



# An explanation for the better brightness stability obtained for ozone bleached pulps - a UV Resonance Raman spectroscopy approach

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agefpi

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## ECF

## TCFz

- + Well-known chemistry and processes
- + No viscosity / DP loss
- + Compliance to current environmental regulation
- Partial effluent recycling
- AOX (in effluents) and OX (in pulp) generation

+ Potential full closure of the plant recycling loop

+ COD / BOD reduction

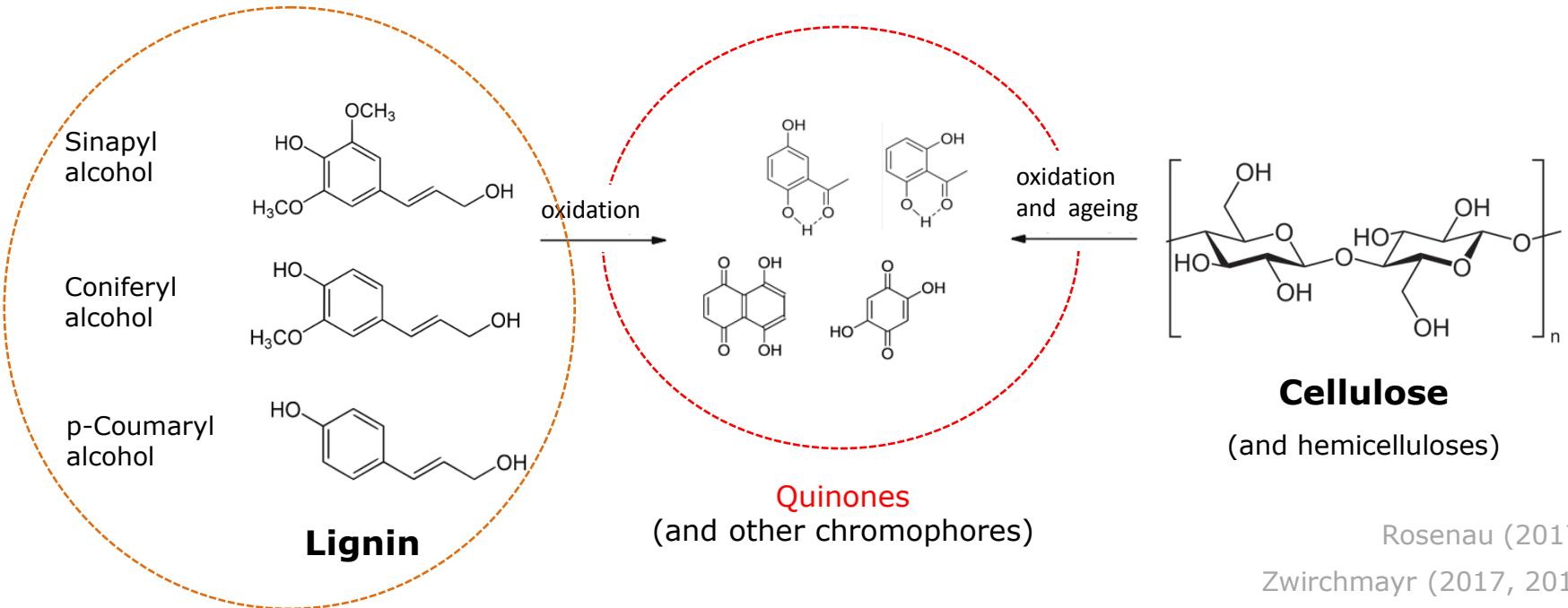
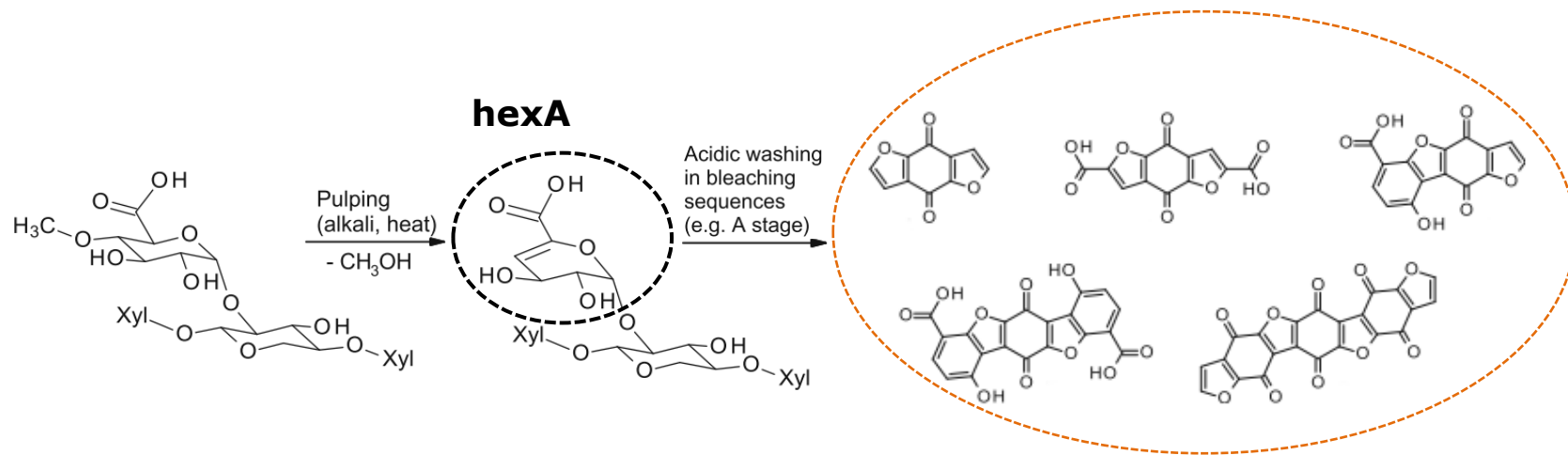
+ No AOX, nor OX

+ High brightness with great stability

- Applied only in a few plants worldwide

- Viscosity / DP loss

→ **without consequence on mechanical properties**



Rosenau (2017),  
Zwirchmayr (2017, 2018)

But...

- Chromophores (and chromophore precursors) include other structures: conjugated lignin fragments, acetophenones, furanoid structures, transition metal complexes, etc.
- Sources of chromophores are diverse: they come from pulping, residual lignin and carbohydrates degradation during bleaching or ageing, etc.

**Why would a TCFz bleached pulp brightness be more stable than for an ECF pulp?**

## Starting material:

O-delignified HW kraft pulp

HC ozone bleaching of acidified fluffed pulp



Ozone glass reactor and experimental set-up

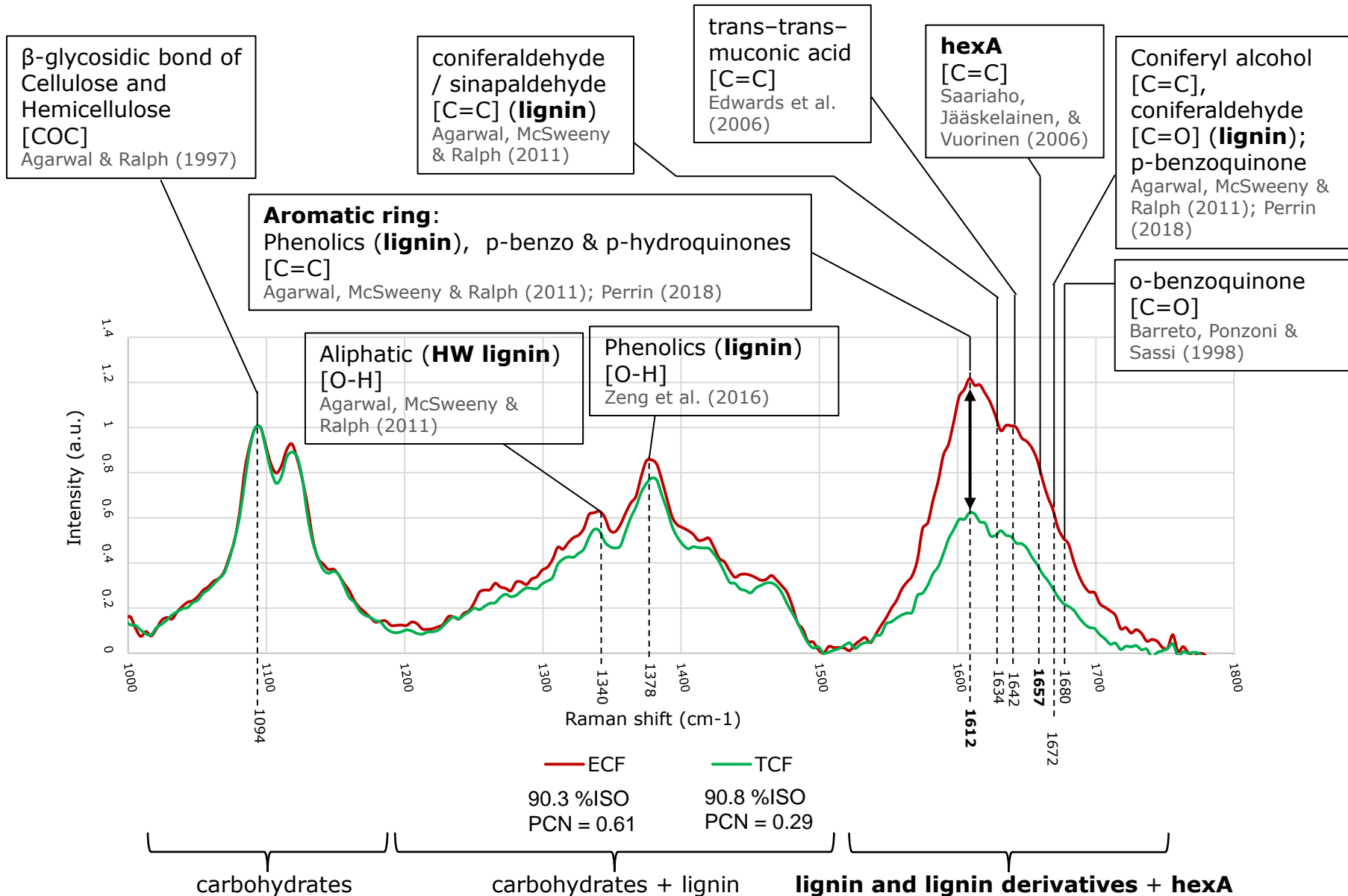
Sequence	Bleaching conditions*	Brightness (%ISO)	PCN
<b>ECF</b> DEpDD	<b>D<sub>0</sub></b> : 0.95 % ClO <sub>2</sub> [55 °C, 1.5 h] <b>Ep</b> : 1.7 % NaOH; 0.45 % H <sub>2</sub> O <sub>2</sub> [70 °C, 1.5 h] <b>D<sub>1</sub></b> : 0.53 % ClO <sub>2</sub> [70 °C, 3 h] <b>D<sub>2</sub></b> : 0.25 % ClO <sub>2</sub> [75 °C, 4 h]	90.3	0.61
<b>TCFz</b> A(ZEo)(ZEo)(ZP)	<b>A</b> : pH = 3 (H <sub>2</sub> SO <sub>4</sub> ) [90 °C, 2 h] <b>Z<sub>1</sub></b> : 0.17 % O <sub>3</sub> ; <b>Eo</b> : 1 % NaOH; P(O <sub>2</sub> ) = 2 bar [70 °C, 1 h] <b>Z<sub>2</sub></b> : 0.17 % O <sub>3</sub> ; <b>Eo</b> : 1 % NaOH; P(O <sub>2</sub> ) = 2 bar [70 °C, 1 h] <b>Z<sub>3</sub></b> : 0.16 % O <sub>3</sub> ; <b>P</b> : 0.45 % H <sub>2</sub> O <sub>2</sub> ; 0.8 % NaOH; 0.3 % MgSO <sub>4</sub> [70 °C, 2 h]	90.8	0.29

PCN = Post-Color Number  
Lower value ⇔ more stable brightness

Heat-induced dry ageing experiments performed at 105 °C for 24 hours

\*: Chemical charges expressed as % wt / od pulp

# UV-RR for lignin and hexA detection



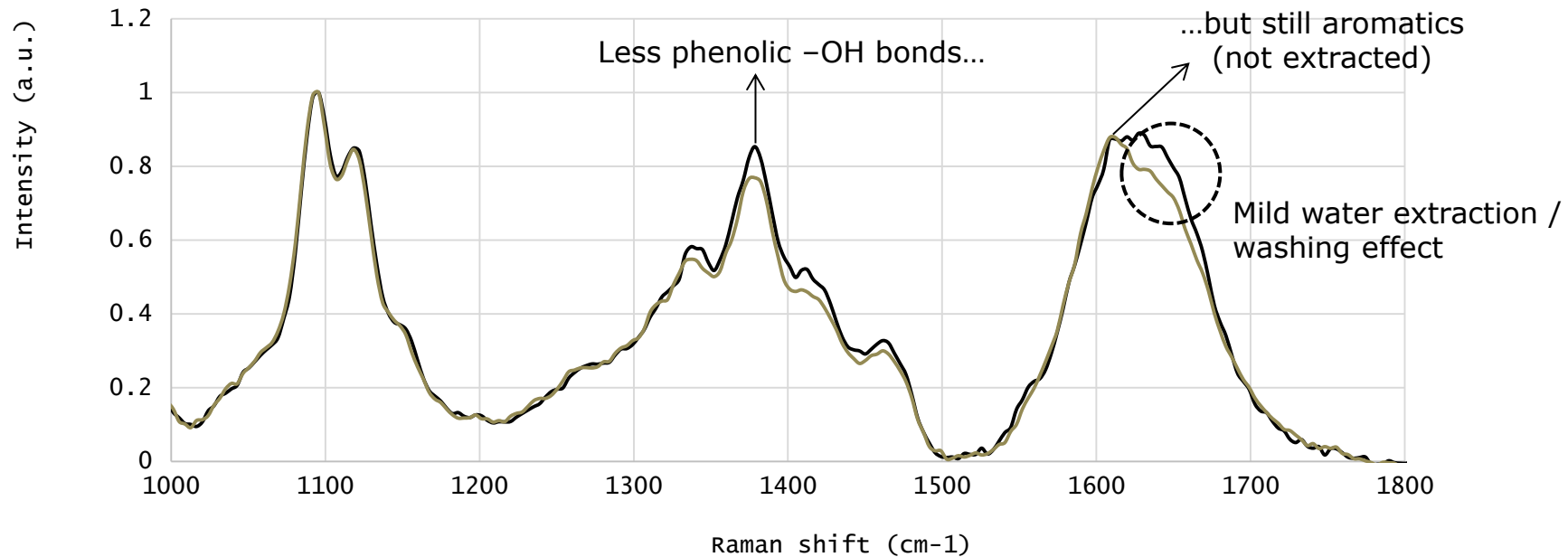
**The ECF pulp exhibits a much higher intensity signal than the TCF one**

In order to assess which chemical groups or products in the pulp are causing this Raman signal discrepancy, several post-bleaching treatments have been applied on a commercial ECF DEpDD bleached pulp

Stage	Chemical	Function	Charge (% wt. / od pulp)	T (°C)	t (h)	pH	PC (%)
SC	NaClO <sub>2</sub>	Delignification similar to D stage	2	65	2	4.7	10
B	NaBH <sub>4</sub> Na <sub>2</sub> CO <sub>3</sub>	C=O reduction to OH	1	T <sub>room</sub>	2	9	2
Ebc	B stage without NaBH <sub>4</sub>						
P	H <sub>2</sub> O <sub>2</sub> NaOH	C=O oxidation to COOH, chromophores destruction	0.45	70	2	12.5	10
Epc	P stage without H <sub>2</sub> O <sub>2</sub>						
Z	O <sub>3</sub>	Delignification, chromophores destruction, carbohydrates oxidation	0.35	T <sub>room</sub>	0.03	2.5	40
ZB, ZEbc, ZP, ZEpc	Eliminate / solubilize compounds oxidized by Z						



## UV-RR spectra of SC treated and control pulps



— c1

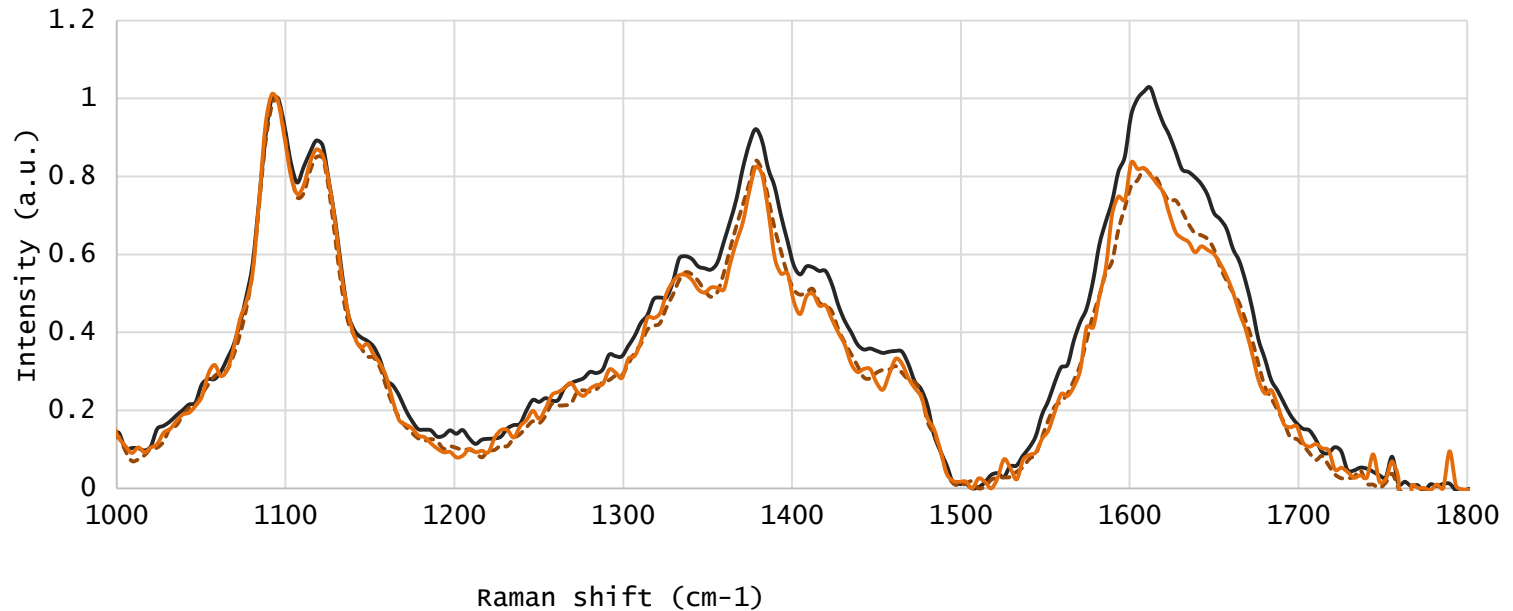
— c1-SC

89.9 %ISO  
PCN = 0.41

90.2 %ISO  
PCN = 0.37

Stage	Chemical	Function	Charge (% wt. / od pulp)	T (°C)	t (h)	pH	PC (%)
SC	NaClO <sub>2</sub>	Delignification similar to D stage	2	65	2	4.7	10
B	NaBH <sub>4</sub> Na <sub>2</sub> CO <sub>3</sub>	C=O reduction to OH	1	T <sub>room</sub>	2	9	2
Ebc	B stage without NaBH <sub>4</sub>						
P	H <sub>2</sub> O <sub>2</sub> NaOH	C=O oxidation to COOH, chromophores destruction	0.45	70	2	12.5	10
Epc	P stage without H <sub>2</sub> O <sub>2</sub>						
Z	O <sub>3</sub>	Delignification, chromophores destruction, carbohydrates oxidation	0.35	T <sub>room</sub>	0.03	2.5	40
ZB, ZEbc, ZP, ZEpc	Eliminate / solubilize compounds oxidized by Z						

UV-RR spectra of Ebc and B treated, and control pulps



— c2

89.6 %ISO  
PCN= 0.44

- - - c2-Ebc

89.7 %ISO  
PCN= 0.32

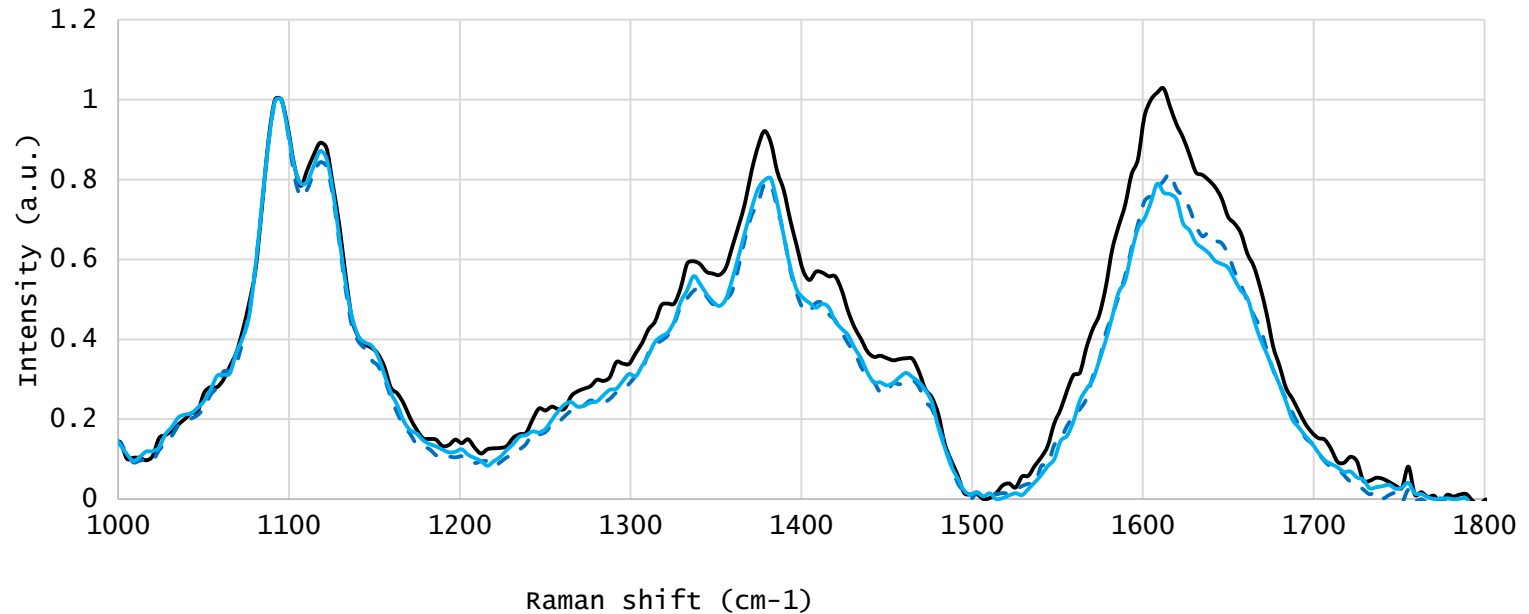
— c2-B

91.2 %ISO  
PCN = 0.28

# Post-bleaching treatments: hydrogen peroxide (P)

Stage	Chemical	Function	Charge (% wt. / od pulp)	T (°C)	t (h)	pH	PC (%)
SC	NaClO <sub>2</sub>	Delignification similar to D stage	2	65	2	4.7	10
B	NaBH <sub>4</sub> Na <sub>2</sub> CO <sub>3</sub>	C=O reduction to OH	1	T <sub>room</sub>	2	9	2
Ebc	B stage without NaBH <sub>4</sub>						
P	H <sub>2</sub> O <sub>2</sub> NaOH	C=O oxidation to COOH, chromophores destruction	0.45	70	2	12.5	10
Epc	P stage without H <sub>2</sub> O <sub>2</sub>						
Z	O <sub>3</sub>	Delignification, chromophores destruction, carbohydrates oxidation	0.35	T <sub>room</sub>	0.03	2.5	40
ZB, ZEbc, ZP, ZEpc	Eliminate / solubilize compounds oxidized by Z						

UV-RR spectra of Epc and P treated, and control pulps

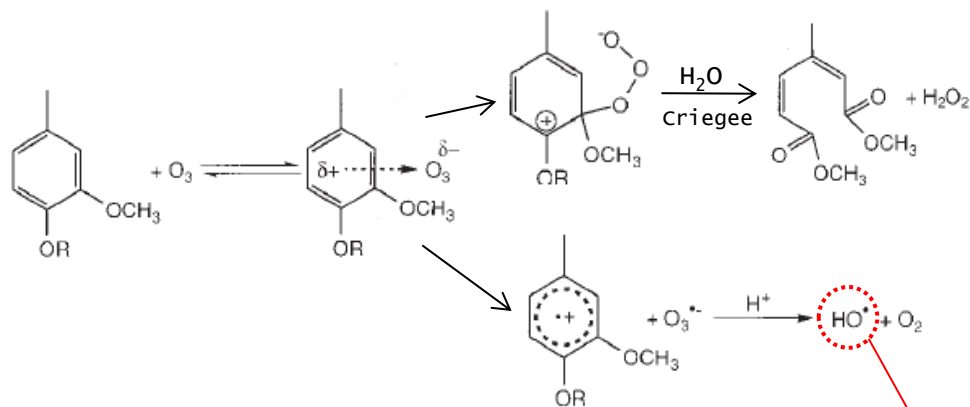


— c2	- - - c2-Epc	— c2-P
89.6 %ISO	89.6 %ISO	91.3 %ISO
PCN = 0.44	PCN = 0.26	PCN=0.23

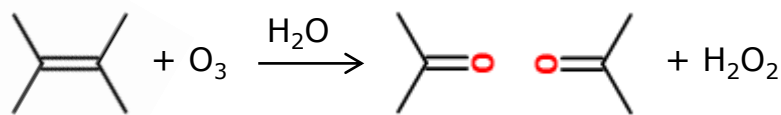
- B, Ebc, P and Epc all decrease the Raman signal intensity indicating solubilization of oxidized materials
- The 4 treatments decrease the PCN value in that order  $P < B < Epc < Ebc$
- Only B and P increase brightness although their UV-RR spectra are identical to Ebc and Epc spectra

Stage	Chemical	Function	Charge (% wt. / od pulp)	T (°C)	t (h)	pH	PC (%)
SC	NaClO <sub>2</sub>	Delignification similar to D stage	2	65	2	4.7	10
B	NaBH <sub>4</sub> Na <sub>2</sub> CO <sub>3</sub>	C=O reduction to OH	1	T <sub>room</sub>	2	9	2
Ebc	B stage without NaBH <sub>4</sub>						
P	H <sub>2</sub> O <sub>2</sub> NaOH	C=O oxidation to COOH, chromophores destruction	0.45	70	2	12.5	10
Epc	P stage without H <sub>2</sub> O <sub>2</sub>						
Z	O <sub>3</sub>	Delignification, chromophores destruction, carbohydrates oxidation	0.35	T <sub>room</sub>	0.03	2.5	40
ZB, ZEbc, ZP, Zepc	Eliminate / solubilize compounds oxidized by Z						

# Post-bleaching treatments: ozone (Z)



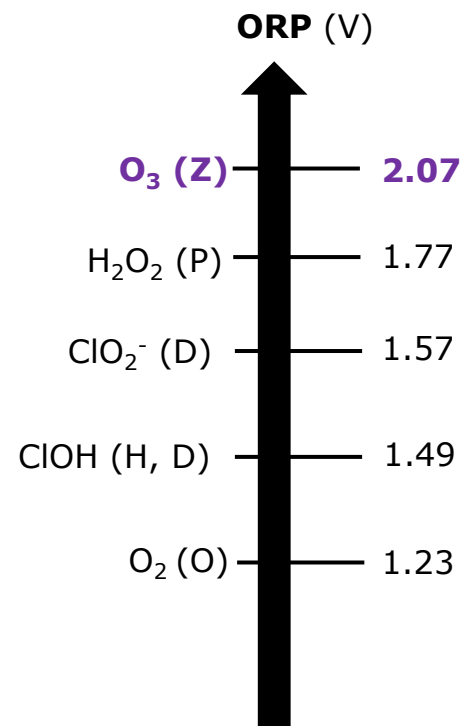
Ragnar et al. (1999)



Pouyet (2014)

Generates C=O  
on carbohydrates

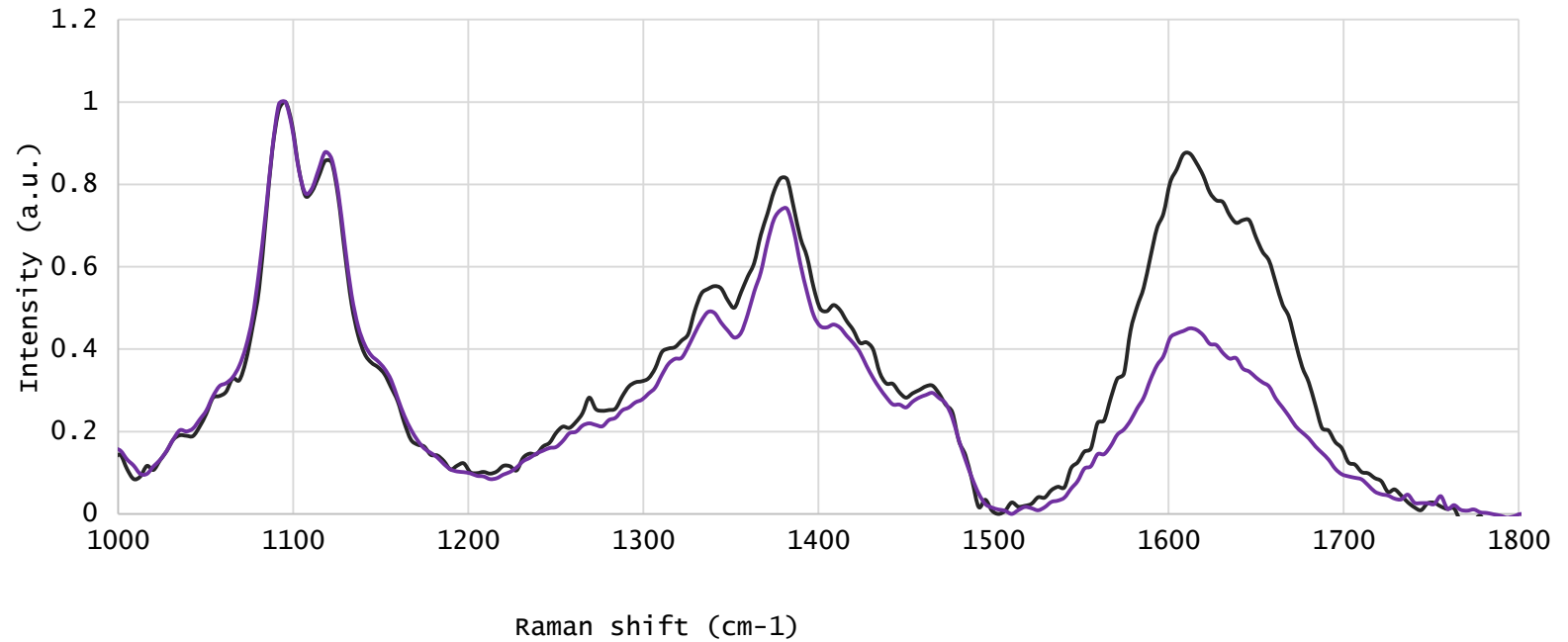
OH•



CRC Handbook of Chemistry and Physics, 88<sup>th</sup> edition



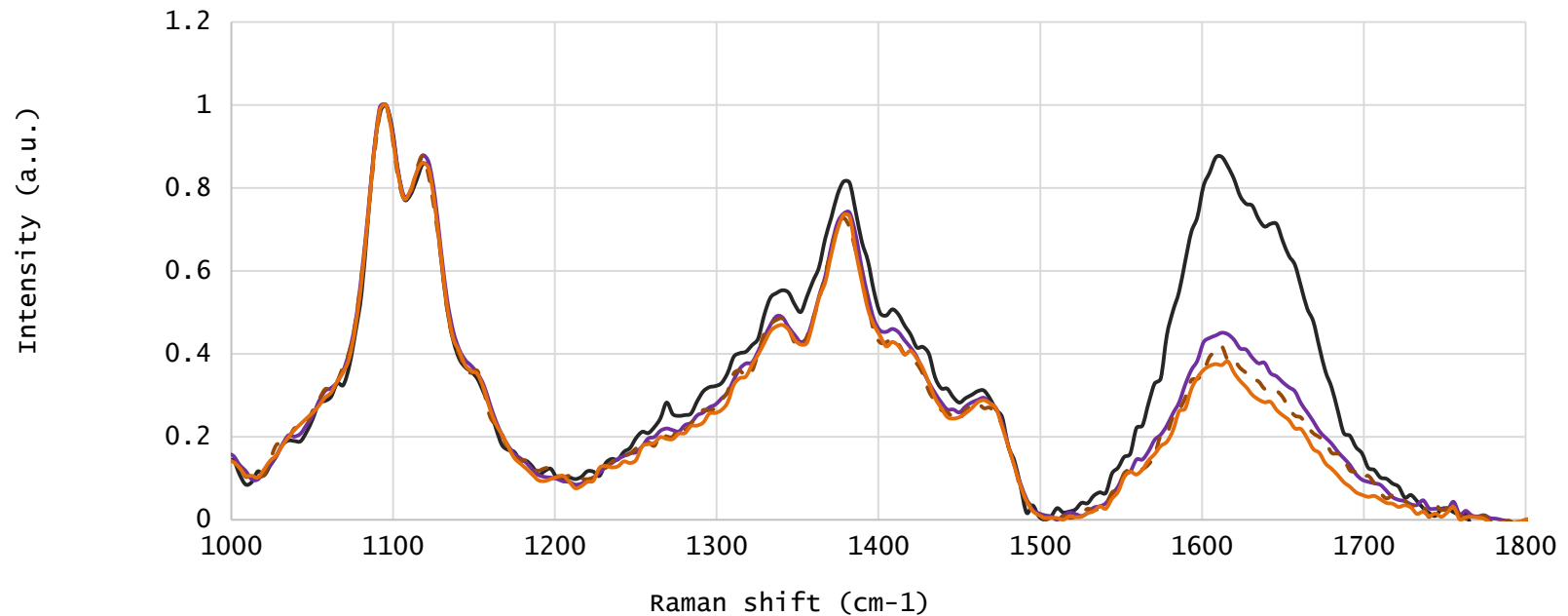
## UV-RR spectra of Z treated and control pulps



— c1  
89.9 %ISO  
PCN = 0.41

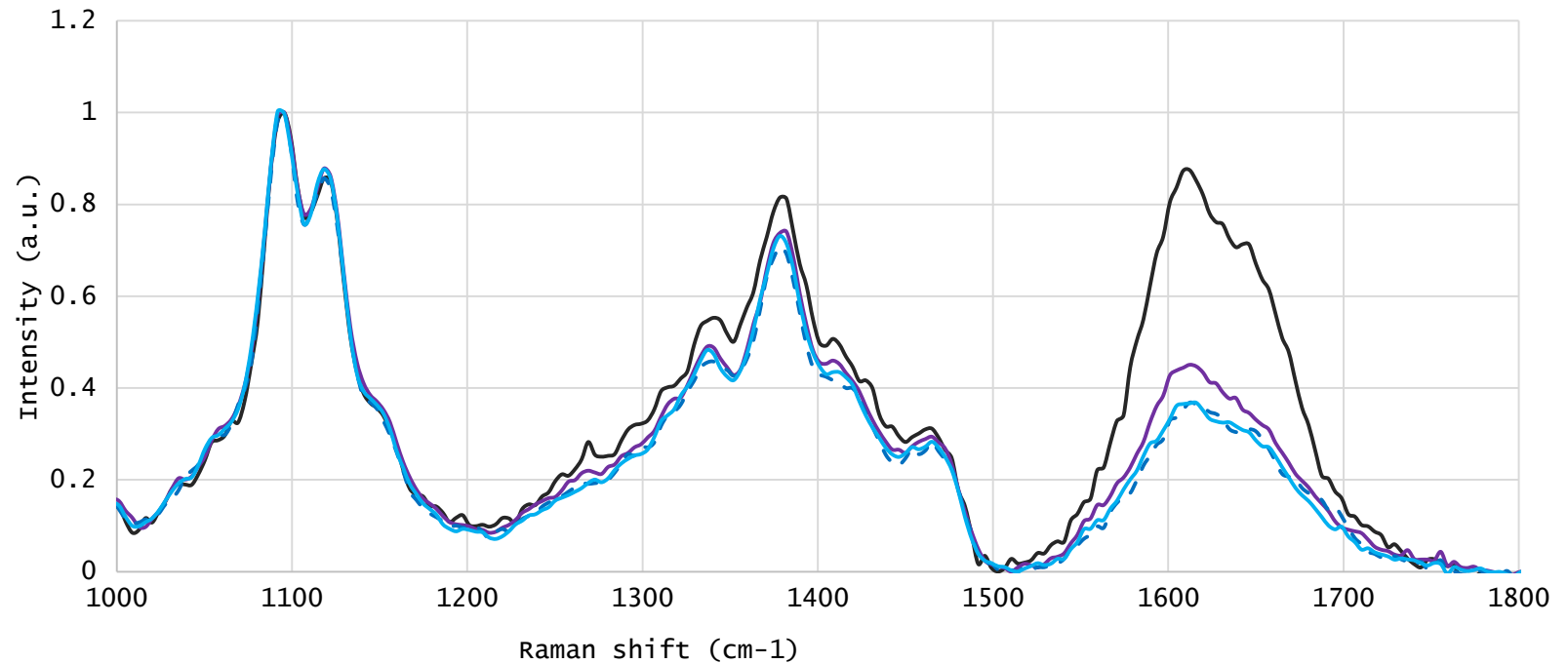
— c1-z(0.35)  
91.1 %ISO  
**PCN = 0.40**

UV-RR spectra of Z, ZEbc and ZB treated, and control pulps



— c1	— c1-Z(0.35)	- - - c1-Z(0.35)Ebc	— c1-Z(0.35)B
89.9 %ISO PCN = 0.41	91.1 %ISO PCN= 0.40	92.2 %ISO PCN= 0.28	92.8 %ISO PCN = 0.23

UV-RR spectra of Z, ZEpc and ZP treated, and control pulps



— c1	— c1-Z(0.35)	- - - c1-Z(0.35)Epc	— c1-Z(0.35)P
89.9 %ISO PCN = 0.41	91.1 %ISO PCN = 0.40	92.1 %ISO PCN= 0.25	93.3 %ISO PCN= 0.21

- Z dramatically decreases the signal intensity but PCN value is unchanged
- The 4 subsequent treatments decrease the PCN value in the same fashion as when applied directly on bleached pulp, as well as increase brightness
- The lowest PCN value of this study is obtained with ZP

- UV-RR spectroscopy shows that the DEpDD ECF pulp has clearly more functional groups – residual lignin, other aromatics, conjugated C=C structures, muconic acid derivatives, hexA, quinones, etc. – than the A(ZEo)(ZEo)(ZP) TCFz pulp
- The large difference of brightness stability of these two pulps is mostly due to oxidized substances in the ECF pulp which are easily extracted by alkaline treatment
- UV-RR spectra intensities are not correlated to PCN values
- ZP ended up being the best combination for obtaining the highest brightness and the best brightness stability. ZE also offers high and stable brightness

PhD sponsors:





Thank you for your attention

