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Formation of Carbonyl and Carboxyl Groups on Cellulosic Pulps: Effect on Alkali Resistance

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Ozone bleaching generates carbonyl groups on the cellulose polymer when applied to unbleached kraft pulps. This suggests that pulp fully bleached with a totally chlorine-free (TCF) sequence may contain more oxidized groups than standard elemental chlorine-free (ECF) bleached pulp. A fully bleached pulp was treated with sodium hypochlorite to form oxidized groups (mostly carbonyls) on the pure carbohydrates, which were investigated during subsequent alkaline treatment. Carbonyl groups had a strong impact on color development during alkaline treatment. Among the carbonyls, the keto groups were the most active. This was confirmed by the behavior of carbohydrate model compounds that contained aldehyde, keto, and/or carboxyl groups when subjected to alkaline conditions. A subsequent hydrogen peroxide (P) stage effectively decreased the carbonyl content, which reduced yellowing during alkaline treatment. However, the oxidized cellulose was severely depolymerized. The addition of magnesium sulfate (Mg) into the P stage minimized depolymerization while maintaining some of the carbonyls in the carbohydrates. It is proposed that Mg cations can hinder alkaline β-elimination, possibly by forming a complex with the carbonyl groups.

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INTRODUCTION

Interest in cellulose-based materials has recently increased because cellulose is a renewable resource available in considerable quantities. Among the most active areas of development is the production of dissolving pulp for textiles, plastics, and various additives (Eichinger 2012). Most of the cellulose available today is produced from wood pulped by the kraft process and subsequently bleached by an oxidative process. The conventional bleaching sequences use chlorine containing oxidants, primarily chlorine dioxide, but also in some cases hypochlorite and even chlorine. They all generate chlorinated organics, which are released in the effluents and may also remain on the cellulose. Whether or not this represents an environmental issue has been a matter of debate for decades (NCASI 2013). Nevertheless, developing alternative chlorine-free processes has been an active subject of research for many years. Totally chlorine-free (TCF) bleaching processes have been proposed, which generally include the use of oxygen, ozone, and hydrogen peroxide (Lachenal and Nguyen-Thi 1994; Metais *et al.* 2013). The implementation of TCF presents several advantages: (1) no chlorinated chemicals should be formed; (2) less organic materials are released in the mill effluent since a portion of the bleaching effluent, which contains only background levels of chloride ions, can be burnt; and (3) less water is required to run the mill. However, the development of TCF bleaching has so far been very

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limited. The primary reason is due to the oxidation and depolymerization of cellulose by the reagents. Among them, ozone is considered to be responsible for most of the oxidative degradation of cellulose (Ragnar *et al.* 1999). Several improvements have been applied to TCF bleaching to minimize cellulose oxidation (Pouyet *et al.* 2013). Nevertheless, it is likely that some carbonyl and carboxyl groups will continue to be introduced onto the cellulose during TCF bleaching to high brightness (Lambert *et al.* 1998).

The effect of carbonyl and carboxyl groups on cellulose properties has been extensively studied. It is generally known that carbonyl groups decrease the brightness stability of fully bleached pulps when exposed to heat (Jullander and Brune 1957; Chirat and de La Chapelle 1999). Moreover, oxidized cellulose is very sensitive to alkaline environments. This is reflected in a substantial reduction of the average degree of polymerization (DP) when oxidized cellulose is exposed to alkali. This reaction is well documented (*i.e.*, β-alkoxy elimination), and is due to the carbonyl groups at the C-2, C-3, and/or C-6 positions of the anhydroglucose unit (Ahn *et al.* 2012). Less investigated is the strong discoloration that takes place when oxidized cellulose is treated with alkali (Lewin 1997).

The problems caused by the presence of oxidized groups may be of particular importance in the manufacture and use of dissolving pulp since several strong alkaline stages are usually performed during the purification and solubilization steps. The quantity of oxidized groups produced on the cellulose during pulp bleaching is usually very low (Chirat and Lachenal 1997), which explains why the methods used to measure their content are very few and not always reliable. Among them is the so-called carbazole-9-carbonyl-oxy-amine method (CCOA), based on the fluorescence measurement after derivatization of carbonyl groups, which has been recently proposed for the quantification of such groups (Röhrling *et al.* 2002a). The method is quite powerful because it allows for locating the carbonyl groups as a function of the molecular size of the carbohydrate chains. However, the values obtained are generally smaller than those measured by simple chemical dosages (Röhrling *et al.* 2002b), like the one based on the formation of cyanohydrins. Although the reason for this observation is not well understood, both methods will be used in this study. Several methods have also been proposed for the determination of carboxyl groups (Davidson and Nevell 1948; Bohrn *et al.* 2006). Even though there is no guarantee that the measured values are correct, there is little discrepancy between them, contrary to what is observed for the quantification of carbonyl groups. The methylene blue technique was selected in this study.

The purpose of this work is to re-examine the effect of the oxidized groups, susceptible to introduction on cellulose during TCF bleaching, on alkali resistance (discoloration and depolymerization) and to propose some ways to minimize this problem. A model pulp produced by sodium hypochlorite treatment of an ECF fully bleached eucalyptus pulp proposed by Lewin and Epstein 1962 was chosen for this study. Under acidic conditions, sodium hypochlorite, like ozone, forms mainly ketone and aldehyde groups (Lewin and Epstein 1962; Chirat and Lachenal 1997; Lemeune *et al.* 2004; Zhou *et al.* 2011). Although several studies have examined the effect of this oxidation treatment on cellulose behavior in an alkaline environment (Lewin 1997), some experiments will be performed during this study with pulp and glucose derivatives in an attempt to obtain a better understanding of the phenomenon. This added knowledge will determine how to best alleviate the potential problems that may occur due to the presence of these oxidized groups.

EXPERIMENTAL

Materials

Pulp samples

Two samples of eucalypt pulp (*Eucalyptus grandis* x *Eucalyptus urophylla* hybrid) were provided by a Brazilian kraft pulp mill. Pulp 1 was an oxygen-delignified eucalypt pulp with a kappa number of 8 and a degree of polymerization (DP) of 1630. Pulp 2 was the corresponding fully bleached pulp obtained by an elemental chlorine-free (ECF) sequence, with a brightness of 90.5% ISO and a DP of 1130.

Formation of oxidized groups by hypochlorite treatment

Hypochlorite treatments (H) were performed in polyethylene bags that were heated to 70 °C in a water bath. Pulp was diluted to 10% consistency using a 0.2 M acetate buffer solution (pH 4.8). The hypochlorite charge was 1% of the oven dry pulp. Sodium hypochlorite solution (13%; Roth, Germany) was titrated prior to each oxidative treatment. After 1 h of reaction, the hypochlorite treatment was stopped by washing the pulp three times with distilled water.

Model compounds

The origin and purity of the glucose model compounds used in this study are given in Table 1. They were subjected to alkaline conditions simulating the alkaline treatment (E) applied to pulp in a 1.0 M phosphate buffer at pH 11.4. A solution of 0.05 M of model in buffer was heated at 70 °C for 1 h, dissolved oxygen was not removed. This solution was diluted 50 times prior analysis. The effect of alkali was analyzed at 400 nm by UV-Visible spectroscopy performed on a Shimadzu UV-1800 instrument (Japan).

Table 1. Glucose Model Compounds Used in This Study

Model compound	Supplier	Purity
Glucose	Sigma-Aldrich, Germany	99%
Glucuronic acid	Sigma-Aldrich, Germany	98%
Gluconic acid	Sigma-Aldrich, France	99%
1-*O*-methyl-D-glucuronic acid	Santa Cruz Biotechnology, Inc.	99%
D-fructosonic acid	Sigma-Aldrich, Israel	98%
D-galactaric acid	Sigma-Aldrich, United Kingdom	98%
1-*O*-methyl-D-glucopyranose	Sigma-Aldrich, Germany	99%
D-arabino-hexos-2-ulose	Sigma-Aldrich, Canada	98%

Methods

Pulp characterization

Pulp brightness was measured according to the ISO 2470 (2009) standard. Pulp (2 g) was diluted with 200 mL of distilled water prior to handsheet formation; the handsheets were dried at 92 °C for 5 min. In some experiments, the pH of the pulp suspension was modified before handsheet formation using either sulfuric acid or caustic soda.

Carbonyl group content was determined by cyanide titration (Lewin and Epstein 1962). Cyanohydrins were formed by the addition of cyanide to the carbonyl group. Residual cyanide was then titrated with silver nitrate. The distribution of carbonyl groups was determined according to the CCOA (carbazole-9-carbonyl-oxy-amine) fluorescence labeling method, as described in the literature (Röhrling *et al.* 2002; Potthast *et al.* 2003),

which was then followed by gel permeation chromatography (GPC). The GPC system consists of a fluorescence detector (TSP FL2000) for monitoring the CCOA label, a multiple-angle laser light-scattering detector (MALLS) (Wyatt Dawn DSP with argon ion laser (λ_0= 488 nm)), and a refractive index detector (Shodex RI-71). Four GPC columns (Variant/Agilent^{TM}, PL gelmixed-ALS, 20 µm, 7.5 mm × 300 mm) were used as the stationary phase. DMAc/LiCl (0.9%,w/v) was used as the eluant. This technique profiled the carbonyl content against the molecular weight (M_w) of carbohydrates. Carboxyl group content was measured by the methylene blue (MB) method (Davidson 1948). This method is based on the reaction of the MB cations with carboxylate anions. The average degree of polymerization of carbohydrates (DP) was calculated from viscosity in 0.5 M cupric ethylenediamine (CED) according to the ISO 5351 (2010) standard. Reduced DP was measured after sodium borohydride treatment (B) of the pulp. Hemicellulose content of the pulp was determined according to the method reported by Sluiter *et al.* (2011). Aldehyde content was calculated as the difference between carboxyl content measured by the MB method after and before a chlorite oxidation, where chlorite oxidizes aldehydes into carboxyl groups. The conditions of the chlorite treatment are given in the next section.

Chemical treatments applied to pulp

Alkaline extraction stage (E) was performed in a plastic bag at a consistency of 10%, 1% NaOH (> 99%; Roth, Germany) on oven dry pulp, for 1 h at 70 °C. Hydrogen peroxide treatment (P) was carried out in the same conditions as the E stage with the addition of 1% H_2O_2 on pulp (35%; Roth, Germany), which was added after NaOH addition. Reaction temperature was controlled with a water bath. Reactions were stopped by washing the pulp. The E stage effluent was characterized by UV-visible spectroscopy at 400-800 nm.

Sodium borohydride stage (B) was performed to reduce both ketones and aldehydes, with 5% $NaBH_4$ on pulp (> 97%; Roth, Germany), at 10% consistency and 25 °C in a plastic bag. After 30 min, the treated pulp was washed three times.

Chlorite oxidation (designated as C_l) was performed to selectively oxidize the aldehyde groups. Reaction was performed in a glass bottle with 3.44 g of $NaClO_2$ (> 80%; Roth, Germany) per gram of oven dry pulp and 13 mL of acetic acid (96%; Panreac, Spain), at 1% consistency, for 48 h at room temperature.

When magnesium was added to alkaline extraction (designated as E*) or to the peroxide stage (designated as P*), 0.5% $MgSO_4 \cdot 7H_2O$ was added first to the pulp. Hand mixing was performed for 10 min before adding the other chemicals.

RESULTS AND DISCUSSION

Introduction of Oxidized Groups on Pulp Carbohydrates by Ozone and Hypochlorite

Effect of ozone treatment on unbleached eucalyptus pulp

Although ozone could in theory react directly with cellulose and induce degradation, it is not *per se* the primary cause of carbohydrate chain scission and oxidation during TCF bleaching sequences. In fact, kinetic studies show that lignin is much more reactive than cellulose toward ozone, which suggests that cellulose in unbleached pulp should only marginally react with ozone. Nevertheless, significant quantities of carbonyl groups, as measured by the CCOA method, were introduced onto the carbohydrates during

the ozone treatment of unbleached eucalypt kraft pulp (Pulp 1), as shown in Fig. 1. Figure 1 plots the shift of the molecular weight distribution and the content of carbonyl groups with the molecular weight fractions before and after ozone treatment. It is clear that a substantial amount of depolymerization occurred and that carbonyl groups were formed, mostly on the lower molecular fractions (*i.e.*, hemicelluloses). However, some carbonyl groups are also formed on cellulose. The addition of carbonyl groups on the cellulose could be caused by hydroxyl radicals (HO•), which are formed by the reaction of ozone with lignin (Ragnar *et al.* 1999), and with hexenuronic and muconic acid groups (Pouyet *et al.* 2013). The amount of carbonyl groups will certainly vary depending on where the ozone stage is used in the TCF bleaching sequence, as well as what other bleaching stages are used after the ozone stage.

To clarify the effect of oxidized groups on the carbohydrates, sodium hypochlorite was used to oxidize a model pulp prepared from an ECF fully bleached pulp under acidic conditions. This oxidation method allows for the generation of oxidized groups onto the carbohydrates in a controlled way.
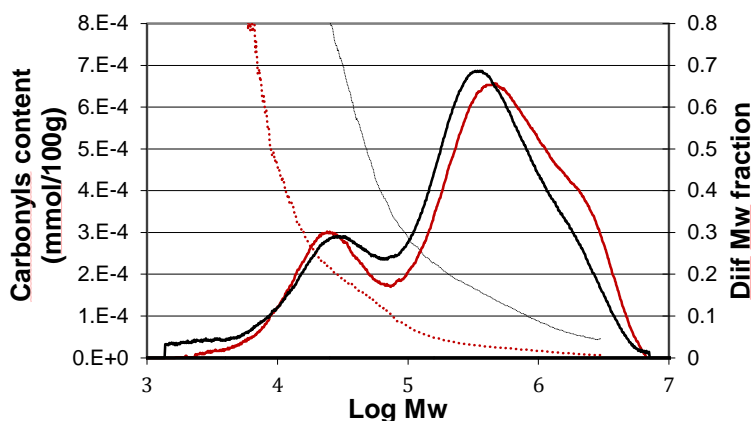

Fig. 1. Carbonyl content (dotted lines) and differential molecular weight fraction (solid lines) as a function of log Mw for pulp 1, before (brown) and after (black) ozone treatment (1% ozone on o.d. pulp)

Effect of hypochlorite treatment (H) on a fully bleached eucalypt kraft pulp

The ECF fully bleached eucalypt pulp (Pulp 2) was treated with sodium hypochlorite. Table 2 shows the formation of carbonyl and carboxyl groups, as well as the DP of the pulp. The hypochlorite treatment carried out in acidic conditions created substantial quantities of carbonyl groups on the fully bleached pulp. Detected carbonyl groups are the ketones located at either C-2 or C-3, and the aldehydes located at either C-6 or C-1. Approximately one-half of all the measured carbonyl groups were aldehydes.

Table 2. Functional Groups Introduced in Bleached Pulp by Hypochlorite Treatment (CN and MB Methods) in mmol/100 g Pulp

	Total CO (CN)	COOH (MB)	CHO (MB)	DP
Bleached pulp (Pulp 2)	10.8	5.2	5.9	1130
Hypochlorite (H) treated	21.8	6.8	9.5	620

Alkali Sensitivity of Oxidized Pulp

Effect of pH of pulp suspension on brightness value

In Fig. 2, the measured brightness is plotted against the pH of the pulp suspension prior to forming the brightness handsheet. As expected, the untreated pulp brightness value was not impacted by the pH of the pulp suspension, whereas the H oxidized pulp brightness was found sensitive to the alkaline environment since the brightness decreased by more than 1 unit when the pH of the pulp suspension increased from 5 to 11. This indicates how much the pH of the pulp suspension is critical to the measured brightness of oxidized cellulose. This observation also suggests that chromophores are formed when oxidized cellulose is subjected to an alkaline environment. Thus, all pulp suspensions reported afterwards were adjusted to a pH of 5 with sulfuric acid prior to forming the handsheets for brightness measurements.
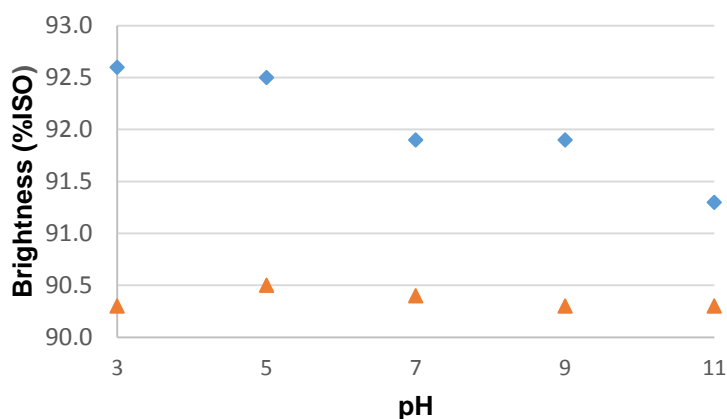

Fig. 2. Brightness of untreated (▲) and H oxidized (♦) pulp against pH of the pulp suspension before sheet formation

Formation of chromophores during an alkaline extraction stage (E) applied to an oxidized pulp

Both the untreated and H oxidized pulps were subjected to a conventional E stage (1% NaOH, 70 °C). The filtrates of the E stage were collected and analyzed by UV spectroscopy (Fig. 3). A very small amount of chromophores was detected in the effluent in the case of the untreated pulp, whereas in the case of the oxidized pulp the E stage filtrates were highly colored. The absorbance spectra indicate, however, that the color of the dissolved materials was strongly, although not totally, reduced upon acidification to a pH of 2. The partial reversibility of the color formation was confirmed when the acidified filtrate was re-alkalinized and the color reappeared almost completely. This behavior is typical of chromophores containing hydroxyl (OH) groups conjugated to unsaturated structures (C=C).

At the same time, the H oxidized pulp yellowed during the E stage, unlike the untreated control (Table 3). This phenomenon has not been extensively investigated to date. Several means to minimize this discoloration were tested (Table 3). Magnesium impregnation prior to E stage did not improve the results. A strong reductive pretreatment of the H oxidized pulp with sodium borohydride (B) prior to the E stage totally suppressed the yellowing. This indicated that carbonyl groups are the main culprits of alkali yellowing of the pulp. A P stage applied before the E stage also reduced the color formation. It is known that hydrogen peroxide reacts with the carbonyl groups, which are converted to

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carboxyl groups. The beneficial effect of P stage suggests again that the carbonyl groups are the main structure responsible for the alkali yellowing and that the newly formed carboxyl groups only have a minor effect, if any. Finally, chlorite oxidation was applied on H oxidized pulp. This pre-treatment reduced the yellowing effect of the E stage, but to a smaller extent than B or P stage pre-treatment. Chlorite oxidizes aldehyde groups into carboxyl groups. Therefore, these observations suggest that among the carbonyl groups on the carbohydrates, some aldehyde groups play a significant role in the alkali yellowing effect, whereas the carboxyl groups play a minor role. The aldehyde groups participating in the alkali yellowing may be either from the reducing end groups at C-1 or the aldehyde at C-6, or from both positions. The fact that the untreated pulp does not yellow more after acid hydrolysis (pH 2, 90 °C, 2 h) (Table 3) suggests that reducing end groups do not play a role. However, effluent of this extraction yellowed more than for untreated pulp (Fig. 3b), which indicates that products released from the peeling reaction are converted to colored substances.

Table 3 also contains the DP values after these different treatments. It is well known that the carbonyl groups (other than the reducing end groups) on oxidized carbohydrates are the origins for alkali-induced polysaccharide depolymerization (*e.g.*, E stage or cupric ethylenediamine (CED) medium) *via* β-elimination (Ahn *et al.* 2012). The fact that DP did not decrease after HB and HP was in line with the destruction of the carbonyl groups during B and P as shown in Table 4.
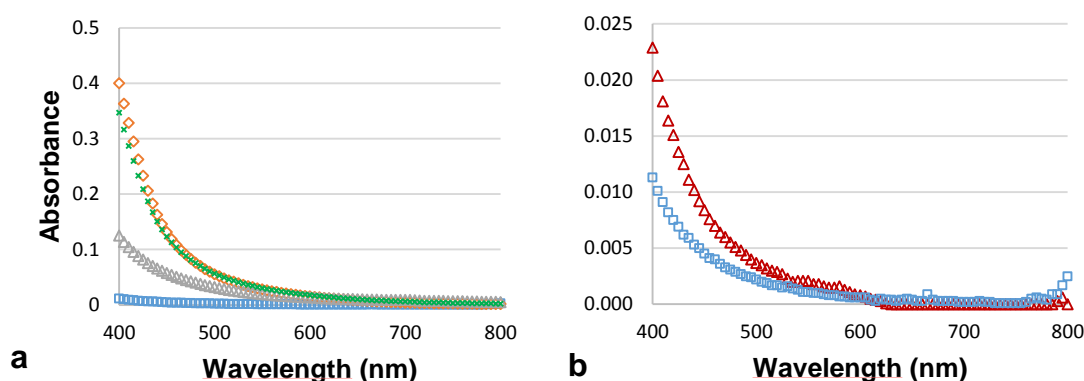

Fig. 3. UV/Vis spectra of effluents from alkaline extraction (E) of pulp 2. (a) Untreated pulp (□), H oxidized pulp (◊), same effluent acidified to pH 2 (△), same effluent after re-adjustment to pH 12 (x) and (b) untreated pulp (□), same after acid hydrolysis (△)

Table 3. Brightness and DP of Pulp Subjected to Different Treatments Prior to Alkaline Extraction

	Brightness (%ISO)	DP		Brightness (%ISO)	DP
Control	90.5	1130	E	91.3	1150
H	92.5	620	HE	89.1	550
			HE*	89.3	555
HB	92.5	870	HBE	92.4	865
HP	93.4	490	HPE	92.5	480
HC$_l$	93.1	690	HC$_l$E	91.2	630
A	90.2	/	AE	91.2	/

H: hypochlorite; E: alkaline extraction; B: borohydride; P: hydrogen peroxide; C$_l$: chlorite;
*denotes the addition of Mg cations prior to the treatment stage

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A peroxide treatment might be a very good option to decrease the yellowing of pulp, which is much cheaper than a borohydride treatment. However, the main drawback of the P stage is the decrease in the DP of the pulp. Thus, an investigation of the carbohydrate degradation occurring in the P stage was carried out. Figure 4 shows that the difference between DP and reduced DP (DPr) (*i.e.*, DP measured after borohydride treatment (B)) was very high after H oxidation but was smaller after HE and HP stages. In fact, the difference was almost nil after HP. The disparity between DP and DPr values is linked to the carbonyl groups on the oxidized carbohydrates besides the ones at the reducing ends. This indicated that carbonyl groups decreased during E and P. Measurement of carbonyl groups (Table 4) confirmed this point. Carbonyl groups were virtually eliminated during P. The small quantity left must belong to reducing ends since they did not affect the reduced DP. When the E stage and the P stage were carried out after HB (crosses in Fig. 4), no DP loss was observed during E, confirming that E does not affect the DP of cellulose, even when it contains carboxyl groups. In the case where the HB pulp was treated with a P stage, there was a small DP drop was. This latter effect must be due to some radicals liberated from hydrogen peroxide under alkaline conditions; this peroxide decomposition reaction can be catalyzed by trace levels of transition metal ions in the pulp. Adding magnesium sulfate just prior to the P stage lessen the DP drop of the cellulose. At the same time, more carbonyl groups were retained in the pulp as indicated by the larger difference between DPr and DP. One hypothesis is that the magnesium cations formed a complex with the carbonyl groups of the oxidized cellulose, which could have prevented the degradation reaction during the P stage, as has been already suggested by Bouchard *et al.* (2011) in the case of oxygen delignification.
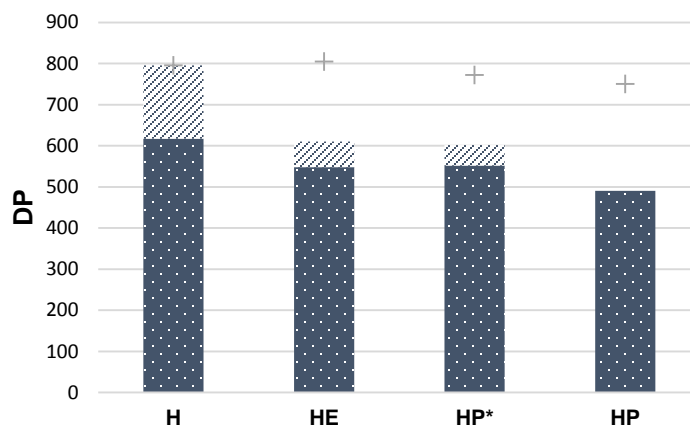

Fig. 4. Degree of polymerization of pulp after various treatments: dotted blue bar = DP of pulp; diagonal gray bar = DPr –DP; and cross (+) = DP value with B stage prior to E and P or P*

Table 4. Impact of E and P Stages on Oxidized Groups

	E	H	HB	HE	HP*	HP
CO (mmol/100g)	3.6	22.0	~0	14.9	12.7	4.8
COOH (mmol/100g)	-	6.8	6.8	12.5	-	10

(- not measured)

Alkali Yellowing of Model Sugar Derivatives

Sugar derivatives containing aldehyde, ketone, and carboxyl groups were treated under alkaline conditions to simulate the E stage as applied to a pulp. The alkaline solution was analyzed by UV visible spectroscopy (Fig. 5). Table 5 gives the absorbance at 400 nm for all the model compounds tested. It is shown that all the model compounds with a carbonyl group at the C-1 or C-2 position yellowed when subjected to alkaline conditions. Yellowing increased when a carboxyl group was also present at C-6 position. However, carboxyl groups alone did not seem to induce any yellowing, which was generally in line with earlier observations with oxidized pulp samples. It must be added that the reducing end groups (*i.e.*, C-1 aldehyde) did not cause any yellowing of the pulp, but did cause the discoloration of the effluent, which was shown with a pulp after acid hydrolysis. In this case, the products from the peeling reaction would turn yellow in solution. This also suggested that the main groups responsible for pulp yellowing are the keto groups. Further investigations are necessary to understand the mechanisms that result in color formation and the chemical effect of the oxidized groups on the yellowing. Theander and Nelson (1988) showed that under alkaline conditions, the degradation of some glucose derivatives may lead to quinonic structure.
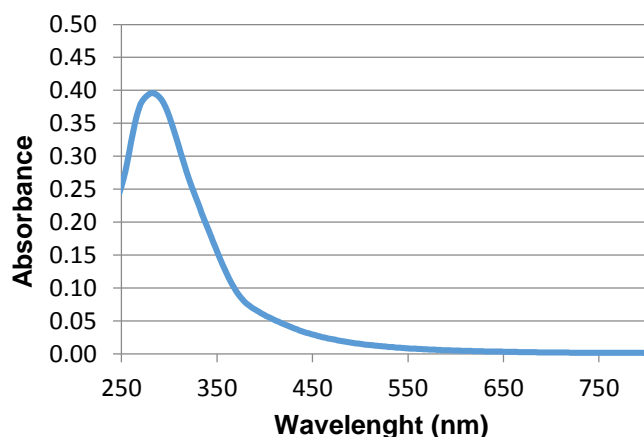

Fig. 5. UV/Vis spectroscopy of glucose solutions under E stage conditions

Table 5. Absorbance of Sugar Derivatives Solutions at 400 nm after 1 h at pH 11.4 and 70 °C

Model	Absorbance at 400 nm
Glucose	0.059
Glucose*	0
Glucuronic acid	0.097
1-*O*-methyl-D-glucuronic acid	0
Gluconic acid	0
D-fructosonic acid	0.129
D-galactaric acid	0
1-*O*-methyl-D-glucopyranose	0
D-arabino-hexos-2-ulose	0.073
D-arabino-hexos-2-ulose *	0.029

*Room temperature

CONCLUSIONS

1. Pulp containing oxidized groups on the carbohydrates, such as ketones, aldehydes, and carboxyls is degraded under mild alkaline conditions, which results in depolymerization and yellowing.

2. Experiments with glucose derivatives subjected to similar alkaline conditions confirm that the ketone groups are primarily responsible for pulp depolymerization and yellowing when subjected to alkaline conditions.

3. Susceptible oxidized groups are formed during TCF bleaching, particularly after an ozone stage.

4. Post-treatment with hydrogen peroxide offers a solution to the yellowing problem because the carbonyl groups are oxidized. However, cellulose depolymerization is not inhibited. The addition of magnesium salt is necessary to alleviate this problem; a possible mechanism for this effect is that the magnesium cations hinder alkaline β-elimination.

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