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Production de celluloses pures à partir de pâte à papier par un procédé propre au peroxyde d'hydrogène catalysé

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I would like to dedicate my thesis to my elder father, father, mother, uncles, aunts, brothers, sistesr, and friends. Without their love and motivation it simply would never have been possible.

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INTRODUCTION

The use of pure cellulose is experiencing a renewed interest in the synthesis of cellulose derivatives (ethers and esters) for additives and plastics and in the production of regenerated celluloses mainly for textile applications. This is caused by the search for products issued from biomass as substitutes for those made from fossil resources. In this context cellulose has a place of choice since it is the most abundant organic product on earth.

To date pure cellulose is produced from wood by kraft pulping of pre-hydrolysed chips (prehydrolysis-kraft process) or by acid sulfite pulping of ordinary chips, and also from cotton linters by appropriate purification treatments. To meet the future demand, wood is the raw material offering the greatest potential since the use of linters is limited by the hazards of the cotton cultivation.

Many kraft paper pulp producers are today in a difficult situation. This is due to the fact that this industry is very capital intensive. Consequently, the capacity of the mill is a key factor in determining the production cost. Wood price is also impacting highly the pulp production cost. So the new giant pulp mills installed in countries where wood is growing fast and is available in the vicinity of the mill, like in Brazil, Indonesia…are in a most favourable economic situation. The only way for the smaller facilities to stay alive is to produce higher value products such as pure cellulose which is sold at a 50% higher price than wood pulp. Instead of shifting to prehydrolysis –kraft, which would represent a major and costly change, some minor adjustments might be introduced in the existing kraft pulping lines to purify the wood pulp so as to obtain pure cellulose. This is the purpose of this thesis work. The objective of this work is thus to develop the production of pure cellulose from wood in a kraft pulp mill by an environmentally friendly purification process. This new process would be implemented in parallel to the current kraft pulp bleaching line.

Cellulosic pulps obtained after wood delignification by the kraft process are brown and still contaminated by some lignin and hemicelluloses. The production of bleached fibres requires an additional bleaching step in order to remove coloured residual lignin. Oxygenated reagents such as oxygen or hydrogen peroxide are now applied in alkaline medium in partial substitution for the usual chlorinated agents (chlorine, chlorine dioxide) responsible for the production of toxic chlorinated organic compounds. However, the combination of oxygen and hydrogen peroxide treatments is not sufficient to fully complete the bleaching. As a consequence, some chlorinated agents are still largely used.

Bleached kraft cellulosic fibers are essentially used for the production of white paper for printing applications. Their hemicellulose content is still high (20-25%). Moreover these fibers lack reactivity and their cellulose has a high degree of polymerization. These characteristics make them unable to enter into any chemical application or to be processed into textile.

Recent studies showed that transition metallic complexes, especially copper-phenanthroline, exhibit a catalytic action on hydrogen peroxide reactions in alkaline medium with cellulosic pulp. Delignification is strongly improved and the carbohydrates (cellulose and hemicelluloses) are also more oxidized as reflected by the large cellulose depolymerization. Consequently this catalytic process has a low selectivity towards the residual lignin, which makes it of low interest in the bleaching of paper pulps. Nevertheless, this drawback could become an advantage regarding the production of pure cellulose for chemical application. Indeed, the production of pure and reactive cellulose requires not only the elimination of residual lignin but also that of hemicelluloses. Moreover the reduction in cellulose DP is necessary for its dissolution. The purpose of this work is thus to develop an entirely environmentally friendly industrial process based on catalyzed hydrogen peroxide and including, if necessary, complementary treatments with chlorine free reagents.

The first chapter is a literature review on the state of the art on wood composition, kraft pulping and TCF bleaching operations (O_2, H_2O_2 and O_3), and on the development of hydrogen peroxide activators for delignification improvement. The last part is devoted to the characteristics that cellulose should possess to be transformed into cellulose derivatives or processed in the current dissolving pulp lines. Justification of the directions to be explored during the thesis will be given as a conclusion to this literature review.

The second chapter is a basic study of the behaviour of the copper-phenanthroline complex with hydrogen peroxide under alkaline conditions. UV-Visible spectrophotometry will be used. The reaction of the copper-phenanthroline / hydrogen peroxide system with a nonphenolic lignin model compound i.e. veratryl alcohol will be followed by HPLC. Special attention will be paid to the formation of veratryl aldehyde which is supposed to be the main reaction production. The results of this study will justify the application of the copper-phenanthroline as catalyst for hydrogen peroxide delignification of kraft pulp

In the third chapter, an industrial kraft pulp, pre-delignified with oxygen, is used as substrate to optimise the hydrogen peroxide catalysed delignification. The effect of the catalyst on delignification (kappa number) and carbohydrate degradation (DPv and hemicelluloses content) is studied. Variable parameters include hydrogen peroxide and sodium hydroxide charge, copper-phenanthroline dose, the strategy of catalyst addition, and reaction temperature. Some pre-treatments before the catalysed H_2O_2 delignification will be investigated in an attempt to accentuate the effect of the catalyst. Finally the chemical composition of the pulp after the catalysed H_2O_2 stage, preceded by suitable treatments, will be analysed.

Further purification of the pulp is studied in the chapter four. Conventional cold caustic extraction and a final ozone stage are applied to target the expected purity, i.e. the cellulose content and brightness requirements. Then a full totally chlorine free sequence for pure cellulose production will be proposed. The produced celluloses will be characterized by classical pulp analyses (brightness, hemicelluloses and hexenuronic acid content, DPv, metal content). Their molecular mass distribution (MMD) will be also analysed in detail using size exclusion chromatography. The carbohydrate MMD profile will be followed all along the sequence giving information on the effect of each single operation on the low and high molecular mass fractions of polysaccharides. Finally the reactivity of the cellulose in a viscose-type process will be assessed and compared with that of market cellulose.

Chapter five will describe the material and methods used during the realization of the experiments.

Finally, a general conclusion covering the main findings of this study and possible applications will be presented. Some perspectives will be also proposed.

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BLEACHING OF HARDWOOD KRAFT PULP WITH H_2O_2/CU-PHENANTHROLINE SYSTEM 91

ABBREVIATIONS

a : Acid (H_2SO_4) stage
O : Oxygen stage
P : Hydrogen peroxide stage
OP : Oxygen and Peroxide
Z : Ozone stage
HexA : Hexenuronic acids
E : Cold Caustic Extraction
ECF : Elemental chlorine free
TCF : Totally chlorine free
DP : Molecular Weight Distribution
CED : Cupriethylenediamine
CMC : Carboxymethyl cellulose
HPLC : High performance liquid chromatography
UV-Vis : Ultraviolet visible

CHAPTER - 1

AN INTRODUCTION TO PULP PRODUCTION AND PURE CELLULOSE PRODUCTION

1.1 Wood and Its Composition

Wood is one of the principal sources for pulp production. Chemical substances in wood can be divided into four groups, (i) cellulose, (ii) hemicelluloses, (iii) lignin and (iv) extractives. But the amounts of these groups are not constant and different in hardwoods and softwood. The typical composition is mentioned in table 1.

Table 1.1: Typical Composition for Hardwoods and Softwoods[1-5]

Parameters	**Hardwoods**	**Softwoods**
Cellulose	45 ± 2 %	42 ± 2 %
Hemicelluloses	30 ± 5 %	27 ± 2 %
Lignin	20 ± 4 %	28 ± 3 %
Extractives	5 ± 3 %	3 ± 2 %

1.1.1 Cellulose

Cellulose is a polysaccharide with formula $(C_6H_{10}O_5)_n$ where n is the number of repeating units or degree of polymerization (DP). The structure of cellulose is shown in figure 1.1. The recurring unit is actually two consecutive glucose anhydride units known as cellobiose unit. The DP value changes from species to species, and from process to process. Cellulose consists of β-D-glucose units linked together by 1-4 glycosidic bonds. Cellulose is a linear polymer of β-(l, 4)-D-glucopyranose units in $^4C_1$ chair conformation.

In this conformation the free hydroxyl groups are positioned equatorially while the hydrogen atoms are placed in axial positions. It is the biggest component in both softwood and hardwood species. Cellulose in wood has an average DP of around 8,000-10,000 whereas in bleached pulp of around 600-1500. Cellulose is an unbranched, linear polymer, which makes several cellulose chains to pack together and form a very ordered crystalline structure. In between the ordered crystalline structure (micelles), there are cellulose chains which are not ordered, they are called as amorphous regions. These bundles of aggregated celluloses are called micro fibrils. Several micro fibrils form a bigger structure and called macrofibrils. The fibrils pack together with hemicelluloses and lignin in between to form the wood fiber wall. Cellulose is not soluble in water but it swells due to the hydrogen bonding between cellulose and water. Cellulose dissolves in cupriethylenediamine, cuprammonium hydroxide, and is completely degraded in hydrochloric acid (44%), sulphuric acid (72%) and phosphoric acid

(85%). Cellulose can be modified and derivatized to produce different products, viz., fiber, film, plastics, explosives, thickeners and etc. For production of cellulose derivatives, pure cellulose (α-cellulose) is used. Derivatization of cellulose takes place at the hydroxyl groups of cellulose.

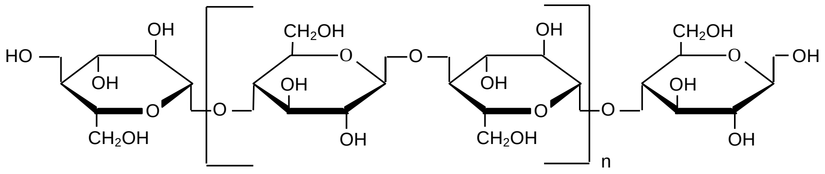


Figure 1.1: Structure of Cellulose[1]

1.1.2 Hemicelluloses

Along with long-chain cellulose, a number of short-chain polysaccharides are also present, which are known as hemicelluloses. There are hetero-polysaccharides since they comprise different types of sugar units: (i) pentose (five carbons) as xylose and arabinose, and (ii) hexoses (six carbons) as glucose, mannose and galactose (figure 1.2). Some uronic acids, resulting from hexose primary hydroxyl oxidation into carboxyl, may be also present. If the hexose is glucose, the generated acid is the glucuronic acid.

Hemicelluloses chains are shorter than cellulose chains and have lower DP than cellulose. Normally their DP is upto 200 units. They are branched polymer and thus cannot form crystalline structures. Some OH groups may be acetylated. In pulping process Hemicelluloses react faster than cellulose. Hemicelluloses are found in the microfibrils. Hemicelluloses are insoluble in water but soluble in strong alkaline solution. They hydrolyze more rapidly than cellulose. Structures of hardwood and softwood xylan are given in figures 1.3 & 1.4.

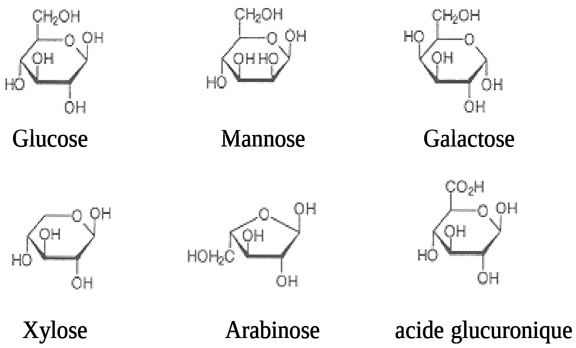


Figure 1.2: Structure of Hemicelluloses[1-5]

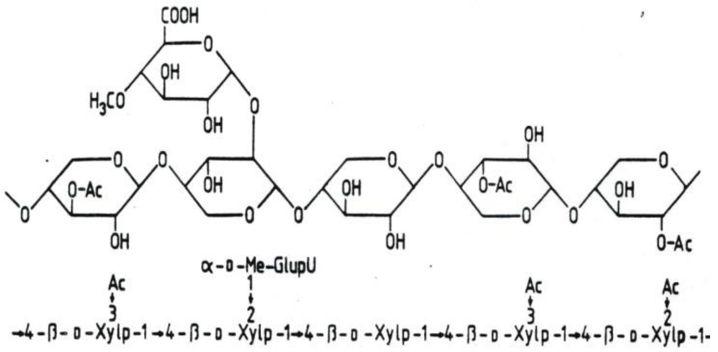


Figure 1.3: Hardwood Xylan[1-5]

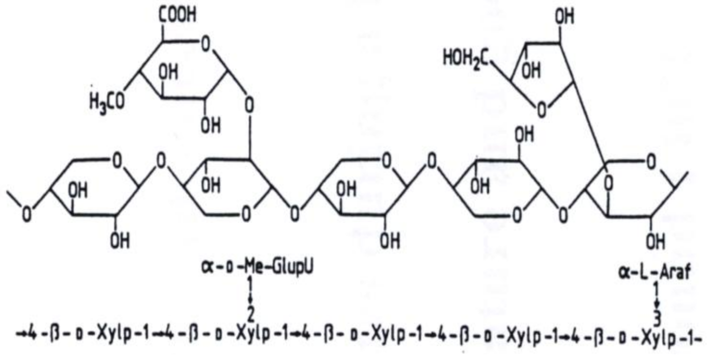


Figure 1.4: Softwood Xylan[1-5]

1.1.3 Lignin

Lignin is a highly branched and three dimensional polymers. Lignin is the cementing material between cells and thus gives mechanical strength to wood. It is composed of three phenyl-propane unit types (figure 1.5) linked by carbon-carbon or ether linkages. Among all linkages, the β-O-4 structure is the most abundant in native lignin (wood lignin) (figure 1.6).

It is reported that bond between lignin and hemicelluloses does exist. Also there are indications of bonds between lignin and cellulose. Hemicelluloses are linked to lignin through ether and ester linkages.

Pulping and bleaching processes are focused to remove lignin from the wood to liberate cellulosic fibres. After kraft delignification, some lignin remains. It is called residual lignin. Its structure differs from that of native lignin. The residual lignin structure will be described in part 1.2.1 of this chapter.

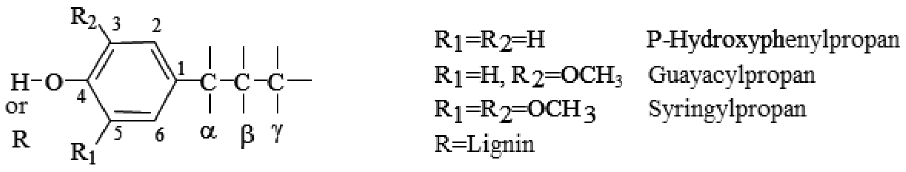


Figure 1.5: Lignin Phenyl-Propane Units[1]

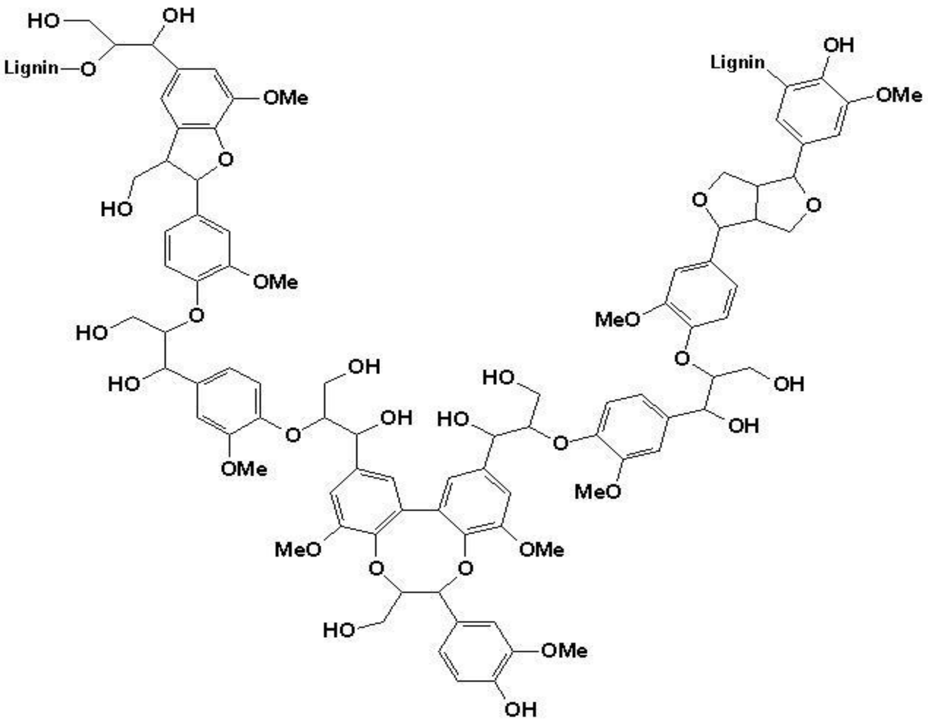


Figure 1.6: Native Lignin

1.1.4 Extractives

Apart from cellulose, hemicelluloses and lignin, a small quantity of resin acids, fatty acids, terpenoid compounds, and alcohols are present in the wood. There are collectively called as extractives[1-5].

1.2 Pulping Processes

Fibrous material is prepared in the pulping process. The raw materials are wood and annual plants. There is a wide range of pulping processes available depending upon the end - products. The processes are:

- Mechanical pulping (wood is fiberized mechanically)
- Chemi-mechanical, chemi-thermo mechanical, semi-chemical pulping (some chemistry is added)
- Chemical pulping (Kraft, acid sulfite, soda) (fiberization is obtained by lignin dissolution)

Kraft pulping is the dominant process worldwide for wood pulping. The acid sulfite chemical pulping is a marginal process used essentially for the production of pure cellulosic products for chemical or textile applications. This will be developed in part 1.5 dealing with market pure celluloses.

Kraft pulping is applicable for both hardwood and softwood. It produces pulp for paper applications by delignification while preserving mechanical strength properties of the cellulosic fibres. It also enables the recovery and reuse of the inorganic pulping chemicals such that a kraft mill is a nearly closed-cycle process with respect to inorganic chemicals, apart from those used in the bleaching process.

The cooking liquor, so called ‘white Liquor’, is composed of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). One of the main chemical reactions that underpin the kraft process is the scission of lignin ether bonds by several nucleoplilic reactions in which HO^- and SH^- are involved. Then the depolymerized lignin, soluble in the alkaline medium, is removed with the liquor.

Under the cooking conditions part of hemicelluloses are also solubilized in the strongly basic liquor after partial or total degradation. The solid pulp (about 50% by weight based on the dry wood chips) is collected and washed. At this point the pulp is quite brown and thus requires subsequent bleaching operations which will be presented later in this chapter. After kraft cooking, the resulting liquor known as black liquor (so called because of its colour), contains lignin fragments, degraded carbohydrates from the breakdown of hemicelluloses, extractives, and inorganic salts derived from the pulping chemicals. This black liquor is sent to the chemical recovery plant to regenerate the white liquor[6-13].

1.2.1 Reaction of Lignin in Kraft Pulping

After delignification, the unbleached kraft pulp contains less than 5% residual lignin. In kraft pulping, lignin dissolution follows three distinct phases. During the initial step (up to 140°C), delignification is rather low as lignin content is reduced by only 10 to 20% compared to about 40% of hemicelluloses removal. The second phase, so called bulk delignification, occurs above 140°C and removes almost 80% of lignin. The final phase is much slower and carbohydrate degradation becomes predominant.

As α- and β-aryl ether linkages are the dominant bonding mode in lignin (70% of the total inter-unit linkages in hardwood lignin) the cleavage of these linkages contributes essentially to lignin degradation. Studies have shown that three types of cleavage reaction occur during kraft pulping. They lead to an increase of the amount of lignin phenolic hydroxyl groups. The three main reactions are summarized as follows:

The cleavage of α-aryl ether bonds (figure 1.7) in free phenolic structures and the elimination of α-substituent lead to the formation of a quinone methide structure, susceptible or not to other degradation reaction with sulphide ions (SH^-).

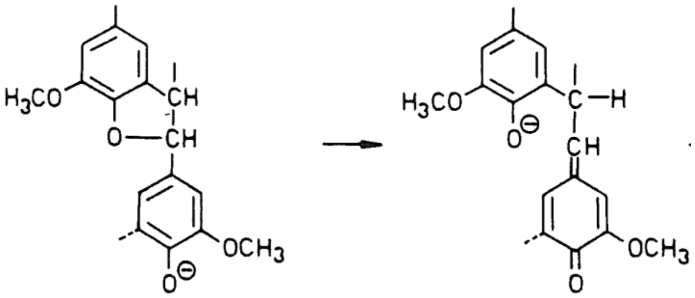


Figure 1.7: Example of Cleavage of α-Aryl Ether Bonds[14, 15]

β-aryl ether bonds in non phenolic structures are cleaved (figure 1.8) at higher temperature (above 140°C) during bulk delignification. This reaction leads to the liberation of new free phenolic structures which may undergo the previous reaction leading to soluble lignin fragments.

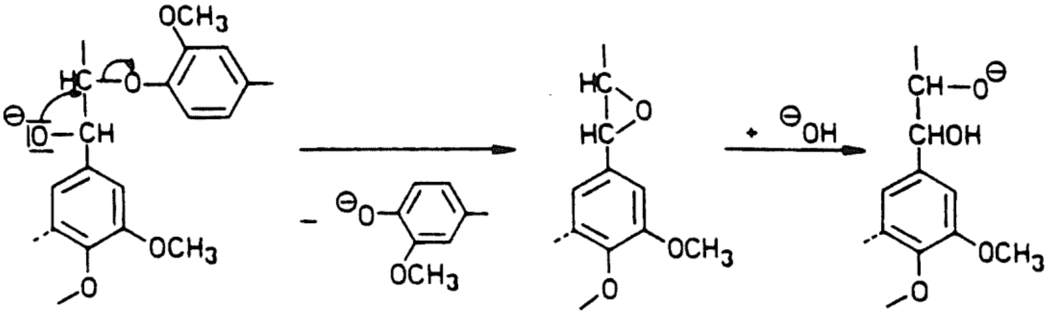


Figure 1.8: Cleavage of β -Aryl Ether Bonds[14]

The methoxyl groups of lignin are cleaved (figure 1.9) by hydrogen sulphide ions giving rise to the formation of methyl mercaptans which can further react with another methoxyl group to form dimethyl sulphide. These products are volatile and are responsible for the odour problem of kraft mills. A new free phenol group is formed, which improve lignin solubility. When this reaction takes place on a free phenol unit in lignin, then a catechol is formed. The latter is readily oxidized by air and converted into a coloured quinone.

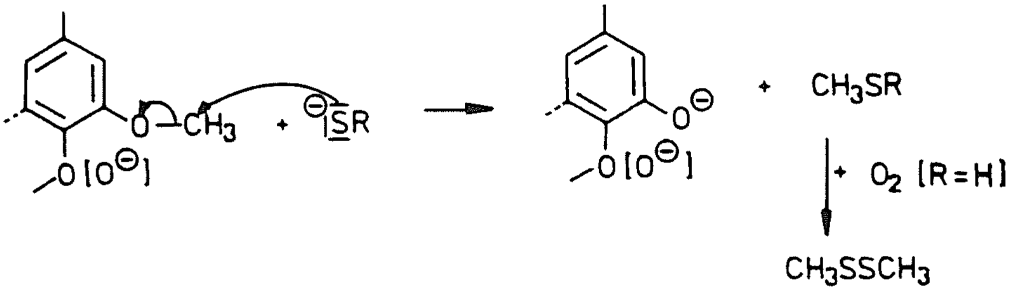


Figure 1.9: Cleavage of Methoxy Groups[16]

Among all reactions, some condensation reactions of lignin units take place simultaneously (figure 1.10) slowing down the lignin degradation. During the kraft pulping process, various carbanions (resonance forms of phenolates anions) are formed. They compete with the reactive nucleophilic anions (SH^-, OH^-) and may eventually fix on the quinone methide intermediates. This leads to the formation of new C-C bonds, generally at the C5 position of the phenolic unit giving rise to a α-5 linkage.

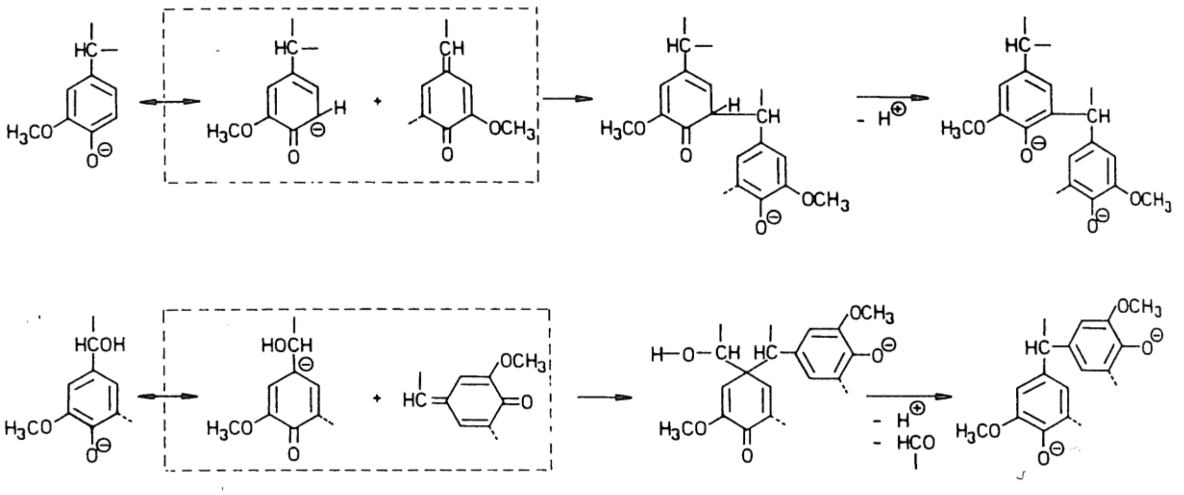


Figure 1.10: Condensation Reactions in Lignin[16]

1.2.2 Reaction of Cellulose and Hemicelluloses in Kraft Pulping

During kraft pulping, in parallel of delignification, carbohydrates are also degraded. Due to its high crystalline structure, high polymerisation degree and strong tendency of intra- and intermolecular hydrogen bonding, cellulose is less reactive than hemicelluloses. Approximately 60 %-70% of the hemicelluloses, depending on the wood species, and 10% of the cellulose are dissolved during kraft pulping. Unbleached kraft pulp contains 65 to 75% cellulose and 20 to 30% hemicelluloses.

Carbohydrate degradation reactions are of two types, (i) peeling reaction and (ii) alkaline hydrolysis[8].

Despite its high stability, cellulose is subject in a limited extent to peeling during kraft pulping (figure 1.11). The reducing hemiacetal end group can take a non-cyclic aldehyde form in alkaline medium. In these conditions cellulose end groups undergo the peeling reaction due to the cleavage of the glucosidic bond at C_4 –position. Around 60 glucose units are removed till a competing reaction takes place and stops the peeling. The hydroxyl group is eliminated at C_3 position of the enol forming a diketone. This last product undergoes a rearrangement leading to the formation of the metasaccharinic acid end group. Since the chain no longer has reducing end group, the peeling reaction is finally halted (figure 1.12).

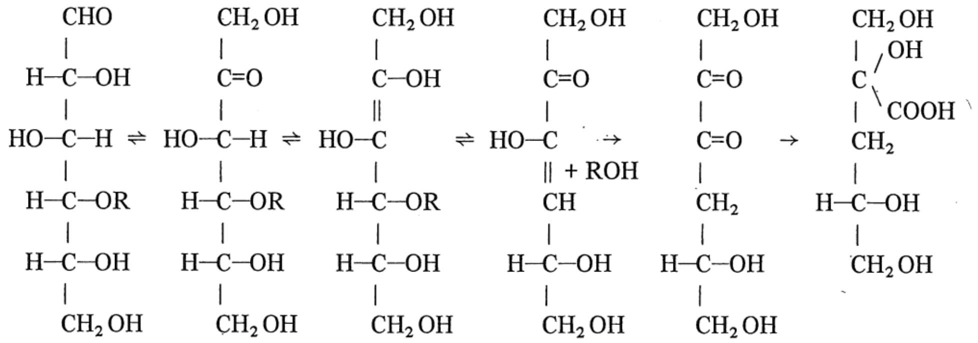


Figure 1.11: Peeling Reactions in Cellulose[17, 18]

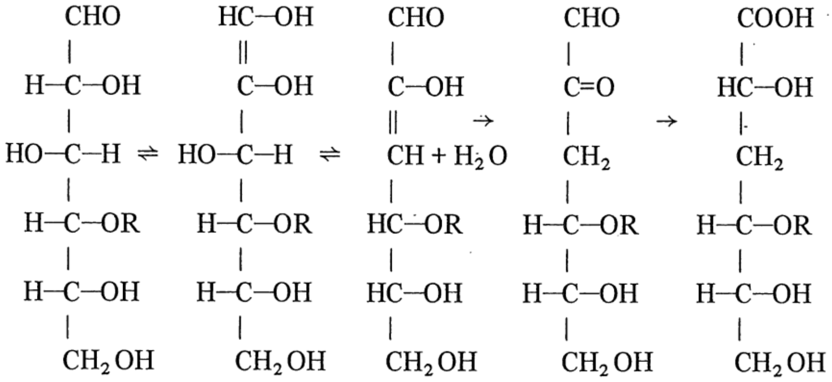


Figure 1.12: Stopping Reactions after Peeling Reaction[19, 20]

Cellulose degree of polymerisation is not significantly affected by the peeling reaction since only around 60 glucose units are removed compared to the 10 000 original value in wood. As the average depolymerisation degree of hemicelluloses is low (50 to 200), the peeling reaction causes substantial hemicelluloses dissolution.

The second reaction on carbohydrates is the alkaline hydrolysis. This reaction takes place at higher temperature (150 °C or higher) and randomly cleaves glucosidic bonds generating new reducing end groups which are sensitive to the peeling reaction previously described. The mechanism is presented in figure 1.13.

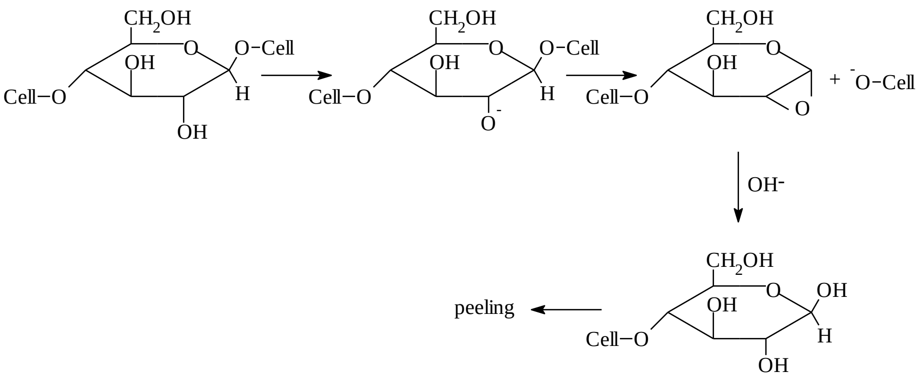
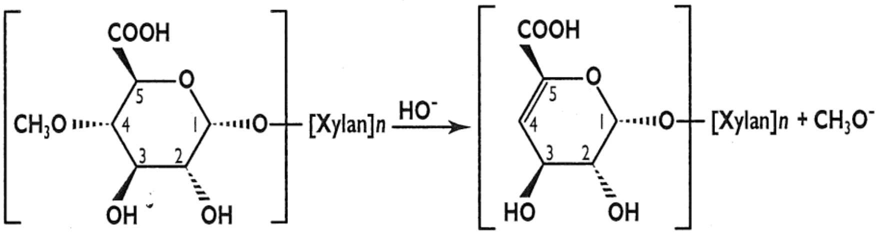


Figure 1.13: Alkaline Hydrolysis of Cellulose[17]

The alkaline hydrolysis of glycosidic bonds strongly affected the polymerisation degree of carbohydrates. During cooking, the cellulose polymerisation degree decreases from 10 000 to around 2 000 and hemicelluloses which initially have DP values of 50 to 200 can be completely degraded. However some hemicelluloses are resistant during cooking. This is the case of xylans, present in a great quantity in hardwood. This will be developed in the next section.

1.2.3 Formation of Hexeneuronic Acid (HexA)

The major hemicelluloses present in hardwood are an acetylated glucuronoxylan (*O*-acetyl-(4-*O*-methylglucurono) xylan). Under the alkaline conditions used in kraft cooking the acetyl groups originally present in the hardwood xylans are rapidly cleaved producing acetic acid together with deacetylated xylans. Furthermore the major part of the 4-*O*-methylglucuronic acid side-groups linked to the xylan chains undergo a β-elimination reaction splitting off methanol and forming hexenuronic acid residues on the xylan backbone according to figure 1.14.



(4-O-methylglucuronic acid) (Hexeneuronic Acid)

Figure1.14: Formation of Hexeneuronic Acid[21, 22]

Hexeneuronic acid groups (HexA) consume the electrophilic bleaching agents (figure 1.15) which operate in acidic conditions and contribute to potassium permanganate consumption during kappa number measurement. 8-12 μmoles of hexenuronic acid per gram of pulp approximately contribute to 1 kappa number[23].

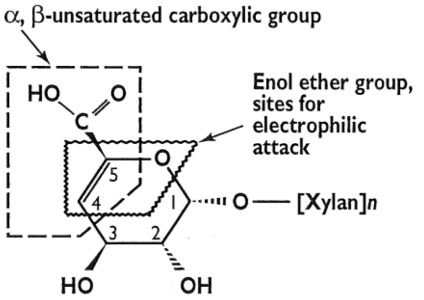


Figure1.15: Functionality of Hexeneuronic Acid Groups attached to Xylan[21, 22]

Hexeneuronic acids are partly removed from pulps before bleaching by an acidic treatment around pH 3-4 at 85-115 °C for several hours. Under these conditions the enol-ether groups in hexeneuronic acid are labile and form furan derivatives (figure 1.16).

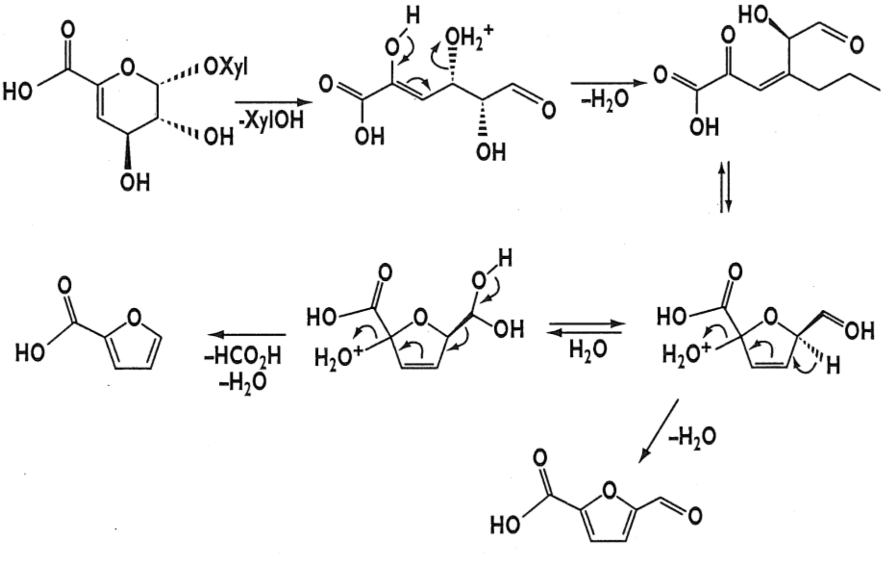


Figure1.16: Acid Degradation of Hexeneuronic Acid[22]

1.2.4 Reaction of Extractives in Kraft Pulping

Wood initially contains less than 5% extractives. After kraft pulping, less than 0.5% extractives are present in pulp since most of them are dissolved in the alkaline cooking liquor[8].

1.3 Oxygen Delignification

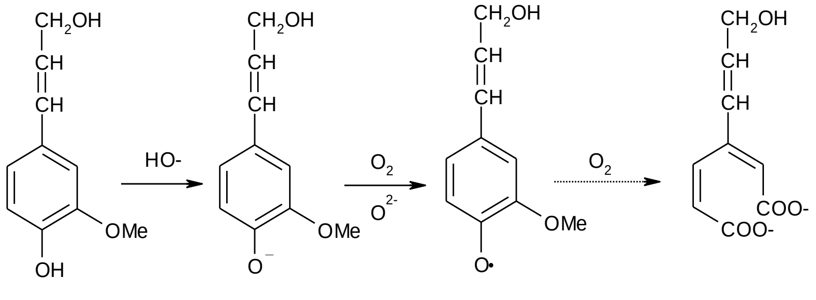
Since 3-5% lignin is still present in pulp after kraft cooking it has become common to continue the delignification process by the use of an oxygen delignification stage. Oxygen (O_2) is an environmentally friendly oxidizing agent which degrades lignin under alkaline conditions. The effluent from oxygen bleaching does not contain chloride ions and can be sent to the pulp mill recovery boiler meaning that no effluent is generated.

Oxygen delignification is carried out in alkaline medium using, at industrial scale, oxidized white liquor from the kraft mill recovery process. Due to its low solubility in water, oxygen is used under pressure (6-8 bars), in excess and at high temperature, between 90 to 120°C. The retention time in the bleaching tower may vary from 30 to 60 minutes. Oxygen delignification can be operated at medium or high consistency (10 to 30%). Magnesium sulphate is added to the pulp to protect cellulose from degradation. Oxygen bleaching delignifies unbleached kraft pulp up to 30 to 50% [24- 27].

Due to the number of reactive intermediate species formed during the reaction of oxygen with a substrate, the resulting pattern is complex. The oxidation that occurs includes a series of radical chain reactions involving both lignin and carbohydrates. As a result cellulose is also partly depolymerised.

1.3.1 Reaction of Lignin in Oxygen Delignification

In oxygen delignification free phenolic groups in residual lignin are first ionized by the alkaline medium. The initial step of the oxidation reaction of lignin is the formation of a phenoxy radical through electron transfer from a phenoxide ion to molecular oxygen. The phenoxy radical is finally oxidized into soluble muconic acid derivatives as shown in figure 1.17.



(Muconic acid derivatives)

Figure 1.17: Oxygen Reaction with Lignin in Alkaline Medium[28-30]

1.3.2 Reaction of Carbohydrates in Oxygen Delignification

Oxygen also degrades carbohydrate in the delignification process either by the cleavage of glucosidic bonds at any point along the polysaccharide chain or by the peeling reaction by which end group units are successively removed. Cleavage of glucosidic linkages is promoted by the presence of oxygen based radicals. Their origin is due to the formation and decomposition of peroxides when oxygen reacts with lignin. Among them the hydroxyl radical (OH◦) is the most dangerous for cellulose. Carbohydrate C_2 sites may be oxidized into carbonyl groups by hydroxyl radicals ($OH^\bullet$). This carbonyl group facilitates the cleavage of an alkali liable glucosidic bond at C_4 by β-alkoxy-elimination reaction and subsequent formation a of new reducing end group (Figure 1.18). This causes reduction in DP and affects pulp and paper strength properties. This explains why delignification is limited to the removal of half of the residual lignin entering the oxygen stage.

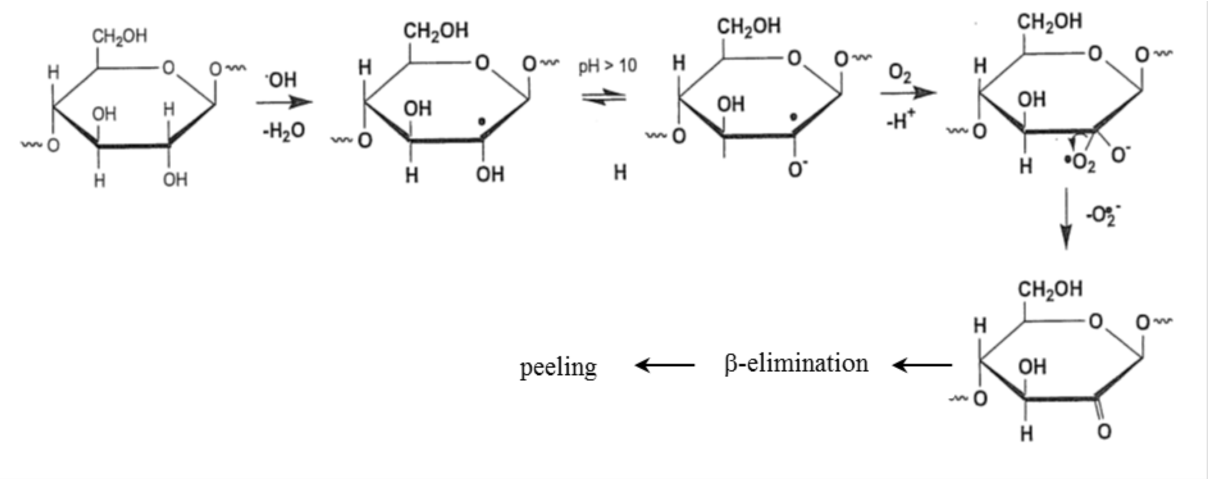


Figure 1.18: Oxidative Cleavage of Carbohydrates by Hydroxyl Radicals[28-32]

1.4 Total Chlorine Free (TCF) Bleaching of Pulps

Pulp mills release organo-chlorine compounds (AOX) in their effluent. Whether or not the level of AOX is susceptible to cause problems to the environment is not known. However the pulp industry is making efforts to minimize the formation of AOX. In that respect the exclusive use of oxygen, ozone, hydrogen peroxides and peracids as replacements for the chlorine containing bleaching reagents (chlorine, chlorine dioxide, and hypochlorites) is a radical solution. This process is called Total Chlorine Free (TCF) bleaching[33].

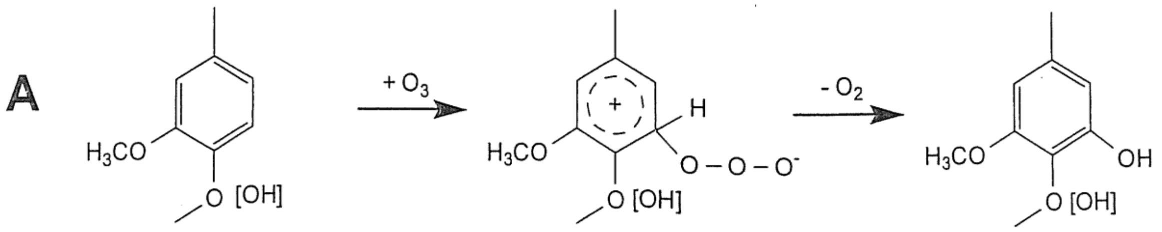
1.4.1 Ozone Bleaching

Among the oxygen based bleaching chemicals, ozone is the most powerful oxidizing agent able to react with most of the organic compounds. Due to its ability to delignify and enhance the brightness of pulps, it represents a promising chemical as replacement for chlorine based reagents. Ozone bleaching effluents are free from organo-chlorine compounds and can be recirculated to the chemical recovery system of the pulp mill.

Ozone (Z stage) is generally applied after oxygen delignification. The conditions are mild since lignin is already active at room temperature. The pH must be acidic (pH 2.5) to get the best result. It is observed that cellulose is partly oxidized during the treatment. Ozone can also be applied as final bleaching stage (Z stage), when addition of chlorine dioxide in excess (ClO_2) does not improve brightness in an efficient way. In these conditions ozone is able to degrade the last chromophores. A neutral pH can then be applied, provided that the charge of ozone is maintained at a low level (1 to 2 kg per ton of pulp), so that cellulose is not affected [34-40].

1.4.1. A Reaction of Ozone with Lignin

The main reaction of ozone on the lignin aromatic groups is an electrophilic attack as shown in figure 1.19.



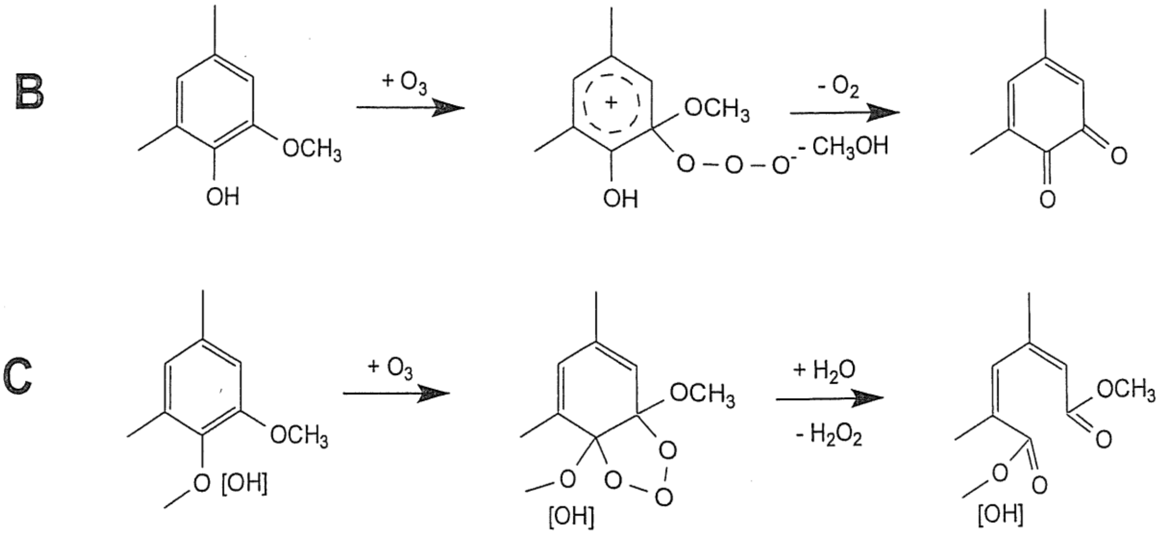


Figure 1.19: Aromatic Lignin Reactions during Ozone Bleaching[41]

Ozone reaction with the aromatic ring may result in hydroxylation and O_2 release (Route A) or demethoxylation and methanol production (Route B). However the most probable reaction would be the opening of the aromatic ring creating muconic acid derivatives which are liable to further degradation (Route C)

Ozone reacts with olefinic double bonds and forms ozonides (Figure 1.20) which are highly unstable and readily decompose in two ways, one to give aldehydes and/or ketones and H_2O_2 (Route D) while the other leads to epoxide (Route E) which could rearrange to a carboxylic acid.

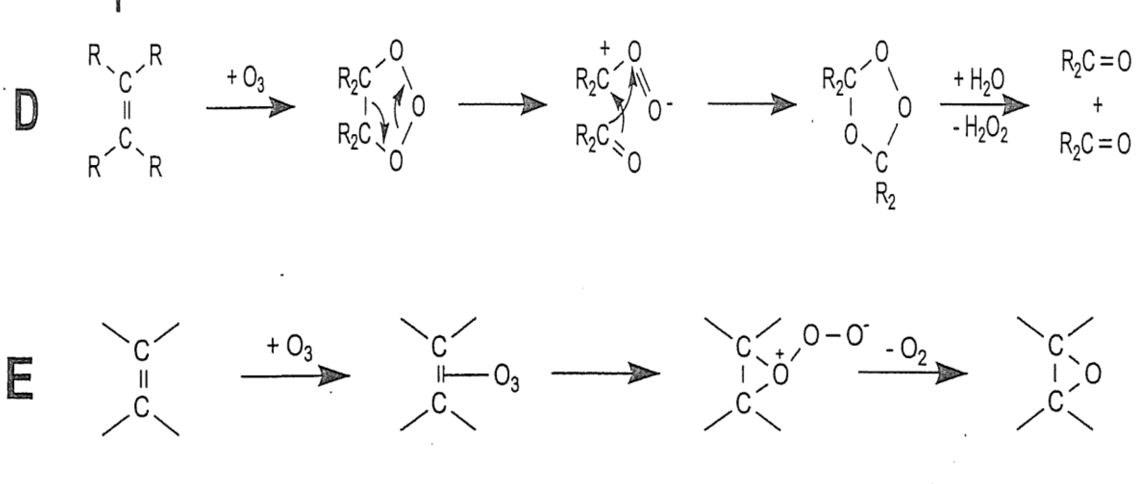


Figure 1.20: Reaction of Ozone with Olefinic Groups[41, 42]

The reactions of ozone on lignin introduce carboxylic acid groups in the molecules. Oxidized lignin is much more hydrophilic. However extensive dissolution of the oxidized lignin requires a subsequent alkaline extraction stage. Condensed phenolic structures are destroyed leading to pulp brightness improvement[41, 42].

1.4.1. B. Reaction of Ozone with Carbohydrates

Ozone is less selective toward lignin than chlorine dioxide and low charges are required to prevent pulp strength loss. The poor selectivity of ozone is due to the presence of highly reactive and non-selective hydroxyl and superoxide radicals originated from ozone decomposition catalysed by transition metals (Fe^{++}/Fe^{+++}, Cu^{++}) or from the reaction of ozone on lignin[34-37].

Ozone reacts with carbohydrates and degrades them. The main factors influencing the extent of the degradation have been extensively studied. Among them the quantity of lignin seems to play a role. However predicting the result is difficult since lignin would have a dual role. On the one hand it would generate radicals but on the other it would act as a protector by reacting with these radicals. It is generally admitted that the worst results are obtained when ozone is used late in the bleaching sequence, when the lignin content is low [38, 43- 45].

1.4.2 Hydrogen Peroxide Bleaching

Hydrogen peroxide (H_2O_2) is an environment friendly bleaching agent widely applied for pulp (mechanical pulp, recycled waste paper pulp and chemical pulp) bleaching. Peroxide can be used as bleaching agent with temperature 50- 70 °C, but also as a delignifying agent at temperature more than 80°C. Operating consistency is 10-20% and time lies from 2 hours to 4 hours. Generally it is supplied to the mill as an aqueous solution of 35% concentration by mass [46-50].

Under alkaline conditions, hydrogen peroxide reacts with the hydroxyl ion (HO^-) to yield the perhydroxyl anion (HOO^-).

$$HOOH + HO^- \leftrightarrow HOO^- + H_2O \qquad pKa=11.6 \text{ at } 25°C$$

The decomposition products of hydrogen peroxide in alkaline medium are thought to cause the oxidation of lignin structures which leads to the introduction of hydrophilic carboxyl groups, the cleavage of some unit bonds and the dissolution of lignin. Alkaline hydrogen peroxide decomposes to hydroxyl radical (OH°), and superoxide anions ($°OO^-$). These radicals react with lignin and carbohydrates causing delignification and cellulose depolymerisation[51-56] as well. Decomposition of hydrogen peroxide is catalysed by transition metals present in pulp.

$$M^{n+} + HOOH \rightarrow M^{(n+1)+} + HO^{\circ} + HO^{-}$$
$$M^{(n+1)+} + HOO^{-} + HO^{-} \rightarrow M^{n+} + O_2^{\circ -} + H_2O$$
$$M^{(n+1)+} + O_2^{\circ -} \rightarrow O_2 + M^{n+}$$
$$O_2^{\circ -} + HO^{\circ} \rightarrow O_2 + HO^{-}$$

In conventional bleaching sequence, hydrogen peroxide decomposition is controlled by the transition metal ions removal from the pulp by an acid washing stage or by chelation.

As already discussed, hydrogen peroxide reactions on lignin involve the perhydroxyl anion (HOO^{-}), which is a strong nucleophilic species, and radicals issued from the hydrogen peroxide decomposition. The perhydroxyl anion mainly reacts with carbonyl type lignin chromophores for bleaching whereas radicals play a major role in delignification.

1.4.2. A. Reactions of Perhydroxyl Anions with Lignin Chromophores

The perhydroxyl anion reacts on lignin through nucleophilic attack. Sites of nucleophilic attack in lignin are shown in figure 1.21. O-quinone groups are not mentioned here but are important targets $C^{\delta+}= O$ too.

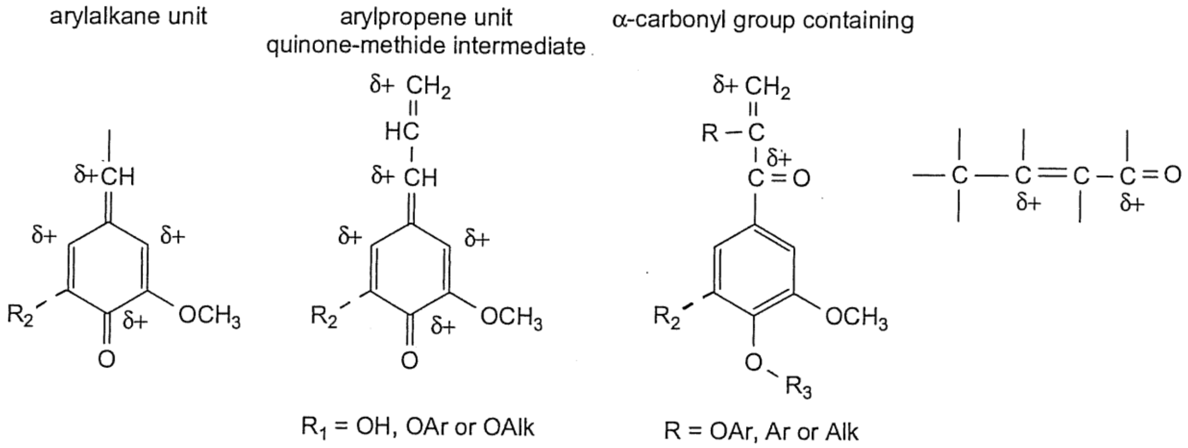


Figure 1.21: Sites of Nucleophilic (δ+) Attack in Lignin[57-59]

Examples of nucleophilic attacks on lignin structures are given in figure 1.9. Perhydroxyl anion (HOO^-) reacts with quinonic structures (Figure 1.22).

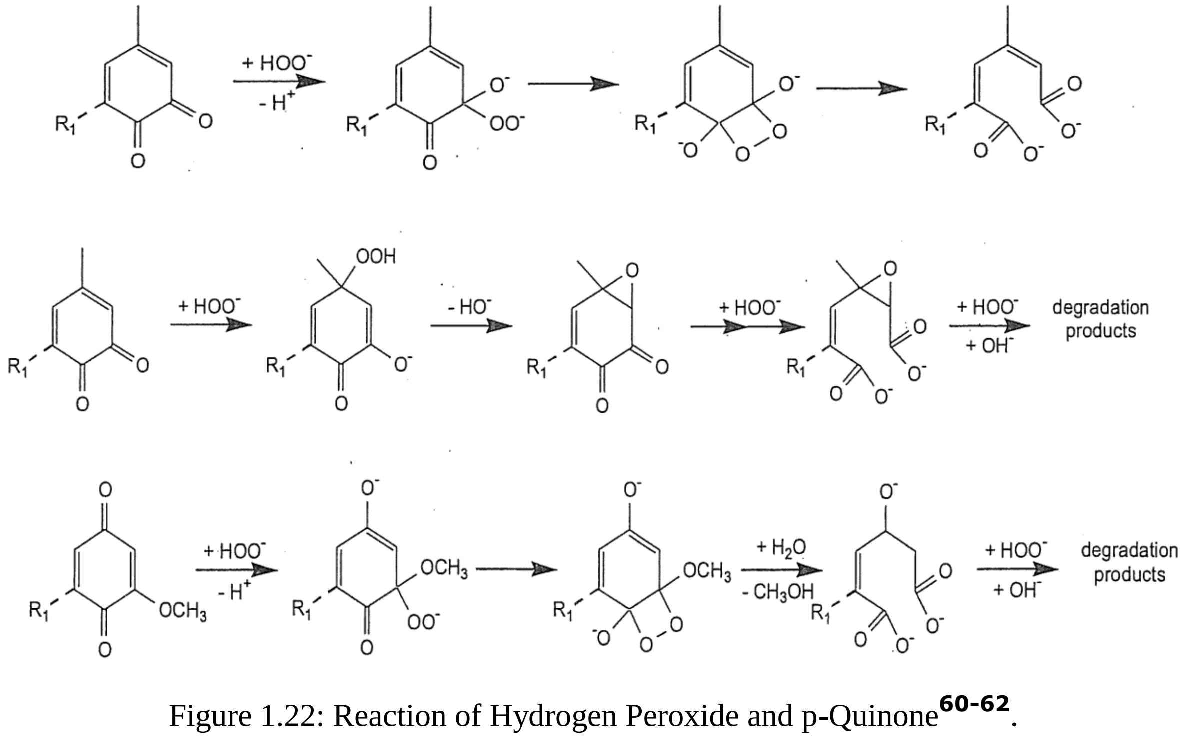


Figure 1.22: Reaction of Hydrogen Peroxide and p-Quinone[60-62].

The reaction of the perhydroxyl anion on ortho- and para-quinonic structures leads to the cleavage of the ring and to the formation of dicarboxylic acid. All these reactions improve the pulp brightness since the quinonic type chromophores are degraded.

Quinone-methide structures are also converted into para-quinones. This product may be degraded further in acids (figure 1.23)

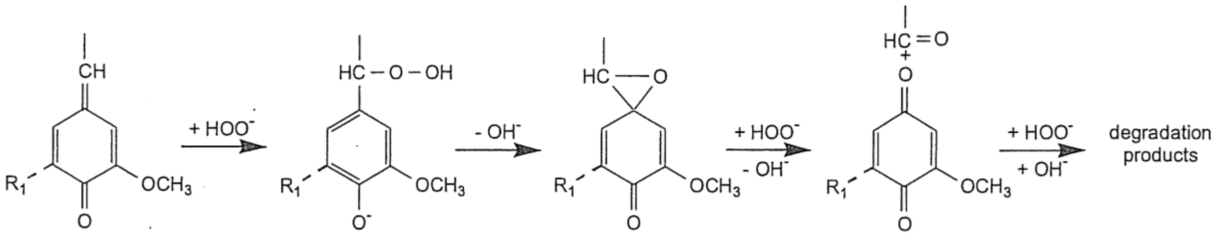


Figure 1.23: Reaction of Perhydroxyl Anion on Quinone-Methide Structures[60-62]

Side chain with enone structures is also attacked by the perhydroxyl anion (HOO^-) and forms oxirane intermediates before leading to the cleavage of Cα-Cβ bond. The reduction of the conjugated system yields to news aldehydes or carboxylic acids (figure 1.24).

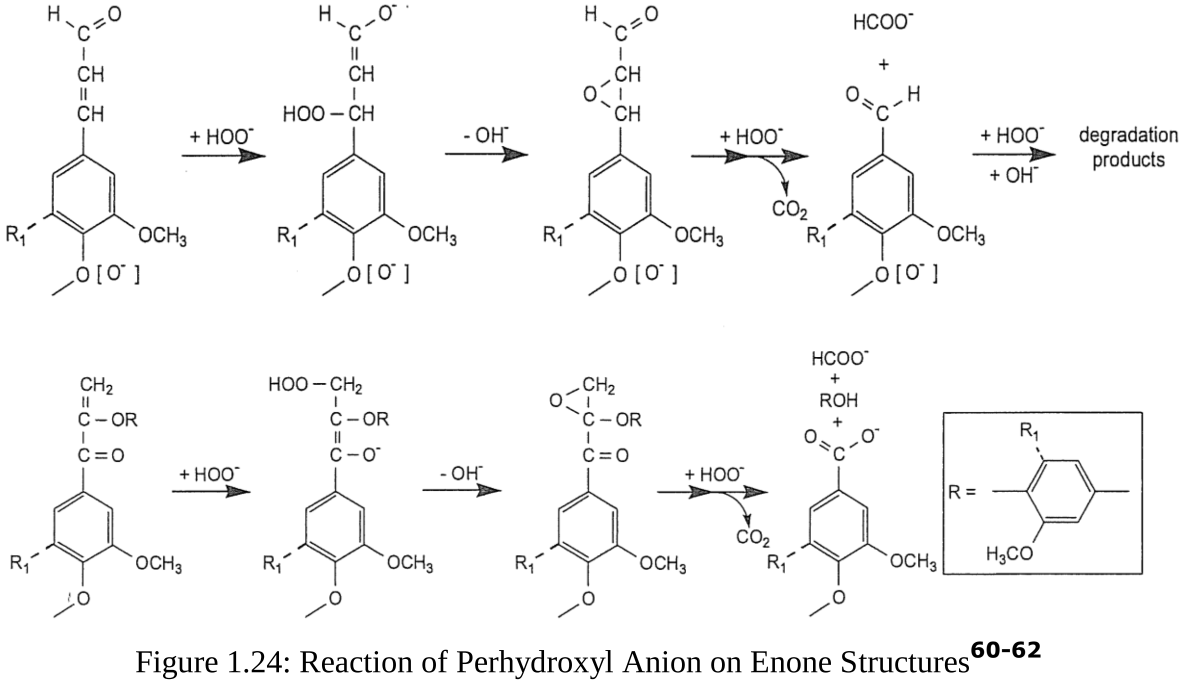


Figure 1.24: Reaction of Perhydroxyl Anion on Enone Structures[60-62]

All these reaction contribute to the increase in brightness. In parallel to chromophores degradation, new ones may be generated during the alkaline hydrogen peroxide bleaching. The following reaction is one example (Figure 1.25).

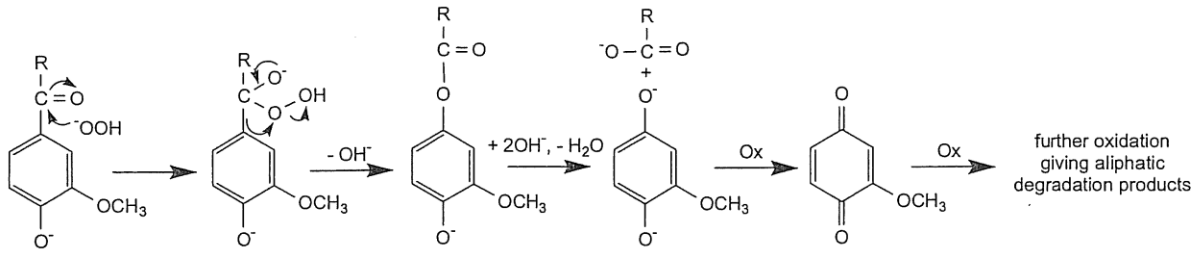


Figure 1.25: Quinone Formation during Alkaline Peroxide Bleaching Starting from a Phenylpropanone[60-62]

Phenyl propanone also follows nucleophilic addition path leading to the formation of hydroperoxide which rearranges into ester. This ester can be cleaved into acid and p-hydroquinone. The latter is oxidised into o-quinone which in turn may be degraded as shown in figure 1.22.

1.4.2. B. Reactions of Radicals with Lignin

Products issued from hydrogen peroxide decomposition in alkaline medium such as hydroxyl radicals are responsible for lignin oxidation and lead to the formation of hydrophilic carboxyl groups, the cleavage of phenylpropane unit linkages and the dissolution of residual lignin. H_2O_2 and O_2 delignification mechanisms have similarities since both bleaching processes involve the same oxygenated species. Reactions of the hydroxyl radicals on lignin are given in figure 1.26.

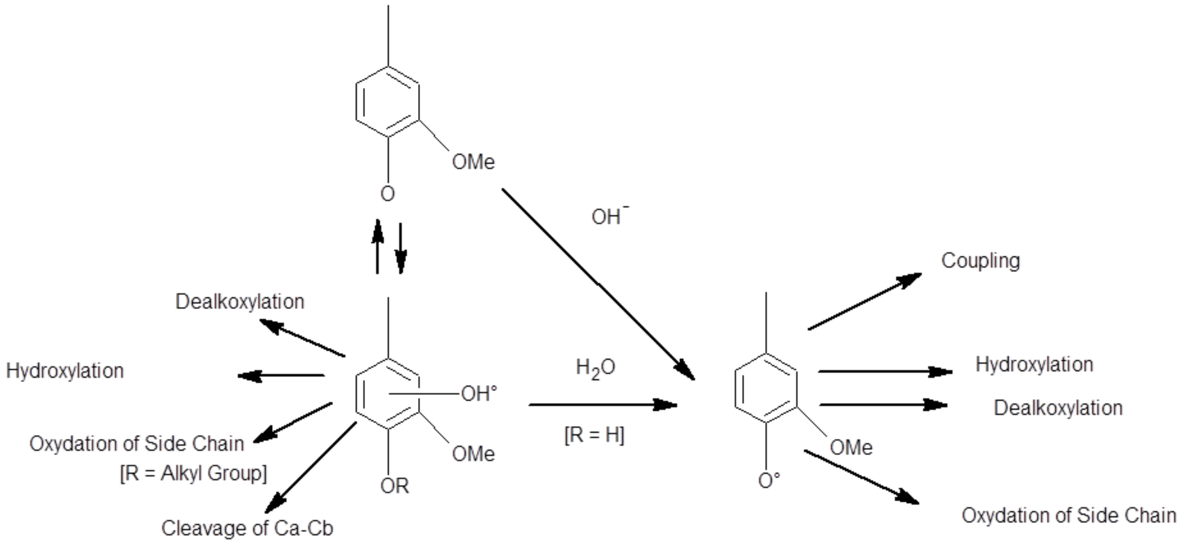


Figure 1.26: Hydroxyl Radical Reaction on Lignin[63]

In the case of phenolic structures (R=H), the hydroxyl radical reacts with lignin to form a phenoxyl radical. This last compound may undergo the reactions listed in the right side of figure 1.29. In the case of non-phenolic structures (R=alkyl), the hydroxyl radical is at the origin of hydroxylation and dealkoxylation reactions, aliphatic chain oxidation or $C\alpha-C\beta$ linkage cleavage (reaction listed in the left side of figure 1.29). The action of hydroxyl radicals is reinforced by that of superoxide radicals ($O_2^{\circ-}$) and oxygen originated from hydrogen peroxide decomposition. These compounds lead to the formation of instable hydroperoxides and to the phenolic unit opening.

1.4.2. C. Peroxide Reaction with Cellulose

Hydroxyl radicals ($OH^{\bullet}$) are the responsible species for cellulose degradation. They form carbonyl groups (which promote β-elimination as already seen) and may also cleave the glycosidic linkages directly. Reaction continues by several ways since then new reducing end groups are created [64-67].

1.4.3 Hydrogen Peroxide Activators

Hydrogen peroxide (H_2O_2) is a promising bleaching reagent for total chlorine free (TCF) bleaching[68]. But as a delignifying agent, its efficiency is far behind that of chlorine dioxide (ClO_2) and oxygen (O_2). To increase peroxide reactivity, harsher conditions can be applied (higher temperature and chemical charges) which do increase delignification but also causes cellulose degradation[68-70]. Using appropriate pre-treatments and activators has been considered as a better approach.

1.4.4. A. Pre-Treatment of Pulps Prior to Bleaching

Different types of pulp pre-treatments are proposed. Transition metals can cause peroxide decomposition and should be removed prior to peroxide bleaching. Acid and chelation pre-treatments (with EDTA or DTPA) generally increase the effect of peroxide[71-73]. Other types of pulp pre-treatment for kraft pulps have been proposed. They include the use of NO_2 or Cl_2 which would form new free phenol groups on lignin (by demethylation) [74-76].

1.4.4. B. Transition Metal Centred Activators

It was found that some transition metals can be used as catalysts for peroxide delignification in acidic medium. Eckert[77] reported on the effect tungsten, molybdenum, chromium, osmium, and selenium species in acidic hydrogen peroxide delignification. Better delignification effect would be due to the formation of transition metal peroxo-complexes which are stronger oxidants as compared to peroxide. Molybdate metal oxides have been more particularly investigated[78]. Their catalytic effect is due to the formation of reactive diperoxo complexes with peroxide in acidic conditions[79]. Tungstate, molybdate and vanadate-based polyoxometalates have also been identified as peroxide activators for delignification in acidic conditions[80, 81].

Other metal complex like the binuclear manganese complex has been proposed [82]. Other ones are iron (III) complexes involving macrocyclic tetraamides[83]. These complexes catalytically active hydrogen peroxide oxidation reactions and promote delignification[83].

1.4.4. C. Enzyme Activators

Bio-bleaching with peroxidases (MnP) has been seen as a promising approach since it may offer some environmental advantages. Manganese peroxidase activity is Mn^{2+} dependent. Mn^{2+} is oxidized to Mn^{3+} which carries out the lignin oxidation at the phenolic subunits[84]. But in the presence of glutathione (GSH), MnP would oxidize non-phenolic lignin model compounds[85]. Some condensation reactions would also occur which reduce the interest of the process.

1.4.4. D. Nitrogen Centred Activators

Peroxide activation in alkaline conditions is possible Different types of nitrogen centred activators have shown some promise. Among them cyanamide and its dimmer, dicyandiamide have received a lot of attention in alkaline peroxide bleaching[86, 87]. They would add to the perhydroxyl anion to give the active species. Another activator is tetra acetyl ethylene diamine (TAED). It generates peracetic acid on interaction with peroxide which actually plays the active role in bleaching[88].

Nitrogen-containing heterocycles are so far the preferred ligands for investigation under alkaline conditions. They have high complex formation constants in aqueous solutions and they form active oxidation catalysts with transition metals e.g., Cu, Co and Fe[89]. These complexes are effective in electron-proton transfer, which makes them oxidizing agents for delignification in the presence of hydrogen peroxide and oxygen. Several complexes e.g., polypyridines etc. have already been tested in that purpose. However most of the work has been done on oxygen delignification and much less on peroxide delignification.

1.4.4. E. Poly-Pyridine Complexes

Polypyridines complexes are considered as very promising for the catalysis of oxygen and hydrogen peroxide delignification. Bipyridine, phenanthroline, terpyridine (Figure 1.27) are among some poly-pyridine compounds which form complexes with metal ions.

2, 2’-bipyridine

4,4'-dimethyl-2,2'-bipyridine

1, 10 - Phenanthroline

2, 2’, 6’, 2"-Terpyridine

Figure 1.27: Bipyridine, Phenanthroline, Terpyridine ligands

Copper complexes of poly-pyridine are known to activate hydrogen peroxide (H_2O_2) and oxygen (O_2) delignifion under alkaline conditions[90]. Electron transfer takes place between Cu (I) and Cu (II). The complex activity is dependent on the pH and the ligand and varies with the nature of the substituents. For example, a Cu-bipyridine complex with electron donating groups (like methyl and methoxyl) located at 4, 4’ and 5, 5’- positions is a more active complexes[91].

Among all the poly-pyridine ligands, phenanthroline is the most promising

1.4.4. F. Phenanthroline

Phenanthroline is a heterocyclic organic compound. It is a bidentate ligand which forms strong complexes with most metal ions. In terms of coordination properties, phenanthroline is similar to 2, 2’-bipyridine.

Although phenanthroline has essentially been proposed as catalyst for oxygen delignification, [92-95] hydrogen peroxide delignifications has also been mentioned as possible application. pH is playing an important role for the catalytic activity of phenantholine. pH higher than 12 are required (pKa H_2O_2= 11.6 at 25^0C). High pH would also contribute to the swelling of pulp, which increases reagent transfer. On addition of 2% of peroxide and 0.15% of phenanthroline, a reduction of 50% in kappa number[96] can be obtained. It was also found that the $Cu^{(II)}(Phen)(OH)_2$ is the active complex for delignification[97]. Effect of methyl substituents has been reviewed. These groups facilitate the oxidation rate of Cu (I) to Cu (II) [98, 99]. However steric effects have to be taken into account in assessing the activity of the complex[100].

Most of the studies have been devoted to the effect of copper-phenanthroline complexes in oxygen delignification. A global reaction mechanism has been given for the oxidation of with veratryl alcohol[97];

$2[Cu^{(II)}(phen)(OH)_2] + RCH_2OH \rightarrow 2[Cu^{(I)}(phen)(OH)] + RCHO + 2H_2O$ …… …(1)

$2[Cu^{(I)}(phen)(OH)] + O_2 + 2H_2O \rightarrow 2[Cu^{(II)}(phen)(OH)] + H_2O_2 + 2\,OH^-$ .... (2)

$2[Cu^{(II)}(phen)(OH)] + 2\,OH^- \rightarrow 2[Cu^{(II)}(phen)(OH)_2]$ ……………………… (3)

Over all, $RCH_2OH \rightarrow RCHO + H_2O_2$ .... (4)

Again it is claimed that the key effect of this type of complex is the oxidation of alcohol group into carbonyl group. In lignin the OH at the α-position on the side chain of the phenyl-propane units would be the main target. Bleaching tests with oxygen or hydrogen peroxide activated with copper phenanthroline complexes have confirmed that delignification is improved. It has been proposed that the formation of α carbonyl groups in lignin would favour the alkaline cleavage of the β-O-4 linkages, thereby making the lignin more soluble[97].

The major drawback of this process is that oxidation of carbohydrates seems to be also catalysed which is reflected in the dramatic DP loss of the pulp. The origin of the degradation could be the oxidation of hydroxyl groups to carbonyl groups in a similar way to what occurs on lignin. It is known that such oxidized cellulose is very sensitive to alkaline medium. It is also possible that radicals are generated during the course of the reactions.

If the DP loss is problematic for the production of paper pulp, the situation may be different in the objective of producing purer cellulose for other purposes like textile of chemical usages. These latter applications will be the focus of this thesis work.

1.5 Pure Cellulose

1.5.1 Introduction

Cellulosic pulp is the raw material for two main applications: (i) for paper and paper board production and (ii) cellulose derivatives. It is also denoted as paper grade and dissolving grade pulp respectively. Paper grade pulp accounts for almost 98% of total wood pulp production[101-104]. Wide varieties of unbleached and bleached mechanical and chemical pulps are used as raw material for paper and board products, where the fibres are mechanically modified to give a coherent sheet. Among all pulp production processes, kraft pulping is the dominant process worldwide for pulp and paper production. Kraft pulp is generally appreciated for its superior strength characteristics and can be used in almost all paper and board grades[6, 7].

Dissolving pulp refers to pulp of high cellulose content which is used to manufacture various cellulose-derived products such as regenerated fibres or films (e.g., viscose, lyocell), cellulose esters (acetates, propionates, butyrates, nitrates) for film- and fiber-forming materials and cellulose ethers (carboxymethyl-, ethyl-, methyl-celluloses) used as additive to bring particular properties to a material (gelling, thermoplastic, thickening effect (Figure 1.28). Despite the world production of dissolving pulp having been constantly reduced in the past, the latest forecast reveals a slight change in this trend. An increasing demand is predicted (Figure 1.29), mainly due to new installations of viscose plants manufacturing regenerated cellulose fibres in Asia.

END USES AND END PRODUCTS OF DISSOLVING PULPS

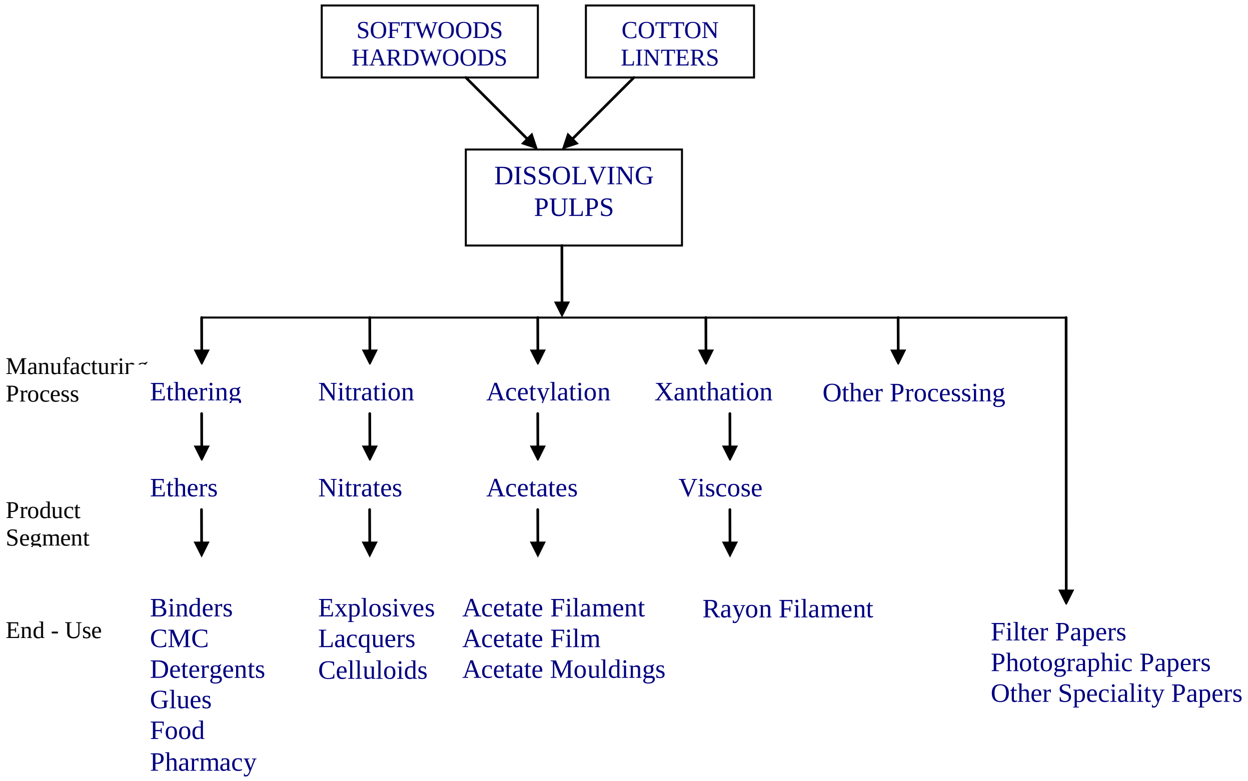


Figure 1.28: End-uses and End-products of Dissolving pulp[104]

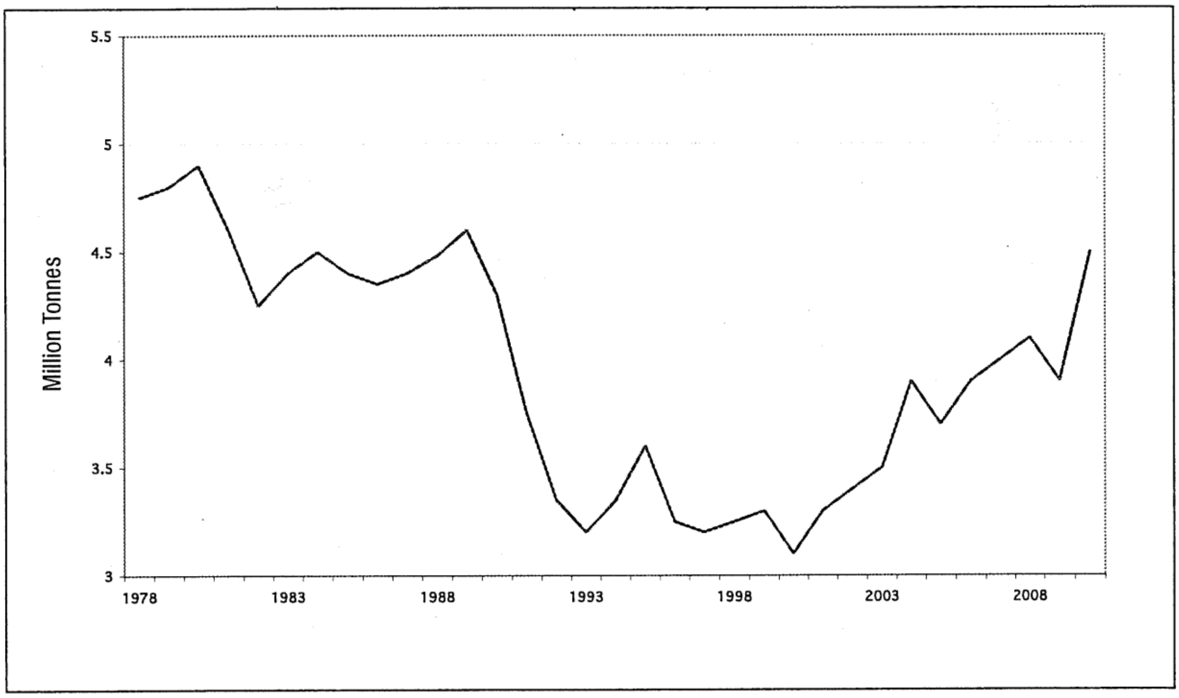


Figure1.29: Dissolving Wood Pulp Demand[104]

1.5.2 Dissolving Grade Pulp

Dissolving grade pulps represent a niche market compared to paper grade with a world production of 5.2 million tonnes in 2011. 85 to 88% of the total dissolving pulp is wood based, whereas the residual amount of dissolving pulps used cotton linters as raw material. Purified cotton linters represent the dissolving pulp of highest cellulose purity particularly used for manufacturing acetate plastics and high viscosity cellulose ethers[104]. However cotton linters are not as sustainable as wood since cotton growing is subjected to drought or other climatic events.

Wood based raw materials (softwoods and hardwoods) require drastic pulping and bleaching conditions to have high quality dissolving pulps. Wood dissolving pulps are produced by pre-hydrolysis kraft and acid sulfite processes. Acid sulfite process accounts for approximately 60-70% of the total dissolving pulp production[102].

1.5.3 Dissolving Pulp Production

1.5.3. A. Pre-hydrolysis Kraft (PHK) Process

The conventional alkaline kraft pulping process is unable to produce pure cellulose because hemicelluloses are resistant to alkaline pulping conditions. Indeed, even if hemicelluloses are depolymerised during alkaline peeling, part of xylans are adsorbed on the cellulose microfibrils during pulping leading to residual hemicelluloses in the pulp. To avoid xylan adsorption on fibres, wood may be pre-hydrolysed before kraft pulping to solubilize hemicelluloses [105-107]. This is the pre-hydrolysis kraft (PHK) process.

Pre-hydrolysis of wood is generally used to remove hemicelluloses by hydrolysis, in water at 160 –180 °C, in dilute sulfuric acid (0.3 – 0.5% H_2SO_4 at 120 – 140 °C), or in concentrated hydrochloric acid (20 – 30% Hcl at 40°C) [109-111]. At industrial scale wood pre-hydrolysis is carried out in water between 160 and 180 °C[107]. In these conditions acetyl groups are cleaved from the β-(1-4)-linked xylan backbone and the acetic acid released acts as a catalyst for the hydrolysis of glycosidic bonds. The resulting pH in the prehydrolyzate is in between 3 and 4. The addition of mineral acid will improve the xylan solubilisation but renders the subsequent alkaline delignification more difficult. To date, pre-hydrolysis is carried out without the addition of mineral acids with liquor to wood ratio of 3-4: 1. It produces huge amount of pre-hydrolyzates, which does not have at present any valorisation. A new process has been recently developed, the Visbatch process, using steam pre-hydrolysis. It limits the effective alkali consumption during the cooking operation and improves the purification efficiency.

Pre-hydrolysis is followed by kraft or soda-anthraquinone pulping to produce high purity dissolving pulps. Water pre-hydrolysis affects the pulping process by formation of highly reactive intermediates undergoing condensation products and organic acids. As a result, pitch compounds are formed and settle on chips surface, affecting chemical diffusion. To prevent extensive condensation reactions before the cooking operation, the prehydrozylate products are neutralized, extracted and displaced prior to cooking. After neutralisation, white liquor is added for cooking. In this step, organic acids are neutralized and oligo saccharides and mono saccharides are solubilized. Due to high temperature and hydroxyl ion concentration, delignification begins parallel to the extraction of prehydrolyzate acidic compounds. Neutralisation liquor is then displaced to remove extractives and alkali is charged into the digester to pursue the cooking operation.

After kraft pulping, bleaching using ECF agents is applied in order to remove lignin[106-108] and a purification stage is carried out to eliminate residual hemicelluloses (See 1.4 of this chapter). But pure cellulose production by PHK process has one disadvantage, i.e. the pulp yield. It is around 35 - 38%, which is not very high[106].

1.5.3. B. Acid Sulfite Pulping

The sulfite process produces wood pulp which is almost pure cellulose fibers by using various salts of sulfurous acid to extract the lignin from wood in acidic conditions. The salts used in the pulping process are either sulfites (SO_3^{2-}), or bisulfites (HSO_3^{-}), depending on the pH. The counter ion (or base) can be sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) or ammonium (NH_4^+).Today magnesium is the dominating base used in sulfite processes since chemical recovery has been developed for this base.

During the sulfite pulping process, both lignin and hemicelluloses are removed from the wood chips. Moreover, cellulose is also strongly affected which explains that sulfite pulps are not used for paper applications. On the other hand the sulfite process is preferred over pre-hydrolysis kraft pulping (PHK) for high-purity cellulose production due to favourable economy, higher yield, higher initial brightness, better bleachability and higher reactivity.

Acid sulfite pulping is carried out in batch digester with a pH varying between 1.5 and 5. The pulp is in contact with the pulping chemicals for 4 to 14 hours and at temperatures ranging from 130 to 160 °C, depending on the base used. The process steps are chip filling, steaming, cooking liquor charging and wood chips impregnation, rising to the desired temperature, maintaining temperature till cooking, pressure relief, cooking liquor displacement and digester discharging.[112, 113].

In acid sulfite pulping, active agents are H^+ and HSO_3^-. The degree of delignification is related to the concentration of H^+ and HSO_3^- while H^+ is responsible for cellulose hydrolysis. The cooking liquor in sulfite process is a combination of free SO_2 (sulfur dioxide in its hydrated form, i.e. H^+, HSO_3^-) and combined SO_2 (combined to the base, i.e. Mg^{2+}, HSO_3^-,), and must be balanced to get optimum delignification and very low condensation reactions. The concentrations of the sulfur species in the aqueous cooking liquor are defined through the following equilibrium and depends on the pH: $SO_2 + H_2O \leftrightarrow H_2SO_3 \leftrightarrow HSO_3^- + H^+$

The general reaction in sulfite process can be divided into sulfonation, hydrolysis, condensation and redox processes.

Sulfonation of lignin is the main reaction in acid sulfite pulping. This reaction, very fast at low pH[114, 115], renders the lignin molecule sufficiently hydrophilic to be soluble in the cooking liquor. A second reaction, slower than lignin sulfonation, is the cleavage of some lignin-carbohydrate and inter-lignin linkages by hydrolysis reaction. In lignin, only α-O-4 linkages are affected (Figure 1.30). As a consequence, the acid sulfite process does not lead to heavy lignin fragmentation, lignin is mainly dissolved.

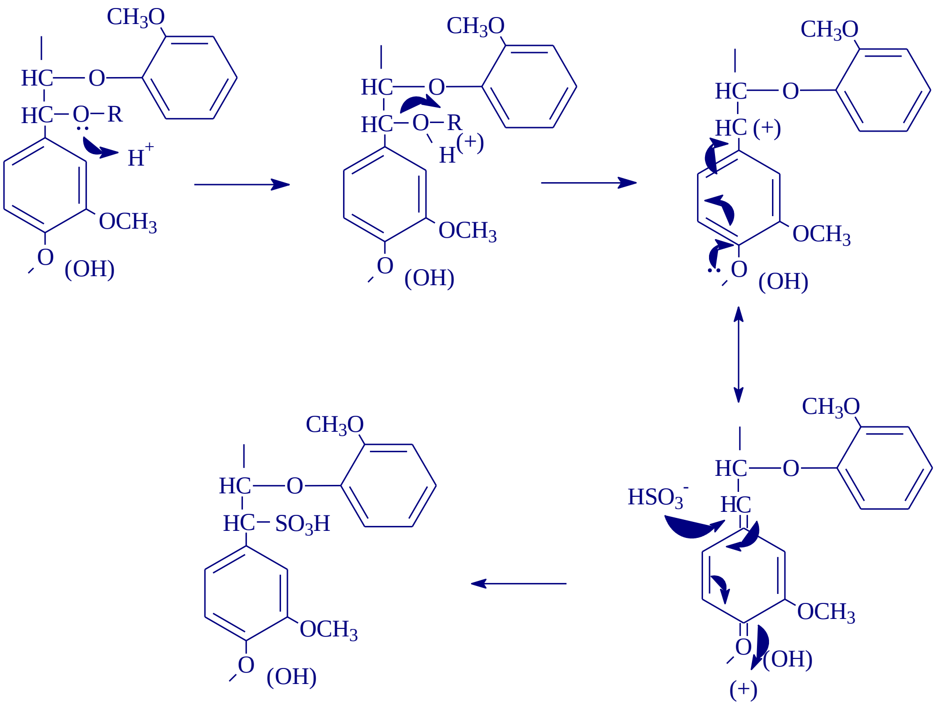


Figure 1.30: Sulfonation of lignin (on α carbon) and cleavage of α-O-4 linkage[116]

Condensation reaction competes with sulfonation and impairs the delignification efficiency by formation of stable carbon-carbon bonds, which increases the lignin molecular weight and makes lignin less hydrophilic. An increase in acidity at the end of the pulping favours condensation whereas condensations are limited with an increasing concentration of bisulfite ions[117]. After cooking the pulp is brighter than that of the pre-hydrolysis kraft process because of lower condensation reactions and better lignin removal.

As far as cellulose is concerned, glycosidic linkages are hydrolysed during the acid sulfite pulping. Cellulose DPv is reduced and depending on the severity of the process conditions, the polymer is degraded to monomers. The rate of the reaction depends on the temperature, acid concentration and molecular environment of glycosidic bond[118]. However the cleavage of glycosidic linkages is slow due to the crystalline structure of cellulose. Acid sulfite pulping is thus able to produce high purity celluloses with high viscosity contrary to the kraft pre-hydrolysis process.

Acid sulfite pulping degrades hemicelluloses much faster than celluloses. The order of heterogeneous hydrolysis is cellulose <mannan < xylan < galactan[119]. Arabinofuranosidic bonds are hydrolyzed more rapidly than glucopyranosidic bonds, so arabinose does appear in the early stage of pulping. Glucopyranosidic bonds are comparably stable and 4-O-methyl glucuronic acids are found in the latter stage when most of the xylan backbone has been removed. Hardwood xylan bonds are also partly stable in sulfite pulping process, because of the presence of glucuronic acids in the side chain, which reduces the rate of hydrolysis[120]. Residual hemicelluloses will be removed in the further purification stage. Apart from all these benefits with acid sulfite process, there are some drawbacks. Recovery of cooking chemicals is not very efficient. All the types of woods cannot be processed in this process[112, 113].

1.5.4. Pulp Purification

After the acid sulfite cooking, pulps contain considerable amount of low molecular weight carbohydrates coming from the acid hydrolysis, which is not suitable for many products such as cellulose acetate, high purity cellulose ethers, and high tenacity regenerated fibres. Pre-hydrolysis kraft pulps also contain hemicelluloses impairing the process-ability in the further cellulose derivatizing steps. These pulps are consequently purified.

Pulp purification aims to remove extractives, lignin and hemicelluloses from the pulp, and to tailor the cellulose molecular mass distribution into a narrow monomodal distribution. The purification process depends on the requirement of the end products. For example, chain – length distribution in the dissolving pulp is a crucial property in the production of rayon fibers[121]. If the amount of low molecular weight fractions in the pulp increases then strength properties will be reduced[122]. Purification is also carried out to render the resulting cellulose product more reactive in the subsequent operation as the viscose process for example.

Purification is carried out using caustic extraction operations. Alkali purification processes are of two types, (i) cold caustic extraction and (ii) hot caustic extraction. Cold caustic extraction (CCE) is carried out at 20 - 40 °C and high sodium hydroxide concentration (1.2 to 3.0 mol/L) whereas the hot caustic extraction (HCE) is carried out at 70 - 130 °C and lower sodium hydroxide concentration (0.1 – 0.4 mol/L). Cold caustic extraction causes physical change in the carbohydrate materials and hot extraction degrades carbohydrate by alkaline peeling reaction. Cold caustic extraction with higher soda concentration produces more α-celluloses (α-celluloses: undegraded and higher molecular weight celluloses [123]) and more yield than hot extraction[124]. However the hot caustic extraction is not applied on pre-hydrolysed kraft pulps because it strongly degrades the carbohydrate quality since the alkaline peeling was already initiated in the kraft pulping.

Caustic extraction has a major impact on molecular mass distribution of pulp. Extraction removes short chain carbohydrates, narrows the cellulose molecular mass distribution thus decreasing polydispersity. Alkaline extraction also removes some lignin from the pulp since kappa number is reduced after this stage[124].

Some researchers are also tried to prepare pure cellulose from paper pulps. Xylan is removed from the pulp initially either by enzyme treatment, i.e., xylanase treatment (X) or by cold caustic extraction (CCE) or both[125-127]. Then pulp is subjected to bleaching and after bleaching pulp is treated with endoglucanase (EG) enzyme to improve its reactivity. It is reported that EG is very useful to improve pulp reactivity[125-130].

1.5.5 Characteristics of Dissolving Grade Pulps

The quality of dissolving pulps is related to their process-ability in the subsequent derivatizing steps. Generally pulp reactivity is estimated by the simulation of the conversion process to the

final product on small pilots. Because the simulation is not always possible, some characterisations were developed to qualify dissolving pulps for their final application.
The main transformation processes of pure celluloses, i.e. viscose and etherification processes involve steeping of the pulp in high alkaline aqueous solution followed by the addition of the required chemical for derivatization (CS_2 for xanthation and alkylhalides for cellulose etherification). The efficiency of this operation, related to the reactivity and quality of dissolving pulps, strongly depends on the chemical compositions of the pulps, on the macromolecular properties, supramolecular structure, cell wall structure, fiber morphology and pore structure and accessibility[131-133].

1.5.5. A. Chemical composition of dissolving grade pulps

The hemicelluloses content of dissolving pulps should be as low as possible[134]. Hemicelluloses are removed from the pulp by cold or hot caustic extraction to an extend depending on the pulp requirements. The presence of hemicelluloses impairs the cellulose derivatization since they consumed caustic soda and they react preferentially with carbon disulfide in the xanthation process. This undesired reaction leads to an inhomogeneous substituted cellulose and affects viscose filtrability. To target the required quality, the viscose solution may content low particles content (less than 3 µm), low amount of noncellulosic impurities in particular xylans since they are responsible for chromophore formation on viscose dopes[134], low inorganic and low resin contents[131-133].

When pulp is processed in an acidic conditions (acetate process), high purity is required than for alkaline processes, because certain pentosans may cause the formation of haze and colour on cellulose tri-acetate and di-acetate solutions. Acetate pulps should contain less than 1.5 % hemicelluloses and no measurable residual lignin. Glucomannan (from both acid sulfite and pre-hydrolysis kraft pulps) is the major source for di-acetate haze, false viscosity and poor filtration[135, 136].

Extractives and resins, determined by acetone or dichloromethane extraction, are also impurities which have dual role. The presence of extractives in the cellulose substrate causes severe problems during the conversion process. Precipitation may occur when pH changes suddenly from alkaline to acid, the spinnerets may be clogged, and yarn yellowing could appear. On the other hand, resins improve the accessibility of chemical reagents to the cellulose substrate by lowering surface tension. Chlorine free bleaching sequences, especially ozone stage, reduce resin content. Resins can also be removed by post treatment as centri-cleaner [137-139].

Residual lignin contributes to the yellowing of the cellulosic products. It may reduce brightness and affect brightness stability and viscose solution filterability. It is an issue for processability of dissolving pulps. It is reported that viscose filterability was affected with increasing residual lignin content. Normally, kappa number of dissolving pulps is between 0.2 and 0.5, which corresponds to residual lignin amount of about 0.05%[140, 141].

Inorganic compounds such as silicate, calcium salts or transition metals (Fe, Cu, Co etc), have a detrimental effect on filterability and spinnability of a cellulose spinning dope (i.e., viscose or lyocell type of fibers). They also lead to spinneret clogging and disturb the uniformity of fibres especially Ca, Fe and silicates. Moreover Cu(II) and Fe(II) promotes light-induced yellowing and are responsible for degradation of fibre in presence of hydrogen peroxide[122].

1.5.5. B. Macromolecular Properties of Dissolving Grade Pulps

The molecular mass distribution (MMD) of carbohydrates in dissolving pulps is an important parameter for the production of regenerated fibres. It is obtained by size exclusion chromatography and gives access to the carbohydrate polymerisation degree counted in weight (DPw) or in number (DPn) and to the polydispersity of the carbohydrate fractions (PDI=DPw/DPn). Characteristics of some dissolving grade pulps are reported in Table 1.2.

Table 1.2: Carbohydrate MMD properties of some dissolving pulps[121]

Preferred Application					
Products →	Viscose	Ether	Viscose	Acetate	Acetate
Raw Material →	Hardwood	Softwood	Hardwood	Hardwood	Cotton Linters
Cooking Process →	Sulfite	Sulfite	PHK	PHK	
Xylan, %	3.6	3.1	1.5	0.9	0.2
DPw	1790	4750	1400	2100	1250
DPn	277	450	460	650	700

PDI	6.5	10.6	3.0	3.2	1.8
DP<100, Wt %	9.0	0.5	2.5	2.0	0.3
DP>2000, Wt %	26.8	61.0	19.9	35.0	15.5

Acid sulfite pulps show a broad MMD (PDI=polydispersity) whereas pre-hydrolysis kraft pulps (PHK) have more uniform MMD[142].

Some studies reported that the chain-length distribution of dissolving pulp is an important property for the production of rayon fibers[143]. The short-chain molecules are the symbol of the weakest section in the fibre. Strength properties are reduced with the increase of low molecular-weight fractions[144] and larger polydispersity.

Carbohydrate functional groups may also affect the dissolving pulp quality. Carbonyl groups are issued from the reducing end-groups and oxidized groups in the cellulose chain, whereas carboxyl groups are mainly present on hemicelluloses and are formed by pulping, bleaching and by other oxidation processes. Carbonyl group causes strength loss and light-induced yellowing[145, 146]. During bleaching, when strong oxidizing agents (i.e., ozone) are used then carbonyl groups are introduced[147, 148]. When carbonyl groups are exposed to oxidative bleaching treatments, they are partly oxidized into carboxyl groups. Fortunately carboxyl groups do not negatively affect viscose fiber processing, but pulp becomes thermally instable[149]. Thus carboxyl groups should be kept as low as possible for acetate-grade pulps which are used for plastic molding[150].

1.5.5. C. Supramolecular Structure and Fibre Morphology of Dissolving Grade Pulps

Supramolecular structure of cellulose plays an important role in the dissolving grade pulps. It is characterised as (i) highly ordered crystalline regions and (ii) low ordered amorphous regions. The ratio between crystalline and amorphous domains, called “degree of crystallinity”, depends on the cellulose source and on the pulping process. The degree of crystallinity, determined by wide-angle X-ray scattering (WAXS) or ^{13}C-CP/MAS-NMR[151, 152], can be altered by the pulping, bleaching and pulp purification process[153]. As an example the removal of hemicelluloses during the cold caustic extraction mainly occurs in the amorphous regions.

Cotton linters exhibit a higher degree of crystallinity than pre-hydrolysis kraft pulp and then sulfite pulps[154]. The NaOH concentration required for the rearrangement of native cellulose crystal structure is thus higher for linters[121]. The reason for high resistance of cotton linters is its supramolecular structure which is different from pre-hydrolysis kraft and sulfite pulps. In cotton linters, cellulose molecules are uniform and arranged in a dense and organized architecture of fibrillar elements leading to a decreased accessibility of reagents due to less pulp swelling in alkaline medium. Pulping followed by purification can influence lattice transformation. During the alkaline purification process, especially for the production of high purity dissolving pulps where high concentration of NaOH solution is used, the cellulose I may shift to cellulose II[155, 156] (Cellulose I: Native Cellulose, Cellulose II: Regenerated or Mercerized Fibres) [157].

It is also reported that after drying, the reactivity of dissolving pulps may be altered and cannot be converted to cellulose acetate in normal processing conditions[158-160]. Reactivity after drying is reduced due to the formation of hydrogen bonds, impairing the accessibility of chemicals.

Cell wall structure is an important property and it mainly depends on the pulping process. Better reactivity was observed with pulps exhibiting more damaged cell wall morphology, i.e with acid sulfite pulps.

The location of hemicelluloses in the fibre wall also influences the dissolving pulp quality.

It is observed that dissolving pulps have higher xylan content on the surface than in the inner fibre wall. Moreover redeposition of xylans during the kraft process may affect the manufacture of cellulose acetates.

Homogeneous fiber morphology will promote the cellulose reactivity. It has been shown that sulfite pulps containing larger amount of short fibre fractions are less reactive due to faster swelling impeding chemicals diffusion.

Finally the carbohydrate swelling ability of the whole cell wall structure is essential for the subsequent conversion of cellulose into its derivatives. Structure swelling depends on pulp supramolecular structure which determines pore volume and pore structure. It was seen that water accessible pore volume of cotton linters is lower than wood pulps, whereas pre-hydrolysis kraft and sulfite pulps exhibit very narrow differences[161]. This explains the lower accessibility of cellulose coming from cotton linters. The accessibility of the pore volume may be determined by the water retention value (weight gain in % of a dry sample after swelling in a large excess of water and subsequent centrifugation) or by inverse size-exclusion chromatography.

Moreover never dried pulps have higher accessibility than dried and rewetted pulps. After drying, irreversible loss of fibre swelling occurs: pores are collapsed or no more accessible. This phenomenon is well-known; this is "hornification"[162-164].

1.6 Conclusion

Dissolving grade pulps represent a niche market in strong evolution. The market demand is increasing with the development of new cellulose conversion installations in Asia. The conventional processes (acid sulfite and pre-hydrolysis kraft cooking) followed by purification stages are able to produce reactive high-purity celluloses. If these processes are efficient, they are unfortunately far to be environmentally friendly practices. There is today a need of new environmentally friendly processes for the production of pure celluloses.

The purpose of this thesis work is to contribute to the establishment of a simpler and hopefully greener chain to produce pure cellulose. The kraft process will still be the retained cooking process but the pre-hydrolysis will not be performed. Instead the purification (mainly the removal of hemicelluloses) will rely on the bleaching steps which will use exclusively oxygen based chemicals and caustic soda. Among them a catalysed hydrogen stage will be introduced as a means to modulate the DP of the cellulose and to contribute to a better purification

The development of such process is not easy since the quality of the final product (cellulose) is very critical. For example the pulp reactivity cannot be described by a single structural feature, but rather by the physical and chemical structure of the cellulosic substrate and the interactions of the derivatizing agent with the carbohydrates. Structure and morphology of the fibre define both the homogeneity of the conversion process and the final product quality. Predicting how these latter aspects will be influenced by the different steps of the new manufacturing chain is a very difficult task.

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CHAPTER - 2

BEHAVIOUR OF Cu-PHENANTHROLINE COMPLEXES DURING HYDROGEN PEROXIDE BLEACHING

2.1 Introduction

Copper phenanthroline is a potential delignification catalyst[1]. In presence of oxygen (O_2) and hydrogen peroxide (H_2O_2), this catalyst enhances the delignification of wood pulps[2, 3]. According to previous literature the active catalyst would be the $Cu(phen)(OH)_2$ species (having only one phenanthroline ligand) which is formed when the $Cu(phen)_2^{2+}$ is placed in an alkaline solution. The active species would easily oxidize alcohol groups into carbonyl groups[4, 5]. A lot of research works are done on lignin model compound i.e. veratryl alcohol. Results have shown the conversion of veratryl alcohol to veratryl aldehyde. This explains that the benzylic OH group in lignin would be the target of this reaction[2, 6]. The first step would be the formation of a new complex between the corresponding lignin moieties and $Cu(Phen)_2^{2+}$. In this oxidation process Cu^{2+} is converted to Cu^{1+}. Then O_2 or H_2O_2 oxidizes Cu^{1+} back to Cu^{2+} and the oxidation goes on[4, 5]. So the change in oxidation state of copper is a key characteristic of the catalytic system. It can be monitored by UV-Visible spectrophotometer. The disappearance of lignin benzylic OH groups and the corresponding formation of carbonyl groups in pulp lignin are difficult to detect. However the use of simple lignin models like veratryl alcohol (VA) makes it possible to follow the extent of this reaction. HPLC is then a very convenient and simple analytical technique for this purpose. The mechanism has been investigated in the case of oxygen bleaching catalysed by copper phenanthroline[2, 6].

The expected oxidation of veratryl alcohol in the alkaline medium is summarized in figure 2.1.

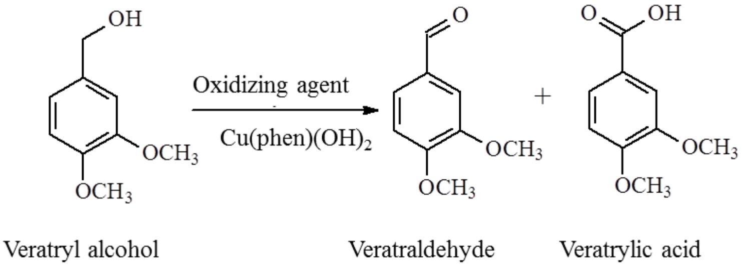


Figure 2.1: Expected Oxidation Reaction of Veratryl Alcohol[6] (3,4 Dimethoxybenzyl Alcohol) in the Presence of $Cu(phen)(OH)_2$

The catalysed oxidation of veratryl alcohol mainly forms veratraldehyde (3, 4-dimethoxybenzaldehyde). However some other products may be formed such as veratrylic acid. Oxygen and hydrogen peroxide were already studied as oxidizing agent. With oxygen, it was shown that the veratryl alcohol consumption is important[2, 4] whereas with hydrogen peroxide, the consumption is less[10]. No explanation was given to date.

To better understand the lower activity of Cu(phen)$(OH)_2$ to catalyse hydrogen peroxide oxidation reactions, we propose to study the behaviour of the copper phenanthroline system in an alkaline solution of hydrogen peroxide. This has never been investigated. The major concern is that H_2O_2 is known to be unstable in alkaline medium especially when transition metal ions are present[7, 11]. The decomposition of H_2O_2 generates radicals and ultimately oxygen gas according to the series of reactions given in figure 2.2.

(i) Decomposition by Transition Metal

$$\mathbf{M^{n+} + H_2O_2 \rightarrow OH^{\circ} + OH^{-} + M^{(n+1)+}}$$

$$\mathbf{OH^{-} + HO_2^{-} + M^{(n+1)+} \rightarrow {}^{\circ}O_2^{-} + M^{n+} + H_2O}$$

$$\mathbf{{}^{\circ}O_2^{-} + H_2O_2 \rightarrow OH^{\circ} + OH^{-} + O_2}$$

(ii) Decompsition in Alkaline Medium

$$\mathbf{H_2O_2 + OH^{-} \rightarrow O_2H^{-} + H_2O}$$

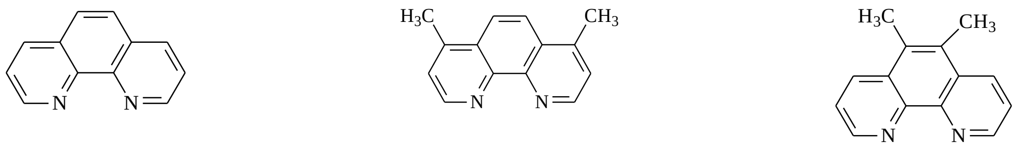
$$\mathbf{H_2O_2 + O_2H^{-} \rightarrow OH^{\circ} + H_2O + {}^{\circ}O_2^{-}}$$

$$\mathbf{OH^{\circ} + {}^{\circ}O_2^{-} \rightarrow OH^{-} + O_2}$$

Figure 2.2: Decomposition Mechanism of H_2O_2 (i) by Transition Metal Ions and (ii) in Alkaline Medium

When the metal ion, here Cu^{2+}, is under a complex form the extent of peroxide decomposition will depend on the redox properties of the complex and is difficult to predict. However this information is of key importance since it will influence the efficiency of the H_2O_2 / Cu-phenanthroline system in the bleaching process. Moreover when radicals are formed, cellulose degradation may occur and becomes difficult to control.

Another point of interest is the capacity of the ligand to influence the extent of the alcohol group oxidation. Indeed in a previous study conducted in our laboratory[12] it has been shown that phenanthroline derivatives used as ligand instead of phenanthroline may modify the copper ligand activity. In particular the 4, 7 and 5, 6 dimethylphenanthroline ligands, complexed with copper (II), were found more active than unsubstituted phenanthroline for the vertaryl alcohol oxidation by dioxygen. And 4, 7 dimethyl phenanthroline found to be better than phenanthroline alone. These ligands were thus also used in our study. The ligand formulas are given in figure 2.3.



1,10-phenanthroline (phen)

4,7-dimethyl-1,10-phenanthroline (4,7-DMP)

5,6-dimethyl-1,10-phenanthroline (5,6-DMP)

Figure 2.3: Phenanthroline Derivatives Used in the Cu-phenanthroline / H_2O_2 system

After a brief description of the experimental procedure, the behavior of the copper(II)-phenanthroline / H_2O_2 system will be studied in the presence of the veratryl alcohol used as a lignin model. To optimize the oxidation, i.e. to maximize the lignin model compound oxidation, substituted phenanthroline will be used instead of phenanthroline and the activity of the corresponding copper complexes was compared to that of the copper(II)-phenanthroline. Finally due to the rapid hydrogen peroxide consumption, oxidation trials using H_2O_2 split addition were studied.

2.2 Experimental Procedures

UV-Vis spectroscopy analyses are carried out in this study for determining the exact nature of the studied complexes: copper oxidation degree and the species coordinated to the copper metallic center.

HPLC was used to follow the reaction of the veratryl alcohol or the reaction of the veratraldehyde in the oxidizing medium.

In all the following trials, the quantity of Cu-(ligand)$_2$ complex is given in copper. The molar ratio of Cu-(ligand)$_2$, veratryl alcohol or veratraldehyde, H_2O_2 and NaOH is set as follows unless indicated in the text, Cu-(ligand)$_2$: veratryl alcohol or veratraldehyde: NaOH: H_2O_2 = 1: 10 : 20: 20.The amount of each product is given in table 2.1.

Table 2.1: Quantity of products used in Analysis

Products used corresponding to the Cu-(ligand)$_2$: veratryl alcohol or veratraldehyde : NaOH : H_2O_2 molar ratio of 1 : 10 : 20: 20

Product	mole
$CuSO_4$	6.88×10^{-5}
Ligand (1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline, or 5,6-dimethyl-1,10-phenanthroline)	13.76×10^{-5}
Veratryl alcohol or veratraldehyde	6.88×10^{-4}
NaOH	13.76×10^{-4}
H_2O_2	13.76×10^{-4}

All reactions were carried out using a two-neck round bottom flask (25 mL) in distilled water or in an alkaline aqueous solution (NaOH 0.05 M). When veratryl alcohol or veratraldehyde are used, they are first introduced in the flask. Then the aqueous solution of Cu-(ligand)$_2$(or copper alone or phenanthroline alone) is added, followed by NaOH solution if required and finally by H_2O_2 solution in the case of oxidizing agent addition. Reactions were performed in the absence of oxygen by bubbling N_2 gas.The reaction was carried out at room temperature for UV-Vis analyses or at 80 °C using an oil bath. For the model compounds oxidation, reaction was performed at 80°Cfor 3 hours under stirring.

For HPLC analyses, the reaction medium was cooled to room temperature before neutralisation using one drop of HCl 1 M (pH 6-7). The solution is filtered through a 0.2 µm nylon filter before injection in the chromatography column.

2.3. Behaviour of the Cu (II)-Phenanthroline / H_2O_2 System

2.3.1 UV-Visible Spectrophotometry - Analysis of the Cu(II)-Phenanthroline / H_2O_2 System

Initially some UV-Visible spectrophotometry blank trials are run to locate individual compounds or complexes. The blank spectra represent veratryl alcohol, phenanthroline, copper-phenanthroline complex alone in water and in the caustic soda solution. The analysis is performed in the 370-800 nm range. As expected no absorption is observed with both phenanthroline and veratryl alcohol in that region. Figure2.4 shows the UV-visible spectra of copper-phenanthroline in water (pH 7) and in the sodium hydroxide medium (pH=12.5). As mentioned by other researchers, the absorption maximum is shifted from 720 nm to 680 nm when the medium is made sufficiently alkaline. This would correspond to a change in the complex structure which would move from $Cu(phen)_2^{2+}$ to $Cu(phen)(OH)_2$(Figure 2.5).

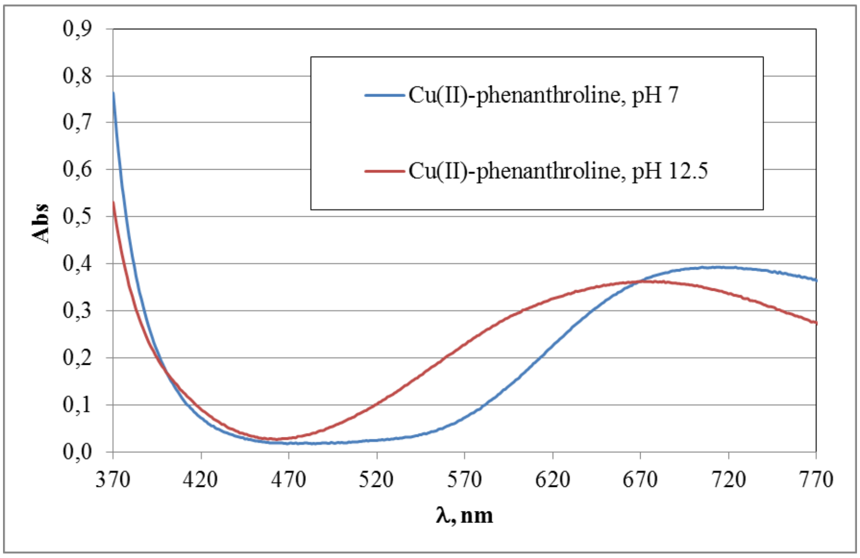


Figure 2.4: UV-visible Spectrum of Copper-Phenanthroline Complex in NaOH Solution

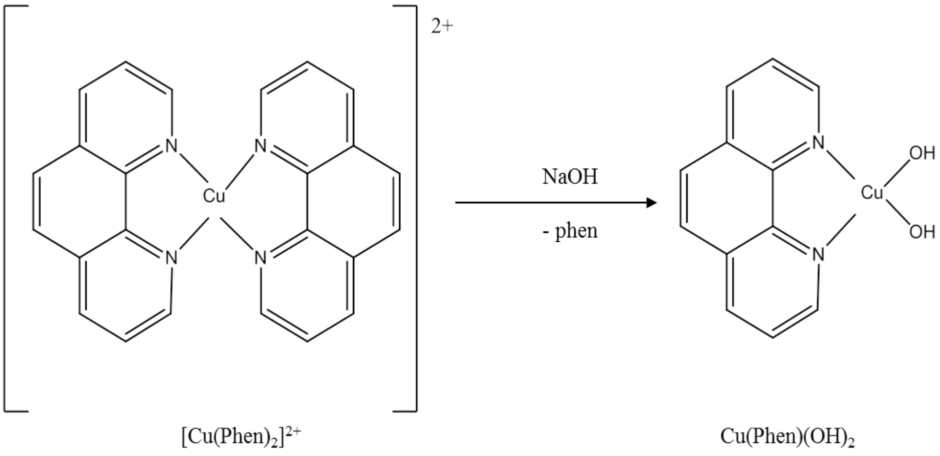


Figure 2.5: Formation of the Cu(phen)$(OH)_2$ in Alkaline Solution from Copper(II) - Phenanthroline

In the absence of any oxidizing agent, when the copper-phenanthroline complex in alkaline medium is added to the veratryl alcohol at room temperature, the UV-visible signal is modified (Figure 2.6) and the absorption below 500 nm is increased substantially, which could correspond to the absorption of a Cu(I)- phenanthroline complex[4, 8].

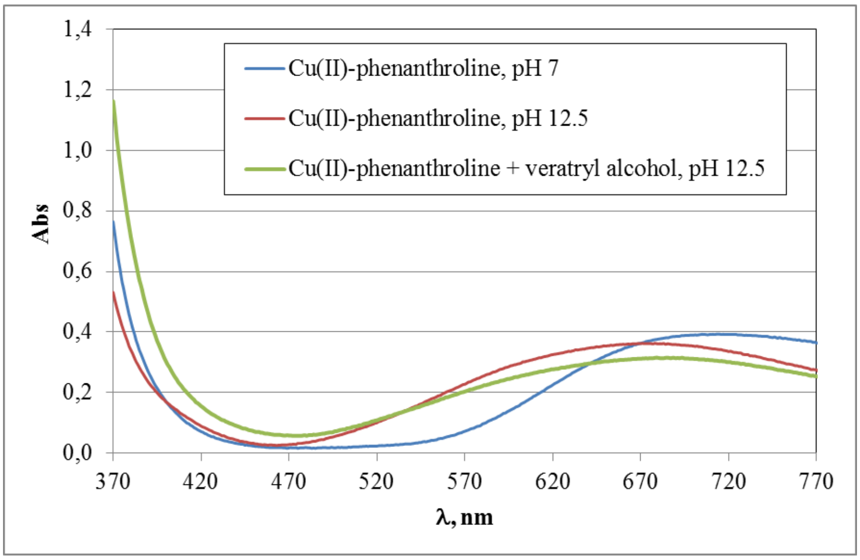


Figure 2.6: UV-visible Spectrum of Copper-Phenanthroline Complex in Alkaline Medium with Veratryl Alcohol

In the next experiment some retention time is given to ensure a more complete formation of Cu(I)-phenanthroline by reaction of Cu(II)-phenanthroline with veratryl alcohol. Figure 2.7 shows the effect of retention time at room temperature. The same experiment is repeated but at 80 °C. Then the sample is cooled and UV-Visible spectra are recorded. The result is shown in figure 2.8.

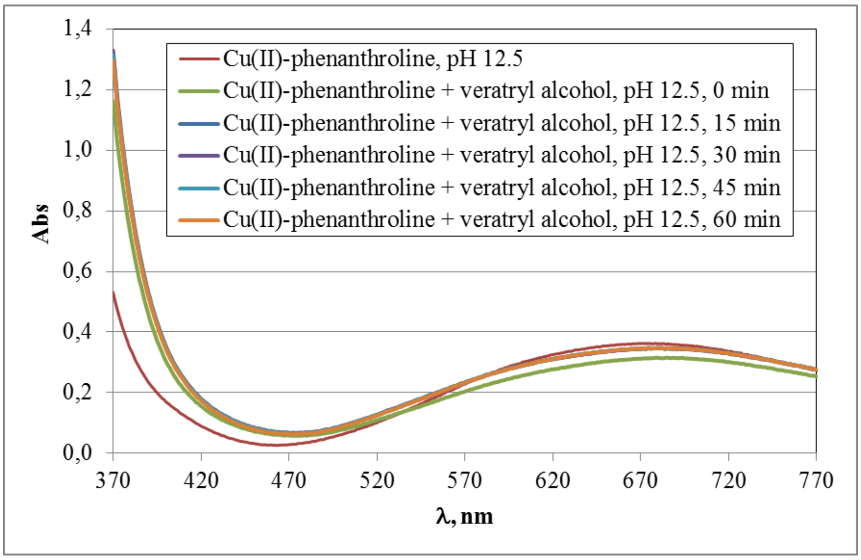


Figure 2.7: Effect of the Retention Time on the Copper-Phenanthroline Complex Structure with Veratryl Alcohol (trials performed at room temperature)

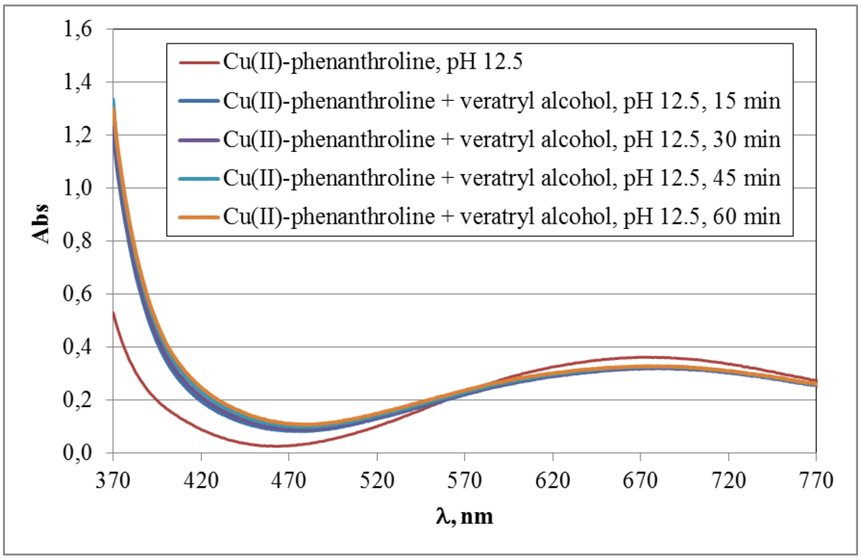


Figure 2.8 Effect of the Retention Time on the Copper-Phenanthroline Complex Structure with Veratryl Alcohol (trials performed at 80°C)

Figures 2.7 and 2.8 show that, whatever may be the reaction temperature, there is almost no effect of the retention time on the formation of Cu(I)-phenanthroline under the applied operating conditions range.

To clearly observe the formation of the Cu(I)-phenanthroline complex, the veratryl alcohol quantity is doubled (for the same copper complex amount) and the reaction time is extended to almost 3 days (Figure 2.9).

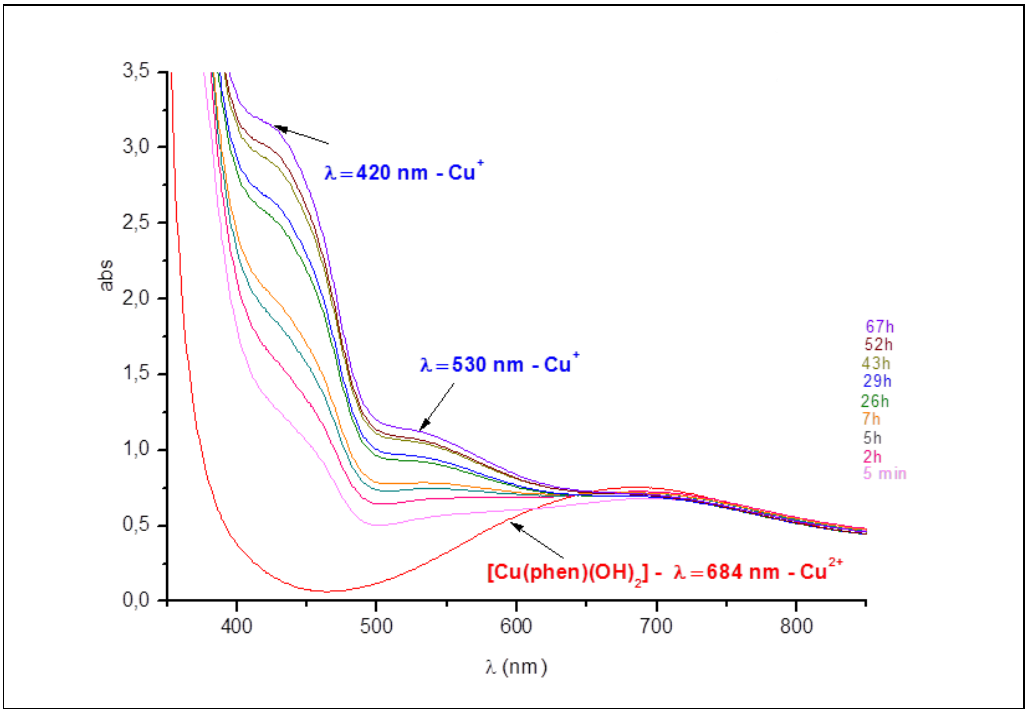


Figure 2.9: Effect of the Retention Time on the Copper-Phenanthroline Complex Structure with an Excess of Veratryl Alcohol (Cu: veratryl alcohol = 1:20) (trials performed at room temperature)

In the presence of an excess of veratryl alcohol, the progressive formation of the Cu(I)-phenanthroline complex is more visible (Figure 2.9). Two signals appear at 530 nm and 420 nm corresponding to Cu(I)[4]. Copper is thus reduced and the veratryl alcohol oxidized. After a rapid start, the reaction of the veratryl alcohol with the Cu(II)-phenanthroline complex is slow. It must be noted that the maximum around 680 nm does not vary when Cu(II)-phenanthroline disappears because Cu(I) also absorbs in this region[4].

Finally, when hydrogen peroxide (H_2O_2) is added to the alkaline copper-phenanthroline solution, the blue colour of the solutionturns brown due to the change in the oxidation state of some copper passing from Cu(II) to Cu(I).This evolution, similar to what was observed with the presence of the veratryl alcohol, is also visible in the UV-visible spectrum recorded immediately after the peroxide addition (Figure 2.10).

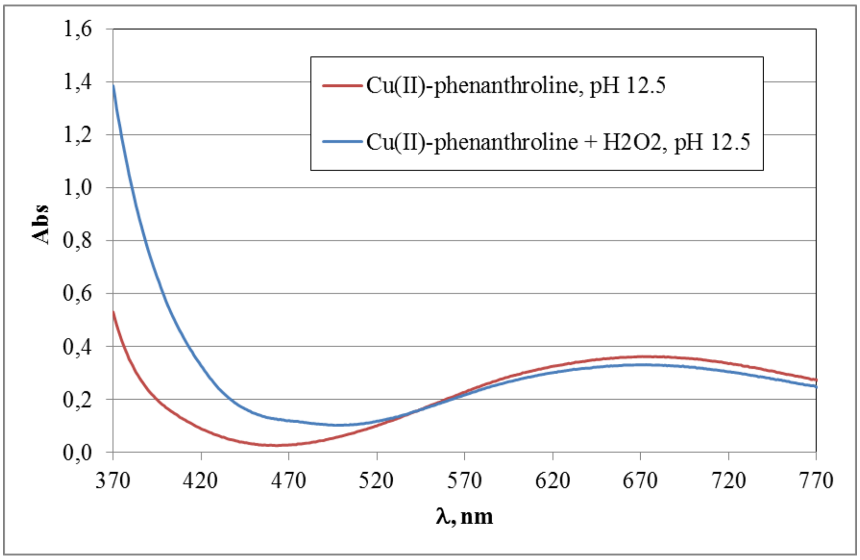


Figure 2.10: Copper- Phenanthroline and H_2O_2 Interaction at Room Temperature

This reaction of copper-phenanthroline complex with H_2O_2 has never been described before. It would indicate that globally some H_2O_2 is acting as a reducing agent and is oxidized to oxygen since bubbles are also observed. Catalytic decomposition of H_2O_2 by Cu(II) species, which is well known when copper is not under a complex form[9] cannot be excluded. Radical species would be formed in a similar way as Cu(II) decomposes H_2O_2 and would affect the course of the catalytic oxidation of the substrate by the Cu(II)- phenanthroline-H_2O_2system. However it would not explain why some Cu(I) is accumulating. Moreover, it is likely that the instantaneous reaction of Cu(II)-phenanthroline with H_2O_2 is responsible for rapid H_2O_2 consumption.

Figure 2.11 shows what happens when the veratryl alcohol is then added in the medium containing H_2O_2 and the Cu(II)-phenanthroline.

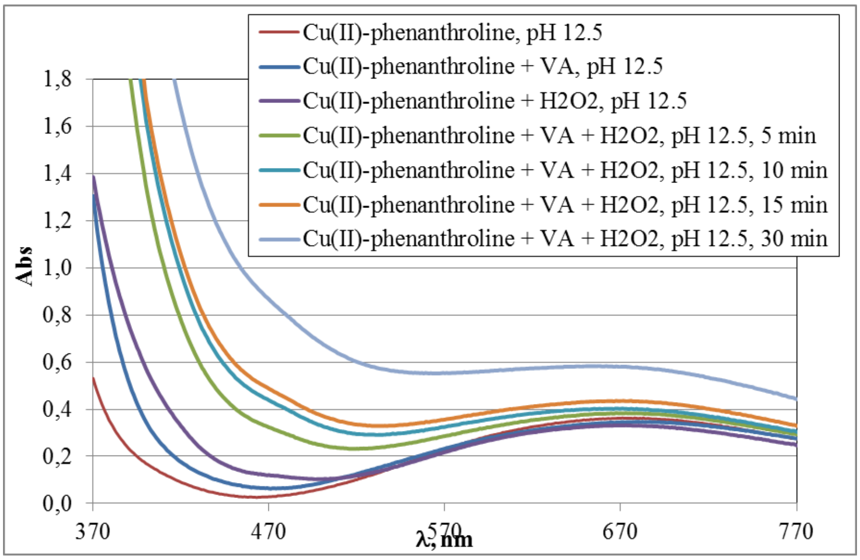


Figure 2.11: Copper-Phenanthroline, Veratryl Alcohol and H_2O_2 Interaction at Room Temperature

The absorption ascribed to Cu(I) increases more rapidly than with the veratryl alcohol alone. Both H_2O_2 and veratryl alcohol are oxidized during the reaction and would contribute to Cu(I) formation. This suggests that the re-oxidation of Cu(I) to Cu(II) is not operating, which may limit the catalysis activity of the copper-phenanthroline system.

In conclusion, the UV-visible spectrophotometry study confirmed that the Cu(II)-phenanthroline has the capability to oxidize the veratryl alcohol. Some Cu(I) complex is formed. According to literature the complex would be[4] 2[Cu(I)(Phen)(OH)]. The quantity of Cu(I) complex increases slowly. Since veratryl alcohol is in large excess compared to Cu(II)-phenanthroline, it can be concluded that the reaction between these two species is rather slow, even at 80°C.

The formation of Cu(I) complex when Cu(II)-phenanthroline is placed in presence of H_2O_2 is quite unexpected. The parallel generation of oxygen bubbles may suggest that H_2O_2 is oxidized and therefore reduces Cu(II) into Cu(I). Catalytic decomposition of H_2O_2 by Cu(II)/Cu(I) is not excluded but then it is difficult to understand why some Cu(I) accumulates. Whatever the mechanism, H_2O_2 is consumed and will certainly disappear from the solution before complete oxidation of the substrate. Moreover radicals are probably produced and may participate in oxidation reactions. Finally, when veratryl alcohol is in solution with both H_2O_2 and Cu(II)-phenanthroline, Cu(I) species accumulate more than without H_2O_2. In this study there is no evidence of any oxidation of Cu(I)-phenanthroline by H_2O_2.

In conclusion the Cu (II)-phenanthroline / H_2O_2 system is not going to operate like the O_2 / Cu(II)-phenanthroline system since nothing indicates that Cu(II) can be re-formed from Cu(I). Moreover the system will suffer from the instability of H_2O_2 and the inevitable parallel formation of radicals which will complicate the course of the lignin oxidation process and will certainly induce the oxidation of cellulose.

2.3.2. Oxidation of the Veratryl Alcohol with the Cu(II)-Phenanthroline / H_2O_2 System, followed by HPLC

Previous studies, focused on the delignification by catalyst, shown that the Cu(II)-phenanthroline complex is able to catalyse alcohol functions oxidation into carbonyl groups using oxygen or hydrogen peroxide as oxidizing agent[1-3].Many authors worked with lignin model compounds to study the catalytic activity of these systems. The veratryl alcohol is often used because it is a simple and non-phenolic lignin model resistant to H_2O_2 applied in conventional delignification conditions. During the catalysed reaction it has been shown that the veratryl alcohol is converted into veratraldehyde. The disappearance of the veratryl alcohol and the formation of the veratraldehyde, quantified by High Performance Liquid Chromatography (HPLC), is an indication of the efficiency of the Cu(II)-phenanthroline/H_2O_2 system. In our study the oxidation of the veratryl alcohol was thus followed by HPLC.

Initially individual compounds are analysed by HPLC to record the corresponding elution time. The C(II)-phenanthroline and/or phenanthroline complex, the veratryl alcohol and the veratraldehyde are eluted at 2-3 minute, 6-7 minute and 16-17 minute respectively.

Figure 2.12 gives an example of HPLC analysis after the reaction of the veratryl alcohol in alkaline medium with hydrogen peroxide and in the presence of the Cu(II)-phenanthroline complex. Three main signals appear: the first one at around 2.5 min may be attributed to phenanthroline and/or phenanthroline degradation product, the second one at 6 min is attributed to the veratryl alcohol and the last one at 16 min to the veratraldehyde.

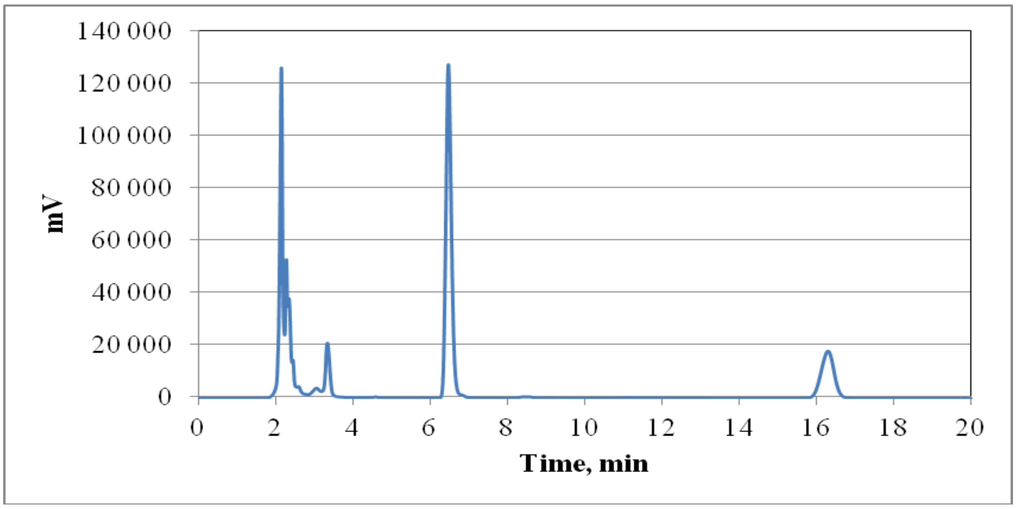


Figure 2.12 Example of HPLC Analysis Obtained after the Reaction of the Veratryl Alcohol in Alkaline Medium with Hydrogen Peroxide and in the Presence of the Cu(II)-Phenanthroline Complex

Several blank trials were carried out, with or without oxidizing agent and with or without the complex. The consumption of the veratryl alcohol and the production of the veratraldehyde measured by HPLC are given in the table 2.2.

Table 2.2: Reaction of the Veratryl Alcohol (VA) Under Various Conditions (80°C, 3h)

Cu(II) or Cu(II)-phenanthroline : veratryl alcohol : NaOH : H_2O_2 molar ratio = 1 : 10 : 20 : 20			
Experiment	Conditions	Veratryl alcohol consumption, %	Veratraldehyde formation, %
1	VA + H_2O	0.3	No
2	VA + NaOH	4.8	No
3	VA + NaOH + Cu(II)-Phen	8.9	No
4*	VA + NaOH + Cu(II)-Phen	16.4	No
5	VA + NaOH + H_2O_2	9.5	1.7
6	VA + NaOH + H_2O_2 + Cu(II)	8.7	0.1
7	VA + NaOH + H_2O_2 + Cu(II)-Phen	13.2	4.8
8*	VA + NaOH + H_2O_2 + Cu(II)-Phen	31.6	3.8

The reactions are performed in the absence of oxygen
*Cu(II)-phenanthroline : veratryl alcohol : NaOH : H_2O_2 molar ratio = 10 : 10 : 20 : 20
Veratryl Alcohol (VA) Consumption % =(VA Initial, mole - VA Final, mole)x100 / VA Initial, mole
Veratryl Aldehyde (VAld)) Formation % = (VAld Formed, mole)x100 / VA Initial, mole

After 3 hours of reaction in water at 80°C, the veratryl alcohol is stable since only 0.3% is consumed (experiment 1). This slight loss is probably due to some physical retention in the chromatography column and/or to the accuracy of the analysis. More surprising, when the reaction is performed in sodium hydroxide, 4.8% of the initial veratryl alcohol disappeared without apparent veratraldehyde formation (experiment 2). The reason is not clear because veratryl alcohol is not supposed to undergo any reaction with sodium hydroxide alone.

Moreover, in the presence of Cu(II)-phenanthroline, about 8.9% of veratryl alcohol disappears (experiment 3). Compared to the blank under alkaline conditions the addition of copper phenanthroline increases the loss of veratryl alcohol by 4.1%, which indicates that copper phenanthroline is reacting with veratryl alcohol. In theory the reaction is the following:

2 Cu(II)-phenanthroline + Veratryl alcohol → 2 Cu(I)-phenanthroline + veratryl aldehyde

Considering the molar ratio of Cu/VA used here (1/10), a complete reaction would consume only 5% of the VA. So we can consider that in experiment 3, the reaction is almost complete. Taking into account the 5% loss of veratryl alcohol due to the alkaline medium, the problem is that no aldehyde is detected. The quantity of Cu(II)-phenanthroline was thus increased (multiplied by 10) in order to accentuate the oxidation of the veratryl alcohol and in an attempt to detect some veratryl aldehyde (experiment 4).

Results of experiment 4 show that even with the Cu(II)-phenanthroline : veratryl alcohol molar ratio of 1 : 1, no aldehyde could be detected after the reaction of the veratryl alcohol with the complex in alkaline conditions. This does not necessarily indicate that aldehyde is not formed because the latter might not be stable or might be oxidized further to veratrylic acid, although no reaction of that type has ever been described. The quantity of veratryl alcohol which has disappeared remains relatively low in experiment 4, which confirms that the oxidation of the veratryl alcohol by the Cu(II)-phenanthroline complex is slow.

A slight quantity of veratraldehyde is produced only in the presence of hydrogen peroxide (experiments 5 - 8). It appears (experiment 5) that hydrogen peroxide alone can oxidize the veratryl alcohol and form some aldehyde, which has never been described earlier under similar conditions. Whether or not the radical species resulting from hydrogen decomposition would participate in this reaction is not known. However experiment 6 where the production of radicals is increased by the addition of Cu^{2+} shows that less aldehyde is formed. Therefore the mechanism by which veratryl aldehyde is formed is still unclear.

Adding together hydrogen peroxide and Cu(II)-phenanthroline improves the oxidation process (experiment 7 and 8). The higher the quantity of Cu(II)-phenanthroline (experiment 8, multiplied by 10), the bigger the disappearance of the veratryl alcohol. However the amount of aldehyde is not increased which would suggest that the veratryl aldehyde is not stable.

In conclusion, it is confirmed that the veratryl alcohol could be substantially oxidized by the Cu(II)-phenanthroline / hydrogen peroxide system. However the oxidation of the α -OH group into carbonyl by Cu(II)-phenanthroline alone could not be demonstrated by HPLC analysis.

In an attempt to detect the formation of the carbonyl group, the veratryl alcohol consumption and the veratraldehyde formation is determined all along the reaction of the veratryl alcohol with hydrogen peroxide under alkaline conditions with and without Cu(II)-phenanthroline. Results are given in table 2.3 and plotted in figures 2.13 and 2.14.

Table 2.3: Kinetics of the Veratryl Alcohol Reaction with Hydrogen Peroxide in the Presence and in the Absence of Cu(II)-Phenanthroline

Time, minutes	Veratryl alcohol + NaOH + H_2O_2		Veratryl alcohol + NaOH + H_2O_2 + Cu(II)-phenanthroline	
	Veratryl alcohol consumption, %	Veratryl adehyde formation, %	Veratryl alcohol consumption, %	Veratraldehyde formation, %
15	4.2	0.0	12.0	3.9
30	7.8	0.8	14.9	4.5
60	8.0	0.5	13.4	4.8
120	8.5	1.3	13.2	3.9
180	9.6	1.7	13.2	4.8

Cu(II)-phenathroline : veratryl alcohol : NaOH : H_2O_2 molar ratio = 1(or 0) : 10 : 20 : 20
The reactions are performed in the absence of oxygen
Veratryl Alcohol (VA) Consumption % = (VA Initial, mole - VA Final, mole)x100 / VA Initial, mole
Veratryl Aldehyde (VAld) Formation % = (VAld Formed, mole) x100 / VA Initial, mole

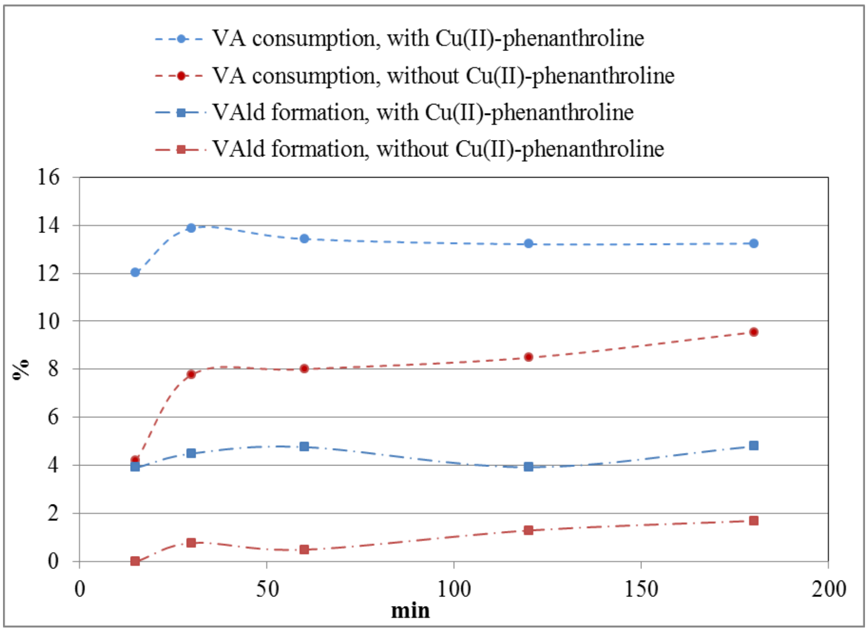


Figure 2.13: Veratryl alcohol (VA) Disappearance and Veratraldehyde (VAld) Formation versus Reaction Time

Figure 2.13 show that, in the absence of Cu(II)phenanthroline, most of the reaction between the veratryl alcohol and hydrogen peroxideis completed during the first 30 minutes. Then, the reaction continues but at a very slow rate. When Cu(II)-phenanthroline is present most of the reaction has already taken place in 15 minutes and then a plateau is rapidly reached. This result is in line with the immediate change of the reaction medium colour from blue to yellow and the appearance of oxygen bubbles as soon as peroxide is added. Hydrogen period is probably rapidly totally consumed during this initial period. Consequently there is certainly no need to run a catalysed P delignifying stage for 3 hours.

Due to the low aldehyde quantity detected (table 2.3) during the reaction, the behaviour of the veratraldehyde in the oxidation process of the veratryl alcohol was studied. Results are presented in the following section.

2.3.3. Behaviour of Veratraldehyde in the Oxidation Process of Veratryl Alcohol, followed by HPLC

The behaviour of veratraldehyde in the reaction medium has been investigated in an attempt to know whether the absence or the low value of detected veratryl aldehyde is due to its oxidation in the reaction medium. The interaction of the veratraldehyde with Cu(II)-phenanthroline was first analysed by UV-visible spectrophotometry (figure 2.14).

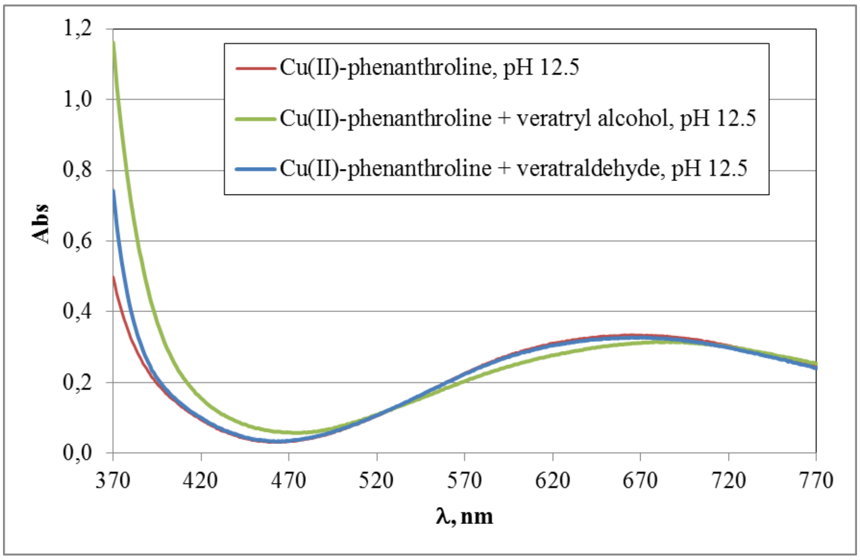


Figure 2.14.Interaction of the Veratryl Alcohol or the Veratraldehyde with Cu(II)-Phenanthroline

(Cu : veratraldehyde or veratryl alcohol : NaOH : H_2O_2molar ratio = 1 : 10 : 20 : 20,
Room temperature, UV-Vis analysis recorded after 15 minutes reaction)

The UV-Visible analysis (figure 2.14) shows that the signal of the Cu(II)-phenanthroline complex in alkaline medium is not changed with the addition of the veratraldehyde indicating that the complex would not lead to any oxidation of the aldehyde, contrary to what is observed with the veratryl alcohol. Consequently, the absence of veratryl aldehyde during the reaction is due to some other reasons.

Reactions of the veratraldehyde in various conditions in the oxidizing medium were carried out and the veratraldehyde quantity was followed during the reaction by HPLC. Results are given in table 2.4.

Table 2.4.Consumption of the Veratraldehyde (V. Ald) in the Reaction Medium under Various Conditions

Cu(II)-phenanthroline : veratraldehyde : NaOH : H_2O_2 molar ratio = 1 : 10 : 20 : 20				
Experiment	Conditions	Temperature, °C	Time, minutes	Veratraldehyde consumption, %
9	V.Ald + H_2O	25	15	0.0
10	V.Ald + NaOH	25	15	19.0
11	V.Ald + NaOH	80	60	24.6
12	V.Ald + NaOH	80	120	25.1
13	V.Ald + NaOH	80	180	26.0
14	V.Ald + NaOH + H_2O_2	80	180	38.5
15	Cu(II)-phenanthroline + V.Ald + NaOH	80	180	35.5
16	Cu(II)-phenanthroline + V.Ald + NaOH + H_2O_2	80	180	53.6

The reactions are performed in the absence of oxygen
Veratryl Aldehyde (Vald) Consumption % = =(VAld Initial, mole - VAld Final, mole)x100 / VAld Initial, mole

At room temperature and in water, the veratraldehyde is stable (table 2.4, experiment 9). On the other hand, in alkaline solution, veratraldehyde was partly disappearing (19% and around 25% disappearance at 25°C and 80°C respectively, whatever the reaction time). One explanation may be the formation of hydrates (Figure 2.15) from addition of water to the veratraldehyde. Indeed, the equilibrium of a ketone (or aldehyde) with a hydrate is a well-known reaction. For most aldehydes and ketones the hydrate is not favoured by equilibrium since hydrates are less stable. However if an electron-withdrawing group is present adjacent to the aldehyde or ketone the hydrate will be more stable. In the case of the veratraldehyde the aromatic part of the molecule may exhibit an electron withdrawing character due to the resonance and thus may shift the equilibrium towards the formation of the hydrate according to the following mechanism.

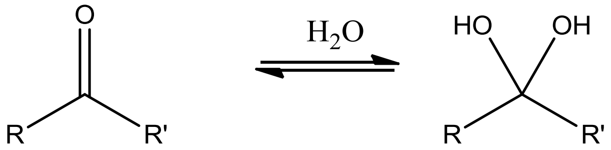


Figure 2.15: Formation of Hydrates from Aldehydes / Ketones and H_2O

The formation of hydrates from the veratraldehyde would be in agreement with the absence of any Cu(II)-phenanthroline reduction as shown by UV-vis spectrophotometry.

The aldehyde consumption increases with the addition of hydrogen peroxide or Cu(II)-phenanthroline alone and is maximal in the case of the simultaneous presence of Cu(II)-phenanthroline and hydrogen peroxide (experiments 14 to 16, table 2.4).The oxidation of aldehyde with hydrogen peroxide in alkaline conditions is not unexpected, the same when both H_2O_2 and Cu(II)-phenanthrolineare present since reactive radical species are probably formed. Whatever the explanations, veratryl aldehyde is not stable under the applied operating conditions and this may explain the absence of veratraldehyde whereas a substantial part of veratryl alcohol has reacted.

2.4 Optimisation of the Veratryl Alcohol Oxidation

2.4.1 Screening of Ligands for the Copper Complex

In another project carried out in our laboratory[12] two substituted phenanthroline ligands combined with copper II have been tested, as catalyst for lignin oxidation by dioxygen. These ligands, the 4, 7-dimethyl phenanthroline (4, 7-DMP) and the 5,6-dimethyl phenanthroline (5, 6-DMP), improved the veratryl alcohol oxidation. These ligands were thus also tested in our study using hydrogen peroxide as oxidizing agent instead of oxygen. As already presented before, the catalytic activity of the H_2O_2/Cu(II)-substituted phenanthroline system was studied using the veratryl alcohol as substrate. The reaction was followed by the veratryl alcohol consumption using HPLC. Results are presented in table 2.5.

Table 2.5: Oxidation of the Veratryl Alcohol with Cu(II)-Substituted Phenanthroline Complexes (80°C, 3h)

Experiment No.	Conditions	Veratryl alcohol consumption, %	Veratraldehyde formation, %
4	VA + NaOH + H_2O_2	9.5	1.7
5	VA + NaOH + H_2O_2 + Cu	8.7	0.1
6	VA + NaOH + H_2O_2 + Cu-Phen	13.2	4.8
18	VA + NaOH + H_2O_2 + Cu-4,7-DMP	9.1	7.9
19	VA + NaOH + H_2O_2 + Cu-5,6-DMP	17.15	7.2

Cu(II)-ligand : veratryl alcohol : NaOH : H_2O_2 molar ratio = 1 : 10 : 20 : 20
The reactions are performed in the absence of oxygen
Veratryl Alcohol (VA) Consumption % =(VA Initial, mole - VA Final, mole)x100 / VA Initial, mole
Veratryl Aldehyde (VAld) Formation % = (VAld Formed, mole) x100 / VA Initial, mole

Results of table 2.6 clearly show that the Cu(II)-5,6-DMP is more efficient to catalyse the oxidation of the veratryl alcohol by hydrogen peroxide, which is consistent with its better effect in delignification[12]. The amount of veratryl aldehyde detected is higher for both substituted derivatives.

2.4.2. Split Addition of H_2O_2

In table 2.3 and figure 2.13, it has been shown that most of the reaction of the H_2O_2 /Cu(II)-phenanthroline system with veratryl alcoholis occurring very quickly and then stops. Our explanation was thathydrogen peroxide decomposes and disappears from the medium. This hypothesis led us to investigate the split addition of hydrogen peroxidewithout any change of the total quantity applied. Table 2.6 gives the results of two different types of split addition. In the first one, hydrogen peroxidewasadded in two parts, half the quantity at 0 minute and second half at 90 minutes. In the second one, hydrogen peroxide was added in three equivalent parts: first part at 0 minute then at 20 minutes and finally at 40 minutes.

Table 2.6: Oxidation of the Veratryl Alcohol with Split Addition of H_2O_2 in the Presence of Cu(II)-Phenanthroline (80°C)

Experiment No.	Conditions	Veratryl alcohol consumption, %	Veratraldehyde formation, %
1	VA + NaOH + H_2O_2 Conventional H_2O_2 Addition Total Time - 3 hr	9.55	1.7
2	VA + NaOH + H_2O_2 + Cu-Phen Conventional H_2O_2 Addition Total Time - 3 hr	13.24	4.8
3	V.A. + NaOH + H_2O_2 H_2O_2 : added in two parts Total Time - 3 hr	13.5	1.34
4	V.A. + NaOH + H_2O_2 + Cu-Phen H_2O_2 : added in two parts Total Time - 3 hr	16.17	6.73
5	V.A. + NaOH + H_2O_2 H_2O_2 : added in three parts Total Time - 1 hr	10.9	0.36
6	V.A. + NaOH + H_2O_2 + Cu-Phen H_2O_2 : added in three parts Total Time - 1 hr	17.6	6.22

Cu(II)-ligand : veratryl alcohol : NaOH : H_2O_2 molar ratio = 1 : 10 : 20 : 20
The reactions are performed in the absence of oxygen
Veratryl Alcohol (VA) Consumption % =(VA Initial, mole - VA Final, mole)x100 / VA Initial, mole
Veratryl Aldehyde (VAld) Formation % = (VAld Formed, mole) x100 / VA Initial, mole

The results are encouraging since the split addition improved theveratryl alcohol oxidation. More alcohol is consumed and more veratraldehyde was produced with the catalyst. Moreover the reaction of 60 minutes with split addition of H_2O_2 leads to similar results as the conventional experiment carried out during 180 minutes, thus confirming the high rate of reaction. The improvement of the results by split addition indicates that $H_2O_2$is probably rapidly consumed and must be charged again for the reaction to continue.

2.5 Conclusions

The results in this chapter bring some useful information about the relevance of the Cu-phen / H_2O_2system in pulp delignification:

- Copper phenanthroline under the Cu(II) form is reduced by veratryl alcohol into the Cu(I) form . This could be observed by UV-visble spectroscopy. However the reaction is very slow even at 80°C. Several hours are necessary to see a substantial formation of Cu(I) species.

- It was not possible to detect any formation of veratryl aldehyde under those conditions by HPLC analysis. This was quite surprising since, according to the literature, veratryl aldehyde should be the oxidation product of veratryl alcohol by Cu(II)-phenanthroline.
- When H_2O_2 is added to the alkaline medium containing Cu(II)-phen the disappearance of veratryl alcohol was further enhanced. However Cu(II) species rapidly disappeared. The colour of the solution was turning yellow and some oxygen bubbles were produced. All indicated that H_2O_2 was not stable in this medium and that Cu(II) species were not re-formed, at least after the first moments of the reaction. Contrary to what is seen in the Cu(II)-phen/O_2 oxidation system the Cu(II)-phen/ H_2O_2 system does not behave like a catalytic system where the Cu(II)-phen would be the oxidant of the substrate and H_2O_2 the regenerating oxidant, re-forming C(II)-phen. The decomposition of H_2O_2 seemed very rapid which implied that radical species were formed and may oxidize veratryl alcohol.
- In all the experiments with H_2O_2, veratryl aldehyde could be detected, even in the absence of Cu(II)-phenanthroline, which has never been described. The disappearance of veratryl alcohol and the quantity of aldehyde were more important when Cu(II)-phenanthroline was present. Whether the radicals are responsible for this result or not is not known.
- It was shown that veratryl aldehyde was not stable under the conditions used in this study. Consequently the fact that veratryl aldehyde was not seen in some experiments does not imply that it was not formed. Moreover the formation of veratrylic acid by further oxidation is quite possible and has been shown in the Cu(II)-phen/O_2 oxidation system.
- Oxidation of veratryl alcohol by Cu(II)-5,6-dimethyl phenanthroline works better than with Cu(II) phenanthroline. This ligand, combined with copper (II), will be thus tested as a novel complex for hydrogen peroxide delignification catalysis (Chapter 4.4.1).
- Since H_2O_2 is rapidly decomposed it is worth splitting the amount of H_2O_2 into several charges added successively. The disappearance of veratryl alcohol and the formation of veratryl aldehyde were substantially increased.
- Considering these results it seems justified to study the delignification of chemical pulps by H_2O_2 in the presence of Cu(II) phenanthroline complexes, even though the

system is not a catalytic one. Pulp delignification should be better than with H_2O_2 alone.

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CHAPTER – 3

BLEACHING OF HARDWOOD KRAFT PULP WITH H_2O_2/Cu-PHENANTHROLINE SYSTEM

3.1 Introduction

Copper- phenanthroline complexes catalyse the oxidation of alcohols groups into carbonyl groups (chapter-2). Several OH groups are present on the residual kraft lignin[1-4] and are therefore susceptible to undergo such an oxidation. Whether or not the formation of carbonyl groups is helping the depolymerization of the lignin macromolecule under the conditions of hydrogen peroxide bleaching is not known. However, it has been shown that the introduction of a ketone group at the α-position of the lignin side chain is making the alkaline cooking of wood much easier. It is explained that the α-carbonyl group facilitates the cleavage of the β-O-4 ether linkage[5-7] under the conditions of an alkaline cook which are more severe than those of a peroxide delignification stage.

Applying the H_2O_2 / copper-phenanthroline system for the delignification of a mixed hardwood kraft pulp is the subject of the present chapter. The ultimate purpose is to develop a totally chlorine-free sequence including this catalysed stage and to produce a pure cellulosic pulp. Pure means that the brightness must be at 90% ISO or more and the content in residual hemicelluloses lower than 5%. For some uses, the DP of cellulose does not need to be as high as for papermaking. However the higher will be the better to meet the requirements for as many applications as possible.

In this study the mixed hardwood kraft pulp was provided by the Fibre Excellence Saint-Gaudens mill in France. It was oxygen delignified at the mill and sampled after washing. However for some trials the oxygen treatment was performed at the laboratory.

The procedure to form the copper-phenanthroline complex and to perform the H_2O_2 stage in its presence needs to be investigated since several alternatives exist and operating conditions have to be adjusted. For the sake of clarity it was chosen to detail the experimental procedures at the beginning of the chapter and along the course of the text whenever needed. This includes all the conditions of the bleaching stages and pre-treatments. The analytical procedures are mentioned. Missing details are given in the chapter-5 “Material and Methods”.

3.2 Experimental Procedures

3.2.1 Preparation of Chemical Solutions

3.2.1 A. Preparation of Phenanthroline Solution

0.1 g of 1, 10-phenanthroline (provided by ALFA AESAR, of purity 99% minimum) is added to 50 ml of demineralised water in a flask and mixed with a magnetic stirrer at room temperature till complete dissolution.

3.2.1 B. Preparation of Copper Solution

0.045 g of $CuSO_4$ (provided by ALDRICH, of purity 98% minimum) is added to 50 ml of demineralised water in a flask and mixed with a magnetic stirrer at ambient temperature till complete dissolution.

3.2.1 C. Preparation of Cu-Phenanthroline Complex Solution

0.1 g of 1,10-phenanthroline and 0.045 g of $CuSO_4$ is added to 50 ml of demineralised water in a flask and mixed with a magnetic stirrer at ambient temperature till complete dissolution. The Cu to phenanthroline molar ratio is 1:2. For other molar ratios, weight of $CuSO_4$ is adjusted accordingly.

3.2.1 D. Preparation of Sodium Hydroxide Solution

40 g/l of NaOH (provided by ROTH, of purity 99% minimum) solution is prepared with demineralised water and used for hydrogen peroxyde bleaching experiments.

3.2.1 E. Preparation of Hydrogen Peroxide Solution

The original H_2O_2 solution (provided by ROTH, at a concentration of 35% minimum) is diluted 10 times in volume with demineralised water. Before every experiment its concentration is checked according to the titration method described in the chapter-5 “Material and Methods”.

3.2.1 F. Preparation of Magnesium Sulphate Solution

10 g/l of $MgSO_4$ (provided by Janssen Chimica) solution is prepared with demineralised water. 0.15% of $MgSO_4$ on pulp is added for oxygen delignification.

3.2.2 Pulp Samples and Characteristics

The pulps used for the experiments are unbleached and oxygen bleached (ODL-Tembec) mixed hardwood kraft pulps received at approximately 7% humidity. They are provided by the Saint-Gaudens mill (Fibre Excellence) in France. Some unbleached pulp samples are also oxygen delignified in the lab (ODL-Lab).

3.2.2 A. ODL-Tembec

The oxygen delignified pulp (ODL-Tembec) has a kappa number of 8.9, a brightness of 45.7 % ISO and a DPv of 1388 (intrinsic viscosity 931 cm^3/g).

3.2.2 B. ODL - Lab

The unbleached kraft pulp which is used for oxygen delignification has a kappa number of 19.4 and a brightness of 32.5% ISO. The oxygen delignified pulps prepared at the laboratory from unbleached samples have the following characteristics:

(ODL-Lab-1) has a kappa number of 9.0, brightness of 45.6 % ISO and DPv of 1378 (intrinsic viscosity 924 cm^3/g).

(ODL-Lab-2) has a kappa number of 9.8, brightness of 45.6 % ISO and DPv of 1398 (intrinsic viscosity 937 cm^3/g).

3.2.3 Pulp Bleaching

3.2.3 A. Oxygen Delignification of Kraft Pulp, (ODL – Lab)

50 g of oven dried kraft pulp is used for all experiments. Water is added to a consistency of 1-2% and then the pulp is disintegrated by a mixer and concentrated on filter no 2. The pulp is placed in a polyethylen bag. Normally its consistency after filtration is around 18-20%. Then 0.15% $MgSO_4$ salt is introduced as cellulose protector followed by 2% NaOH (40g/L solution). Finally demineralised water is added to adjust the consistency at 10%. Pulp is mixed properly to ensure even distribution of NaOH and $MgSO_4$. Then the pulp is put in the oxygen reactor (see chapter-5 “Materials and Methods”) and the polyethylene bag is removed. 5 bar of oxygen gas is applied. After that, the temperature - time programme is launched (30 minutes to 100°C, 60 minutes at 100°C and 20 minutes down to 50°C). After the completion of the treatment, the pulp is recovered and washed properly. Then pulp is air dried (or kept wet) and stored for further experiments and analyses.

3.2.3 B. Hydrogen Peroxide Bleaching (P)

20 g of oven dried pulp is taken for all experiments. Demineralised water is added to a consistency of 1-2% and then the pulp is disintegrated by a mixer and concentrated on filter no 2. The pulp is kept in a polyethylene bag. Normally its consistency after filtration is around

18-20%. The solution containing the catalyst is added first. Then, NaOH and H_2O_2 solutions are added in this order (the quantities will be précised all along the discussion). Finally demineralised water is added to adjust the consistency at 10%. Pulp is mixed thoroughly with the chemicals by hand. Then the polyethylene bag is tied and put in another polyethylene bag. Finally, the polyethylene bags containing the pulp are put into a water bath for two hours or less if mentioned (temperature is maintained as per requirement). After the desired reaction time the polyethylene bag is removed from the water bath and kept for some time in tap water till cool. Around 20 ml of filtrate is recovered for residual peroxide measurement. Residual peroxide is measured using iodometric titration according to the standard procedure (see chapter-5 "Materials and Methods"). The pulp is washed till the filtrate is clear. After washing, the pulp is air dried (or kept wet) and preserved for further experiments and analyses.

3.2.3 C. Oxygen- Hydrogen Peroxide Bleaching (OP)

As before, 20 g of oven dried pulp are used for all experiments. Water is added and then the pulp is disintegrated by a mixer and concentrated on filter no 2. After filtration its consistency is normally 18-20%. The pulp is placed in a polyethylene bag. The solution containing the catalyst is added first (no magnesium salt is introduced as cellulose protector) followed by NaOH and H_2O_2 solutions and water to 10% pulp consistency (2% NaOH and 2% H_2O_2). Then the pulp is introduced in the oxygen reactor and polyethylene bag is removed. 5 bar of oxygen gas is applied. The temperature - time programme is launched (30 minutes to 90°C, 60 minutes at 90°C and 20 minutes down to 50°C). After the completion of the treatment, the pulp is washed thoroughly and air dried. The air dried (or wet) pulp is kept for further treatments and analyses.

3.2.3 D. SO_2 Washing

After every peroxide bleaching (both, with and without catalyst), pulp is washed with SO_2 water (H_2SO_3). H_2SO_3 is prepared by bubbling SO_2 gas through demineralised water for 2-3 h (up to saturation). This helps to remove metal ions from the pulp after treatment.

3.2.4 Pulp Pre-Treatment before Bleaching

3.2.4 A. Acid Pre-Treatment (a)

20 g of oven dried oxygen delignified pulp are used for all experiments. Demineralised water is added to a consistency of 1-2%. Then the pulp suspension is disintegrated and filtered on filter no 2. Again demineralised water is added to the pulp to a consistency of about 1%. 0.5 N H_2SO_4 is added drop wise and mixed with a glass rod. pH is checked after every 2 drops of acid. Addition is stopped when the pH is 3.0 (around 3 ml of 0.5 N H_2SO_4). Then the acidified pulp suspension is filtered on filter no 2 and the filtrate is kept. The consistency is adjusted to 10% by adding filtrate. Then, the plastic bag is placed into a water bath for 3h at 90 °C. After cooling under tap water, the pulp is washed properly, air dried (or kept wet) and preserved for other experiments.

3.2.4 B. Chelation (Q)

10 g/L of EDTA (purity - 99% minimum) solution in demineralised water is prepared at ambient temperature. Normally 20 g of oven dried pulp is taken for every experiment. Demineralised water is added to a consistency of 1-2% and then the pulp is disintegrated and filtered on filter no 2. Pulp is kept in a polyethylene bag at a consistency around 18-20%. Then 0.2 g EDTA in solution (1 % pure EDTA based on pulp weight) is added to the pulp[8] and mixed thoroughly with hand. Then the consistency is adjusted to 10% by adding demineralised water. The pH should be around 5-6. Finally, the polyethylene bag is introduced into a water bath for 30 minutes at 90°C. After cooling, the pulp is washed, air dried (or kept wet) and preserved for other experiments.

3.2.4 C. Acid Pre-Treatment Followed by Chelation (a-Q)

These two treatments are performed in series according to the conditions described above. First, the a-stage (acid stage) is performed, then, the pulp is filtered and the Q-stage (chelation stage) is carried out. After that, the pulp is filtered, air dried (or kept wet) and preserved for other trials.

3.2.4 D. Acid Pre-Treatment and Chelation Together in a Single Stage (aQ)

Pulp is disintegrated first and then filtered. Water is added to reach a consistency of about 1% and 0.5 N H_2SO_4 is added drop wise to pH 3. After that the pulp suspension is filtered and the filtrate is kept (as mentioned for the a-stage). After filtration, the pulp consistency is 18-20%. 0.2 g EDTA in solution (1 % pure EDTA based on pulp weight) is added followed by part of the filtrate to reach 10% pulp consistency. Then, the pulp is kept in a polyethylen bag which is placed into a water bath for 3 hours and 30 minutes at 90°C.

3.2.4 E. Copper, Phenanthroline and Cu-Phenanthroline Impregnation in Pulp

Initially copper solution, phenanthroline solution and Cu-phenanthroline solution should be prepared (see solution preparations above). 20 g of oven dried pulp is taken and demineralised water is added to reach a consistency of 1-2%. Then the pulp suspension is disintegrated and concentrated by filtering on filter no 2. After filtration distilled water is added up to a consistency of 1%. Either copper or phenanthroline or Cu-phenanthroline solution is added and the suspension is stirred with a glass rod. This pulp slurry is retained for 1 hour. Then the pulp suspension is filtered on filter no 2 and the impregnated pulp are used in the bleaching stages. It is supposed here that copper[9], phenanthroline and Cu-phenanthroline[11] are retained by the pulp during the procedure, which has been shown in some studies.

3.2.4 F. In Situ Formation of Cu-phenanthroline Complex in Pulp

In-situ formation of complex gives better results for the oxidation of veratryl alcohol to veratryl aldehyde[10-12]. So it is decided to in-situ formation of copper phenanthroline complex for pulp bleaching. The procedure for in situ formation of the complex in pulp is the same as for impregnation (mentioned above). Desired amount of copper is added first to the pulp slurry at 1% consistency and then, after 10 minutes of gentle stirring, phenanthroline solution is added. This slurry is retained for 1 hour and then concentrated on filter no 2. Then the pulp is used in the peroxide bleaching stage.

3.2.5 Testing Procedure

Before and after treatment the pulp is characterized using the following tests:
Pulp brightness: ISO Method ISO 2470-2:2008.
Kappa number: ISO 302-2004
Degree of polymerization: Tappi Test Method T230 om-99
Pentosan content in pulp: Tappi Test Method T223 cm-01
Hexeneuronic acid in pulp: Test Method T282 pm-07
The detailed experimental techniques are presented in the chapter 5 “Materials and Methods”

3.3. Results and Discussions

3.3.1 Optimization of the use of Copper and Phenanthroline to Catalyse a Hydrogen Peroxide Stage

3.3.1 A. Effect of Adding the Cu-Phenanthroline Complex in a Conventional P stage

In this first series of experiments, conventional conditions are chosen for the P stage (2% NaOH and 2% H_2O_2 on pulp, 10% consistency, 90°C and 2h). The Cu-phenanthroline complex is the one previously tested in some other studies (copper to phenanthroline molar ratio of 1:2)[12]. Its amount is 0.1% (expressed as the quantity of phenanthroline on pulp). Results are compared with blanks (no additive, or 0.045% Cu alone, or 0.1% phenanthroline alone). Kappa number, brightness and DPv are compared.in figure 3.1.

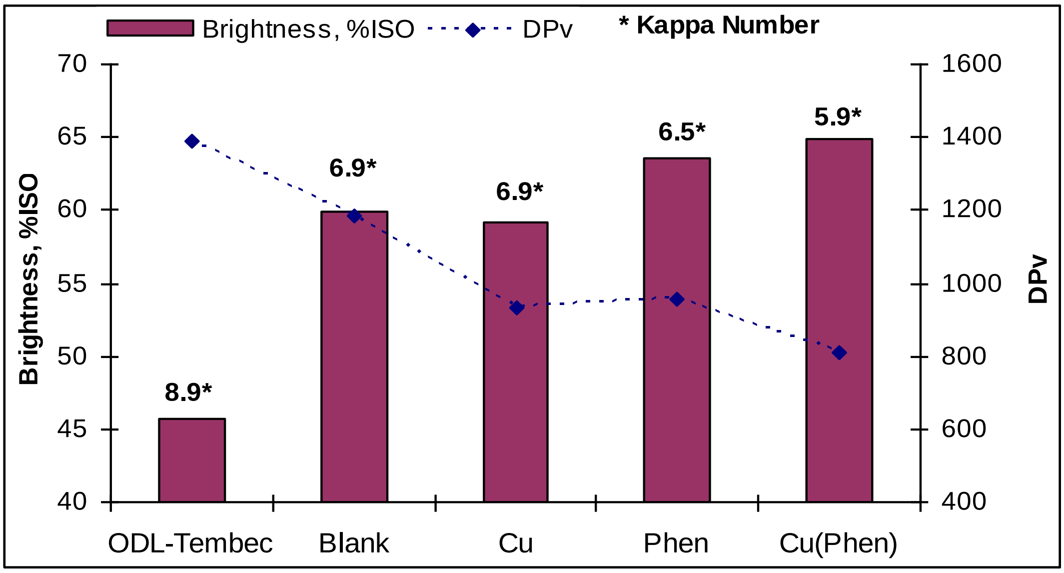

Figure 3.1: Effect of Cu-Phenanthroline Complex on H_2O_2 Delignification of ODL-Tembec Pulp

Figure 3.1 shows that under the applied conditions, peroxide delignification amounts to 22% (2 kappa unit reduction) without Cu-phenanthroline addition and 33% (3 kappa unit reduction) with addition of the Cu-phenanthroline complex. Alone, copper is not playing any role on delignification since the resulting kappa number, 6.9, is the same as that of the blank trial. Phenanthroline alone has a slight effect on delignification. It may be due to the formation of metal complex because of the presence of metal ions in the pulp (possibly copper complex). Addition of Cu-phenanthroline complex gives the best result with respect to brightness gain. There is a drastic reduction in DPv especially when Cu-phenanthroline is added. It indicates that the action of the complex is not selective. It favours both the oxidation of lignin by H_2O_2 and the de-polymerization of cellulose. This latter effect may be the result of radical formation in greater quantity (from hydrogen peroxide) or of the formation of carbonyl groups on cellulose followed by β elimination in the alkaline environment[13]. This was discussed in chapter-1. Cu^{2+} alone leads also to substantial cellulose degradation because of the formation of radicals from peroxide decomposition[14]. The loss of DPv when phenanthroline is added alone could be due to the in situ formation of some metal-phenanthroline complexes.

Trials are also performed using a varying copper: phenanthroline molar ratio to favour the formation of the Cu-phenanthroline complexation. Results are given in figure 3.2.

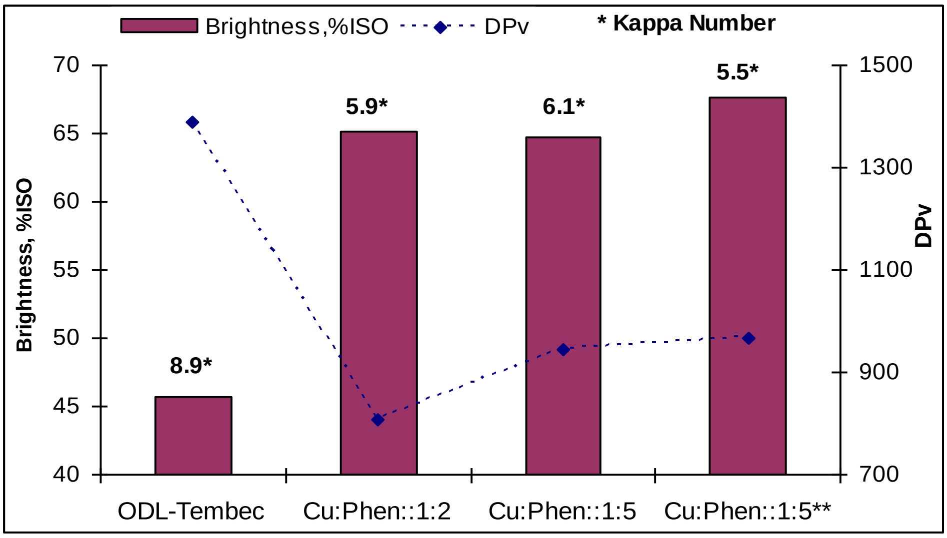

Figure 3.2: Effect of Cu to Phenanthroline Molar Ratio on H_2O_2 Delignification of ODL-Tembec Pulp

(**) the quantity of phenanthroline on pulp is higher in this experiment

The copper to phenanthroline molar ratio is set at 1:5 during the preparation of the complex instead of 1:2. In one experiment the quantity of complex is again 0.1% (of phenanthroline on pulp) meaning that the quantity of copper on pulp is reduced when compared to the previous case with the 1:2 molar ratio. In the second experiment, the complex is prepared with a copper to phenanthroline molar ratio 1:2 and added to the pulp as in figure 3.1. Immediately after, an extra quantity of phenanthroline solution is added to the pulp to reach the ratio 1:5 (noted ** on figure 3.2). The second trial is performed to exclude any presence of free copper, because this extra phenanthroline ensures that all copper make ions make bond with phenthroline. Results in figure 3.2 show that there is less degradation of cellulose when phenanthroline is in excess (ratio 1:5). This may indicate that part of the degradation with the 1:2 ratios would be due to some free copper. A slightly better delignification is observed when the amount of phenanthroline is higher which could be due to the effect of other complexes with the metals in the pulp.

3.3.1 B. Effect of In-Situ Addition of Cu and Phenanthroline

In the previous experiments the copper-phenanthroline complex is prepared separately and added to the pulp. Then the question arises whether the complex is properly diffused in the pulp and eventually inside the fibre walls. Another procedure is tested by which the complex is formed in situ. In this purpose the pulp is first impregnated with the Cu cations and then phenanthroline (0.1% on pulp) is added. Complexes with copper to phenanthroline molar ratio 1:2** and 1:5** are formed in situ by this procedure. But since the amount of phenanthroline is set at 0.1% on pulp, the amount of copper added is varied. For the 1:2 and the 1:5 ratios, 0.045% and 0.018% of copper is added on pulp respectively. After in situ formation of the complex, 2% of NaOH and 2% of H_2O_2 are added. Bleaching takes place at 90°C for 2 hours. Results are given in Figure 3.3.

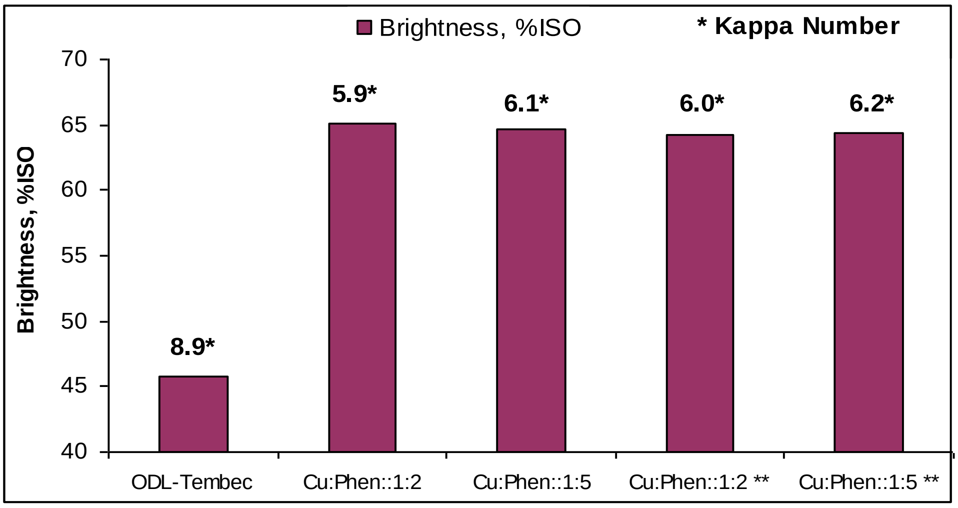

Figure 3.3: Effect of In-Situ Formation of Cu-Phenanthroline Complex on H_2O_2 Delignification of ODL-Tembec Pulp

*** in situ formation of the Cu-phenanthroline complex*

Figure 3.3 show that the in situ formation of the complex does not change the performance of the process. So for future experiments the $Cu(Phen)_2^{2+}$ complex will be prepared separately and added to the pulp.

3.3.1 C. Effect of Impregnation of the Cu-Phenanthroline Complex in Pulp

It has been claimed that the Cu- phenanthroline complex may form a new complex with some lignin sites[11]. So this would make sense to leave some time for the complex to reach these lignin sites after its addition to the pulp. For that purpose, the Cu-phenanthroline complex is first mixed with the pulp at lower pulp consistency (1-2%) for a better diffusion and some retention time is given. The pulp is then pressed to 10% consistency and the P stage is performed. When the pulp is pressed from 1% consistency to 10%, it is supposed that the complex stays bonded to the lignin sites and is not washed out with the filtrate[11]. Results for different times of impregnation are given in Figure 3.4.

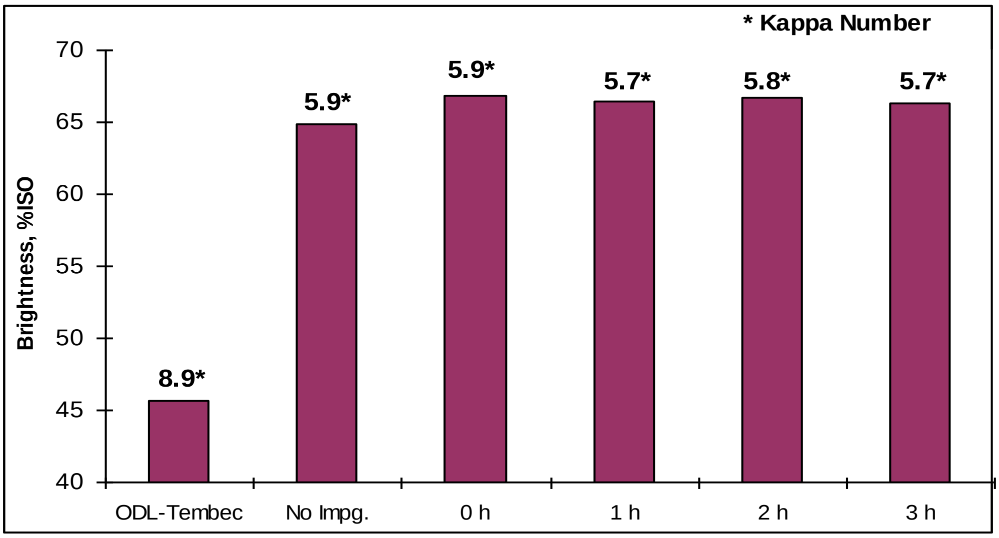

Figure 3.4: Effect of Cu-Phenanthroline Impregnation on Pulp on H_2O_2 Delignification of ODL-Tembec Pulp

According to results in figure 3.4, brightness and kappa number values with and without impregnation are similar whatever the impregnation duration. Therefore, this impregnation procedure does not enhance the performance of the Cu-phenanthroline complex. Nevertheless, the fact that identical results are obtained confirms that the complex remains attached to the fibers during pressing from 1% to 10% which suggests the formation of a new complex with some of the pulp components.

3.3.1 D. Effect of Temperature on H_2O_2 Delignification with Cu-Phenanthroline Complex

In the previous experiments the temperature of the H_2O_2 delignification was 90°C, which was the conventional one for peroxide delignification. It is checked here whether a temperature lower than usual would be acceptable (Figure 3.5).

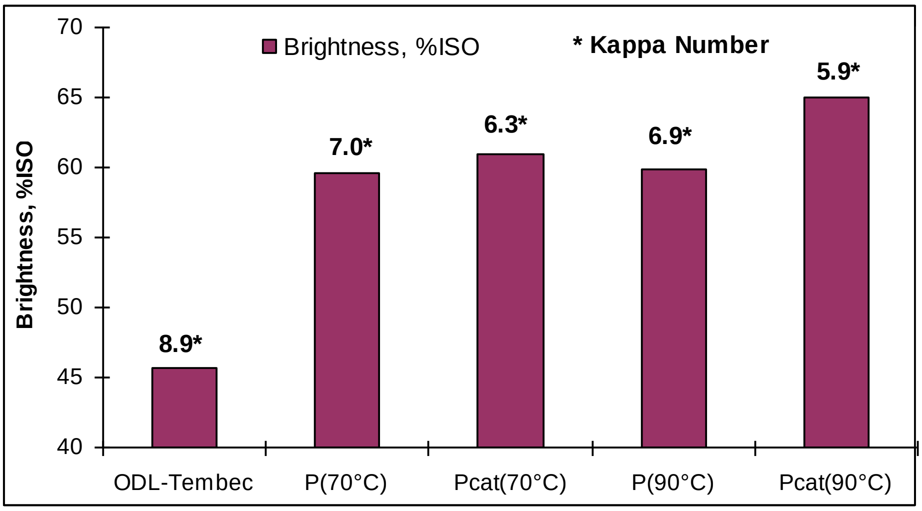

Figure 3.5: Effect of the Temperature on H_2O_2 Delignification of ODL-Tembec Pulp with and without the Complex

Pcat = P stage with the complex Cu-phenanthroline (1:2 molar ratio)

The results in Figure 3.5 show that the beneficial effect of the complex (referred as “cat” here and in the following results) on brightness and delignification is lower at 70°C compared to 90°C. Working at 90°C being more interesting for delignification and brightness development, this temperature will be kept in the following.

3.3.1 E. Effect of NaOH dose on H_2O_2 Delignification with Cu-Phenanthroline Complex

In an alkaline oxidative bleaching stage, the caustic soda is consumed by the organic acids which are formed. Since the catalyzed H_2O_2 stage appeared to be less selective than a conventional H_2O_2 stage, one may expect a higher requirement of caustic soda than normal. For this study oxygen delignified pulp (ODL- Lab-2) of initial kappa number 9.8 is used. Figure 3.6 shows the effect of increasing the sodium hydroxide charge on delignification in the case where the Cu-phenanthroline complex (molar ratio 1:2) is added.

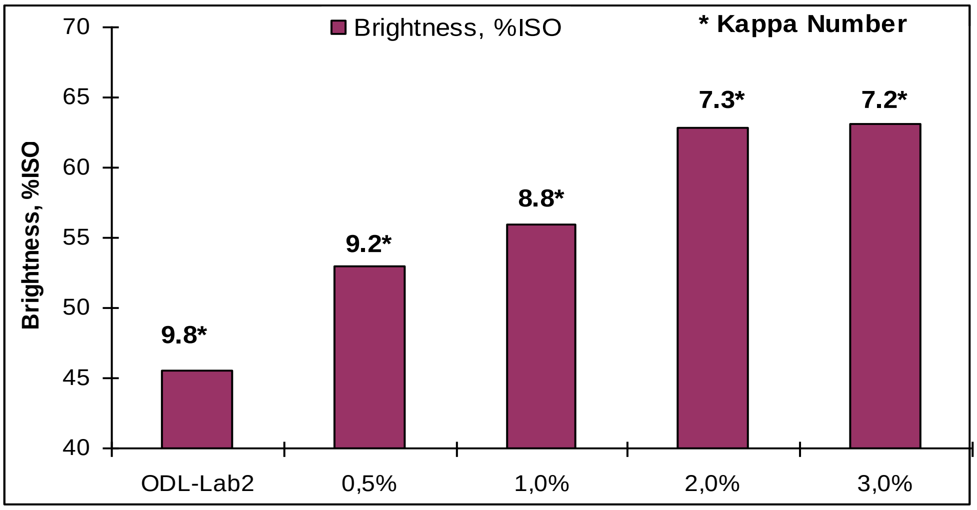

Figure 3.6: Effect of Increasing the NaOH Charge on H_2O_2 (2%) Delignification of ODL-Lab-2 in Presence of the Cu-Phenanthroline Complex

No significant difference is observed between 2% and 3% sodium hydroxide charge. 2% NaOH will be kept in the next experiments.

3.3.1 F. Effect of the Quantity of Cu-Phenanthroline Complex on H_2O_2 Delignification

Several doses of Cu-phenanthroline complex (0.05, 0.075, 0.1, 0.125, and 0.15% expressed as phenanthroline on pulp) are added in a conventional P stage (2% of H_2O_2, 2% NaOH). The results are shown in Figure 3.7.

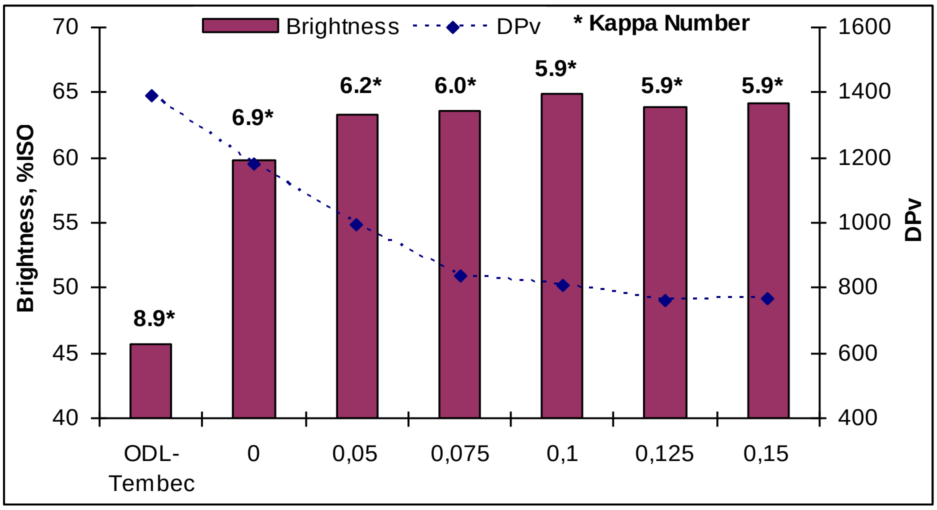

Figure 3.7: Effect of the Quantity of Cu-Phenanthroline Complex on H_2O_2 Delignification of ODL-Tembec Pulp

It is seen that 0.075 to 0.1% is a suitable dose since no improvement is observed at higher charges, neither in delignification, nor in brightness gain. For future experiments the complex charge, expressed as phenanthroline dose, will be set at 0.1% (on pulp).

From above experiments it is decided that copper to phenanthroline molar ratio will be 1:2 and phenanthroline dose will be 0.1% (on pulp). 2% NaOH is sufficient for delignification and the process will be operated at 90°C.

3.3.2 Optimization of the Pulp Delignification by using Hydrogen Peroxide Catalysed by the Copper-Phenanthroline Complex

3.3.2. A. Effect of Hydrogen Peroxide Charge on H_2O_2 Delignification with Cu-Phenanthroline Complex

It has been observed that there is no residual peroxide after the P stage using 2% H_2O_2 on pulp. Moreover the overall performance of the P stage remains moderate even when the Cu-phenanthroline complex is added. Higher doses of H_2O_2 are tried with and without catalyst to examine the potential of this P stage (Figure 3.8).

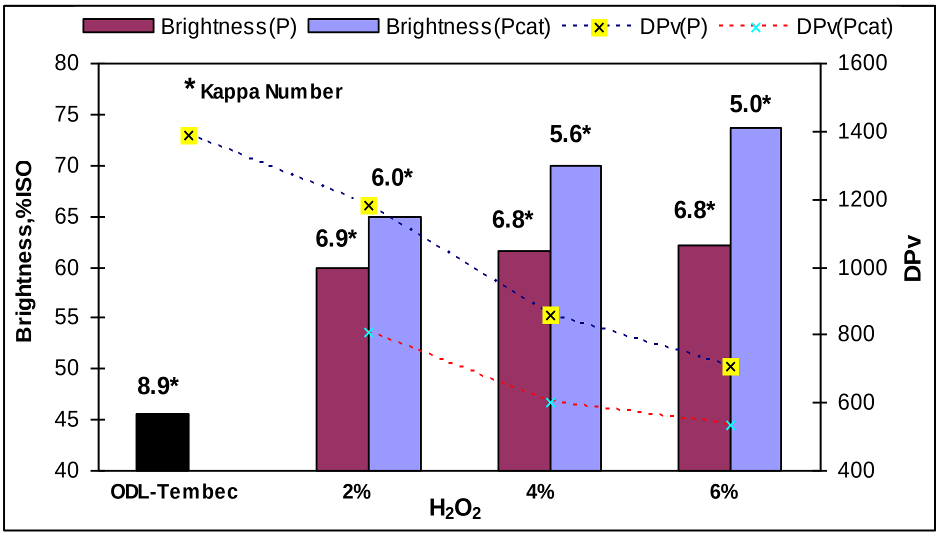

Figure 3.8: Effect of Hydrogen Peroxide Charge on P and Pcat stages (90°C, 2% NaOH) applied on ODL-Tembec Pulp

As the peroxide charge is increased from 2% to 6% on pulp, the P stage without catalyst is not improved significantly. Adding H_2O_2 at higher charges than 2% offers no interest. The presence of Cu-phenanthroline has a marked effect on the results and the higher the peroxide charge, the bigger the effect of the complex on both delignification and brightness gain. However the loss in pulp viscosity is also greater which indicates that in the presence of catalyst delignification and cellulose depolymerisation are going together. 75% brightness is reached at 6% H_2O_2 on pulp, which is still far from the 90% brightness target for pure cellulose.

The addition of Cu-phenanthroline to the peroxide stage leads to some improvement in delignification and brightness but the benefit is rather small and counterbalanced by a loss in cellulose quality. The reason for the cellulose depolymerization is not known. Some peroxide decomposition into radicals must be involved but may not be the only cause. Metal ions play a key role in peroxide decomposition. Consequently some pre-treatments which have an effect on the content of metal ions in pulp are carried out.

3.3.2 B. Effect of Acid Pre-Treatment (a) on P stage, aP and aPcat

The pulp used is a mixed hardwood kraft pulp and hardwood has more xylans than softwoods. As a consequence it is expected that a healthy amount of hexenuronic acids (HexA) is present[16]. It is well known that a hot acid treatment (90° C, H_2SO_4 at pH 3.0), for several hours is capable of removing most of HexA[16], which causes some kappa number decrease. It has been shown that the HexA may retain some metal ions[17]. The partial elimination of HexA is therefore one way to get rid of part of the transition metal ions. Moreover it is known that a significant portion of the metal ions is soluble in acidic medium and should be removed during washing after the “a” treatment. Both actions must combine to reduce the content of metal ions in pulp. P and Pcat are applied with 2%, 4% and 6% H_2O_2 on the “a” treated pulp (Figure 3.9)

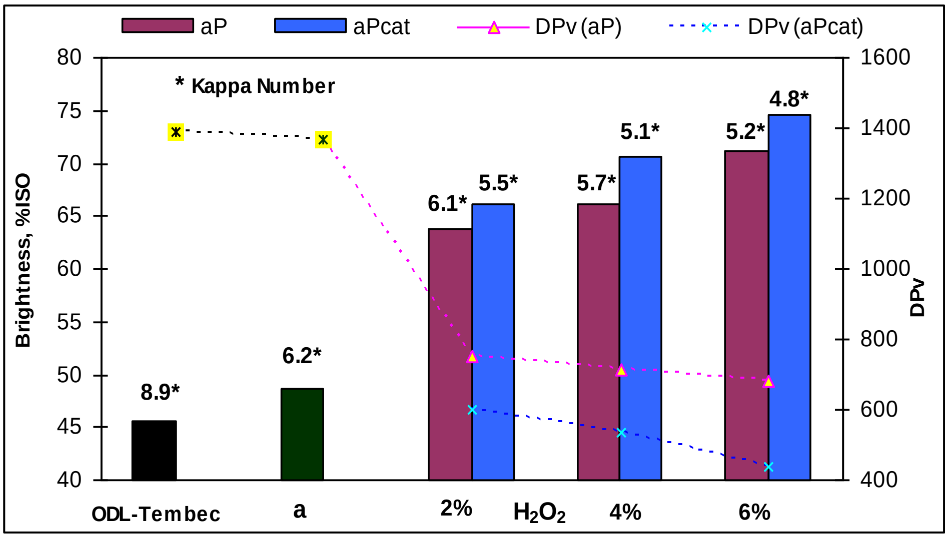

Figure 3.9: Effect of Acid Pre-Treatment on P and Pcat Stages Applied on ODL-Tembec Pulp

The acid pre-treatment alone reduces the kappa number by almost 30%, which corresponds to the removal of some HexA. It has very little effect on brightness gain and DPv. After acid pre-treatment, the effect of the catalyst on peroxide delignification becomes very marginal (around 10% kappa number reductions). Also very little brightness gain is observed. Actually, considering that 3 kappa units are removed during the (a) stage and that H_2O_2 does not react with the HexA[18], one may conclude that both P and Pcat are working less than without pre-treatment, which is quite unexpected.

3.3.2 C. Effect of a Chelation Pre-Treatment (Q) on P stage, QP and QPcat

Another way to remove some metal ions is to perform a chelating stage with a complexing agent like EDTA. In this experiment chelation takes place at a pH near neutral (5-6) and at 90°C. The charge of EDTA is 1% on pulp, which is higher than usual for such applications but the aim is to unambiguously see the effect of metal ions on P and Pcat. As before, 2 %, 4 %, and 6 % H_2O_2 are applied and the results are shown in Figure 3.10.

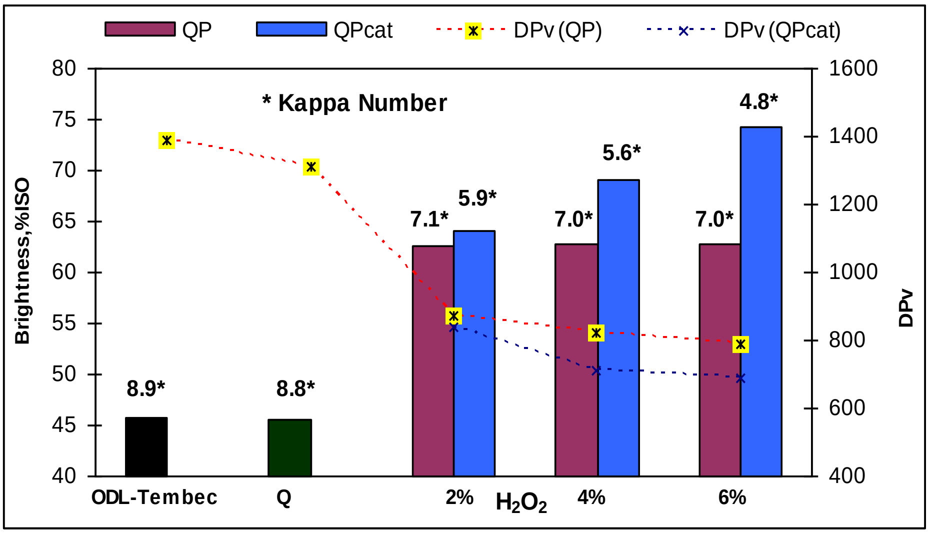

Figure 3.10: Effect of a Chelation Pre-Treatment with EDTA on P and Pcat Stages Applied on ODL-Tembec Pulp

As expected, chelation alone does not have any impact on the kappa number and polymerization degree of cellulose. After P and Pcat the kappa number and brightness are not significantly modified by the implementation of the Q pre-treatment. The only difference brought about by the Q stage is the slightly higher final DPv. Consequently, it seems that the removal of metal ions by Q does not substantially modify the performance of the Cu-phenanthroline complex in the P stage.

3.3.2 D. Combined Effect of Acid Pre-Treatment and Chelation on P stage, aQP and aQPcat

The two pre-treatments are performed in series, with intermediate washing, under the conditions already mentioned above (Figure 3.11). By doing so one may expect a most efficient metal removal prior to the application of the P stage and Pcat stages.

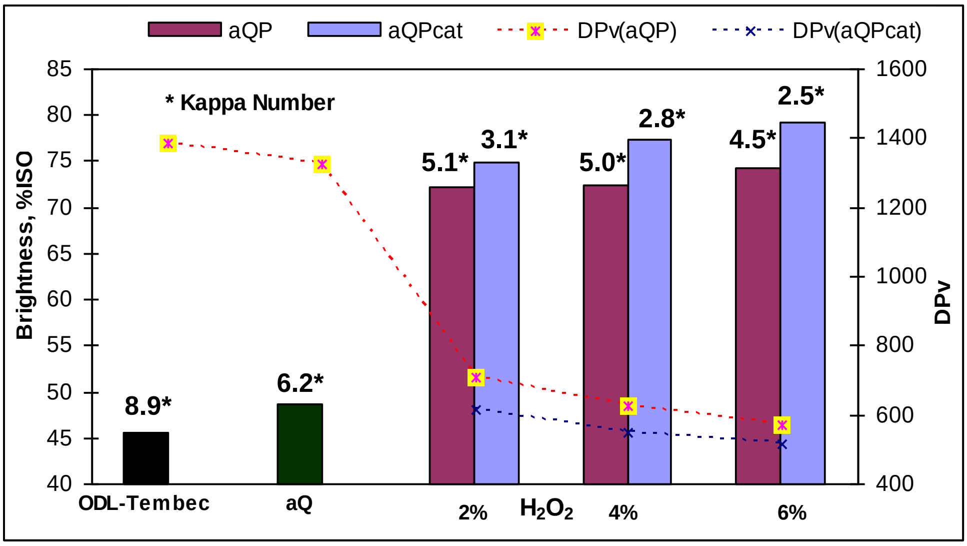

Figure 3.11: Combined Effect of Acid (pH 3) and Chelation (EDTA) Pre-Treatments on P and Pcat stages Applied on ODL-Tembec Pulp

Results in Figure 3.11 are very encouraging in several aspects. Delignification during the P stage is better than expected since it exceeds the result after the “a” pre-treatment while the “Q” pre-treatment has no effect (see Figure 3.10). Brightness gain is also unexpectedly much better. Therefore the peroxide stage is made more efficient by these two pre-treatments in series. The effect of adding Cu-phenanthroline contributes to a further 40% reduction in kappa number as compared to peroxide alone, which was not observed when the “a” pre-treatment was applied as the only pre-treatment. Unfortunately the final DPv remains very low.

It can be concluded that the two pre-treatments have a synergistic effect on the P and Pcat stages performance. Kappa numbers lower than 3 and brightness levels as high as 80% can be obtained after aQPcat. Unfortunately these pre-treatments do not prevent cellulose from degradation.

3.3.2 E. Post Hydrogen Peroxide Treatment applied on aQP and aQPcat pulps, aQP-P and aQPcat-P

Although interesting, the combined effect of acid treatment and chelation does not meet the required target. So, complementary treatments of pulp are necessary. In Figure 3.12 a post bleaching peroxide stage with 2% H_2O_2 at 70° C for 2 hours is added.

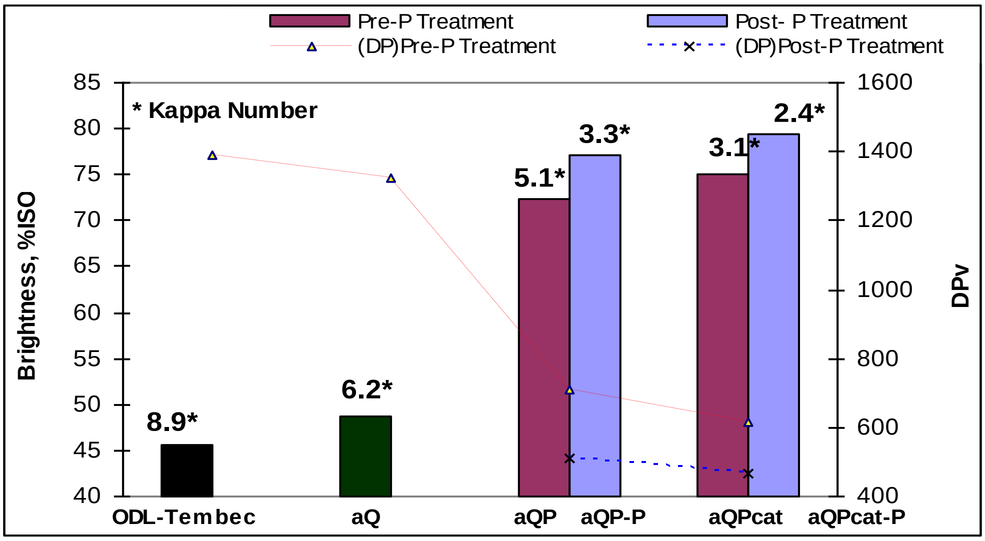

Figure 3.12: Post Hydrogen Peroxide Treatment (70°C) after aQP and aQPcat sequence Applied on ODL-Tembec Pulp (aQP-P and aQPcat-P)

In figure 3.12 it is observed that the post treatment reduces by almost 40% the kappa number of aQP pulp and 20% that of aQPcat pulp. Then it is interesting to note, by comparison with Figure 3.11, that for the same total amount of H_2O_2 (4%), the aQP-P and aQPcat-P processes are working better than the aQP and aQPcat processes respectively. However the brightness target of 90% ISO is not reached. Again no major beneficial effect on DPv is noticed.

3.3.2 F. Post Catalysed Hydrogen Peroxide Treatment applied on aQP pulp, aQP-Pcat

After aQP another P stage is added, as seen before, but the P stage is performed with Cu-phenanthroline, at 90°C instead of 70°C (Figure 3.13). It must be mentioned that these trials were conducted on the oxygen delignified pulp produced at lab scale (ODL-Lab 2, Initial Kappa Number 9.8), which explains the slight difference in kappa number at the beginning.

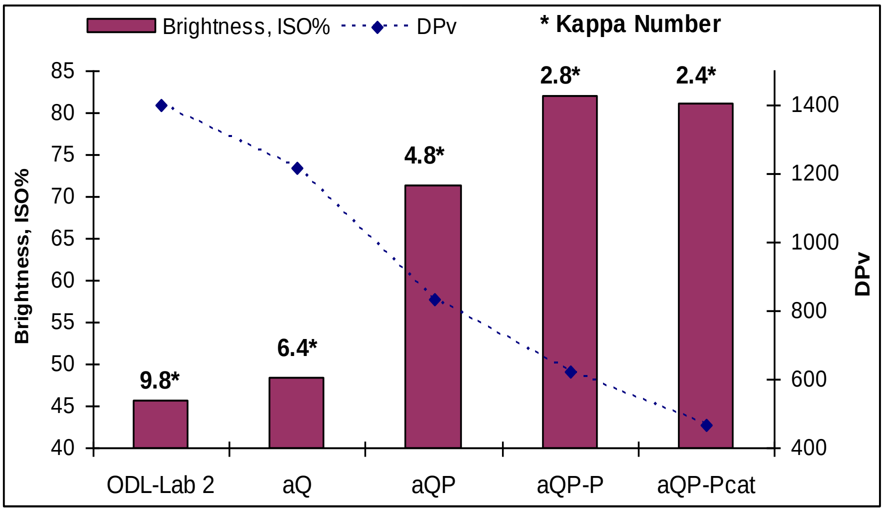

Figure 3.13: Post P and Pcat (Hydrogen Peroxide Treatment at 90°C) after the aQP sequence Applied on ODL-Lab 2 (aQP-Pcat and aQP-P)

In comparison with the results in Figure 3.12, the second P stage is more efficient at 90°C as the brightness reaches 82% ISO against 77% ISO when the temperature of the last P stage is 70°C. The presence of catalyst in the second P stage does not seem to be interesting since delignification is not much increased and the brightness not improved. The catalyst has a beneficial effect on delignification if it is introduced in the first P delignifying stage when lignin is present in quantity.

3.3.2 G. Effect of Adding Oxygen in the P stage, aQ(OP) and aQ(OP)cat

The above mentioned processes use conventional P treatments, catalysed or not by Cu-phenanthroline. A significant progress is made by applying an appropriate pre-treatment (aQ). Performing a P stage under oxygen pressure is common practice in the industry[19]. Moreover Cu-phenanthroline is also a catalyst in oxygen delignification[10-12]. Consequently, putting some oxygen pressure in a Pcat stage deserves some consideration. Results are shown in Figure 3.14. The pulp used here and in the next experiments is produced in the lab (ODL-Lab-1) having initial kappa number 9.0.

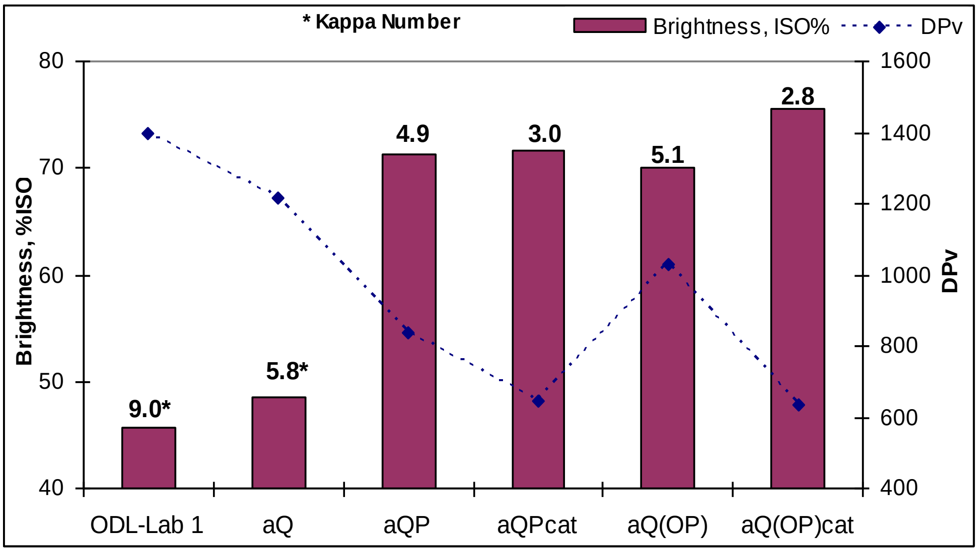

Figure 3.14: Effect of Adding Oxygen (5 bars) in the Hydrogen Peroxide Stage of aQP and aQPcat applied on ODL-Lab 1 [aQ(OP)and aQ(OP)cat]

No improvement is observed when oxygen is present, neither in delignification nor in brightness gain. The main different is the final DPv after aQ(OP) which is unexpectedly much higher than after aQP. Since a too low DPv may be a concern in the production of pure cellulose, this result is quite interesting.

3.3.2 H. Combining Acid Pre-Treatment and Chelation in one Single stage, (aQ) in (aQ)(OP) and (aQ)(OP)cat

From a practical point of view it would be much simpler at industrial scale to carry out the acid pre-treatment and chelation in a single stage to avoid filtering between the two stages. In that case the chelation would be made at the pH of the acid stage which is 3.0 instead of 5-6 and during 3 hours and 30 minutes (see experimental procedures). Results are given in Figure 3.15.

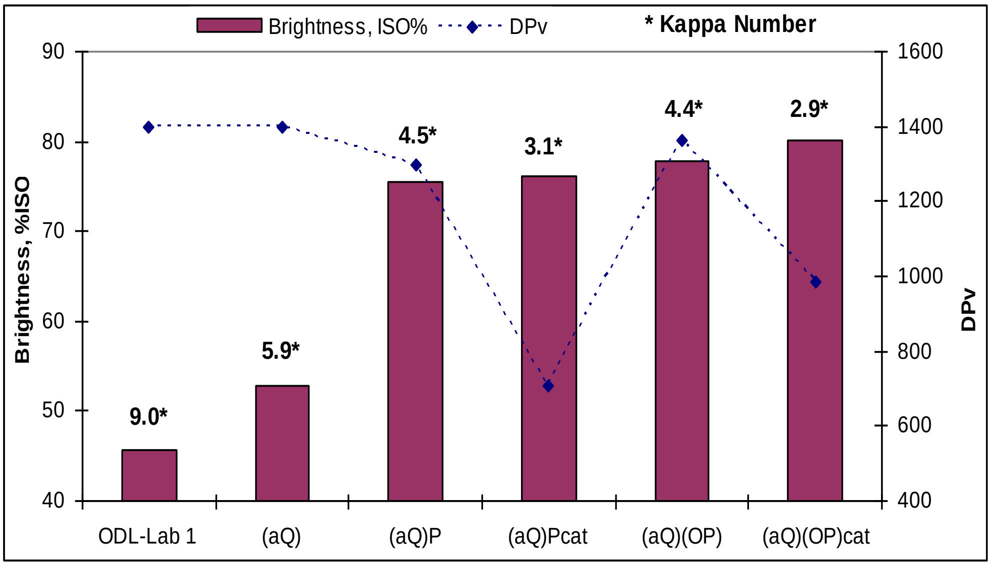

Figure 3.15: Effect of Acid Pre-Treatment and Chelation in One Single stage (aQ) on Hydrogen Peroxide stage Applied on ODL-Lab 1, [(aQ)P, (aQ)Pcat, (aQ)(OP) and (aQ)(OP)cat]

Acid pre-treatment and chelation in a single stage (aQ) is found to be a better option than in series and (aQ)(OP)cat is found to be the best sequence tested so far with the lowest kappa number never reached. The reason, why (aQ) is better than a-Q may lie in the fact that the conditions for the chelation step are different, i.e. longer time and lower pH than in the former case. After the best sequence, (aQ)(OP)cat, kappa number is lower than 3.0 and brightness higher than 80% ISO. Pulp characterisation and calculation will show that most of the residual kappa number is due to residual hexA and not to residual lignin. The DPv is still at a low level but the (aQ) pre-treatment is improving both brightness and delignification significantly, especially in the case of (aQ)P and (aQ)(OP).

3.3.3 Overall Results Summary

One may summarize the main findings obtained so far:

- The introduction of Cu-phenanthroline (called complex or catalyst) in a peroxide delignification stage has a positive effect on delignification and brightness gain. Unfortunately the cellulose DPv is affected negatively. The exact origin of the greater degradation of cellulose is not known precisely. It could be the formation of radicals by decomposition of H_2O_2 by the copper complex or the catalysed oxidation of the alcohol groups of cellulose followed by alkali induced β elimination.

- Adding a pre-treatment consisting of an acid treatment (a) and a chelation step (Q) in series improves the process. Although the lower kappa number is essentially due to the known removal of some HexA by the acid treatment, the higher brightness is a reflection of a more powerful peroxide treatment. Even better result is obtained when acid (a) and chelation (Q) are made together in one single stage (aQ). The improvement of the DP is then spectacular, especially when there is no catalyst
- Adding oxygen in the P stage does not modify the performance of the P stage significantly. However the cellulose DPv and the brightness are generally slightly better.
- Applied on an oxygen bleached eucalyptus kraft pulp of kappa number around 9, the (aQ)(OP) stage (2% peroxide on pulp) gives a kappa number of 4.4 and a brightness of 77.8 % ISO. The cellulose DPv remains at a high level (1364). The most efficient sequence (aQ)(OP)cat leads to a kappa lower than 3 and a brightness higher than 80% ISO. Unfortunately the DPv is then below 1000.

3.3.4 Tentative Explanation of the Results Given by the Hydrogen Peroxide Processes Defined Previously

The next experiments will bring some light on the possible origin of the results obtained previously with the peroxide processes applied on the mixed hardwood kraft pulp.

3.3.4 A. Analysis of the Content in Hexenuronic Acids (HexA) after Each Step of the Sequence

The eucalyptus kraft pulp contains some hexenuronic acid groups (HexA) which contribute to its kappa number[20]. It is known that an alkaline peroxide treatment should not affect the HexA content[18]. Consequently the loss in kappa number should be exclusively due to lignin removal by oxidation. The situation is different when hot acid pre-treatment is performed since then the pre-treatment is supposed to dissolve part of the HexA groups (Figure 3.16) without affecting the lignin[16]. Consequently the loss in kappa number after a peroxide stage performed with an acid pre-treatment is the addition of lignin and HexA removal. Following both the loss in kappa number and the removal of HexA during the previous peroxide processes allows an indirect measure of the lignin removal.

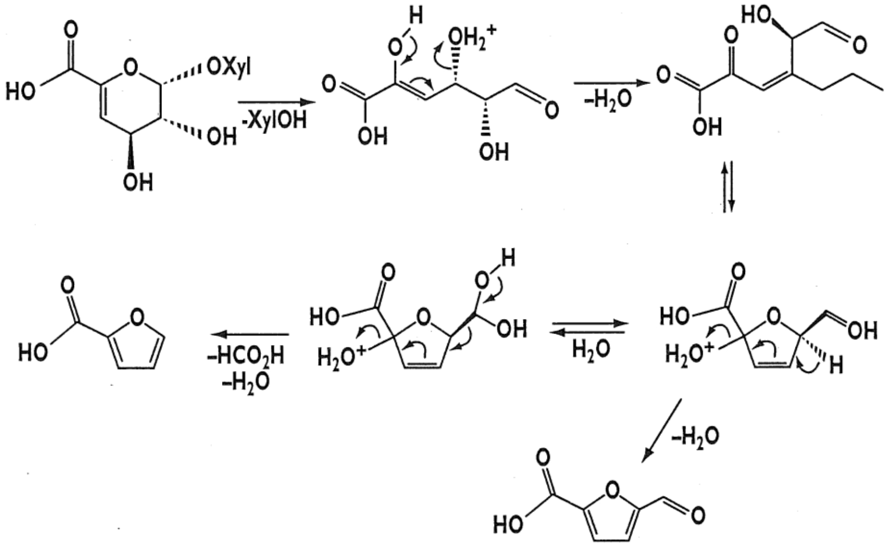

Figure 3.16: Acid Catalyzed Hydrolysis of HexA

The content in HexA after each step of the (aQ)(OP)cat sequence is given in Figure 3.17. The measurements were made according to the procedure given in material and methods chapter. They are expressed in µmol per g of pulp. The initial value is the average value of the three ODL pulps used in this study. It is close to 54 µmol/g of HexA.

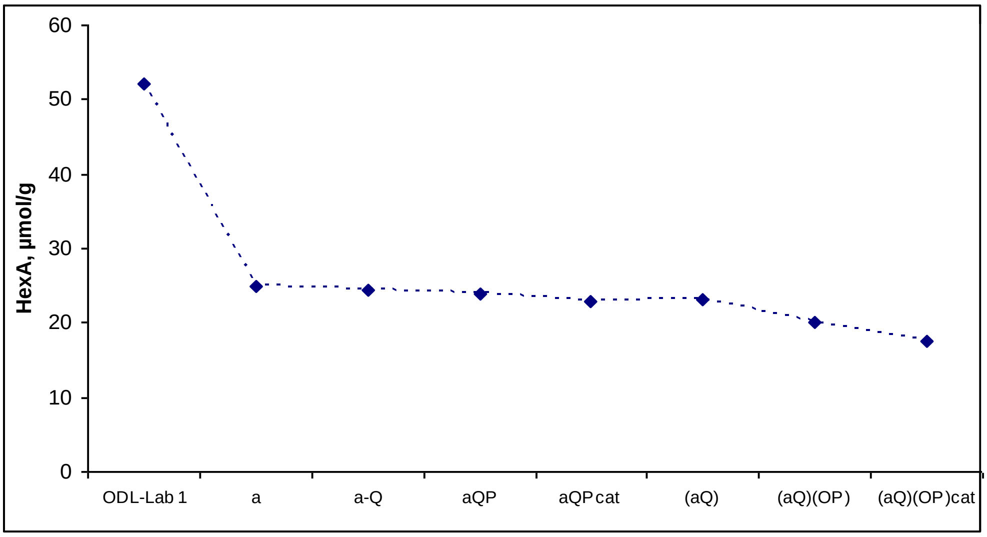

Figure 3.17: HexA Content of the ODL-Lab 1 Pulps after each Treatment of the (aQ)(OP)cat Sequence

Figure 3.17 allows drawing the following conclusions. A slight decrease in HexA is observed after the P stage and especially after the (OP) stage. Even though hydrogen peroxide or oxygen is not supposed to degrade the HexA, it is quite possible that some HexA attached to lignin through the xylan chain are removed with the oxidized lignin. Another possibility could be the oxidation of HexA by some radicals produced by hydrogen peroxide decomposition. A similar effect is observed when Cu-phenanthroline is added. The same explanations may be valid here too, which would mean that the catalyst has no specific effect on the HexA.

The effect of the (a) treatment is rather pronounced. 50% (≈ 27 µmol/g) of the HexA is disappeared. According to Figure 3.9, this corresponds to a kappa number decrease of about 2.7 units (i.e. 1 kappa unit for 10 µmol /g HexA) [20]. Therefore the remaining HexA contribute for 2.4 units to the kappa number. After aQPcat the HexA content is around 24, which represents a contribution of around 2.4 units to the kappa number. According to Figure 3.11 the kappa number after aQPcat is 3.1. One may conclude that roughly 2/3 of this kappa number is given by the residual HexA.

Since neither P nor O have a specific action on HexA it is not possible to go down to a kappa number lower than around 2 by the treatments tested in this study. Having reached 2.9 kappa number with the (aQ)(OP)cat sequence is a very satisfactory result.

3.3.4 B. Metal Ions Content in Pulp after each Step of the Sequence

Peroxide delignification is affected by metal ions. The most detrimental metal ions are the transition metal ions like iron (Fe), copper (Cu) and manganese (Mn) which are present in wood and pulp in substantial quantities[15]. These metals catalyse the decomposition of HOO^- into radicals HO° and $O_2^{\circ -}$. These radicals may contribute to the delignification, since they are oxidants, however if they are produced too rapidly their contribution is not efficient and globally delignification is less because the contribution of HOO^- is much reduced. Other problems are that the radicals, contrary to HOO^-, HO° can degrade cellulose[21, 22]. Several articles indicate that metal ions should be removed as much as possible prior to hydrogen peroxide delignification[23, 24]. The improvement observed with some of the processes investigated above must be linked to a modification of the metals profile in pulp.

Metal content was measured by X-Ray Fluorescence (XRF) Technique. The analysis was performed at the Arkema Research Centre (CRRA, Pierre Bénite, France), a partner in this project. Results are given in Tables 3.1 and 3.2 (*For Metal Ion Analysis – Pulps were sent without SO_2-Water washings*).

As mentioned previously two kinds of oxygen delignified pulp samples were used. One was directly provided by the Tembec mill in Saint Gaudens (ODL Tembec) and the second has been oxygen delignified at the lab in a metallic pressurized reactor (ODL-Lab-1 & 2). Consequently it is not a surprise that these 2 samples have not the same metal profile. Results in Table 3.1 refer to the ODL-Tembec pulp and Table 3.2 shows the results of ODL-Lab pulp (1 or 2). The nature of the treatment is given in the first line. The contents given are those obtained after the indicated treatment. Values indicated as <5 ppm mean that the corresponding metal ion cannot be measured quantitatively because its content is too low.

Table 3.1: Metal Ion Contents in Pulp after each Step of the Sequence (ODL Tembec Pulp)

Metal ion, ppm	ODL Pulp	P	Pcat	a	Q	aQ	aQP	aQPcat
Cu	<5	<5	75	6	<5	<5	<5	83
Mn	60	37	38	22	10	7	<5	<5
Fe	32	<5	<5	5	<5	<5	<5	<5
Al	45	24	12	46	46	20	<5	<5
Mg	510	260	270	55	416	45	35	30
Ca	2860	2350	2720	570	2200	490	260	190

Table 3.2: Metal Ion Contents in Pulp after each Step of the Sequence (ODL Lab Pulp)

Metal ion, ppm	ODL Pulp	a	Q	(aQ)	(aQ)P	(aQ)Pcat	(aQ)(OP)	(aQ)(OP)cat
Cu	<5	<5	<5	<5	<5	15	<5	110
Mn	90	10	5	<5	<5	<5	<5	<5
Fe	44	5	<5	<5	<5	<5	<5	<5
Al	106	154	46	40	18	13	<5	20
Mg	570	57	416	61	14	15	85	15
Ca	3700	600	452	570	150	130	440	50

As expected, the level of Cu ion is very low in the ODL pulp. Consequently the positive effect of the phenanthroline ligand alone on peroxide delignification is not easily explained. However low quantity does not mean zero and also iron-phenanthroline or manganese-phenanthroline complexes may be formed and may have an effect on delignification.

This pulp is rather rich in manganese and iron which are known to decompose hydrogen peroxide very efficiently. Magnesium cations are coming from the magnesium sulphate

($MgSO_4$) added as a cellulose protector in oxygen delignification. The presence of high levels of magnesium should be beneficial to peroxide stability in alkaline medium[25]. The other cations should not cause any problem in peroxide delignification. Their only influence could be on the Cu-phenanthroline complex, which may be decomposed by other cations that would have a stronger affinity for the phenanthroline ligands or be present in larger quantity. But copper-phenanthroline is a very stable complex[26].

It is shown that the (a) treatment eliminates most of iron ions and a substantial part of manganese ions. Moreover it reduces the content in calcium and magnesium. (Q) is better for the removal of manganese but has no action on calcium and magnesium. The most important point is that the combination of (a) and (Q) reduces manganese and iron ions to the lowest amounts. This is likely the reason for the good performance of aQP (Table 3.1). When the catalyst is added to the pulp, the pulp after treatment is enriched in copper which must belong to residual Cu-phenanthroline complex. The same conclusions can be drawn from the findings of Table 3.2. More particularly it is shown that the (aQ) pre-treatment, made in a single operation, removes the metal ions in a very efficient manner.

Although these results should be viewed with caution given the difficulty of having a homogeneous sampling for metal analysis and of avoiding any contamination, it seems that the interesting results given by the combination of (a) and (Q) pre-treatments are due to proper elimination of the transition metal ions.

3.3.4 C. Analysis of the Content of Pentosan after each Step of the Sequence

The objective of this work is not only to produce a fully bleached (90% brightness) pulp at zero kappa number; the pulp should also exhibit a very low content in hemicelluloses. In eucalyptus kraft pulp most of the hemicelluloses are polymers of C5 sugars (pentose). Therefore it is relevant to measure the pentose (Xylose, Arabinose) content in pulp. Pentosans are quantitatively transformed to furfural by boiling in 3.85 N HCl acid, which is collected in the distillate and determined colorimetrically with orcinol-ferric chloride reagent (for details see chapter-5 ‘Methods’).

It is expected before the experiments that decrease in DPv must be parallel to the pentosan content in pulp. Pentosan in pulp must be removed because xylans are more reactive than cellulose. Results are given in Figure 3.18.

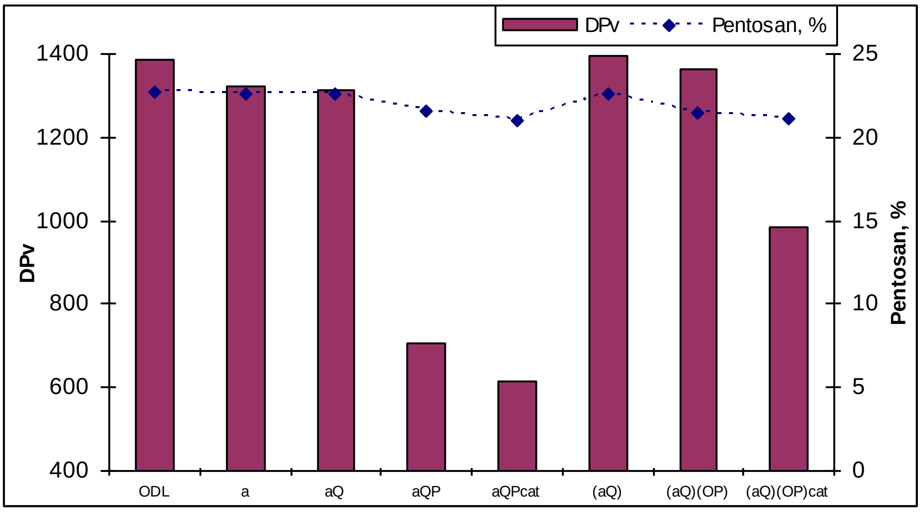

Figure: 3.18. Pentosan Content after each Step of the Sequence

Results in Figure 3.18 show that the reductions in pentosan and DPv are not parallel. In comparison with DPv reduction, pentosan reduction is almost negligible (maximum 10% for the better sequence i.e., (aQ)(OP)cat). Therefore the pentosan amount in the treated pulps remains at a high level (about 20%). It has to be noted that the catalyst does not help the removal of xylan despite its strong effect on the carbohydrate depolymerisation.

3.4 Conclusions

The oxygen delignified eucalyptus kraft pulp can be bleached to 80% ISO brightness with 3.0 kappa number by a hydrogen peroxide/oxygen treatment (OP) catalysed by Cu-phenanthroline and proceeded by a metal ion removal step. Residual HexA contribute for 2/3 to the final kappa number. Residual lignin is therefore very low.

The treated pulp suffers from a rather low DPv and a high level of residual hemicelluloses. According to what was found in this study, it does not seem that an increase in the charge of catalyst nor of sodium hydroxide would modify the result. The only parameter which could make the delignification more powerful is the charge of hydrogen peroxide. However this is not going to reduce the content in hemicelluloses and to lead to a higher DPv. Finally, the addition of oxygen to Pcat has a marginal beneficial effect. Brightness gain, 2-3 %ISO has been observed in the pulp.

The implementation of an efficient pre-treatment which eliminates most of the transition metal ions (aQ) is a pre-requisite. In that case the loss in DPv is caused mainly by the presence of the catalyst. The pulp obtained after the peroxide treatment without catalyst has kept a DPv value close to that before peroxide bleaching.

In the next chapter post-treatments will be performed in an attempt to prepare a pulp which will meet the quality targets in terms of brightness, purity and DPv of cellulose for chemical purposes.

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CHAPTER – 4

PREPARATION OF PURE CELLULOSE WITH A PROCESS CONTAINING A CATALYSED PEROXIDE STAGE

4. Production of Pure Cellulosic Pulp

4.1 Introduction

Peroxide delignification alone has not the capability to produce a fully bleached pure cellulose pulp from an oxygen delignified eucalyptus kraft pulp. Even though the Cu-phenanthroline catalyst improves the delignification power of hydrogen peroxide, but the process does not lead to produce pure cellulose. Entire lignin is not removed; some hexenuronic acids (HexA) and most of the hemicelluloses remain in the pulp. Moreover the better delignification is obtained at the expense of a very serious viscosity (DP) loss which may limit the range of potential application of cellulose.

The purpose of the work described in this chapter is to find the appropriate post treatments which will make it possible to produce pure cellulose.

4.2 Experimental Procedures

Most of the experimental procedures have been described in the previous chapter. Several new treatments have been applied:

4.2.1 Cold Caustic Extraction (NaOH Treatment) (E)

An 8% soda solution (80 g/L) is prepared with distilled water. 20 g of (o.d.) pulp, placed in a beaker, is mixed with the caustic soda solution at a consistency of 10%. Mixing is assured by an overhead propeller rotating at 300 rpm for one hour at room temperature. Then the pulp is washed with distilled water and filtered through filter no. 1 until neutral pH. After filtration, pulp is air dried (or kept wet) and stored for further experiments or analyses[1, 2].

4.2.2 Ozone Bleaching (Z)

30 g of oven dried pulp is taken for each experiment. When the purpose is delignification, ozonation is normally carried out at acidic pH. Here the objective is to remove the hexenuronic acids which are the main contributors to the residual kappa number. Ozonation is thus performed at neutral pH. Working under neutral conditions has already been proposed when ozone is used in a final bleaching stage[3] and is easier when it comes to industrialization. Pulp is disintegrated and filtered as before. Then, it is dewatered by centrifugation to a consistency of 35-40% and fluffed in a fluffer (see principle in the chapter 5 “Material and

Methods"). Fluffed pulp is introduced into the ozone reactor and a pre-decided amount of ozone is passed. After ozonation, the pulp is washed and air dried.

4.3 Results and Discussions for Production of Pure Cellulose

4.3.1 Tentative Removal of the Hemicelluloses with a Cold Caustic Soda Treatment

The hemicelluloses present in eucalyptus kraft pulp are mainly xylans. As seen before, their content is around 25% on pulp[1]. It was found that none of the treatments tested so far are able to reduce this content.

The removal of residual xylans is very difficult. They resisted to the kraft cooking conditions. One reason is that the peeling reaction, which is supposed to eliminate most of the hemicelluloses, is working well with the glucomannans but only marginally with the xylans[4]. The only acting reaction on the xylans is the alkaline hydrolysis which reduces their average DP, but not enough to make them soluble[4].

Oxidation of the xylans should in theory be one way to make them more soluble by the formation of new carboxylic groups. Such an oxidation was expected to happen during catalysed peroxide delignification, because it is known that the carbohydrates in general are oxidized by this system[5, 6]. The results in the previous chapter showed that this was not the case. It might be that xylans are not prone to oxidation, contrary to cellulose, because of their lack of primary alcohol groups which are easier targets than secondary alcohol groups during most of the oxidation processes. Another way which has been described is the solubilization of the xylans in a cold concentrated caustic soda solution[1, 2]. Xylans naturally possess some carboxyl groups which explain their solubility in such solutions. This approach is investigated in the following.

After delignification with peroxide, pulps (ODL-Lab 1) are treated with a concentrated cold caustic soda solution to remove as much hemicelluloses as possible. The results are given in figures 4.1, 4.2 & 4.3.

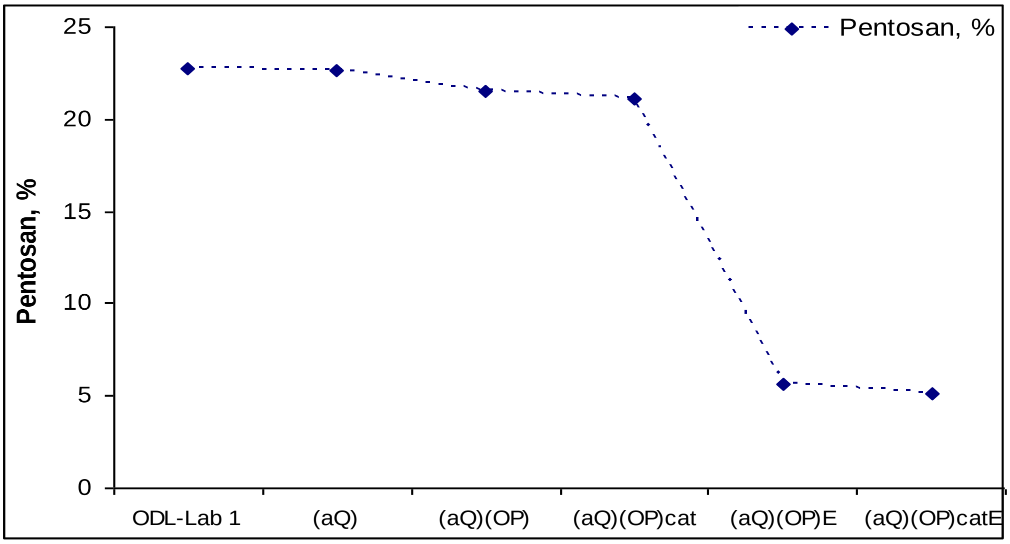


Figure 4.1: Effect of the Cold Caustic Soda Treatment on the Pentosan Content of the (aQ)(OP) and (aQ)(OP)cat ODL-Lab 1 Treated Pulps

Figure 4.1 shows that most of the xylans get solubilized during the caustic soda treatment. The fact that the catalyst has been present in the peroxide stage has no impact on the result. After extraction the level in pentosans is around 5% which is the target set at the beginning of this project.

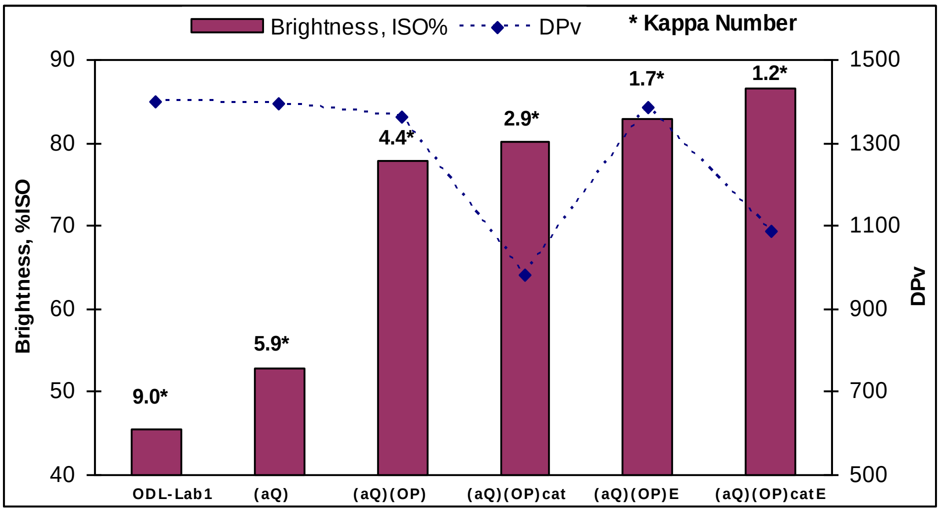


Figure 4.2: Effect of the Cold Caustic Soda Treatment on the Kappa Number, Brightness and DPv of the (aQ)(OP) and (aQ)(OP)cat ODL-Lab-1 Treated Pulps

After the E treatment, around 60% kappa reduction is observed (Figure 4.2) which could be due to lignin and/or HexA removal. Kappa number values as low as 1-2 are reached. At the same time brightness is slightly improved and 82-85 % ISO is obtained depending on the presence of catalyst in (OP) or not. The DPv is interestingly at the level of that of the ODL pulp when no catalyst is added to (OP). Part of this result is certainly due to the removal of lower molecular weight xylans which do not contribute any more to the value of the DPv. In the case where some catalyst is present in (OP), the DPv is again at a lower value but it becomes higher than before the E treatment, likely for the same reason as previously explained. The fibre yield of the E treatment is close to 85% on pulp, which corresponds roughly to the loss in pentosans indicating that the E treatment is very selective to the hemicelluloses.

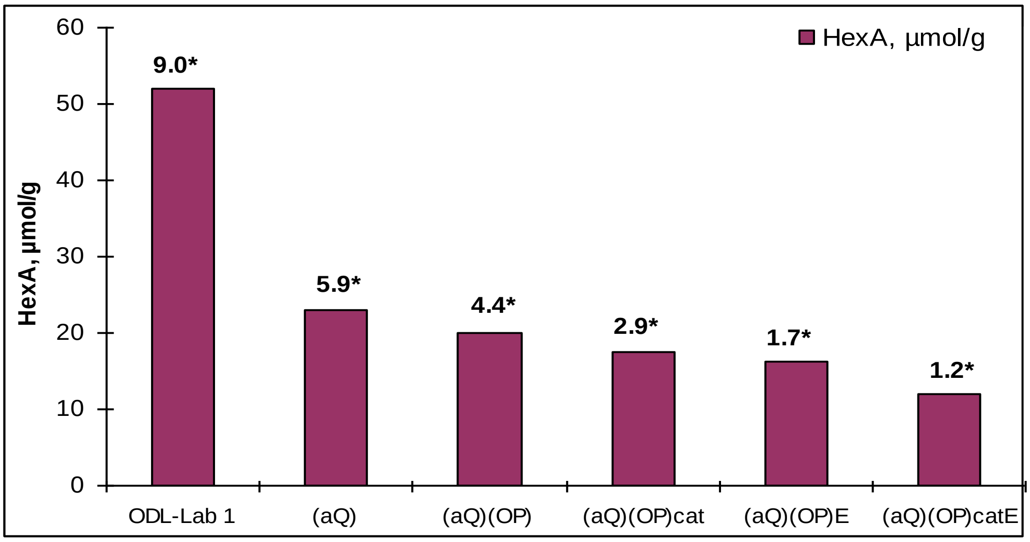


Figure 4.3: Effect of the Cold Caustic Soda Treatment on the Amount of HexA of the (aQ)(OP) and (aQ)(OP)cat ODL-Lab 1 Treated Pulps

Figure 4.3 shows that the HexA are slightly solubilized by the caustic soda extraction. It is interesting to note that the residual amount of HexA is 17 µmol/g without catalyst and 12 µmol/g with catalyst, contributing to 1.7 and 1.2 kappa number units respectively (see previous chapter). Therefore the residual kappa number would be exclusively given by HexA still present in pulp. The conclusion is that there is no lignin left in the pulp after the caustic extraction stage. The conclusion is that there is virtually no lignin left in the pulp after the caustic extraction stage. The fact that most of the xylans are removed by the cold caustic extraction without any parallel decrease in the number of HexA is quite unexpected. It could mean that the xylans with HexA groups have a higher molecular weight than those without, or that solubilization is essentially due to peeling reaction.

The removal of the HexA must be achieved to get pure cellulose. Since the HexA have a carbon-carbon double bond they should react very easily with ozone[7]. This is the subject of the next part.

4.3.2 Implementation of an Ozone Treatment as a Final Bleaching Stage

An ozone treatment was implemented after (aQ)(OP)E and (aQ)(OP)catE to oxidize the HexA groups. Contrary to what is practiced in mills using ozone in bleaching[8], it is chosen to work under neutral conditions. Although it is known that ozone delignification is working better in acidic conditions (pH 2), where ozone stability and selectivity are better, the addition of sulphuric acid to such a low pH is a complication and a drawback in terms of chemical cost and effluent management. It has been shown that ozone, when applied at the end of bleaching where very few amount of lignin is left, has a marked bleaching action under neutral conditions, without any penalty on cellulose viscosity[3]. Its action is then limited to the elimination of some residual chromophores. This should be the case here after (aQ)(OP)E and (aQ)(OP)catE. Ozonations using 0.1 and 0.2% ozone were carried out. Results are given in figure 4.4.

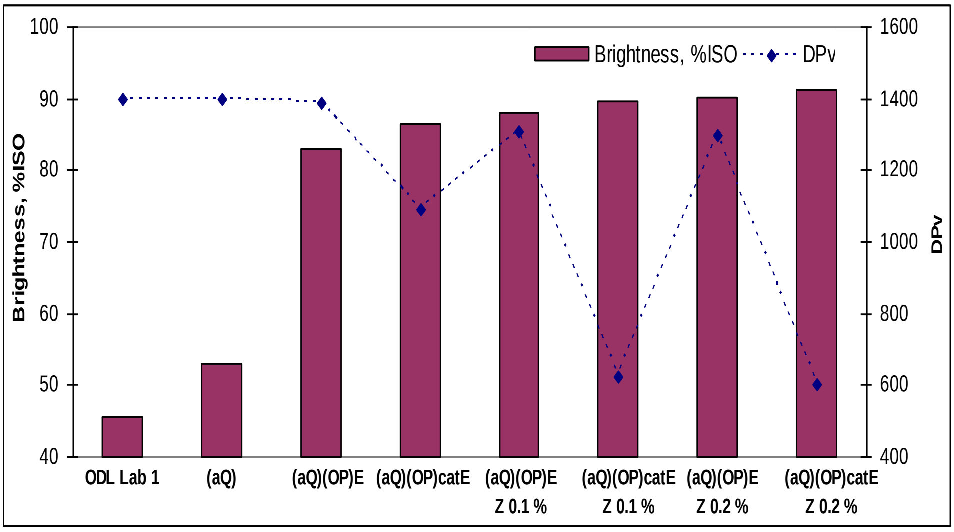


Figure 4.4: Effect of the Ozone Treatment on Brightness, Kappa Number and DPv of the (aQ)(OP)E and (aQ)(OP)catE ODL Treated Pulps

Results in figure 4.4 indicate that 0.1% to 0.2% ozone is sufficient to lead to 90% brightness and the quantification of the HexA content (figure 4.5) shows that at least half of the residual HexA disappears during the Z stage (0.2% ozone). After ozonation, HexA content is at the detection limit (5µmol/g).

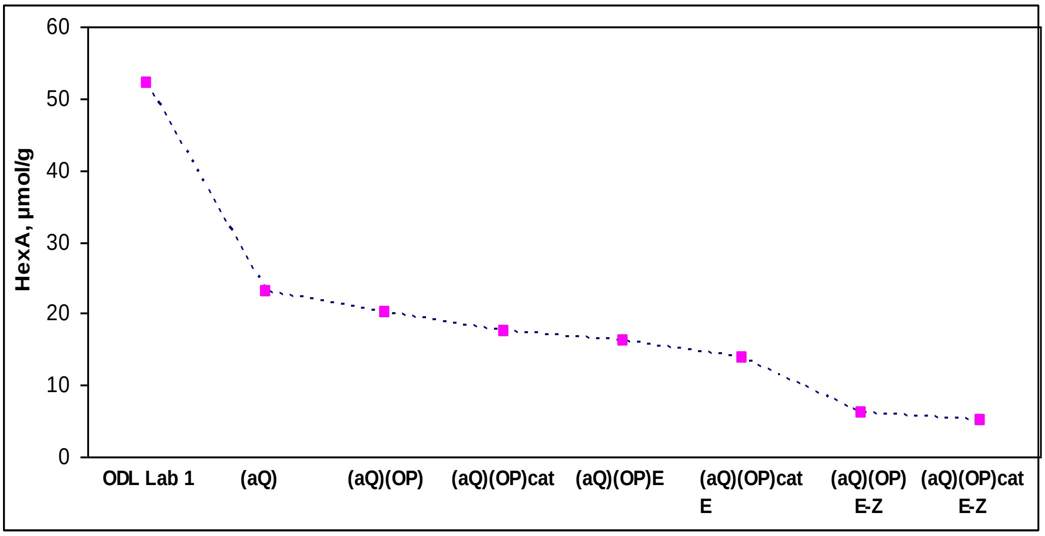


Figure 4.5: Effect of Ozone Treatment (0.2% O_3) on the HexA

Unfortunately, figure 4.4 also shows that the cellulose DPv is further reduced in the case where the catalyst is present in (OP). The reason why cellulose is depolymerised by ozone only in that case is not known

Such effect could be attributed to the ozone decomposition into radicals detrimental for cellulose. As a matter of fact ozone is known to be instable with metals under neutral or alkaline conditions[9]. Metal ions content was measured after the different bleaching treatments. Results are given in Table 4.1.

Table 4.1: Metal Ion Content in (aQ)(OP) and (aQ)(OP)cat Pulps after E and Z Stages (Pulp- ODL-Lab 2)

Metal ion, ppm	ODL-(aQ)(OP)-E	ODL-(aQ)(OP)cat-E	ODL-(aQ)(OP)-E-Z	ODL-(aQ)(OP)cat-E-Z
Cu	<5	<5	<5	<5
Mn	<5	<5	<5	<5
Fe	<5	<5	<5	<5
Al	<5	30	20	<5
Mg	80	25	25	30
Ca	200	40	65	65

The content in Cu, Fe and Mn ions may be very low since the pulp is washed with SO_2 water after (OP) and (OP)cat stages. As shown in table 4.1., there is no copper-phenanthroline complex or free copper left in the peroxide treated pulp since the copper content is less than 5 ppm. Thus copper is not the origin of ozone decomposition. The DPv drop may be mainly attributed to the reaction of ozone with phenathroline. To study this hypothesis, free copper, phenanthroline, or copper-phenanthroline complex are voluntarily added to the pulp (phen-0.1%, Cu-0.045%) before the Z stage carried out with 0.2% O_3 dose. Results are given in figure 4.6.

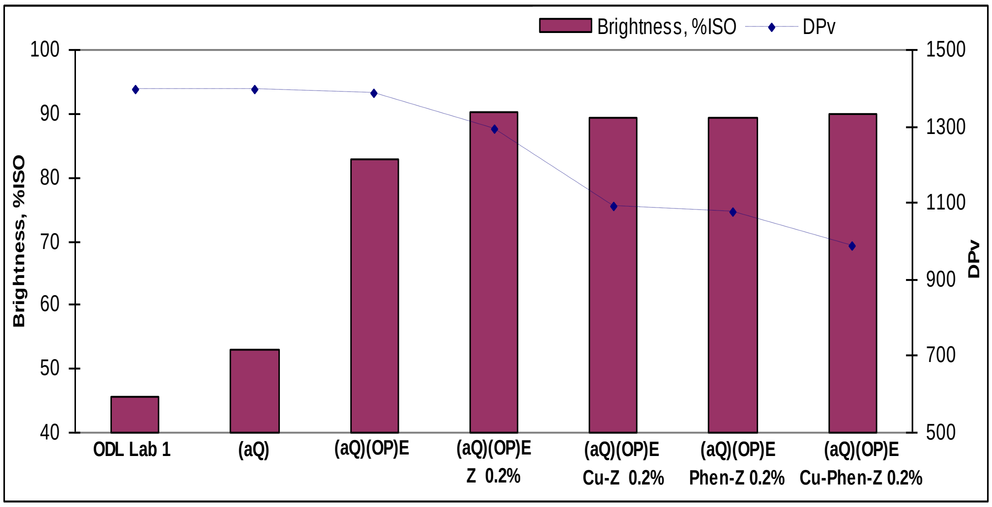


Figure 4.6: Addition of Cu^{2+}, Phenanthroline and Cu-Phenanthroline in (aQ)(OP) Pulps after E and prior to Ozone Treatment

The results in figure 4.6 indicate that when either copper, phenanthroline, or Cu-phenanthroline complex are added to the pulp, some DPv reductions are observed after the Z stage. In the presence of copper and/or phenanthroline, ozone probably contributes to the formation of radicals detrimental to the cellulose. Since the fully bleached pulp does not contain any copper (free copper or complexed copper with phenanthroline) (table 4.1), it is supposed that the phenanthroline ligand alone may give radicals when it reacts with ozone. The presence of the phenanthroline ligand (or one derivative) in the partially bleached pulps was assessed through nitrogen titration (after SO_2 washing). Results are presented in table 4.2.

Table 4.2: Nitrogen Content in the (aQ)(OP) and (aQ)(OP)cat Pulps

Pulps	Nitrogen, ppm
ODL-Lab 1	105
(aQ)	115
(aQ)(OP) / (aQ)(OP)cat	105 / 145

** Pulp samples were not washed with SO_2-Water*

When the catalyst was added in the sequence, the pulp contained more nitrogen (145 ppm with the catalyst compared to 105 ppm without it) indicating the presence of the phenanthroline ligand (table 4.2). A UV-visible analysis of phenanthroline in aqueous solution, without any fibre, with and without ozone addition (with different molar ratios between ozone and phenanthroline), confirms that phenanthroline is partially degraded and converted to (coloured) compound(s) by ozone (Figure 4.7). There is no proof that radicals are formed during phenanthroline oxidation. However since cellulose is degraded one may suggest that radicals[9, 10] are produced through the following mechanistic pathway;

$O_3 + \text{Phen} \rightarrow O_3^{-} + \text{Ox Phen}$

$O_3^{\circ -} + H^+ \rightarrow HO^{\circ} + O_2$

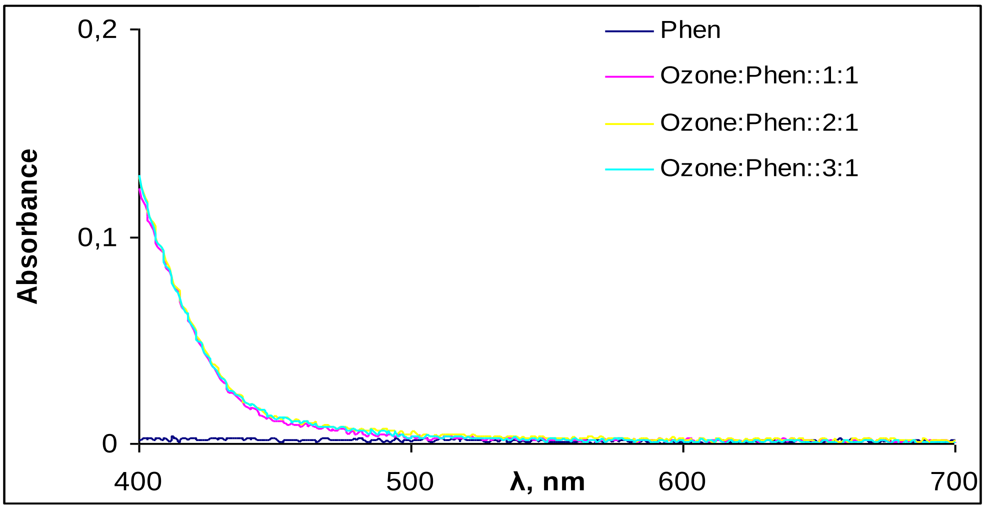


Figure 4.7: UV-Visible Analysis of Phenanthroline in Aqueous Solution before and after Ozone Addition

(Conditions: Phenanthroline – 13.76.10^{-5} moles, ozone - 13.76.10^{-5}, 27.52.10^{-5}, 41.28.10^{-5} moles, Temperature – Ambient, pH-Neutral)

4.3.3 Conclusion –the Sequence for Pure Cellulose Production

In conclusion, the (aQ)(OP)cat EZ sequence makes it possible to reach the targets for pure cellulose grades. A fully bleached cellulosic pulp with a low amount of residual hemicelluloses (5% by weight on pulp) and without hexenuronic acid can be obtained. The DPv of the cellulose is at the lower side of the target interval, which means that some cellulosic materials cannot be produced.

The low DPv is entirely the result of the use of the catalyst. Avoiding the addition of the copper-phenanthroline catalyst does not change the bleaching efficiency of the sequence substantially (1 brightness unit loss), despite the fact that delignification is less during the P stage. It does not change either the quantity of residual hemicelluloses or the removal of the hexA groups. However the DPv is much better. The choice of adding the catalyst or not will depend on the target DPv, depending on the final destination of the cellulose.

In the next part of this chapter, some attempts are made to render the process more efficient or simpler.

4.4 Attempts to Make the Process Simpler and to Improve its Efficiency

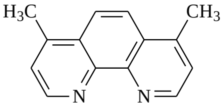
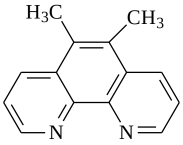
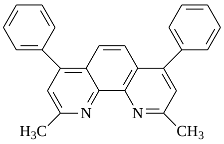
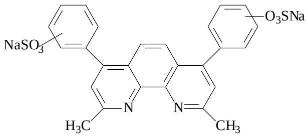
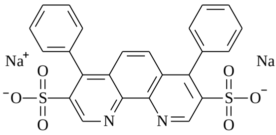
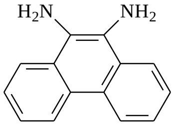
4.4.1 Use of Different Ligands

Although the copper-phenanthroline complex is described as an efficient catalyst in the oxygen oxidation of alcohol groups into carbonyl[11] which should favoured the alkaline delignification, the activity of this catalyst in the proposed bleaching sequence remains moderate.

Copper(II)-poly pyridine complexes are already described as efficient species to catalyze the oxidation of lignin model compounds[12]. The catalytic activity highly depends on the complex structure (geometry, steric surrounding provided by the ligand, presence of electron donor or acceptor groups, etc) [13]. Consequently the nature of the ligand should have a marked effect on the catalytic efficiency. Some other ligands, known to form active catalyst with copper (II), were then tested in an attempt to improve the process. 6 ligands were selected (table 3.3). 5 among them are substituted phenanthrolines at different positions with methyl or phenyl groups (ligands i to vi) and the last ligand is a phenanthrene already described as an active catalyst to oxidize alcohols when combined with copper (II) [14]. Alkyl groups, known as electron donor groups[15], may favor the copper reduction during the oxidation reaction. The bulky phenyl groups increase the hydrophobic character of the ligand which may favor lignin oxidation. However the bulky phenyl groups may also hinder the complex formation with copper. Hydrophilic sulfonated phenyl phenanthrolines were also selected for comparison.

The activity of these complexes was tested in P delignification of the pulp substrate.

Table 4.3: Selected Ligands for the Copper Complex used to Catalyse the Hydrogen Peroxide Delignification

	Name of Ligands	Chemical Formula
i	4, 7-dimethyl phenanthroline (4, 7-DMP)	
ii	5, 6-dimethyl phenanthroline (5, 6 -DMP)	
iii	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP)	
iv	2,9-dimethyl-4,7-diphenyl-1,10- phenanthroline disulfonic acid, sodium salt (BCS)	
v	4,7-diphenyl-1,10-phenanthroline disulfonic acid, sodium salt trihydrate (BPS)	
vi	9, 10-diamino phenanthrene (Daphen)	

The copper complexes were prepared with a copper to ligand molar ratio of 1:2 as already done with the copper phenanthroline complex. Results are given in figure 4.8 and compared with phenanthroline (Phen).

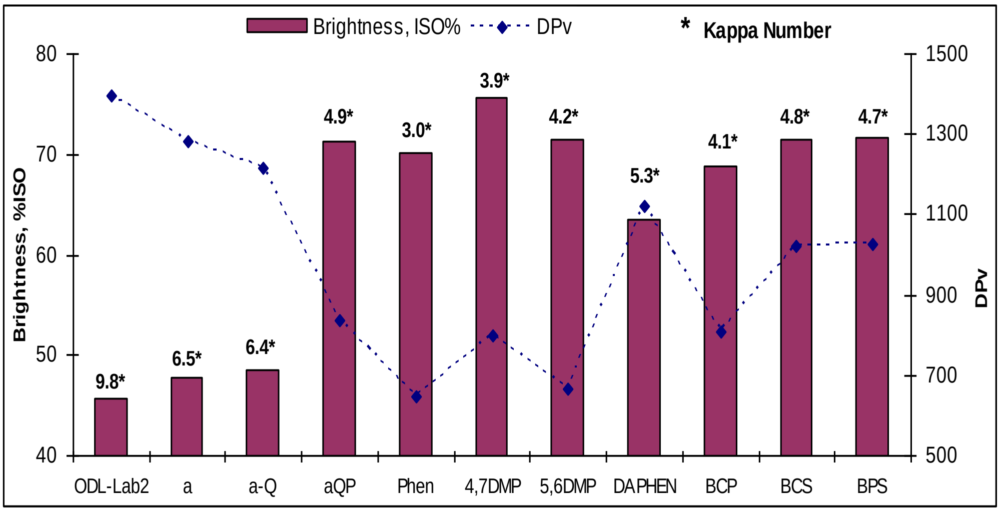


Figure 4.8: Effect of the Addition of Copper-Ligand in the P stage of the aQP Bleaching Sequence.

The catalytic activity of the different complexes is evaluated through the kappa number measurement. Results given in figure 4.8 clearly show that phenanthroline is by far the best ligand among all for delignification since it leads to the lowest kappa number (3.0). Contrary to what was observed in chapter 2, where a lignin model was used as substrate, 4,7- dimethyl or 5,6-dimethyl phenanthrolines do not exhibit better activity, whatever the substitution position. The presence of alkyl groups on phenanthroline could lead to a steric overcrowding rendering more difficult the copper oxidation and the access to the substrate. The sulfonation of the ligand, improving its solubility, has also no effect on the activity of the phenyl phenanthroline complexes. Despite interesting results observed for the oxidation of the veratryl alcohol[14], the copper-Daphen system is not an activator of hydrogen peroxide delignification since the kappa number is higher than that obtained after a conventional P stage. Previous studies on oxygen delignification already found that Daphen is a singular ligand, insoluble in the alkaline delignification medium, able to improve the oxidation of a soluble non phenolic lignin model[14] but inactive on a pulp substrate.

Some previous studies, including one thesis conducted in our laboratory[16], showed that copper-polymine complexes were fairly active in oxygen delignification This explained that addition of oxygen in the P stage (i.e.(OP) stage) improved the catalytic activity of the copper-phenanthroline ligand (chapter 3). Some experiments with addition of complexes in (OP) were performed. Only phenanthroline and methylated phenanthrolines were tested. Results are presented in figure 4.9.

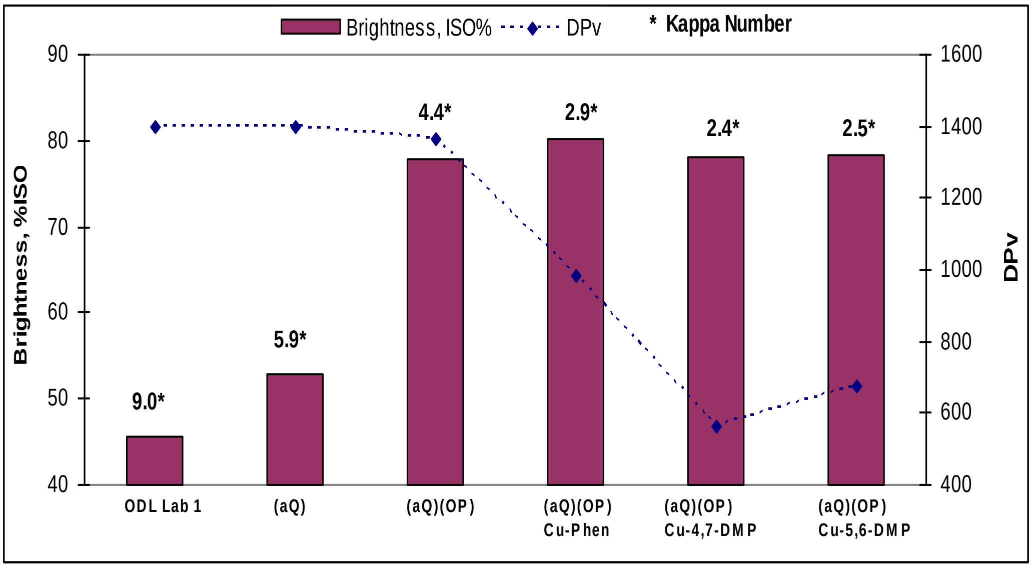


Figure 4.9: Effect of the Addition of Copper-Phenanthrolines (Phen, 4, 7-DMP and 5, 6-DMP) in the (OP) stage of the (aQ)(OP) Bleaching Sequence.

Using copper complexes with 4, 7 DMP and 5, 6 DMP ligands instead of un-substituted phenanthroline slightly improved delignification as the kappa number decreased by 0.4 to 0.5. Thus methylated phenanthrolines in positions 4, 7 and 5, 6 are of interest only when oxygen is present. The reason of the better performance of the methylated phenanthroline in a (OP) must reflect a better activity of these complexes in oxygen delignification. Explanation has still to be found. In parallel brightness is also slightly enhanced. Unfortunately cellulose is more degraded, since the DPv is substantially lower. Either the copper-4, 7 DMP and copper-5,6 DMP complexes are more active on carbohydrate oxidation than the copper-phenanthroline complex (formation of more carbonyl groups on cellulose), or more radicals are generated with these two substituted complexes. Consequently, phenanthroline was selected for the rest of the work.

4.4.2 Effect of the Hydrogen Peroxide Reaction Time on the Catalysed Delignification

Another way to improve the performances of the process is to optimise the reaction conditions of the catalysed delignification. Several parameters such as soda, hydrogen peroxide doses and temperature were already optimised in chapter 3. Only reaction time was not studied although oxidation trials conducted on a lignin model compound (chapter 2) showed that the oxidation of the veratryl alcohol by H_2O_2 with the copper-phenanthroline complex takes place in a few minutes. Then the question arises whether the catalysed peroxide delignification of pulp could be performed in less than the 2 hours used in the previous trials. The effect of the reaction time on P and Pcat stages, with or without the aQ pre-treatment, carried out on the oxygen de-lignified pulp (ODL) is thus studied. Results are shown in figures 4.10 and 4.11.

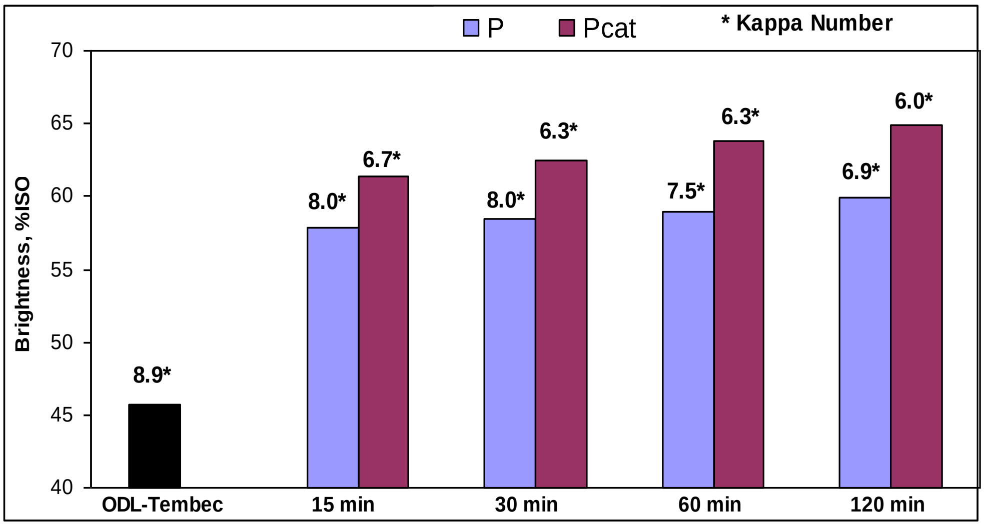


Figure 4.10: Effect of the Reaction time on the P and Pcat stage Performances

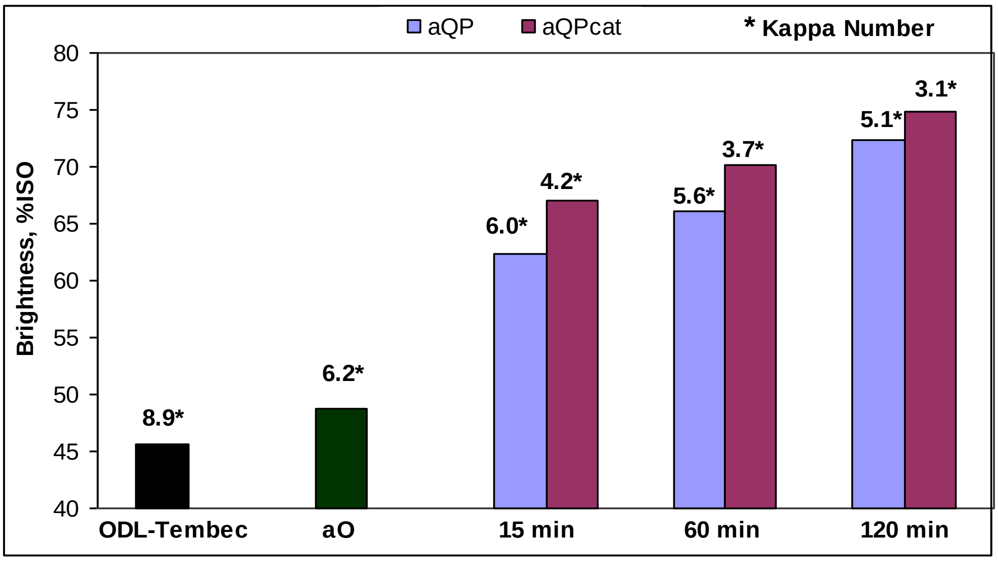


Figure 4.11: Effect of the Reaction Time on the aQ-P and aQ-Pcat Sequence Performances

Table 4.4: Residual Hydrogen Peroxide in Different Time Intervals

Time, minutes	P, %	Pcat, %	aQP, %	aQPcat, %
15	3.6	0.5	3.8	0.5
30	2.8	0.3	3.0	0.4
60	1.2	0.2	1.7	0.3
120	0.5	0.1	0.2	0.1

Kappa number values presented in figures 4.10 and 4.11 clearly show that P delignification is more efficient in the presence of the catalyst and that from the beginning of the reaction. Indeed most of the delignification takes place in the early stage (15 minutes) of the catalysed treatment. Beyond, the kappa number decreases slowly and regularly. Moreover hydrogen peroxide is almost entirely consumed (almost 99.5% H_2O_2 consumption) before the first 15 minutes when the catalyst is present. To explain the slow decrease in kappa number when no peroxide is present, it should be admitted that either oxidized lignin dissolution is a slow process or oxygen in air takes the role of the oxidant in the catalytic system, assuring the re-oxidation of the copper (I) complex[11]. The rapid hydrogen peroxide consumption is probably due to a reaction of the copper complex with H_2O_2.

Without catalyst the situation is somewhat different. Delignification is not as fast since kappa number after 15 min reaction is still high, but its evolution is more regular. Hydrogen peroxide decomposition is slightly slower since peroxide residuals after 15, 30, 60 and 120 minutes are 3.6, 2.8, 1.2 and 0.5% respectively (Table 4.4).

The aQ pre-treatment improves both P and P cat stages with a greater benefit for the catalytic activity since the kappa number difference between aQP and aQPcat is higher than between P and Pcat. With the aQ pre-treatment, hydrogen peroxide is still totally consumed at the early stage of the reaction when the catalyst is present meaning that the pre-treatment cannot stabilise H_2O_2 in the catalysed reaction.

The evolution of brightness is parallel to that of kappa numbers. However the difference between aQP and aQPcat is smaller than would be expected from the difference of the kappa values. It is quite possible that the colour of the copper complex handicaps the evolution of brightness. Longer reaction times for P and Pcat stages (figure 4.12) were also tested after (aQ) pre-treatment (Remember; in figure 4.10 & 4.11 the pre-treatment was ‘aQ’ i.e. acid stage followed by chelation. But in figure It is (aQ) i.e., acid stage and chelation in a single stage).

Again although most of the reaction takes place within 1 hour with the catalyst, there is a slight benefit to extend the time to 2-3 hours for both delignification and bleaching. With (aQ)P it is remarkable to gain more than 5 brightness points between 1 hour and 3 hours reaction time. This is clearly an indication that in (aQ)P, hydrogen peroxide is more stable than in any other peroxide treatment tested in this study, probably due to the efficient metal ion removal during (aQ). For (aQ)Pcat the brightness gain is lower certainly likely because, as already mentioned, of the presence of residual copper(II) at the end of the sequence giving a bluish colour to the pulp.

Considering the cellulose DPv evolution during the (aQ)P treatment, it appears that carbohydrate degradation occurs beyond 1 h of treatment. This justifies stopping the reaction after 2 hours maximum. With the catalyst, cellulose degradation is much stronger as already seen. While most of the DP loss takes place after 2h in (aQ)P, in (aQ)Pcat the DP loss has entirely occurred within 2h, which again reflects the faster kinetics when the catalyst is present.

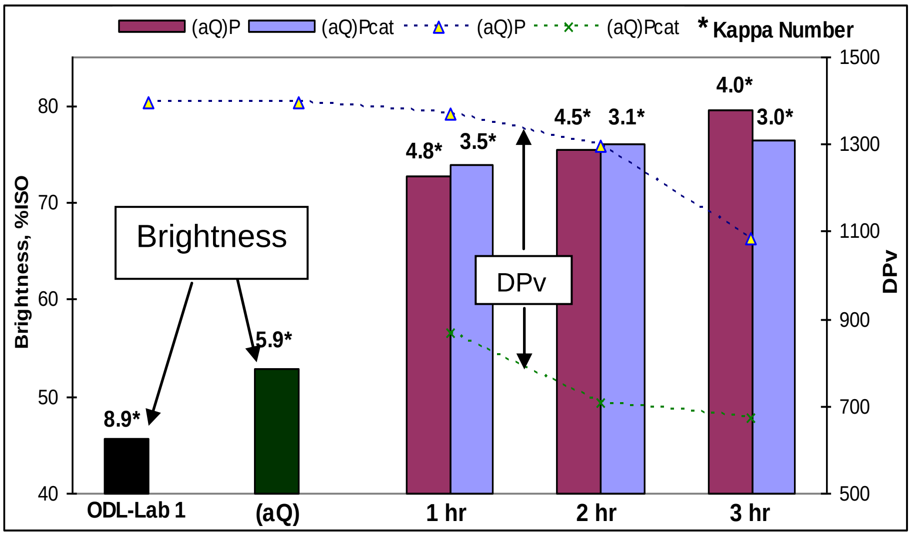


Figure 4.12: Effect of the Reaction Time on the (aQ)-P and (aQ)-Pcat Sequence Performances

4.4.3 Effect of the Hydrogen Peroxide Charge Splitting on the Catalysed Delignification

In chapter 2, it has been shown that the addition of copper-phenanthroline to a hydrogen peroxide solution free of fibre causes a rapid decomposition of the latter. It would explain why hydrogen peroxide is rapidly consumed during pulp delignification well before the end of the stage. Consequently, as mentioned earlier, part of the Pcat stage proceeds without any peroxide left. One way to alleviate this problem would be to split the addition of hydrogen peroxide into two or three parts (Chapter 2). This has been tested in the following. The oxygen delignified pulp (ODL-Lab 1) was treated by (aQ)P for 1 to 3 hours with a total of 2% H_2O_2 on pulp according to the strategy given in table 4.5. Results are presented in figures 4.13, 4.14 and 4.15.

Table 4.5: Strategy of Hydrogen Peroxide Addition in the Catalysed Peroxide Delignification

Total P time	First addition 0.66% H_2O_2	Second addition 0.66% H_2O_2	Third addition 0.66% H_2O_2
1 hour	0 min	20 min	40 min
2 hours	0 min	40 min	80 min
3 hours	0 min	60 min	120 min

**Other reagents are added at the beginning of the reaction*

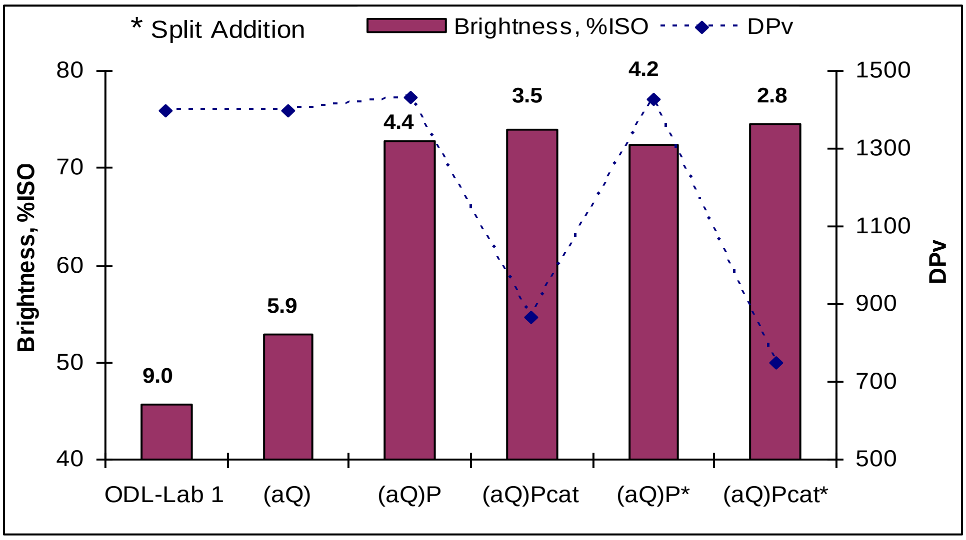


Figure 4.13: H_2O_2 Charge Splitting – 1 hour Reaction Time

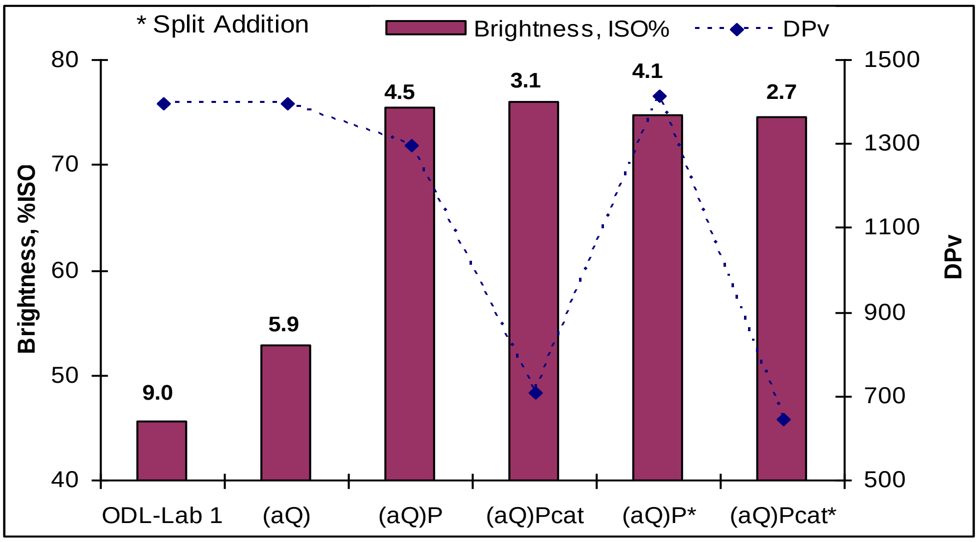


Figure 4.14: H_2O_2 Charge Splitting – 2 hours Reaction Time

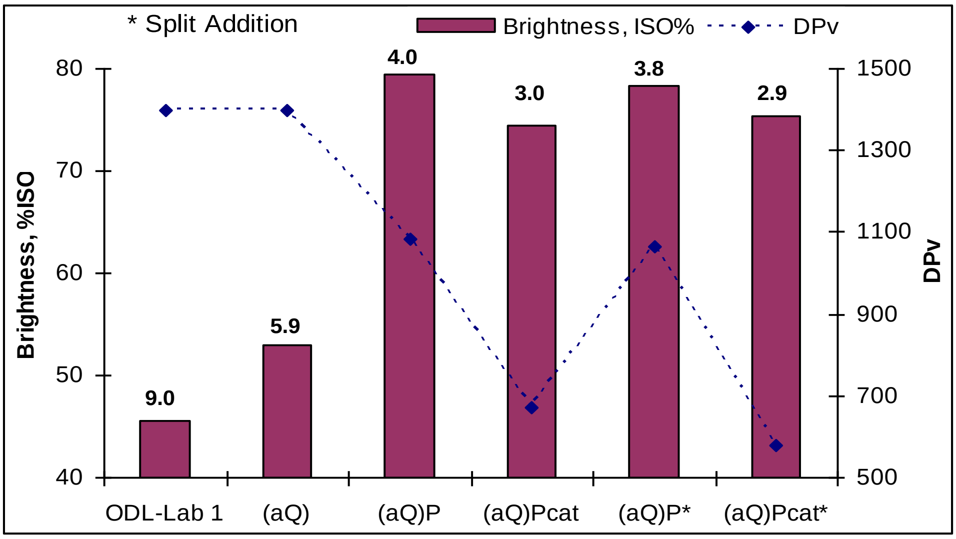


Figure 4.15: H_2O_2 Charge Splitting – 3 hours Reaction Time

The results show some substantial improvement of delignification rate in the case of a total reaction time of 1 hour (figure 4.13). The splitting of the peroxide charge makes it possible to reduce the time of the catalysed peroxide stage down to 1 hour, at equal delignification performance to that obtained in 3 hours, with less detrimental effect on cellulose DPv (figure 4.15). However the charge splitting is an industrial complication which might not be justified, given the relatively modest magnitude of the improvement. The benefit is less for longer reaction times (figures 4.14 and 4.15). Moreover the fact that cellulose viscosity is decreased further when applying this strategy in Pcat, shows again that cellulose degradation is roughly parallel to lignin removal.

4.5 Design of the Process Selected to Produce Pure Cellulose

To summarize all the previous results, a full process has been successfully designed to produce purified cellulose from eucalyptus kraft pulp. This process is intended to be placed after the oxygen delignification stage. The main stages of the process and the cellulosic pulp properties are given in table 4.5. It has been found that the process should include the following steps:

- (aQ) pre-treatment of ODL pulp (preferably in one stage), which removes most of the hexenuronic acids and the transition metal ions. The latter effect explains why the pulp becomes then very reactive with hydrogen peroxide.

- P treatment with a quantity of H_2O_2 of the order of 2% on pulp (in our case). This treatment is aimed at removing most of the lignin. Due to the (aQ) pre-treatment, no substantial degradation of cellulose is observed when the catalyst is absent. Adding copper-phenanthroline improves the P stage. However this occurs at the expense of some cellulose depolymerisation. Some substituted phenanthroline gives slightly better delignification results than un-substituted phenanthroline but only when oxygen is added in the P stage (OP). Unfortunately the better delignification is accompanied by an enhanced depolymerisation of cellulose.
- E treatment (cold caustic extraction) which dissolves most of the residual hemicelluloses. The quantity of caustic soda is such that it will be necessary to recover or recycle it in one way or another. It happens that the E treatment dissolves also the residual lignin. Then after E, the measured kappa number is due to residual hexenuronic acids.
- Z treatment performed in neutral condition with a low ozone charge (0.2% on pulp). Most of the residual hexenuronic acids are degraded and dissolved during this treatment.

As shown in table 4.6, the cellulosic pulp meets the quality targets defined at the start of the study. Cellulose is slightly purer when copper-phenanthroline is added in the P stage. However the DPv is affected dramatically by this catalyst, which may limit the applications. Further characterizations are needed to be able to conclude about the suitability of the cellulose to be processed into interesting cellulosic products.

Table 4.6: Process stages and the cellulosic pulp properties

Sequence	Brightness, % ISO	Intrinsic Viscosity, mL/g	DPv	Pentosan, %	HexA, µmol/g
(aQ)(OP)-E-$Z_{0.2\%}$	90.3	874	1295	5.5	6
(aQ)(OP)cat-E- $Z_{0.2\%}$	91.2	437	602	4.6	2

4.6 Characterisation of the Produced Celluloses

4.6.1 Introduction

As already reported in the literature review (chapter - 1), pure celluloses are used for the production of viscose products, cellulose ether, acetate, nitrocellulose and microcrystalline cellulose. Viscose fibres are used for textile applications (standard rayon, textile filament, lyocell), cellophane and cellulosic sponges are belong to standard grades, specialty and high grade celluloses are purer which includes chemical celluloses such as cellulose ethers and esters[17]. Depending on the cellulose grades, chemical properties are varying. Pure celluloses should contain high alpha cellulose content (cellulose material insoluble in strong alkaline solutions), low amount of minerals, and high degree of homogeneous and high degree of polymerisation.

One of the key parameters for pure cellulose is the alkali resistance (or solubility) of the material (R_{18} or S_{18}) which is an indication of the cellulose quality. Pulp Substrates issued from wood contain short chain carbohydrates, i.e. helicelluloses and degraded celluloses, and long chain carbohydrates, i.e. cellulose. All processes affecting the degree of polymerisation are detrimental to the production of pure cellulose and its end products.

The carbohydrates in pulp may be partially soluble in aqueous alkali, their solubility depending heavily on alkali concentration. A major part of the alkali soluble components are removed during the alkaline stages of pulping and bleaching. Only that part of material which is only soluble at higher concentration (i.e. higher than 10% NaOH solution) may be found in the pulp. These carbohydrates mainly consist of more - or less – oxidized hemicelluloses and strongly degrades and/or oxidized cellulose. These components have a strong influence on the pulp properties and on their end-uses, consequently the alkali solubility (S_{18}) and the insoluble residue (R_{18}), measured after pulp treatment in a 18% NaOH solution, gives an information on the cellulose quality. Lower the S_{18} (or higher R_{18}), better the cellulose quality. The relation between S_{18} and R_{18} is given in the equation 4.1[18, 19].

$$S_{18}, \% = 100 - R_{18}, \% \qquad \text{……………………….Equation 4.1}$$

4.6.2 Key Properties of Cellulose

Key parameters of different cellulosic products are given in table 4.7 and compared with those of the celluloses produced from kraft pulp after the bleaching sequence with or without the catalyst.

Table 4.7: Key Parameters Required by Special Applications of Dissolving Pulp[20] and Comparison with the Produced Celluloses from Kraft Pulp

Products	S_{18} %	Brightness, % ISO	Viscosity, mL/g
Acetate (Plastics)	1.5 - 2.0	93<	500 - 750
Acetate (Filter Tow)	2.0 - 2.5	90-92	500 - 750
Nitro cellulose	2.0 - 2.5	90-92	500 – 650
High Tenacity Filament	2.0 - 2.5	88-89	500 – 650
Ether	2.5 - 3.0	not given	250 - 750
Lyocell	3.0 - 3.5	not given	300 - 500
Textile Filament	3.0 - 3.5	90-92	400 - 600
Cellophane	3.5 - 4.0	89-90	300 - 500
Standard Rayon	3.5 - 4.0	89-90	300 - 500
Celluloses issued from kraft pulp			
(aQ)(OP)-E-$Z_{0.2\%}$	3.26	90.3	874
(aQ)(OP)cat-E- $Z_{0.2\%}$	3.43	91.2	437

Table 4.6 shows that the celluloses produced from the kraft pulp possess similar brightness, viscosity and alkaline solubility (S_{18}) as lyocell, cellophane and standard rayon. These products belong to viscose low grade applications. This last application is very interesting since the viscose market represents 3/4th of the pure cellulose world market and is in expansion[20].

Pulp produced with the catalyst has higher brightness but viscosity is very less. As already discussed the lower viscosity is due to the presence of the catalyst in the peroxide delignification. Moreover, with the catalyst, the alkaline solubility (S_{18}) does not increased contrary to what was expected, meaning that the catalysed peroxide stage is not able to remove more hemicelluloses than the conventional P stage. The action of the copper-phenanthroline complex is thus probably focused on long-chain carbohydrates, i.e. cellulose.

To follow the carbohydrate degradation, intrinsic viscosity measurement is not sufficient. Viscosity is related to the length of the cellulose chains and can be measured in different solvents, but the result is only a mean value calculated using all the carbohydrate fractions. A more suitable analytical technique was used to study in detail the effect of the catalyst on the different carbohydrate fractions, i.e. hemicelluloses and cellulose. This is size exclusion chromatography (SEC) which gives access to the molecular mass distribution of carbohydrates. The analytical method and the results are presented in the following sections.

4.6.3 Carbohydrate Molecular Mass Distribution (MMD) of Cellulosic Products - Principle

Cellulosic products contain various carbohydrates, of different chain lengths. They have a molecular mass distribution (MMD). The MMD of a polymer may be illustrated by calculating molecular mass averages of the distribution in number and in weight.

Mn, the number –average molecular mass (g/mole), is historically significant since it has been correlated with a number of polymers physical properties, before size exclusion chromatography (SEC) becomes available. It is defined as the mass of the sample in grams ∑Wi or ∑ni.Mi, divided by the number of chains present, ni, which is ∑Ni. Here Wi and ni are the weight and number of molecules of molecular mass Mi, respectively, and i is an incrementing index overall molecular mass present.

$$Mn = \sum ni.Mi / \sum ni \qquad \ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation 4.2}$$

Another molecular mass average that can be correlated with physical properties is the weight average molecular mass, Mw (g/mole), which is determined in the laboratory by size exclusion chromatography (SEC). It is defined as;

$$Mw = \sum ni.Mi^2 / \sum ni.Mi \qquad \ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 4.2}$$

The value of Mw is generally higher than Mn, except in the case of a monodisperse distribution. The ratio Mw/Mn, termed the molecular mass polydispersity or more simply, the polydispersity (PD), is a measure of the breadth of the polymer molecular mass distribution.

To determine the molecular mass (Mw) of each carbohydrate fractions, SEC equipped with light scattering detection is used (see Material and Methods).

With a viscosimetry detector, this analysis also gives access to the intrinsic viscosity, [η] (mL/g), related to the molecular massof the polymer, M, by the empirical Mark-Houwink equation:

$[\eta] = KM^a$ ………..………………………………………Equation 4.3

Where, [η] is the intrinsic viscosity of a sample dissolved in a specific solvent and M is the molecular mass. K and a are empirical parameters known for the polymer in the specified solvent[22, 23].

4.6.3. A. Size-Exclusion Chromatography

Polymer chains take various forms or conformation in solution and solid states depending on their primary structures and surroundings, and this is one of their unique and critical characteristic. Because some specific properties and functionalities of polymers are influenced by their conformations, accurate determination of temporal molecular conformations of polymers under certain conditions is important for elucidating and designing properties and functionalities of the polymer systems. At the same time, such a conformational study leads to elucidation of the intrinsic properties of the polymer. This principle is also applicable to cellulose, a linear semi-flexible polysaccharide consisting of β-1,4-linked anhydroglucose units, which has been extensively utilized in various forms such as fibers, films, gels, thickeners, retarding materials, membranes, paper and others with or without certain kind of modifications[24]. Size exclusion chromatography (SEC) is thus an important tool in polymer science for determining the molecular mass distribution (MMD), polymer size and mixtures composition. SEC has been used in some industrial laboratories to characterise cellulose and to investigate its degradation. Unfortunately, cellulose is not soluble in the main good solvents used for SEC analysis. Cellulose derivatives, more soluble, are thus prepared. Cellulose can be derivatized by introducing functionalities at the primary and at the secondary hydroxyl groups of the glucose unit. Because of the high molar weight of cellulose, substitutions other than at C2, C3 or C6 are disregarded and the maximum degree of substitution is assumed to be 3. It is difficult to get complete substitution or an even distribution of substituents in cellulose molecules. It is because of the heterogeneous nature of cellulose, i.e., within the ordered crystalline regions and between ordered and less ordered regions. Generally the preferable cellulose derivative is cellulose tricarbanilate (CTC) (Figure 3.16), which is produced by the reaction of phenylisocyanate and alcoholic groups of cellulose. DMSO (dimethylsulfoxide) and pyridine are common solvents used[25-28]. DMSO is considered as the suitable solvent for most of the cellulosic substrates for its high polarity that increases cellulose swelling and reagent access. THF is commonly used as eluent in SEC[29].

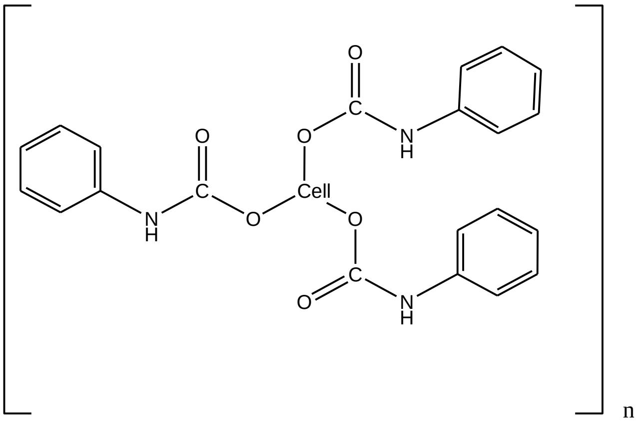


Figure 4.16: Cellulose Tricarbanilate (CTC) after Cellulose Derivation, (M=519 g/mole)

Cellulose molecular mass distribution was analysed with a Viscotek TDA-302 apparatus equipped with 3 coupled detectors: UV, Light Scattering (LS)/Refractive Index (RI) detector and viscometry detector (see details and operating conditions in the chapter 5 “Material and Methods”).

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.
By cross-linking the data of the multiple detectors (RI, LS and Viscosimetry), and data of size exclusion chromatographic behaviour of the column, information on the cellulose molecular mass distribution and conformation could be obtained. The refractometer (RI) gives the relationship between molecular fraction abundance and elution volume, in the line light-scattering (LS) detector coupled to the RI detector gives access to the molecular mass distribution and the viscometer enables to calculate the hydrodynamic radius, <Rh> (nm), through the measurement of the intrinsic viscosity of the polymer, [η].

The mean hydrodynamic radius of the polymer is the radius of an equivalent sphere for the solvated polymer. It gives an estimation of the volume occupied by the polymer in solution. This is an indication of the polymer size, i.e. on its conformation[22, 23].

Finally, SEC results also enable to calculate the cellulose degree of polymerisation in weight, DPw, knowing the weight-molecular mass of the polymer and the molecular mass of the monomer, i.e. the CTC;

DPw = Mw/519

4.6.3. B. Interpretation of Carbohydrate Molecular Mass Distribution of Cellulosic Substrates

The result of a SEC characterisation is normally given as the differential mass fraction plotted versus the logarithm of the molar mass (dw/dLogM). The ordinate describes the mass fraction eluted between LogM and Log M + dLog M. This mass fraction describes the mass of the polymer, i.e. the number of molecules multiplied by its molar mass.

In the case of a fully bleached kraft pulp, the MMD presents a bimodal profile. The first fraction, eluted first, is composed of cellulose with the highest molecular mass. The second fraction, delayed in the SEC column, is attributed to hemicelluloses exhibiting lower molecular mass[23].

4.6.4 Molecular Mass Distribution (MMD) of a Fully Bleached Pulp Treated by P, Pcat and E

As shown previously, the presence of the catalyst in the P stage strongly affected the DPv of the cellulosic products. To better understand the effect of the catalyst added in the P stage only on cellulose and hemicelluloses, a preliminary study was conducted on a fully bleached hardwood pulp, free of lignin. The fully bleached pulp was submitted to 3 different treatments: a hydrogen peroxide stage (P), a hydrogen peroxide stage with the catalyst (Pcat) and a cold caustic soda extraction (E) to remove hemicelluloses (pentosan) (E). Main results are presented in the table 4.8.

Table 4.8: Pulp Properties and Mean Molecular Data of the Fully Bleached Hardwood Pulp Submitted to P, Pcat and E Treatments

	Pulp properties			**SEC results**			
Pulp	**Brightness, %ISO**	**DPv (Tappi)**	**Pentosan, %**	**DPw**	**Polydispersity**	**[η], mL/g**	**<Rh>, nm**
Untreated	87.5	796	17.4	2206	3.85	470	40.7
P	92.0	649	15.1	2062	3.88	455	40.1
Pcat	89.9	365	14.7	853	3.42	258	25.1
E	90.5	1169	4.6	2555	5.08	450	43.4

Table – 4.7 shows that the P stage slightly modified the pulp properties. The brightness increased due to the removal of the chromophores, the DPv decreased because of cellulose depolymerisation induced by radical attack and the pentosan content was not much affected. Moreover cellulose properties after the P stage, given by the SEC results, are similar to that of the untreated cellulose. The mean DPw and intrinsic viscosity were slightly affected but the hydrodynamic radius and polydispersity were unchanged meaning that the P stage had a poor effect on the molecular weight and size of the cellulose and no effect on its conformation.

The Pcat treatment induced much more modifications. The brightness gain was reduced compared to that obtained after the P stage because of the presence of copper (II) which gave a bluish colour to the pulp. The lower DPv indicates that the catalyst caused a severe degradation of the high molecular mass fraction of the cellulose without removing the hemicelluloses as shown by the pentosan dosage. Intrinsic viscosities and mean hydrodynamic radii were logically strongly affected, same as the DPv and mean DPw. Finally the Pcat treatment had a major effect on the hydrodynamic radius and thus on the cellulose molecular size.

When a cold caustic soda extraction (E) was applied, most of the hemicelluloses were removed as shown by the pentosan quantity. The DPv, which is an average value of the polymerisation degree, logically increased since short-chain carbohydrates were eliminated from the cellulosic substrate. Moreover the mean DPw and polydispersity increased because the proportion of high molecular size carbohydrates increased. Other cellulose properties are similar to that of the untreated and P-treated pulps.

The molecular mass distribution profiles of the fully bleached hardwood pulp and the corresponding P, Pcat and E treated pulps are presented in the figure 4.17.

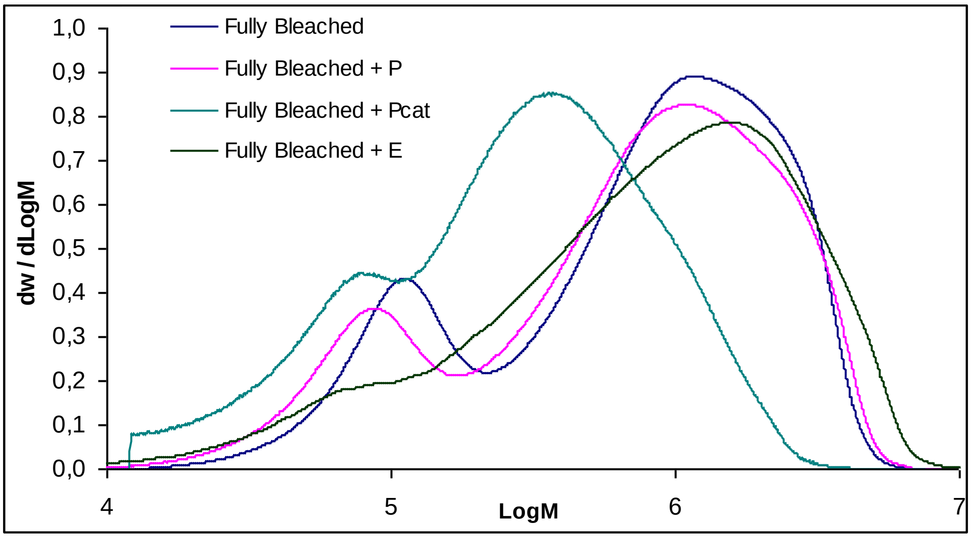


Figure 4.17: Presents the Molecular Mass Distribution of the Fully Bleached Hardwood Pulp and the Corresponding P, Pcat and E Treated Pulps.

For the untreated and P treated pulps, a bimodal MMD profile is observed: a first fraction between logM=4.5 and logM=5.5 (DP of the CTC between 60 and 600), and a second fraction between logM=5.5 and logM=6.5 (DP of the CTC higher than 600). The first fraction, corresponding to low molecular mass, contained hemicelluloses and low molecular mass cellulose fragments; the second one was attributed to the main cellulose fraction[30].

As already shown in table 4.7, figure 4.17 confirmed that the fully bleached and P treated pulps are similar in the high and low molecular mass regions. The P stage slightly shifted the MMD profile towards lower molecular masses.

The Pcat treatment caused a severe degradation of the high molecular mass fraction without removing the hemicelluloses, which was already confirmed by the pentosan dosage (table 4.7). The catalyst mainly acted on cellulose, contrary to what was expected.

When a cold caustic soda extraction (E) was applied, a drastic loss of hemicelluloses was observed. Cellulose was not degraded and the molecular mass distribution tended to a mono-modal MMD profile.

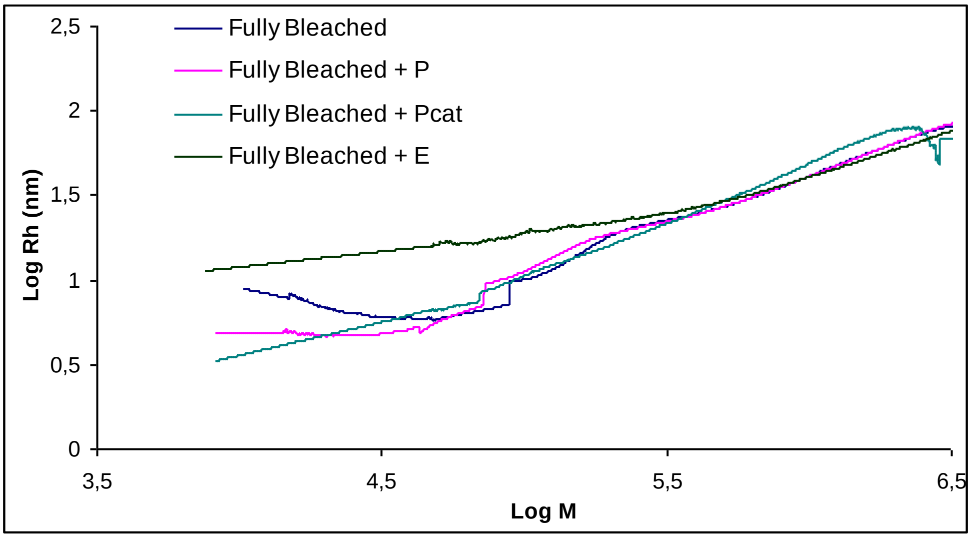


Figure 4.18: Log Rh versus Log M curves – Cellulose Conformation Analyses from the Fully Bleached Hardwood Pulp and the P, Pcat and E Treated Pulps

Figure 4.18 shows the relationship between the carbohydrate size (hydrodynamic radius, Rh) and the molecular mass (M). According to results in figure 4.18, there is no change in the relationship between size with respect to the molecular mass of the CTC molecules coming from the fully bleached, the P and the P cat pulps. Derivatized as carbanilates and solvated in THF, the cellulose chains exhibit the same conformation. The catalyst did no modify the structure of the carbohydrates. However some differences were observed with the E treated pulp. In the low molecular mass region, the E pulp carbohydrate chains appear to be less compact than the others meaning that the cold alkaline extraction treatment induced some modifications in the hemicelluloses structures, perhaps due to a bulky effect of sodium hydroxide. However, due to interpolation calculation in the short-chain carbohydrate region, and also due to the low abundance of this carbohydrate fraction in the E treated pulp; comments on hemicelluloses lead to this hypothesis.

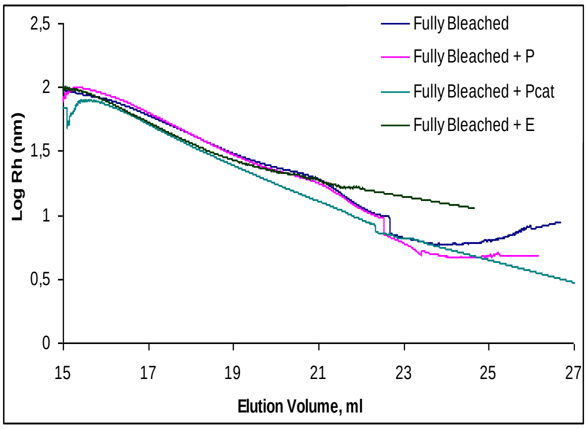


Figure 4.19 : Log Rh versus Elution Volume - Fully Bleached Hardwood Pulp and P, Pcat and E Treated Pulps

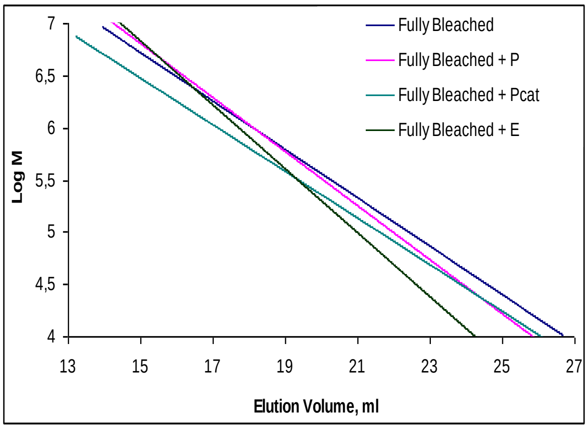


Figure 4.20 Log M versus Elution Volume – Fully Bleached Hardwood Pulp and P, Pcat and E Treated Pulps

Figures 4.19 and 4.20 present the SEC behavior of the pulp carbohydrates. Figure 4.19 shows some differences in the elution behavior of the different pulps in the high retention volume region, i.e. in the low molecular mass region. At same hydrodynamic radius, the hemicelluloses of the E treated pulp are more delayed in the column pores confirming that the cold alkaline extraction strongly modified the short-chain carbohydrate structure. A hypothesis is that these molecules are more flexible and penetrate more easily in the nano-pores of the SEC column or the diffusion of these molecules is reduced (higher Rh for a given M) with the consequence that there are delayed in the SEC column.

In figure 4.20, the log M versus elution volume relationship appears to be a combination between the molecular size effect (P and Pcat pulp curves shifted but remained almost parallel to the untreated pulp curve) and the cellulose substrate effect (E pulp curve non-parallel to the untreated pulp curve).

From the analyses of the fully bleached pulp before and after the P, Pcat and E treatments, it appears that the P stage only slightly shifted the molecular mass distribution to lower particle size. Hemicelluloses and cellulose are not much affected.

With the catalyst, cellulose is more damaged whereas hemicelluloses are not degraded to a great extent. Finally P and Pcat pulps presented similar conformation to that of the untreated pulp.

On the other hand the cold alkaline extraction stage induced much more modifications. The E treatment removed almost all the hemicelluloses leading to higher DPv and DPw, but it also increased the carbohydrates polydispersity. Moreover the E stage rendered the remaining short-chain carbohydrates, become less compact than the other pulps. This could be an interesting property since pure cellulosic products may be more accessible to chemicals used in further post-treatments for example, as the viscose process.

4.6.5 Molecular Mass Distribution (MMD) of the Cellulosic Products Originating from the Oxygen-Delignified Pulp Treated by the Bleaching Sequence Containing P or Pcat

In this section, the MMD of the celluloses were analysed produced after each treatment with different sequence using P or P cat.

4.6.5. A. Effect of the Catalyst used in the P Stage on the Carbohydrate Molecular Distibution

The ODL-Tembac pulp, coming from Fibre Excellence Saint Gaudens, was treated by a single P and Pcat stage. The effect of the peroxide treatment with or without the catalyst on the pulp properties was studied. Results are given in the table 4.9.

Table 4.9: Pulp Properties and Mean Molecular data of the ODL[1] Pulp Submitted to P and Pcat Treatments

	Pulp properties				**SEC results**		
Pulp	**Kappa Number**	**Brightness, %ISO**	**DPv (Tappi)**	**Pentosan, %**	**DPw**	**[η], mL/g**	**<Rh>, nm**
ODL^T	8.9	45.6	1388	22.6	3391	545	51.5
ODL^T+P	6.9	59.9	1182	22.1	1806	385	36.7
ODL^T+ Pcat	6.0	64.9	809	21.3	1500	333	32.2

ODL-Tembec: ODL^T

The P delignifying effect was detrimental for the cellulose carbohydrate fraction since the DPv and the DPw decreased after the H_2O_2 treatment. The intrinsic viscosity was also affected whereas the polydispersity remained unchanged. As already shown, the hemicelluloses could not be removed, even with the addition of the catalyst in the P stage. Moreover the use of the catalyst led to the degradation of higher molecular mass carbohydrates as the DPw is lower than P.

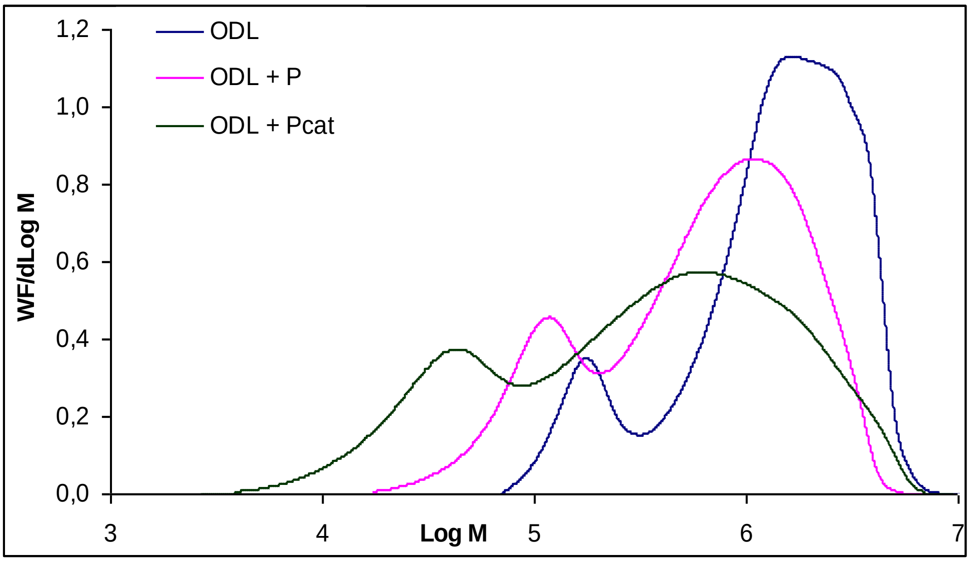


Figure 4.21: Molecular Mass Distribution (MMD) of CTC's from the ODL^T Pulp and the P and Pcat Treated Pulps

Figure 4.21 presents the molecular mass distribution of the ODL^T pulp and the corresponding P and Pcat treated pulps. As already observed peroxide effect (P) on the MMD with the fully bleached pulp, the P stage shifted the MMD profile of the ODL^T pulp to lower molecular mass (figure 4.21). This treatment mainly affected the cellulose fraction, hemicelluloses were less degraded.

With the presence of the catalyst, the MMD profile was much more modified. The bimodal response shifted to lower molecular mass and the fraction of high molecular mass carbohydrates is less abundant. Cellulose was strongly affected whereas hemicelluloses were still present.

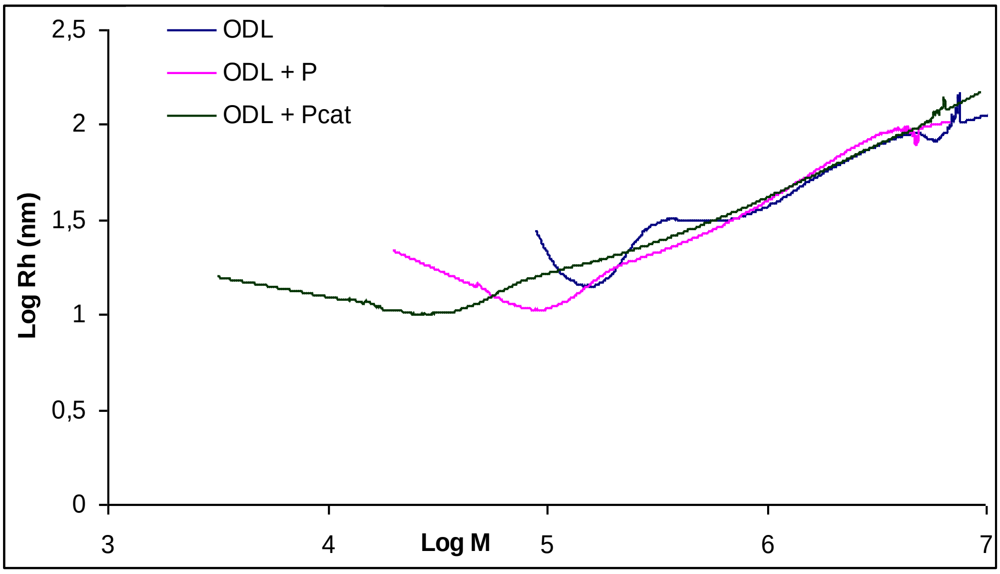


Figure 4.22: Log Rh versus Log M curves – Cellulose Conformation Analyses from ODL^T Pulp and P and Pcat Treated Pulps

Figure 4.22 represents the molecular conformation of the ODL^T pulp and the corresponding P and Pcat treated pulps. In the region of cellulose (high molecular weight, logM>5.5), the 3 pulps exhibited the same conformation (same Rh for a given M, figure 4.22). H_2O_2 and the catalyst did not modify the cellulosic structure of the pulp. Same results were already observed with the fully bleached pulp.

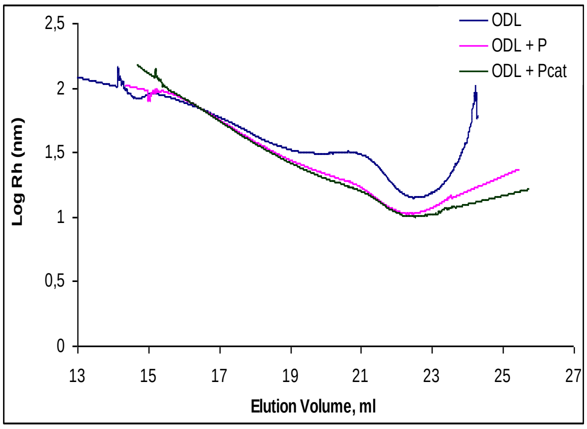


Figure 4.23 Log Rh versus Elution Volume – ODL^T Pulp, P and Pcat Treated Pulps

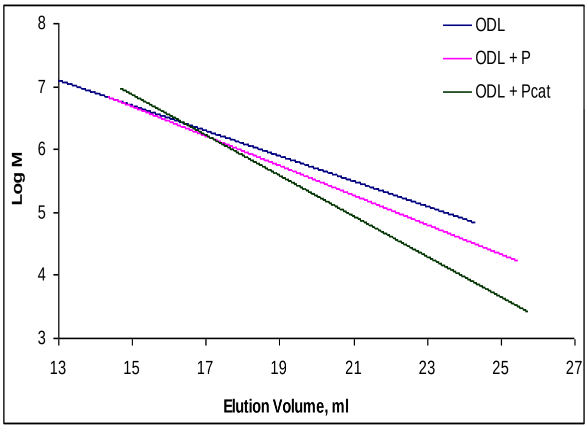


Figure 4.24 Log M versus Elution Volume – ODL^T pulp, P and Pcat Treated Pulps

Figure 4.23 shows only minor differences in the elution behavior of the 3 pulps. ODL^T and P pulps behaved similarly whereas CTC’s from Pcat pulp were more delayed in the column for the same hydrodynamic volume. The catalyst had a slight effect on the short-chain carbohydrate conformation.

On the same, figure 4.24, given the relationship between the molecular mass and the elution volume, confirmed that the catalyst induced some changes in the cellulose conformation since for a given molecular mass, CTC's from Pcat pulp were eluted faster. But this effect is not pronounced.

4.6.5. B. Effect of the aQ Pre-Treatment on the Carbohydrate Molecular Mass Distribution

To improve the delignifying effect of the P stage while limiting cellulose degradation with or without the catalyst, it was shown that an acid stage followed by chelation pre-treatment ("aQ") should be added. The "a" stage is an acidic treatment removing the hexenuronic acids and the "Q" stage is a metal ion chelation step required for hydrogen peroxide stabilisation.

The MMD of the ODL^T pulp treated with aQ, aQP and aQPcat sequences were analysed. Results are detailed in table 4.10.

Table 4.10: Pulp Properties and Mean Molecular data of the ODL^T Pulp Submitted to P, Pcat, aQ, aQP and aQPcat Treatments

	Pulp properties				**SEC results**			
Pulp	**Kappa Number**	**Brightness, %ISO**	**DPv (Tappi)**	**Pentosan, %**	**DPw**	**Polydis-persity**	**[η], ml/g**	**<Rh>, nm**
ODL^T	8.9	45.6	1388	22.6	3391	3.45	545	51.5
ODL^T+P	6.9	59.9	1182	22.1	1806	3.43	385	36.7
ODL^T+ Pcat	6.0	64.9	809	21.3	1500	2.72	333	32.2
ODL^T+ aQ	6.2	48.7	1323	22.6	1636	2.31	375	33.2
ODL^T+ aQP	5.1	72.3	708	21.6	1530	2.33	365	33.6
ODL^T+ aQPcat	3.1	74.9	616	21.0	820	2.18	217	23.2

ODL-Tembec: ODL^T

The addition of the "aQ" pre-treatment improved the delignifying effect of peroxide with or without the catalyst, the cellulose DPv was strongly affected (708 after aQP and 616 after aQPcat). This detrimental effect does not seem to be due to the "aQ" treatment since the DPv drop after "aQ" is marginal. The SEC analysis gave a contradictory result since after the "aQ" treatment the DPw is divided by two. On the same, the intrinsic viscosity was strongly reduced. The "aQ" treatment probably degraded high molecular weight carbohydrates in priority. The further P stage did not lead to an additional detrimental effect on cellulose as DPw after aQP is in the same range as after aQ. This is quite different for the Pcat stage since the DPw after aQPcat is twice less than the DPw after aQP: the catalyst impaired the cellulose quality.

The molecular mass distribution of the aQ pre-treated ODL^T pulp after P and Pcat are given in figures 4.25 and 4.26.

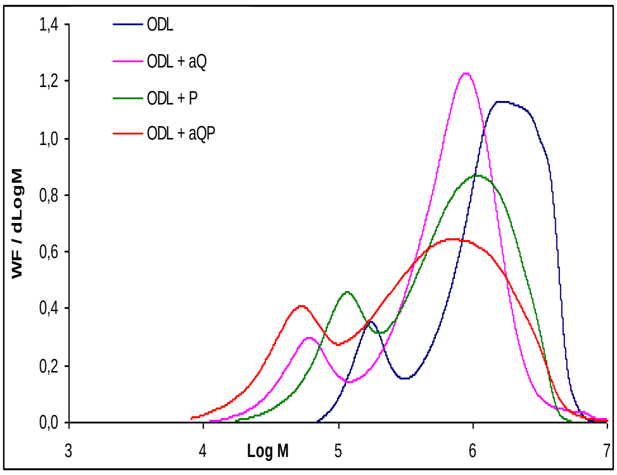


Figure 4.25: Molecular Mass Distribution (MMD) of CTC's from;
ODL^T Pulp and the (aQ), P, aQP

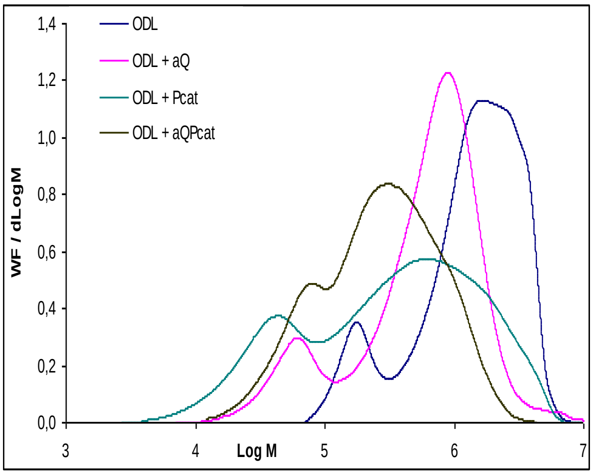


Figure 4.26: Molecular Mass Distribution (MMD) of CTC's from;
ODL^T Pulp and the (aQ), Pcat, aQPcat

The "aQ" pre-treatment shifted the MMD profile towards lower molecular weight region. The depolymerisation of both cellulose and hemicelluloses is probably due to the acidic conditions and the high temperature applied in the "a" stage leading to some carbohydrates dissolution[31, 32]. The further P stage did not change the MMD profile, as confirmed by the SEC results given in table 3.9. Finally the Pcat stage still shifted the MMD profile towards the short-chain carbohydrate region and the major effect of the catalyst is the gradually change from a bimodal to a monomodal MMD profile.

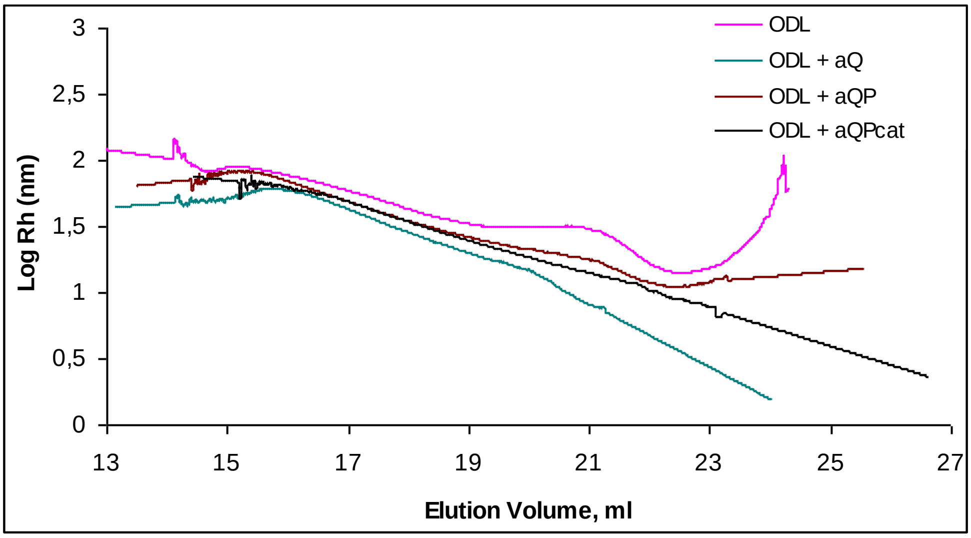


Figure 4.27: Log Rh versus Elution Volume – ODL^T Pulp, aQ, aQP and aQPcat Treated Pulps

Figure 4.27 show the elution behavior of the pulps. The elution behaviour of the pulps is almost similar for higher molecular size (i.e. low elution volumes) but it differs in the lower molecular size region. The aQ pulp is more compact than the other pulps (lower Rh at a given elution volume) but after P or Pcat stage, the pulp became less compact and tended to the ODL pulp conformation. The acidic conditions used in the aQ treatment probably modified the cellulosic substrate conformation leading to compaction while the further P or Pcat stage, carried in alkaline conditions, enabled to bulk the cellulose substrate as in its original state in the ODL pulp.

4.6.5. C. Replacement of P by (OP) – Effect on the Carbohydrates Molecular Mass Distribution

To reinforce the copper-phenanthroline catalytic activity on delignification, oxygen was introduced in the P stage. For these trials, a new pulp sample, ODL^1, was used because all the ODL^T pulp stock was consumed by previous experimentations. ODL^1 is also a hardwood kraft pulp as ODL^T but the oxygen delignification step was performed at the lab scale whereas ODL^T was recovered from the pulp mill after the O stage. ODL^1 and ODL^T exhibit similar pulp properties as seen in table 4.11.

Table 4.11: ODL^1 and ODL^T pulp properties

	Pulp properties			
Pulp	**Kappa Number**	**Brightness, %ISO**	**DPv (Tappi)**	**Pentosan, %**
ODL^T	8.9	45.7	1388	22.6
ODL^1	9.0	45.6	1378	22.7

The molecular mass distribution of the ODL^1 pulp after the (OP) or (OP)cat stage is compared to that of the P and Pcat treated pulps (figures 4.28 and 4.29).

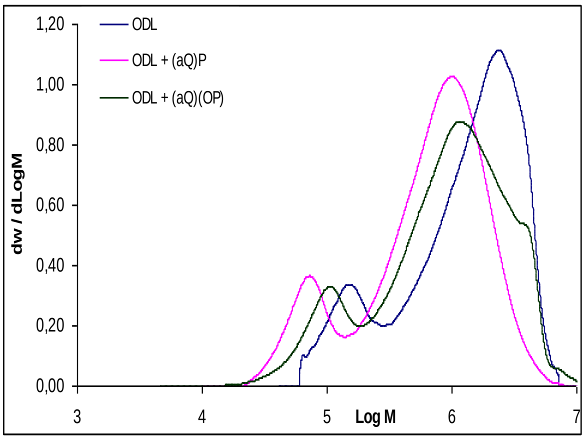


Figure 4.28: Molecular Mass Distribution (MMD) of CTC's from; ODL^1 Pulp and the (aQ)P and (aQ)(OP) Treated Pulps

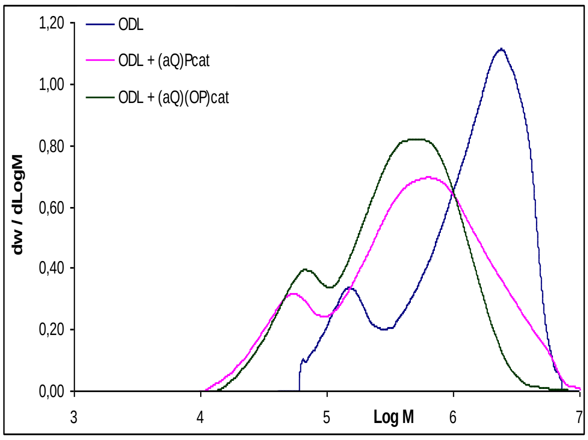


Figure 4.29: Molecular Mass Distribution (MMD) of CTC's from; ODL^1 Pulp and the (aQ)Pcat and (aQ)(OP)cat Treated Pulps

In figure 4.28, carbohydrates seemed to be more preserved with the (aQ)(OP) treatment compared to the (aQ)P treatment since the bimodal MMD signal was less shifted toward lower molecular weight. However the shoulder observed at high molecular weight for the (OP) treated pulp curve is certainly due to cellulose aggregation during the SEC analysis. The aggregation phenomenon probably originated from the insufficient shear stresses in the SEC column. The MMD of the (aQ)(OP) pulp cannot be compared to the MMD of the (aQ)P pulp. Fortunately, the SEC analyses of the (aQ)Pcat and (aQ)(OP)cat pulps did not reveal any carbohydrate aggregation (Figure 4.29). The (aQ)(OP)cat pulp MMD is similar to that of the (aQ)Pcat pulp, except at high molecular weight. The (OP) stage probably had the same effect as the P stage on carbohydrates even if the high molecular weight carbohydrate fraction seemed to be more preserved when oxygen in present in the peroxide stage[33, 34].

4.6.5. D. Effect of the Cold Caustic Soda Extraction, E, on the Carbohydrate Molecular Mass Distribution

The post E treatment was added to remove hemicelluloses. The pentosan dosages (chapter-4, Table – 4.11) confirmed that a cold caustic soda stage is able to remove most of the hemicelluloses. The SEC analyses of the E treated pulp should also corroborate the pentosan results. Molecular mass distributions after the E stage are given in figures 4.30 and 4.31.

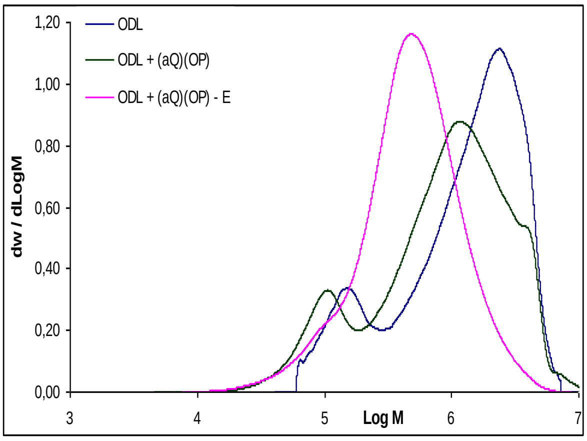


Figure 4.30: Molecular Mass Distribution (MMD) of CTC's from; ODL[1] Pulp and the (aQ)(OP) and (aQ)(OP)-E Treated Pulps

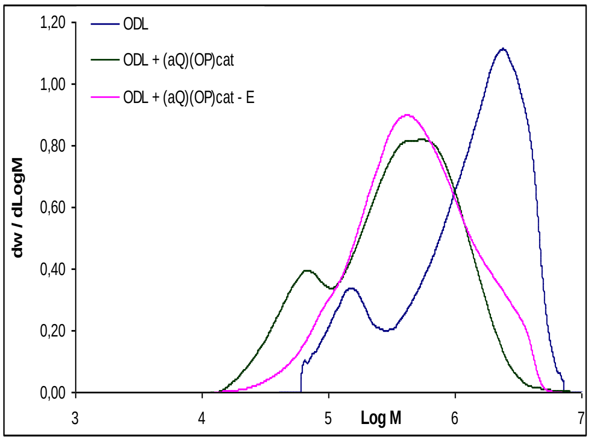


Figure 4.31: Molecular Mass Distribution (MMD) of CTC's from; ODL[1] Pulp and the (aQ)(OP)cat and (aQ)(OP)cat-E Treated Pulps

As shown in figures 4.30 and 4.31, after the cold alkaline extraction, the MMD distribution shape has changed. Again, only SEC results of figure 4.31 will be comment since the SEC analysis of the (aQ)(OP) pulp is probably not correct due to cellulose aggregation.

Figure 4.31 shows that the remained cellulose after (aQ)(OP)cat is not further degraded by the E stage. The molecular mass distribution tended to a monomodal MMD, where almost all hemicelluloses were removed. The SEC analysis confirmed the efficiency of the E stage to eliminate the hemicelluloses[1, 2].

4.6.5. E. Effect of the Final Z stage on the Molecular Mass Distribution

A final neutral ozone treatment was applied to target 90% ISO brightness, required for pure cellulosic products. The pulp DPv measured after the final Z stage showed that ozone strongly affected cellulose if the catalyst was applied in the previous (OP) stage (table 4.11). As already discussed in this chapter, residual phenanthroline may probably react with ozone generating radicals, which causes pulp depolymerisation. In this part, the effect of ozone on carbohydrates after the (OP) and (OP)cat stages is also analysed by SEC. Results are presented in table 4.12 and in figures 4.32 and 4.33.

Table 4.12: Pulp Properties of the ODL[1] Pulp Submitted to a Z stage after (aQ)(OP)-E and (aQ)(OP)cat-E Treatments

	Pulp properties			
Pulp	Kappa Number	Brightness, %ISO	DPv (Tappi)	Pentosan, %
ODL[1]	8.9	45.7	1398	22.7
ODL[1]+(aQ)(OP)	4.4	77.8	1364	21.5
ODL[1]+(aQ)(OP)-E	1.7	83.0	1385	5.5
ODL[1]+(aQ)(OP)-E-Z	----	90.3	1295	5.5
ODL[1]+(aQ)(OP)cat	2.9	80.2	983	21.1
ODL[1]+(aQ)(OP)cat-E	1.2	86.5	1089	4.6
ODL[1]+(aQ)(OP)cat-E-Z	----	91.2	602	4.6

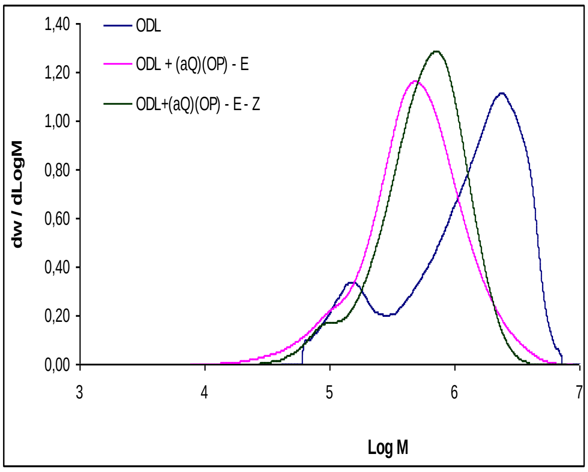


Figure 4.32: Molecular Mass Distribution (MMD) of CTC's from; ODL[1] Pulp and the (aQ)(OP)-E and (aQ)(OP)-E-Z Treated Pulps

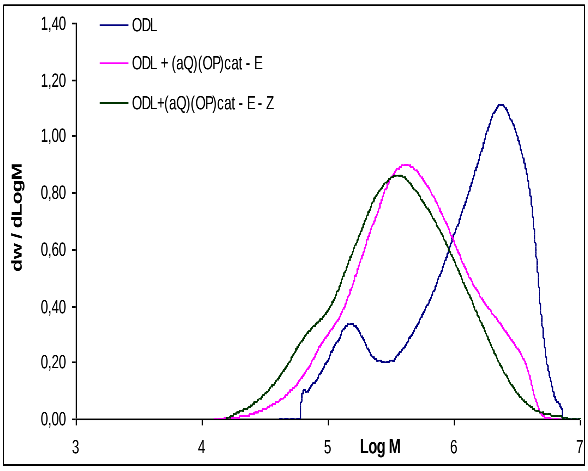


Figure 4.33: Molecular Mass Distribution (MMD) of CTC's from; ODL[1] Pulp and the (aQ)(OP)cat-E and (aQ)(OP)cat-E-Z Treated Pulps

As shown in figure 4.32, the ozone stage applied after the (OP)-E treatment did not impair the cellulose quality since the (aQ)(OP)-E-Z carbohydrate distribution shifted a little to the higher molecular mass after the last Z stage. On the contrary, after the (OP)cat-E treatment (figure 4.33), the Z stage slightly affected carbohydrates since the MMD moved toward lower molecular mass region. This last result confirmed the detrimental effect of the ozone stage implemented after the (OP)cat-E treatment.

4.6.5. F. Carbohydrate Molecular Mass Distribution of the Produced Celluloses Compared to that of the Un-Treated pulp and Market Dissolving Pulps

The pulp properties and SEC characterizations of the two celluloses produced with or without the catalyst are given in table 4.13. Results for the untreated kraft pulp, ODL[1], and standard viscose pulps are presented for comparison.

Table 4.13: Pulp Properties and Mean Molecular data of ODL[1] before and after the Bleaching Sequence with or without the Catalyst and of Standard Viscose Pulps

	Pulp properties				**SEC results**			
Pulp	**Kappa Number**	**Brightness, %ISO**	**DPv (Tappi)**	**Pentosan, %**	**DPw**	**Polydis-persity**	**[η], ml/g**	**<Rh>, nm**
ODL[1]	8.9	45.7	1398	22.7	5468	5.6	461	48.23
ODL[1]+(aQ)(OP)-E-Z	----	90.3	1295	5.5	1368	3.9	313	31.90
ODL[1]+(aQ)(OP)cat-E-Z	----	91.2	602	4.6	1137	3.0	233	25.32
Viscose hardwood sulfite[32]	ng	92.2	ng	3.6	1790	6.5	ng	ng
Viscose hardwood pre-hydrolysis kraft[32]	ng	90.7	ng	1.5	1400	3.0	ng	ng

ng=not given

If lignin is no more present and hemicelluloses almost removed in the treated ODL[1] (final bleached pulp after Z-stage), the bleaching sequence applied affected long-chain carbohydrates since the DPw and viscosity are lower compared to that of the unbleached pulp. Even if the catalyst improved the brightness (1 point of brightness gain), its interest is limited because (1) the brightness target for viscose application is already obtained without the catalyst and (2) the presence of the catalyst had a strong detrimental effect on cellulose, as shown by the huge reduction of DPv, DPw and intrinsic viscosity.

The sequence without the catalyst is thus more interesting. The comparison with standard viscose pulps originating from conventional processes shows that the pure cellulose produced without the catalyst exhibits similar properties as viscose prehydrolysis kraft pulps. The brightness is in the same range (90.3% for the cellulose produced in this project versus 90.7% for the viscose pulp), as DPw (1368 for the cellulose produced in this project versus 1400 for the viscose pulp). The hemicelluloses content, measured by the pentosan dosage, is higher for the pulp produced in this project but it has been shown that hemicelluloses may be totally removed using higher caustic soda charge in the E stage (10% for example). Finally the polydispersity of the pulp produced in this project is between 3.0 and 6.5, corresponding to the polydispersity of the pre-hydrolysis kraft pulp and that of the sulfite pulp. All these results tended to show that the produced cellulose without the catalyst behaves like a viscose substrate produced from pre-hydrolysed kraft pulp.

The MMD of the produced celluloses and of the unbleached pulp are presented in the figure 4.34. Figure 4.35 gives the MMD of viscose pulps originating from different dissolving pulps for comparison.

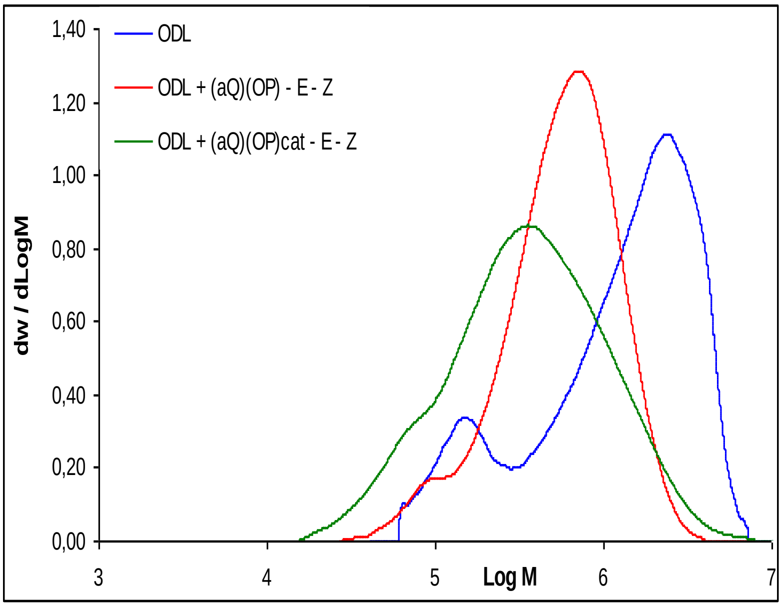


Figure 4.34: Molecular Mass Distribution (MMD) of CTC's from ODL[1] Pulp and the Produced Celluloses with or without the Catalyst

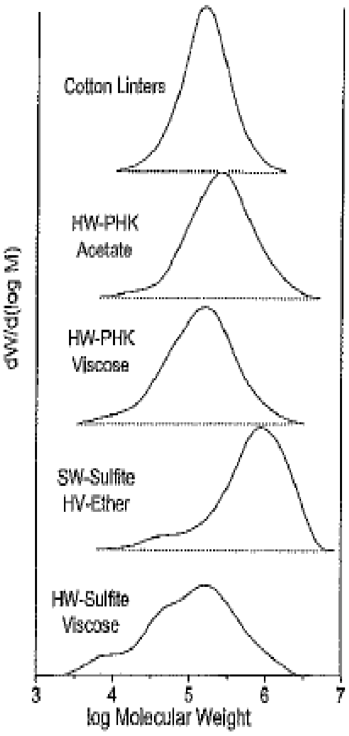


Figure 4.35: Molecular Mass Distribution (MMD) of Dissolving Pulps[35]

Figure 4.34 again confirmed that almost all hemicelluloses were removed by the bleaching sequence and showed a rather uniform carbohydrate MMD profile, especially when the sequence was performed without the catalyst, as required for homogeneous pure cellulosic products. Moreover, in comparison with standard viscose pulps (figure 4.35), the MMD profile of the produced cellulose is more uniform and is centred at higher molecular mass (LogM of the CTC=5.8 for the produced cellulose versus LogM of the CTC=5.2 for the standard viscose, sulphite or pre-hydrolysis kraft). The produced celluloses have thus comparable MMD as the standard viscose pulp.

To ensure that the produced celluloses are suitable for viscose application, the viscose ability should be tested. Results are presented in the next section.

4.6.5. G. Viscose Process Ability of the Produced Celluloses

The viscose ability test enables to evaluate the reactivity of a cellulosic product in the viscose process. As described in literature, during viscose production the cellulose is first reacted with caustic soda at high concentration for cellulose hydrolysis. After an ageing waiting period, so called the ripening process during which depolymerisation occurs, carbon disulphide is added (xanthation). This forms a yellow crumb known as cellulose xanthate, which is easily dissolved in more caustic soda to form a viscous yellow solution. This solution is filtered to remove impurities and pumped through a spinneret, which may contain thousands of holes, into a dilute sulphuric acid bath where the cellulose is regenerated as fine filaments as the xanthate decomposes. Contrary to most of cellulosic derivatives, the cellulose xanthate has no interest by itself since it is only used to solubilize the cellulose.

The preparation of viscose filaments from cellulosic substrates requires the use of a viscose pilot and huge amount of cellulose in the form of sheets for the alkalinisation by immersion before xanthation. To measure the viscose ability of small laboratory pulp samples, another method is employed using the Treiber pilot, a miniature viscose pilot treating 20g of cellulose. The viscose test gives as response a filtration indicator (Filter clogging value) of the cellulose xanthate solution in caustic soda (step before spinning). These trials were subcontracted to Lenzing, expert in viscose products. The relation between the viscose quality and the filter value measured during the Treiber test is given in the table 4.14.

Table 4.14.Classification Treiber Viscose Quality

Viscose quality	Filter value
Excellent	F>550
Very good	450<F<550
Good	350<F<450
Satisfactory	200<F<350
Poor	F<200

The results of the filter value obtained after testing the two cellulose samples produced are presented in table 4.15.

Table 4.15: Viscose Process Ability of Celluloses

	ODL-(aQ)-P-E-Z	ODL-(aQ)-Pcat-E-Z
Filter Value	67	47
Particle Content, ppm	81.5	60.2
Number of Particles	236620	195157

Courtesy: Lenzing, Austria

Unfortunately, the two cellulosic products exhibit a poor viscose ability. The low reactivity of these celluloses may have many explanations. The first one is that the celluloses may contain impurities impairing the filtration of the viscose solution. Hemicelluloses, still present (around 5%), are well known to react preferentially with carbon disulphide in the xanthation step thus leading to inhomogeneous substituted cellulose which consequently adversely affects viscose filterability. The presence of certain inorganic impurities such as silicates, calcium salts and catalytic active transition metal ions (Fe, Mn, Co, etc.) are also responsible for low viscose filtrability[18]. As shown in table 4.15, the pulp contamination with inorganic compounds is very low and thus could not be incriminated since all necessary measures were undertaken in the bleaching sequence to remove active cations (acid washing and acid chelation).

Table 4.16: Transition Metal Ions Content in the Produced Celluloses (Pulp -ODL [1])

Metal ion, ppm	ODL-(aQ)(OP)-E-Z	ODL-(aQ)(OP)cat-E-Z
Cu	<5	<5
Mn	<5	<5
Fe	<5	<5
Al	20	<5
Mg	25	30
Ca	65	65

Among all impurities, resins may also cause severe problems in the viscose process, such as pitch deposit. Hardwoods generally do not disturb the viscose production due to their low extractives content. Moreover kraft cooking is removes resins because most of acidic extractives are dissolved in the cooking liquor, leaving little resin in the unbleached pulp[36]. Even if resins are still present after cooking, the applied ozone bleaching step will also decrease the content of extractives while improving the viscose quality[37].Thus the presence of residual resins is probably not at the origin of the poor viscose ability of the produced celluloses.

The viscose quality of fibrous substrates is influenced not only by its chemical composition (lignin, hemicelluloses, resins etc.) and macromolecular properties (molecular mass distribution) but also by the supramolecular properties and the morphology of the fibers. During the viscose process, cellulose should react with caustic soda and carbon disulphide to form a viscose solution with a high filtrability. Before xanthation, the cellulosic substrate is swelled by caustic soda leading to the transformation of crystal lattice into amorphous structures. As xanthation occurs only in amorphous region, the xanathate groups are distribute randomly on the cellulose macromolecule following the fiber morphology. It could be concluded that all the hydroxyl sites of cellulose are not accessible for CS_2 substitution and that the xanathation efficiency depends on the crystal lattice of the cellulosic substrate. The fiber morphology of the produced celluloses should be investigated in details. Indeed, in a previous work using kraft pulp as substrate for viscose production, the use of enzymes to remove hemicelluloses seems a good approach to improve the viscose reactivity. These enzymes mainly enable to open the fibre pore structures thus increasing swelling ability and reactivity of the pulp[38, 39].

4.7 Conclusion

In in this chapter, it was shown that it is possible to produce pure cellulosic substrate from a harwood kraft pulp bleached with a TCF bleaching stage. As the peroxide catalyst is not able to remove hemicelluloses, a cold alkaline extraction stage is required in the sequence. Moreover to target the 90% ISO brightness a final ozone stage is applied.

With the bleaching (aQ)(OP)EZ or (aQ)(OP)cat EZ sequences, the produced celluloses have similar chemical and macromolecular properties as dissolving pulps used for viscose applications. However a viscose ability test revealed that the produced celluloses exhibit a poor viscose filterability. Differences in supramolecular properties or fibre morphology may be at the origin of the low viscose ability of the produced celluloses. Further characterisations will be required to conclude such as the distribution of crystalline and amorphous regions in the fibre, the fibre fibrillation, the fibre swelling ability, etc.

Since the DP of the TCF bleached pulp is relatively high when the catalyst is omitted, then some other applications may be investigated like the production of cellulose derivatives.

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CHAPTER – 5

MATERIALS AND METHODS

5.1 Pulp Raw Materials

Pulps used for the experiments are unbleached and oxygen delignified (ODL) mixed hardwood Kraft pulps provided by Fibre Excellence, Saint-Gaudens pulp mill, France (formerly Tembec group). They were received at approximately 30-40 % humidity and they were washed with tape water before centrifugation to 30-40% and air dried to consistency 90-93%. Then it stored in a tightly closed plastic bag for future experiments.

The industrial unbleached Kraft pulps were delignified with oxygen in the laboratory as follows. 50 g of Kraft pulp (oven dried basis) is used for all experiments. Water is added to adjust the pulp consistency to 1-2% before pulp mixing (soft mixer) and filtration (filter n°2). Magnesium as $MgSO_4$ salt solution (0.15% on pulp dry weight) is introduced as cellulose protector followed by sodium hydroxide (NaOH) (2% on pulp dry weight). Finally water is added till 10%consistency is reached. Pulp is homogenised to ensure uniform distribution of NaOH and $MgSO_4$. Then the pulp is introduced in an autoclave placed in the oil bath of the ERTAM rotating reactor. Oxygen gas is introduced in the autoclave till 5 bars on the reactor manometer. After, the temperature and time programme values are entered in the software piloting the reactor: 30 minutes for temperature rise to 100°C, 60 minutes reaction at 100°C and 20 minutes down to 50°C. Final pH is between 12 and 13. After the reaction, the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

The kappa number, brightness and viscosity of the pulps used in the thesis work are given in table 5.1.

Table 5.1: Kappa number, Brightness and Viscosity of the Oxygen Delignified Mixed Hardwood Kraft Pulps used

	ODL-Tembec	ODL-Lab1	ODL-Lab2
Kappa number	8.9	9.0	9.8
Brightness, % ISO	45.7	45.6	45.6
Viscosity, ml/g	931	925	937
DPv	1388	1378	1398

5.2. Pre-Treatment, Bleaching and Purification of Pulp

5.2.1 Acid Pre-Treatment, a stage

20 g of oxygen delignified pulp (oven dried basis) are used for all experiments. Distilled water is added to the pulp till 1-2%consistency. Then the pulp suspension is mixed (soft mixer) and filtered (filter n°2). Again distilled water is added to adjust the pulp consistency to about 1-2%. After, 0.5 N H_2SO_4 is added drop wise and mixed with a glass rod. Acid addition is stopped when the pH is 3.0 ± 0.5. Then the acid pulp suspension is filtered (filter n°2) and the filtrate is kept. The consistency is adjusted to 10% by adding the acid filtrate. The pulp suspension is finally placed in a polyethylene bag in a thermo stated water bath for 3 hours at 90 °C. After reaction, the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

5.2.2 Chelation Treatment, Q stage

20 g of pulp (oven dried basis) are used for all experiments. Distilled water is added to the pulp till 1-2% consistency. Then the pulp is mixed (soft mixer) and filtered (filter n° 2). 0.2 g of EDTA (1 % pure EDTA based on pulp dry weight[1]) previously diluted in water, is added to the pulp and homogenised in a polyethylene bag. Then the consistency is adjusted to 10% by adding distilled water. The pH should be around 5-6. Finally, the polyethylene bag is placed in a thermo-stated water bath for 30 minutes at 90°C. After reaction, the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

5.2.3 Acid Pre-Treatment followed by Chelation, a-Q sequence

These two treatments are performed in series according to the conditions described above. First, the a-stage (acid pre-treatment stage) is performed, then the pulp is washed and filtered before running the Q stage (chelation stage). After Q-stage, the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

5.2.4 Acid Pre-Treatment and Chelation Together in a Single stage, (aQ) stage

20 g of pulp (oven dried basis) is disintegrated in distilled water (soft mixer) and filtered (filter n°2). Distilled water is added to reach an approximate consistency of 1-2% and 0.5 N H_2SO_4 is introduced drop wise till pH 3. The pulp suspension is then filtered (filter n°2) and the filtrate is kept (as mentioned for the a-stage). By filtration the pulp consistency is increased to 18-20%. 0.2 g of EDTA (1 % pure EDTA based on pulp dry weight) previously diluted in water, is added and consistency is finally adjusted to 10% with the acid filtrate. After reaction (3h30 at 90°C) the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

5.2.5 Copper (II), Phenanthroline and Cu (II)-Phenanthroline Impregnation on Pulp

Initially copper (II) solution (using $CuSO_4$ salt), phenanthroline solution (using 1,10 phenanthroline) and Cu(II)-phenanthroline solution (using both $CuSO_4$salt and 1,10 phenanthroline) are prepared and stored separately in a clean glass flask.

20 g of pulp (oven dried basis) are placed in distilled water to reach an approximate consistency of 1-2%. The pulp suspension is mixed (soft mixer) and filtered (filter n°2). Copper (II) or phenanthroline or Cu(II)-phenanthroline solution is added while the suspension consistency is adjusted to 1% with distilled water. The pulp suspension is stirred with a glass rod for 2-3 minutes before 1 hour impregnation time at room temperature. The pulp suspension is finally filtered and treated immediately with hydrogen peroxide. Here it is supposed that copper(II), phenanthroline and Cu(II)-phenanthroline are retained by the pulp during the procedure, which has been already shown in a previous study.

5.2.6 In Situ Formation of Cu(II)-Phenanthroline Complex in Pulp

In this procedure, the Cu(II)-phenanthroline complex is directly formed in the pulp. This procedure is similar to the pulp impregnation already described above.

The required quantity of copper(II) (taken from a $CuSO_4$ aqueous solution) is first added to the pulp slurry at 1% consistency and after 10 minutes of gentle stirring, phenanthroline solution is added. This slurry is retained for 1 hour and then filtered (filter n°2). After filtration the pulp is immediately used for hydrogen peroxide treatment.

5.2.7 Hydrogen Peroxide stage with or without the Cu(II)-Phenanthroline Complex, P and Pcat stages

20 g of pulp (oven dried basis) are used for all experiments. Distilled water is added till1-2% consistency for pulp disintegration (soft mixer). Pulp suspension is then filtrated (filter n°2) and introduced in a polyethylene bag. The Cu(II)-phenanthroline complex is added first. Then, NaOH and H_2O_2 are added in this order (NaOH and H_2O_2 amounts are mentioned in results and discussions). Finally distilled water is again added to adjust the consistency at 10%. Chemicals are homogenised. The polyethylene bag, used as reactor, is placed in a thermostatedwater bath for 2 hours at the required temperature (mentioned in results and discussions). After reaction, around 30 ml of filtrate is recovered for residual peroxide titration (iodometry method). The pulp is finally washed with distilled water till the filtrate is clear and air dried (or kept wet) before further experiments and/or analyses.

Hydrogen Peroxide Concentration Calculation

Hydrogen peroxide is commercialised as concentrated solutions (30 – 35%). These instable solutions had to be titrated before use.

Hydrogen peroxide solution of approximately 40 g/l is prepared by precise dilution of the concentrated solution (dilution of 10 in volume). 2 ml of the diluted H_2O_2 solution is let react with20ml of 4N H_2SO_4 and 15 ml of 1M KI solutions. 5 ml of ammonium molybdate solution is added to catalyse the reaction. After 5 minutes reaction, the produced iodine is titrated with sodium thiosulfatesolution ($Na_2S_2O_3$) according to these reactions:

$$H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow H_2O_2 + I_2 + 2\,H_2O$$

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

The concentration of H_2O_2 in g/l is calculated as follows:

$$H_2O_2 = \frac{N_{thio} \text{ x } V_{thio} \text{ x } 17}{V_{H_2O_2}}$$

Where:

- N_{thio} is the normality of the $Na_2S_2O_3$ solution,
- V_{thio} is the volume of the $Na_2S_2O_3$ solution consumed during the titration
- 17 is the equivalent weight of hydrogen peroxide

5.2.8 Oxygen-Hydrogen Peroxide Bleaching with or without the Cu(II)-Phenanthroline Complex, (OP) and (OP)cat stages

20 g of pulp (oven dried basis) are used for all experiments. Distilled water is added till 1-2% consistency for pulp disintegration (soft mixer). Pulp suspension is then filtrated (filter n°2) and introduced in a polyethylene bag. The Cu(II)-phenanthroline complex is added first. Then, NaOH and H_2O_2 are introduced in this order (2% on pulp dry weight for both chemicals). Distilled water is finally added to adjust the consistency at 10%. No magnesium salt ($MgSO_4$) is introduced. Pulp is homogenised before being introduced in the autoclave of the ERTAM oxygen reactor. 5 bars of oxygen gas were applied. Then the temperature and time programme valuesare entered in the software piloting the reactor: 30 minutes for temperature rise to 90°C, 60 minutes reaction at 90°C and 20 minutes down to 50°C. After the reaction, the pulp is washed properly with distilled water and air dried (or kept wet) before further experiments and/or analyses.

5.2.9 SO_2 Washing

After eachhydrogen peroxide bleaching (both, with and without Cu(II)-phenanthroline complex), pulps are washed with SO_2 water (H_2SO_3) to remove metal ions from the pulp after treatment. H_2SO_3 is prepared by passing SO_2 gas through distilled water for 2-3 hours (up to saturation).

5.2.10 Cold Caustic Extraction, E stage

The cold caustic extraction was also called "NaOH treatment" in the discussion. 8% of sodium hydroxide solution is prepared with distilled water. 20 g of pulp (oven dried basis) are placed in a beaker and mixed with the caustic soda solution till consistency of 10%. Mixing is ensured by an overhead propeller rotating at 300 rpm for one hour at room temperature. After the reaction, pulp is washed with distilled water and filtered (filter n°1) until neutral pH. Pulp is finally air dried (or kept wet) before further experiments and/or analyses[2].

5.2.11 Ozone Bleaching, Z stage

Ozonation is performed at neutral pH as the Z stage will be placed at the end of the sequence to remove hexenuronic acids, the main contributors to the residual kappa number. Working under neutral conditions has already been proposed when ozone is used in a final bleaching stage and is easier when it comes to industrialization[3].

30 g of pulp (oven dried basis) are used for each experiment due to the design and the size of the ozonation reactor.Pulp is disintegrated in distilled water and filtered as before. Then, it is dewatered by centrifugation to a consistency of 35-40% and fluffed to work at high consistency. Fluffed pulp is introduced into the ozone reactor and a pre-decided amount of ozone is introduced. After washing, pulp is finally air dried (or kept wet) before analyses.

Ozone Concentration Calculation[4]:

The exact concentration of ozone in the oxygen/ozone mixture is determined before passing into the reactor. The concentration of ozone is determined by passing the oxygen/ozone mixture (two turns on the turn counter) into 250 ml glass bottle containing 1M of KI solution. The solution with liberated iodine is then poured into a 500 ml Erlenmeyer flask containing 20 ml of a 4N H_2SO_4 solution. The total iodine liberated is then titrated by a 0.2N sodium thiosulfate solution ($Na_2S_2O_3$) to the colourless end point using iodine indicator. The titration reactions are the following:

$$O_3 + 2\,I^- + H_2O \longrightarrow I_2 + 2\,OH^- + O_2$$

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

The concentration of ozone in mg/l is calculated as follows:

$$O_3 = \frac{N_{thio} \times V_{thio} \times 48}{2 \times n^\circ \text{ of turn} \times fc}$$

Where:

- N_{thio} is the normality of $Na_2S_2O_3$ solution,
- V_{thio} is the volume of the $Na_2S_2O_3$ solution consumed during the titration,
- 48 is the molecular weight of ozone in g/mole,
- 2 is the number of electrons transferred during the reaction with ozone,
- fc is the correction for temperature to 0°C, $fc = \frac{273}{273 + T°C}$, where T is the temperature of the ozone gas in Celsius.

The number of rotations needed for a particular ozone dose, noted Z (in g/l), is calculated as follows:

$$\text{Number of rotations} = \frac{\frac{Z \times 1000}{[O_3]}}{fc}$$

5.3 Pulp Characterisations

5.3.1 Kappa Number

The kappa number measurement followed the ISO 302-2004 standard[5].

Amount of residual lignin in pulp is one of the important pulp characterisations. It indicates the degree of delignification obtained after pulping and bleaching. Kappa number is an indirect methodfor the determination of the residual lignin in the chemical, semi-chemical and unbleached pulps. Determination of the kappa number is based on the oxidation of the residual lignin with a standard solution of potassium permanganate and determination of the residual permanganate iodometrically.

Kappa number is defined as the number of ml of 0.2 N $KMnO_4$solution consumed by 1 gram of oven dried pulp in 10 minutes at 25 °C.The results are corrected to 50% consumption of the permanganate added.

The reagents used are:

- sulfuric acid (H_2SO_4), 4N
- potassium iodide (KI), 1M
- potassium permanganate ($KMnO_4$), 0.2 N
- sodium thiosulfate ($Na_2S_2O_3$), 0.2 N

Kappa number testisperformed on air-dried pulp samples of known moisture content. The weight of the pulp is chosen such that the consumption of potassium permanganate would be about 50%. For all the consumption between 30-70% a correction factor should be used. The pulp sample is mixed well (mixer) with 600 ml of distelled water in a 2l glass beaker and after this 250 ml of distilled water is added. Then 50 ml of $KMnO_4$ and 100 ml of H_2SO_4 solutions are introduced. After 10 minutes, the reaction is stopped by adding 20 ml of KI solution and the liberated iodine was titrated with the sodium thiosulfate solution to a colourless end point using starch or iodine indicator. The test is carried out at 25°C, or at room temperature but then corrected to 25°C by application of a temperature correction factor.

Kappa number (X) is calculated as follows:

$$X = \frac{V_1 \, x \, d}{m}, \quad with \quad V_1 = \frac{(V_2 - V_3) x \, c}{0.02 \, x \, 5}$$

Where,

- V_1 is the volume of the potassium permanganate solution consumed in ml
- V_2 is the volume of the sodium thiosulfate solution consumed during blank test in ml
- V_3 is the volume of the sodium thiosulfate solution consumed during sample test in ml

- c is the concentration of the sodium thiosulfate solution in mole/l
- d is the correction factor to 50% potassium permanganate consumption
- m is the weight of the pulp (oven dried basis)

Correction for the temperature:

$$X = \frac{V_1 \text{ x } d}{m} \text{ x } [\, 1 + 0.013 \text{ x } (25 - T°C)]$$

Where T°C is the temperature measured during the test.

5.3.2 Viscosity

The viscosity measurement followed the T230 om-99.

The viscosity test measures the average polymerization degreeof the pulp (DPv). This test gives an idea of the extent of cellulosic sample degradation caused by pulping and bleaching processes. After the pulp sample dissolution in 0.5M cupriethylenediamine (CED) solution, the viscosity of the solution is determined using standardized conditions in a capillary viscometer.

250 mg of air-dried pulp (oven dried basis) are dispersed well with 25 ml of distilled water in a 50 ml capped vial. 25 ml of 1M cupriethylenediamine solution are then added and mixed till complete sample dissolution. The resulting solution is poured into a Cannon-Fenske capillary viscometer and the time to pass the solution between two points (of known calibration constant) at 25°C was noted. The viscosity of the pulp was calculated as follows[6]:

$$\eta = c \text{ x } t \text{ x } d$$

Where,

- η is the viscosity in mPa.s,
- c is the viscometer constant in mm^2/s^2,
- t is the times in s,
- d is the density of the cellulose solution, d=1.052 kg/dm^3

The polymerization degree (DPv) of the cellulose was calculated as follows:

$$DPv = 0.75 \text{ x } [(954 \text{ xlog}\eta) - 325]^{1.105}$$

5.3.2 A. Holocellulose

For unbleached and semi-beached pulps, samples undergo a complete delignification treatment to produce hollocelluloses free of lignin. This is achieved with an acid sodium chlorite treatment which does not degrade carbohydrates.

2 grams of pulp (oven dried basis) are mixed with 160 ml distilled water, 20 ml sodium chlorite solution at 34 g/l and 20 ml acetic acid buffer solution (pH 4.9) and heated in a water bath at 70°C for 1h30.After reaction and chlorinated organic species neutralisation, holocellulose is washed, filtered and air dried before viscosity measurement.

5.3.2. B. Borohydride Reduction

After ozonation, bleached pulps should undergo a reducing treatment in order to remove carbonyl groups present on cellulose. Indeed, carbonyl groups are at the origin of cellulose chain cleavage en alkaline medium, which may occurs during the dissolution of the sample in the alkaline cupriethylenediamine solution.

The reduction uses sodium borohydride ($NaBH_4$). 10 g of pulp (oven dried basis) were submitted to a sodium borohydride reduction at 10% consistency using 1% $NaBH_4$ (on pulp dry weight) at room temperature during 1 hour. After reaction, the pulp is washed with distilled water and air dried to determine its moisture content[7].

5.3.3 ISO Brightness

The brightness measurement followed the ISO 2470-2:2008.

ISO brightness is the intrinsic diffuse reflectance factor. Its measurement is based on the reflectance by white or near-white papers at a single wavelength of 457 nm. The measure is done on a sample thick enough to be opaque, often represented by several layers of simply folded sheet of sample. A spectrophotometer Colour Touch DATA COLOR from Technidyne Corporation is used in the present research[8]. To measure the pulp brightness, handsheets were formed using distilled water.

5.3.4 Determination of Hexeneuronicacid (HexA) Content in Pulp

The determination of hexeneuronicacid content in pulp followed the T 282 pm-07 standard[9].

Hexeneuronic acid (HexA) quantification procedure is based on the method developed by Chai et al[10]. HexA in pulp are hydrolyzed by mercuric chloride-sodium acetate solution and quantified y UV-Vis spectrophotometry.

50 mg of pulp (oven dried basis), placed in a 25 ml capped bottle, are hydrolysed with 10 ml of a hydrolysis solution containing 0.6% $HgCl_2$ and 0.7% of CH_3COONaat 60-70°C for 30 minutes with constant agitation. After hydrolysis, the solution is cooled to room temperature. The solution is then sucked in a 5 ml syringe and filtered with an Anatopmembrane filter

(diameter 10 mm and pore size 0.2µm). The filtered solution was analysed by UV-Vis spectrophotometry using a UV 1800 Shimadzu UV spectrophotometerat 260 nm and 290 nm. Fresh hydrolysis solution is taken as reference. The quantity of HexA in the pulp, in µmole/g, is calculated as follows:

$$C_{HexA} = 0.287 \text{ x } \frac{(A_{260} - 1.2 \text{ x } A_{290}) \text{x } V}{w}$$

Where,

- C_{HexA} is the hexenuronic acid content in µmol/g,
- A_{260} and A_{290} are the absorbance values of the solution at 260 and 290 nm,
- V is the volume of the testing hydrolysis solution in ml,
- w is the weight (oven dried basis) of the pulp sample in hydrolysis in g,
- 1.2 is the ratio between lignin absorption at 260 nm and 290 nm that is used to correct lignin absorption on HexA determination
- 0.287 is the calibration factor for the dual wavelength method obtained by Chai et al.

5.3.5 Determination of Pentosancontent in Pulp

The determination of pentosan content in pulp followed the T 223 cm-01 standard.

This method is based on the quantification of furfural compounds formed by hydrochloric acid hydrolysis of pulp (Figure 1). The furfural formed under these conditions may originate from pentosans and uronic acids. In this method hydroxylmethyl-furfural formed from hexoses (cellulose) does not interfere.

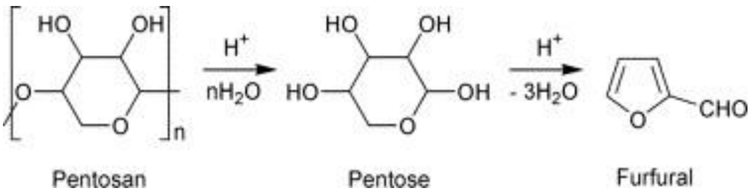

Figure 5.1 Hydrolysis of Pentosan by Hydrochloric Acid into Furfural

Pentosans are transformed into furfural by boiling ina 3.85N hydrochloric acid solution. After being collected in the distillate, furfurals are colorimetrically quantified with orcinol-ferric chloride reagent.

Pulp sample is placed in 250 ml round bottom flask (0.5 g - 2.0 g oven dried basis) with 20 g NaCl, 100 ml 3.85N HCl and some pumice stones. This flask is connected to a distillation apparatus. The rate of distillation was regulated so as to get a uniform rate of 2.5 ml/minute. During distillation, the volume of the flask is maintained constant at 100 ml by simultaneous HCl addition through a separate funnel. Around 225±10 mL of distillate are collected in a 250 ml volumetric flask. HCl is added to maintain the final volume at 250 ml. 5ml of distillate is precisely introduced in a 50 ml volumetric flask. 25 mL orcinol-ferric chloride solution (0.4 g orcinol, $CH_3C_6H_3(OH)_2$, and 0.5 g of ferric chloride, $FeCl_3.6H_2O$, in 1000 ml of 11N HCl) are added and mixed. It is kept in a water bath at 25±1°C for 60±5 minutes. Then ethanol is added till 50 ml and kept for 60±5 minutes. This solution was analysed by UV-Vis spectrophotometry, with the 3.85N HCl solutionas reference. Absorbance at 630 nm is recorded.

The number of milligrams of xylan in the pulp sample is red from a previously prepared calibration graph using xylose (known quantities, for example 10, 20, 40, 60, 80, 100 mg) as substrate instead of the pulp sample[11]. The conversion of xylose into xylan uses by the ratio of their molecular weight (xylan in mg = 0.88 x xylose in mg).

The pentosan content in a pulp sample, in %, is calculated as follows:

$$\text{Pentosans} = \frac{A}{10 \times w}$$

Where

- A = xylan in the pulp sample in mg
- w = oven-dry weight of the pulp sample in g

5.3.6 Alkali Resistance and Solubility of Pulp (R_{18} and S_{18})

The alkali solubility of pulp followed the standard: ISO 699 /1982.

2.5 g of pulp (oven dried basis) are used for the determination. 25 ml of 18% NaOH solution (215.5 g of NaOH/l, specific gravity=1.197) are poured on the sample. After 3 minutes, 25 ml18% NaOH solutions are further added. Again, after 3 other minutes 100 ml of 18% NaOH solution is added and the sample is let to react for 54 minutes (without stirring). After the reaction, the sample is filtered on a pre-weighted n ° 2 crucible with 200 ml of 10% acetic acid solution and finally it is washed with distilled water till neutral pH. After filtration the crucible with pulp is let to dry in an oven at 105°C untill constant mass. The alkaline resistance of the sample is directly weighted[12]. It is also called R_{18}. The alkali solubility is the part of the sample which did not resist to the 18% NaOH treatment. R_{18} and S_{18} are linked by the following equation: $S_{18}, \% = 100 - R_{18}, \%$

5.3.7 Viscose Ability

The viscose ability test enables to evaluate the reactivity of a cellulosic product in the viscose process. The Treiber method was used[13]. Due to the lack of the required equipment in our laboratory, the viscose ability tests have been subcontracted to Lenzing, Austria.

5.3.8 Transition Metal ion Content in Pulp

Transition metal ion content in pulp was subcontracted to the CNRS (Vernaison) and to Arkema CRRA.

5.4 Determination of the Molecular Mass Distribution (MMD) of Carbohydrates

The carbohydrate molecular mass distribution of the pulp samples has been determined by size exclusion chromatography (SEC).

SEC is a separation technology used to separate molecules according to their size in solution. The sample is dissolved in a solvent and introduced into a separating column which is filled with a porous packing material. The size of the pores of the packing material determines the molecular range over which the column is active. A constant flow of solvent is applied to the column and separation takes place by trapping of the molecules within the pores. Smaller molecules are retained for a longer time in the column, as they penetrate the porous phase to a greater extent than larger molecules. Molecules larger than the pores are not retained in the column at all and they are eluted first. They are followed by the molecules that are small enough to penetrate the pores and finally the smaller molecules are eluted[14].

5.4.1 Carbanilation

Before chromatography analysis, lignin should be removed and the resulting cellulosic substrate is derivatized into soluble cellulose tri-carbanilate (CTC). CTC (figure 5.2) are produced by the reaction of phenylisocyanate and alcoholic groups (ROH) of the cellulose[15].

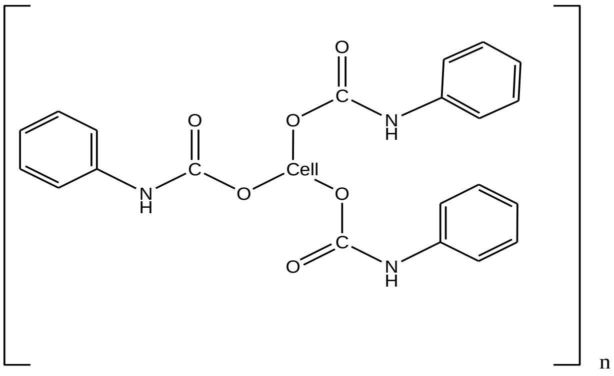

Figure 5.2 Cellulose Tricarbanilate (CTC) after Cellulose Derivation, (M=519 g/mole)

CTC are produced using the following conditions:

250 mg of air dry holocellulose or fully bleached pulp are mixed with 30 ml dimethylsulfoxide (DMSO)for 48 hours at 225 rpm and room temperature in aclosed glass reactor connected to a thermostated water bath. After pulp sample swelling in DMSO, temperature is raised to 70°C and 10 ml of phenylisocyanateare added slowly, drop by drop. Immediately after, 20 ml of DMSO is added again. This reaction processes under magnetic stirring at 225 rpm during 48 hours. At the end 20 ml of filtered acetone is added to the hot reaction medium. After 20 minutes, the medium was left to cool slowly under stirring. A sample of the medium was up taken and diluted 10 or 4 times in tetrahydrofuran (THF), and the dilute solution was directly injected (100 µL) in the SEC system.

5.4.2 SEC/LS/Viscometry – Apparatus and Analysis Conditions

A Viscotek TDA-302 apparatus was equipped with 3 TSK Viscogel^{TM} columns GMH$_{HR}$-H (7.8×300) or 3 PLgel^{TM} mixed B columns (7.5×300), with guard columns. SEC worked with THF at 1 ml/min, 35°C. Samples were injected at around 0.5 mg CTC/ml. PLgel columns have a 2 ml smaller porous volume and 40% reduced head pressure than TSK columns, with comparable linearity with CTC’s.

Coupled detection: UV at 260 nm, RALS/LALS/RI at 670 nm (laser 3 mW) and viscometry, all at 35°C.Refractometry was used as concentration detector and UV as control. The dn/dC was taken at a fixed value of 0.168 in good accordance with literature data and measurements of sample recovery through the column[15].

5.4.3 Molecular Mass Distribution (MMD) Calculation

The OmniSec^{TM} program (Viscotek Co.) was used with some choices in the calculation method: the most influencing parameters being peak integration limits (based on RI signal) and molecular mass versus elution volume fit. Both greatly influence the polydispersity and molecular mass distribution calculations, especially in the low molecular mass range. Molecular mass curve fit was based on (1) measured data in the medium molecular mass range (almost linear part), and (2) optimised linear extrapolation of low and high molecular mass curve ends[15].

5.5 UV-Visible Spectrophotometry – Apparatus and Analysis Conditions

UV-Vis measurements were performed in aqueous solutions (in H_2O, pH 7 or in a 0.05 M hydroxide solution, pH 12.50) on a UV 1800 Shimadzu UV spectrophotometer, equipped with quartz cuves of 1cm.

5.6 High Performance Liquid Chromatography – Apparatus and Analysis Conditions

HPLC analyses were conducted on a Spectra SYSTEM with a Spectra-Physics 1500 pump instrument using a reverse-phase ODS Hypersil C18column(250 x 4.6 mm, 5µ particle size)and a UV 2000 Spectra-Physicsdetector set at 260 nm. A mix of filtered water and acetonitrile (80:20 v/v ratios) was used as eluent. Pressure was around 1100 PSI and the eluent flow was set at 1 ml/min. Acquisitions were treated with the Borwin software.

External calibrations were carried out to quantify veratryl alcohol and veratraldehyde.

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CONCLUSION OF THIS WORK AND PERSPECTIVES

This thesis work aimed at developing a new environmentally friendly catalytic process for the bleaching and purification of cellulosic paper pulp using hydrogen peroxide as main delignifying agent, able to degrade and solubilize residual lignin and hemicelluloses in order to produce reactive and pure celluloses of adjustable polymerization degree. The goal is to provide the kraft pulp producers with a simple and green way to produce higher added value cellulose by a process which could be implemented in parallel to the paper pulp production line.

The selected catalyst is the copper-phenanthroline complex, already reported as an efficient activator of oxygen and hydrogen peroxide delignification. This catalyst is also known to accelerate the oxidation and depolymerization of the carbohydrates. This latter effect, which represents a serious handicap for the production of paper pulp, might be taken into profit when the objective is to degrade the hemicelluloses and obtain cellulose of variable degree of polymerization

The relevance of the Cu(II)-phenanthroline / H_2O_2 system for pulp delignification has been first studied in aqueous solution using a nonphenolic lignin model, i.e., the veratryl alcohol, resistant to conventional alkaline hydrogen peroxide oxidation.

UV-visible analyses revealed that without H_2O_2 the Cu(II)-phenanthroline complex is reduced by the veratryl alcohol into its Cu(I) form. However the reaction is very slow even at 80°C. Surprisingly, after the reaction, no veratraldehyde could be detected by HPLC even though the literature reported that the veratraldehyde is the main oxidation product of veratryl alcohol by Cu(II)-phenanthroline.

The veratryl alcohol consumption increases when hydrogen peroxide is added. It is shown in parallel experiments that the Cu(II) complex reacts with H_2O_2. This is demonstrated by the disappearance of the UV absorption band of Cu(II) phenanthroline and the formation of oxygen bubbles. Therefore hydrogen peroxide is not stable in this medium, which must rapidly affect the re-formation of the active Cu(II) species. It is concluded that, contrary to what was expected, the Cu(II)-phenanthroline / hydrogen peroxide system does not behave like the Cu(II)-phenanthroline / dioxygen system. With H_2O_2 the catalytic cycle must become rapidly inoperative. Part of the veratryl alcohol consumption is certainly due to the radicals generated during H_2O_2 decomposition.

In all the experiments where H_2O_2 was present veratraldehyde could be detected, even in the absence of the complex. The oxidation of veratryl alcohol into veratraldehyde by H_2O_2 alone has never been described. When the complex is present, more veratraldehyde is produced. Radicals resulting from H_2O_2 decomposition may be responsible for the conversion of the veratryl alcohol into veratraldehyde.

It was also shown that veratraldehyde was not stable in the reaction medium. This may explain why no veratraldehyde could be detected after the Cu(II)-phenanthroline reaction with veratryl alcohol. Moreover, with the Cu(II)-phenanthroline / H_2O_2 system veratraldehyde may be further oxidized into veratrylic acid as already described for the Cu(II)-phenanthroline / dioxygen oxidation system or may react with the generated radicals.

As the oxidation process suffers from the H_2O_2 decomposition by the copper-phenanthroline complex, split addition of hydrogen peroxide was tested. It has been shown that split addition not only enhances the formation of veratryl aldehyde but also reduces the oxidation time to reach the same veratryl alcohol consumption.

Even though the Cu(II)-phenanthroline / H_2O_2 combination is probably not a good catalytic system, it would probably lead to better delignification than conventional hydrogen peroxide treatment since benzylic OH groups located on nonphenolic units might then be substantially oxidized. This reaction is supposed to promote the alkaline cleavage of adjacent β-O-4 linkages in lignin.

H_2O_2 délignification of an oxygen delignified mixed hardwood kraft pulp (starting kappa number around 10) has been investigated in the presence or not of Cu(II)-phenanthroline complex. As expected, the presence of the complex improves the delignification but also increases the degradation of the carbohydrates. An acid chelation pre-treatment, noted (aQ), was also added to remove both the transition metal ions, responsible for the H_2O_2 decomposition into radicals, and the hexenuronic acids, present in large quantity in hardwood kraft pulp. This pre-treatment rendered the Cu(II)-phenanthroline / H_2O_2 system more active for delignification and less aggressive towards carbohydrates. In an attempt to further increase the activity of the complex, pressurised oxygen was successfully added in the activated hydrogen peroxide system (OP)cat.

After (aQ)(OP)cat treatment the pulp substrate can be bleached up to 80% ISO brightness with a residual kappa number of 2.9. Pulp analysis revealed that after (aQ)(OP)cat very few lignin is left since residual hexenuronic acids contribute for 2/3 to the final kappa number.

In this sequence the presence of the complex improved the delignification by 40%. Even though the DP of cellulose is seriously affected by the addition of the complex in the treatment the hemicelluloses are not degraded to such a degree where they would become soluble, contrary to what was expected. Their content in the pulp stayed at around 20%. Finally, as shown using the veratryl alcohol as substrate, split addition of H_2O_2 facilitates the delignification further. Since hemicelluloses and hexenuronic acids were still present after the (aQ)(OP)cat treatment further purification steps had to be performed to meet the required purity level (no hexenuronic acid, 90% brightness, less than 5% hemicelluloses).

A cold caustic extraction, E stage, generally used for dissolving pulp purification, enabled to remove most of the hemicelluloses (5% left in pulp). Moreover the E stage also removed the last residual lignin traces. To reach the 90% ISO brightness and to eliminate hexenuronic acids from the pulp, an ozone stage (Z) carried out under neutral conditions with very low ozone charges was applied.

After the full (aQ)(OP)catEZ sequence, the chemical composition of the produced cellulose (brightness, hemicelluloses content, DP) is similar to that of market pure celluloses used for viscose application. Supramolecular properties have been also compared through the study of the carbohydrate molecular mass distribution (MMD). This analysis confirmed that (i) in the presence of the complex, carbohydrates are more degraded since their MMD profile shifted to lower molecular mass, and (ii) hemicelluloses are removed by the cold caustic extraction as the carbohydrate molecular mass distribution tended to a monomodal profile. Finally it has been shown that the MMD of the produced cellulose is comparable to that of acid sulfite or pre-hydrolysis kraft pulps used for viscose application. To strengthen the comparison with market viscose grade cellulose, viscose ability has been tested. Unfortunately results concluded that the produced cellulose exhibits a poor viscose filtrability which means that the reactivity is lower than that of dissolving grade pulps. The reason is not known. Further characterizations would be required to explain this last result with the objective of modifying the sequence accordingly. Indeed, the pulp reactivity cannot be described only by the chemical composition of the pulp, but rather by the whole structure of the cellulosic substrate and the interactions of the derivatizing agent with the carbohydrates. Structure and morphology of the fibres are particularly important since they define the homogeneity of the conversion process and the final product quality.

However since the DP of the TCF bleached pulp is relatively high when the catalyst is omitted, then some other applications may be investigated like the production of cellulose derivatives.

To finally conclude, the activation of hydrogen peroxide by the Cu(II)-phenanthroline complex improved delignification efficiency, adjusted the cellulose DPv but could not enhance the removal of hemicelluloses. Thus the activated H_2O_2 treatment should be assisted by complementary purification steps. After purification stages using only chlorine free chemicals, the produced celluloses are pure but they lack reactivity. The reasons should be studied and some process corrections should be proposed. Moreover the adequation of the celluloses produced with market cellulose derivatives should be also explored.

From a fundamental point of view, it has been shown that the Cu(II)-phenanthroline / H_2O_2 oxidation system could not be considered as a catalytic system since H_2O_2 is decomposed by the complex, which rapidly prevents Cu(II) from been regenerated during the reaction. However the oxidative properties of hydrogen peroxide are really activated by this complex. The mechanism by which this system activates the oxidation of benzylic alcohol groups is not known and should be clarified for further improvement.

Résumé en Français

INTRODUCTION

On observe aujourd’hui un regain d’intérêt pour l’utilisation de cellulose pure dans la synthèse des dérivés cellulosiques (éthers et esters) employés comme additifs dans les plastiques et dans la production de cellulose régénérée pour application textile principalement. Ce nouvel élan découle de la recherche de produits issus de la biomasse en substitut de produits trouvant leur origine dans les ressources fossiles. Dans ce contexte, la cellulose occupe une place de choix puisqu’elle est le composé organique le plus abondant sur Terre.

Actuellement la cellulose pure est produite à partir de bois par une cuisson kraft de copeaux pré-hydrolysés (pré-hydrolyse kraft) ou par cuisson de copeaux ordinaires par le procédé bisulfite acide, ou à partir de linters de cotons soumis à différents traitements de purification. Afin de répondre à la future demande croissante, le bois est la matière première qui offre le plus grand potentiel puisque l’utilisation de linters est soumise aux aléas de la culture du coton.

De nombreux producteurs de pâte à papier kraft sont aujourd’hui dans une situation difficile car l’industrie papetière absorbe beaucoup de capitaux. Par conséquent, la capacité d’une usine est un facteur clé qui détermine les coûts de production. Le prix du bois affecte également fortement le coût de production de la pâte de sorte que les nouvelles usines gigantesques installées dans les pays où le bois croit rapidement à proximité de l’usine, comme au Brésil ou en Indonésie, sont dans une situation économique plus favorable. La seule issue pour les unités de production plus petites est de produire des produits de forte valeur ajoutée comme de la cellulose pure qui est vendue 50% plus chère que la pâte papetière. Au lieu de se tourner vers la pré-hydrolyse-kraft qui représente un changement majeur avec des investissements élevés, des ajustements mineurs pourraient être réalisés sur la ligne de pâte kraft existante afin de purifier la pâte papetière de manière à obtenir de la cellulose pure, c’est l’objet de ces travaux de thèse. L’objectif est de développer la production de cellulose pure à partir de bois dans une usine de pâte kraft par un procédé de purification propre, sans agent chloré. Ce nouveau procédé sera installé en parallèle de la ligne de blanchiment actuelle de l’usine.

Les pâtes cellulosiques obtenues après délignification par le procédé kraft sont brunes et encore contaminées par de la lignine et des hémicelluloses. La production de fibres blanchies nécessite des étapes de blanchiment additionnelles afin d'éliminer la lignine résiduelle colorée. Les réactifs oxygénés comme l'oxygène ou le peroxyde d'hydrogène, appliqués en milieu alcalin, remplacent aujourd'hui en partie les agents chlorés (dioxyde de chlore, dichlore) responsables de la production de composés organochlorés toxiques. Cependant la combinaison des traitements à l'oxygène et au peroxyde d'hydrogène n'est pas suffisamment efficace pour permettre le blanchiment complet de sorte que certains agents chlorés sont encore largement utilisés.

Les pâtes cellulosiques kraft blanchies sont majoritairement utilisées pour la production de papiers blancs en vue de leur impression. Leur teneur en hémicelluloses est encore élevée (20 à 25%), la cellulose possède un haut degré de polymérisation et ces pâtes souffrent d'un manque de réactivité aux procédés de dérivation pour des applications chimiques. Ces propriétés ne permettent pas aux pâtes cellulosiques kraft blanchies d'être utilisées pour des applications chimiques ou textiles.

Des études récentes ont montré que les complexes de métaux de transition, en particulier le complexe cuivre-phénanthroline, présentaient une activité catalytique sur les réactions au peroxyde d'hydrogène en milieu alcalin avec les pâtes cellulosiques. La délignification est fortement améliorée et les hydrates de carbone (cellulose et hémicelluloses) sont aussi plus oxydés comme en témoigne le plus faible degré de polymérisation de la cellulose. Par conséquent, ce procédé catalytique est peu sélectif de la lignine résiduelle ce qui limite son intérêt pour le blanchiment des pâtes à papier. Toutefois cet inconvénient peut devenir un avantage pour la production de cellulose de haute pureté pour des applications chimiques. En effet la production de cellulose pure et réactive requiert non seulement l'élimination de la lignine résiduelle mais aussi des hémicelluloses. De plus la réduction du degré de polymérisation de la cellulose est nécessaire pour sa dissolution. L'objectif de ce travail est donc de développer un procédé industriel, propre, de production de cellulose pure à partir de pâte kraft non blanchie, basé sur la catalyse du peroxyde d'hydrogène et utilisant si nécessaire des traitements complémentaires sans chlore.

Le manuscrit de thèse comporte cinq chapitres. Le premier consiste en une revue de la littérature sur la composition du bois, la cuisson kraft et les opérations de blanchiment TCF (O_2, H_2O_2 et O_3). Cette bibliographie aborde également les récents développements dans le domaine de la délignification au peroxyde d'hydrogène avec notamment l'activation de cet

agent, et présente les caractéristiques des celluloses de haute pureté aptes à être transformées en dérivés cellulosiques pour l'industrie chimique ou textile.
Les chapitres suivants développent les résultats.

Le deuxième chapitre présente une étude fondamentale du comportement du complexe cuivre-phénanthroline, activateur choisi dans cette étude, avec du peroxyde d'hydrogène en milieu alcalin. Cette étude a été réalisée par spectrophotométrie UV-visible. Ensuite la réaction du système cuivre-phénanthroline / peroxyde d'hydrogène avec un composé modèle de lignine non phénolique, l'alcool vératrylique, a été suivie par HPLC. Une attention particulière a été portée à la production du vératraldéhyde supposé être le produit principal de réaction. Les résultats obtenus ont permis de justifier l'application du complexe cuivre-phénanthroline comme catalyseur de la délignification au peroxyde d'hydrogène des pâtes kraft.

Dans le troisième chapitre, une pâte kraft industrielle pré-délignifiée à l'oxygène a été utilisée comme substrat afin d'optimiser la délignification au peroxyde d'hydrogène catalysé. L'effet du catalyseur sur la délignification (indice kappa) et sur la dégradation des hydrates de carbone (DP de la cellulose et teneur en hémicelluloses) a été examiné. Plusieurs paramètres ont été étudiés : la charge en peroxyde d'hydrogène et en hydroxyde de sodium, la quantité de cuivre-phénanthroline introduite, la stratégie d'addition du catalyseur et la température de réaction. Des pré-traitements, avant la délignification au peroxyde d'hydrogène catalysé, ont également été développés afin d'accentuer l'effet du catalyseur. Enfin, la composition chimique de la pâte après le stade au H_2O_2 catalysé, précédé des pré-traitements adéquates, a été analysée.

La purification des pâtes ainsi obtenues fait l'objet du chapitre IV. Une extraction alcaline, à froid ainsi qu'un stade de blanchiment final à l'ozone ont été appliqués afin d'atteindre la pureté requise, c'est-à-dire une teneur élevée en cellulose et une forte blancheur. Ainsi, une séquence de production de cellulose pure à partir de pâte kraft, sans agent chloré, a pu être proposée. Les celluloses produites ont été caractérisées par les analyses papetières classiques (blancheur, teneurs en hémicelluloses et acides héxènuroniques, DP de la cellulose, teneur en ions métalliques). Leur distribution de masses moléculaires (DMM) a également fait l'objet d'une étude approfondie par chromatographie d'exclusion stérique. Le profil de la distribution de masses moléculaires des hydrates de carbone a été suivi tout le long de la séquence donnant des informations sur l'effet de chaque opération sur les fractions de faibles et hautes masses. Enfin, la réactivité de la cellulose dans le procédé viscose a été étudiée et comparée à la réactivité des celluloses chimiques du marché.

Le chapitre V décrit les méthodes et matériaux utilisés dans ce projet.
Enfin, une conclusion finale reprenant les principaux résultats du projet est présentée à la fin du manuscrit. Des perspectives sont également proposées.

Les parties suivantes de ce résumé présentent les principaux résultats des chapitres II à IV, avant de reprendre la conclusion finale des travaux de thèse.

Chapitre II. Comportement du complexe Cuivre-phénanthroline pendant le blanchiment au peroxyde d'hydrogène

De récentes études ont montré que les complexes de type cuivre-phénanthroline (Figure 1) permettaient d'améliorer la délignification des pâtes kraft par le peroxyde d'hydrogène et l'oxygène.

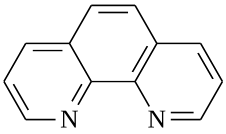


Figure 1 : Structure de la 1,10-phénanthroline (phen)

Beaucoup de travaux ont été conduits sur un composé modèle de lignine simple non phénolique, l'alcool vératrylique. Les résultats montrent que l'alcool vératrylique est oxydé en vératraldéhyde, ce qui laisse supposer que les fonctions alcool benzylique de la lignine seraient le siège de la réaction de délignification. La première étape serait la formation d'un nouveau complexe entre la lignine et le complexe $Cu(Phen)_2^{2+}$, avec oxydation de la lignine. Le Cu(II) serait alors réduit en Cu(I) et l'oxygène ou le peroxyde d'hydrogène ré-oxyderait le Cu(I) en Cu(II), entretenant ainsi la réaction d'oxydation via un mécanisme catalytique. Le changement de l'état d'oxydation du cuivre est donc une caractéristique importante du système catalytique. Il peut être suivi par spectrophotométrie UV-vis. La disparition des fonctions alcool benzylique de la lignine et la formation des fonctions carbonyle correspondantes est plus difficile à détecter. L'utilisation d'un composé modèle de lignine simple non phénolique comme l'alcool vératrylique (noté VA) permet de suivre plus facilement la réaction par HPLC.

Un mécanisme a déjà été proposé dans le cas de la catalyse de la délignification à l'oxygène par le complexe cuivre-phénanthroline. Il est présenté dans la figure 2. L'oxydation de l'alcool vératrylique conduirait à la formation du vératraldéhyde ainsi qu'à des traces d'acide vératrylique.

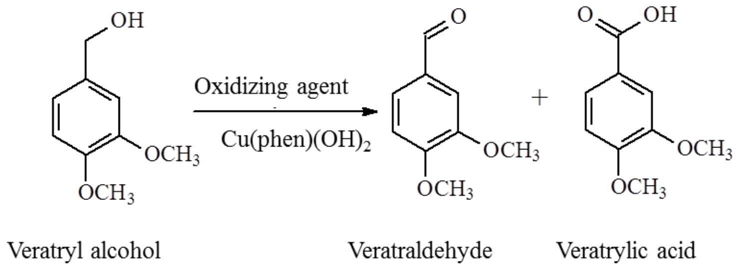


Figure 2 : Réaction d'oxydation par O_2 de l'alcool vératrylique (alcool 3,4 diméthoxybenzylique) en présence du complexe Cuivre-phénanthroline

La littérature montre que la consommation d'alcool est plus importante avec l'oxygène utilisé comme oxydant qu'avec le peroxyde d'hydrogène. Aucune explication n'a été donnée à ce jour. Afin de mieux comprendre la faible activité du complexe cuivre-phénanthroline pour catalyser les réactions d'oxydation au peroxyde d'hydrogène, nous avons donc étudié le comportement du système cuivre-phénanthroline / H_2O_2 en milieu alcalin.

Une étude par spectrophotométrie UV-vis a permis de confirmer qu'en milieu alcalin le complexe cuivre-phénanthroline était du type $Cu(phen)(OH)_2$ (déplacement de la longueur d'onde maximale d'absorption du complexe de 720 nm en milieu neutre à 680 à pH 12,5 – figure 3). La figure 4 présente la structure du complexe actif lors de la délignification en milieu alcalin.

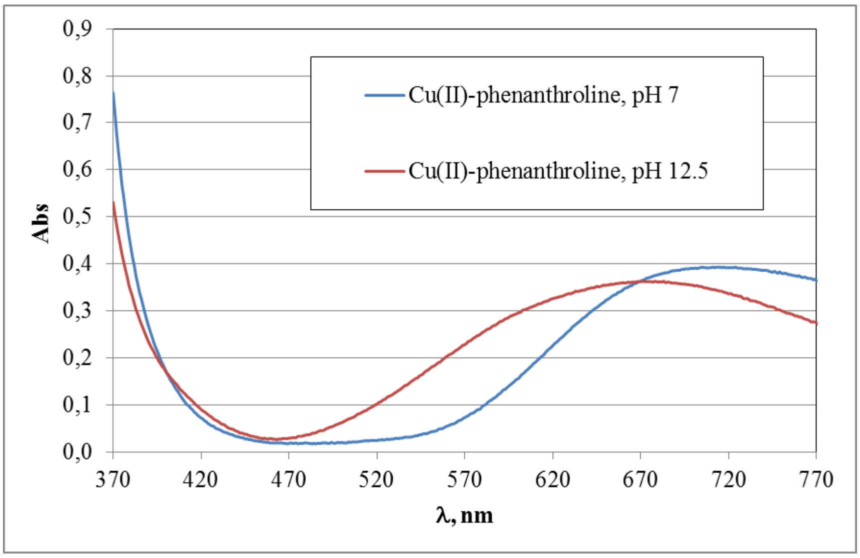


Figure 3 : Spectre UV-visible du complexe Cuivre-Phénanthroline en milieu neutre et pH 12,5

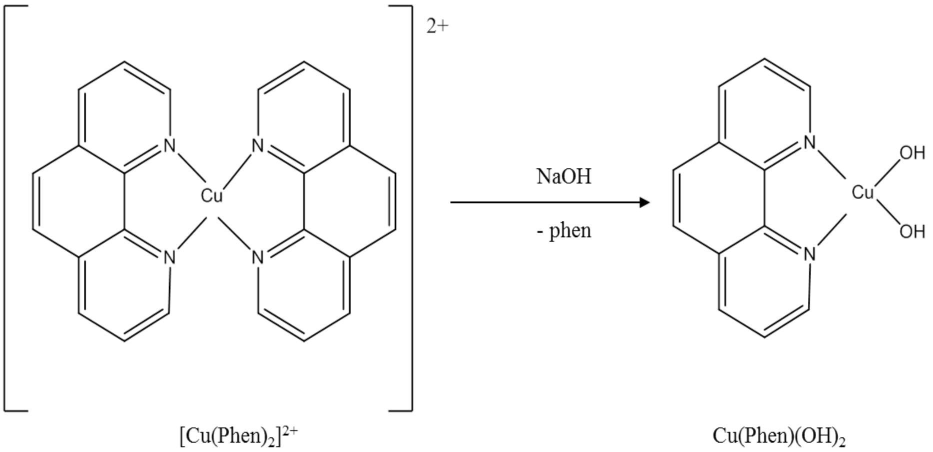


Figure 4 : Formation du complexe $Cu^{II}(phen)(OH)_2$ en milieu alcalin

Par ailleurs, l'étude par spectrophotométrie UV-visible confirme que le complexe Cu(II)-phénanthroline seul, en l'absence d'oxydant, est capable d'oxyder l'alcool vératrylique et que du Cu(I) est formé lentement que ce soit à température ambiante ou à 80°C (apparition de signaux caractéristiques du Cu(I) à 420 et 530 nm, figure 5, essais réalisés à température ambiante).

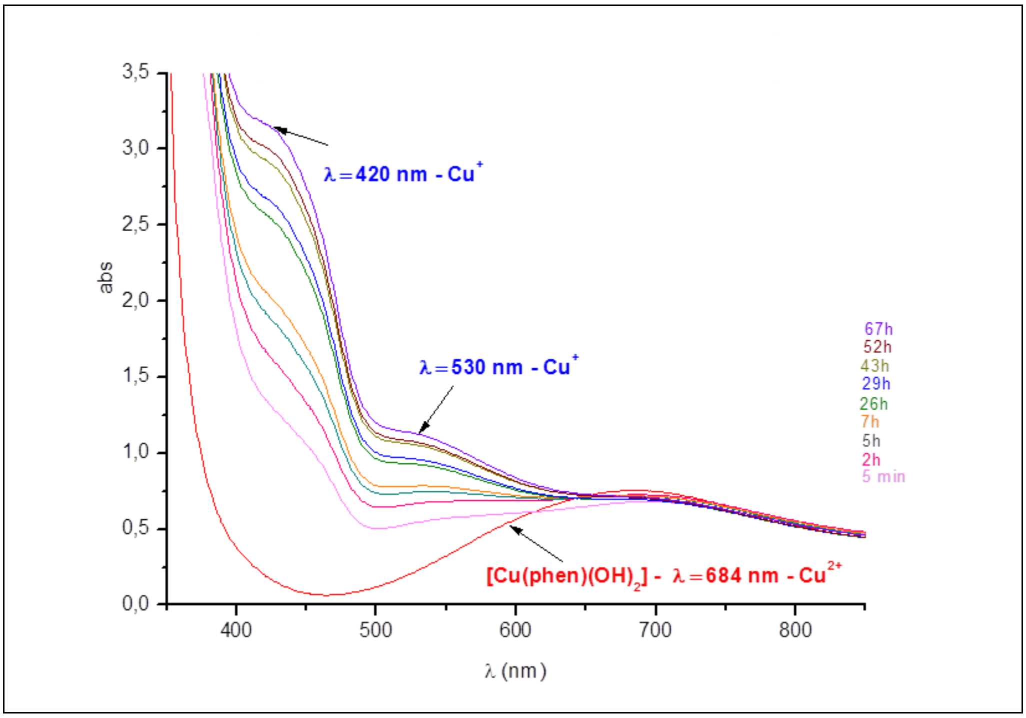


Figure 5 : Evolution de la structure du complexe Cuivre-Phénanthroline, en l'absence d'oxydant, mais en présence d'excès d'alcool vératrylique (ratio molaire Cu: alcool vératrylique = 1:20, essais réalisés à température ambiante)

Lorsque le peroxyde d'hydrogène est ajouté à une solution alcaline de complexe Cu(II)-phénanthroline, en l'absence d'alcool vératrylique, la couleur bleue du complexe disparaît immédiatement pour virer au marron et des bulles d'oxygène se dégagent dans le milieu. H_2O_2 est donc probablement oxydé par le complexe qui change alors d'état d'oxydation pour devenir du complexe Cu(I)-phénanthroline. Ceci est confirmé par analyse spectrophotométrique UV-visible où les signaux caractéristiques du Cu(I) apparaissent comme dans le cas de l'oxydation de l'alcool vératrylique par le complexe (Figure 6).

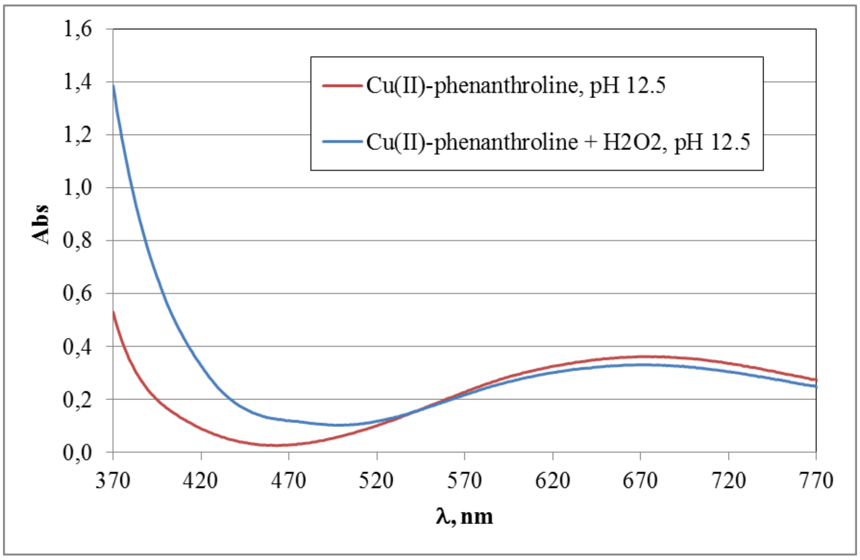


Figure 6 : Interaction entre le complexe Cuivre(II)- Phénanthroline en milieu alcalin et H_2O_2 à température ambiante

Il est donc probable que H_2O_2 soit décomposé par les espèces Cu(II) et/ou Cu(I) présentes en solution mais l'accumulation de Cu(I) reste difficile à expliquer. Quel que soit le mécanisme, H_2O_2 est consommé et disparaît certainement avant complète oxydation du substrat. Des radicaux sont également probablement produits et pourraient participer aux réactions d'oxydation. Enfin, quand l'alcool vératrylique est en solution avec H_2O_2 et le complexe Cu(II)-phénanthroline, du Cu(I) s'accumule davantage qu'en l'absence de H_2O_2. Il est donc impossible de prouver que le complexe Cu(I)-phénanthroline est ré-oxydé par H_2O_2. Il apparaît donc que le système Cu(II)-phénanthroline / H_2O_2 est très différent du système Cu(II)-phénanthroline / O_2 puisque rien n'indique que le Cu(II) peut être reformé à partir de Cu(I). Enfin ce système souffre de l'instabilité de H_2O_2 et la formation inévitable de radicaux ce qui complexifie les réactions d'oxydation de la lignine et qui conduit aussi certainement à l'oxydation de la cellulose.

Afin d'évaluer l'efficacité du système Cu(II)-phénanthroline / H_2O_2 pour oxyder la lignine, nous avons travaillé avec l'alcool vératrylique, composé modèle de lignine non phénolique résistant à H_2O_2 seul, et nous avons suivi la consommation ainsi que la production de l'aldéhyde correspondant par HPLC. Plusieurs essais ont été réalisés, avec ou sans oxydant, et avec ou sans complexe. Les résultats sont présentés dans le tableau 1.

Table 1 : Réaction de l'alcool vératrylique (VA) dans différentes conditions (80°C, 3h)

Ratio molaire Cu(II) ou Cu(II)-phénanthroline : alcool vératrylique : NaOH : H_2O_2 = 1 : 10 : 20 : 20			
essai	Conditions	Consommation de l'alcool vératrylique, %	Formation du vératraldéhyde, %
1	VA + H_2O	0,3	0
2	VA + NaOH	4,8	0
3	VA + NaOH + Cu(II)-Phen	8,9	0
4*	VA + NaOH + Cu(II)-Phen	16,4	0
5	VA + NaOH + H_2O_2	9,5	1,7
6	VA + NaOH + H_2O_2 + Cu(II)	8,7	0,1
7	VA + NaOH + H_2O_2 + Cu(II)-Phen	13,2	4,8
8*	VA + NaOH + H_2O_2 + Cu(II)-Phen	31,6	3,8

Les réactions sont réalisées en l'absence d'oxygène
* Ratio molaire Cu(II)-phénanthroline : alcool vératrylique : NaOH : H_2O_2 = 10 : 10 : 20 : 20
Consommation de l'alcool vératrylique (VA) % =(VA Initial, mole - VA Final, mole)x100 / VA Initial, mole
Formation du vératraldéhyde (VAld) % = (VAld Formé, mole)x100 / VA Initial, mole

Les résultats montrent que l'alcool vératrylique est instable puisque 0,3% disparaissent lorsque l'alcool est introduit dans l'eau. Cette perte est peut-être due à une rétention physique dans la colonne de chromatographie et/ou à la précision de l'analyse (essai 1). Plus suprenant, en milieu alcalin, 4,8% d'alcool est consommé sans production d'aldéhyde (essai 2). Ceci n'est pas expliqué car l'alcool n'est pas sensé réagir avec l'hydroxyde de sodium.

En présence de Cu(II)-phénanthroline, 8,9% d'alcool est consommé (essai 3). Après comparaison avec l'essai témoin en milieu alcalin, l'ajout de complexe permet une consommation supplémentaire de l'alcool de 4,1%, ce qui indique que le cuivre-phénanthroline réagit avec l'alcool vératrylique, même sans oxydant. La réaction serait la suivante :

2 Cu(II)-phénanthroline + alcool vératrylique → 2 Cu(I)-phénanthroline + vératraldéhyde

En considérant le ratio molaire Cu/VA utilisé ici (1/10), une réaction totale consommerait 5% d'alcool vératrylique. Nous pouvons donc considérer que dans l'essai 3, la réaction est complète, en revanche l'analyse ne permet pas de détecter d'aldéhyde. La quantité de Cu(II)-phénanthroline a donc été augmentée (multipliée par 10) de façon à oxyder davantage l'alcool vératrylique et à former l'aldéhyde correspondant (essai 4). L'aldéhyde n'est toujours pas détecté. Nous pouvons émettre deux hypothèses, soit il n'est pas formé, soit il est instable dans le milieu réactionnel (oxydation en acide vératrylique), ceci n'a jamais été décrit auparavant. Enfin la consommation d'alcool vératrylique reste relativement faible même en présence d'une forte quantité de complexe ce qui confirme que l'oxydation de l'alcool par le Cu(II)-phénanthroline est lente.

Une faible quantité d'aldéhyde est produite en présence de peroxyde d'hydrogène (essais 5 – 8). H_2O_2 seul est capable d'oxyder l'alcool vératrylique et de l'aldéhyde est formé en faible quantité. Il est possible que des espèces radicalaires résultant de la décomposition de H_2O_2 participent à cette réaction. Toutefois, dans l'essai 6 où la quantité de radicaux est augmentée par ajout de Cu(II) seul, la quantité d'aldéhyde formée est plus faible. Le mécanisme dont est issue la formation de l'aldéhyde reste non élucidé.

L'ajout conjoint de H_2O_2 et de Cu(II)-phénanthroline (essais 7 et 8) améliore l'oxydation de l'alcool. Une plus forte quantité de Cu(II)-phénanthroline (multipliée par 10) permet d'augmenter encore la consommation de l'alcool vératrylique mais la quantité d'aldéhyde formée reste faible ce qui suggère que l'aldéhyde n'est pas stable dans le milieu.

En conclusion, ces résultats confirment que l'alcool vératrylique est bien oxydé par le système Cu(II)-phénanthroline / peroxyde d'hydrogène mais l'oxydation du groupe α –OH en carbonyle par le complexe Cu(II)-phénanthroline seul n'a pas pu être montrée par HPLC. Afin de détecter la formation de groupement carbonyle, la consommation de l'alcool vératrylique et la formation de vératraldéhyde ont été suivies tout au long de la réaction de l'alcool vératrylique avec H_2O_2 en présence ou non de complexe. Les résultats montrent qu'en l'absence de complexe, la réaction se déroule dans les 30 premières minutes puis le système évolue peu. En présence de complexe, la réaction est plus rapide et à partir de 15 min, les quantités de produits dosés atteignent un plateau. Ceci peut être mis en relation avec le changement immédiat de couleur du milieu du bleu au marron et l'apparition de bulles d'oxygène dès lors que le peroxyde est ajouté dans le milieu. H_2O_2 est donc probablement très vite consommé. Par conséquent la délignification au H_2O_2 catalysée devra être réalisée en un temps très court, inférieur à 3 heures.

Afin d'expliquer l'absence d'aldéhyde détecté au cours de la réaction, le comportement du vératraldéhyde dans le milieu réactionnel, en l'absence d'alcool vératrylique, a été étudié.

L'étude par spectrophotométrie UV-visible de l'interaction entre le vératraldéhyde et le complexe Cu(II)-phénanthroline (Figure 7) montre que le signal du Cu(II)-phénanthroline en milieu alcalin n'est pas modifié en présence de l'aldéhyde. Le vératraldéhyde ne serait donc pas oxydé par le complexe contrairement à l'alcool vératrylique. L'absence d'aldéhyde pendant la réaction est donc due à une autre raison.

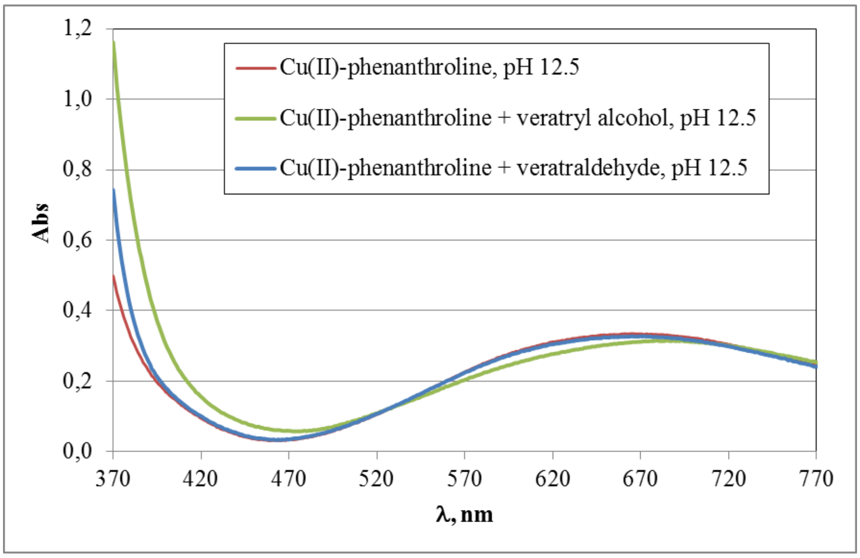


Figure 7 : Interaction de l'alcool vératrylique ou du vératraldéhyde avec le complexe Cu(II)-Phénanthroline en milieu alcalin

(ratio molaire Cu : alcool vératrylique ou vératraldéhyde : NaOH : H_2O_2 = 1 : 10 : 20 : 20, température ambiante, analyse UV-Vis enregistrée après 15 minutes de réaction)

L'évolution de la quantité de vératraldéhyde présent dans le milieu réactionnel a été suivie par HPLC. Les résultats sont présentés dans le tableau 2.

Tableau 2 : Consommation du vératraldéhyde (V. Ald) dans le milieu réactionnel (conditions variables)

Ratio molaire Cu(II)-phénanthroline : vératraldéhyde : NaOH : H_2O_2 = 1 : 10 : 20 : 20				
Essai	Conditions	Température, °C	Temps, minutes	Consommation vératraldéhyde, %
9	V.Ald + H_2O	25	15	0,0
10	V.Ald + NaOH	25	15	19,0
11	V.Ald + NaOH	80	60	24,6
12	V.Ald + NaOH	80	120	25,1
13	V.Ald + NaOH	80	180	26,0
14	V.Ald + NaOH + H_2O_2	80	180	38,5

15	Cu(II)-phénanthroline + V.Ald + NaOH	80	180	35,5
16	Cu(II)-phénanthroline + V.Ald + NaOH + H_2O_2	80	180	53,6

Les réactions sont réalisées en l'absence d'oxygène
Consommation de Vératrylaldéhyde (Vald)% = =(VAld Initial, mole - VAld Final, mole)x100 / VAld Initial, mole

Alors que l'aldéhyde est stable dans l'eau à température ambiante (tableau 2, essai 9), une partie de l'aldéhyde disparaît en solution alcaline (19% et 25% à 25°C et 80°C respectivement). Une explication serait la formation d'hydrate par addition d'eau sur l'aldéhyde. Cette équilibre est bien connu mais la forme hydrate est souvent moins stable que la forme aldéhyde. Toutefois la présence de groupements attracteurs d'électrons adjacents à la fonction aldéhyde pourrait rendre l'hydrate plus stable. Dans le cas du vératraldéhyde, la partie aromatique de la molécule présence un caractère attracteur d'électrons dû à sa structure conjuguée et pourrait donc favoriser la forme hydrate. La formation d'hydrate à partir de l'aldéhyde est en accord avec l'absence de réduction du complexe Cu(II)-phénanthroline, démontrée par spectrophotométrie UV-visible.

La consommation de l'aldéhyde augmente avec l'addition de peroxyde d'hydrogène ou de Cu(II)-phénanthroline seul et est maximale en présence simultanée de Cu(II)-phénanthroline et de H_2O_2 (essais 14 à 16, tableau 2). L'oxydation de l'aldéhyde par le peroxyde en milieu alcalin est possible, de même en présence de H_2O_2 et Cu(II)-phénanthroline puisque des radicaux sont probablement formés pendant la réaction. Tous ces essais permettent de conclure que l'aldéhyde supposé formé suite à l'oxydation de l'alcool vératrylique n'est pas stable dans le milieu réactionnel.

La consommation de l'alcool vératrylique restant faible, des essais d'optimisation de la consommation de l'alcool ont été entrepris.

Une première stratégie a consisté à réaliser un screening de ligands pour le complexe de cuivre. Sur la base de projets antérieurs conduits au LGP2 sur la catalyse de la délignification à l'oxygène, deux phénanthroline substituées, la 4,7-diméthyle phénanthroline (4,7-DMP) et la 5,6-diméthyle phénanthroline (5, 6-DMP) ont été sélectionnées. Des essais d'oxydation de l'alcool vératrylique par le système H_2O_2/Cu(II)-phénanthroline substituée ont été réalisés et la consommation de l'alcool a été suivie par HPLC.

Les résultats montrent que la substitution de la phénanthroline permet d'améliorer la consommation de l'alcool mais les quantités d'alcool oxydées restent encore faibles.

Une deuxième stratégie a consisté à faire des ajouts fractionnés de peroxyde pendant la réaction car il a été montré précédemment que la consommation de l'alcool se déroulait essentiellement dans les premières minutes de la réaction. Ceci serait expliqué par une rapide décomposition de H_2O_2. La charge en H_2O_2 appliquée a donc été introduite en plusieurs fractions au cours de la réaction (ajout en 2 ou 3 fractions, avec une quantité de H_2O_2 totale fixée). Les résultats montrent que davantage d'alcool est consommé par ajout fractionné de H_2O_2 et que la quantité d'aldéhyde formé est plus importante en présence du complexe. De plus une réaction de 60 minutes avec ajouts fractionnés de H_2O_2 conduit au même résultat qu'une réaction conventionnelle de 180 minutes. Le succès de cette stratégie confirme que H_2O_2 est probablement très vite consommé au cours de la réaction.

Ce premier chapitre apporte des informations primordiales sur le fonctionnement du système Cu(II)-phénanthroline/H_2O_2 que nous souhaitons appliquer à la délignification :

- Le Cu(II) du complexe Cu-phénanthroline est réduit par l'alcool vératrylique en Cu(I). Toutefois la réaction est lente même à 80°C. Plusieurs heures sont nécessaires pour observer une formation substantielle de Cu(I).
- Il n'a pas été possible de détecter la formation de vératraldéhyde dans les conditions de la réaction d'oxydation par HPLC. Ceci est surprenant car d'après la littérature le vératraldéhyde serait le produit d'oxydation de l'alcool vératrylique par le complexe Cu(II)-phénanthroline.
- Quand H_2O_2 est ajouté dans le milieu alcalin contenant le Cu(II)-phénanthroline, la consommation de l'alcool vératrylique augmente mais les espèces Cu(II) disparaissent aussi rapidement. La couleur de la solution initialement bleu devient jaune-marron et des bulles d'oxygène se dégagent. Tout semble indiquer que H_2O_2 n'est pas stable dans le milieu et que le Cu(II) n'est pas reformé. Contrairement au système Cu(II)-phénanthroline/O_2, le système Cu(II)-phénanthroline/ H_2O_2 ne se comporte pas comme un système catalytique où le Cu(II)-phénanthroline serait l'oxydant et H_2O_2 chargé de régénérer l'oxydant en reformant le Cu(II)-phénanthroline. La décomposition de H_2O_2 semble très rapide ce qui implique probablement que des espèces radicalaires seraient formées et seraient responsables de l'oxydation de l'alcool vératrylique.
- Dans tous les essais avec H_2O_2, le vératraldéhyde a été détecté même en l'absence de Cu(II)-phénanthroline, ceci n'a jamais été décrit auparavant. La disparition de l'alcool

vératrylique et la quantité d'aldéhyde produit sont plus importantes en présence de Cu(II)-phénanthroline. La présence de radicaux pourrait en être la raison.

- Le vératraldéhyde n'est pas stable dans les conditions de réaction. L'absence d'aldéhyde lors de certains essais ne signifie pas qu'il n'est pas formé. Par ailleurs la formation d'acide vératrylique suite à l'oxydation de l'aldéhyde n'est pas à exclure et a été démontrée dans le cas du système Cu(II)-phénanthroline/O_2.
- L'oxydation de l'alcool vératrylique par le complexe Cu(II)-5,6-diméthyle phénanthroline est plus efficace qu'avec le Cu(II)-phénanthroline. Ce nouveau ligand sera testé lors d'une délignification de substrat lignocellulosique.
- Comme la décomposition de H_2O_2 est rapide, l'ajout fractionné de H_2O_2 en plusieurs charges successives permet d'améliorer l'oxydation de l'alcool.
- Tous ces résultats confirment que le Cu(II)-phénanthroline/H_2O_2 pourrait permettre d'améliorer la délignification des pâtes cellulosiques même si le système n'est pas un système catalytique. La délignification devrait être plus importante qu'avec H_2O_2 seul.

Chapitre III. Blanchiment d'une pâte kraft de feuillus par le système Cu(II)-phénanthroline/H_2O_2

Il a été montré dans le chapitre II que le complexe cuivre-phénanthroline catalysait l'oxydation des fonctions alcool en carbonyle. Les groupements alcool, présents en nombre dans la lignine résiduelle kraft, seraient donc susceptibles de subir cette oxydation. Ainsi la formation de groupements carbonyle en position α de la chaîne aliphatique de la lignine pourrait favoriser la dépolymérisation de la molécule de lignine lors de la délignification au H_2O_2 catalysé, comme c'est le cas dans la cuisson alcaline du bois, beaucoup plus agressive.

Le système H_2O_2 / cuivre-phénanthroline est donc appliqué, dans ce chapitre, à la délignification d'une pâte kraft de feuillus. L'objectif est de développer une séquence de blanchiment sans chlore incluant le stade catalysé, afin de produire une pâte cellulosique pure : blancheur minimale de 90% ISO et teneur en hémicelluloses inférieure à 5%. Pour certains usages, le DP de la cellulose peut être inférieur à celui des pâtes papetière, toutefois un DP plus élevé permettra de diversifier les applications du produit final.

La pâte kraft utilisée provient de l'usine de Fibre Excellence Saint- Gaudens, France. C'est une pâte papetière ayant subi une pré-délignification à l'oxygène à l'usine. Certains essais ont également été réalisés sur une pâte industrielle pré-délignifiée au laboratoire. Au total, 3 différentes pâtes de propriétés similaires (tableau 3) ont été utilisées dans cette étude.

Table 3 : Indice kappa, blancheur, viscosité et DP des pâtes kraft de feuillus délignifiées à l'oxygène utilisées dans cette étude

	ODL-Tembec	ODL-Lab1	ODL-Lab2
Indice kappa	8,9	9,0	9,8
Blancheur, % ISO	45,7	45,6	45,6
Viscosité, ml/g	931	925	937
DPv	1388	1378	1398

Les premiers essais ont été réalisés dans les conditions usuelles d'un stade au peroxyde d'hydrogène (noté stade P) : 2% de NaOH et 2% de H_2O_2 / pâte comptée en sec, 10% de concentration fibreuse, 90°C et 2h de réaction. Le complexe Cu-phénanthroline, utilisant un ratio molaire Cuivre : phénanthroline de 1:2, est introduit à hauteur de 0,1% (exprimé en quantité de phénanthroline par rapport à la pâte). Les résultats sont comparés à des essais témoins, sans additif, ou avec 0,045% de Cu(II) seul, ou 0,1% de phénanthroline seule (figure 8).

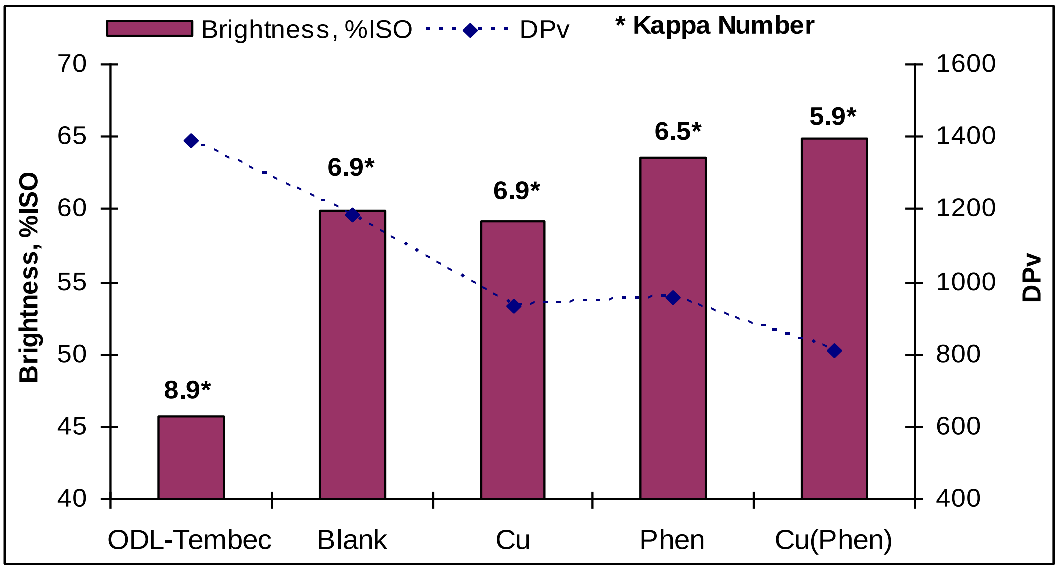


Figure 8 : Délignification au H_2O_2 sans additif (blank), avec du cuivre II (Cu), avec de la phénanthroline seule (Phen) et avec un mélange cuivre-phénanthroline (Cu(Phen))

La figure 8 montre clairement qu'en l'absence d'additif ou qu'en présence de cuivre ou phénanthroline seuls, les niveaux de délignification restent inférieurs à celui obtenu en présence d'un mélange cuivre-phénanthroline. Toutefois, en présence du complexe, le degré de polymérisation de la cellulose est davantage affecté. L'action du complexe n'est donc pas sélective de la lignine. L'effet serait dû soit à la production de radicaux par réaction de H_2O_2 avec le complexe, soit à la formation de groupes carbonyles sur la lignine favorisant la délignification alcaline mais aussi sur la cellulose conduisant à une β élimination.

Le ratio molaire Cu : phénanthroline = 1 : 5 a également été testé afin de s'assurer que tout le cuivre était effectivement complexé au ligand introduit en large excès. La délignification et le DP ne sont que très légèrement améliorés. Ceci montre que la présence de cuivre libre n'est pas seule responsable de l'effet du complexe. Le ratio molaire Cu : phénanthroline utilisé par la suite sera donc 1 :2.

La façon d'introduire le complexe a également été étudiée. Dans les essais précédemment décrits, le cuivre et la phénanthroline ont été mélangés en solution aqueuse puis introduits sur la pâte. Des essais d'imprégnation avec le cuivre solubilisé puis avec la phénanthroline, solubilisée à part, n'ont montré aucune différence avec les essais réalisés avec le complexe formé avant addition sur la pâte. De même des essais d'imprégnation du complexe sur la pâte (introduction du complexe sur la suspension diluée puis concentration de la suspension avant essai), visant à augmenter la diffusion du catalyseur au sein des fibres, n'ont pas conduit à une amélioration de la délignification. Les essais seront donc conduits par la suite avec le complexe préformé en solution aqueuse. Enfin, des doses variables de complexe (0,05 à 0,15% / pâte) ont été introduites lors de la délignification au H_2O_2. A partir de 0,075% d'ajout aucune amélioration de la délignification n'a été observée. Nous avons donc décidé de travailler avec une dose de 0,1% en complexe.

Afin d'optimiser la délignification au peroxyde d'hydrogène catalysé, plusieurs autres conditions opératoires ont fait l'objet de variations : la température, la quantité de soude et de peroxyde d'hydrogène (stades notés P et Pcat, sans et avec complexe respectivement). Les résultats sont présentés dans les figures 9 à 11.

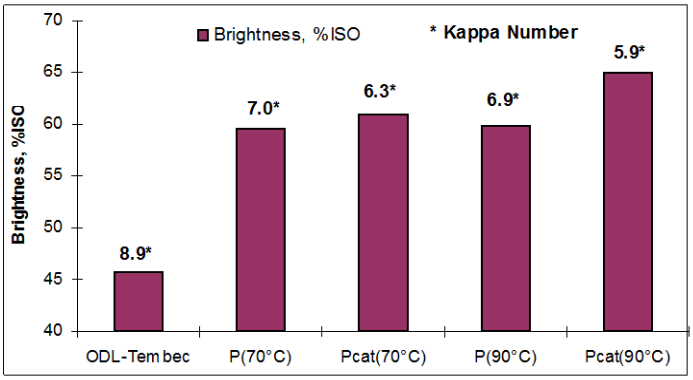


Figure 9 : Effet de la température sur l'effet délignifiant des stades P et Pcat

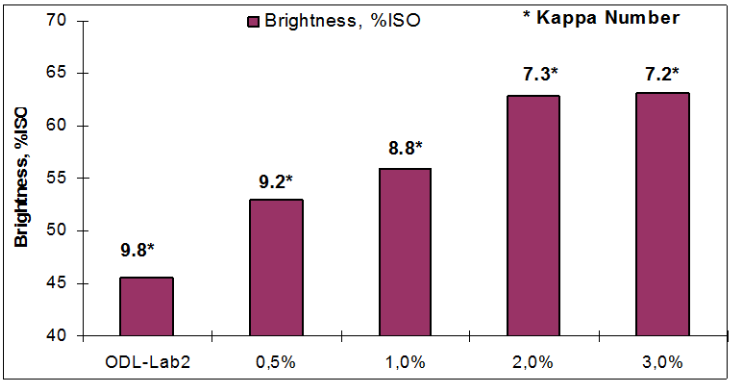


Figure 10 : Effet de la charge en hydroxyde de sodium (0,5 à 3%) sur l'effet délignifiant des stades P et Pcat

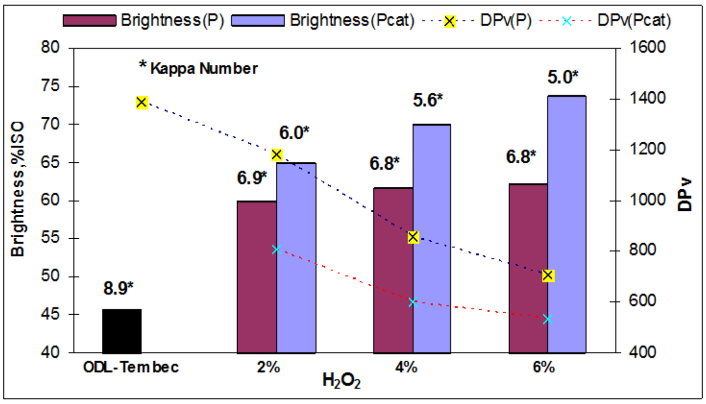


Figure 11 : Effet de la charge en peroxyde d'hydrogène sur l'effet délignifiant des stades P et Pcat

Le complexe Cu-phénanthroline est plus actif à 90°C qu'à 70°C, il permet un gain en délignification et blancheur supérieur par rapport au stade P sans catalyseur (Figure 9). L'augmentation de la quantité de soude a un effet sur l'efficacité du stade P catalysé mais au-delà de 2%, aucune amélioration supplémentaire n'est observée (Figure 10). Enfin, l'augmentation de la charge en H_2O_2 permet une meilleure délignification mais au détriment de la qualité de la cellulose qui est plus dégradée (Figure 11). Les conditions opératoires que nous avons retenues pour le stade P catalysé sont donc 90°C, 2% NaOH, 2% H_2O_2, 0,1% de complexe Cu-phénanthroline (compté en phénanthroline) préformé en milieu aqueux, avec un ratio molaire Cu : phénanthroline de 1 : 2. Le temps de réaction est fixé à 2 heures, temps de réaction classique pour un stade de délignification au peroxyde d'hydrogène.

Bien que l'addition de complexe conduise à une amélioration de la délignification et de la blancheur, le bénéfice reste faible par rapport à la perte en qualité de la cellulose. La blancheur n'excède pas 65% avec 2% de H_2O_2 (ou 75% avec 6% de H_2O_2), ce qui reste loin de l'objectif fixé, 90% de blancheur pour des celluloses pures. La dépolymérisation supplémentaire de la cellulose observée en présence de complexe est mal connue. Plusieurs explications peuvent être avancées, comme la production de radicaux en présence du complexe ou d'ions métalliques de transition présents naturellement dans la pâte. Afin de limiter une éventuelle décomposition de H_2O_2 et donc de renforcer l'action du complexe, des pré-traitements ont été introduits avant le stade Pcat.

Un prétraitement à l'acide, noté (a) et une étape de chélation (Q) permettent, (1) l'élimination de la majeur partie des ions métalliques (tableau 4) responsables de la décomposition de H_2O_2 en radicaux, en partie à l'origine de la dépolymérisation de la cellulose, ainsi que (2) la suppression d'une partie des acides héxènuroniques contenus dans les pâtes de feuillus, responsables d'une surconsommation d'agent oxydant lors de la délignification. Ainsi la présence de ces prétraitements améliore la délignification des stades P et Pcat tout en limitant la réduction du degré de polymérisation de la cellulose. Lorsque la chélation et le stade acide sont réalisés en une seule étape, l'élimination des ions métalliques est plus efficace, il s'en suit une délignification encore plus performante et plus sélective (Figure 12).

Si le renforcement des stades P et Pcat par l'oxygène n'améliore que légèrement la délignification, l'effet principal est une meilleure blancheur et une réduction du degré de polymérisation de la cellulose plus faible, surtout pour le stade (OP)cat (comparaison avec le stade Pcat) (Figure 12). Enfin, en présence du complexe, la pâte sortie (OP) contient beaucoup de cuivre absorbé par les fibres. Nous avons pu montrer que ce cuivre pouvait être facilement éliminé dans les effluents par un lavage SO_2 de la pâte en fin de séquence de blanchiment.

Tableau 4 : Ions métalliques présents dans la pâte après chaque stade de la séquence

Ion métallique, ppm	Pate initiale	a	Q	(aQ)	(aQ)P	(aQ)P$_{cat}$	(aQ)(OP)	(aQ)(OP)$_{cat}$
Cu	<5	<5	<5	<5	<5	15	<5	110
Mn	90	10	5	<5	<5	<5	<5	<5
Fe	44	5	<5	<5	<5	<5	<5	<5
Al	106	154	46	40	18	13	<5	20
Mg	570	57	416	61	14	15	85	15
Ca	3700	600	452	570	150	130	440	50

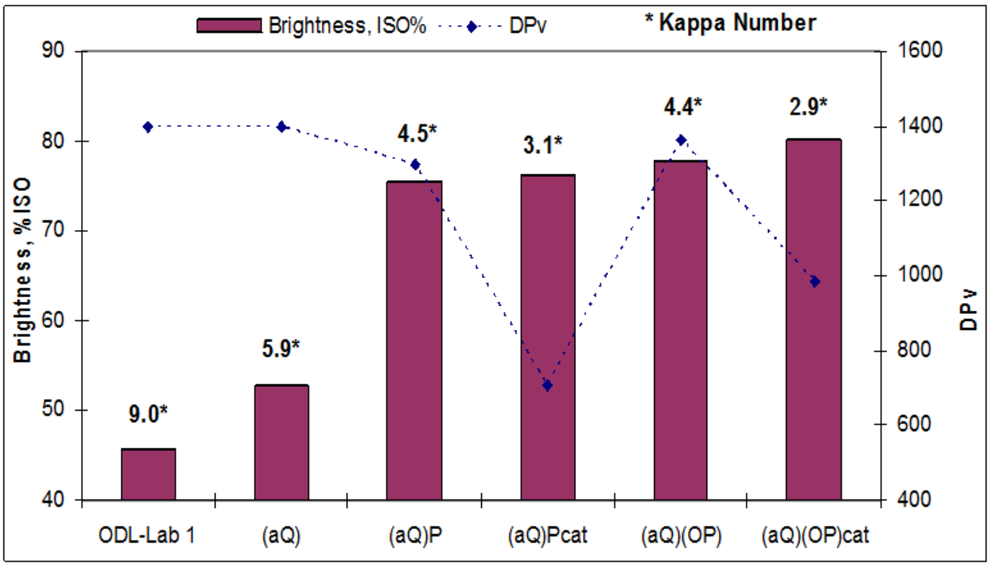


Figure 12 : Addition d'un prétraitement (aQ) avant le stade de délignification au H_2O_2, renforcé ou non à l'oxygène

A ce point de l'étude, la séquence (aQ)P, réalisée avec 2% de H_2O_2, permet d'obtenir une pâte délignifiée avec un indice kappa de 4,5 et une blancheur de 75% ISO avec un degré de polymérisation de la cellulose qui reste élevé (1300 au lieu de 1400 avant traitement). La séquence la plus efficace en termes de délignification est celle qui utilise le complexe et l'oxygène : (aQ)(OP)cat. Cette séquence permet en effet d'atteindre un indice kappa de 3 seulement et une blancheur supérieure à 80%. Malheureusement le degré de polymérisation de la cellulose est faible dès que le catalyseur est utilisé, il est inférieur à 1000.

L'analyse plus détaillée des pâtes après les séquences (aQ)(OP) et (aQ)(OP)cat a permis d'expliquer certains résultats.

L’analyse du taux d’acides héxènuroniques a montré que le prétraitement à l’acide permettait une forte réduction du taux d’acides héxènuroniques dans la pâte mais qu’après le stade (OP)cat il en reste encore (Figure 13). Les 2/3 de l’indice kappa sont dus à ces acides résiduels. La pâte ne renferme donc quasiment plus de lignine, la délignification est maximum.

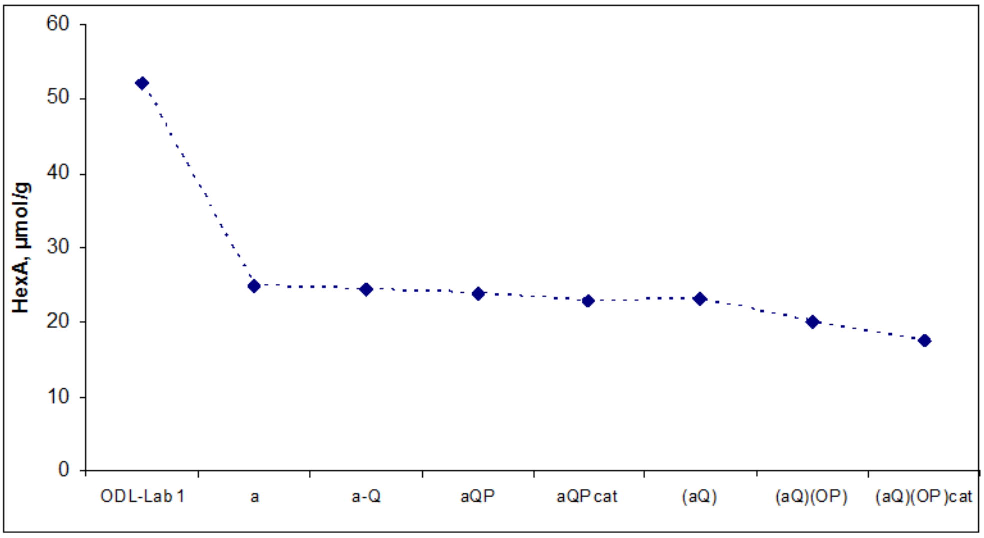


Figure 13 : Dosage des acides héxènuroniques le long de la séquence (aQ)(OP) avec ou sans complexe

La production de celluloses pures, en plus d’une forte blancheur et de hauts degrés de polymérisation, nécessite l’élimination complète des hémicelluloses. Les hémicelluloses ont été quantifiées par la méthode de dosage des pentosanes (pentoses sucres en C5 majoritaires dans les hémicelluloses de feuillus). Les résultats montrent que le complexe, contrairement à ce qui était supposé, n’a aucun effet sur l’élimination des hémicelluloses, bien que la présence du complexe Cu-phénanthroline affecte fortement le degré de polymérisation de la cellulose.

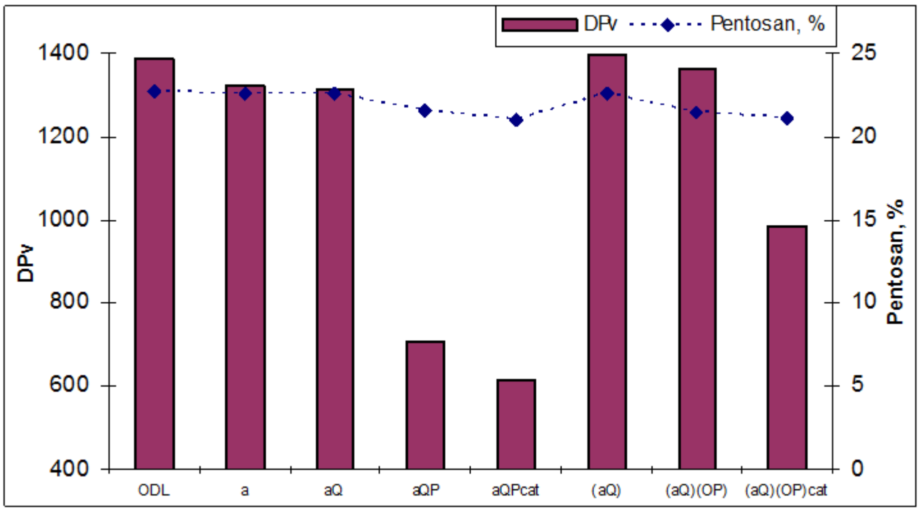


Figure 14 : Dosage des hémicelluloses le long de la séquence (aQ)(OP) avec ou sans complexe

La séquence (aQ)(OP)cat permet donc une délignification quasi-totale de la pâte mais les objectifs de blancheur et de pureté (élimination des hémicelluloses) ne sont pas atteints. Des post-traitements ont donc été ajoutés à la séquence. Ceci fait l'objet du chapitre IV.

Chapitre IV. Préparation de cellulose pure dans une séquence contenant un stade de délignification au H_2O_2 catalysé

La délignification au peroxyde d'hydrogène de pâte kraft de feuillus, bien que catalysée par le complexe Cu-phénanthroline, n'est pas capable de conduire à de la cellulose pure. De la lignine résiduelle subsiste, des acides héxènuroniques (HexA) sont toujours présents et la majeure partie des hémicelluloses reste dans la pâte. Par ailleurs les gains en délignification sont au prix d'une forte diminution de la viscosité (DP) de la pâte ce qui réduit les applications potentielles pour les celluloses produites à partir de ce procédé.
L'objectif de cette partie est donc de mettre au point des post-traitements à la délignification au H_2O_2 catalysé, permettant de conduire à la production de cellulose pure.

Les hémicelluloses des pâtes de feuillus sont principalement des xylans. Leur élimination lors de la cuisson du bois est connue pour être difficile car seule l'hydrolyse alcaline peut réduire leur DP, sans toutefois les solubiliser. La présence du complexe Cu-phénanthroline dans la délignification au peroxyde d'hydrogène pourrait conduire à l'oxydation des xylans, qui seraient alors rendus plus solubles par formation de groupements carboxyliques.

Malheureusement ce n'est pas le cas, les essais présentés dans le chapitre précédent ne montrent pas de diminution du taux d'hémicelluloses après le stade Pcat. Les xylans, contrairement à la cellulose, sont probablement moins sensibles aux réactions d'oxydation sans doute car ils contiennent peu l'alcool primaire, plus réactifs que les alcools secondaires. Les xylans, contenant quelques fonctions carboxyle peuvent en revanche être solubilisés dans une solution alcaline concentrée, à froid. C'est cette approche qui a été appliquée ici. Après la délignification au peroxyde catalysé, la pâte a donc été soumise à une extraction alcaline à froid, notée E. Ce type de traitement est déjà utilisé pour purifier les pâtes sulfite acide.

Après le stade E, réalisé avec une solution d'hydroxyde de sodium à 8% et une concentration fibreuse de 10%, la quantité d'hémicelluloses résiduelles est de 5% (Figure 15) soit la quantité maximale tolérée pour la production de cellules pures. Cette extraction permet donc d'atteindre les niveaux de pureté souhaités. De plus cette étape permet également de réduire encore l'indice kappa (1,2 après (aQ)(OP)catE) (Figure 16). Une analyse de la pâte montre que l'indice kappa mesuré est dû uniquement aux acides héxènuroniques résiduels, toute la lignine a été éliminée. La blancheur est légèrement améliorée puisqu'elle atteint entre 82 et 85% ISO. Le DP de la cellulose, quant à lui, atteint les niveaux de celui de la pâte ODL, sans traitement lorsque le complexe est absent. Ce résultat est probablement dû à l'élimination des xylans de petites masses moléculaires qui ne contribuent alors plus à la valeur du DP. Enfin, le rendement de l'extraction E est de 85% ce qui correspond à la perte des pentosanes et qui indique que le traitement est très sélectif des hémicelluloses.

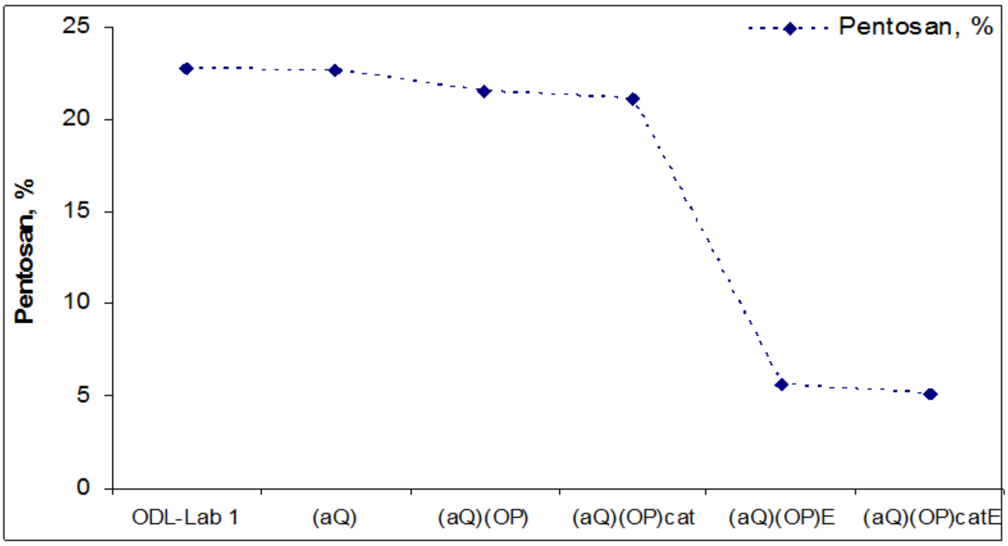


Figure 15 : Dosage des hémicelluloses le long de la séquence (aQ)(OP)E avec ou sans complexe

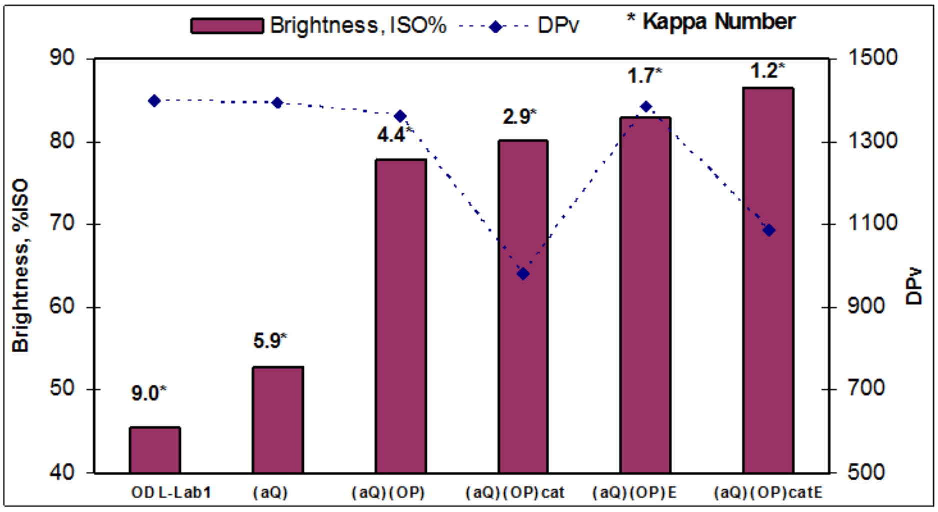


Figure 16 : Effet du stade E sur les propriétés de la pâte obtenue par la séquence (aQ)(OP) avec ou sans complexe

Une mesure du taux d'acides héxènuroniques le long de la séquence (aQ)(OP) avec ou sans complexe montre que les HexA ne sont pas éliminés par l'extraction alcaline E. Ceci signifie que les xylans contenant les HexA ont probablement des masses moléculaires supérieures à ceux sans HexA ou que la solubilisation des hémicelluloses est due essentiellement à des réactions de peeling.

Pour obtenir une pâte pure, il reste donc à éliminer les acides héxènuroniques restants. L'ozone est un agent de blanchiment dont l'effet sur les acides héxènuroniques est bien connu. Des essais d'ozonation ont donc été réalisés, en stade final en présence ou non de complexe dans le stade (OP), à différents pH et différentes doses d'oxydant. Les résultats montrent qu'un stade à l'ozone conduit en milieu neutre avec 0,2% d'ozone permet d'atteindre les blancheurs requises (>90% ISO) (Figure 17) et d'éliminer les acides héxènuroniques (Figure 18). Malheureusement le degré de polymérisation de la cellulose en fin de blanchiment est faible (environ 600) lorsque le catalyseur est présent dans la séquence (Figure 17). Les résultats sont beaucoup plus intéressants lorsque le catalyseur est absent (DPv > 1300). Des essais complémentaires ainsi que des analyses de métaux dans les pâtes ont montré que l'ozone réagissait probablement avec la phénanthroline fixée sur les fibres, générant des radicaux à l'origine de la très forte dépolymérisation de la cellulose lorsque le complexe est présent dans la séquence de production de cellulose pure.

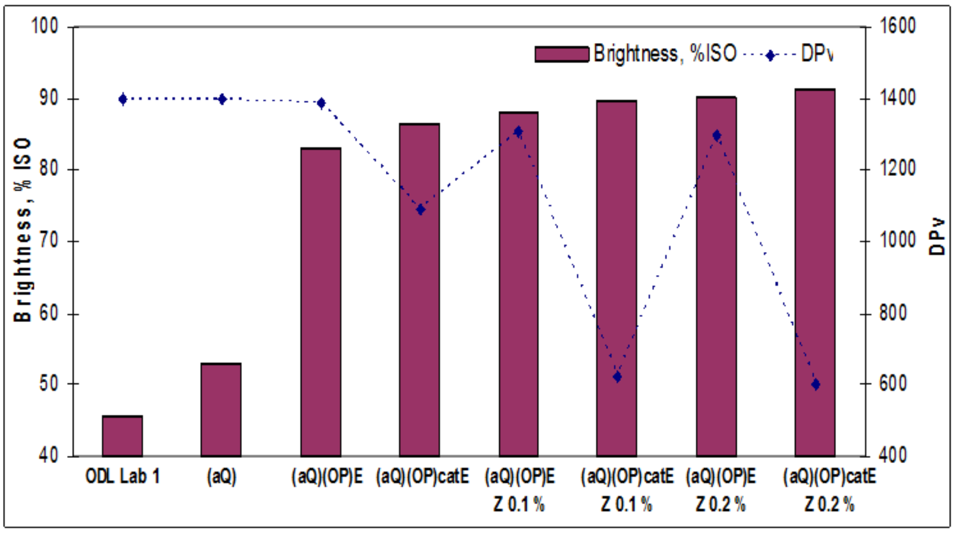


Figure 17 : Addition d'un post-blanchiment à l'ozone après (aQ)(OP)E avec ou sans complexe

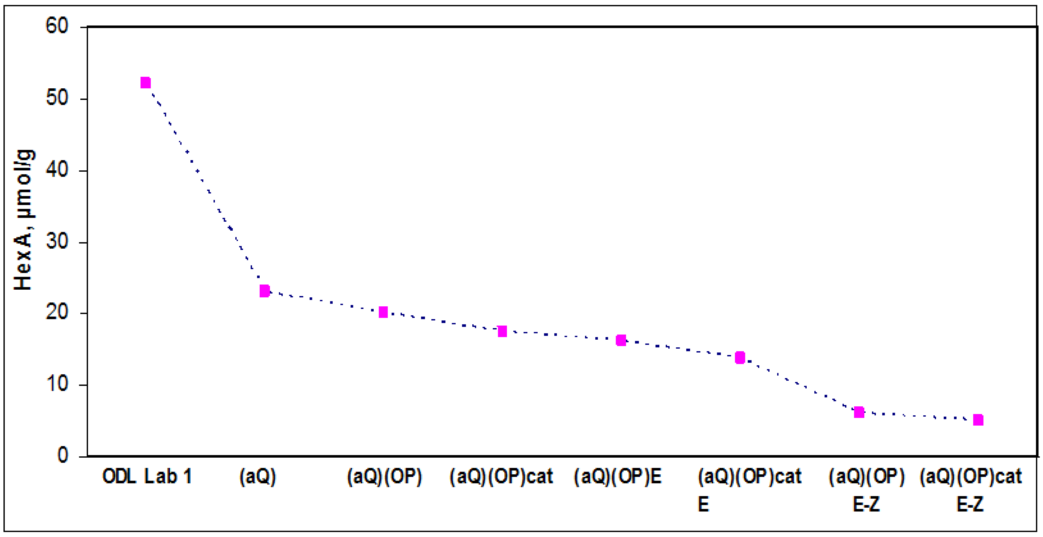


Figure 18 : Effet de l'ozone (0,2%) sur les HexA

En conclusion, la séquence (aQ)(OP)catEZ permet de produire des celluloses pures (sans lignine, peu d'hémicelluloses, sans acide héxènuronique et sans cuivre résiduel si un lavage au SO_2 est réalisé en fin de séquence) et de forte blancheur. Le degré de polymérisation est faible mais les celluloses produites avec cette séquence pourraient être réservées aux applications qui ne nécessitent pas de haut degré de polymérisation. Le faible DP mesuré est dû à l'utilisation du complexe. Pour obtenir des celluloses pures de plus haut degré de polymérisation, il est possible de ne pas utiliser le complexe. En son absence, la délignification est plus lente mais les pâtes produites possèdent de meilleurs degrés de polymérisation.

Afin d'améliorer l'efficacité de cette séquence en termes de délignification et de degré de polymérisation de la cellulose, d'autres ligands ont été testés à la place de la phénanthroline. En effet, nous avons montré dans le chapitre II que des phénanthrolines substituées pouvaient permettre au système complexe de cuivre / H_2O_2 d'être plus oxydant envers l'alcool vératrylique, composé modèle de la lignine non phénolique. Comme prévu, les résultats ont montré une légère amélioration de la délignification avec le ligand 4, 7 diméthyle phénanthroline ou le ligand 5, 6 diméthyle phénanthroline mais la cellulose est aussi davantage dégradée de sorte que nous ne retiendrons pas ces ligands pour la séquence de production de cellulose pure. Comme dans le chapitre II, nous avons également envisagé l'ajout de H_2O_2 fractionné au cours de la délignification afin de préserver au mieux le peroxyde susceptible d'être décomposé pendant la réaction. Sans surprise, l'ajout fractionné de H_2O_2 permet d'améliorer la délignification avec une réduction de la dégradation de la cellulose. Toutefois, cette solution n'est pas retenue dans ce projet suite aux complications qu'elle engendrerait pour des applications industrielles.

La séquence de production de cellulose pure à partir de pâte kraft finalement retenue est donc (aQ)(OP)EZ avec ou sans complexe dans la délignification au H_2O_2, selon les applications visées.

Les qualités papetières des celluloses produites par la séquence (aQ)(OP)EZ avec ou sans complexes ont été étudiées plus en détail afin de cibler les applications chimiques. Les propriétés clés sont la résistance (ou la solubilité) à la soude (R18 ou S18) qui donne une indication de qualité de cellulose, la blancheur et la viscosité de la cellulose.

Le tableau 5 montre que les celluloses produites ne contiennent plus de lignine, très peu d'acides héxènuroniques, moins de 5% d'hémicelluloses, peu de cuivre si un lavage SO_2 est réalisé, et que le degré de blancheur excède les 90% ISO. Le degré de polymérisation, quant à lui, est beaucoup plus faible lorsque la séquence utilise le catalyseur. Toutefois, ces niveaux de viscosité et de S18 permettent aux celluloses produites une éventuelle application viscose, qui représente les 2/3 du marché des celluloses pures.

Tableau 5 : Propriétés papetières des celluloses produites – comparaison avec les celluloses pour application viscose

Séquence	Blancheur, % ISO	viscosité, mL/g	DPv	Pentosanes, %	HexA, µmol/g	S18, %
Objectif viscose	90-92	400-600	546-855	<5	Non donné	3-3,5
(aQ)(OP)EZ	90,3	874	1295	5,5	6	3,26
(aQ)(OP)$_{cat}$EZ	91,2	437	602	4,6	2	3,43

Une analyse de distribution des masses moléculaires des substrats par chromatographie d'exclusion stérique (SEC), a permis d'étudier l'effet des différents traitements sur les hydrates de carbone, et cela tout le long de la séquence de production de cellulose pure. Cette technique permet en outre d'analyser la polydispersité des celluloses, propriété très importante pour la réactivité du produit. En effet, plus la distribution des hydrates de carbone est uniforme, plus la cellulose produite sera réactive dans les procédés de conversion comme le procédé viscose par exemple.

Le tableau 6 et la figure 19 présentent respectivement les propriétés papetières et la distribution des masses moléculaires des celluloses produites après les stades P et Pcat appliqués sur la pâte industrielle ODL.

Table 6 : Propriétés des pâtes ODL soumises aux traitements P et Pcat

	Propriétés des pates			
Pâte	**Indice kappa**	**Blancheur, % ISO**	**DPv (Tappi)**	**Pentosanes, %**
ODL^T	8,9	45,6	1388	22,6
ODL^T+P	6,9	59,9	1182	22,1
ODL^T+ Pcat	6,0	64,9	809	21,3

ODL-Tembec: ODL^T

Les stades de délignification P et Pcat affectent le DP des hydrates de carbone mais aucune élimination de pentosanes n'est observée (mesure du taux d'hémicelluloses), même en présence du complexe pourtant très agressif envers la cellulose. La figure 19 confirme ces résultats. En effet, le stade P déplace la distribution des masses moléculaires (DMM) des hydrates de carbone vers les faibles masses. Ce traitement affecte surtout la fraction de cellulose (hautes masses), les hémicelluloses (fraction de faibles masses) sont beaucoup moins dégradées. En présence du complexe, le profil de DMM est davantage modifié. La réponse bimodale est déplacée vers les faibles masses et la fraction de fortes masses est moins abondante. La cellulose est donc fortement affectée alors que les hémicelluloses sont toujours présentes.

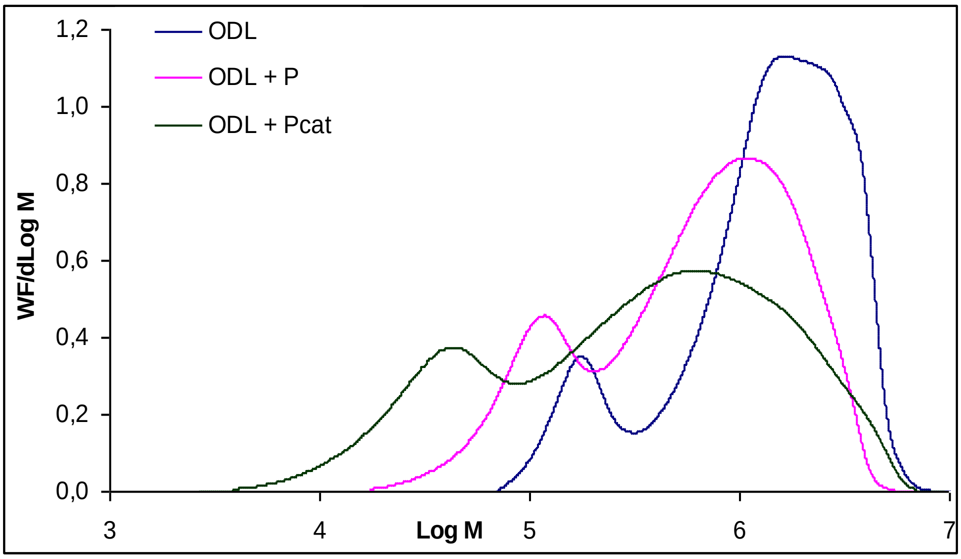
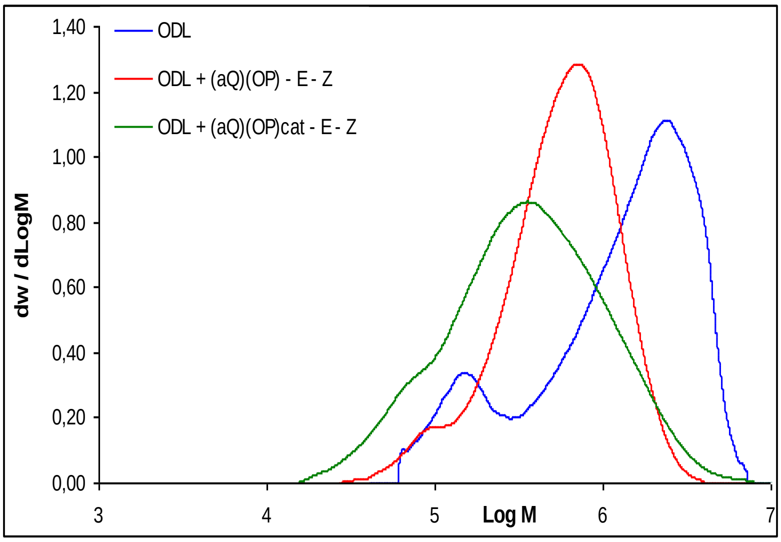


Figure 19 : Distribution des masses moléculaires (DMM) des dérivés de cellulose issus des pâtes ODL, ODL traitée P et ODL traitée Pcat

L'effet des pré- et post-traitements sur la DMM de la cellulose a également été étudié par SEC. Les résultats montrent que le pré-traitement (aQ) (chélation acide) déplace légèrement la DMM de la cellulose vers les plus faibles masses. Les conditions acides et la forte température de ce traitement sont sans doute à l'origine de la dégradation observée. L'introduction d'oxygène dans les stades P ou Pcat permet de limiter légèrement la dégradation de la cellulose. Ceci a été confirmé par les mesures des DMM des celluloses traitées (OP) et (OP)cat. L'extraction alcaline quant à elle, permet d'éliminer la majeure partie des hémicelluloses. En effet, après le stade E, la DMM de la cellulose tend vers un profil monomodal correspondant aux chaînes de cellulose. Enfin, le stade à l'ozone (Z) affecte peu la DMM de la cellulose traitée au H_2O_2 en l'absence de complexe alors que la présence de complexe nuit fortement à la cellulose après traitement Z. Il est probable que l'ozone réagisse avec le complexe Cu-phénanthroline, produisant des radicaux très agressifs envers la cellulose.

Finalement, les DMM des celluloses produites à partir de la séquence (aQ)(OP)EZ avec ou sans complexe ont été comparées aux DMM des celluloses pour application viscose (Figures 20 et 21).

La figure 20 montre que la séquence (aQ)(OP)EZ avec ou sans complexe dans le stade à base de peroxyde d'hydrogène, permet effectivement une élimination des hémicelluloses. La distribution des masses moléculaires de la cellulose est uniforme et cette distribution est étroite notamment lorsque le catalyseur n'est pas utilisé. La comparaison avec les distributions de masses moléculaires de pâte viscose (Figure 21), montre que les celluloses produites dans ce projet présentent une distribution plus étroite et centrée sur une masse moléculaire plus élevée (LogM 5,8 pour les dérivés de cellulose produits dans le projet contre LogM =5,2 pour la viscose standard issue de pâte sulfite acide ou kraft pré-hydrolysée). On peut donc conclure que les celluloses produites présentent des propriétés comparables à celles des pâtes viscose et que le catalyseur permet de moduler le DP de la cellulose en fonction des applications visées.



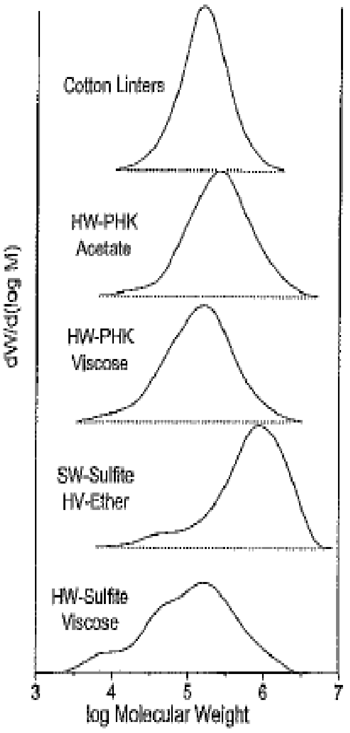


Figure 19 : Distribution des masses moléculaires des celluloses produites (en vert et rouge) et de la pâte initiale (en bleu)

Figure 20 : Distribution des masses moléculaires de celluloses de pâtes à dissoudre

Enfin, afin de s'assurer que les celluloses produites peuvent être utilisées pour des applications de type viscose, un test d'aptitude viscose (méthode Treiber) a été réalisé. Celui-ci a été sous-traité chez Lenzing, spécialiste des pâtes de cellulose de haute pureté. Malheureusement les analyses révèlent que les celluloses produites ont une faible aptitude viscose. La faible réactivité de ces celluloses avec les produits de dérivation du procédé viscose pourraient s'expliquer de plusieurs façons. La première explication serait la forte teneur en impuretés des celluloses testées ce qui diminue la filtrabilité de la solution de viscose. Les hémicelluloses, toujours présentes (environ 5%) sont bien connues pour réagir en priorité avec le réactif CS_2 (disulfure de carbone) utilisé pour la xanthation de la cellulose. Cette réaction conduirait à une substitution inhomogène de la cellulose réduisant ainsi sa filtrabilité. La présence d'impuretés comme des silicates, des sels de calcium et des ions métalliques de transition (Fe, Mn, Co, etc.) seraient également responsable de la diminution de la filtrabilité des solutions de viscose. Enfin la présence de résines provenant du bois et mal éliminées de la pâte peut aussi affecter l'aptitude viscose de la cellulose.

La qualité viscose du substrat n'est pas seulement influencée par la composition chimique de la cellulose (lignine, hémicelluloses, résines, etc.) ou ses propriétés macromoléculaires (distribution des masses moléculaires) mais aussi par ses propriétés supramoléculaires et par la morphologie des fibres. Pendant la dérivation viscose, la cellulose doit réagir avec la soude et le disulfure de carbone (CS_2) pour former une solution de viscose filtrable. Avant la xanthation, le substrat cellulosique est mis à gonfler avec la soude conduisant à la transformation de la structure cristalline de la cellulose en structure amorphe. Comme la xanthation se produit uniquement dans les zones amorphes, les groupes xanthate sont distribués au hasard le long de la chaîne de cellulose en suivant sa morphologie. Certains sites de dérivations sont donc probablement inaccessibles au CS_2. La morphologie de la fibre devra donc être étudiée plus en détail.

Conclusion des travaux de thèse et perspectives

Ces travaux de thèse ont consisté à développer un nouveau procédé propre de blanchiment et de purification des pâtes cellulosiques papetières en utilisant le peroxyde d’hydrogène catalysé comme principal agent délignifiant, capable de dégrader et solubiliser la lignine résiduelle et les hémicelluloses afin de produire des celluloses pures et réactives avec des degrés de polymérisation ajustables. L’objectif est de fournir aux producteurs de pâte kraft un procédé simple et propre de production de cellulose de haute valeur ajoutée, facilement intégrable dans la ligne de production actuelle de pâte à papier.

Le catalyseur sélectionné est le complexe cuivre-phénanthroline, déjà étudié pour activer la délignification à l’oxygène et au peroxyde d’hydrogène. Ce catalyseur est connu pour accélérer les réactions d’oxydation et de dépolymérisation des hydrates de carbone. Cet effet, qui est un sérieux handicap pour la production de pâte à papier, pourrait être un atout dans ce projet puisque l’objectif est de dégrader les hémicelluloses et d’obtenir des celluloses de degré de polymérisation variable.

L’efficacité du système Cu(II)-phénanthroline / H_2O_2 utilisé en délignification a tout d’abord été étudiée en solution aqueuse, en utilisant un composé modèle de lignine non phénolique, l’alcool vératrylique, résistant à l’oxydation conventionnelle par le peroxyde d’hydrogène en milieu alcalin. Des analyses UV-visible ont révélé que sans H_2O_2 le complexe Cu(II)-phénanthroline est réduit par l’alcool vératrylique en Cu(I). Cette réaction est lente même à 80°C. Plus surprenant, après réaction, aucune trace de vératraldéhyde n’a pu être détectée par HPLC alors que la littérature rapporte que le vératraldéhyde est le principal produit d’oxydation de l’alcool vératrylique par le complexe Cu(II)-phénanthroline.

La consommation de l’alcool vératrylique augmente quand du peroxyde d’hydrogène est ajouté dans le milieu contenant le complexe. Nous avons montré également que le complexe de Cu(II) réagit avec H_2O_2. Ceci a été démontré par la disparition de la bande d’absorption dans l’UV du complexe Cu(II)-phénanthroline et par la formation de bulles d’oxygène. Par conséquent le peroxyde d’hydrogène n’est pas stable dans le milieu de réaction, ce qui affecte très rapidement la régénération des espèces Cu(II) actives. Contrairement à ce qui était supposé, le système Cu(II)-phénanthroline / peroxyde d’hydrogène ne se comporte pas comme le système Cu(II)-phénanthroline / dioxygène. Avec H_2O_2 le cycle catalytique ne peut pas être entretenu. Une partie de la consommation de l’alcool vératrylique est donc probablement dû à la génération de radicaux pendant la décomposition de H_2O_2. Dans tous les essais où H_2O_2 été présent, le vératraldéhyde a été détecté, même en l’absence de complexe.

L’oxydation de l’alcool vératrylique en vératraldéhyde par H_2O_2 seul n’a jamais été décrite dans la littérature. Lorsque le complexe est présent, la quantité de vératraldéhyde détectée est supérieure. Les radicaux issus de la décomposition de H_2O_2 pourraient être responsables de l’oxydation de l’alcool vératrylique en aldéhyde correspondant.

Nous avons également montré que le vératraldéhyde n’était pas stable dans le milieu réactionnel. Ceci pourrait expliquer qu’il n’est pas possible de détecter l’aldéhyde après réaction du complexe Cu(II)-phénanthroline avec l’alcool vératrylique. De plus le système Cu(II)-phénanthroline / H_2O_2 est également susceptible d’oxyder l’aldéhyde en acide vératrylique comme cela a déjà été décrit dans le cas des systèmes oxydants de type Cu(II)-phénanthroline / dioxygène. Enfin, l’aldéhyde peut avoir réagi avec des radicaux produits lors de la réaction.

Le procédé d’oxydation souffrant de la décomposition de H_2O_2 par le complexe de cuivre phénanthroline, l’addition fractionnée de peroxyde a été étudiée. Les résultats ont montré une augmentation de la quantité d’aldéhyde formé ainsi que la possibilité de réduire le temps de la réaction d’oxydation pour atteindre la même quantité d’alcool vératrylique consommé.

Même si le système Cu(II)-phénanthroline / H_2O_2 n’est probablement pas un système catalytique, il permet certainement d’améliorer la délignification conventionnelle au H_2O_2 puisque les fonctions alcool de la chaîne aliphatique des unités lignine non phénoliques seraient oxydées. Cette réaction est supposée favoriser la rupture, en milieu alcalin, des laissons β-O-4 adjacentes.

La délignification au peroxyde d’hydrogène et à l’oxygène de pâte kraft de feuillus (indice kappa initial de 10 environ) a été conduite en présence ou non de complexe Cu(II)-phénanthroline. Comme prévu, la présence du complexe améliore la délignification mais accentue aussi la dégradation des hydrates de carbone. Une chélation acide, notée (aQ), a été ajoutée en pré-traitement pour éliminer les ions métalliques de transition responsables de la décomposition de H_2O_2 en radicaux, ainsi que les acides héxènuroniques présents en grande quantité dans les pâtes kraft de feuillus. Ce traitement rend le système Cu(II)-phénanthroline / H_2O_2 plus actif en délignification et moins agressif envers les hydrates de carbone. Afin d’accroître encore la réactivité du complexe, de l’oxygène sous pression a été introduit avec succès dans le stade P activé. Cette opération est notée (OP)cat.

Après le traitement (aQ)(OP)cat, la blancheur de la pâte atteint 80% ISO et l’indice kappa résiduel est de 2,9. L’analyse de la pâte révèle qu’après ce traitement, très peu de lignine résiduelle subsiste puisque les acides héxènuroniques contribuent pour 2/3 à l’indice kappa final. Dans cette séquence, le complexe améliore la délignification de 40%. Même si le DP de la cellulose est sérieusement affecté par l'addition du complexe, les hémicelluloses ne sont pas dégradées, du moins pas assez pour permettre leur solubilisation, contrairement à ce qui avait été supposé. La teneur en hémicelluloses après ce traitement est de 20% environ. Enfin, l'ajout fractionné de H_2O_2 permet d'améliorer la délignification.

Les hémicelluloses et des acides héxènuroniques étant toujours présents dans la pâte après le traitement (aQ)(OP)cat, des étapes de purification ont été réalisées de façon à atteindre le niveau de pureté requis (pas d'acide d'héxènuronique, 90% de blancheur finale, moins de 5% d'hémicelluloses).
Une extraction alcaline à froid, notée stade E, généralement utilisée pour purifier les pâtes à dissoudre, permet d'éliminer la majeure partie des hémicelluloses (teneur en hémicelluloses résiduelles de 5%). Ce traitement élimine aussi les dernières traces de lignine résiduelle. Pour atteindre la blancheur de 90% ISO et pour éliminer les acides héxènuroniques de la pâte, un stade à l'ozone, (Z), conduit en milieu neutre avec une faible charge en ozone a été appliqué. Après la séquence (aQ)(OP)catEZ, la composition de la cellulose produite (blancheur, teneur en hémicelluloses, DP) est similaire à celle des celluloses pures du marché utilisées pour des applications viscose. Les propriétés macromoléculaires ont également été comparées grâce à la mesure de la distribution des masses moléculaires des celluloses (DMM). Cette analyse confirme (1) qu'en présence de complexe les hydrates de carbone sont davantage dégradés car le profil de DMM est déplacé vers les faibles masses, et (2) que les hémicelluloses sont éliminées par le traitement d'extraction à la soude, à froid, car le profil de DMM des celluloses produites tend vers une distribution monomodale. Enfin, il a été montré que les DMM des celluloses produites étaient comparables à celles des pâtes au bisulfite acide ou pré-hydrolyse kraft utilisées pour les applications viscose. Pour renforcer la comparaison avec les celluloses du marché pour viscose, un test d'aptitude viscose a été réalisé. Malheureusement les celluloses produites possèdent une faible aptitude à la filtration viscose ce qui rend ces substrats moins réactifs que les pâtes à dissoudre. Nous n'en connaissons pas la raison. Des analyses complémentaires pourraient expliquer cette faible aptitude viscose et permettre ensuite d'ajuster au mieux la séquence de traitement proposée. En effet, la réactivité du substrat ne dépend pas uniquement de la composition chimique de la pâte, elle résulte également de la structure globale du substrat cellulosique et des interactions entre l'agent de dérivation et les hydrates de carbone. La structure et la morphologie des fibres sont

particulièrement importantes puisqu'elles sont à l'origine de l'homogénéité du procédé de conversion et la qualité du produit final.

Quoi qu'il en soit, comme le DP des pâtes blanchies TCF est relativement élevé en l'absence du complexe, d'autres applications (hors procédé viscose) pourraient être envisagées comme la production de dérivés cellulosiques pour la chimie.

Pour conclure, l'activation du peroxyde d'hydrogène par le complexe Cu(II)-phénanthroline améliore la délignification, permet d'ajuster le DP de la cellulose mais n'élimine pas les hémicelluloses. Par conséquent le traitement au H_2O_2 doit être complété de traitements de purification. Après ces étapes de purification, réalisées sans agent chloré, les celluloses produites sont pures mais manquent de réactivité. Les raisons doivent maintenant être étudiées et des corrections dans la ligne de production de ces celluloses doivent être apportées. Enfin l'adéquation des celluloses produites avec les dérivés cellulosiques marchands devra aussi être explorée.

D'un point de vu fondamental, il a été montré que le système Cu(II)-phénanthroline / H_2O_2 ne pouvait pas être considéré comme un système catalytique car H_2O_2 est décomposé par le complexe, ce qui empêche rapidement la régénération du Cu(II) pendant la réaction. En revanche, les propriétés oxydantes du peroxyde d'hydrogène sont réellement activées par le complexe. Le mécanisme d'activation de l'oxydation des groupes alcool benzylique n'a pas pu être identifié et devra être clarifié afin d'améliorer l'efficacité du système.

SUMMARY

This research work describes the production of pure cellulose from hardwood kraft pulp by an environmental friendly process. To achieve this goal two main strategies are approached: (i) pulp deilgnification and (ii) pulp purification. For pulp delignification hydrogen peroxide is chosen with copper phenanthroline complex. Initially oxidation efficiency of copper phenanthroline with hydrogen peroxide is studied with lignin model compound, i.e., veratryl alcohol. Then its delignification effect is studied with oxygen delignified kraft pulp. After delignification pulp is purified by cold caustic extraction and ozone treatment. With this approach pure cellulose is produced, whose chemical properties are similar the different grades of pure celluloses available. By this process a wide rang of pure celluloses can be produced for different products.

RÉSUME

L'objectif de ce travail est donc de développer un procédé industriel, propre, de production de cellulose pure à partir de pâte kraft non blanchie, basé sur la catalyse du peroxyde d'hydrogène et utilisant si nécessaire des traitements complémentaires sans chlore. A cet effet, deux approches sont adoptées : (i) délignification de pâte kraft avec du peroxyde d'hydrogène et (ii) purification de la pâte à la soude et ozone. La réaction du système cuivre-phénanthroline / peroxyde d'hydrogène avec un composé modèle de lignine non phénolique, l'alcool vératrylique a été étudié. L'effet du catalyseur sur la délignification et sur la dégradation des hydrates de carbone a été examiné. La purification des pâtes ainsi obtenues par une extraction alcaline à froid ainsi qu'un stade de blanchiment final à l'ozone. Enfin, il a été montré que les moléculaires des celluloses (DMM) des celluloses produites étaient comparables à celles des pâtes au bisulfite acide où pré-hydrolyse krafts utilisés pour les applications viscose.