

Oxidation of Fully Bleached Paper-grade Kraft Pulps with H₂O₂ Activated by Cu(Phen) and the Effect of the Final pH

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Hydrogen peroxide is an environmentally friendly bleaching chemical that is widely used in alkaline media in the pulp and paper industry. In this study, unconventional reaction conditions of the conventional bleaching P-stage were performed to evaluate its effect on cellulose. The objective was to “tailor” the cellulose degradation according to different applications, such as dissolving pulps. Different operating conditions were studied: pH variation (alkaline or acidic medium), as well as the addition of Cu(II) or the Cu(II)-phenanthroline complex. The hypotheses considered were (1) Using H₂O₂ in unconventional conditions will favor hemicelluloses removal after depolymerization and will lead to the desired cellulose degradation, and (2) H₂O₂ oxidation carried out under unconventional conditions will favor the dissolving ability of cellulose.

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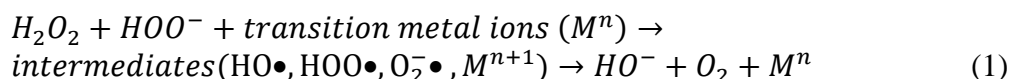
INTRODUCTION

Hydrogen peroxide has been used in alkaline medium as a bleaching agent for virgin wood chemical pulps since the 80's. Nowadays, due to its versatility, it is also used as a reinforcement delignifying agent after oxygen delignification, and in alkaline extraction stages to avoid the yellowing induced by sodium hydroxide (Carvalho *et al.* 2008). The P-stage is considered a complementary stage in an elementary chlorine free (ECF) sequence, to enhance the final brightness and brightness stability; and it is also a major bleaching stage in totally chlorine free (TCF) bleaching sequences, for delignification. The P stage (H₂O₂) could be used as a delignifying and/or a color-stripping treatment, depending on the temperature applied during bleaching and can be performed alone or in combination with oxygen. The classic operation conditions of the P-stage are 10 to 15% pulp consistency, 60 to 90 °C, 30 to 240 min of retention time, 0.2 to 4% NaOH charge, 0.2 to 4% H₂O₂ charge, and pH range of 10 to 12 (Walger *et al.* 2017).

As lignin is responsible for the color in the pulp, bleaching can be obtained either by delignification and/or by color-stripping, resulting in an oxidized lignin and partially depolymerized, which renders lignin soluble in the bleaching medium. Later, lignin is removed during washing steps placed between bleaching stages. Parallel to delignification, cellulose may also be damaged. In the case of D stage, cellulose is preserved, which is the reason why chlorine dioxide in acidic conditions is widely used in bleaching sequences.

The structures responsible for color in the pulp are polarizable groups (conjugated carbonyl groups, enones, and quinones), able to react with hydrogen peroxide in alkaline medium by the action of the perhydroxyl anion (HOO^-) at moderate temperature between 60 to 75 °C. The reaction leads to selective oxidation into non-colored compounds (Castellan and Grelier 2016). The destruction of these chromophores results in the whitening of the pulp, without significant lignin removal. Such reactions typically occur during the bleaching of mechanical pulps (Dence and Reeve 1996). In addition, the Dakin (or pseudo-Dakin) reaction is involved in the bleaching of chemical pulps. In alkaline medium, HOO^- can react on some of the free phenolic structures in lignin (the ones bearing a carbonyl group on the $\text{C}\alpha$ carbon, or on the $\text{C}\alpha$ carbon of quinone methide induced structures, obtained at higher temperature in alkaline medium from the free phenolic structures bearing a benzyl alcohol). Yet, depending on the alkalinity and temperature, the reactivity of HOO^- with lignin-containing pulps remains rather moderate. Contrary to lignin, polysaccharides in this range of temperatures do not react with H_2O_2 and HOO^- ($\text{pK}_a = 11.6$ at 25 °C), except in a strongly acidic medium.

At higher temperatures (above 80 °C), HOO^- can decompose by the well-known Fenton reaction mechanism, giving rise to the formation of highly reactive intermediate oxygenated radicals, namely HO^\bullet , HOO^\bullet and O_2^\bullet ($\text{pK}_a(\text{HOO}^\bullet/\text{O}_2^\bullet) \sim 4.8$ at 25 °C). Such a decomposition involves the catalysis by metal cations (M^n) that are generally present as traces in the pulp. The global reaction for peroxide decomposition can be given as follows:



HO^\bullet is a strong electrophilic oxidant ($E^\circ > 2 \text{ V}$) with the capacity of electron abstraction on the alcoholic $-\text{OH}$ groups of polysaccharides, leading to cellulose oxidation (carbonyl formation) and further cellulose depolymerization. Contrary to HO^\bullet , O_2^\bullet is a nucleophilic species that can be oxidized into HO^\bullet , while HO^\bullet is reduced into H_2O . In the presence of organic reducers, O_2^\bullet can behave as a weak oxidant and react with them, since it is a long-life radical compared to HO^\bullet , and it can diffuse at a certain distance from the point where it was generated.

It is generally desired to monitor the effect of oxygenated radicals during alkaline bleaching or delignification stages applied on chemical pulps involving hydrogen peroxide (P stages). This is usually obtained by controlling the alkalinity, the temperature, and the metal cations profile in the pulp, with the possibility to apply chelating stages (Dence and Reeve 1996).

Not only lignin, but also dyes in cellulosic pulps can be fully removed or discolored by hydrogen peroxide. But depending on the dye's molecular structure and the applied reaction conditions, peroxide's efficiency can be poor with some recalcitrant dyes. Walger *et al.* (2016) focused on the possible ways of improving dye decolorizing of a fully bleached chemical pulp, impregnated by recalcitrant red dyes, which are not easily removed using conventional alkaline P stages. The study focused on the possible ways of monitoring and regulating the intensity of the hydroxyl radical flow generation, by the addition of copper additives at different pH values: either free copper (CuSO_4), or the copper-phenanthroline complex (referred as $\text{Cu}(\text{Phen})$ in this paper). The addition of $\text{Cu}(\text{Phen})$ in near-neutral or alkaline aqueous solution promotes the formation of different complexes, which depend on the phenanthroline-to-copper ratio and on the concentration of OH^- (Korpi *et al.* 2007). Walger *et al.* (2018) listed the abundance of the main copper

species, either free, hydroxylated, or complexed with phenanthroline, according to different pH and Cu:Phen molar ratios (Walger *et al.* 2018). In the absence of phenanthroline, some of the obtained speciation results are given in Table, where it is evidenced that free copper dominates at near-neutral pH, whereas various hydroxylated copper complexes dominate at alkaline pH. In the presence of phenanthroline, various complexes are introduced, depending both on the alkalinity and the phenanthroline dose. In Table, speciation results for a (Cu:Phen) ratio of (1:2) are presented.

Table 1. Speciation of Copper at Different pH, in the Absence of Phenanthroline (Walger 2016)

Copper Species	Relative Abundance (%)		
	pH 6.5	pH 10.7	pH 12.3
Cu ²⁺	90.2	trace	trace
CuOH ⁺	8.8	0.5	trace
Cu(OH) ₂	0.1	48.1	1.6
CuSO ₄	0.3	trace	trace
Cu ₂ (OH) ₂ ²⁺	0.6	trace	trace
Cu(OH) ₃ ⁻	trace	51.2	77.4
Cu(OH) ₄ ²⁻	trace	0.2	21.0

Table 2. Speciation of Copper at Near-neutral and Alkaline pH, in the Presence of Phenanthroline at a Cu:Phen Molar Ratio of 1:2 (Walger 2016).

Copper Species	Relative Abundance (%)		
	pH 6.5	pH 10.7	pH 12.3
Cu ²⁺	trace	trace	trace
CuOH ⁺	trace	trace	trace
Cu(OH) ₂	trace	0.1	0.1
CuSO ₄	trace	trace	trace
Cu ₂ (OH) ₂ ²⁺	trace	trace	trace
Cu(OH) ₃ ⁻	trace	0.1	3.1
Cu(OH) ₄ ²⁻	trace	trace	0.8
(CuPhen) ₂ ⁺	15.9	trace	trace
(CuPhen ₂) ₂ ⁺	72.8	0.6	trace
(CuPhen ₃) ₂ ⁺	10.6	1.4	trace
(CuPhenOH) ⁺	0.8	5.9	0.2
(CuPhenOH) ₂ ²⁺	trace	0.9	trace
CuPhen(OH) ₂	trace	91.1	95.9
Phen	6.1	96.8	104.0

From Table it is apparent that the higher the pH, the more dominant the CuPhen(OH)₂ complex, but also, traces of hydroxylated copper complexes arise with higher amounts of OH⁻ ligands at higher pH. At near-neutral pH, free copper is completely replaced by the CuPhen₂²⁺ complex. As free Cu²⁺, the latter is also involved in the catalysis of peroxide decomposition, as shown by Korpi *et al.* (2007) and Walger *et al.* (2016). Vladut *et al.* (2011) demonstrated that HO• generation during P stages (at alkaline pH) was much more intense with Cu(Phen), when compared to a classical non-activated stage. Walger *et al.* (2016) showed that copper II alone, and the copper II-phenanthroline complex, both significantly improved the reactivity of H₂O₂. The results were a better color-stripping of dyed pulps, while cellulose became also more depolymerized during pulp decolorizing. Similar results about the effect on pulp viscosity had already been

observed in previous studies on delignification (Vladut *et al.* 2011; Das 2012). delignification was improved using copper and phenanthroline species but the cellulose DP_v was significantly affected.

In a detailed mechanistic study, Walger *et al.* (2021) showed the presence of free hydroxyl radicals in the pH conditions given in Tables 1 and 2, with the use of EPR spectroscopy and the spin-trapping technique, using DMPO (5,5-dimethylpyrroline-N-oxide). When present, the latter reacts almost instantaneously with the hydroxyl radicals generated in the medium to form the DMPO-OH adduct, which can be unambiguously identified by its characteristic four-lines EPR spectrum. Figure 1 presents two spectra, one at near-neutral pH with a strong signal, and the other one with a moderate signal at slightly alkaline pH.

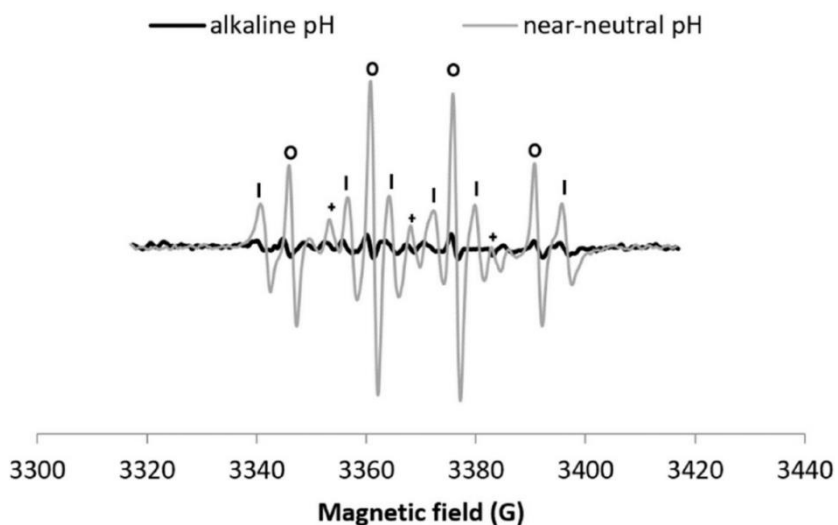


Fig. 1. Comparison between near-neutral and alkaline pH (Walger *et al.* 2021; CC BY 4.0)

Figure 1 provides evidence that the presence of copper stimulated an intense generation of HO• radicals at near-neutral pH, while the effects were more moderate but still present at alkaline pH. The Cu:Phen molar ratio was 1:2. Comparison of the results were done at near-neutral pH (between 7.5 and 9) or at alkaline pH (pH around 12.5).

In the presence of H₂O₂, copper II is the activating species, and phenanthroline only acts as a stabilizing agent to adjust the solubility, the stability, and the redox potential of copper II. The activation of H₂O₂ is mainly due to its decomposition into HO• by the copper species, and the extent of the activation is strongly dependent on the pH of the medium. Finally, the mentioned study concluded that the H₂O₂/Cu(II) system is an interesting generator of HO• radicals with adjustable flow. All details about the conditions for controlling HO• flow intensity, qualitatively identified and measured by ESR spectroscopy, are described in the studies cited. Overall, the use of free copper (CuSO₄) at acidic or neutral pH promotes a non-inhibited, strong radical flow, together with fast peroxide decomposition. Such a flow can be strongly attenuated at alkaline pH, or even regulated by adding adjusted doses of NaOH and phenanthroline.

The main application of bleached pulps with low degree of polymerization considered in this study is the dissolving pulps for viscose applications. When referring to a high-quality dissolving pulps for viscose applications, the intrinsic viscosity should be in the range of 400 to 600 mL/g; a uniform molecular weight distribution is desirable to ensure homogeneous reactions, as well as high alpha-cellulose content (> 92%) (Sixta 2006).

Pulps with high surface area, high porosity, and large pore size often can have high accessibility and reactivity. In summary, the key parameters to monitor in dissolving pulps include high α -cellulose content, alkali solubility, intrinsic viscosity, uniform molecular weight distribution (MWD), and good accessibility and reactivity.

In the present study, the results published by Walger *et al.* (2016, 2018, 2021) have been the main guide to be directly reused (without further measurement of HO• radical flow), in the context of a new focused objective, *i.e.*, modifying a lignin-free cellulosic pulp by hydrogen peroxide to increase its dissolving ability and the control of its degree of polymerization, for further applications of chemical celluloses.

MATERIALS AND METHODS

All the oxidation trials in the present section were carried out at high temperature (90 °C) to favor the formation of hydroxyl radicals. The effects on the final pH, chemical charge of H₂O₂ and NaOH have been explored.

Cellulosic Substrates

The screening of the most interesting conditions for cellulose oxidation with hydrogen peroxide was carried out on paper-grade kraft pulps from hardwood and softwood. The cellulosic samples selected were a softwood (SW) and a hardwood (HW) with low intrinsic viscosity values (IV) of 563 and 496 mL/g, respectively. For comparison with a substrate without hemicelluloses, cotton linters (CL, IV of 695 mL/g) were also included in the study. Other initial conditions are presented along the document in tables and figures as REF, referring to the non-treated sample.

Oxidation trials using H₂O₂ alone were carried out, as well as trials with copper (II) activators, either Cu(II) from copper sulfate or from the Cu(Phen) complex. The pH of the oxidation reaction varied with the addition of different amounts of sodium hydroxide: 0, 0.2 or 2% NaOH, for a constant H₂O₂ charge (2%). The aim was to investigate the behavior of the three H₂O₂-based systems in acidic, neutral, and alkaline medium.

Table 3. Conditions using 2% H₂O₂ and 0.02% Cu or Cu(Phen) with Different Doses of NaOH

Conditions	
0% NaOH	H ₂ O ₂ alone
	H ₂ O ₂ / Cu
	H ₂ O ₂ / Cu(Phen)
0.2% NaOH	H ₂ O ₂ alone
	H ₂ O ₂ / Cu
	H ₂ O ₂ / Cu(Phen)
2% NaOH	H ₂ O ₂ alone
	H ₂ O ₂ / Cu
	H ₂ O ₂ / Cu(Phen)

After oxidation, the pulps were analyzed through intrinsic viscosity (IV), alkali resistance (R18), crystallinity, and brightness (%ISO). The final pH and the consumption of H₂O₂ were also monitored for the purpose of optimizing the conditions. Finally, the dissolving ability of the pulp was assessed using the methods proposed by Vera-Loor *et al.* (2023), where the derivatization of cellulose was performed while measuring the particle

size by DLS; as well as by the dissolution in the NaOH:urea:water system (Vera-Loor *et al.* 2023). The chemical doses used for the oxidation trials are detailed in Table. These conditions have been extracted from previous work done at LGP2 by E. Walger and S. Das. Note: the percentage values mentioned are considered as weight of the chemical per weight of dry pulp.

Cellulose Oxidation

20 g of oven-dried pulp were weighed and later disintegrated in deionized water using a Lombardy apparatus for 1 min, following the guidelines for pulp disintegration of ISO 5263-1995. The pulp was then concentrated by filtration in a sintered glass crucible of porosity No. 2 and introduced in a polyethylene (PE) bag used as reactor. The total weight was completed up to 5% consistency (400 g of fiber suspension, considering the chemicals to be added). The pulp was preheated in a water bath at 95 °C for 20 min, and the chemicals were added and mixed by hand in each step in the following order: Cu(Phen) or CuSO₄, NaOH, and H₂O₂. The pH was measured before closing the PE bag, right before putting it in the water bath for 1 h to start the oxidation. After the reaction, the fiber suspension was filtered, and the first effluent collected for pH measurement and determination of H₂O₂ consumption. Finally, the pulp was washed with deionized water until neutral pH. 2 g of oven-dried pulp were separated for brightness measurements, which were performed the same day of the oxidation. The remaining pulp was air-dried for further measurements such as intrinsic viscosity and functional group quantification.

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

The Cu(Phen) complex was prepared using CuSO₄·5H₂O and 1,10-phenanthroline, as detailed by Walger *et al.* (2017). It was prepared in aqueous solution by dissolving phenanthroline and adding CuSO₄, using 2 moles of phenanthroline for 1 mole of CuSO₄. The complex is referred to in the document as Cu(Phen).

pH

The pH was measured at the beginning of the reaction, after the oxidative chemical addition, and at the end of the reaction before washing.

Hydrogen Peroxide Titration

The consumption of H₂O₂ was determined immediately after each oxidation trial, and it was performed by iodometric titration in the presence of sulfuric acid. The titration chemical was sodium thiosulfate (0.2 M).

Pulp Brightness

The brightness was determined according to the standard ISO 2470-1:2016. Two grams (oven-dried basis) of pulp were homogenized in deionized water, and handsheets were formed the same day after the oxidation trial was performed. Once the sample was dried in the sheet former, the brightness was measured 4 times per sample, and its average was reported.

Alkali Resistance

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

COOH Quantification

Carboxyl group quantification was estimated following the standard method TAPPI T237 cm-08.

Viscosity-average degree of polymerization of the pulp in CuED

The viscosity-average cellulose degree of polymerization approximately indicates the weight-average number of monomeric glucose units in the cellulose polymer. A viscosimetric method can be used. The determination was done using 50 mg of sample (oven-dried basis), following the procedure of the standard method ISO 5351:2010.

Cellulose Accessibility

The accessibility of the cellulosic samples can be assessed based on morphological changes, such as fiber length, crystallinity, pore structure, and specific surface area. The fiber length and width were measured using a MorFi analyzer to monitor the physical changes of the fibers before and after treatments. For the estimation of the crystallinity index (CI), the samples were cryo-ground to obtain a fine powder, which was analyzed by X-Ray Diffraction. The analyses were performed using a diffractometer X'Pert Pro MPD (PANalytical, Netherlands) equipped with a copper anode ($K\alpha \lambda = 1.5419 \text{ \AA}$). The diffractometer was working in the Bragg-Brentano geometry, with the angle 2θ ranging from 6° to 60° (0.05° interval). The measurements were analyzed with FULLPROF software to obtain the crystallinity profiles. For the calculation of the CI, the Segal peak height method was used. The method uses a maximum intensity value (I_{200}) found between the scattering angles $2\theta=22^\circ$ and 23° . The minimum value (I_{min}) is typically between $2\theta=18^\circ$ and 19° . The CI is simply the difference between these two intensities, divided by the intensity of the highest (Segal *et al.* 1959; French and Santiago Cintr3n 2013). The CI was calculated as follows:

$$CI = \frac{I_{200} - I_{min}}{I_{200}} \quad (1)$$

Carbohydrate Composition

The carbohydrate composition was determined following the guidelines of TAPPI T-249 cm-00. A specimen of 350 g (oven dried basis) was put in a glass test tube, and 3 mL of 72% H_2SO_2 was added. The tube was then placed in a water bath at $30^\circ C$ for one hour, and the sample was mixed often with a stirring rod. When the hour was over, the solution was transferred into a 100 mL glass resistant flask, and exactly 84 mL of distilled water was added. The flask was closed and then put in an autoclave for 1 h at $120^\circ C$. At the end of the hydrolysis, and when the flask was cooled down, the solution was filtered and later used for the preparation of dilutions for further analysis in the DIONEX-HPLC.

Cellulose Tricarbanilation

This reaction was done following the publication of Vera-Loor *et al.* (2023). An amount 250 mg of oven dried basis ground cellulosic substrate was weighed in a 250 mL glass bottle with a screw cap and mixed with 25 mL of the reaction solvent, DMSO. Then it was left under stirring at 250 rpm overnight at room temperature. After 18 h, with continuous stirring, the temperature was raised to 70 °C (approximately 1 hour). Then 5 mL of phenyl isocyanate was added slowly under stirring (t_0), followed by 20 mL of DMSO. The reaction proceeded for 48 h.

To monitor the particle size evolution during the tri-carbanilation by Dynamic Light Scattering (DSL), 1 mL of the sample was collected from the reacting system and diluted 10 times as follows: 5 mL of DMSO and 1 mL of acetone into a 10 mL volumetric flask, followed by 1 mL of the cellulosic substrate undergoing dissolution was sampled, and the 10 mL volume was completed with DMSO. This sampling procedure was performed for the first 6 h of the reaction. The repeatability was evaluated by triplicate testing. As for the DLS information input, a DMSO refractive index of 1.4772 and a viscosity of 1.99 mPa-s were considered at 25 °C. The instrument used was a VASCO™ particle size analyzer with a light source from a diode laser emitting at 657nm. Z-average and PDI from the Cumulants method, as the parameters recommended by ISO 22412:2017, were used in this study to evaluate the particle size.

Size-exclusion Chromatography

At the end of the carbanilation, with 48 mL left when 8 samples of 1 mL were taken, 16 mL of acetone were added carefully in the hot reactional mixture, and it was left to cool down slowly under stirring. 1 mL of this solution was diluted in 10 mL of THF, and 100 μ L of the diluted solution was injected in the SEC system for MWD analyses. A multi-detector SEC system (The Viscotek-Malvern TDA 302-GPCmax system) was used for the analyses, and the MWD profiles were obtained using the software OmniSEC 4,5 (Malvern Co.). Some of the parameters studied included peak integration limits (based on RI signal), and MW versus elution volume fit, both influenced by the dispersity index (PD) and MW calculations (Mortha *et al.* 2011).

Dissolution in NaOH:urea:water Mixture

This experiment was performed following the guidelines proposed by Vera-Loor *et al.* (2023). A mass 0.25 g (1 wt%) of cellulosic substrates was dispersed in 24.75 g of pre-cooled (-12 °C) solvent made of NaOH:urea:water with a ratio of 7:12:81 wt%, The liquid fraction was pre-cooled in the system under agitation at 400 rpm for 15 min before adding the sample in a 250 mL glass bottle with a screw cap. After the pre-cooling time, the bottle was opened, and the sample transferred in very slowly with the help of a tweezer. The transfer duration was exactly 5 min, while maintaining 400 rpm agitation. After the addition of the sample, it was verified that there was no sample left on the walls of the bottle. The system was closed and allowed to dissolve for 15 min. Then, the solution was transferred to centrifuge tubes and centrifuged for 30 min at 4000 rpm. The supernatant was removed with a pipette, and the undissolved fraction was washed with distilled water until reaching neutral pH (~600 mL water was needed). The pre-weighted crucible (pore No.2), which had been used for washing, was then placed in the oven at 105 °C for 24 h. Before measuring the final weight, the hot crucible was placed in a desiccator for 15 min. The cellulose solubility (S_a) in NaOH:urea:water solution was calculated as presented in Eq. 2, where w_0 is the weight of the sample and w_1 the undissolved fraction.

$$S_a (\%) = \frac{w_0 - w_i}{w_0} * 100 \quad (2)$$

RESULTS AND DISCUSSION

Figure 2 presents the final pH and intrinsic viscosity for the studied cellulosic substrates and the above-described oxidation treatments.

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

Figure 2(B), presents the results after the oxidation took place with 2% H₂O₂ and 0.02% Cu(II). IV values of HW were reduced significantly when the final pH was acidic. But it was only reduced to 396 mL/g at alkaline pH, which was a similar behavior as with H₂O₂ alone. Such behavior was also observed for SW, where the lowest IV value was reached with the lowest pH. Yet, CL behaved differently, since degradation only took place at alkaline pH, going from its initial value of 695 mL/g to 317 mL/g. Alkaline medium provided conditions for cellulose swelling and not too fast generation of radicals during peroxide decomposition, as copper ions are hydroxylated in alkaline medium, contrary to the acidic medium where the radicals flow is intense. Moreover, cellulose in CL is not protected by a hemicelluloses' barrier around the microfibrils when it becomes more accessible by swelling.

When focusing on Fig. 2(C), a general observation can be made: with Cu(Phen), CuSO₄-H₂O₂ or H₂O₂ alone, for SW and HW, the lowest cellulose degradation took place at a higher final pH (2% NaOH). This is in contrast to CL, which achieved its highest IV value at pH close to neutral (0.2% NaOH). In general terms, at acidic pH, the intrinsic viscosity values decreased down to three times the initial values, the hydrogen peroxide decayed down to 20% consumption, and the brightness %ISO was more affected compared with the other scenarios.

The H₂O₂ oxidation activated with CuPhen in CL at pH 7.8 allowed a slow and constant radical generation, which slightly degraded the sample, in comparison to the acidic condition with pH 3.6, where it is presumed that the radical generation was too fast, and thus the degradation was too strong. Both behaviors are likely to be explained by a Fenton-like decomposition of H₂O₂ in cellulose, where traces of Fe²⁺ promote the degradation of fibers in acidic medium (Walter 2009). Yet, in the scenario with pH 11.7, a slight degradation was observed, and it can be presumed that is due to the residual Fenton decomposition. The overall resistance of CL against degradation, when comparing to SW and HW, can be explained by its compact cell wall and highly crystalline structure.

Nevertheless, these were not the only parameters monitored. The final brightness and the H₂O₂ consumption, when no copper was involved, are presented in Fig. 3.

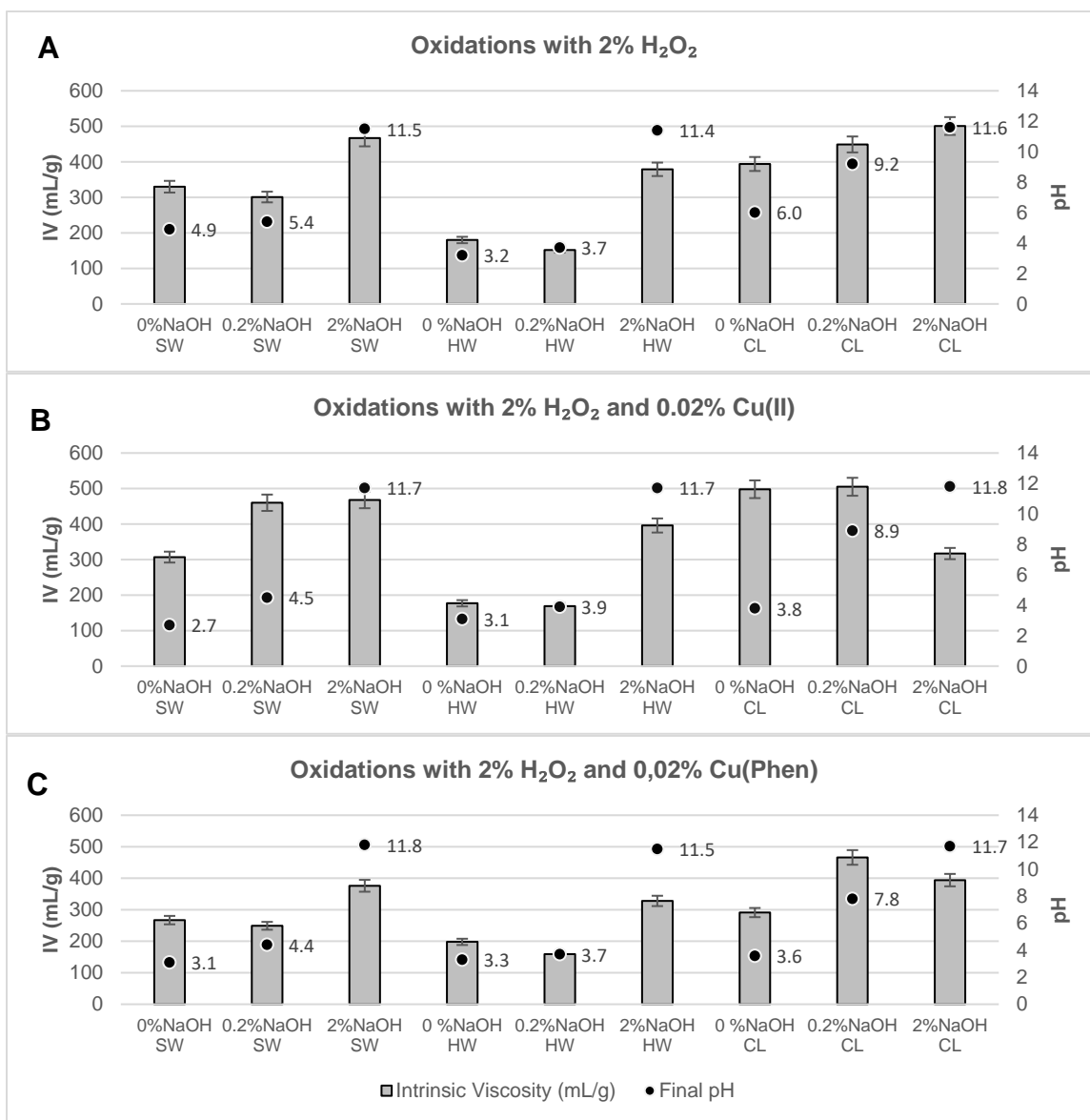


Fig. 2. Intrinsic viscosity (IV) in CuED and final pH after oxidations. (IV_{initial}: 563 ml/g for SW, 496 ml/g for HW, and 695 ml/g for CL)

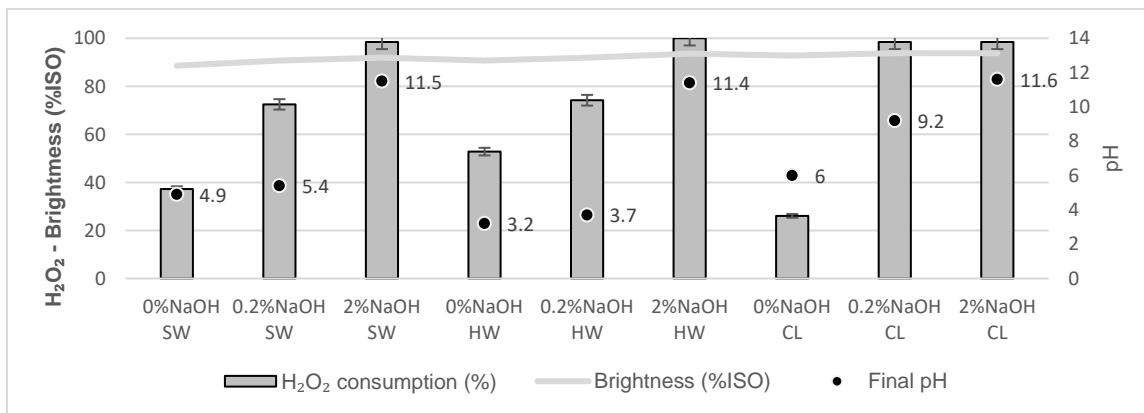


Fig. 3. H₂O₂ consumption, brightness (%ISO), and final pH after oxidations with only 2% H₂O₂. (Initial ISO brightness: 87.9% for SW, 87.9 % for HW, and 90.2% for CL)

The results presented in Fig. 3 provide evidence that HW, SW, and CL behaved similarly. The H₂O₂ consumption increased when the final pH was higher. When considering intrinsic viscosity values higher than 400 mL/g, which is interesting for dissolving applications, the acidic pH did not give interesting results, as well as not achieving total consumption of H₂O₂ (see Fig. 2(A)). H₂O₂ consumption was not directly related to the decrease of IV, and the peroxide consumption was higher in alkaline medium despite a reduced bulk attack of cellulose, due to slower rate of HO• generation. In acidic medium, the bulk attack of cellulose was more important, but H₂O₂ consumption was lower.

The role of copper as an activated species was evaluated but is not presented in this paper. Indeed, for both scenarios with Cu(II) and Cu(Phen), it was possible to achieve the complete H₂O₂ consumption (>95%) because of copper catalysis, and the brightness (%ISO) was rather not affected or slightly increased.

Comparison of the Three H₂O₂-based Oxidation Systems

The section above showed similar reactivities for SW and HW, but significant differences with CL. For the latter, the cellulose structure was much more compact (high crystallinity) and hemicelluloses were absent, as shown in Table.

Cellulose swells in alkaline medium, which allows better bulk penetration of reagents, under conditions promoting a regulated flow of radicals (by copper complexation, Cu(OH)₂ or Cu(Phen)). SW and HW are more accessible and thus reactive to the flow of radicals, despite the presence of hemicelluloses, especially in acidic medium. Finally, alkaline pH provides a better control of the radical flow, which is almost nonexistent in the absence of copper, leading to a light cellulose degradation and the highest brightness level.

Cellulose Oxidation by H₂O₂/Cu(Phen) – Towards Optimization

Additional tests were performed to determine the most interesting conditions to get a final pH close to neutral or slightly alkaline, and still reaching interesting final properties, with the aim of improving the dissolution ability of the studied substrates. For these tests, the concentrations of H₂O₂ and Cu(Phen) remained the same, 2% and 0.02% respectively, while the dose of NaOH was explored until reaching the desired final pH. The results are shown in Table 4.

Table 4. Characteristics of the Most Interesting Conditions When Using 2% H₂O₂ and 0.02% Cu(Phen) (REF=untreated pulp)

Sample	Final pH	Intrinsic Viscosity (mL/g)	Brightness (%ISO)	H ₂ O ₂ consump. (%)	Alkali Resistance, R18 (%)	Crystallinity Index (%)
SW REF	-	563	87.8	-	84	73
SW 0.3%NaOH	8.1	434	87.8	99	91	70
SW 0.4%NaOH	9.5	438	87.9	98	87	54
HW REF	-	496	87.9	-	93	78
HW 0.4%NaOH	6.7	300	88.5	98	94	60
HW 0.5%NaOH	9.1	381	90.9	98	97	64
CL REF	-	695	90.2	-	98	88
CL 0.2%NaOH	7.8	466	90.3	98	99	80
CL 0.3%NaOH	9.9	439	90.4	99	99	84

The determined conditions allowed full H₂O₂ consumption ($\approx 100\%$) and high brightness values ($\approx 90\%$ ISO). Intrinsic viscosity values around 400 mL/g were reached for CL and SW, as shown in Table 4. However, HW did not achieve intrinsic viscosity values in the desirable range (400 to 600 mL/g) for viscose applications. Complementary alkali resistance tests were performed to assess the cellulose purity. No differences between the reference and the oxidized substrate were observed for CL (as only hemicelluloses are expected to dissolve in the R18 test). For HW, a slight improvement in the cellulose purity was observed, especially at 0.5% NaOH, reaching a good R18 value; and for SW, purification was slight but better with 0.3% NaOH than with 0.4% NaOH.

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

Dissolving Ability Evaluation

Dissolution trials were performed in duplicate and analyzed by the carbanilation reaction and monitored by DLS. The particle size measurements during carbanilation for SW, HW, and CL are displayed in Fig. 4.

Only the oxidized samples CL 0.2% NaOH, SW 0.3% NaOH, and HW 0.4% NaOH dissolved more slowly than their corresponding untreated reference sample. When focusing on the final pH after the oxidations (Fig. 3), it can be presumed that a pH around 9 resulted in a better dissolution, at least for hardwoods, and for CL only at the beginning. Yet, the dissolution behavior in DMSO may be affected by the creation of functional groups during the oxidation of the substrates. It is well established that carboxyl groups react at a much slower rate with phenyl isocyanate than alcohols do. The detailed observation in Fig. 4 shows that for the pulps treated at the highest alkalinity, its dissolution was accelerated at the beginning but rapidly became slower after a certain time. This could be an indication of better accessibility to the bulk of the substrate and to the R-OH groups, but slower reactivity at the end with the presence of RCOOH groups.

MWD Profiles of the Oxidized Substrates

Further analyses of the carbanilated samples were done by HPSEC, as described in the methods section. As already shown by intrinsic viscosity values of Table 4, the degradation of the samples after the different oxidation treatments was confirmed by the MWD profiles (Fig. 5) and the acquired SEC data (Table 5), compared to the reference. The dispersity index (M_w/M_n) is an interesting indicator of the narrowness of the MWD profile. Intrinsic viscosity (weight-average), DP_w and hydrodynamic radius R_h are also derived for all the samples. Figure 5 displays the MWD profiles of SW, HW, and CL, respectively obtained before and after oxidation.

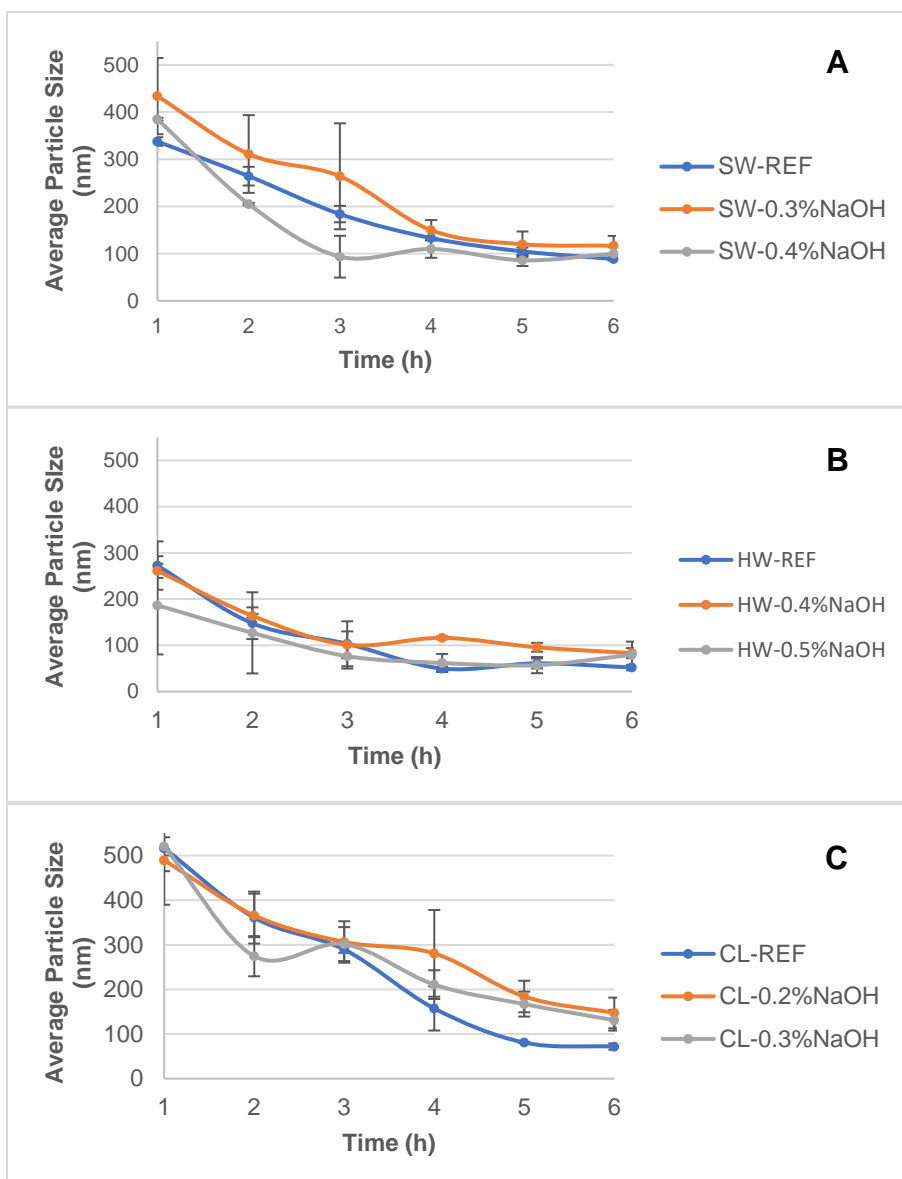


Fig. 4. Average particle size during carbanilation (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp)

Table 5. SEC Analysis of the Oxidized Substrates (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) Using Varied NaOH Doses. REF=untreated pulp)

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

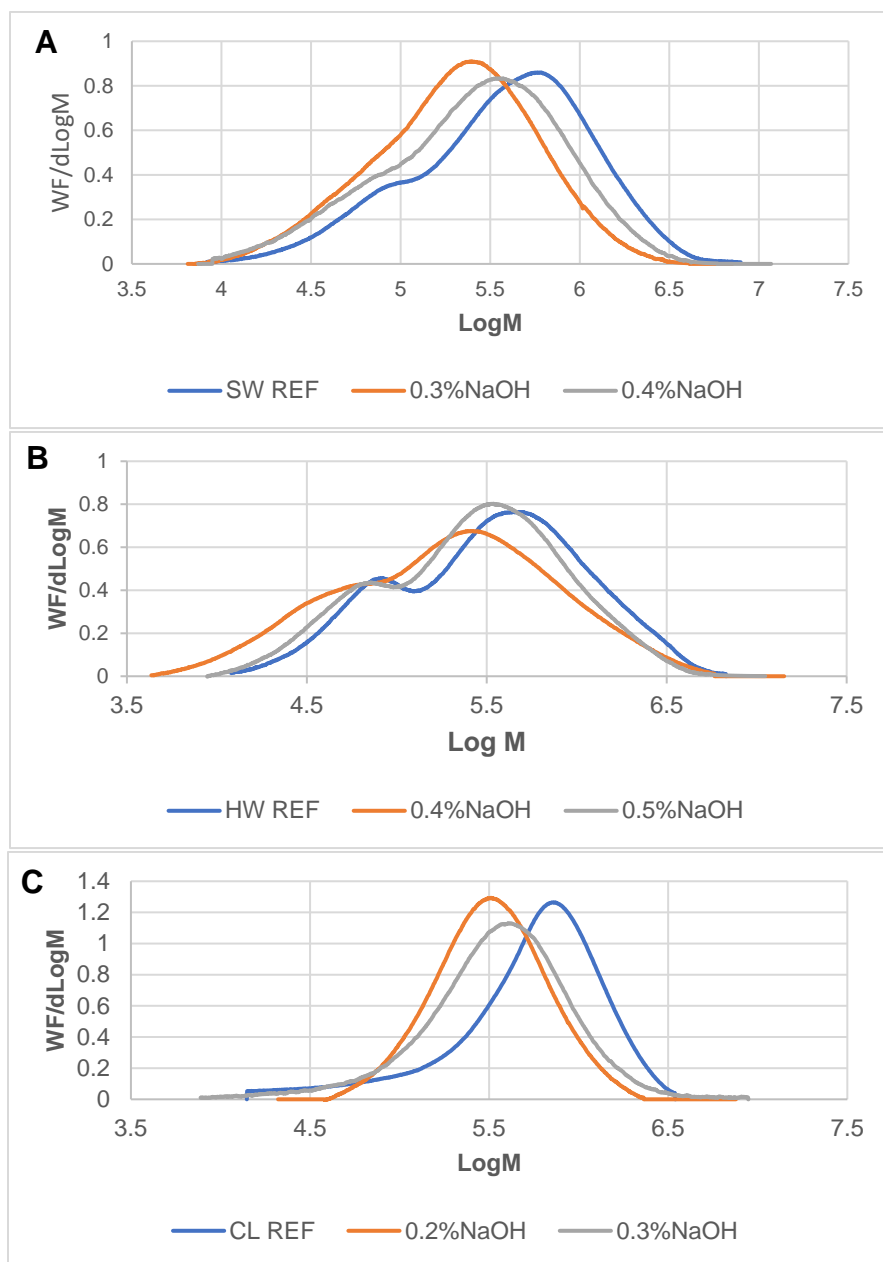


Fig. 5. Molecular weight distribution (oxidation with 2% H₂O₂ and 0.02% Cu(Phen) using different NaOH doses. REF=untreated pulp)

Softwood (SW) and hardwood (HW), both containing hemicelluloses and cellulose, displayed a classical bimodal MWD profile. In the reference samples (blue curves), hemicelluloses were present in the range of $\log M=4.5$ to 5 , whereas the cellulose fraction appeared at higher molar mass, centered around $\log M=5.8$ to 6 . After oxidation (red and green curves), MWD profiles were shifted towards lower molar mass. This is also evidenced by the drop of DP_w, IV and R_h (Table). All oxidized kraft pulps (SW and HW) still presented a signal in the hemicelluloses range, revealing that hemicelluloses were not completely removed during oxidation. Additionally, in the intermediate range, between $10^{5.1}$ and $10^{5.3}$, whose abundance is increasingly marked, the corresponding DP values, between 240 and 400 (considering a monomer molar mass for the CTC of 519 g/mol), correspond to the characteristic zone of short chains, degraded cellulose. The enlargement

of this zone was evident for the three pulps, and in the case of the HW and SW pulps, it tended to gradually mask the initially well-marked separation between long chains of cellulose and short chains of hemicelluloses.

For both kraft pulps, degradation was related to the final pH. The most important degradation occurred at the lowest alkalinity dosage, producing either near neutral or very slightly alkaline medium. Again, this seems to have been under the control of the hydroxyl radical generation flux, which was less important in alkaline medium when copper was complexed. Moreover, the more accessible substrate, HW, tended to increase its dispersity value, showing that oxidation was less selective and operates on all chain sizes, compared to the less accessible SW pulp.

The behavior of CL could be slightly distinguished from that of the kraft pulps. MWD profiles were still monomodal after oxidation, meaning a non-deep attack (which would create a bimodal profile, as already observed with other oxidants). Here, cellulose was more depolymerized at near-neutral pH, as seen by the higher shift of the MWD mode (curve peak), but the difference seemed less under the alkaline conditions. Moreover, at alkaline pH, a higher dispersity was observed. This shows the effect in alkaline medium, where the solids were more swollen and accessible. However, the reaction was more limited due to a lower flux of radicals, and it was less selective with respect to chain size and accessibility.

No modifications in terms of fiber morphology and water retention values were observed (results not presented). It seems that the oxidation treatments did not deeply affect the substrates at the fiber morphological level.

Comparison of the Oxidation Systems: H₂O₂/Cu(Phen) vs. H₂O₂ Alone

The presence of Cu(Phen) with peroxide generates a regular flow of radicals, with a strong dependence on the pH. H₂O₂ alone generates much less radicals, especially in alkaline medium (the usual conditions for pulp bleaching). Therefore, for the HW (the most accessible substrate), a pH close to neutral was selected, since at this pH radical's formation takes place with or without Cu(Phen). For the SW, a slightly alkaline pH was selected since it favors the substrate accessibility while keeping some radical generation in the presence of Cu(Phen).

Table 6. Comparison of the Final Parameters When Using or Not 0.02% Cu(Phen) in the Oxidations with 2% H₂O₂ (REF= untreated pulp)

Samples	Final pH	IV (mL/g)	Brightness (%ISO)	H ₂ O ₂ consump. (%)	R18 (%)	Cl (%)	COOH (mEq/100g dry pulp)
SW REF	-	563	87.8	-	84	73	6.4
0.3%NaOH 0.02%Cu(Phen)	8.1	434	87.8	98.6	91	70	6.2
0.3%NaOH	9.3	461	90.0	98.4	87	70	6.7
HW REF	-	496	87.8	-	93	78	7.0
0.4%NaOH 0.02%Cu(Phen)	6.7	300	88.5	97.8	94	60	7.7
0.4%NaOH	7.5	334	91.4	98.4	92	72	9.2
CL REF	-	695	90.2	-	98	88	5.0
0.3%NaOH 0.02%Cu(Phen)	9.9	439	90.4	98.7	99	80	5.4
0.3%NaOH	10.5	513	91.9	98.4	99	82	4.6

For CL, the choice of the pH was dictated by the poor substrate accessibility except at alkaline pH where swelling occurs, as discussed in the previous paragraphs. For the mentioned trials, all the samples showed an increased H₂O₂ consumption (higher than 97%), and with Cu(Phen), the final pH decreased, and the intrinsic viscosity was more affected, as shown in Table 6. It could also be noticed that the R18 values increased, and the CI was slightly affected. Table 7 presents the information extracted from SEC.

Table 7. Additional Information Extracted from SEC and HPLC Analyses (REF= untreated pulp)

Samples	SEC				HPLC		
	IV (mL/g)	Rh (nm)	Mw/Mn	DPw	Cellulose (%)	Hemicelluloses (%)	
						Glucos.	Xylans
SW REF	289	28	3.6	1218	77	15	8
0.3%NaOH 0.02%Cu(Phen)	180	19	2.9	638	81	10	9
0.3%NaOH)	236	24	3.1	915	77	12	11
HW REF	284	28	4.0	1215	79	-	21
0.4%NaOH 0.02%Cu(Phen)	167	19	5.8	845	71	-	29
0.4%NaOH	170	19	4.2	682	74	-	26
CL REF	422	35	2.8	1433	-	-	-
0.3%NaOH 0.02%Cu(Phen)	261	26	2.6	1017	-	-	-
0.3%NaOH	287	28	2.0	1139	-	-	-

As a general observation, cellulose depolymerization was accentuated in the presence of Cu(Phen), by observing IV values. For the three samples studied, the DP_w decreased after both kinds of oxidations. Degradation was generally higher in the presence of Cu(Phen). In the case of the HW, this was revealed by the increase of the dispersity index, which caused an increase of DP_w, being influenced by the higher proportion of long chains (as seen on the MWD profile, Fig. 5(B)). The same tendency can be observed looking at the intrinsic viscosity values (IV) in Table 7. The values of hydrodynamic radius confirm what was observed with the particle size measurements by DLS during carbanilation, showing an average particle size below 100 nm at the end of the derivatization. No significant changes were observed in the MWD, and the dissolution behavior of the samples oxidized in the mentioned conditions without Cu(Phen). (Results not included in the paper).

No important formation of carboxyl groups was observed on the three substrates (Table 6). The more significant enrichment could be observed for HW, possibly linked to its better accessibility/reactivity observed above, and possibly the type of hemicelluloses in each sample. Perhaps part of the polysaccharides was effectively carboxylated but also depolymerized and solubilized, and for these reasons no important changes could be observed.

It is important to highlight that for dissolving applications, a high purity is required. But for microfibrillated cellulose (MFC) applications, a fair amount of hemicelluloses may enhance the microfibrillation (Foster *et al.* 2018), and the target may be the creation of carboxyl groups to favor wettability, swelling, and cellulose final dissolution in water or in a polar medium (Vera-Loor *et al.* 2022). In such cases, the fastest dissolution measured by cellulose carbanilation may not be the right indication for the best dissolution behavior. Brightness values above 90% ISO were achieved, as well as cellulose content above 90%,

when referring to R18 trials. However, the cellulose was strongly degraded by the oxidation conditions. The range of cellulose purity for the kraft pulps was not reached, and the intrinsic viscosity for viscose applications (dissolving pulps), ideally in the range of 400 to 500 mL/g, was only reached for some samples. Considering that IV initial values in the present study were low, it is fair to believe that dissolving-grade characteristics could be achieved in the case of higher IV initial values.

Dissolving Ability in the NaOH:urea:water System

To finish the analysis described in the methods section, the solubility in the NaOH:urea:water system was studied, and the results are presented in Fig. 6. In this solvent system, solubility was dominated by the cellulose DP_v (measured in CuED), which is also the general tendency presented in Fig. 6. For the three reference samples, a higher DP_v implies lower solubility, and solubility varied in the expected order of CL < SW < HW. Nevertheless, the two kraft pulps values were close to each other and quite far from the CL pulp, which was hardly dissolved. This shows the significant impact of the presence of hemicelluloses in the kraft pulps on the solubility in this system.

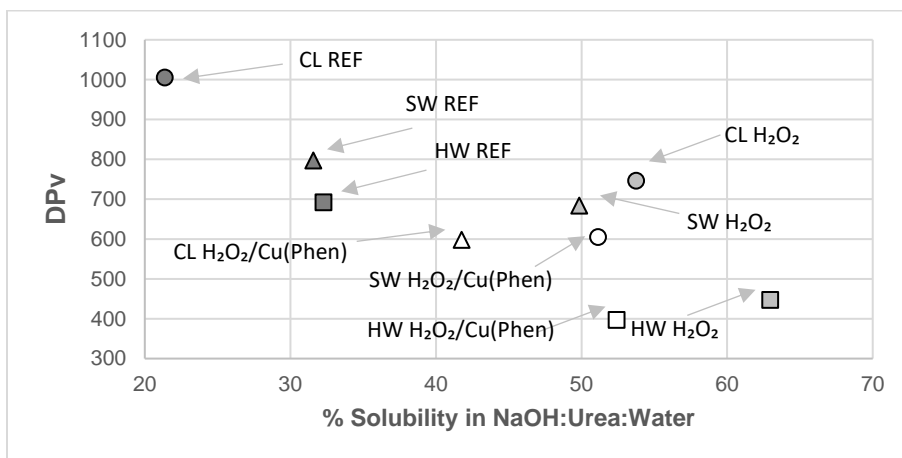


Fig. 6. Solubility in the NaOH:urea:water system for the oxidized substrates with and without Cu(Phen) (REF=untreated pulp)

After oxidation, unexpectedly, a stronger degradation was observed when CuPhen was used, compared to the corresponding substrates oxidized with H₂O₂ alone. This was verified for the three samples. This was likely due to some chemical modifications induced by the presence of Cu(Phen) and radicals during the peroxide oxidation. Overall, the presented tests gave indication that the use of Cu(Phen) does not improve the dissolving ability of the oxidized samples in this polar system. The reference samples exhibited a dissolution ability in the same order as that observed by the carbanilation test.

Overview of the Dissolving Ability of the Different Substrates

The methodology focused on the kinetics of carbanilation in DMSO, a reaction on the -OH groups of polysaccharides without a strong impact on the cellulose DP_v, using a powerful reagent, phenyl isocyanate, and an organic polar solvent, DMSO. The latter was chosen for its ability to swell cellulose to a certain extent. It has been shown by Vera-Loor *et al.* (2023) that the improvement of the carbanilation kinetics was linked to a loosening of the compactness of the cell wall structure, as well as to a decrease in substrate

crystallinity, but not necessarily linked to the length of the cellulose chains. In this medium, reagents and solvent access the cellulose chains by diffusion around and inside the microfibrils. One of the components of this inner accessibility is therefore the crystallinity of the cellulosic substrate. Moreover, the presence of hemicelluloses located on the surface of the microfibrils increases the swelling ability of the substrate, in the case of a polar solvent such as DMSO. The latter might also contribute to locally dissolving the hemicelluloses. Contrary to this organic medium, studies of cellulose solubility in the aqueous NaOH:urea system show that for cellulosic substrates of different natures, the length of the cellulose chains (DP_v) strongly contributes to the solubility yield. Finally, the studies of MWD, mean DP values, polymer dispersity and hydrodynamic radius make it possible to understand the evolution of the molecular characteristics, in connection with the values of DP_v , measured in the CuED.

It was also possible to observe that the oxidations with H_2O_2 generally improved the solubility in the NaOH:urea:water system, for all the studied substrates. On the other hand, the presence of Cu(Phen) did not bring a positive effect on cellulose solubility and the DP_v , compared to the cases without Cu(Phen). CL, the less accessible substrate, was the most impacted by the presence of Cu(Phen), both on DP_v and aqueous solubility. The characteristics of molar masses and hydrodynamic radius were in good accordance with the evolutions of DP_v . Contrary to the expectations, the treatment with H_2O_2 /Cu(Phen) does not eliminate the hemicelluloses but increases the amount of degraded cellulose. It was during the most alkaline H_2O_2 treatments that the fastest carbanilation reaction was observed, an effect which would be explained by a better relaxation in alkaline medium of the interfibrillar network and better access to amorphous cellulose. The fact that the carbanilation did not seem to be improved by the presence of Cu(Phen), might be attributed to the possible formation of carboxyl groups, which are less reactive than the alcohol groups with the phenyl isocyanate. Overall, the decrease in DP_v in the presence of Cu(Phen), does not contribute to a faster carbanilation reaction in this organic medium.

All these elements lead to the general conclusion that treatments with H_2O_2 improve solubility in a NaOH:urea:water system but not in an organic medium. The addition of Cu(Phen) decreases the DP_v without an improvement in solubility. Conversely, a deterioration in solubility was observed, whether aqueous or organic media were employed.

CONCLUSIONS

1. The impact of the use of copper as a catalyst for oxidations with commonly-used-in-mills chemicals, H_2O_2 and NaOH, was evaluated for three selected samples: cotton linter (CL), bleached softwood kraft pulp (SW), and bleached hardwood kraft pulp (HW). Copper was present in $CuSO_4$, in $Cu(OH)_2$ in alkaline medium, and in the copper-phenanthroline complex, and it has different forms depending on the pH of the medium.
2. The main differences of behavior for all samples can be attributed to the pH reached after every oxidation, as well as the type of hemicelluloses present in the substrate, enhancing or not the action of copper, which generates a flux of oxidizing radicals in the presence of H_2O_2 . The latter appears to be regulated by the freeness of copper.

Indeed, the effect of pH and the presence of phenanthroline makes it possible to regulate the intensity of radical's generation from H₂O₂ decomposition.

3. Even though it was not observed a significant improvement of the dissolution ability by the carbanilation reaction, the dissolution in NaOH:urea:water system was improved for the three selected samples, SW, HW, and CL. But in the latter case, the best dissolution improvements were observed without the use of the Cu(Phen). Finally, some potential applications were identified, such as interesting conditions to produce microfibrillated cellulose (MFC) with a previous oxidation stage with H₂O₂ and Cu(Phen), as the presence of hemicelluloses and the possible formation of carboxyl groups may enhance the microfibrillation.

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