_{initial}: 563 ml/g for SW-K-2, 496 ml/g for HW-K-2, and 695 ml/g for CL).

The determined conditions allowed the full H_2O_2 consumption ($\approx 100\%$), high brightness values ($\approx 90\%$ ISO). Intrinsic viscosity values around 400 mL/g were reached for CL and SW-K-2, as shown in Figure III-9. However, HW-K-2 did not achieve intrinsic viscosity values in the desirable range (400-600 mL/g) – for viscose applications. Complementary alkali resistance tests have been performed to assess the cellulose purity. The results are shown in Figure III-10.



Figure III-10. Alkali resistance (R18) of the pulps after oxidation using 2% H₂O₂ and 0.02% Cu(Phen) with different NaOH doses. (REF = reference pulp).

No difference between the reference and the oxidized substrate was observed for CL (as only hemicelluloses are expected to dissolve in the R18 test). For HW-K-2, a slight improvement in the cellulose purity was observed, especially at 0.5% NaOH, reaching a good R18 value; and for SW-K-2, purification was slight but better with 0.3% NaOH than with 0.4% NaOH.

To examine if the oxidation treatment had an impact on the physical structure of cellulose, the crystallinity has been also analysed. The crystallinity profiles (displayed in the Appendix) were measured by XRD, and the Segal peak height method was used to calculate a crystallinity index.



Figure III-11. Crystallinity index of the pulps after oxidation using 2% H₂O₂ and 0.02% Cu(Phen) with different NaOH doses (REF=untreated pulp).

As observed in Figure III-11, the crystallinity was affected by the oxidation for all the substrates, but to different extents. It seems related to the final pH. For the SW-K-2, a high crystallinity drop is observed as soon as the final pH becomes alkaline. A strong drop is also observed for the HW-K-2, even at near-neutral pH. This agrees with the fact that HW-K-2 is more accessible and more degraded than SW-K-2 at this pH. In contrast, CL was less degraded (lower IV variations) and did not show an important CI decrease, compared to Kraft pulps. As already discussed, CL is the least accessible substrate, especially when it is not much swelled by NaOH. It is also possible to consider that in CL, cellulose recrystallization during drying of the wet pulp, fully washed after oxidation, is not hindered by the presence of hemicelluloses.

III.4.5. Dissolving ability evaluation

Dissolution trials were performed by duplicate, and analysed by the carbanilation method, as detailed in Chapter II. The particle size measurement during carbanilation of the SW-K-2 is given in Figure III-12.



Figure III-12. Average particle size during carbanilation of the oxidized SW-K-2 (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).

From Figure III-12, and according to the discussion in Chapter II, an average particle size value can be calculated along the dissolution, which serves as an index for the rate of dissolution. Values were: SW-K-2 REF, 185 nm; SW-0.3% NaOH, 232 nm; SW-0.4%NaOH, 168 nm. A ranking of dissolution rate can be estimated, where the highest average diameter implies the slowest dissolution. The SW-0.4%NaOH was thus the fastest one, followed by the SW-REF, and then by the SW-0.3%NaOH, for which the end-pH was near-neutral.



Figure III-13. Average particle size during carbanilation of the oxidized HW-K-2 (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).

In the case of HW-K-2 (Figure III-13), the ranking of the average diameter values are: HW-K-2 REF, 114 nm; HW-0.4%NaOH, 137 nm; and HW-0.5%NaOH, 98 nm. Thus, the oxidized samples presented a faster dissolution than the reference sample; the higher the pH, the fastest the dissolution was, also corresponding to a higher reactivity (loss in IV) than SW pulp.

Finally, the dissolving behaviour of cotton linters is presented in Figure III-14. The obtained average diameter values are: CL-REF, 246 nm; CL-0.2%NaOH, 296 nm; CL-0.3%NaOH, 268 nm. None of the oxidized CL were ranked faster to dissolved, compared with REF.



Figure III-14. Average particle size during carbanilation of the oxidized CL (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).

Overall, only oxidized CL 0.2%NaOH, SW 0.3%NaOH, and HW 0.4%NaOH dissolved slower that the initial pulps. When pointing out the final pH after the oxidations (Figure III-9), it can be presumed that a pH around 9 resulted in a better dissolution, at least for hardwoods, and for CL only at the beginning. Yet, the dissolution behaviour in DMSO may be affected by the creation of functional groups during the oxidation of the substrates. It is well established that carboxyl groups react at a much slower rate with phenylisocyanate than alcohols do. In Figure III-12, Figure III-13, and Figure III-14, the detailed observation shows that for the pulps treated at the highest alkalinity, dissolution is accelerated at the beginning but rapidly slower after a certain time. This could be an indication of a better accessibility to the bulk of the substrate and to the R-OH groups, but slower reactivity at the end with the presence of RCOOH groups.

In some cases, like MFC production, the target may be the creation of carboxyl groups to favour wettability, swelling and cellulose final dissolution in water or in a polar medium (this is the object of the study in Chapter V). In such cases, the fastest dissolution measured by cellulose carbanilation may not be the right indication for the best dissolution behaviour.

MWD profiles of the oxidized substrates

Further analysis of the carbanilated substrates was done by HPSEC, after dilution in THF of the fully dissolved substrate samples in DMSO, as CTC. As already seen by the IV in CuED measurements, MWD profiles and the acquired SEC data in Table III-3, allow to observe the degradation of the samples after the different oxidation treatments, compared to the reference. The dispersity Index (Mw/Mn), also shown in Table III-3, is an interesting indicator of the narrowness of the MWD profile. Intrinsic viscosity (weight-average), DPw and hydrodynamic radius (weight average) are also derived for all the samples. Figure III-15, Figure III-16, and Figure III-17 display the MWD profiles of SW-K-2, HW-K-2, and CL, respectively obtained before and after oxidation.

Table III-3. SEC analysis of the oxidized substrates (oxidation with 2% H2O2 and 0,02% Cu(Phen) using
varied NaOH doses. REF=untreated pulp).

	IV (mL/g)	Rh (nm)	Mw/Mn	DPw
SW-K-2 REF	289	28	3.6	1218
SW-K-2 0.3%NaOH	180	19	2.9	635
SW-K-2 0.4%NaOH	212	22	3.6	851
HW-K-2 REF	284	28	4	1215
HW-K-2 0.4%NaOH	167	19	5.8	845
HW-K-2 0.5%NaOH	262	25	3.9	943
CL REF	422	35	2.8	1433
CL 0.2%NaOH	230	24	1.6	791
CL 0.3%NaOH	261	26	2.6	1017



Figure III-15. Molar weight distribution of the oxidized SW-K-2 substrate (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).



Figure III-16. Molar weight distribution of the oxidized HW-K-2 substrate (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).



Figure III-17. Molar weight distribution of the oxidized CL (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).

The SW-K-2 and HW-K-2 pulps, both containing hemicelluloses and cellulose, display a classical bimodal MWD profile. In the reference samples (blue curves), hemicelluloses are present in the range of logM=4.5-5, whereas the cellulose fraction appears at higher molar mass, centred around logM=5.8-6. After oxidation (orange and grey curves), MWD profiles were shifted towards lower molar mass. This is also evidenced by the drop of DPw, IV and Rh (Table III-3). All oxidised pulps still presented a signal in the hemicelluloses range, meaning that they were not completely removed during oxidation.

For both types of Kraft pulps, degradation is related to the final pH: the most important degradation occurs at the lowest alkalinity dosage, producing either near-neutral or very slightly

alkaline medium. Again, this seems to be under the control of the hydroxyl radical generation flux, less important in alkaline medium when copper is more complexed. Moreover, the more accessible substrate, HW-K-2, tends to increase its dispersity value, showing that oxidation is less selective and operates on all chain sizes, compared to the less accessible SW-K-2 pulp.

The behaviour of cotton linters can be slightly distinguished from that of the Kraft pulps. MWD profiles are still monomodal after oxidation, meaning a non-deep attack (which would create a bimodal profile, as already observed with other oxidants). Here, cellulose is more depolymerised at near-neutral pH, as seen by the higher shift of the MWD mode (curve peak), but the difference seems less with the alkaline case. Moreover, at alkaline pH, a higher dispersity is observed, which shows that the effect in alkaline medium, more swelled and accessible, although more limited due to a lower flux of radicals, is less selective referring to chain size and accessibility.

Oxidising tests at higher pH (CL-0.4%NaOH, HW-0.6%NaOH and SW-0.5%NaOH) have also been applied, and the corresponding substrates characterised by IV in CuED, carbanilation dissolution test and HPSEC. All data are reported in the Appendix. They all confirm the substrate behaviours and pH effect, as discussed above.

In order to explore further the possible changes occurring during the oxidation with $H_2O_2/Cu(Phen)$, complementary morphological characterisations were performed, and are detailed in the section below.
Morphology analyses

No important changes can be noted in the morphology of fibres, as measured by the MorFi analyser after the oxidation trials (Table III-4). Weight-average fibre width, length, and fine contents can be observed. Figure III-18, presents the water retention values (WRV), which can reflect some changes in fibre swelling and accessibility to water. Again, very similar values can be observed with the studied treatments. It seems that the oxidation treatments did not affect deeply the substrates at the fibre morphological level. SEM images were also taken and did not exhibit visible modification. They are presented in the Appendix, as well as all the compiled information of the conditions of all the oxidation trials.

Table III-4. MorFi analysis of the oxidized substrates (oxidation with 2% H2O2 and 0.02% Cu(Phen) using
different NaOH doses. REF=untreated pulp).

SW-K-2	REF	0.3%NaOH	0.4%NaOH	
Mean arith. Length, um	1246	1415	1432	
Fibre width	27.5	26.6	27.5	
Fine Content, % length	28.9	26.8	21.4	
HW-K-2	REF	0.4%NaOH	0.5%NaOH	
Mean arith. Length, um	646	664	665	
Fibre width	15.5	15.1	15.0	
Fine Content, % length	23.8	23.4	31.5	
CL	REF	0.2%NaOH	0.3%NaOH	
Mean arith. Length, um	909	999	952	
Fibre width	21,1	20.4	20.9	
Fine Content, % length	43.9	42.0	45.7	



Figure III-18. Water retention value of the oxidized substrates (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp).

III.5. Comparison of oxidations: H₂O₂/Cu(Phen) vs H₂O₂ alone

As already discussed, the presence of Cu(Phen) with peroxide generates a regulated flow of radicals, with a strong dependence on the pH. H₂O₂ alone generates much less radicals, especially in alkaline medium (the usual conditions for pulp bleaching). Therefore, for the HW-K-2 pulp (the most accessible substrate), a pH close to neutral was selected, since at this pH radical's formation takes place with or without Cu(Phen). For the SW-K-2, the choice of a slightly alkaline pH was retained, since it favours the substrate accessibility while keeping some radical generation in the presence of Cu(Phen). For CL, the choice of the pH was dictated by the poor substrate accessibility except at alkaline pH where swelling occurs, as discussed in the previous paragraphs. For the mentioned trials, H₂O₂ consumption was higher than 97% in all cases, and with Cu(Phen), the final pH decreased and the intrinsic viscosity was more affected, as shown in Table III-5.

Conditions	Final pH	IV (mL/g)	Brightness (%ISO)	H ₂ O ₂ cons.(%)
SW-K-2 REF		563	87.8	
0.3%NaOH/0.02%Cu(Phen)	8.1	434	87.8	98.6
0.3%NaOH	9.3	461	90.0	98.4
HW-K-2 REF		496	87.8	
0.4%NaOH/0.02%Cu(Phen)	6.7	300	88.5	97.8
0.4%NaOH	7.5	334	91.4	98.4
CL REF		695	90.2	
0.3%NaOH/0.02%Cu(Phen)	9.9	439	90.4	98.7
0.3%NaOH	10.5	513	91.9	98.4

Table III-5. Final pH, intrinsic viscosity (mL/g), brightness (% ISO), H₂O₂ consumption (%). All oxidations with 2% H₂O₂.

Carbanilation – dissolving ability and SEC analyses

The evolution of the particle size measured by DLS during carbanilation in DMSO is presented in Figure III-19, Figure III-20, and Figure III-21. Compared to the reference samples, dissolution is not favoured by oxidation. For the case for HW-K-2 and CL, the oxidations without Cu(Phen) were even slower that the ones with Cu(Phen). As mentioned along the chapter, the insertion of oxidised groups on cellulose, like carboxyl groups, may affect the dissolution rate during carbanilation, especially after some hours of reaction, as observed for HW-K-2 and CL. SW-K-2 presented very similar behaviour in the dissolution when using or not Cu(Phen), less degradation was observed when not using it, referring to the IV values in Table III-5. MWD profiles and cellulose conformation obtained by HPSEC is discussed below.







Figure III-20. Average particle size during carbanilation of HW-K-2 with and without Cu(Phen)











Figure III-23. Molar weight distribution of HW-K-2 with and without Cu(Phen).



Figure III-24. Molar weight distribution of CL with and without Cu(Phen).







Figure III-26. Cellulose conformation of HW-K-2 with and without Cu(Phen).



Figure III-27. Cellulose conformation of CL with and without Cu(Phen).

The MWD profiles obtained by HPSEC are displayed in Figure III-22, Figure III-23, and Figure III-24, for SW-K-2, HW-K-2, and CL respectively. As a general observation, cellulose depolymerisation is accentuated in the presence of Cu(Phen). In the case of the HW-K-2 pulp, the same peak shift is observed with or without Cu(Phen), but dispersity is increased with Cu(Phen) which shows a less selective degradation of all chain size, as already discussed in the previous paragraph. The polymer conformation studied through the representation of Log Rh versus Log M, presented in Figure III-25, Figure III-26, and Figure III-27, shows a similar behaviour for the 3 samples, with or without oxidation. No significant modification of cellulose conformation was induced by the oxidation.

Finally, Table III-6 summarizes the main results of the size exclusion chromatography analyses.

SAMPLE	IV (mL/g)	Rh (nm)	Mw/Mn	DPw
SW-K-2 REF	289	28	3.6	1218
0.3%NaOH/0.02%Cu(Phen)	180	19	2.9	638
0.3%NaOH)	236	24	3.1	915
HW-K-2 REF	284	28	4.0	1215
0.4%NaOH/0.02%Cu(Phen)	167	19	5.8	845
0.4%NaOH	170	19	4.2	682
CL REF	422	35	2.8	1433
0.3%NaOH/0.02%Cu(Phen)	261	26	2.6	1017
0.3%NaOH	287	28	2.0	1139

Table III-6. Additional information from HPSEC for the oxidised samples with and without Cu(Phen).

For the three substrates, the DPw decreased after both kind of oxidations. Degradation was generally higher in the presence of Cu(Phen). In the particular case of the HW-K-2 substrate, this is revealed by the increase of the dispersity index, which causes an increase of DPw, being influenced by the higher proportion of long chains (as seen on the MWD profile). The same tendency can be observed looking at the intrinsic viscosity values (IV) obtained by HPSEC Table III-6. The values of hydrodynamic radius confirm the particle measurements by DLS during carbanilation, showing an average particle size below 100 nm at the end of the derivatization.

Complementary analyses

Crystallinity index of the reference and all oxidised substrates are presented in Figure III-28.



Figure III-28. Crystallinity index of the oxidized substrates with and without Cu(Phen).

Oxidized SW-K-2 presented a slight decrease but not much significant when comparing the presence or absence of Cu(Phen); the same behaviour was observed in CL. However, for the oxidized HW-K-2, a higher affectation of the CI was observed when Cu(Phen) was used.

Carboxyl groups, as well as sugar analyses were also investigated, to examine the effect of the oxidation treatments on the possible formation of polar groups remaining on the substrate, and on the removal of hemicelluloses.





No important formation of carboxyl groups was observed on the three substrates. The more significant enrichment can be observed for the HW-K-2, possibly linked to its better accessibility/reactivity, and also possibly the fact that it contains only xylans, less easily dissolved than mannans in aqueous solutions.

The sugar content was measured by ionic chromatography, after full hydrolysis of the substrate. As shown in Table III-7, the SW-K-2 contained more glucomannans than xylans, and HW-K-2 contained only xylans. CL (not shown in the table) contained only glucose.

	SW-	SW	SW	HW-	HW	HW
	REF	H ₂ O ₂ /Cu(Phen)	H_2O_2	Ref	H ₂ O ₂ /Cu(Phen)	H_2O_2
Cellulose (%)	77	81	77	79	71	74
Hemicellulose (%)	23	19	23	21	29	26
Glucomannans (%)	15	10	12	-	-	-
Xylans (%)	8	9	11	21	29	26

Table III-7. Sugar content of the substrates oxidized with or without Cu(Phen) (REF=untreated pulp).

After oxidation, some changes can be observed. In HW-K-2, the hemicelluloses proportion increased (more pronounced with Cu(Phen), showing that cellulose was more affected and dissolved after oxidation than xylans. Xylans also remained undissolved in the SW-K-2 pulp, whereas mannans proportion decreased. Globally, in the case of H_2O_2 alone, this leads to the same proportion of cellulose, but in the case of $H_2O_2/Cu(Phen)$, a slight enrichment in cellulose is observed, since mannans are more dissolved. But globally, it can be considered that modifications are rather small and that cellulose is not significantly purified from the hemicelluloses, a necessary condition for most dissolving pulps. These results also confirm the observations of the MWD profiles, in which hemicelluloses still remain after oxidation.

The above sugar results also confirm the R18 trials (see Figure III-30), where no differences in the purity for HW-K-2 is observed. However, SW-K-2 became more pure when using Cu(Phen) in the oxidation, compared to H_2O_2 alone, in agreement with the sugar profiles presented in Table III-7, in which one can see the better elimination of mannans than xylans or cellulose.



Figure III-30. Alkali Resistance, R18 (%) of the oxidized substrates with and without Cu(Phen).

III.6. Dissolving ability in the NaOH:urea:water system

As done for the reference samples in Chapter II, the dissolution ability of the substrates in the NaOH:urea:water system was also evaluated. The reference substrates and the oxidized substrates were compared, as presented in Figure III-31.



Figure III-31. Solubility in the NaOH:urea:water system for the oxidized substrates with and without Cu(Phen) (ref=untreated pulp)

In this solvent system, solubility is dominated by the cellulose DPv (measured in CuED), as shown in Chapter II. This is also the general tendency displayed in Figure III-31. For the three reference samples, the lower the solubility implies the higher DPv, and solubility varies in the expected order of: CL < SW-K-2 < HW-K-2. Nevertheless, the two Kraft pulps are close to each other, and quite far from the CL pulp which is hardly dissolved. This shows the significant impact of the presence hemicelluloses in the Kraft pulps on the solubility in this system.

After oxidation, unexpectedly, the more depolymerised substrates when Cu(Phen) was used were the less soluble ones, compared to the corresponding substrates oxidised with H_2O_2 alone. This is verified for the three substrates. This is likely due to some chemical modifications induced by the presence of Cu(Phen) and radicals during the peroxide oxidation, but to our knowledge, this cannot be explained.

Overall, the presented tests give indication that the use of Cu(Phen) does not improve the dissolving ability of the oxidised samples in this polar system. The reference samples exhibited a dissolution ability in the same order as the one observed by the carbanilation test.

III.7. Conclusions

The impact of the use of copper as a catalyst for oxidations with commonly-used-in-mills chemicals, H₂O₂ and NaOH, was evaluated for three selected samples: CL, SW-K-2, and HW-K-2. Copper was present in CuSO₄, in Cu(OH)₂ in alkaline medium, and in the copper-phenanthroline complex which has different forms depending on the alkalinity of the medium.

Intrinsic viscosity, as well as total consumption of H_2O_2 and brightness were monitored after the oxidation trials. Nevertheless, the final pH played an important role when selecting the more interesting conditions, which were further characterised with the dissolution ability in the carbanilation reaction, cellulose solubility in NaOH:urea:water system, the alkali resistance test (R18), sugar content analyses, water retention value, and morphological analyses by MorFi. The quantification of COOH groups was also part of the monitored characteristics.

Brightness values above 90% ISO were achieved, as well as cellulose content above 90%, when referring to R18 trials. But the cellulose DPv was strongly affected by the oxidation conditions. The range of cellulose purity for the Kraft pulps was not reached, and the intrinsic viscosity for viscose applications, ideally in the range of 400-500 mL/g, was only reached for some pulps. Even though it was not observed a significant improvement of the dissolution ability by the carbanilation reaction, the dissolution in NaOH:urea:water system was improved for the three selected samples, SW-K-2, HW-K-2, and CL. But in the latter case, the best dissolution improvements were observed without the use of the Cu(Phen).

The main differences of behaviour for all samples can be attributed to the pH reached after every oxidation, as well as the type of hemicelluloses present in the substrate, enhancing or not the action of copper which generates a flux of oxidising radicals in the presence of H_2O_2 . The latter appears to be regulated by the more or less freeness of copper. Indeed, the effect of pH and the presence of phenanthroline allows to regulate the intensity of radical's generation from H_2O_2 decomposition. Additionally, it was observed on the softwood pulp that glucomannans exhibited a better removal, compared to xylans when exposed to the $H_2O_2/Cu(Phen)$ system.

It is important to highlight that for dissolving applications, a high purity is required, but for MFC, a fair amount of hemicelluloses may enhance the microfibrillation. In the following chapter IV, other treatments that generates carboxyl groups on cellulose are explored with the purpose of reaching characteristics for dissolving pulp applications. And, in Chapter V, MFC applications will be studied, considering the use of Cu(Phen).

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IV. Cellulose oxidation with H_2O_2 in combination with other stages: periodate oxidation and alkaline extraction

IV.1. Introduction

In the previous chapter, it was evidenced that the activation of hydrogen peroxide oxidation using copper or the copper/phenanthroline complex, did not improve the cellulose dissolving ability. It was also not very efficient to extract substantial amounts of hemicelluloses from the Kraft pulps, HW or SW, in order to reach the cellulose purity targeted for dissolving pulp applications. As the objective of the thesis project is to evaluate the use of hydrogen peroxide, another strategy has been investigated in this chapter, i.e. the unconventional combination of hydrogen peroxide with other treatments.

Two systems have been studied. The first one based on the combination of hydrogen peroxide oxidation with alkaline extraction of hemicelluloses, referring to the well-known HCE (hot caustic extraction) or CCE (cold caustic extraction) treatments. The idea is to combined two effects: hemicelluloses extraction and cellulose oxidation. The hemicelluloses extraction should favour the pulp dissolution, and the oxidation should introduce hydrophilic groups on the cellulose, improving the reactivity. The second system investigates the use of only oxidative agents: sodium periodate and hydrogen peroxide. The purpose will be, first, to introduce some carbonyl groups in the cellulose by periodate oxidation of the alcohols, followed by over-oxidation of the carbonyls into carboxyl groups, since in Chapter III it was observed that hydrogen peroxide alone did not enrich the pulp with sufficient amount of carboxyl groups to favour substrate dissolution in a significant manner.

IV.2. Alkaline treatments to extract hemicelluloses

The purification aimed to produce dissolving pulps (R18>96%) involves both the removal of non-cellulosic materials, such as lignin, extractives, or hemicelluloses; as well as the change of molecular weight distribution to a narrow, monomodal type, with a minimum amount of low molecular weight carbohydrates; as it has been demonstrated that it can negatively affect the pulp process behaviour or significantly reduce strength characteristics, thus lowering its final quality¹. Conventional CCE is performed at high consistency, above 35%, at temperatures 25-45°C, with concentrations lower than 100 g/L NaOH, and 10 min reaction time. It has been observed that the hemicelluloses decrease linearly with the increase of NaOH concentration, leading to the increase of R18 values. Contrary to CCE that relies on physical effects such as swelling to enhance hemicelluloses dissolution in the polymer network, HCE uses the chemical reactivity of sodium hydroxide for hemicelluloses degradation by peeling/dissolution after acid sulfite pulping. Indeed, such treatment reproduces the same carbohydrate degradation as the

one that undergoes during alkaline Kraft pulping. HCE requires lower alkalinity than CCE, 3-18 g/L NaOH concentration, with 10-15% pulp consistency, and at temperatures ranging from 70-120°C. HCE should take place before an oxidative stage, as the efficiency of the purification is affected when the aldehyde groups are oxidized to carboxyl groups.

As an alternative to pre-hydrolysis prior Kraft pulping, CCE is conducted at room temperature after the Kraft pulping. As a drawback of CCE, some mercerisation might happen and may compromise the pulp dissolving ability and reactivity to certain chemicals. Mercerisation is the conversion of cellulose I to cellulose II, leading to stronger inter and intra molecular bonding. Another negative effect is cellulose fibril aggregation, due to the removal of low molecular weight cellulose and hemicelluloses². As reviewed in previous chapters, the cellulose reactivity is a key parameter for a dissolving-grade pulp, which is defined by the ability of the hydroxyl groups at C2, C3 and C6 to react with other chemicals³. A CCE post treatment may allow to increase such reactivity by decreasing the cellulose degree of polymerisation or by increasing the surface area of the fibres. For example, mercerised cellulose is resistant to acetylation under conventional conditions, while being reactive in the viscose process⁴.

As a consequence, the use of caustic extraction steps for the upgrading of paper-grade pulp became of interest. A modified CCE, at 84 mg/L NaOH, with lower consistency than usual, allowed the upgrade of a commercial bleached Kraft pulp by performing twelve CCE stages at 25°C for 30 min each⁵. Good dissolving-grade pulps properties were observed when optimising the extraction step during the bleaching sequence, with 60-80 g/L NaOH at 80°C. Optimised treatments allowed reaching high selectivity towards xylans removal while cellulose was preserved⁶. Two systems have been formerly studied in LGP2 on bleached softwood Kraft pulp: a modified caustic extraction, allowing 70% of hemicelluloses removal at temperatures above 90°C; likewise, a two-step operation was performed, which consisted in an acid stage (>150°C) followed by a hot caustic extraction (HCE) at 110°C, allowing more than 60% hemicelluloses removal. The latter process led to strong cellulose degradation, yet it remained in the good range for dissolving-grade pulps, in addition to the fact that no cellulose II was formed, compared to the modified caustic extraction formerly mentioned⁷.

In this context, the first section of the chapter studies the insertion of a purification step, combining conditions of CCE and HCE, prior the hydrogen peroxide oxidation. The procedures followed and their effect on the dissolving ability, are discussed in the following section.

IV.3. Hydrogen peroxide with caustic extraction

As in the previous chapter, two pulps have been selected for the study: the fully bleached hardwood Kraft pulp, HW-K-2 (IV in CuED of 496 mL/g, DPv of 692), and the fully bleached softwood Kraft pulp, SW-K-1 (IV in CuED of 745, DPv of 1086).

IV.3.1. Oxidation conditions

The present section investigates the peroxide oxidation and hemicelluloses caustic extraction in one single step, referred as EP. A combination of conditions between CCE and HCE have been selected for the treatment of 10 g cellulosic substrate: a temperature of 75°C as in the lower range for HCE, and at the same time still in the range of a P stage; the NaOH concentration should be carefully chosen, not too high to avoid the conversion of cellulose I into cellulose II, and not too low, at the risk of limiting the hemicelluloses extraction. 75g/L NaOH has been selected, as in a conventional CCE; Yet, the pulp consistency was set at 10% as usually done in the conventional P stage for bleaching, and as in HCE treatment. Moreover, a high dose of H_2O_2 was applied, i.e. 10%, to compensate the high alkaline charge.

To study the effect of the EP treatment, P, E and also E+P treatments with an intermediate washing after E were carried out as controls. The conditions are gathered in Table IV-1.

Step	Conditions HW-K-2 and SW-K-1
E	60 min, 75°C, 75 g NaOH/L
Р	60 min, 75°C, NaOH = 2%, H ₂ O ₂ = 10%
E+P	E step + washing until neutral pH + P step
EP	60 min, 75°C, 75 g NaOH/L, and 10% H_2O_2

Table IV-1. Operating conditions of EP, E, P and E+P treatments

After applying the above described treatments, characterisations were performed, and the results are discussed below.

IV.3.2. Pulp characterisation

The consumption of H_2O_2 was monitored, as well as the final viscosity and brightness (% ISO) (Figure IV-1 and Figure IV-2). For all the cases, final pH was higher than 11.



Figure IV-1. HW-K-2 after strong H₂O₂ oxidation combined with alkaline extraction (IV_{initial}, 496 mL/g).



Figure IV-2. SW-K-1 after strong H₂O₂ oxidation combined with alkaline extraction (IV_{initial}, 745 mL/g).

As a general observation, for the applied treatments and for both substrates, even using high alkalinity, not detrimental effect on the brightness (%ISO) was observed.

For both SW-K-1 and HW-K-2, the use of the extraction alone (E), did not affect strongly the intrinsic viscosity, since for the HW-K-2 it goes from 496 mL/g before E to 517 mL/g after E (thus, a slight increase rather than a decrease); for SW-K-1 it goes from 745 mL/g to 688 mL/g. The E stage alone affects mostly the hemicelluloses and short chains of cellulose, which are in minority in the cellulosic pulps, this explains the low effect of the E stage.

When pointing at the results of the single P stage (10% H_2O_2 , and 2%NaOH), it is observed that the intrinsic viscosity is highly affected for both pulps. H_2O_2 at high dosage is known to

depolymerise cellulose, which was observed. In the case of the E+P treatment, a stronger cellulose depolymerisation occurs, even more pronounced than with P only. This could be explained by the fact that after E, less hemicelluloses are present; thus, in P after E, H₂O₂ mainly reacts with cellulose which is much more affected. Finally, after EP (no intermediate wash included), the values of intrinsic viscosity are decreased due to the high dosage of H₂O₂. It can be noted that the chosen conditions did not allow the total consumption of H₂O₂ in all the trials containing hydrogen peroxide, even in the case of EP where both H₂O₂ and alkali doses are high. The high quantity of H₂O₂ applied is thus responsible of the strong cellulose degradation. To target intrinsic viscosity values around 400 mL/g for dissolving pulp applications, the hydrogen peroxide dose should be lowered.

In the following trials, P and EP treatments had been tested using lower H_2O_2 doses, from 10%, to 2 and 5%. The other conditions given in Table IV-1 are maintained. The effect on the pulp brightness, pulp IV and H_2O_2 consumption are given in Figure IV-3 and Figure IV-4.

In these new trials, with reduced H_2O_2 doses while maintaining high alkalinity in EP, the peroxide consumption is higher and the cellulose depolymerisation is lesser, but intrinsic viscosity values are still very low for viscose applications. For both substrates, the more interesting overall results in terms of brightness (%ISO), and chemical consumption, were observed when using only 2% H_2O_2 . In the case of 5% H_2O_2 , the oxidant consumption is less because the alkali dose, i.e. 2% NaOH, is too low. In the latter case, the cellulose oxidation is probably poor. EP again leads to more cellulose depolymerization than P alone. But the difference has become rather small. Considering peroxide consumption, it seems to be slightly less at higher alkalinity for EP stage than in a P stage. The reason for this is not clear, especially since an opposite trend is observed in the case of SW-K-1.

Globally, HW-K-2 and SW-K-1 reached the highest intrinsic viscosity at low peroxide dosage and when no strong extraction step was included. Brightness values were kept around 90% ISO, and almost full consumption of H₂O₂ was evidenced.



Figure IV-3. HW-K-2 after mild H₂O₂ oxidation combined with alkaline extraction (IV_{initial}, 496 mL/g).





Other parameters were studied in order to evaluate their potential interest for dissolving pulps, such as a MWD profiles, solubility, and purity. All of them, are discussed below.

Cellulose purity measured by R18

To investigate the effects of the above treatments on hemicelluloses removal, R18 analyses have been performed on the pulps treated with 2% and 5% H_2O_2 . The single P stage with low alkalinity (2%), has been included for comparison.

Results are presented in Figure IV-5 and Figure IV-6.



Figure IV-5. Alkali resistance of HW-K-2 treated with P and EP, with 2% or 5% H₂O₂



Figure IV-6. Alkali resistance of SW-K-1 treated with P and EP, with 2% or 5% H₂O₂

A cellulose content above 95% is the general target for high quality dissolving pulps, yet 90% is acceptable for some specialty pulps⁸.

For the HW-K-2 in Figure IV-5, the R18 value is 90.6 % before any treatment. After P alone (2% or 5% H₂O₂), cellulose purity did not improve significantly (91.3 and 90.7% respectively). Thus, a single oxidation with hydrogen peroxide seems to slightly remove hemicelluloses, but this effect is not sufficient. However, when pointing at the combined EP treatment, R18 increased until 96.9% for HW-EP(2%), and 95.3% for HW-EP(5%). Thus, more than 60% of the initial hemicelluloses were removed with EP, which reaches the general target for dissolving pulps. However, it appears that EP is less performing than E alone, where the R18 values reached 99.1%. Therefore, the addition of H₂O₂ in the E stage has a negative effect on hemicelluloses extraction. Globally, to explain the above effects, the following assumption can be proposed: HW-K-2 is a rather accessible substrate containing xylans, which can go to solution in a single E stage (very strong alkalinity). Introducing H₂O₂ in this strongly alkaline

medium lead to both hemicelluloses' extraction, but also polysaccharides oxidation and depolymerization. Some oxidised/depolymerised chains in the substrate can dissolve in the R18 test, leading to apparently less pure cellulose compared to E. Contrary to E and EP, P alone (at low alkalinity) does not have the capacity to dissolve the hemicelluloses, thus leading to unchanged R18 values after oxidation.

For the softwood substrate SW-K-1, the dissolution pattern, presented in Figure IV-6, exhibited similar tendencies, with R18 values ranking in the order E > EP > P > REF. The difference with HW-K-2 is that SW-K-1 has a lower initial purity (R18 of 79.7% for the REF sample). P alone removes some hemicelluloses but the dissolving pulp target is not reached. Yet, P removed hemicelluloses in the SW substrate, compared to HW where no changes were observed. Differences in hemicelluloses composition is perhaps the reason: glucomannans of softwoods may be more sensitive to oxidation and depolymerisation that xylans of hardwoods. The EP treatment in SW-K-1 removed more hemicelluloses than P but the R18 remains too low. E was more efficient that EP, leading to the highest R18 value, above 92%, which is at the very low limit of the target range for dissolving pulps.

COOH quantification

To better understand the action of P and EP on the fully bleached pulp, the carboxylic groups of the substrates have been quantified. The method followed is detailed in Chapter VI, and the results presented in Figure IV-7 and Figure IV-8.



Figure IV-7. COOH quantification of HW-K-2 treated with P and EP, with 2 or 5% H₂O₂



Figure IV-8. COOH quantification of SW-K-1 treated with P and EP, with 2 or 5% H₂O₂

Regarding the softwood substrate, SW-K-1 as in Figure IV-8, no changes in COOH can be observed compared to the initial pulp, whatever the treatment applied, P or EP. In the tested conditions, H₂O₂ is not able to insert COOH groups in the substrate. For the HW-K-2 substrate, in Figure IV-7, the alkaline P treatment slightly oxidized the pulp but when the extraction step E is included, this effect is reduced, which may be likely due to the dissolution of the carboxylated fragments. In any case, the oxidation extent is poor compared to what was expected. Such rate of oxidations may not be sufficient to improve significantly the dissolving ability of the studied substrates.

IV.3.3. Dissolving ability of the pulps during carbanilation

The dissolving ability of the cellulosic substrates has been assessed using the method developed in chapter II, i.e. particle size measurement during pulp carbanilation. This method ranks pulps according to their dissolution ability during derivatisation, and in addition it enables to study the molecular weight distribution (MWD) of the substrate.

Figure IV-9 and Figure IV-10 gather the dissolution behaviours monitored by DLS during the carbanilation reaction in DMSO.



Figure IV-9. Dissolution during carbanilation of HW-K-2 treated with E, P and EP (2% H₂O₂).





For the hardwood substrate, identified as the most accessible pulp in the previous chapter, the reference sample dissolved the fastest compared to all the treated HW pulps (E, P, and EP). Additionally, when a caustic extraction step was included, HW-E and HW-EP(2%), the particle size decrease was rapid during the first two hours, and later the dissolution slowed down. This is not the case of the P(2%) treated pulp, where a more regular evolution of the particle size is observed. One explanation might be that with caustic extraction, part of cellulose I is converted into cellulose II, and during the first two hours of reaction cellulose I dissolves while cellulose II dissolves more slowly. Anyhow, the dissolving behaviour of HW-P(2%) is not better than the reference pulp meaning that the partial oxidation of the substrate did not modify its dissolving ability in an organic reaction system (carbanilation in DMSO).

The softwood pulp behaved differently. All the dissolution curves presented very similar dissolution behaviour. It can be concluded that dissolving ability was not modified compared to that of the reference pulp, whatever the treatment applied.

HW-K-2 and SW-K-1 did not behave similarly: this is may be due to the hemicelluloses type and their ease to dissolve in the carbanilation system, but this is also likely related to the SW substrate structure, much less accessible and less reactive than the HW, as observed in the previous chapter. For HW-K-2, a too high dose of NaOH was probably applied to extract the hemicelluloses, since in Figure IV-5, it is observed that after E and EP, almost all hemicelluloses were removed. Additionally, it is assumed that part of cellulose I was converted into cellulose II, limiting the dissolution in DMSO. For the case of SW-K-1, containing more hemicelluloses, the NaOH dose was possibly insufficient to remove all hemicelluloses, as observed in Figure IV-6. Cellulose I was not significantly converted into cellulose II and soda just acts as hemicelluloses carrier. In SW, reagents reactions improved the substrate accessibility, even when only P was applied, at low alkalinity. A better accessibility in SW is probably a main factor that contributes to its dissolution, contrary to HW more readily accessible and easily dissolved without the need of chemical agents.

For dissolving-grade pulps, high purity cellulose and uniform MWD profiles with low dispersity are required. Thus, following the derivatisation method described in chapter II, MWD profiles after carbanilation were determined by HPSEC, and the obtained curves are presented in Figure IV-11 and Figure IV-12. Complementary information derived from HPSEC analyses are given in Table IV-2.



Figure IV-11. MWD of HW-K-2 treated with E, P and EP (2% H₂O₂).



Figure IV-12. MWD of HW-K-2 treated with E, P and EP (2% H₂O₂).

Untreated HW-K-2 pulp presented a bimodal profile, typical of the presence of cellulose and hemicelluloses. After P(2%), the MWD profiles was shifted toward slightly lower mass, but the characteristic peak of hemicelluloses was still present. This indicates that P at low alkalinity, even with a high peroxide charge, partially depolymerises the cellulose but does not extract the hemicelluloses (mostly xylans in this case). In Table IV-2, it is seen that he DPw decreased from 1215 to 814, but the dispersity, as an indication of the narrowness of the profile, remained unchanged (4.1 before and after P treatment). Using treatments with strong alkalinity, E and EP, the hemicelluloses signal vanished and the dispersity was reduced to 2 and 3, respectively.

	IV(dL/g)	Rh(nm)	Mw/Mn	DPw
HW-REF	2.8	27.8	4.1	1249
HW-E	2.4	23.9	2.3	873
HW-P(2%)	2.1	21.6	4.1	814
HW-EP(2%)	2	18	3	635
SW-REF	6.4	51.7	6.3	4025
SW-E	2.9	28.0	2.6	1222
SW-P(2%)	2.4	23.9	5.0	1066
SW-EP(2%)	2	21	2	742

Table IV-2. Additional SEC information - substrates treated with E, P and EP (2% H₂O₂)

For the SW-K-1 substrate, the same trends were observed. The untreated SW bleached pulp exhibited a bimodal profile with both cellulose and hemicelluloses fractions, but with an additional shoulder around log M = 6.5 which typically represents aggregates. For SW-P(2%) the cellulose signal was shifted towards lower mass without hemicelluloses removal, as in the HW case. E and EP treatments in SW-K-1 were able to remove hemicelluloses since the signal disappeared, with a significant reduction of the dispersity, meaning a much better uniformity

of the MWD profile. A lower dispersity is obtained for SW-K-1 when H_2O_2 was added in the caustic extraction stage; Here, H_2O_2 addition is positive, except for the strong effect on the cellulose DPw (Table IV-2).

Summary

For viscose applications there are some properties that should be reached in order to ensure a good quality product, and to avoid potential difficulties at industrial scale. i.e. uniform MWD, to avoid to plug systems when pumping the dissolved pulp through nozzles to form the fibres. To discuss the key characteristics, a summary is presented in Table IV-3.

		REF	E	P(2%)	EP(2%)
HW-K-2	IV in CuED, mL/g	496	517	345	273
	Brightness, % ISO	87.9	88.9	92.9	93.2
	R18, %	90.6	99.1	91.3	96.9
	meq COOH/100g dried pulp	7.0	5.6	7.7	4.3
	Dispersity (Mw/Mn)	4.1	2.3	4.1	3
SW-K-1	IV in CuED, mL/g	745	688	436	343
	Brightness, % ISO	86.9	85.4	90.5	91.2
	R18, %	79.7	92.2	84.5	90.3
	meq COOH/100g dried pulp	5.9	4.7	5.2	5.1
	Dispersity (Mw/Mn)	6.3	2.6	5.0	2

Table IV-3. Combination of hydrogen peroxide with caustic extraction - summary of the main results

High brightness values (>90% ISO), and high cellulose content (>90%), is expected for viscose applications. HW-K-2 and SW-K-1 reached both values for the oxidation conditions of EP(2%); SW-K-1 reached the minimum accepted in cellulose purity, 90.3%, yet HW-K-2 reached a high value which corresponds to a high quality dissolving pulp, >95%. A more uniform MWD was as well observed with EP(2%) for both substrates, compared to their references. Normal content of COOH for dissolving pulps are in the range of 30 μ mol/g¹. Even though, the treatments did not increase significantly the presence of COOH groups, this is not a condition to be fulfilled for dissolving-grade pulps.

Regarding the intrinsic viscosity, a range between 400-600 mL/g is recommended for viscose applications. As shown in Table IV-3, HW-K-2 starting conditions were low, and the treatments did not allow to reach a good value. However, the values of SW-K-1 remained in a good range for all the treatments but not EP(2%), which reached all the other properties. Unfortunately, none of the substrates reached the desired properties for viscose applications, but maybe interesting for ether applications (IV>300 mL/g), if we refer to the diagrams given by LGP2

industrial partners, presented in Chapter I. Concerning dissolving pulp applications, other combination of oxidations was studied, and is detailed in the section below.

IV.4. Cellulose oxidation using periodate

The aim of oxidising carbohydrates by the periodate ion is to introduce dialdehyde groups into polysaccharides, as explained in Chapter I. Periodate oxidised cellulose is often referred as dialdehyde cellulose (DAC). Moreover, DAC is biodegradable, biocompatible, and the aldehyde compound can be further converted into carboxylic groups, primary alcohols, or amines, which can serve as useful intermediates for cellulose-based specialty materials⁹. Additionally, it is used for the generation of aldehyde functions for crosslinking reactions or further modifications of nanocellulose, for applications as a paper wet strength additive¹⁰, or bio-based adhesives produced from microcrystalline cellulose¹¹.

Periodate is capable to oxidise the vicinal hydroxyl groups at carbon 2 and 3, in an anhydroglucose unit (AGU), into two aldehyde groups, simultaneously breaking the C-C bond. As a result, one mol of iodate is liberated when one AGU is oxidised. The reaction is illustrated in Figure IV-13. Peroxide oxidation is accompanied by a decrease in crystallinity and uneven distribution of the aldehydes¹². As a consequence of the described mechanism, the higher the aldehyde content, the more the degradation¹⁵.

$$* \begin{bmatrix} OH & OH \\ + \begin{bmatrix} 0 & -\frac{4}{5} & 0 \\ HO & -\frac{3}{2} & OH \end{bmatrix} * \begin{bmatrix} NalO_4 & * \begin{bmatrix} 0 & -\frac{4}{5} & 0 \\ 0 & -\frac{3}{2} & 0 \end{bmatrix} * + NalO_3 + H_2O$$

Figure IV-13. Periodate oxidation of cellulose.

The periodate oxidation is conventionally done in water, and due to its low reactivity with cellulose (limited by cellulose accessibility), great amounts of periodate and long oxidation times are required to achieve high aldehyde contents. As a consequence, large amounts of iodine are present in the waste¹³. Sodium periodate has proven to be unstable and decomposes over time into radicals, particularly in the presence of light. Hence, periodate oxidations are preferentially carried out in dark conditions, and in the absence of oxygen, using freshly prepared solutions¹⁴.

In the present section, periodate oxidation is applied as a first oxidative stage to convert the OH alcohols in C2 and C3 into carbonyls (CO), followed by a classical hydrogen peroxide stage, P

stage, to over-oxidized carbonyls into carboxyl groups (COOH). The procedures and results are presented below. The more interesting conditions are to be identified for potential applications of dissolving-grade pulps, as a strong cellulose degradation is expected after the two successive oxidations.

IV.5. Hydrogen peroxide with a previous periodate oxidation

The substrates used in this section are the same as the previous ones, HW-K-2 and SW-K-1. Some trials have been also conducted on cotton linters, to observe the effects of the treatment on a hemicelluloses-free substrate, and for a better comprehension.

IV.5.1 Oxidation conditions

The periodate stage was performed with an excess of sodium periodate. 20 g (oven-dried weight basis) of cellulosic substrate were homogenised in a Lhomargy disintegrator for 1min, and later filtrated on a sintered glass crucible of porosity No. 2 to remove the excess water. The substrate was then transferred into a 2 L Erlenmeyer flask and filled with 1 L of NaIO₄ titrated solution; water was then added to reach a weight of 1250 g and 1,6% pulp consistency. Different amounts of sodium periodate were tested: 54%, 27%, or 13.5% (% expressed as weight of NaIO₄/ weight substrate). The reaction took place in dark conditions and left under stirring for two hours reaction at room temperature. After the reaction, the suspension was filtered and washed with deionised water. Yet, it was not enough to remove the acidic medium. For this reason, after a couple of washes with water and filtration, the suspension was soaked for 10 min in 100 mL of a 20 g/L of NaHCO₃ solution, before filtering again and continuing the washing with deionised water until reach neutral pH.

The washed and filtrated substrate was divided in two parts of same weight: one part to proceed with the characterisation to evaluate the effect of the periodate oxidation, and the second part to start the next oxidation with H_2O_2 (P stage).

To monitor the consumption of chemicals during the periodate oxidation step, 5 mL of the initial NaIO₄ solution (54%, 27%, or 13,5%) were titrated by iodometry, as described in Chapter VI. The same was done with the effluent after oxidation.

The overoxidation was performed with low dosage of hydrogen peroxide and slight alkalinity. The H_2O_2 dose was adjusted to 2% (% expressed as weight H_2O_2 / weight of substrate) and NaOH was set at 1.2% or 1.5% depending on the substrate (% expressed as weight of NaOH /

weight of substrate), the objective being that the P stage proceeds in classical alkaline conditions. Other operating conditions are 75°C, 1 hour of reaction time, and 10% pulp consistency. After the second oxidation, the H_2O_2 consumption was monitored in the effluent, at the end of the reaction by iodometry, as detailed in Chapter VI.

After the oxidations, several analyses were performed, some of them right after the oxidation trials: monitoring of the final pH, chemical consumption, and cellulosic substrate brightness (% ISO); and others later on, as cellulose DPv (or IV), R18, COOH quantification, and dissolution ability through carbanilation in DMSO, MWD by HPSEC analyses, and dissolution in the NaOH:urea:water system.

For the discussion, the periodate oxidation will be referred as the first oxidation and, the oxidation with hydrogen peroxide in alkaline medium, as the second oxidation.

IV.5.2. Pulp characterisation



Figure IV-14 presents the final pH after the second oxidation step, i.e. after the P stage.

Figure IV-14. Final pH values after the substrate oxidation by the combination of NaIO₄ followed by H₂O₂ in alkaline medium.

A blank test was also carried out. The blank test consisted in the same two steps oxidation procedure but without $NaIO_4$ addition in the first step; where the pulp was placed into water at room temperature in dark conditions during 2 h. After, the wash steps were reproduced as if a normal periodate oxidation had taken place, with the 10 min soaking in NaHCO₃. Later, the second oxidation was performed with no further modifications. Results in Figure IV-14 show

that the blank trials were alkaline, as expected with pH values of 12.4, 12.3 and 12.2 for HW, SW and CL substrates, respectively.

The final pH after the two oxidations was acidic (below 5) for both Kraft pulps, SW-K-1 and HW-K-2, when using the highest dose of NaIO₄, and close to neutral for CL. Even if bicarbonate is used to neutralise the acidic effluent of the periodate oxidation, the second oxidation required more alkali to end at alkaline pH. As a general observation, the lower the dose of NaIO₄, the higher the final pH after the second oxidation. It is important to highlight that, like in the previous section, the targeted final pH is alkaline, with the aim of reaching similar bleaching effluents as in a Kraft mill after P-stage. Alkaline effluent after the second oxidation was obtained when using 27% of NaIO₄ and 13.5% NaIO₄ enabling to reach a final pH, similar to a P stage, between 11.3 and 12, as presented Figure IV-14.

As explained earlier, combination of NaIO₄ oxidation prior H₂O₂ oxidation aims the insertion of dialdehyde groups during the first oxidation, followed by their conversion into di-carboxyls during the second oxidation. H₂O₂ oxidation may not have converted all the carbonyl groups, and the cellulosic pulps may still contain functional groups sensitive to β -elimination under alkaline conditions. The consequence is that during the IV analysis in CuED, the cellulose is depolymerised resulting in false values. To ensure the elimination of all carbonyl groups prior the DPv analysis, sodium borohydride (NaBH₄) reduction was carried after the second oxidation (protocol detailed in Chapter VI). The intrinsic viscosity, after the reduction with NaBH₄, as well as the brightness and the H₂O₂ consumption of the substrates, all after the second oxidation, are presented in Figure IV-15, Figure IV-16, and Figure IV-17.

For the three substrates, whatever the treatment applied, full H_2O_2 consumption was almost achieved (above 95%). Therefore, peroxide consumption was not affected by conditions of periodate oxidation after washing. The brightness values were all around or above 90 %ISO. The main effect observed was on cellulose degradation, i.e. the decrease of IV in CuED.

Regarding the blank trials of the three substrates, they all presented a decreased IV. This was more accentuated when the substrate exhibited higher starting intrinsic viscosity values: CL and SW-K-1, with initial IV of 695 and 745 mL/g respectively, were more affected by the oxidations than HW-K-2, with initial IV of 496 mL/g. Yet, after the second oxidation with H_2O_2 , all the blank trials exhibited sufficient IV for dissolving-grade pulps, i.e. higher than 400 mL/g.



Figure IV-15. Intrinsic viscosity (mL/g), brightness (% ISO) and H₂O₂ consumption (%) of CL after the second oxidation (IV_{initial}, 695mL/g).



Figure IV-16. Intrinsic viscosity (mL/g), brightness (% ISO) and H₂O₂ consumption (%) of SW-K-1 after the second oxidation (IV_{initial}, 745 mL/g).



Figure IV-17. Intrinsic viscosity (mL/g), brightness (% ISO) and H₂O₂ consumption (%) of HW-K-2 after the second oxidation (IV_{initial}, 496 mL/g).

When including NaIO₄ oxidation prior H₂O₂ oxidation, a stronger degradation was observed, compared to the blank trials. The higher the dose of NaIO₄, the more the decrease in the IV value, as expected. Using 54% and 27% NaIO₄ lead to IV values is lower than 200 mL/g after the second oxidation, a too low value for viscose application. A reduced dose of 13.5% NaIO₄, lead to an IV of 317 mL/g for the SW-K-1, not so far from the objective. HW-K-2 was more affected with an IV of 282 mL/g, probably because the IV of its reference is the lowest one. Regardless the initial IV before oxidation, the most affected substrate was CL with a final IV of 233 mL/g. The absence of hemicelluloses in this substrate makes the cellulose more reactive during oxidation, thus more damaged.

The intrinsic viscosity has also been measured after the first oxidation, with or without NaBH₄ reduction prior the dissolution in CuED. Results for 13.5% NaIO₄ are presented in Figure IV-18, and for the blank in Figure IV-19.



Figure IV-18. Intrinsic viscosity (mL/g) measured with and without NaBH₄ reduction for 13.5%NaIO₄.



Figure IV-19. Intrinsic viscosity (mL/g) measured with and without NaBH₄ reduction for the blank trials.

It was confirmed, for all the three substrates, the IV values obtained after periodate oxidation without the reduction with NaBH₄ were significantly lower than after NBH₄ reduction (more than 30% difference), as seen in Figure IV-18, which evidences the formation of carbonyl groups during the first oxidation. Even with NaBH₄ reduction, IV values of the periodate oxidised substrates were lower than those of the reference substrates. This shows that periodate is also responsible for cellulose depolymerisation. In Figure IV-19, the values obtained with the blank trial are presented, confirming the reliability of the method: as no NaIO₄ was used in the blank trial, no carbonyl were formed, and there is no IV change, compared to the reference.

During the second oxidation with H_2O_2 , the depolymerization was continued, as lower IV values were obtained, compared to the values after the first oxidation. However, the values obtained after the second oxidation were similar with and without reduction with NaBH₄. These results confirm that the oxidation with H_2O_2 in alkaline conditions at 75°C converted all the carbonyls created in the periodate oxidation into carboxyls. The IV presented in Figure IV-18 after the two-step oxidation are thus confirmed. No changes were as well observed for the blank trials with or without NaBH₄ reduction, Figure IV-19, as expected.

As consequence, the values which will be considered for further discussion are the ones obtained without NaBH₄ reduction after the second oxidation, as no changes where observed, compared to when the reduction was performed.

Carbonyl quantification

The titration of the periodate consumed during the first oxidation allows to give an estimate of the amount of aldehyde groups formed during the reaction. The titration procedures are detailed in Chapter VI, and the results are presented in Table IV-4.

According to the redox equation:

$$IO_4^- + 8 H^+ + 8e^- \rightarrow I^- + 4 H_2O$$

The number of equivalents (n-eq) titrated at the beginning of the reaction by iodometry is four times the molar amount of NaIO₄ introduced for the reaction (as an example, 0.05 mol of NaIO₄ is introduced when using 54% NaIO₄ w/w on pulp, for 20 g of pulp). At the end of the reaction, the n-eq final is titrated, from which the n-eq consumed is derived. Since 1 mol of C=O is formed per equivalent consumed, the number of C=O per 100 AGU is calculated.

Looking at the results in Table IV-4, it seems that the number of C=O was the lowest for the CL substrate, and the highest for the SW substrate. However, the evolution is unexpected when comparing values for a given substrate, since the higher number of C=O does not correspond to the highest charge of NaIO₄. Some experimental errors have possibly arisen in these titrations, or instead, they do not reflect the carbonyl formation accurately, since they appear in contradiction with the decrease of the final pH observed in Figure IV-14, and also, with the increased cellulose degradation at higher periodate charge. The latter variations should be closely related to the increase of C=O formation during the periodate stage.

Samples	NalO₄	n-Eq initial	n-Eq final	nCO	nCO/100
	Consu. (%)			groups	AGU
CL-54%NalO ₄	7.4	0.3956	0.3872	0.0084	6.81
CL-27%NalO ₄	9.5	0.2028	0.1921	0.0107	8.67
CL-13,5%NalO ₄	12.1	0.1116	0.0979	0.0137	11.05
SW-54%NalO ₄	22.3	0.3956	0.3704	0.0252	20.42
SW-27%NalO ₄	11.6	0.2028	0.1896	0.0132	10.67
SW-13,5%NalO ₄	14.0	0.1116	0.0957	0.0159	12.86
HW-54%NalO ₄	15.3	0.3956	0.3783	0.0173	14.01
HW-27%NalO ₄	6.6	0.2028	0.1953	0.0075	6.07
HW-13,5%NalO ₄	11.8	0.1116	0.0982	0.0134	10.85

Table IV-4. Carbonyl groups of the substrates after the (NaIO₄) oxidation.

Carboxyl quantification

Figure IV-20 presents the carboxyl groups quantification after the second oxidation.



Figure IV-20. COOH quantification (mEq COOH for 100g of dry pulp) of the substrates after the (NaIO₄) + (H₂O₂) combination (13.5% NaIO₄ during the periodate oxidation)

The COOH quantification was done after the second oxidation and the details of the procedure are in Chapter VI. No carboxyls were generated without periodate (blank trials). When periodate oxidation was performed with 13.5% NaIO₄, some COOH were introduced but in very low amounts: for CL, values increased from 3.8 to 4.7 meq/100g of pulp; SW-K-1 did not show relevant changes, and for HW-K-2, it increased from 6.3 to 7.9 meq/100g, being the highest increase. To explain these differences between HW and SW, it can be hypothesised that the oxidised mannans in the SW substrate may dissolve more easily than the oxidised xylans in the HW substrate. In all cases, the alkaline conditions during the P stage offer very good conditions for the dissolution of the carboxylated moieties of polysaccharides, which probably explains why the carboxyl amounts left on all substrates are quite small.

Cellulose purity measured by R18

The R18 test was also performed. Figure IV-21 presents the results obtained with the lower charge of NaIO₄ (13.5%), the blank, and the reference values.

Considering the purity required for dissolving-grades pulps, only CL and the HW-blank pulp offered acceptable values. The two other HW pulps (REF and NaIO₄-oxidised) are at the very low limit of acceptability, whereas none of the SW substrates are acceptable. In Figure IV-21, typical variations can be observed which reflects that the R18 test not only eliminates hemicelluloses in these oxidised substrates, but also dissolved part of the oxidised cellulosic fragments of cellulose. For the case of the Blank tests (no use of NaIO₄), accessibility is better in HW than in SW. When periodate oxidation was applied, some polysaccharides were oxidised, and were removed during the R18 test, thus producing lower R18 values. This effect was more pronounced in the HW substrate, probably due to its better accessibility and easier dissolution of oxidised polysaccharides chains during the R18. This effect can also be related to depolymerisation induced by NaIO₄, as the blank trials were much less degraded, compared to NaIO₄ oxidations (Figure IV-15, Figure IV-16, Figure IV-17).



Figure IV-21. Alkali resistance (%) of the substrates after the second oxidation, using 13.5%NaIO4.

IV.5.3. Dissolving ability of the pulps - carbanilation

Despite the low amount of carboxyl groups introduced into the substrates, the potential changes in the dissolving ability were evaluated. First, dissolution has been followed during carbanilation. The results are presented in Figure IV-22, Figure IV-23, and Figure IV-24. Later, the dissolution results in NaOH:urea:water polar system are discussed.

Concerning CL and SW-K-1, as already observed in the previous section, Hydrogen peroxide with caustic extraction, the P stage alone (the blank trials) did not modify the behaviour of the substrates through the carbanilation test, as the particle size evolution was very similar. The same was observed for the substrates oxidised with NaIO₄, regardless of the charge applied. This organic dissolution system did not allow the discrimination of the substrates.

More differences were observed for HW-K-2, especially during the first three hours of carbanilation. The REF pulp dissolved faster than oxidized ones. However, compared to the blank trial (P alone), the use of NaIO₄ accelerated dissolution, yet without reaching the dissolving ability of the untreated pulp. Therefore, the dissolving ability by carbanilation in DMSO was affected compared to the reference pulp, which may be a consequence of the insertion of COOH groups. The blank trial, presented the more important affectation. Moreover, at the end of the carbanilation reaction, all the substrates, oxidized or not, were fully dissolved.


Figure IV-22. Dissolution ability during carbanilation monitored by DLS for CL when using different doses of NaIO₄ prior H₂O₂ oxidation.



Figure IV-23. Dissolution ability during carbanilation monitored by DLS for SW-K-1 when using different doses of NaIO₄ prior H₂O₂ oxidation.



Figure IV-24. Dissolution ability during carbanilation monitored by DLS for HW-K-2 when using different doses of NaIO₄ prior H₂O₂ oxidation.

SEC analyses

After the carbanilation reaction, the MWD of the substrates have been analysed by HPSEC, and the profiles are presented in Figure IV-25, Figure IV-26, and Figure IV-27. Additional information extracted from the SEC analyses are reported in Table IV-5.

The reference profiles for hardwoods, SW-K-1 and HW-K-2, displayed a bimodal profile: at high molecular weight, the cellulose fraction was present, and at lower mass, the hemicelluloses fraction, as displayed in Figure IV-26 and Figure IV-27 respectively. For both hardwoods, the peroxide oxidation shifted the signal towards lower weight, but a small fraction of hemicelluloses seems to be still present for SW-blank. The degradation extent is confirmed in the decrease of DPw values presented in Table IV-5. As noticed before, the addition of NaIO₄ oxidation prior H_2O_2 oxidation made more prominent the shift of the MWD profiles towards lower Log M.

Regarding the blank trials for the hardwoods, oxidations with peroxide alone, the degradation is lessened as the MWD profile is shifted toward slightly lower mass, but two fractions are observed, with a light shoulder in the region of hemicelluloses, as the effect of a classical P stage, where the substrates can be partially depolymerised without a major impact on hemicelluloses. The effect of the dose of NaIO₄ on hemicelluloses removal is more difficult observe; the signal attributed to hemicelluloses seems to be absent but due to the strong depolymerisation, no clear conclusion can be drawn. What is observed is that the lowest dose of periodate, i.e. 13.5%, leads to the lower depolymerisation whereas using 27% or 54% lead to pulps with similar MWD profiles, shifted to the lower Log M. Another noticeable feature is that the peak of aggregates in the SW-REF disappeared after oxidation, clearly showing that even P oxidation improves the accessibility/reactivity of the substrate during carbanilation.

CL-REF, in Figure IV-25 displayed one peak only, evidencing the absence of hemicelluloses, as expected. The results obtained on SW-K-1 and HW-K-2 substrates confirms those obtained on the CL: The NaIO₄ oxidation followed by H_2O_2 oxidation was more aggressive for the carbohydrates than the peroxide oxidation alone (blank trial), but the dose of periodate did not introduce important changes in the MWD profiles (except when using 13.5% NaIO₄, where degradation was attenuated). Nevertheless, to produce dissolving-grade pulp quality, the depolymerisation should be controlled. Thus, the more interesting dosage could be selected, being the lower dose, 13.5% NaIO₄.





Figure IV-25. MWD profiles of CL using different doses of NaIO₄ prior H₂O₂ oxidation.

Figure IV-26. MWD profiles of SW-K-1 using different doses of NaIO₄ prior H₂O₂ oxidation.



Figure IV-27. MWD profiles of HW-K-2 using different doses of NaIO₄ prior H₂O₂ oxidation.

	IV(dL/g)	Rh(nm)	Mw/Mn	DPw
CL-13,5%NalO₄	1.7	18.2	2.5	569
CL-27%NalO₄	1.3	15.6	2.5	470
CL-54%NalO₄	1.4	16.0	1.9	424
CL-Blank	2.9	27.8	1.8	1072
CL-REF	4.2	34.9	2.9	1433
SW-13,5%NalO₄	2.0	20.9	4.8	883
SW-27%NalO₄	1.7	18.6	4.1	644
SW-54%NalO₄	1.5	18.2	7.3	835
SW-Blank	2.6	25.6	3.7	1205
SW-REF	6.4	51.7	6.3	3699
HW-13,5%NalO₄	1.6	17.9	7.1	683
HW-27%NalO₄	1.3	15.1	5.8	456
HW-54%NalO₄	1.3	16.3	9.3	588
HW-Blank	2.2	22.4	4.1	862
HW-REF	2.8	27.8	4.1	1215

Table IV-5. Additional SEC information – Different doses of NaIO₄ prior H₂O₂ oxidation.

Data displayed in Table IV-5 reflects the previous discussion about the MWD profiles. In general terms, the DPw of the three substrates was strongly affected by the trials including NaIO₄ oxidations, more than if only a P oxidation was used (blank). It was previously stated that the sample with the more interesting viscose-grade characteristics was the blank, which also presents a narrower profile, with less degradation than the others, confirmed in Table IV-5. A narrow MWD is preferred for dissolving pulp applications to ensure a more homogeneous final product. Unfortunately, when NaIO₄ oxidation was included, the dispersity increased.

IV.6. Dissolving ability of the pulps in NaOH:urea:water system

As the objective of the chapter was to study the effect of introducing carboxyl groups in the substrates to improve their dissolution behaviour, while controlling the substrate depolymerisation in order to reach acceptable dissolving-grade pulp properties, the dissolving ability has also been tested in the NaOH:urea:water system. The protocol followed is detailed in Chapter II. Results of the cellulose solubility (%) of the more interesting substrates observed in the present chapter are also included in Figure IV-28.

As previously observed in chapter II and III, the pulp dissolution in this system is highly correlated with the DPv, also correlated with the intrinsic viscosity in CuED. Regardless of the substrate origin or treatment, except for HW-EP(2%) and HW-P(2%), the lower the DPv, the better the cellulose dissolution. The non-compliance of HW-EP(2%), may be due to the

cellulose II formed, thus limiting the dissolution, despite the strong reduction of the DPv in this pulp. In the case of HW-P(2%), the formation of cellulose II cannot be invoked, but this pulp was rather strongly oxidised, as seen by the decreased IV in CuED and DPv values in Table IV-5 (as well as DPw and other HPSEC data included in the same tale)



Figure IV-28. Cellulose solubility (%) in NaOH:urea:water system of the more interesting substrates.

Introducing NaIO₄ oxidation led to much improved dissolution of both Kraft pulps in this solvent. This is evidenced when comparing the REF sample, P or EP samples to the NaIO₄ sample, even at the lowest dosage of 13.5%.

The highest improvement can be observed for the HW pulp, which at DPv values close to 400, presented two to three times higher solubility after periodate treatment, when compared to HW-Blank, HW-P(2%) or HW-EP(2%). SW-K-1 had the highest initial DPv and its solubility reached about 55% after periodate oxidation, a double value compared to the reference (25%). To conclude, the insertion of a periodate oxidation stage prior peroxide oxidation led to a major solubility improvement in the NaOH:urea:water system, for both HW-K-2 and SW-K-1 substrates.

IV.7. Conclusions

In the present chapter, two combinations of treatments using hydrogen peroxide as the main oxidant were studied in order to convert paper-grade bleached pulp to dissolving-grade pulp.

In the first section, an alkaline extraction step was applied prior a hydrogen peroxide oxidation. More uniform molar weight distributions were obtained when performing the extraction alone (E treatment). When adding the hydrogen peroxide oxidation, EP, higher polymer dispersity was observed, which translates in a broader MWD, compared to E alone. E and EP combinations were also able to remove a large part of hemicelluloses, whereas P alone did not. The extraction of hemicelluloses seemed easier for the hardwood pulp, which after EP, reached 96,9% cellulose. For the softwood pulp, after EP, cellulose purity reached 90%. The different behaviours could be related to the type of hemicelluloses present in the SW substrate. Despite interesting results in terms of brightness (> 91%) and cellulose purity (> 90%) reached by the EP treatment, the intrinsic viscosity values were under the target of a dissolving pulp for viscose applications, 400-600 mL/g. Moreover, the cellulose solubility in the NaOH:urea:water system decreased for HW, whereas SW resulted in 100% improvement. Not important improvements were observed during cellulose derivatisation. As a conclusion, EP treatment was not sufficient to convert bleached Kraft pulp into dissolving grade pulps.

The second strategy investigated the use of periodate oxidation prior hydrogen peroxide oxidation, to depolymerise the substrate, and to enrich the pulp with functional groups that may enhance its reactivity. The depolymerisation is started by periodate oxidation and is accentuated by the hydrogen peroxide treatment. IV values higher than 300mL/g were difficult to reach, whereas interesting cellulose solubility in the NaOH:urea:water system was observed, i.e. with a solubility which was more than double, compared to the reference. A slightly slower dissolution during the carbanilation reaction was also observed, which may be an indication of the insertion of functional groups probably affecting the dissolution in DMSO.

The upgrading of fully bleached Kraft paper-grade pulps into dissolving-grade pulps, using hydrogen peroxide as main chemical, was a challenge. Removal of hemicelluloses by alkaline extraction reinforced by H₂O₂ oxidation was not sufficient to improve their dissolving ability, and the oxidative treatments which aimed to insert COOH groups in the pulp, damaged too much the cellulose leading to very low IV values, off the target... Hence, another way of valorisation is proposed: interesting oxidation conditions for the production of microfibrillated cellulose (MFC). Chapter V will investigate the potential use of the proposed treatments for the production of MFC, with chemicals commonly found in paper mills.

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V. Peroxide-based treatments to convert bleached Kraft pulps into microfibrillated cellulose

V.1 Introduction

As mentioned in Chapter I, Microfibrillated cellulose (MFC) refers to cellulosic material, moderately degraded, with expanded high-volume and large surface area, and fibre diameter in the range of 20-60 nm¹; but with lengths that can reach more than $10 \,\mu m^2$. MFC materials merge the advantages of renewable sourced material, biodegradable, and non-toxic with a high surface area, high aspect ratio, and a large amount of surface hydroxyl groups³. The presence of such hydroxyl groups along the material results in the formation of a network of inter- and intramolecular hydrogen bonds, which as a consequence, exhibits impressive mechanical properties, either individually or as a network⁴. At the nanoscale it also provides a wide variety of possible surface functionalization such as physical adsorption, molecular grafting or polymer grafting⁵. MFC has shown enormous potential in the forest products industry, and its interest has increased notably over recent decades as it can be used to improve the quality and performance of a broad array of polymers ranging from paper and board materials, coatings, and films, to nano-composite materials.

The production of MFC requires intensive mechanical treatment, and for this reason its production is still a subject of optimization, as the high-energy consumption of the fibrillation process represents an important barrier for large-scale industrialization. Depending on the raw material, chemical treatments, aimed to produce purified cellulose, may be applied prior to mechanical fibrillation⁶; and, lower energy demand has been observed when enzymatic treatments are applied prior to mechanical fibrillation⁷. Finally, depending on the final application, different properties remain more important than others. For food packaging, low permeability and high transparency are expected⁸; while for adhesive applications, the presence of lignin does not represent a limitation⁹; as for the paper industry, MFC is established as a filler for cost reduction or quality improvement¹⁰. For the latter, it is relevant to improve structural and mechanical properties such as tear, burst, Young's modulus, strain at break, z-strength, as well as other properties such as uniform printability and reduced opacity¹¹.

In previous chapters, the use of peroxide in unconventional ways has been investigated to convert fully bleached Kraft pulp into dissolving pulp, which depolymerised the cellulosic substrates with light addition of functional groups. The present chapter aims to evaluate the possibility of producing MFC from the oxidative systems studied, as well as to assess the more relevant properties of the final product. Because of time constraints, only one initial substrate has been selected, HW-K-2, which characterisation is discussed in the beginning of the chapter.

V.2 The selected cellulosic substrate

The hardwood Kraft pulp No. 2 (HW-K-2) has been selected as it exhibits interesting behaviour after applying the different peroxide-based treatments. As a reminder, the properties of the fully bleached HW-K-2 pulp are: 87.9% ISO brightness, an IV value of 496 mL/g and DPv of 692. About the alkali resistance (R18), 90.6%, referring to the cellulose content.

Systems to be investigated:

- Reference HW-K-2. No treatment applied.
- Two-step oxidation using first periodate followed by hydrogen peroxide oxidation, to introduce COOH groups. The presence of COOH groups may ease fibrillation. It is referred as (*NaIO*₄)+(*H*₂*O*₂).
- H_2O_2 oxidation activated by the Cu(Phen) complex, known to produce strongly oxidant hydroxyl radicals. The idea is to weaken the cellulose matrix by radical species reaction, to favour fibrillation. Referred in this chapter as $H_2O_2+Cu(Phen)$. The same oxidation without the use of Cu(Phen) is also considered, and is referred as H_2O_2 .

Extraction followed by H_2O_2 oxidation is part of the introductory discussion but it was not assessed as potential MFC, due to the high purity achieved. The operational conditions of each treatment are detailed in Figure V-1.

Conditions	Operating conditions
(NaIO ₄)+(H ₂ O ₂)	20g of pulp with 13% NaIO ₄ at 1.6% pulp consistency under stirring during 2 h at room temperature and dark conditions. Washing step. Followed by an oxidation of 2% H_2O_2 and 1.5% NaOH for 60 min in a 75°C water bath. 5% pulp consistency.
H ₂ O ₂ + Cu(Phen)	20g of pulp with 0.02% Cu(Phen), 0.4% NaOH and 2% H ₂ O ₂ at 5% pulp consistency for 60 min in a 95°C water bath.
H_2O_2	20g of pulp with 0.4% NaOH and 2% H_2O_2 at 5% pulp consistency for 60 min in a 95°C water bath.
Extraction+ H ₂ O ₂	Extraction: 10g of pulp, at 10% pulp consistency with 75 g NaOH for 60 min in 75°C water bath. No washing step, and immediately after, the addition of 10% H_2O_2 , for another 60 min at 75°C water bath.

Table	V-1.	Peroxide-based	treatment	-	operating	conditions
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The derivatisation of cellulose into tricarbanilates was studied, for each of the oxidation treatments performed on the HW-K-2 substrate. Figure V-1 presents the dissolution behaviour monitored with DLS during carbanilation.



Figure V-1. Average particle size during carbanilation for the different oxidations of HW-K-2

All the oxidised samples dissolved slower than the reference substrate. This could be considered as an indication of the presence of polar functional groups which may influence dissolution in non-polar DMSO. The pulp treated with only H₂O₂ dissolved the slowest, whereas the reference pulp dissolved the fastest. The dissolution ability in an aqueous system, the NaOH:urea:water system, was also evaluated. Figure V-2 gathers the results obtained for the different oxidized HW pulps, which are related to cellulose DPv.





In the previous chapters it was evidenced that the higher the DPv, the lower the dissolution ability in the polar system of NaOH:urea:water. Even though, the final DPv values were similar for most of the oxidised samples (values around 400), the dissolution behaviour showed to be

different. Extraction+H₂O₂ presents the lowest dissolution ability in this medium, possibly due to the high dose of soda which may convert part of cellulose I into cellulose II, as discussed in the previous chapter. When comparing the treatment with only H₂O₂, with the (NaIO₄)+(H₂O₂), or H₂O₂+Cu(Phen), oxidative systems, better dissolution is obtained with the latter. The dissolution was not only dependent on the cellulose DPv but also on the cellulose modifications.

Hemicelluloses content in the cellulosic substrates was estimated by R18 measurements, and by observation of MWD profiles obtained by SEC; both are presented below in Figure V-3, and Figure V-4 respectively.



Figure V-3. R18 (%) for the different oxidations of HW-K-2



Figure V-4. MWD profiles for the different oxidations of HW-K-2

Except for the extraction treatment, none of the others reached major purification after oxidation, hemicelluloses are still present. As a consequence, it can be concluded that among the tested systems, $H_2O_2+Cu(Phen)$ and $(NaIO_4)+(H_2O_2)$ conserve the hemicelluloses, whereas

extraction+H₂O₂ remove them. For MFC applications, hemicelluloses have proven to enhance microfibrillation, which is likely due to the negative charges on hemicelluloses that lead to charge repulsion between the fibrils¹². In this chapter, oxidations that preserve hemicelluloses will be investigated for potential MFC production, as well as others that removed them.

The MWD profiles confirmed that only the Extraction+ H_2O_2 removed hemicelluloses (Figure V-4), since a monomodal signal is obtained with the suppression of the signal generally attributed to hemicelluloses (log M close to 4.8). For the case of the other oxidation systems, even though there is a modification in the MWD (a shift toward lower log M), the hemicelluloses signal is still present with a light shoulder in the lower log M. As already discussed in previous chapters, there is a significant impact of the H_2O_2 +Cu(Phen) and $(NaIO_4)+(H_2O_2)$ oxidative systems on the cellulose DPv, being $(NaIO_4)+(H_2O_2)$ the one with the lowest value, 372.

V.3 Production of MFC - method

The MFC production is based on disintegration of the fibres mechanically, and chemically, into high aspect ratio nanosized fibrils¹². Yet, mechanical treatment leads to irreversible changes in the fibres, increasing their bonding potential by modification of their morphology and size. Additionally, refining tends to either damage the microfibril structure by reducing molar mass and the degree of crystallinity, or fail to sufficiently disintegrate the pulp fibre⁷. On the other hand, aggregates originated from drying are difficult to re-disperse without significant mechanical treatment, which generally result in losing a portion of the high aspect ratio component¹³.





The use of mechanical treatment exclusively for the production of MFC has shown to be highly energy demanding, up to 70,000 kW h/t without pre-treatment strategy¹¹. In the present chapter, the combination of mechanical treatments plus an oxidation step is studied. The fully bleached HW substrate was first homogenised, and later refined prior to oxidation. After washing, the pulp suspension was passed through the Masuko grinder until a gel was obtained. The pulp

suspension, before and after the mentioned treatments was characterised, and the effect on the quality of the produced MFC discussed, as well as energy requirements. The sequence is displayed in Figure V-5. As an intermediate oxidation step is included, lower exposure to refining treatments is intended.

V.3.1 Refining in the Valley beater

In this study, 420 g of the bleached HW pulp were soaked overnight in water. Cellulose fibres were homogenised with deionized water into a 2 wt% suspension with a laboratory scale pulper and later refined in a Valley beater (Voith, Heidenheim Germany) until fibrillation degree of 47° SR as measured with a Shopper Riegler tester following the ISO 5267-1:1999 standard (initial 20°SR for HW substrate, and refining time of 40min). To proceed with the oxidation steps, the refined pulp suspension was separated by weight in four equal parts (100 g each, as 20 g loss was assumed during the transfers). Three of them were filtered with a nylon sieve with a mesh size of 1 μ m, to keep the fine elements. The non-filtered part is to be considered as the reference sample (filtration was avoided to observe the impact of the fines in the following steps). The pulper, and the valley beater refiner used are showed in Figure V-6.



Figure V-6. Valley Beater refiner (left), and Masuko grinder (right)

V.3.2 Oxidation treatments

After refining, three oxidation treatments were performed. Thus, four samples are listed from now on:

- 1. **REF**, The reference. No oxidation treatment, and no filtration performed.
- (NaIO₄)+(H₂O₂). This oxidation proceeded following the more interesting conditions observed in Chapter IV for periodate oxidation. 13,5% NaIO₄ were used for two hours oxidation under agitation in dark conditions at 1.6%, followed by a wash with NaHCO₃ and distilled water until reaching neutral pH. After filtration (nylon sieve, 1µm to keep the fine elements), and addition of distilled water until 5% of pulp consistency, and preheating for 20 minutes, an oxidation step followed with 1,5%NaOH, and 2% H₂O₂ at 75°C.
- 3. H₂O₂+Cu(Phen). This oxidation was performed by replicating the more interesting conditions observed when using Cu(Phen) complex in Chapter III. After refining, the sample was filtrated (nylon sieve, 1µm to keep the fine elements), and distilled water added until 5% pulp consistency. Before oxidation, the sample was pre-heated for 20 minutes, and the chemicals added in the following order: 0,02% Cu(Phen), 2%NaOH, and 2%H₂O₂. The oxidation took place for one hour at 95°C.
- 4. **H**₂**O**₂. This oxidation was performed in the exact same way as the previous one with Cu(Phen) oxidation described above (3) but no Cu(Phen) complex was included.

For the three cases, all the samples were washed with distilled water after oxidation until reaching a neutral pH, and using a nylon sieve of $1\mu m$ to prevent the loss of fines. The four samples are to be grinded for the MFC production.

V.3.3. Pulp homogenisation with the Masuko grinder

A pilot scale ultra-fine friction grinder (Model MKZA6-2, Disk model MKG-C 80, Masuko Sangyo Co., Ltd., Japan) has been used for an efficient high-quality MFC production. The principle consists on the breakdown of the cell wall structure by the shearing forces generated by two grinding stones: the static and a rotating. The pulp is passed several times between the two revolving stones at about 1500 rpm. As a consequence, the nanofibres composing the cell wall in a multilayer structure are individualised after the grinding¹. It is important to highlight that this process can degrade the fibres, and decrease their length, which may affect the reinforcement, and physical properties of MFC.

Grinding was performed using conditions used in previous studies at LGP2 with Eucalyptus bleached pulp. Even though, it was intended to use the same settings for the four samples, each of them behaved differently, and only two of them allowed to use the intended number of passes through the Masuko grinder: the pulp treated by only H_2O_2 and the pulp treated with $H_2O_2+Cu(Phen)$. The reference pulp and the pulps treated with $(NaIO_4)+(H_2O_2)$ required much more time per pass, thus energy to complete the desired number of passes, as the gel was too viscous. For this reason, the passes were reduced from 20 to 10 in the last stage. The details are presented in Table V-2. Figure V-7 is a picture of the final gel (2 wt-%) obtained after Masuko grinding, when the treatment with $(NaIO_4)+(H_2O_2)$ was used.

Distance between the	REF	(NaIO ₄)+(H ₂ O ₂)	H ₂ O ₂ +Cu(Phen)	H ₂ O ₂
discs, and rpm				

0, 1000

-5, 1500

-10, 1700

Table V-2. Setting in the Masuko grinder for the different oxidations - number of passes

r			No.		J
4		4	-		5
-	7		N. V.	0	100

Figure V-7. Gel obtained after Masuko grinding by the (NaIO₄)+(H₂O₂) oxidative system

V.4 Characterizations before and after mechanical treatments

As described in the previous section, after the Masuko grinding, it was possible to form gels from the four samples studied. With the aim to compare the quality of each sample, several characterisation trials were performed using the produced gel, as well as a nanopaper prepared out of it. The characteristics of the materials before the grinding have been also evaluated.

V.4.1. Nanopaper formation

To be able to evaluate interesting characteristics such as the mechanical properties, crystallinity, and transparency, the preparation of a nanopaper was required. 2 g of cellulosic substrate were diluted in 400 g of water and a nylon sieve (1 μ m) was used in the bottom as a filter to avoid the excessive loss of fines. The apparatus Rapid Köthen sheet former was used. When the excess of water was removed by the vacuum, a second nylon sieve was placed on the top of the filtered suspension (in addition to the one previously placed in the bottom for filtration) and was dried for 15min at 85°C. The nanopaper produced presented a basis weight in the range of around 65 g/m², and it was kept in a conditioned room (controlled conditions: 23°C and 50% relative humidity, as recommended by ISO 187:1990) for at least 48h prior to the mentioned analyses. At least three nanopapers were produced for each sample.

V.4.2. Optical properties of MFC

In Table V-3 is presented the compilation of the optical properties evaluated during the study for the four samples. The transparency of the nanopaper can be observed by the pictures displayed, but it is also estimated by the measurement of the transmittance in a UV Spectrophotometer at 550nm. An average of six measurements were considered per sample. The highest number can be related to the more transparent sample obtained. Being ranked from the more transparent to the most opaque: the untreated pulp (REF), the pulp treated by (NaIO₄)+(H₂O₂), the pulp treated by H₂O₂+Cu(Phen), and the lowest value was presented by the pulp submitted to the oxidation with only H₂O₂.

Optical microscopy images were obtained with the use of Axio Imager microscope (Carl Zeiss, Germany) equipped with AxioCam MRc 5 digital camera. For the measurements, MFC suspensions were diluted to 0.1 wt%, and magnifications of x5, and x10 were used. At least 10 images were taken per sample, but the most representative were selected. From the microscopic images presented in Table V-3, it can be observed that the samples presenting less large fibres are the reference pulp and the treated with $(NaIO_4)+(H_2O_2)$. In contrast, pulps treated with only H_2O_2 presented largest fibres. These results agree with the transmittance, since the larger the fibres, the less transparent the paper. Transmission electron microscopy (TEM) images presented in Table V-3 were acquired from the supernatant of MFC suspensions at 0.1 wt% in an external laboratory, CERMAV. The microfibrillation is more evident for the pulp treated with (NaIO_4)+(H_2O_2) and H_2O_2+Cu(Phen), whereas it is less evident for the other two samples.

Table V-3. Optical and morphological properties

Transmittance	Nanopaper	Optical microscopy (scale: 200μm and 100μm)	TEM (scale: 200nm and 100nm)		
REF 21.41%		200 Jun			
(NaIO ₄)+(H ₂ O ₂) 18.49%		200 µm			
H ₂ O ₂ +Cu(Phen) 3.85%					
H ₂ O ₂ 1.96%		No ha			

V.4.3. Mechanical properties of MFC films

For several MFC applications, the mechanical properties play an important role when evaluating the quality. Transparency values have evidenced a strong correlation with four other parameters: turbidity, tear resistance, Young's modulus, and porosity³. Interestingly, some of the following properties have shown to correlate in this study as well.

In Figure V-8 are presented the measurements of the tensile test, expressed as Young's modulus (GPa) for the four studied nanopapers. Tensile properties of nanopapers were measured with a dual column testing system 5965 of 50 kN maximum force (Instron, USA), following the NF Q03-004 standard. Samples with dimensions $15 \times 100 \text{ mm}^2$ were tested with a tensile cross-head speed of 10 mm/min. The Young's modulus of each sample was calculated using the thickness values of the nanopaper, as measured for porosity. Four measurements of thickness were done on each of the nanopaper analysed. Six tensile tests per sample were performed, average values have been calculated, and are displayed below. The porosity was calculated as in the equation below,

$$Porosity (\%) = 1 - \frac{BW}{e \times \rho_c} \times 100$$

Where BW refers to the basis weight (kg/m²), e is the thickness (m), and ρ_c is the density of cellulose (1540 kg/m³). The more homogeneous the fibres are, the more cohesive the material, and the lower the porosity value³. As displayed in Figure V-8, the lowest porosity value, and the highest modulus were observed for the sample oxidised with H₂O₂+Cu(Phen) followed by (NaIO₄)+(H₂O₂), and the reference sample, which is an indication of the MFC homogeneity.





When considering the oxidation with only H_2O_2 , it has not a significant effect on the tensile test (Figure V-8), compared to the reference pulp. Even though the reference substrate presented the lowest Young's modulus value, it is interestingly higher than for some other MFC produced from hardwoods^{14,15}.

The turbidity (expressed in Nepbelometric Turbidity Units, NTU) has been also studied. The gel suspensions were diluted to 0.1 wt% with deionised water, and later homogenised for 1 min with an ULTRA TURRAX T-25 disperser at 8000 rpm prior the measurement with a turbidity meter AL250T-IR (Aqualytic). Twelve measurements were done for each sample, and the average value was calculated. Results are presented in Figure V-9.





Turbidity in MFC suspension is related to the reduction in transparency due to the presence of light-scattering, and can be used to assess the dispersion and the size of suspended objects. Thus, lower turbidity means less aggregated nanoparticles or more fibrillated samples¹⁶. In Figure V-9, it can be noted that samples oxidised with $H_2O_2+Cu(Phen)$ and $(NaIO_4)+(H_2O_2)$ displayed lower turbidity compared to the reference, thus better microfibrillation, as already observed in Table V-3. However, even though the sample treated with H_2O_2 only displayed the lowest turbidity, the presence of large fibres did not allow to get higher transparency. Which may be an indication of MFC mixed with fibres.

The tear resistance of the nanopapers was evaluated with a tear tester equipped with a 4000 mN pendulum (Noviprofibre, France). Samples of $50 \times 65 \text{ mm}^2$ were pre-cut, and the force (in mN) to complete the propagation of the cut, was measured. Six measurements per samples were performed, and the average value was calculated. The results are presented in Figure V-10.



Figure V-10. Tear Resistance (mN) measured in the nanopaper produced after Masuko grinding.

Depending on the MFC application, a low or high tear resistance is expected. However, the shorter the fibres, or no fibre at all, will display low tear resistance compared to MFC combined with long fibres. The two more interesting results were observed for the reference and the sample treated with $(NaIO_4)+(H_2O_2)$, with the lowest values. Followed by $H_2O_2+Cu(Phen)$, and by far by the one treated only with H_2O_2 . The latter result can be related to the presence of long fibres in the nanopaper, already observe in previous results.

V.4.4. Morphological analysis of MFC

Morphological changes were evaluated with a MorFi fibre analyser. 40 mg of oven-dried sample were diluted in 1 L of water, and it was exposed to magnetic agitation for 30 min for homogenisation prior to the constant recirculation in the image acquisition system. The fines limit was set at 80 μ m in length, and the analyses were carried out for 5 min. For the MFC produced from the reference pulp, pulp treated with (NaIO₄)+(H₂O₂), with H₂O₂+Cu(Phen), and the one treated only with H₂O₂, different amount of fibres were analysed during this time: 969, 740, 35 123, and 50 003 respectively. Which means that the MFC produced from the reference pulp, and the pulp treated with (NaIO₄)+(H₂O₂), presented a lower amount of analysed fibres > 80 μ m in 5 min. Even though, MorFi analyses are not commonly considered for MFC quality evaluation, these values can be used as an indication of the long fibres present in the gel produced after the grinding. Before Masuko grinding and after the mentioned treatments, the same analyses gave values in the order of 45 000 as an indication of a fibrous suspension, for all the four samples. The MorFi analysis results are presented in Figure V-11 and Figure V-12.

Figure V-11 presents the fine content (% in area), which gave an indication of the fines in the suspension. The reference pulp and the pulp treated by $(NaIO_4)+(H_2O_2)$ present the highest content of fines after Masuko grinding, and at the same time, the highest transparency, and the lowest tear resistance of the nanopaper. The lowest fines content was obtained with H₂O₂ only, which so far displays the less interesting properties. The latter oxidation did not reveal important effects on the fibre matrix.



Figure V-11. Fines content - Morfi Analyses before and after Masuko grinding





The fibre length findings are presented in Figure V-12. A strong decrease in length after Masuko grinding has been noticed, being the largest difference for the reference pulp, which goes from 452 μ m to 149 μ m, which represents a decrease of 66%. Somehow, the oxidation treatments lessen the effect, up to only 269 μ m for the pulp treated with H₂O₂ alone.

V.4.5. Other properties

All the characterisation methods followed in the present section are detailed in Chapter VI.

The effect of the Masuko grinding on the crystallinity was also evaluated and the results are displayed in Figure V-13. As discussed in chapters III and IV, there were no important changes in crystallinity index (CI) after the oxidative treatment (grey bars). However, after grinding, CI values significantly decreased and the decrease extend depended on the substrate. The highest CI reduction was for the reference pulp (13% decrease), whereas all the oxidative treatments partially lessen this effect, i.e. 5%, 7%, and 12% for the treatments with H₂O₂ alone, H₂O₂+Cu(Phen) and (NaIO₄)+(H₂O₂), respectively. As observed by *Alila et al*¹⁷, the impact in the crystallinity was more accentuated on the more fibrillated samples.



Figure V-13. Crystallinity Index (%) before and after Masuko grinding.

Brightness was also monitored, and the refining effect can be observed in Figure V-14, which gathers the results obtained without refining, from the previous chapters, and results with a refining until 47°SR prior to oxidations, from the present chapter. It is noted that the refining step affected importantly the brightness of the reference pulp but not the values of the oxidized pulps, as similar values were reached with or without a previous refining step.

The fibrillation degree can be linked to the water retention value (WRV) of the pulp, as the WRV increases due to an increase in surface area¹⁵. The WRVs presented in Figure V-15 were measured prior to Masuko grinding, which means after refining and oxidation treatments. The reference pulp and the pulp treated with (NaIO₄)+(H₂O₂) exhibit the same WRV values. Despite a high standard deviation of the measurements, the H₂O₂ and H₂O₂+Cu(Phen) treatments led to pulps with lower WRV. These results suggest that the better microfibrillation was obtained by (NaIO₄)+(H₂O₂) and the reference pulp, which matches with the previous findings.



Figure V-14. Brightness (%ISO) of the oxidized pulps with and without previous refining.



Figure V-15. Water Retention Values (%) of the oxidized pulps

The cellulose DPv was evaluated both after pulp refining and after grinding. Results are given in Figure V-16. Refining did not affect significantly the cellulose DPv. Moreover, cellulose DPv after Masuko grinding was affected for all the samples, as observed by other authors^{7,18,19}. The H₂O₂+Cu(Phen) treatment evidenced the capacity to lessen the DPv decrease.





V.4.6. Energy consumption

As presented earlier in Table V-2, it was intended to use the same amount of passes through the Masuko grinder for the four studied samples. However, the reference pulp and the pulp treated with $(NaIO_4)+(H_2O_2)$ became too viscous, and their passes took so much longer compared to the other two pulps. Thus, not all the intended passes were done for the first two samples. After each pass, the power (in kW) was recorded, and for each stage of the grinding, the energy consumed was calculated (different stages depended on the disks' gap, and rotation). The values of the total energy consumed for each sample are displayed in Figure V-17.



Figure V-17. Energy consumption during Masuko grinding

The samples that took the longest to complete the passes was the pulp treated with $(NaIO_4)+(H_2O_2)$, followed by the reference pulp, the pulp oxidized by $H_2O_2+Cu(Phen)$ and finally oxidized with only H_2O_2 , with 6 h, 5.3 h, 3.4 h, and 0.9 h, respectively. It must be highlighted that the pulp treated by $(NaIO_4)+(H_2O_2)$ achieved an homogeneous gel quality (visually), two hours before the completion of the established sequence.

The most interesting mechanical and optical properties were observed for the pulp oxidized with $(NaIO_4)+(H_2O_2)$. But, when looking at Figure V-17, this pulp consumed the most within the studied samples; followed by reference pulp. When pointing at the pulp oxidized with $H_2O_2+Cu(Phen)$, and comparing to that oxidized with $(NaIO_4)+(H_2O_2)$, 58% energy could be saved to obtain similar MFC, referring to the mechanical properties, or even better, when specifically observing the values of the tensile test. However, energy consumption, and Young's Modulus values are not enough as information to establish the quality of MFC produced. To analyse better the weight of each studied parameter, and to be able to rank the

more interesting MFC produced, a tool called 'quality index', developed at LGP2, was used. It is detailed in the next section.

V.5 Quality index of the produced MFC

The quality of MFC depends on the large number of possible combination of pre-treatments, mechanical disintegration processes, and post-treatments; which directly lead to a vast range of shapes, morphologies, and properties in the final product. Thus, defining an index of quality is a challenging issue. According to the proposed method developed in LGP2 by *Desmaisons et al*³, the influence of different parameters allows for the benchmarking of different commercial microfibrillated cellulose products. The parameters considered for the quality index (QI) estimation, and their weight in the calculation are detailed below:

$$Q.I. = 0,20 * x_1 + (-0,02 * x_2) - 0,035 * x_3^2 + 1,27 * x_3 - 0,16 * x_4 + 1,65ln(x_5) - 3,59ln(x_6) - 2,67ln(x_7) + 0,18 * x_8 + 69,6$$

Where x_1 represents the nanosized fraction (%), x_2 the turbidity (NTU), x_3 the Young's modulus (GPa), x_4 the porosity (%), x_5 the transmittance at 550 nm (%), x_6 the tear resistance (mN), x_7 the macro-size (μ m²), and x_8 the macroscopic homogeneity (%). The method has been validated for several nanocellulose samples by the authors, i.e. MFC obtained from refined cotton presented a quality index of 47.4 ± 3.4 compared to 75 ± 5.7 for MFC from refined eucalyptus³. However, the intention of the present chapter is to produce MFC, and do not intentionally aim to produce nanocellulose, thus the nanosized fraction was not considered, which gives an important weight to the percentage of fibres < 10µm in the above described method.

A simplification of the method has been proposed by *Desmaisons et al*³, and studied afterwards at LGP2 for enzymatic pre-treated pulp followed by a combination of homogenisation and twinscrew extrusion, as mechanical treatments²⁰. Additionally, *Banvillet et al*¹⁵, studied the production of MFC from eucalyptus pulp: enzymatic hydrolysis was performed on refined pulp (70°SR), and after NaOH treatments at concentrations of 5, 10 and 15 wt% respectively. Later, the suspension was homogenised, and then passed through the Masuko grinder. To evaluate the quality index in the produced MFC, the above described method was adapted as follows:

$$Q.I. = -0.02 * x_1 + 1.65 ln(x_2) - 7.18 ln(x_3) - 0.07 * x_4^2 + 2.54 * x_4 - 0.32 * x_5 + 89.6$$

where x_1 is the turbidity (NTU), x_2 is the transmittance (%), x_3 is the tear resistance (mN), x_4 is the Young's modulus (GPa), and x_5 is the porosity (%). In the latter study, the nano-fraction-related properties were not included as they presented poor repeatability, high standard deviations, and inaccurate values observed¹⁵.

For the calculation of the quality index in this chapter, it was considered the adapted approach of *Banvillet et al*¹⁵. Table V-4 presents the collection of all the values needed.

MFC sample	Turbidity (NTU)	Transmittance 550 nm (%)	Tear Resistance (mN)	Young M (GPa)	Porosity (%)	QI
Reference pulp	417 ± 11	21.4 ± 1.9	28 ± 4	7.8 ± 0.5	25 ± 4	70 ± 2
$(NalO_4)+(H_2O_2)$	387 ± 21	18.5 ± 0.9	26 ± 3	8.6 ± 0.4	24 ± 5	73 ± 2
H ₂ O ₂ +Cu(Phen)	373 ± 9	3.9 ± 0.2	63 ± 1	9.7 ± 0.3	20 ± 3	67 ± 1
H ₂ O ₂	295 ± 35	2.0 ± 0.2	134 ± 21	8.0 ± 0.2	33 ± 2	55 ± 2

Table V-4. Quality Index using the adapted method of Banvillet et al.

The pulp oxidized with $(NaIO_4)+(H_2O_2)$ presents the highest quality index, followed by the reference pulp. The high quality of the reference pulp is probably due to the high hemicelluloses content (Chapter II), which enhances microfibrillation¹². The lowest QI was obtained for the pulp oxidized with H₂O₂ alone which presents the lowest transparency and mechanical properties. Even though some QI values are lower than others, the results show a quality comparable to that of commercial MFC³. Moreover, for the pulp oxidized by H₂O₂+Cu(Phen), the lower QI value is compensated by the fact that it required much less energy in the grinding step, and that the Young's Modulus is the highest.

Finally, Figure V-18 presents the relationship between the energy consumed and the QI obtained. The two highest QI values were also the two with the more energy consumption. Moreover, it remains the doubt of being able to produce a similar quality of MFC from the $(NaIO_4)+(H_2O_2)$ oxidized pulp, with lower energy consumption, as discussed previously.



Figure V-18. Quality index vs Energy Consumption

V.6 Conclusion

MFC has been produced using novel peroxide-based oxidative systems, i.e. with Cu(Phen) and with $(NaIO_4)+(H_2O_2)$. Comparison has been made with the untreated pulp and the one treated only with H_2O_2 .

The more interesting properties were observed for the $(NaIO_4)+(H_2O_2)$ oxidized pulp, with a quality index >70, a Young's Modulus of 8.6 GPa, and a transparency estimated with the transmittance value of 18.5%. This performance may be partially explained by the introduction of COOH groups in the fibre matrix favouring fibrillation. The reference pulp also provided MFC of good quality, close to that of the $(NaIO_4)+(H_2O_2)$ oxidized pulp, with slightly lower mechanical properties but very interesting optical properties evidenced in the nanopaper. The high quality of the untreated pulp may be due to the highest hemicelluloses content, which enhances microfibrillation.

The pulp oxidized by the H_2O_2 alone is the least interesting sample, as it evidenced the presence of large fibrils and poor mechanical properties. The use of hydroxide peroxide alone is not enough to improve the later mechanical fibrillation.

During the characterisation, it was observed that some properties correlated: the higher the fine content estimated by MorFi, the higher transmittance (performed at 550nm, as an indication of transparency), and the lower the tear resistance (mN). When pointing at the tensile strength, it was observed that the higher the porosity, the lower the Young's Modulus (GPa). With respect to other properties, not important changes were observed for WRV. The values of brightness

(% ISO) and DPv were very similar with and without a refining step prior to oxidation. And, it was evidenced drop in the DPv and crystallinity after the Masuko grinding.

Regarding the energy consumption, to produce the MFC with the highest quality, i.e. MFC produced from the $(NaIO_4)+(H_2O_2)$ oxidized pulp, 23,2 MWh/t were required. It may be possible to produce similar MFC quality to the $(NaIO_4)+(H_2O_2)$ with much lower energy consumption during the Masuko grinding, if the effect of the number of passes is studied, as visually, the same aspect was obtained, 2h before the passes performed. On the other hand, the pulp oxidized by $H_2O_2+Cu(Phen)$ displayed the more interesting mechanical properties within all the samples, and almost 60% less energy requirement during the Masuko grinding, compared to the $(NaIO_4)+(H_2O_2)$ oxidized pulp. This could be explained by the partial fibre matrix embrittlement due to the action of radicals. Yet, the pulp did not reach a good transparency, which may limit its potential applications.

It should be highlighted that, previous studies in LGP2 refined their hardwood substrates until 80°SR¹⁵, while the present study targeted lower refining, 47°SR, and the effect of chemical treatments studied, compensated the quality of the final product.

The HW-K-2 substrate proved to be an interesting and versatile substrate, which was able to be converted into MFC. The addition of functional groups inserted by the oxidation treatments, allowed to compensate the lack of hemicelluloses present and required to enhance microfibrillation. It can be concluded that the $(NaIO_4)+(H_2O_2)$ oxidizing system did not only presented interesting findings in the matter of dissolving pulps but also for MFC applications.

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VI. Methods

To better understand the different behaviours of the cellulosic substrates, characterizations are needed. Most of them were performed at LGP2. Those procedures are already established by TAPPI, ISO standards, or protocols found in the literature. Below is given more detail of the procedures not yet included in the previous chapters.

Prior oxidation trials

Finally, prior every oxidation trial, the samples were hydrated following the guidelines for pulp disintegration of ISO 5263-1995. The disintegrator used was the Lhomargy. The samples were later filtered and taken to a consistency of 5% for the oxidation trials, which means 20g of oven dried cellulosic substrate in 400g of suspension (water and added chemicals considered).

рΗ

pH adjustment or measurement is of high importance from a process point of view. For most of the treatments applied, the pH was measured at the beginning of the reaction, after the oxidative chemical addition, and at the end of the reaction before washing. The pH-meter was calibrated before its use.

Hydrogen peroxide titration

The consumption of H_2O_2 was determined immediately after each oxidation trial. For this purpose, the residual hydrogen peroxide (or concentrated peroxide in the commercial solutions) titration was performed by iodometric titration in the presence of sulfuric acid. Hydrogen peroxide is capable of oxidising potassium iodide added in excess, which generates iodine. The reactions are the following:

$$2I^{-} \rightarrow I_{2} + 2e^{-}$$

$$H_{2}O_{2} + 2H^{+} + 2e^{-} \rightarrow 2H_{2}O$$
Thus,
$$H_{2}O_{2} + 2H^{+} + 2I^{-} \rightarrow 2H_{2}O + I_{2}$$

The reaction is slow; thus, a catalyst is used, ammonium molybdate. The quantity of iodine formed is proportional to the quantity of H_2O_2 . Hence, the iodine released is titrated by sodium thiosulfate, as shown below:

$$I_2 + 2S_2O_3^{-2} \rightarrow 2I^- + S_4O_6^{-2}$$

The chemicals for the titration were added in an Erlenmeyer flask with containing a stirring magnet in the following order: 100 mL of distilled water, 15 mL of KI (166 g/L), 10 mL of H_2SO_4 4 N, 2 mL of ammonium molybdate (50 g/L), and 1 mL of commercial hydrogen peroxide (40% in volume) or 10 mL of the effluents after the oxidation trial. 5 min under agitation were placed before the titration by sodium thiosulfate (0.2 M). The final concentration of hydrogen peroxide, expressed in g/L, was calculated as in the equation below:

$$[H_2O_2] = \frac{V_{titration}}{V_{sample}} * [Na_2S_2O_3] * 17$$

Sodium periodate titration and estimation of the quantity of carbonyl inserted on cellulose

- -

Sodium periodate consumption is calculated in the residual effluent, knowing the exact quantity of periodate applied initially. In an Erlenmeyer flask, the it was added in the following order: 100 mL of distilled water, 20 mL of KI (10% w/w), 20 mL of H₂SO₄ 4 N, and 5 mL effluent, or the starting solution, using iodometry. Titration is done with sodium thiosulfate 0.1 N. The normality of NaIO₄ solution was calculated:

$$N_{NaIO_4} = n_{Eq} = \frac{V_{titration} * C_{Na_2S_2O_3}}{V_{sample}}$$

For the periodate consumption calculation, the difference of equivalents between the starting solution and the effluent after the reaction is considered:

$$IO_4^- Consumption (\%) = \frac{(n_{Eq} \text{ initial} - n_{Eq} \text{ final})}{g_{oven-dried \, pulp}} * Molar \text{ mass of } IO_4^-$$

Finally, the number of carbonyl groups produced:

$$n_{Eq\ CO} = n_{Eq\ initial} - n_{Eq\ final}$$

 $n_{CO}/n_{AGU} = CO\ per\ 100g\ of\ AGU$

Where nAGU = 20 g/162 g = 0.1235.

Reduction of carbonyls groups of cellulose by Sodium Borohydride

2 grams of the oxidized grinded dry pulps were weighted (oven-dried basis) in an Erlenmeyer flask, and 100ml of deionized water were added and put into stirring. Later, 20mg of Sodium Carbonate (NaCO₃) were added, and the pH measured (around 7). After a fez minutes of stirring, 20mg of Sodium Borohydride (NaBH₄) were added, the bottle was rinsed with the

remaining water and the Erlenmeyer was under stirring for 2 hours. Meanwhile, an acetic solution was prepared which was used after the reaction to rinse the glassware. For this solution, 16ml of Acetic Acid were diluted in 200ml of deionized water.

At the end of 2 hours, the suspensions were filtered and washed with deionized water, through a crucible of porosity 2, until the filtrate had a conductivity of less than 5 μ S/cm. The washed pulps were spit into small pieces and placed into a screen for 2-days drying at room temperature. All the glassware, that were used during the reaction, were washed initially 3 times with deionized water, then they were rinsed with 5ml of acetic acid, to neutralize any possible traces of hydride, and finally they were rinsed with acetone.

After 2-days at least of drying, the samples were grinded in the FORPLEX hammer-grinder, and the DMC% was measured. The samples were prepared for DP_v measurement with copper ethylene-diamine (CuED) solution.

Brightness

<u>The brightness</u> was determined according to ISO 2470-1:2016. 2g (oven-dried basis) of pulp were homogenized in water, and the sample prepared in the hand-sheet former the same day after the oxidation trial was performed. Once the sample was dried in the sheet former, the brightness was measured 4 times per sample and its average was reported.

Alkali resistance

The alkali resistance of pulp is commonly addressed as *R18* and it was calculated following the standard method ISO 699-1982, applicable on bleached and delignified pulps only. It is used for the determination of the alkali-insoluble fraction of pulps using sodium hydroxide solution of fixed concentration. The analysis requires 2.5 g of pulp (oven-dried basis), a solution of 18% NaOH for the reaction, and a 10% acetic acid solution for washing as detailed in the standard. To calculate the R18, the weight of cellulose is expressed per gram of dry pulp sample. This method assumes that only hemicelluloses are soluble in 18% NaOH solution.

Average degree of polymerization in CuED

The cellulose degree of polymerisation (DPv) indicates the number of monomeric glucose units in the cellulose polymer. A viscosimetric method can be used. In that case, this is the DPv. The standard method ISO 5351:2010 was followed for the determination of the cellulose DPv.

To estimate the cellulose DPv, 50 mg of the sample (oven-dried basis) were dissolved in bis(ethylenediamine)copper(II) hydroxide solution (CuED) under stirring. After 2 hours dissolution, the cellulose solution is transferred into a capillary viscometer and the flowtime in seconds was measured. The IVL (referred as $[\eta]$), is the limiting viscosity number in cupriethylendiamine solution. It is estimated using the table presented in the ISO standard which presents different values for the ratio η/η_0 , where η_0 is the limiting viscosity for the solvent only (no cellulose). The ratio η/η_0 is equal to the ratio t/t_0 , where t_0 is the flowtime of the pure CuED solution, and t is the flowtime of the solution with the cellulosic substrate at a concentration C. In the mentioned table, select the corresponding value of $[\eta]C$ which is expressed as g/mL. Calculate $[\eta]$ by dividing $[\eta]C$ by C, the result is expressed as mL/g. Finally, the DPv is calculated with the equation below.

$$DPv = 10^{\frac{1}{0,905}\log(0.75*IVL)}$$

Sugar content analyses

Sugar analyses were performed by HPLC-DIONEX after performing hydrolyses. 350 mg of oven-dried pulp were hydrolysed with 3 mL of sulfuric acid for 1 hour at 30°C, with constant agitation with a glass rod. After, the sample was transferred into glass bottles and 84 mL of deionised water were added. The bottles were put in the autoclave for 1 h at 120°C. Subsequently, different dilutions were prepared. 1 mL of fucose standard was added for each *50mL* of the solution prepared. Dilutions of 25, 50 and 100 were done after hydrolysis for the reference samples: for detection of hemicelluloses, dilutions of 25 were considered; and for detection of celluloses, dilutions of 100 were suitable. The HPLC gives results in terms of sugars (glucose, xylose, mannose...), and to convert this value to cellulose and hemicelluloses, the following conversions and later, calculations were performed:

$$[Glucan] = [Glucose] * \frac{162}{180}$$
$$[Mannan] = [Mannose] * \frac{162}{180}$$
$$[Galactan] = [Galactose] * \frac{162}{180}$$
$$[Xylan] = [Xylose] * \frac{132}{150}$$
$$[Arabinan] = [Arabinose] * \frac{132}{150}$$

$$Cellulose = \frac{Glucan - \frac{mannan}{Factor}}{m_{sample (O.D)}}$$

$$Hemicellulose = 1 - Cellulose$$

$$Glucomannans = \frac{\left[Mannans * \left(1 + \frac{1}{Factor}\right)\right] + Galactans}{m_{sample (O.D)}}$$

Where the factor will vary according to the nature of the cellulosic substrates: 1.6 for hardwoods and 4.15 for softwoods.

Carboxyl group quantification

Carboxyl group quantification was estimated by following the method TAPPI T237 cm-08. The cationic charge of the methylene blue dye allows to have good adsorption on cellulose fibers and good interaction with its anionic charges. The procedure includes 2 parts. The first one is performed a day before the measurements, and proceeds as detailed below:

125 mg of pulp is let to react without stirring overnight with a solution of methylene blue in dark conditions and the next day filtered. The absorbance of the filtrate is measured at 664 nm. The number of carboxyl groups per 100g of cellulose is given by the formula:

$$[COOH] = \frac{C.0,05 - C'(0,05 + E.10^{-3})}{M - M'}.100$$

Where C is the initial concentration of the methylene blue solution; C' is the concentration of the methylene blue solution after overnight reaction (C and C' are given in mM/L); E is the weight of the substrate in the Erlenmeyer flask before the addition of methylene blue; M is the weight of the initial sample weighed in the crucible and M' is the weight left in the crucible after the overnight drying in the oven (M and M' are given in g).

The methylene blue solution was prepared prior its utilisation, and the volume depended on the number of samples to be analysed. For 250mL volume, 0,0374g of methylene blue (0,1mmol) were dissolved in 200mL of water. As it can be hard to dissolve, the amount of water was added

gradually. 2.5mL of the barbital buffer solution is added and finally, the 250mL volume completed. The pH of this solution is 8.6 at 25°C.

Crystallinity Index

The traditional two-phase cellulose model describes the containing both ordered (crystalline) and less ordered (amorphous) regions. To estimate the relative amount of crystalline material, a parameter Crystallinity Index (CI) is used.

For the estimation of the CI, the initial samples were cryo-grinded to obtain a fine powder which was analysed by X-Ray Diffraction. The analyses were performed using a diffractometer X'Pert Pro MPD (PANalytical, Netherlands) equipped with a Bragg-Brentano geometry. A copper anode ($K_{\alpha}\lambda = 1.5419$ Å) was used, with the angle 2 θ ranging from 6 to 60 with a 0.05 interval. Later, the resulting data was treated in the FULLPROF software to obtain the crystallinity profiles. For the calculation of the CI, the Segal peak height method was used. The method uses a maximum intensity value (I_{200}) found between the scattering angles $2\Theta=22^{\circ}$ and 23° . The minimum value (I_{min}) is typically between $2\Theta=18^{\circ}$ and 19° . The CI was calculated as follows:

$$CI = \frac{I_{200} - I_{min}}{I_{200}}$$

The Segal method is an empirical method which was not meant to be used to compare different types of samples but rather quantify changes within a single sample set. The values obtained from the Segal peak height method should be considered relative values and comparisons of values obtained from different studies should be avoided.

Water Retention Value

The water retention value (WRV) was estimated following the guidelines of the standard method ISO 23714-2014. 2 g were used for this test, which were hydrated and submitted to suction to obtain 3 equal test pads. All the sample pads were placed in special holders and submitted to centrifugation with 3000 g force for 30 min. Immediately after the centrifugation, the weight of the samples was recorded before placing them for overnight drying in an oven at 105° C. The weight after drying was also recorded and the WRV was calculated as in the equation below. Where m₁ is the centrifuged sample and m₂ is the dried sample. WRV is expressed in g/g.

$$WRV = \frac{m_1}{m_2} - 1$$

Conclusions

The PhD work attempted to investigate processes to produce dissolving grade pulps and MFC from classical paper-grade pulps by using hydrogen peroxide in unusual operating conditions. Six different fully bleached substrates have been tested: cotton linters with high crystallinity and no hemicelluloses, a sulfite pulp with low hemicelluloses' content and high dissolving ability, 2 hardwood Kraft pulps with different hemicelluloses amount and cellulose DPv and 2 softwood Kraft pulps, again with different hemicelluloses amount and cellulose DPv.

Because a key characteristic of dissolving pulps is the dissolving ability, and as the widely used Fock test presented important drawbacks, an alternative method to evaluate the dissolving ability was proposed. Like the Fock test, this method uses cellulose derivatisation to favour its dissolution. Cellulose carbanilation with phenyl isocyanate in DMSO has been chosen as this reaction is recognised to preserve cellulose from degradation and it is usually applied to analyse the molar mass of cellulosic substrates. The dissolving behaviour of several cellulosic pulps has been investigated by the monitoring of particle size by dynamic light scattering (DLS) along the dissolution during the derivatisation reaction.

Contrary to the Fock test, this method proposed in this thesis enables to rank the substrates: as expected, the dissolving-grade sulfite pulp is easy to dissolve whereas the cotton linters pulp dissolves the slowest because of their high crystallinity, and long molecular chain, in the case of the sulfite pulp. Paper-grade pulps (Kraft pulps) exhibit poor dissolving ability, without any correlation with cellulose DPv nor hemicelluloses content. A slight difference is observed between hardwood and softwood pulps, hardwood being easier to dissolve. This difference may be explained by differences in hemicelluloses nature, i.e. xylans in hardwood and glucomannans in softwood. The carbanilation is perhaps less disturbed by the presence of xylans compared to glucomannans. Thus, the presence of hemicelluloses and their nature strongly affect the substrate dissolution during carbanilation. This method, similar to the Fock test since it involves cellulose derivatisation, has several advantages over the Fock test: it exhibits a good ability and repeatability to differentiate the dissolving ability of various cellulosic substrates, while avoiding the use of CS₂, a harmful chemical. In addition, DLS measurements are easy to make. At the end of the dissolution/derivatization, the method allows the obtention of the cellulose molecular weight distribution (MWD) by SEC. A complete analysis of the sample is thus possible. Despite this method is close to the Fock test, no correlation has been found between the two tests. One of the reasons is that the Fock test seems to be not suitable for the analysis of substrates containing hemicelluloses.

The solubility of the substrates in an aqueous system, NaOH:urea:water, has also been investigated for comparison. The main difference is that cellulose is not derivatised, dissolution occurs after swelling and intermolecular hydrogen bond release. As shown for carbanilation, in this method, high crystallinity disturbed the substrate solubility because of the poor diffusion of the solvent, but the presence of hemicelluloses is not an issue. The cellulose solubility is mainly correlated with the cellulose DPv because solvation starts from the end-group of polysaccharides. Pulps with low DPv will dissolve faster.

Then, three different oxidation systems with hydrogen peroxide were investigated in order to convert paper-grade pulps into dissolving-grade pulps.

First, the activation of H₂O₂ with copper species has been studied, by varying the pH (alkaline or acidic medium), as well as the addition of additives Cu(II) or the Cu(II)-phenanthroline complex. The hypothesis made are the following: (1) the use of H₂O₂ in unconventional conditions will favour the hemicelluloses removal after depolymerization and will lead to the desired cellulose degradation, and (2) the H₂O₂ oxidation carried out in unconventional conditions will convert part of the hydroxyl groups of the anhydroglucose unit of cellulose into carboxyl groups, favouring the dissolving ability of cellulose. Results showed that in all the tested conditions, cellulose DPv is strongly affected, without substantial hemicelluloses removal nor carboxyl group enrichment. The target of viscosity in the range of 400-500 mL/g was not achieved. It has been highlighted that the pH of the activated H₂O₂ oxidation is a key parameter. Playing with the pH enhanced or reduced the action of copper, which generates a flux of oxidising radicals in the presence of H₂O₂. The dissolving behaviour observed by the carbanilation method is decreasing probably because the amount of COOH introduced during the activated oxidation disturbs the derivatisation. In the aqueous NaOH:urea:water system, the dissolving ability is linked to the cellulose DPv and not to other parameters. To conclude, the conditions studied with activated peroxide oxidation were not able to produce dissolving-grade pulps from paper-grade pulps.

The second oxidation system consists in the combination of hydrogen peroxide oxidation with alkaline extraction of hemicelluloses, using a caustic extraction as complementary treatment. The idea was to combined two effects: hemicelluloses extraction and cellulose oxidation. The hemicelluloses extraction should favour the pulp dissolution, and the oxidation should introduce hydrophilic groups on the cellulose, improving the reactivity. An alkaline extraction step using high NaOH dose (E) was applied prior hydrogen peroxide oxidation. More uniform

molar weight distributions were obtained when performing the extraction alone, whereas the addition of hydrogen peroxide (EP) led to higher polymer dispersity. Hemicelluloses extraction was also better with E compared to EP, whereas P alone did not remove them. The extraction of hemicelluloses is easier for the hardwood pulp substrate. The different behaviours could be related to the type of hemicelluloses present in each substrate. In conclusion, the EP treatment strongly affected the cellulose DPv, is under the target for viscose application, and the dissolving ability (in carbanilation and NaOH:urea:water) was not improved.

The third oxidation system which has been investigated is a two-step oxidation system. First, the substrate is oxidized by sodium periodate to introduce some carbonyl groups in the cellulose chains, and after, an over- oxidation of the carbonyls into carboxyl groups is carried out using H_2O_2 oxidation. The idea was to enrich the pulp with sufficient amount of carboxyl groups to favour substrate dissolution and reactivity. However, this system is too aggressive for cellulose: periodate oxidation starts to depolymerise cellulose and the cellulose DPv drop is pursued by the H_2O_2 over-oxidation. Cellulose DPv values obtained are not in the target for viscose application. However, one interesting feature is that solubility in the NaOH:urea:water system is improved, especially for the hardwood Kraft pulp. The presence of COOH groups, even in low quantity, seems to be beneficial for the dissolution in an aqueous alkaline solvent. On the contrary, during the carbanilation reaction, a slightly slower dissolution was observed probably due to the presence of COOH which may affect the dissolution in DMSO.

These results show that the conversion of fully bleached Kraft pulp into dissolving pulp is a real challenge. Hemicelluloses removal and/or cellulose COOH enrichment may improve the dissolving ability of the Kraft pulp but in all tested treatments, this was done at the expense of the cellulose DPv. That is why another way of valorisation was proposed for the Kraft pulp, the production of microfibrillated cellulose (MFC). For this study, only one hardwood Kraft pulp was selected, and wo oxidative systems were tested: the activated H₂O₂ oxidation with the copper-phenanthroline complex, and the periodate-peroxide two-steps oxidation. They were applied after pulp refining and before mechanical grinding to produce MFC (microfibrillated cellulose). Different qualities were obtained, some exhibiting high strength properties whereas other showing high level of transparency, depending on the chemical treatment applied.

This PhD work opens several perspectives:

For dissolving pulp applications, the main issue seems to be the extended depolymerisation after all the tested oxidative stages. To reduce the cellulose DPv loss, the dosages of oxidant (hydrogen peroxide, periodate) can be decreased. Ongoing work at LGP2 showed that periodate strongly depolymerises cellulose but if low charges are applied the depolymerisation could be controlled. The periodate-peroxide system is the most promising since only low amounts of COOH seem to be required to improve the cellulose dissolution in an aqueous solvent. This is very interesting since derivatisation, and usage of harmful chemicals, could be avoided and aqueous solvents are cheap and environmentally friendly. The results obtained with the combination of periodate-peroxide oxidation open the door for the development of new cellulose regeneration systems, aqueous based. Another way of optimisation is to use Kraft pulp with high DPv since in the present work, the initial substrates contained cellulose with already low DPv.

Concerning MFC production, a comparison with the well-known TEMPO oxidation could be studied and a focus on energy saving should be made. Only few trials have been made and very promising results are already acquired. Only one fully-bleached hardwood Kraft pulp has been tested but other substrates could be also investigated.

Finally, it can be considered that this work was guided by the idea of "exploring multidimensional analytical methods" for the characterization of the dissolving ability of cellulosic substrates. Indeed, as a complement to classical characterisations, it was developed in this work a "three-component method" to evaluate the properties of different substrates: (1) DLS analysis during derivatization in an organic medium (tricarbanilation in DMSO), (2) MWD analysis by HPSEC of the derivatized substrates, and (3) substrate solubility in an alkaline aqueous medium, the NaOH:urea:water system. Our work could be the starting point of a new methodology, including other characterizations to be developed and included as new components of the "multi-dimensional vector" representing the dissolving ability of cellulosic substrates. APPENDIX



Appendix: Chapter III. Crystallinity profiles. Oxidation 0.02% Cu(Phen).



Appendix: Chapter III. Crystallinity profiles. Cu(Phen) vs No Cu(Phen).

Trial No.	1	2	3	4	5	6	7	8	9
Date	29/08/2019	29/08/2019	29/08/2019	09/09/2019	09/09/2019	09/09/2019	17/09/2019	17/09/2019	17/09/2019
Sample	HW-K-1 FE	HW-K-1 FE	HW-K-1 FE	SW-K-2 T	SW-K-2	SW-K-2	HW-K-2	HW-K-2	HW-K-2
Pre-treatment	20g pulp homogenise d and later pre-heated at 95°C								
Conditions									
Reaction Time	60 min								
Bath/Pulp T (°C)	95°C/90°C								
Conc. Cu (%)	0	0	0	0	0	0	0	0	0
Conc. Cu(Phen) (%)	0	0	0	0	0	0	0	0	0
Conc. NaOH (%)	0	0,2	2	0	0,2	2	0	0,2	2
Conc. H ₂ O ₂ (%)	1,78	1,78	1,78	2	2	2	2	2	2
pH before Rx	6	9,7	11,4	4,7	9,6	11,4	5	8,7	11,5
pH after Rx	4,5	5,7	11,4	4,9	5,4	11,5	3,2	3,7	11,4
Characterisation									
H ₂ O ₂ Consumption (%)	31	40	100	37	72	98	53	74	100
Brightness (%ISO) REF	85,6	85,6	85,6	87,8	87,8	87,8	87,9	87,9	87,9
Brightness (%ISO) final	84,1	87,6	89,3	88,6	90,7	91,9	90,7	91,9	93,6
IV final, η (mL/g)	294	388	446	330	301	467	180	152	379
DPv REF	876	876	876	797	797	797	692	692	692
DPv final	388	528	615	442	398	648	226	187	514

Appendix: Chapter III. Information about the oxidation trials with/without Cu(Phen).

Trial No.	10	11	12	13	14	15	16	17	18
Date	18/09/2019	18/09/2019	18/09/2019	15/10/2019	15/10/2019	15/10/2019	16/10/2019	16/10/2019	16/10/2019
Sample	Cotton Linter	Cotton Linter	Cotton Linter	HW-K-2	HW-K-2	HW-K-2	SW-K-2	SW-K-2	SW-K-2
Pre-treatment	20g pulp homogenise d and later pre-heated at 95°C								
Conditions									
Reaction Time	60 min								
Bath/Pulp T (°C)	95°C/90°C								
Conc. Cu (%)	0	0	0	0,02	0,02	0,02	0,02	0,02	0,02
Conc. Cu(Phen) (%)	0	0	0	0	0	0	0	0	0
Conc. NaOH (%)	0	0,2	2	0	0,2	2	0	0,2	2
Conc. H ₂ O ₂ (%)	2	2	2	2	2	2	2	2	2
pH before Rx	6,2	10	11,6	4,2	7,7	12	3,9	9,6	12
pH after Rx	6	9,2	11,6	3,1	3,9	11,7	2,7	6,8	11,7
Characterisation									
H ₂ O ₂ Consumption (%)	26	98	98	98	98	100	100	100	100
Brightness (%ISO) REF	90,2	90,2	90,2	87,9	87,9	87,9	87,8	87,8	87,8
Brightness (%ISO) final	92,8	93,8	93,8	89,8	91,6	92,7	89,2	89,2	88,9
IV final, η (mL/g)	394	449	501	177	169	396	307	460	468
DPv REF	1005	1005	1005	692	692	692	797	797	797
DPv final	536	621	700	221	211	539	408	637	649

Trial No.	19	20	21	22	23	24	25	26	27
Date	30/10/2019	30/10/2019	30/10/2019	31/10/2019	31/10/2019	31/10/2019	10/12/2019	28/01/2020	28/01/2020
Sample	SW-K-2	SW-K-2	SW-K-2	HW-K-2	HW-K-2	HW-K-2	SW-K-2	HW-K-2	HW-K-2
Pre-treatment	20g pulp homogenise d and later pre-heated at 95°C								
Conditions		1	Not well disso	lved Cu(Phen).	r	1		1	
Reaction Time	60 min								
Bath/Pulp T (°C)	95°C/90°C								
Conc. Cu (%)	0	0	0	0	0	0	0,02	0	0
Conc. Cu(Phen) (%)	0,02	0,02	0,02	0,02	0,02	0,02	0	0,02	0,02
Conc. NaOH (%)	0	0,2	2	0	0,2	2	0,2	0	0,2
Conc. H ₂ O ₂ (%)	2	2	2	2	2	2	2	2	2
pH before Rx	4	9,4	11,8	4,3	9,1	11,6	9,6	4,7	9,7
pH after Rx	2,9	4,5	11,6	3,2	3,8	11,6	4,5	3,3	3,7
Characterisation									
H ₂ O ₂ Consumption (%)	83,01	96,38	100,00	74,36	91,98	98,43	98,43	85,53	89,15
Brightness (%ISO) REF	87,83	87,83	87,83	87,88	87,88	87,88	87,83	87,88	87,88
Brightness (%ISO) final	83,95	84,06	88,16	77,67	79,72	90,96	87,81	79,45	83,06
IV final, η (mL/g)	250	268	380	213	146	339	294	198	159
DPv REF	797	797	797	692	692	692	797	692	692
DPv final	325	351	517	272	179	455	388	251	198

Trial No.	28	29	30	31	32	33	34	35	36
Date	28/01/2020	30/01/2020	30/01/2020	30/01/2020	05/02/2020	05/02/2020	05/02/2020	26/02/2020	26/02/2020
Sample	H/W-K-2	SW/-K-2	SW/-K-2	S\N/_K_2	Cotton	Cotton	Cotton	Cotton	Cotton
Jampie		5W K 2	500 K 2	500 K 2	Linters	Linters	Linters	Linters	Linters
	20g pulp								
	homogenise								
Pre-treatment	d and later								
	pre-heated								
	at 95°C								
Conditions			·					·	
Reaction Time	60 min								
Bath/Pulp T (°C)	95°C/90°C								
Conc. Cu (%)	0	0	0	0	0	0	0	0,02	0,02
Conc. Cu(Phen) (%)	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0	0
Conc. NaOH (%)	2	0	0,2	2	0	0,2	2	0	0,2
Conc. H ₂ O ₂ (%)	2	2	2	2	2	2	2	2	2
pH before Rx	11,6	4,5	9,6	11,8	6	9,9	11,7	5	10
pH after Rx	11,5	3,1	4,4	11,8	3,58	7,8	11,7	3,8	8,9
Characterisation									
H ₂ O ₂ Consumption (%)	100,00	79,08	91,19	98,27	76,40	97,64	100,00	94,81	97,64
Brightness (%ISO) REF	87,88	87,83	87,83	87,83	90,2	90,2	90,2	90,2	90,2
Brightness (%ISO) final	91,52	82,28	86,73	88,66	87,56	90,25	89,8	90,25	86,6
IV final, η (mL/g)	328	267	249	376	291	466	394	498	505
DPv REF	692	797	797	797	1005	1005	1005	1005	1005
DPv final	439	349	323	510	384	646	537	695	707

Trial No.	37	38	39	40	41	42	43	44	45
Date	26/02/2020	06/03/2020	06/03/2020	06/03/2020	11/03/2020	11/03/2020	11/03/2020	19/05/2020	19/05/2020
Sample	Cotton Linters	Cotton Linters	HW-K-2	SW-K-2	Cotton Linters	HW-K-2	SW-K-2	HW-K-2	HW-K-2
Pre-treatment	20g pulp homogenise d and later pre-heated at 95°C								
Conditions		1	1		1	1	1	Repetition	Repetition
Reaction Time	60 min								
Bath/Pulp T (°C)	95°C/90°C								
Conc. Cu (%)	0,02	0	0	0	0	0	0	0	0
Conc. Cu(Phen) (%)	0	0,02	0,02	0,02	0,02	0,02	0,02	0,02	0,02
Conc. NaOH (%)	2	0,4	0,4	0,4	0,3	0,5	0,3	0,4	0,5
Conc. H ₂ O ₂ (%)	2	2	2	2	2	2	2	2	2
pH before Rx	11,9	10,7	10,1	10,4	10,6	10,6	10,1	10	10,5
pH after Rx	11,8	10,3	6,7	9,5	9,9	9,1	8,1	6,4	9
Characterisation									
H ₂ O ₂ Consumption (%)	100,00	100,00	97,80	97,64	98,74	98,11	98,58	87,88	87,88
Brightness (%ISO) REF	90,2	90,18	87,88	87,83	90,18	87,88	87,83	87,88	87,88
Brightness (%ISO) final	89,89	89,96	88,46	87,9	90,43	90,9	87,83	87,9	91,04
IV final, η (mL/g)	317	433	300	438	439	381	434		
DPv REF	1005	1005	692	797	1005	692	797	692	692
DPv final	423	595	397	604	605	517	598	370	508

Trial No.	46	47	49	51	52	53	54	55	56
Date	20/05/2020	20/05/2020	10/09/2020	07/10/2020	07/10/2020	07/10/2020	08/10/2020	08/10/2020	08/10/2020
Sample	Cotton Linters	SW-K-2	HW-К-2	Cotton Linters	SW-K-2	HW-K-2	Cotton Linters	SW-K-2	HW-K-2
Pre-treatment	20g pulp homogenised and later pre-heated at 95°C	20g pulp homogenised and later pre-heated at 95°C	20g pulp homogenised and later pre-heated at 95°C	20g pulp with LHOMARGY and 2 hours pre-heating at 95°c					
Conditions	Repetition								
Reaction Time	60 min	60 min	60 min	60 min	60 min	60 min	60 min	60 min	60 min
Bath/Pulp T (°C)	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C	95°C/90°C
Conc. Cu (%)	0	0	0	0	0	0	0	0	0
Conc. Cu(Phen) (%)	0,02	0,02	0,02	0	0	0	0	0	0
Conc. NaOH (%)	0,2	0,5	0,6	0,3	0,3	0,4	0,3	0,3	0,4
Conc. H ₂ O ₂ (%)	2	2	2	2	2	2	2	2	2
pH before Rx	9,8	10,9	10,7	10,4	10,3	10,2	10,5	10,3	10,4
pH after Rx	7,9	9,9	9,5	10,3	8,9	6,7	10,5	9,3	7,5
Characterisation									
H ₂ O ₂ Consumption (%)	90,18	xxx	98,58	98,43	98,43	95,28	98,43	98,74	98,43
Brightness (%ISO) REF	90,18	87,83	87,88	90,18	87,83	87,88	90,18	87,83	87,88
Brightness (%ISO) final	88,7	87,7	90	91,87	90	92	91,87	90	91,4
IV final, η (mL/g)		365	316	513	461	296	531	491	334
DPv REF	1005	797	692	1005	797	692	1005	797	692
DPv final	577	493	421	719	639	392	746	684	447



Appendix: Chapter III. MWD profiles by HPSEC when using more NaOH.



Appendix: Chapter III. Carbanilation by DLS when using more NaOH.

Appendix: Chapter III. SEM. CL. 2%H₂O₂ and 0.02% Cu(Phen).



Appendix: Chapter III. SEM. SW-K-2. 2%H₂O₂ and 0.02% Cu(Phen).





Appendix: Chapter III. SEM. HW-K-2. 2%H₂O₂ and 0.02% Cu(Phen).

Appendix: Chapter IV. Extraction prior oxidation with $H_2O_{2.}$

Trial No.	1	2	3	4	5	6
Date	15/04/2021	15/04/2021	15/04/2021	15/04/2021	16/04/2021	16/04/2021
Sample	HW-K-2	SW-K-1	HW-K-2	SW-K-1	HW-K-2	SW-K-1
Step I: Extraction			P10	P10		
Pre-treatment	10g pulp, and 20min pre- heating.					
Reaction Time	60min	60min	60min	60min	60min	60min
Bath/Pulp Temperature	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10	10	10	10	10
Conc. NaOH	7,50%	7,50%	2%	2%	7,50%	7,50%
Charge of H ₂ O ₂ (%)	0	0	10	10	0	0
pH before Rx	13	13,1	11,1	10,9	13,1	13,1
pH after Rx	12,7	12,8	11,8	11,5	13	13
Step II: H ₂ O ₂ oxidation						
Pre-treatment	none	none	none	none	5L wash and 10 min pre- heating	5L wash and 10 min pre- heating
Reaction Time					1h	1h
Bath/Pulp Temperature					75°C/70°C	75°C/70°C
Pulp consistency (%)					10	10
Conc. NaOH (%)					2	2
Conc. H ₂ O ₂ (%)					10	10
pH after NaOH addition					12,6	12,6
pH before Rx					11,1	10,9
pH after Rx					11,8	11,8
Characterisation						
H ₂ O ₂ Consumption (%)			94,5	48,5	68,8	63,3
Brightness (%ISO) REF	87,9	86,9	87,9	86,9	87,9	86,9
Brightness (%ISO) final	88,2	85,4	93,8	92,9	93 <i>,</i> 8	92,5
IV final, η (mL/g)	488	736	241	360	270	328
DPv REF	692	1086	692	1086	692	1086
DPv final	680	1070	313	486	354	438

Trial No.	7	8	9	10	11	12
Date	16/04/2021	16/04/2021	31/05/2021	31/05/2021	31/05/2021	31/05/2021
Sample	HW-K-2	SW-K-1	HW-K-2	SW-K-1	HW-K-2	SW-K-1
Step I: Extraction			E	E	EP10	EP10
Pre-treatment	10g pulp, and 20min pre- heating.					
Reaction Time	60min	60min	60min	60min	60min	60min
Bath/Pulp Temperature	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10	10	10	10	10
Conc. NaOH	7,50%	7,50%	75g/L	75g/L	75g/L	75g/L
Charge of H ₂ O ₂ (%)	0	0	0	0	0	0
pH before Rx	13	13,1	13,8	13,8	13,8	13,8
pH after Rx	13	13				
Step II: H ₂ O ₂ oxidation						
Pre-treatment	none	none			none	none
Reaction Time	1h	1h			1h	1h
Bath/Pulp Temperature	75°C/70°C	75°C/70°C			75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10			10	10
Conc. NaOH (%)	0	0			0	2
Conc. H ₂ O ₂ (%)	10	10			10	10
pH after NaOH addition						
pH before Rx	12,1	12,3				
pH after Rx	12,7	12,6			13,5	13,5
Characterisation						
H ₂ O ₂ Consumption (%)	51,8	-4,0			-18,4	10,9
Brightness (%ISO) REF	87,9	86,9	87,9	86,9	87,9	86,9
Brightness (%ISO) final	93,7	91,8	88,9	85 <i>,</i> 4	93,3	91,9
IV final, η (mL/g)	272	401	517	688	218	304
DPv REF	692	1086	692	1086	692	1086
DPv final	356	547	725	995	280	403

Trial No.	13	14	15	16	17	18
Date	31/05/2021	31/05/2021	09/06/2021	09/06/2021	09/06/2021	09/06/2021
Sample	HW-K-2	SW-K-1	HW-K-2	HW-K-2	HW-K-2	HW-K-2
Step I: Extraction	E+P10	E+P10	EP2*	EP5*	EP2	EP5
Pre-treatment	10g pulp, and 20min pre- heating.					
Reaction Time	60min	60min	60min	60min	60min	60min
Bath/Pulp Temperature	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10	10	10	10	10
Conc. NaOH	75g/L	75g/L	75g/L	75g/L	75g/L	75g/L
Charge of H ₂ O ₂ (%)	0	0	2	5	0	0
pH before Rx	13,8	13,8	13,6	13,6	13,6	13,6
pH after Rx			13,3	13,3	13,6	13,6
Step II: H ₂ O ₂ oxidation						
Pre-treatment	5L wash and 10 min pre- heating	5L wash and 10 min pre- heating			none	none
Reaction Time	1h	1h			1h	1h
Bath/Pulp Temperature	75°C/70°C	75°C/70°C			75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10			10	10
Conc. NaOH (%)	2	2			0	0
Conc. H ₂ O ₂ (%)	10	10			2	5
pH after NaOH addition						
pH before Rx						
pH after Rx	11,8	11,9			13,3	13,3
Characterisation						
H ₂ O ₂ Consumption (%)	52,3	64,9	95,6	69,8	95,7	65,7
Brightness (%ISO) REF	87,9	86,9	87,9	87,9	87,9	87,9
Brightness (%ISO) final	94,0	91,7	93,0	93,1	93,2	93,3
IV final, η (mL/g)	169	222	264	310	273	242
DPv REF	692	1086	692	692	692	692
DPv final	211	285	345	413	357	313

Trial No.	19	20	21	22	23	24
Date	10/06/2021	10/06/2021	10/06/2021	10/06/2021	10/06/2021	10/06/2021
Sample	HW-K-2	HW-K-2	SW-K-1	SW-K-1	SW-K-1	SW-K-1
Step I: Extraction	P2	P5	EP2	EP5	P2	P5
Pre-treatment	10g pulp, and 20min pre- heating.					
Reaction Time	60min	60min	60min	60min	60min	60min
Bath/Pulp Temperature	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Pulp consistency (%)	10	10	10	10	10	10
Conc. NaOH	2%	2%	75g/L	75g/L	2%	2%
Charge of H_2O_2 (%)	2	5	0	0	2	5
pH before Rx	12	11,5	12,1	11,6	13,7	13,7
pH after Rx	12,4	12,4			13,6	13,6
Step II: H ₂ O ₂ oxidation						
Pre-treatment			none	none		
Reaction Time			1h	1h		
Bath/Pulp Temperature			75°C/70°C	75°C/70°C		
Pulp consistency (%)			10	10		
Conc. NaOH (%)			0	0		
Conc. H ₂ O ₂ (%)			2	5		
pH after NaOH addition						
pH before Rx						
pH after Rx			12,4	12,2		
Characterisation						
H ₂ O ₂ Consumption (%)	99,6	99,3	99,6	99,5	95,7	76,1
Brightness (%ISO) REF	87,9	87,9	86,9	86,9	86,9	86,9
Brightness (%ISO) final	92,9	93,5	91,2	91,9	90,5	91,4
IV final, η (mL/g)	345	284	343	299	436	333
DPv REF	692	692	1086	1086	1086	1086
DPv final	464	375	460	396	601	446

Appendix: Chapter IV. Periodate oxidation prior oxidation with $H_2O_{2.}$

Trial No.	13	14	15	16	17	18
Date	06/04/2021	06/04/2021	06/04/2021	26/04/2021	26/04/2021	26/04/2021
Sample	CL	SW-K-1	HW-K-2	CL	SW-K-1	HW-K-2
	20g pulp					
	prior 1 st					
	oxidation,	oxidation,	oxidation,	oxidation,	oxidation,	oxidation,
Pre-treatment	and pre-					
	75°c prior	75°c prior	75° c prior	75°c prior	75°c prior	75°c prior
	2 nd					
	oxidation	oxidation	oxidation	oxidation	oxidation	oxidation
Step I: NaIO ₄ oxidation	NalO ₄					
Reaction time	120 min					
Reaction Temperature	RT	RT	RT	RT	RT	RT
Pulp consistency (%)	1,6	1,6	1,6	1,6	1,6	1,6
Sol. NaIO ₄ (M)	0,05	0,05	0,05	0,05	0,05	0,05
Charge of NaIO ₄ (%)	54	54	54	27	27	27
g NalO ₄ /g suspension	10,8/1250	10,8/1250	10,8/1250	5,4/1250	5,4/1250	5,4/1250
pH before Rx	5,22	5,18	4,71	4,89	4,4	4,27
pH after Rx	5,35	4,23	3,94	4,88	3,77	3,57
Step II: H ₂ O ₂ oxidation	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2
Reaction Time	60 min					
Bath/Pulp	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Temperature	, 	, 	, 	, 	,	,
Pulp consistency (%)	5	5	5	5	5	5
Charge NaOH (%)	1,2	1,5	1,5	1,5	2,0	2,0
Charge H ₂ O ₂ (%)	2,0	2,0	2,0	2,0	2,0	2,0
pH before Rx	11,2	10,6	10,4	11,5	11,5	11,5
pH after Rx	7,9	5,34	5,8	10,91	7	8,33
Characterisation						
H ₂ O ₂ Consumption (%)	97,4	94,55	95,81	99,3	98,58	99,35
NalO ₄ equivalents	7,43	22,3	15,3	9,47	11,66	6,63
Brightness (%ISO) REF	90,2	86,9	87,9	90,2	86,9	87,9
Brightness (%ISO)						
NaIO ₄	no	no	no	89,96	87,47	89,15
Brightness (%ISO) H ₂ O ₂	91,93	91,59	92,85	92,0	91,7	93,0
DPv initial REF	1005	1086	692	1005	1086	692
DPv after NalO ₄	214	233	207	279	342	294
IV, η (mL/g) after H ₂ O ₂	134	162	145	158	199	173
DPv final after H ₂ O ₂	163	201	178	196	253	216

Trial No.	19	20	21	22	23	24
Date	04/05/2021	04/05/2021	04/05/2021	12/05/2021	12/05/2021	12/05/2021
Sample	CL	SW-K-1	HW-K-2	CL	SW-K-1	HW-K-2
	20g pulp	20g pulp	20g pulp	20g pulp	20g pulp	20g pulp
	prior 1 st	prior 1 st	prior 1 st	prior Blank	prior Blank	prior Blank
	oxidation,	oxidation,	oxidation,	trial, and	trial, and	trial, and
Pre-treatment	and pre-	and pre-	and pre-	pre-	pre-	pre-
	75°c prior	75°c prior	75°c prior	75°c prior	75°c prior	75°c prior
	2 nd	2 nd	2 nd	2 nd	2 nd	2 nd
	oxidation	oxidation	oxidation	oxidation	oxidation	oxidation
Step I: NaIO ₄ oxidation	NalO ₄	NalO ₄	NalO ₄	BLANK	BLANK	BLANK
Reaction time	120 min	120 min	120 min	120 min	120 min	120 min
Reaction Temperature	RT	RT	RT	RT	RT	RT
Pulp consistency (%)	1,6	1,6	1,6	1,6	1,6	1,6
Sol. NaIO ₄ (M)	0,05	0,05	0,05	no	no	no
Charge of NaIO ₄ (%)	13,5	13,5	13,5	blank	blank	blank
g NalO ₄ /g suspension	2.7/1250	2.7/1250	2.7/1250	0	0	0
pH before Rx	5,64	5,6	4,41	7,27	6,2	6
pH after Rx	5 <i>,</i> 8	5,12	4,06	6,6	6,56	6,64
Step II: H ₂ O ₂ oxidation	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2	H_2O_2
Reaction Time	60 min	60 min	60 min	60 min	60 min	60 min
Bath/Pulp Temperature	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C	75°C/70°C
Pulp consistency (%)	5	5	5	5	5	5
Charge NaOH (%)	1,5	2,0	2,0	1,5	2,0	2,0
Charge H ₂ O ₂ (%)	2,0	2,0	2,0	2,0	2,0	2,0
pH before Rx	11,68	11,9	11,84	11,34	11,93	11,8
pH after Rx	11,97	11,25	11,74	12,2	12,33	12,35
Characterisation						
H ₂ O ₂ Consumption (%)	99,01	99,22	99,35	99,09	99,35	98,7
NalO ₄ equivalents	12,07	14,04	11,85	no	no	no
Brightness (%ISO) REF	90,2	86,9	87,9	90,2	86,9	87,9
Brightness (%ISO)						
NalO ₄	91,63	86,49	88,54	90,83	86,74	88
Brightness (%ISO) H ₂ O ₂	92,54	89,85	93,31	92,37	90,79	93,23
DPv initial REF	1005	1086	692	1005	1086	692
DPv after NaIO ₄	435	607	484	1017	1098	691
IV, η (mL/g) after H_2O_2	233,4	317,0	282	467	555	399
DPv final after H ₂ O ₂	301	422	372	647	785	545