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Use of UV resonance Raman spectroscopy for assessing the brightness stability of ozone TCF bleached pulp

Original article

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Abstract: This study intends to explain the difference in brightness stability between hardwood ECF and TCFz kraft pulps bleached by DEpDD and A(ZEo)(ZEo)(ZP) sequences respectively, using UV Resonance Raman (UVRR) spectroscopy. The brightness stability of the pulps was tested via dry aging experiments where the Post-Color Number (PCN) of the ECF pulp was twice that of the TCF pulp. The aged and non-aged bleached pulps were analyzed with UVRR spectroscopy to identify the cause of the large difference in PCN. The spectra of ECF and TCF bleached pulps presented clear differences in the intensities of the Raman shifts associated to lignin, lignin-like compounds, and degradation products such as muconic acids. To identify more specifically the compounds affecting the PCN, several post-bleaching treatments were applied on the ECF pulp including single stages (E, B, P, Z) or combinations (ZE, ZB, ZP), and their UVRR spectra analyzed. It was found that alkaline-soluble compounds were the main culprits for the difference in PCN values between ECF and TCFz pulps. ZP combination was the most efficient in eliminating residual lignin and other unsaturated components and for the development of brightness and brightness stability.

Keywords: brightness stability; chromophores; ECF and TCF bleaching; ozone; paper pulp; UV resonance Raman spectroscopy.

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1 Introduction

Totally Chlorine Free (TCF) bleaching sequences using ozone, or 'TCFz', may offer several advantages when compared to conventional Elemental Chlorine Free (ECF) sequences (Bajpai 2010). Among them, a reduced chemical cost resulting from the high reactivity of ozone with lignin. However, TCF bleached pulp has often been thought to exhibit low brightness and poor brightness stability. When bleaching solely combines oxygen and hydrogen peroxide (H_2O_2), this has been explained by incomplete delignification (Lancaster et al. 1992). But, that fact has never been substantiated regarding TCFz pulps. According to literature contradictory conclusions may be drawn: while chlorine dioxide reacts primarily with free phenolic groups (Brage et al. 1991a,b), all aromatic rings can be oxidized by ozone which should contribute to easier lignin removal. Moreover, ozone reacts on any C=C double bond and is thus able to readily eliminate chromophores and chromophore precursors (chromogens) moieties such as quinones and hexenuronic acids (hexA) (Pouyet et al. 2014). Since in theory bleaching with ozone should remove more of these substances than chlorine dioxide, it should lead to better brightness stability. Conversely, each time ozone reacts on a C=C double bond hydroxyl radicals OH• may be formed. This highly unstable radical can further oxidize lignin and carbohydrates alike, generating C=O carbonyl groups which favor yellowing (Pouyet et al. 2014; Ragnar et al. 1999). Moreover, in subsequent alkaline extraction stage, part of the carbohydrates C=O groups initiate β-elimination and alkaline rearrangements that ultimately result in chain scissions, lowering the pulp degree of polymerization (DP) (Lewin and Herman, 1997) and giving rise to unsaturated substances (Perrin et al. 2014; Zhou et al. 2011). Thus, the effect of Z stages on brightness stability can be both beneficial by destroying chromophores and chromogens and detrimental by generating heat-sensitive degradation products (Pouyet et al. 2013; Röhrling et al. 2002). Some of the chromophores still present in bleached chemical pulps have been identified and quantified (Rosenau et al. 2004, 2011). They are of the quinone or

aromatic furan type. Their recalcitrance towards bleaching has been attributed to a strong resonance-induced stabilization. Hydrogen peroxide has been recently proved capable to eliminate some of these chromophores (Zwirchmayr et al. 2017). As a potent oxidant ozone is also assumed to target these moeties. It was proposed to perform a combination of ozone and H_2O_2 (ZP) to obtain both high and stable brightness (Davies et al. 2009; Rosenau et al. 2017).

Recent work on TCFz bleaching of dissolving pulp not only confirmed this trend but gave additional information on the bleaching efficiency of ECF and TCFz sequences by means of UV Resonance Raman (UVRR) spectroscopy (Perrin et al. 2017). A gap between Raman spectral intensities of ECF and TCFz dissolving pulps of the same brightness was found, indicating that the ECF bleached pulp would contain more aromatics and other unsaturated substances. In fact, UVRR spectroscopy has been used to detect the presence of residual lignin and hexA in pulp (Agarwal and Ralph 1997; Halttunen et al. 2001). They can be detected even when present in minute amounts (ppm to ppb) since the resonance effect amplifies the signal up to 10^6 times. Detection of C=O groups (Potthast et al. 2005) and aromatics-based chromophores (Loureiro et al. 2010) has also been reported for different laser wavelengths. Several quantification procedures have even been proposed (Halttunen et al. 2001; Jääskeläinen et al. 2005; Loureiro et al. 2010; Saariaho et al. 2003) but they are unreliable when analyzing fully bleached pulps since the variety of color contributors cannot be assessed when using one single laser wavelength.

The aim of this work was a deeper understanding of the effect of ozone and other bleaching chemicals on pulp brightness stability. The UVRR spectroscopy was used with a 244 nm laser wavelength to understand the role of the bleaching chemistry on both the nature of the residual substances in ECF and TCFz bleached pulps and their role in brightness reversion. In this work, the ECF sequence was that currently applied in the Fibre Excellence-Saint Gaudens kraft pulp mill DEpDD and the TCFz sequence A(ZEo)(ZEo)(ZP) was designed and optimized according to the principles recently developed to minimize the decrease of the cellulose DP (Pouyet et al. 2013).

2 Materials and methods

2.1 Materials

Hardwoods (HW) mix kraft oxygen-delignified and DEpDD bleached (control pulp 'cp') pulps were provided by Fibre Excellence paper mill of Saint-Gaudens, France. Ozone was produced in the lab with an Ozonia laboratory generator. Sodium borohydride was bought from Fisher Scientific. Model-compounds p-benzoquinone and p-hydroquinone, and hydrogen peroxide were ordered from Millipore Sigma. Other bleaching chemicals were purchased from Roth (Germany). All the chemicals were used without further purification.

2.2 Methods

Oxygen assisted alkaline extraction stages Eo were carried out in a stainless steel reactor under 2 bars of oxygen, at 10% PC. All other bleaching reactions were performed at 10% PC, inside double thermosealed bags, in a thermo-stated water bath, and manually homogenized every 15 min. Chemical charges are expressed in % of o.d. pulp by weight.

2.3 Pulp ozonation

Pulp preparation for high consistency ozonation consists of pH adjustment to 2.5 with (4N) H_2SO_4 at 1–2% pulp consistency (PC), filtration on No. 2 filtration funnel, followed by centrifugation of the pulp to obtain 35–45% PC. Then, pulp is fluffed and put in a spherical glass reactor. The ozone generator settings are: input oxygen pressure of ~2 bars, current in the ozonator of 0.7 A and ozone concentration of ~65 mg/l. The real ozone concentration of the gas flow is determined by indirect titration using potassium iodide and sodium thiosulfate so the needed amount of ozone is calculated and injected in the rotating reactor containing the pulp (expressed as per cent ozone based on pulp by weight).

2.4 Laboratory-scale ECF and TCFz bleaching

The commercial HW oxygen-delignified kraft pulp was bleached by an ECF and a TCFz sequences, details given below:
ECF: DEpDD
D_0: 0.95% ClO_2 [55 °C, 1.5 h]
Ep: 1.7% NaOH, 0.45% H_2O_2 [70 °C, 1.5 h]
D_1: 0.53% ClO_2 [70 °C, 3 h]
D_2: 0.25% ClO_2 [75 °C, 4 h]
TCFz: A(ZEo)(ZEo)(ZP)
A: pH = 3 (H_2SO_4) [90 °C, 2 h]
$Z_{1,2}$: 0.17% O_3; **Eo:** 1% NaOH, P(O_2) = 2 bar [70 °C, 1 h]
Z_3: 0.16% O_3; **P:** 0.45% H_2O_2, 0.8% NaOH, 0.3% $MgSO_4$ [70 °C, 2 h, pH 11.5]

2.5 Post-bleaching treatments applied on commercial ECF bleached pulp

The commercial HW DEpDD bleached kraft pulp was treated in various post-bleaching stages, details given below:
B: 1% NaBH4, Na_2CO_3 [T_{room}, 2h, pH around 10], reaction carried out in sealed Erlenmeyers, under vigorous magnetic agitation, at 2% PC
Ebc ('Extraction stage in B conditions'): Na_2CO_3 [T_{room}, 2h, pH around 10], at 2% PC
P: 0.45% H_2O_2, 0.8% NaOH [70 °C, 2 h, pH 11.5]
Epc ('Extraction stage in P conditions'): 0.8% NaOH [70 °C, 2 h, pH 11.5]
Z: 0.35% O_3
H: 2% ClOH, acetate buffer [T = 70 °C, 1 h, pH 4.9]

Z followed by alkaline stages B, Ebc, P, and Epc were carried out without inter-stage washing.

2.6 Pulp handsheets brightness and brightness stability

Paper handsheets from bleached hardwoods pulps were prepared at pH 6 and dried under vacuum at 85 °C for 7 min. ISO 3688, 1999 and ISO 5630-1, 1991 were followed for brightness determination and dry aging of samples (24 h in an oven at 105 °C), respectively. Post-Color Number (PCN) accounted for the brightness stability (Davies et al. 2009).

2.7 UV resonance Raman spectroscopy

The UVRR spectra were obtained in Aalto University (Espoo, Finland) using a Renishaw 1000 UV Raman spectrometer. The laser source was an Innova 90C FreD frequency-doubled Ar+ ion from Coherent Inc. with an excitation wavelength of 244 nm, a power output of 10 mW, and the measuring transmittance set at 25%. The system was coupled with a DMLM microscope from Leica Microsystems GmbH. The data acquisition and handling were done according to Jääskeläinen et al. 2005 using Grams AI spectroscopy software. The spectra were normalized to the cellulose-related peak at 1094 cm^{-1}. In the framework of this study, a measurement of pure p-benzoquinone and p-hydroquinone has been performed. There were observed the expected ring band at 1605 cm^{-1} for both molecules, and a specific band for p-benzoquinone at 1685 cm^{-1} probably corresponding to C=O stretch.

Relevant Raman bands assignation is summarized in 1.

3 Results and discussion

3.1 TCFz versus ECF

The HW kraft oxygen-delignified pulp was bleached through an ECF and a TCFz sequences, details given in Table 2. The PCN accounting for the brightness stability underlines a brightness about twice more stable for the TCFz pulp compared to the ECF pulp. The UVRR spectra of ECF and TCFz on Figure 2 show a large gap for the broad Raman band at [1500–1800 cm^{-1}] representing the contribution of C=C and C=O containing substances (band **III**), as showed in Figure 1 and detailed in Table 1. Despite having approximately the same brightness, TCFz brightness is about twice more stable than that of ECF. It is assumed that the residual chemical substances which are in larger amounts in the ECF pulp are responsible for most of the yellowing under heat exposure.

The industrial ECF pulp 'cp' underwent the same bleaching sequence as the lab-made ECF, with similar conditions. However, the difference of equipment between industrial and laboraty scales is responsible for cp lower PCN (0.43 vs. 0.61, respectively) albeit showing a similar brightness level. This is probably due to better inter-stage washing using hot water while only cold water was used in

Table 1: Reported Raman bands assignation from the literature and from present work.

| Band no.	Raman shift (cm^{-1})	Assignation	References
–	800–1000	Carbohydrates and lignin, weak signal	(Wiley and Atalla 1987a,b)
1	1094	*(Asymmetric stretch) C–O–C β-glycosidic bond* of cellulose and hemicelluloses	(Agarwal and Ralph, 1997; Cao et al. 2006; Edwards et al. 1994)
2	1120	*(Symmetric stretch) C–O–C β-glycosidic bond* of cellulose and hemicelluloses	
3	1345	*CH$_2$ and OH cellulose; O–H (bend)* aliphatic HW lignin	(Agarwal et al. 2011; Edwards et al. 1994)
4	1380	*CH$_2$ cellulose, phenolic O–H (bend)*	(Agarwal and Atalla 2010)
5	1412	*CH$_2$ cellulose; HCC, HCO, HOC (bend)* carbohydrates and lignin	(Edwards et al. 1994; Wiley and Atalla, 1987a,b)
6	1453	*CH$_3$ (bend)* in OCH$_3$ of carbohydrates and HW lignin	(Agarwal et al. 2011; Agarwal and Ralph, 1997)
	1465	*OH (bend)* of 1st and 2nd groups alcohol	(Edwards et al. 1994)
7 (C=C stretch)	1612	Aromatic ring and p-benzoquinone conjugated ring*	(Agarwal et al. 2011) *Measured in this work
	1625	*cis–cis–dimethylmuconic acid*	(Edwards et al. 2006)
	1634	Coniferaldehyde/sinapaldehyde	(Agarwal et al. 2011)
	1638	Stilbene	(Saariaho et al. 2005)
	1642	*trans–trans–muconic acid*	(Edwards et al. 2006)
	1657	Hexenuronic acid	(Halttunen et al. 2001)
8 (C=O stretch)	1661	*Ring conjugated stretch* of coniferyl/sinapyl alcohol	(Saariaho et al. 2005)
	1661	Coniferaldehyde/sinapaldehyde	(Saariaho et al. 2005)
	1668	p-benzoquinone *C=O* *	*Measured in this work
	1680	o-benzoquinone	(Barreto et al. 1998)
	1662–1695	C=O conjugated monomers	(Saariaho et al. 2005)

Table 2: Characterics of hardwood kraft bleached pulps: laboratory-made 'ECF' and 'TCFz', and industrial ECF pulp 'cp'.

Pulp	Bleaching sequence	Brightness (%ISO)	PCN
ECF	DEpDD	90.3	0.61
TCFz	A(ZEo)(ZEo)(ZP)	90.8	0.29
cp	DEpDD	89.8	0.43

the laboratory. Nevertheless, the ECF industrial control pulp (cp) and the ECF lab-produced pulp are assumed to be comparable since they are produced from the same starting material and bleached with the same sequence. For this reason and larger availability of cp pulp the latter was used to continue the study on identification of chromogens by using several post-bleaching treatments.

3.2 Effect of single alkaline post-bleaching treatments (E, B, P) on ECF pulp

In this study, the commercial ECF control pulp was post-treated by several stages. As shown in Figure 3, B and Ebc stages cause some elimination of lignin, aromatics, C=C and C=O containing substances. Most of the change on the spectra intensity is due to the alkaline conditions and affect brightness stability albeit the specific effect of $NaBH_4$ is marginal. Small brightness improvement is observed for B, likely because of the reduction of some C=O containing chromophores. A noteworthy result is the identical brightness PCN values for both TCF and B treated ECF pulp, despite the difference in spectral intensities. This discrepancy accounts for a larger quantity of unsaturated materials present in the B treated pulp which are uncolored and not
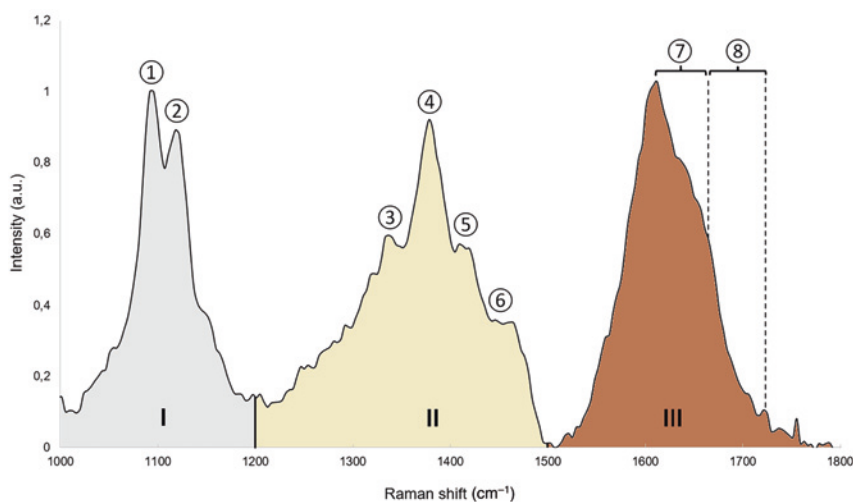
Figure 1: UVRR spectrum of an industrial ECF hardwood bleached pulp showing relevant Raman bands numbered and their corresponding assignations are listed in Table 1.

	%ISO	PCN
—ECF	91.5	0.61
—TCF	91.0	0.29
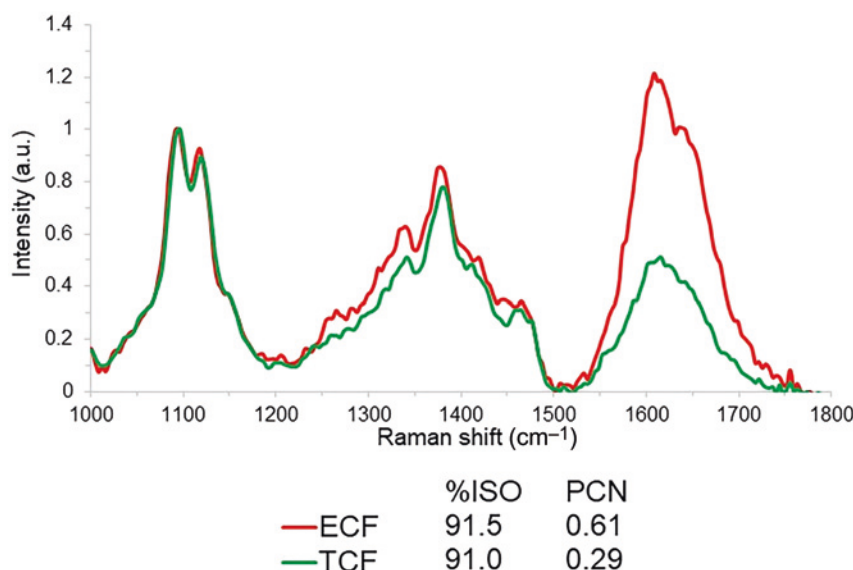
Figure 2: UVRR spectra of ECF and TCFz bleached pulps. ISO brightness and PCN values are showed next to the legend. Details are given in Table 2.
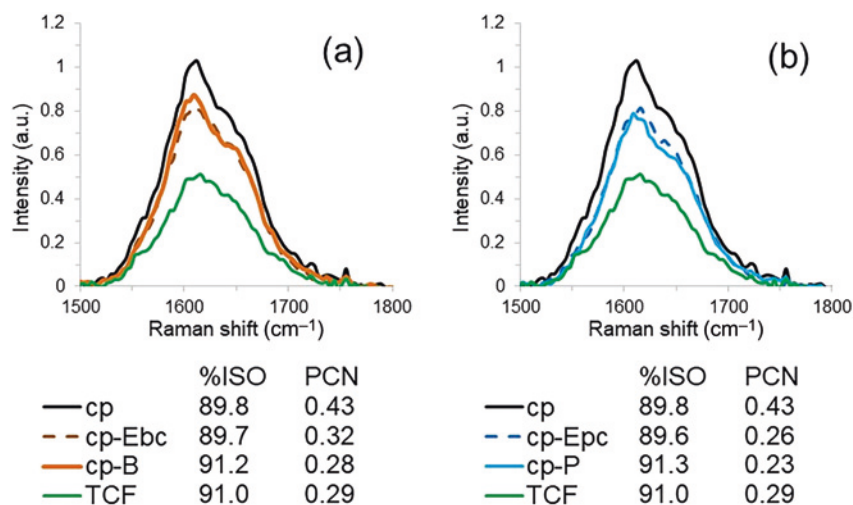
	%ISO	PCN
—cp	89.8	0.43
- - cp-Ebc	89.7	0.32
—cp-B	91.2	0.28
—TCF	91.0	0.29

	%ISO	PCN
—cp	89.8	0.43
- - cp-Epc	89.6	0.26
—cp-P	91.3	0.23
—TCF	91.0	0.29

Figure 3: UVRR spectra of Ebc, B (a), Epc, P (b) treated, TCF and control pulps.

responsible for pulp yellowing upon the aging conditions used in this study. UVRR spectra after P and Epc are very similar to those obtained after B and Ebc showing again that most of the effect is due to the alkaline conditions. Then again the specific attack on carbonyl groups by H_2O_2 cannot be observed on the UVRR spectra. Brightness stability is even more improved by the harsher alkaline and temperature conditions of the Epc and P treatments, whereas the specific effect of H_2O_2 on brightness stability remains small. However, there is a marked positive effect on brightness which indicates that some C=O containing chromophores have been eliminated by H_2O_2, even though this is not detectable by UVRR spectroscopy. Better stability after P than after B was expected since in the chosen experimental conditions H_2O_2 readily oxidizes carbonyl groups to uncolored carboxylic acids while $NaBH_4$ reversibly reduces C=O into alcohols which can convert back to C=O. However, results from Ebc and Epc treatments show that the better brightness stability is primarily due to the stronger alkalinity and does not reflect the better C=O removal with P. One has to admit that brightness stability is affected essentially by alkali soluble insaturated substances present in the ECF pulp.

3.3 Effect of single ozone post-bleaching treatment (Z) on ECF pulp

On Figure 4, the UVRR signal lowers dramatically after Z, about the same level as the TCF pulp. Interestingly, the Z stage does not lower the PCN of the pulp significantly (0.40 vs. 0.43), albeit a remarkable increase in brightness (+2.3 % ISO). The decrease in the signal and the better brightness are in accordance with the well known reactivity of ozone with unsaturated structures. The fact that no improvement in brightness stability is observed may come from the

simultaneous formation of C=O groups on carbohydrates, counteracting the beneficial effect of the destruction of conjugated structures (Perrin et al. 2017; Pouyet et al. 2014).

3.4 Effect of combined [ozone + alkaline] post-bleaching treatments (ZE, ZB, ZP) on ECF pulp

Raman spectra on Figure 5 show that while the signal lowers after Z does not change significantly after the following alkaline stages whether they contain $NaBH_4$, H_2O_2 or no brightening agent. However, the PCN value that was quasi-identical after Z alone is now dramatically reduced after the B and P stages. Actually, the change is essentially due to the alkaline conditions prevailing in these stages, as shown by the results observed after Epc and even after the mild treatment Ebc. The slight
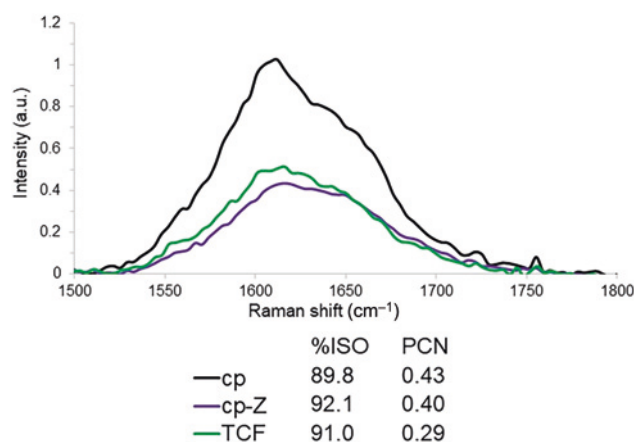

	%ISO	PCN
—cp	89.8	0.43
—cp-Z	92.1	0.40
—TCF	91.0	0.29

Figure 4: UVRR spectra of Z treated, TCF and control pulps.

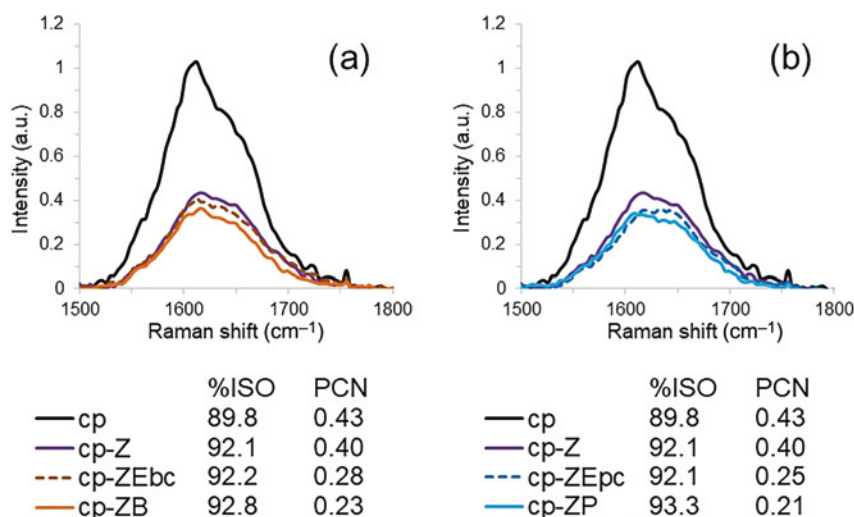|	%ISO	PCN			%ISO	PCN
—cp	89.8	0.43		—cp	89.8	0.43
—cp-Z	92.1	0.40		—cp-Z	92.1	0.40
---cp-ZEbc	92.2	0.28		---cp-ZEpc	92.1	0.25
—cp-ZB	92.8	0.23		—cp-ZP	93.3	0.21

Figure 5: UVRR spectra of Z treated, ZEbc, ZB (a), ZEpc, ZP (b) and control pulps.

advantage of ZEpc over ZEbc on PCN (0.03 points difference) is likely due to the lower alkalinity and temperature of Ebc.

Brightness after ZP is slightly better than after ZB, because of the greater effect of H_2O_2 on conjugated C=O groups. Superiority of P over B to eliminate C=O groups may originate from the irreversible character of their reaction with H_2O_2. Brightness stability after ZP and ZB is better than after ZEpc and ZEbc respectively, which reflects the specific effect of H_2O_2 and $NaBH_4$ on C=O groups. Better brightness stability is observed after ZP compared to ZB. One explanation could be again either the more efficient elimination of C=O groups with H_2O_2 or the result of the higher alkalinity in P.

3.5 Effect of aging

Figure 6 shows the effect of aging of the TCF and the ECF control pulps on the UVRR signals. A general increase of band **III** (Figure 1) intensity is observed which indicates that new unsaturated and aromatic structures are formed under the conditions of aging (105 °C, 24 h). Since brightness is decreased, these new unsaturated structures must contain C=O carbonyl groups. This signal increment is almost undetectable for the alkaline treated pulps on Figure 7 (B and Epc spectra were identical to Ebc and P). Unfortunately, no correlation can be observed between this increase of spectral intensity and the PCN values of the samples.

However, for pulps with oxidized carbohydrates (here, the ozone Z and hypochlorous acid H treated pulps) a clear increase of the spectral band no. 8 (Table 1) corresponding to C=O groups can be observed on Figure 8. In fact, shoulders between 1680 and 1695 cm^{-1} indicate the

presence of quinones in the aged Z and H samples, thus confirming the prevalence of C=O containing carbohydrates on quinones formation during aging (Rosenau et al. 2011). The spectra general shift to the right observed for the H treated pulp may be a consequence of chlorination (Linvien et al. 1991).

This trend is not observed after Z followed by an alkaline treatment (e. g. ZEbc and ZP, Figure 9) anymore. ZB and ZEpc UVRR spectra were similar to ZEbc pulp. This seems to point out that most of the C=O groups generated by Z can be eliminated in an alkaline stage. In particular, for ZP no new aromatic structures are formed, and the aged sample spectrum is quasi-identical to the non-aged one, which corroborates its low PCN value (0.21).

These measurements of aged samples seem to point out that samples with oxidized carbohydrates (C=O and
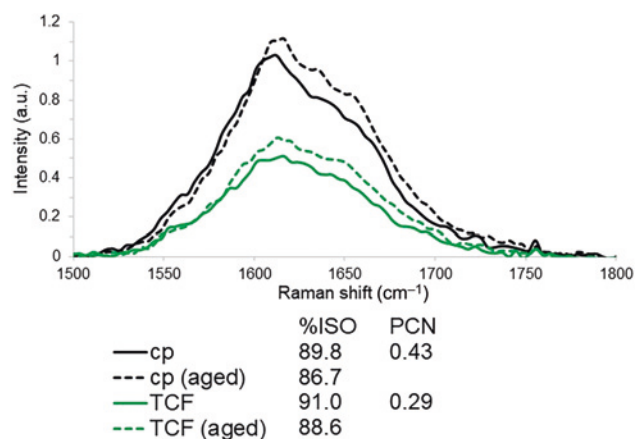

	%ISO	PCN
—cp	89.8	0.43
---cp (aged)	86.7	
—TCF	91.0	0.29
---TCF (aged)	88.6	

Figure 6: UVRR spectra of TCF and control pulps, as well as their aged versions.
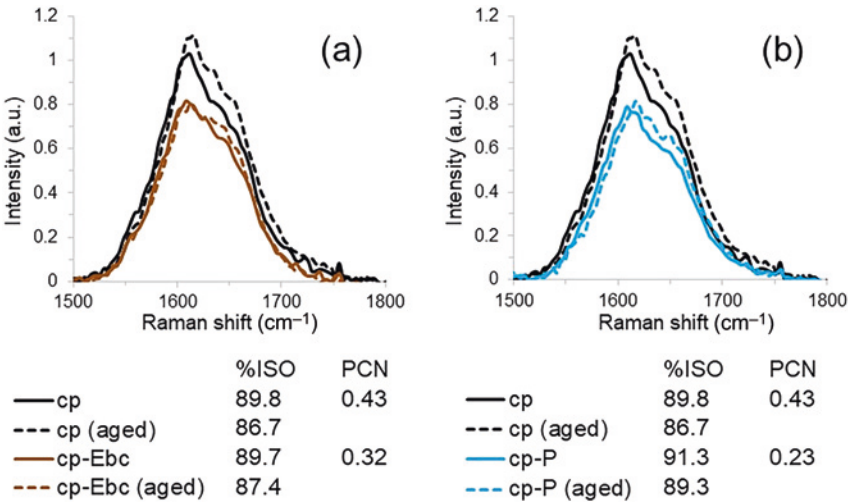
Figure 7: UVRR spectra of Ebc (a), P (b) treated and control pulps as well as their aged versions. Conditions for Ebc and P were unchanged in that section.
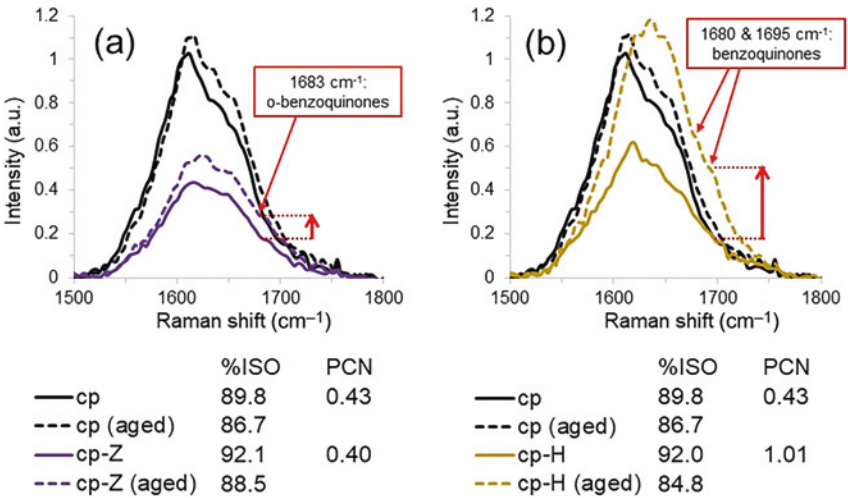
	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-Ebc	89.7	0.32
cp-Ebc (aged)	87.4	

	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-P	91.3	0.23
cp-P (aged)	89.3	

Figure 8: UVRR spectra of Z (a), H (b) treated and control pulps as well as their aged versions.

1683 cm⁻¹: o-benzoquinones

1680 & 1695 cm⁻¹: benzoquinones

	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-Z	92.1	0.40
cp-Z (aged)	88.5	

	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-H	92.0	1.01
cp-H (aged)	84.8	
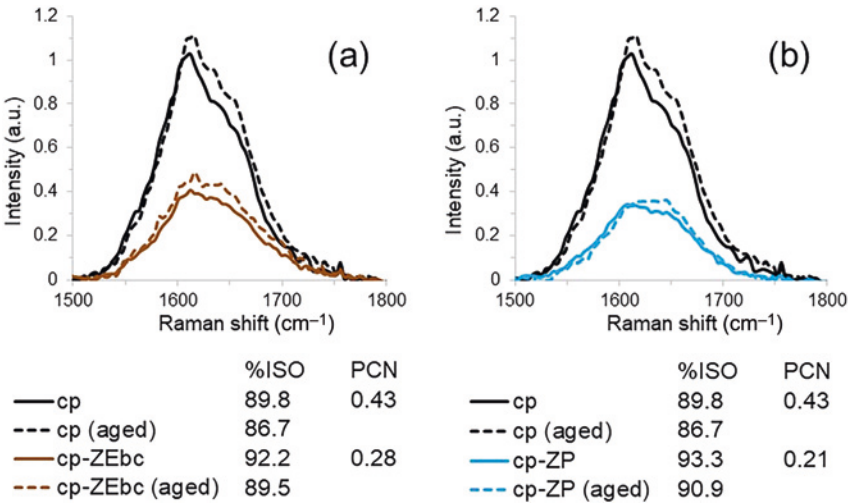
Figure 9: UVRR spectra of Z, ZEbc (a), ZP (b) treated and control pulps as well as their aged versions.

	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-ZEbc	92.2	0.28
cp-ZEbc (aged)	89.5	

	%ISO	PCN
cp	89.8	0.43
cp (aged)	86.7	
cp-ZP	93.3	0.21
cp-ZP (aged)	90.9	

COOH groups) tend to generate quinones detrimental to brightness stability when aging, while the chromophores generated during the aging of samples with rather unoxidized cellulose are less obvious and may simply result from the increased conjugation of unsaturated compounds thus favoring absorption of visible light.

4 Conclusions

UVRR spectroscopy clearly shows that ECF pulp contains more functional groups than TCFz pulp. According to the spectra, these functional groups may belong to residual lignin, other aromatics, conjugated C=C structures (e. g. muconic acid derivatives, hexenuronic acids) and C=O containing stuctures (e. g. quinones). These groups and structures are partly removed from ECF pulp by several post-treatments, like B, P, Z, ZP stages. However, only the Z-based post-treatments allow for lowering UVRR spectra intensity to their level in TCFz pulp. This is in accordance with the fact that ozone may react on all these structures, which is not the case for D. However there is no direct correlation between the intensity of the UVRR bands and the PCN values. Very strong improvement of the ECF PCN value is observed by alkaline treatment of the pulp while the UVRR bands are not much affected indicating that some of the heat sensitive subtances are soluble and removable in alkaline solution and that their amount is low and hardly detected in our UVRR spectroscopic method. Excitation with another laser wavelength, e. g. favoring C=O group resonance, might complement this study (Loureiro et al. 2010; Potthast et al. 2005). Also, Z alone has dramatic effect on the intensity of the UVRR bands while the PCN value is not substantially modified. The degradation of unsaturated conjugated substances and quinones by ozone might be counterbalanced by the formation of new C=O groups on carbohydrates which are known to favor heat yellowing. The high performance of ZP for brightness stability would be due to the combination of the destruction of conjugated unsaturated and aromatic substances (residual lignin, muconic acids, hexenuronic acids, quinones …) by ozone and the oxidation of carbohydrates C=O groups by the latter. According to our results the implementation of a final ZP stage in the TCFz sequence surely explains the good brightness stability of the corresponding pulp.

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