



Ozone Days



# New generation green bleaching processes using ozone stages – comparison with conventional bleaching

Dr Etienne Montet – 23 March 2022



agefpi

TekLiCell



**Introduction**

**TCFz bleaching potential and chemical cost**

**Residual impurities and pulp brightness stability**

**Cellulose preservation and paper strength**

**Conclusion and prospects**



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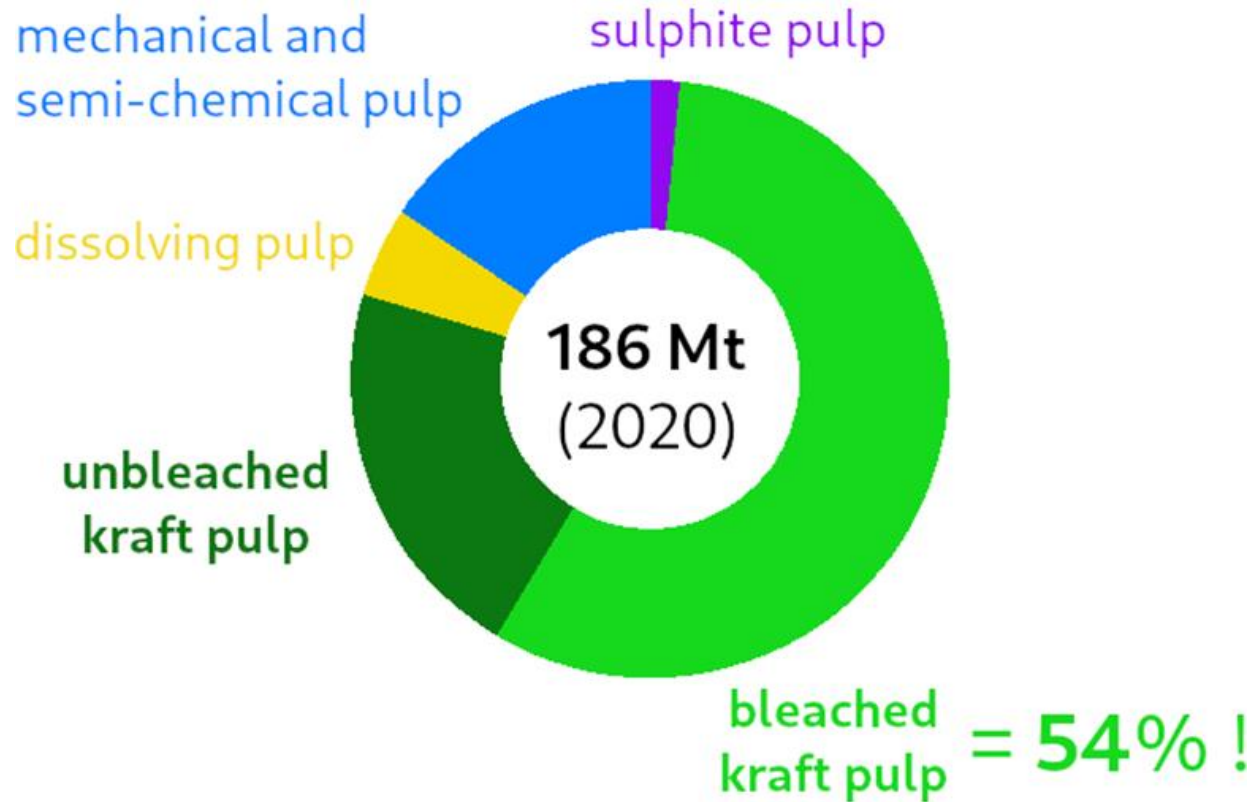


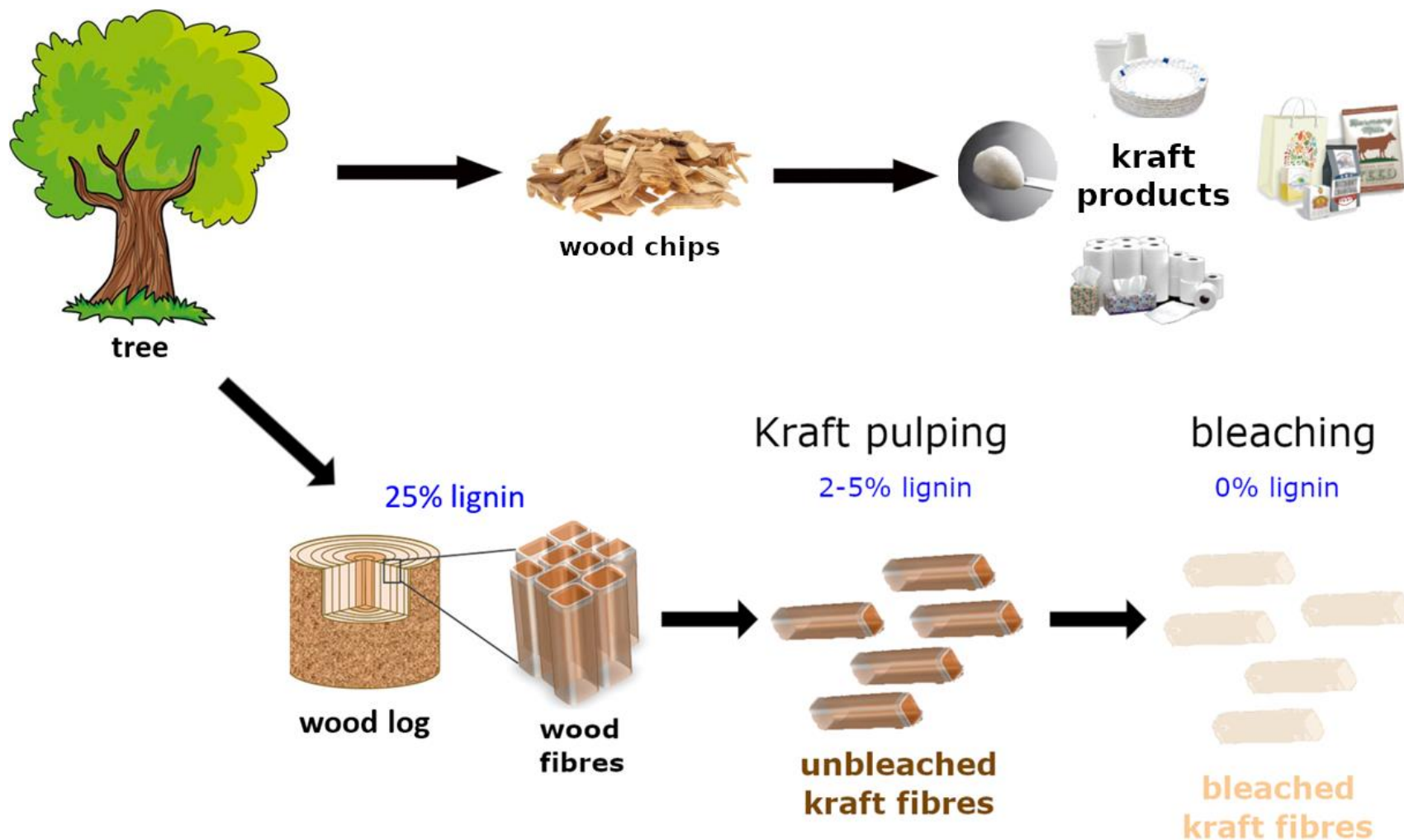
There are **several benefits** in substituting ozone for chlorine dioxide in Totally Chlorine Free (TCF) bleaching sequences:

- ❑ **No more** hazardous chlorinated organics (**AOX**) are generated
- ❑ Possibly **cheaper bleaching sequences** due to favorable displacement ratio of ozone over chlorine dioxide
- ❑ **Better pulp quality** overall due to ozone elimination of all C=C unsaturated substances



## Global wood pulp production in 2020:

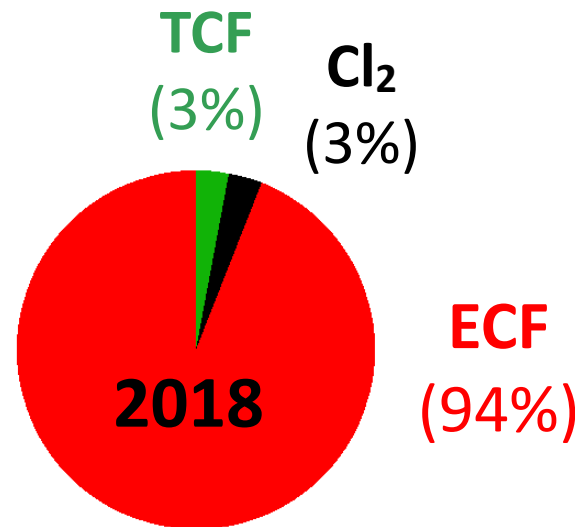




**Most polluting part!**



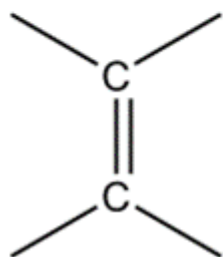
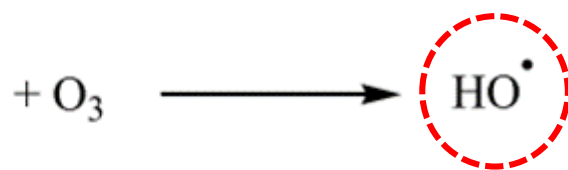
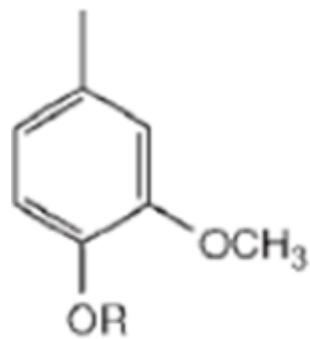
□ At the moment, ECF bleaching is considered the Best Available Technology.



Kraft pulp bleaching

□ Future environmental regulation could benefit TCF bleaching.

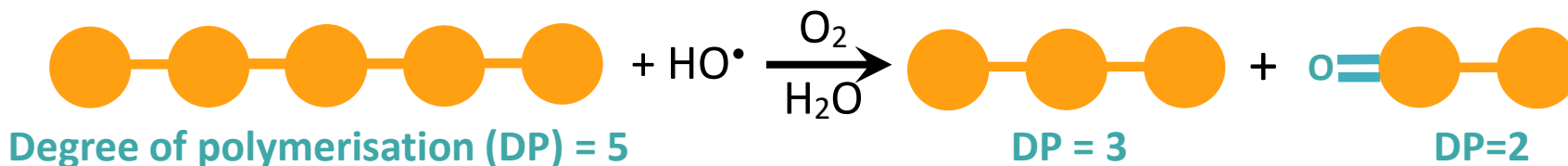




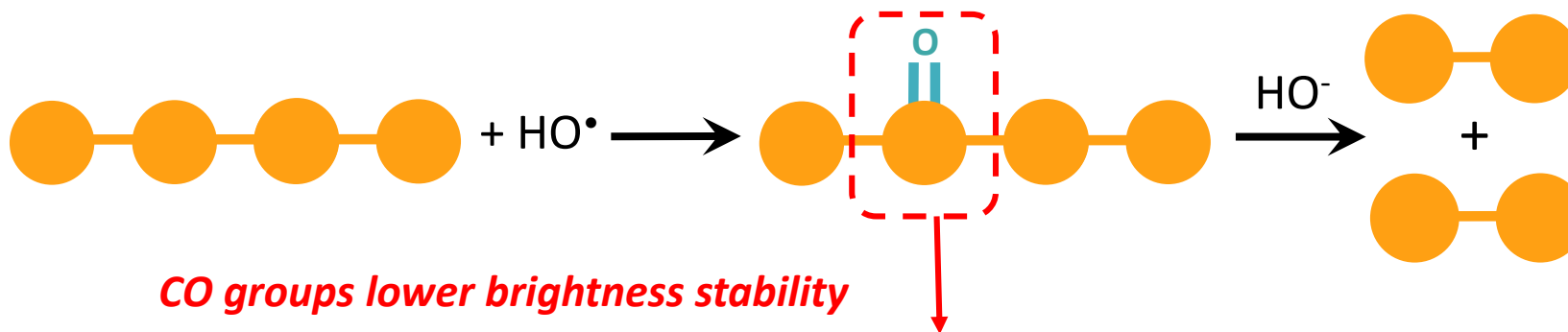


❑ Direct depolymerisation:

cellulose DP ~ 2000 in kraft pulp



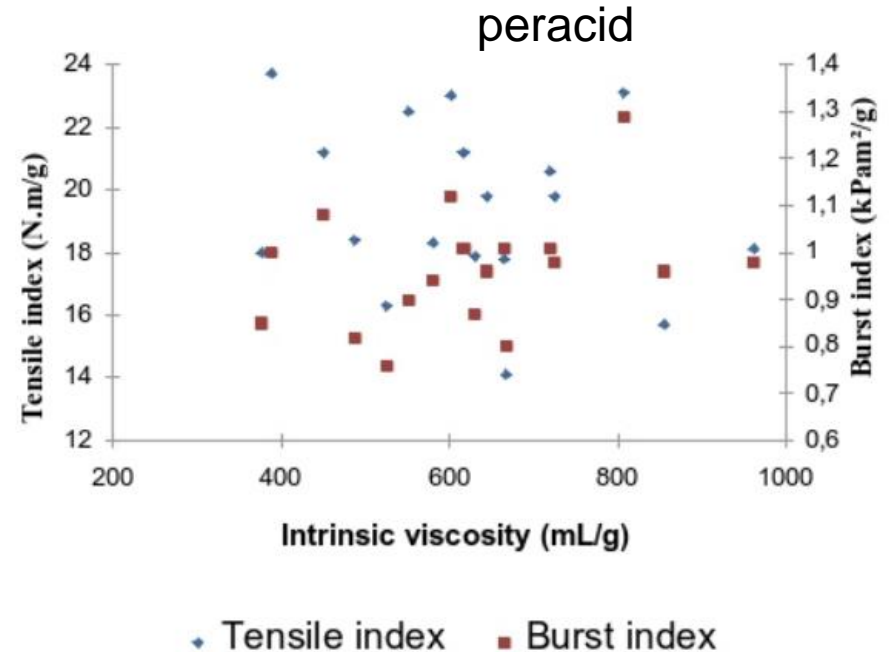
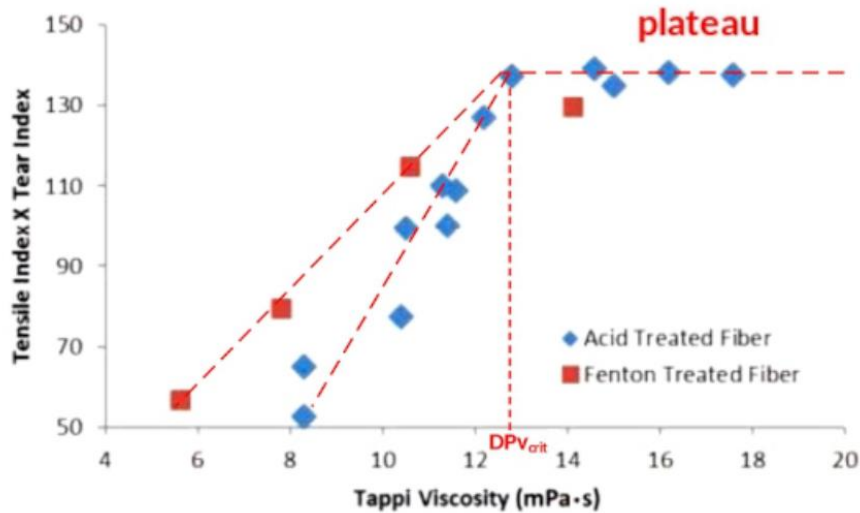
❑ Indirect depolymerisation in **alkaline conditions** (β-elimination reaction):



aging



It is commonly believed that paper strength and cellulose average DP follow a linear relationship...



But paper strength is a complex problem as many parameters come into play: single fibre strength, hemicellulose/cellulose ratio, surface charges etc.

**➡ There is no indication that ozone-induced depolymerisation of cellulose decreases paper strength, following a simple correlation!**



## Observation:

- ❑ Ozone stages are implemented worldwide as a **unique (Z) stage**, generally within “ECF-light” bleaching sequences (combined with ClO<sub>2</sub> stages)
- ❑ **Noticeable paper strength loss and high chemical cost** were reported for very large ozone doses
- ❑ Multi-stage ozone bleaching has been proposed to mitigate cellulose DP loss and improve pulp brightness while decreasing the total required ozone charge:

**(Z)(Z)...(Z) > (Z)** at equal ozone charge



## Jordan Perrin

(P) = good for stabilising brightness when at the end of the bleaching sequence

(E) decreases oxidised pulp brightness when after (Z)

(ZEO)(ZEO)(ZP)

2021

Etienne Montet

2017

2014

Frédéric Pouyet

TCF sequences with multi-(Z) improves brightness and preserves cellulose DP

A(ZEO)(ZEO)P


2010

4 theses on ozone bleaching

1994

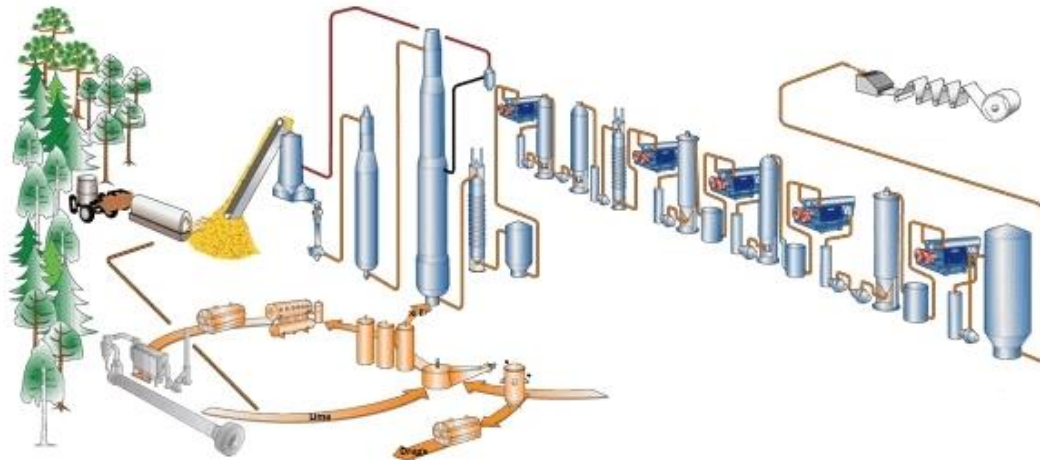
Christine Chirat

- |    |  |
|----|--|
| A  | Hot acid (H <sub>2</sub> SO <sub>4</sub> ) stage         |
| Z  | Ozone (O <sub>3</sub> ) stage                            |
| P  | Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) stage |
| E  | Alkaline extraction stage                                |
| Eo | Oxygen reinforced alkaline extraction stage              |

<b>ECF</b> <i>Elemental Chlorine Free</i>	<b>TCFp</b> <i>Totally Chlorine Free                      with <u>hydrogen peroxide</u> and  <u>oxygen</u></i>	<b>TCFz</b> <i>Totally Chlorine Free                      with <u>ozone</u></i>
<ul style="list-style-type: none"> <li>+ no carbohydrates degradation</li> <li>+ well-known chemistry and process based on ClO<sub>2</sub> bleaching chemical</li> </ul>	<ul style="list-style-type: none"> <li>+ no carbohydrates degradation</li> <li>+ no AOX generation</li> </ul>	<ul style="list-style-type: none"> <li>- carbohydrates degradation <i>impacts mechanical properties?</i></li> </ul>
<ul style="list-style-type: none"> <li>+ high brightness (over 90% ISO)</li> </ul>	<ul style="list-style-type: none"> <li>- moderate brightness</li> </ul>	<ul style="list-style-type: none"> <li>+ high brightness (over 90% ISO)</li> </ul>
<ul style="list-style-type: none"> <li>- No effluent recycling (corrosion from Cl<sup>-</sup>): requires large waste-water treatment plant and high process water consumption)</li> </ul>	<ul style="list-style-type: none"> <li>- poor brightness stability</li> </ul>	<ul style="list-style-type: none"> <li>? </li> </ul>
	<ul style="list-style-type: none"> <li>- relatively expensive</li> </ul>	<ul style="list-style-type: none"> <li>? potentially cheaper than ECF sequences: ozone is more effective than ClO<sub>2</sub> regarding lignin degradation</li> </ul>
 <p><b>95%</b> of total bleached kraft pulp capacity in the world</p>	<p><b>2%</b> of total bleached kraft pulp capacity in the world</p>	<p><b>1%</b> of total bleached kraft pulp capacity in the world</p>

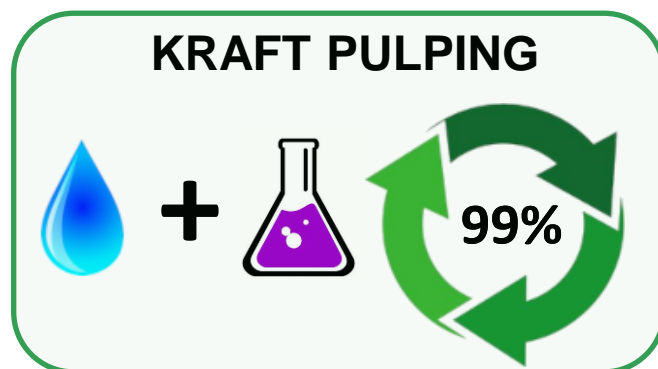


hardwoods  
or  
softwoods

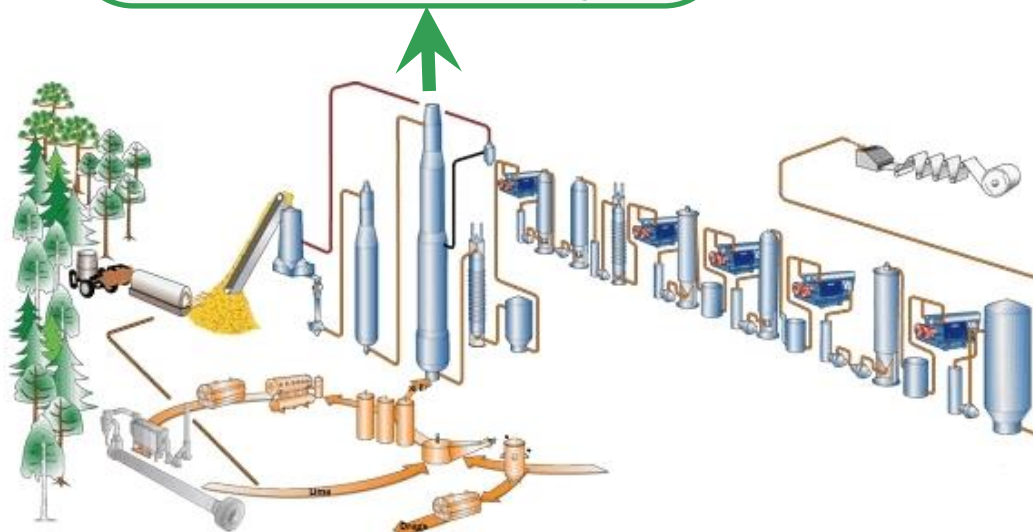


bleached kraft pulp



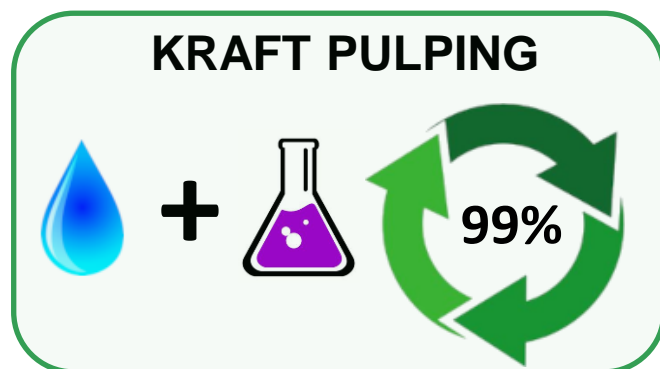


hardwoods  
or  
softwoods

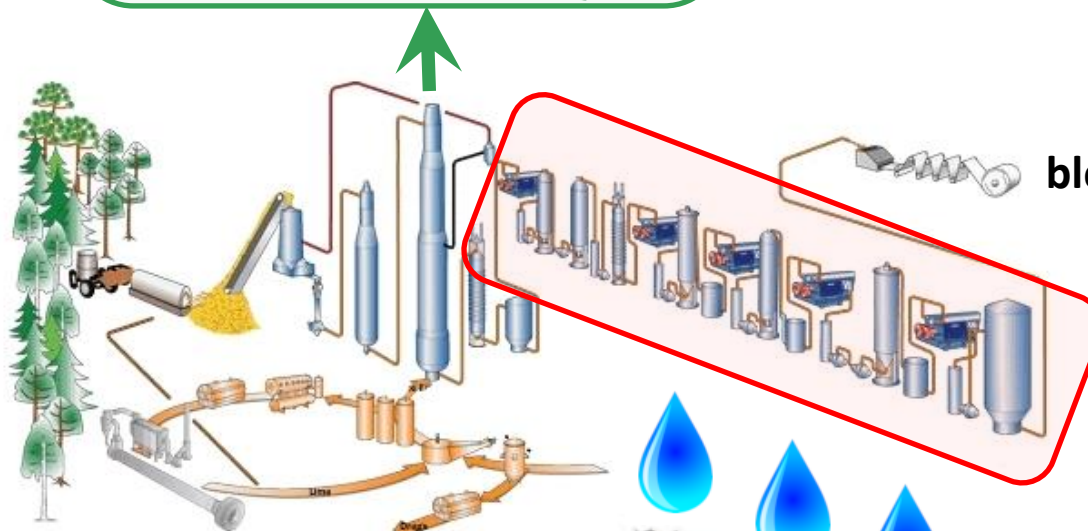


bleached kraft pulp





hardwoods  
or  
softwoods

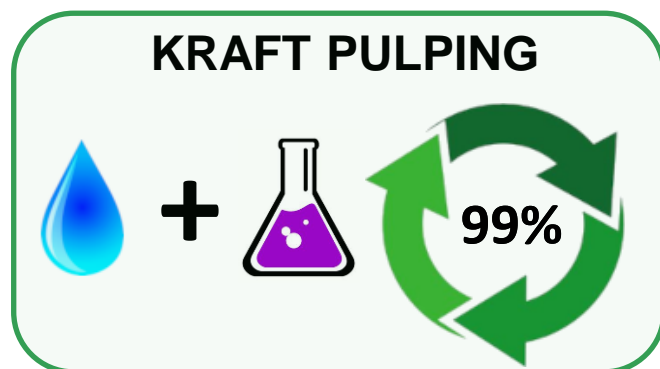


bleached kraft pulp

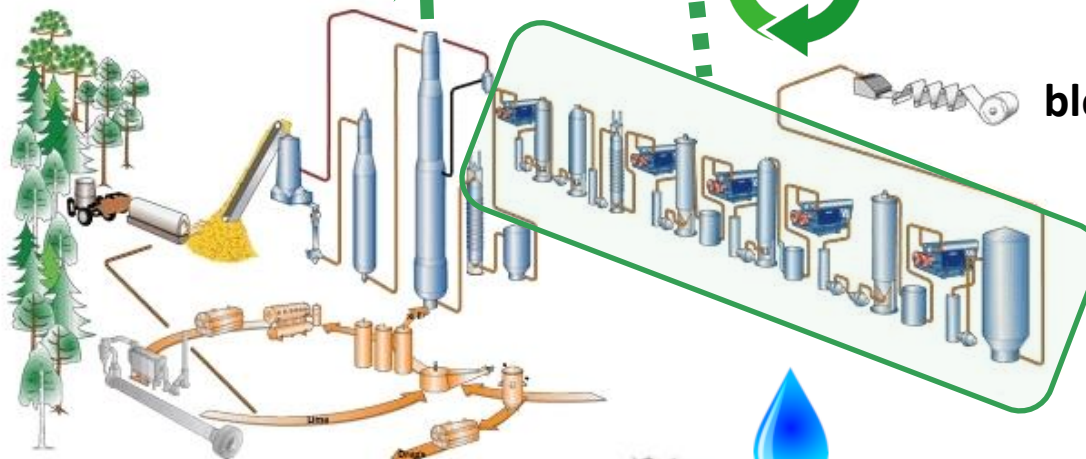
**ECF  
BLEACHING  
ClO<sub>2</sub>**







hardwoods  
or  
softwoods



bleached kraft pulp

**TCF**  
**BLEACHING**  
**O<sub>3</sub>**

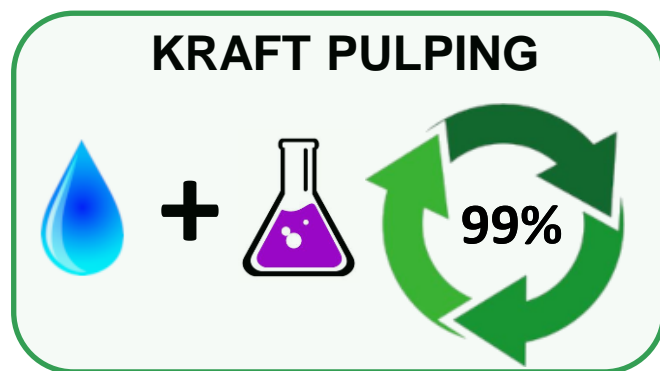


Ozone Days

23/03/2022

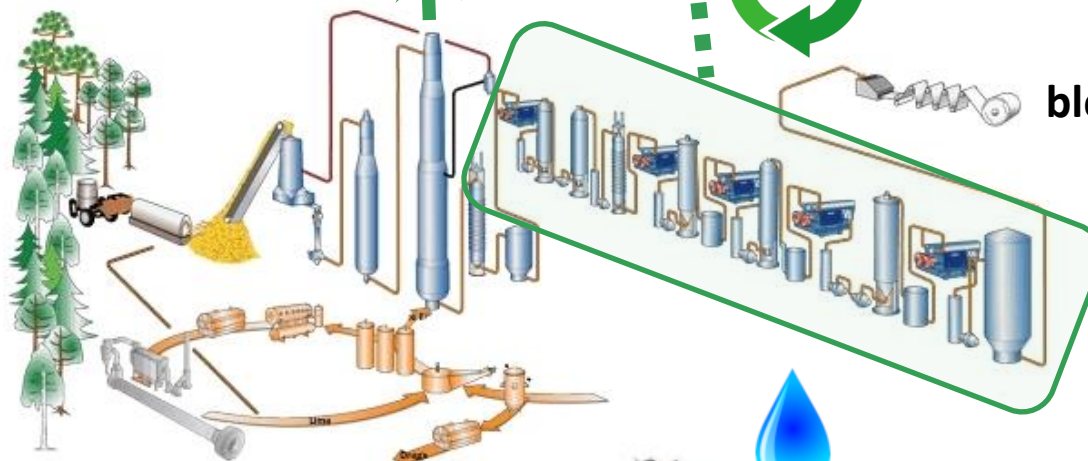


# Context and scope of the PhD thesis



quality?  
cost?

hardwoods  
or  
softwoods



bleached kraft pulp

TCF  
BLEACHING  
O<sub>3</sub>



Ozone Days

23/03/2022



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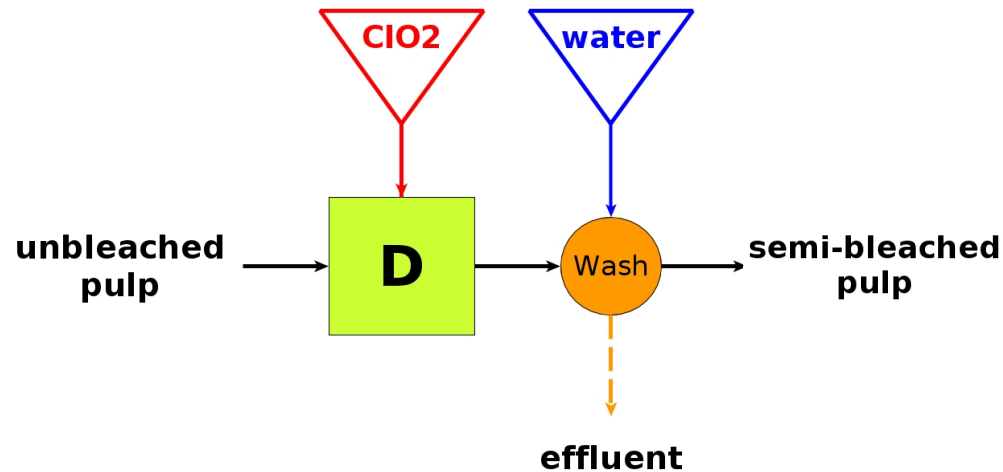
<b>A</b>	Hot acid (H <sub>2</sub> SO <sub>4</sub> ) stage
<b>D</b>	Chlorine dioxide (ClO <sub>2</sub> ) stage
<b>O</b>	Oxygen (O <sub>2</sub> ) stage
<b>Z</b>	Ozone (O <sub>3</sub> ) stage
<b>P</b>	Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) stage
<b>H</b>	Hypochlorous acid (HOCl) stage
<b>E</b>	Alkaline extraction stage
<b>Eo</b>	Oxygen reinforced alkaline extraction stage
<b>Ep</b>	Hydrogen peroxide reinforced alkaline extraction stage

Sequence type	Nomenclature
---------------	--------------

ECF-light	OZEoD (DZ)EopD
TCFp	OQOpZq(PO) Q(OP)Q(PO)
TCFz	OAZP OQOpZq(PO)

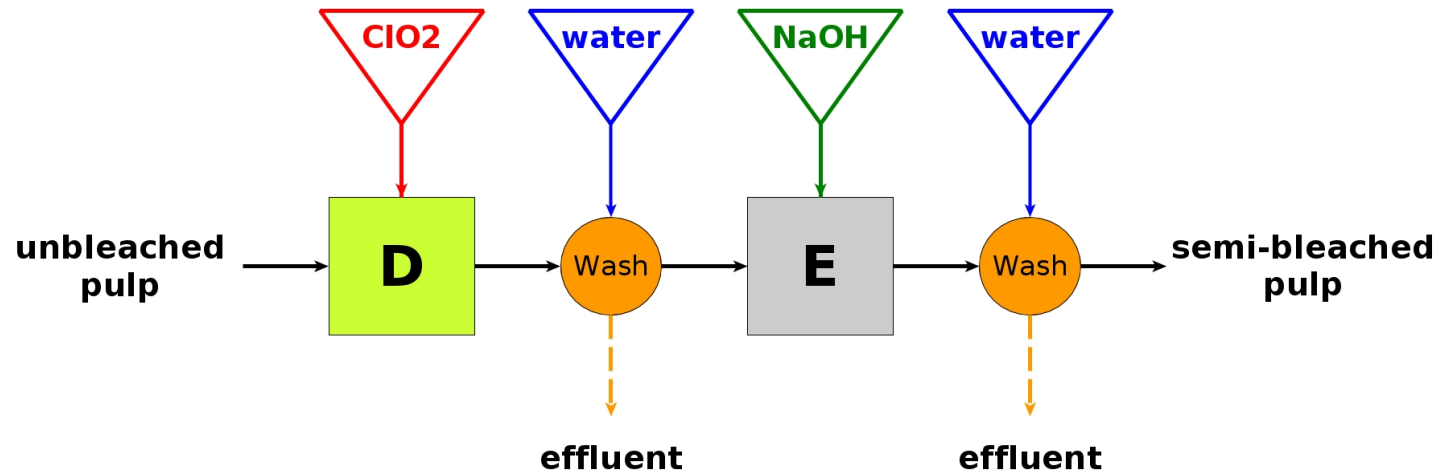
Brackets indicate pulp washing





□ (D) = chlorine dioxide stage ( $\text{ClO}_2$ ): lignin oxidation / dissolution, used in **ECF** bleaching sequences.





□ (D) = chlorine dioxide stage ( $\text{ClO}_2$ ): lignin oxidation / dissolution, used in **ECF** bleaching sequences.

□ (E) = Alkaline extraction stage ( $\text{NaOH}$ ): oxidised lignin dissolution



Goal is to demonstrate that a modern TCFz bleaching sequence can perform as well as St-Gaudens ECF sequence: DEpDD

⇒ reach a **high brightness** equal to that of the ECF pulp

⇒ TCF-ozone sequence must be economically competitive

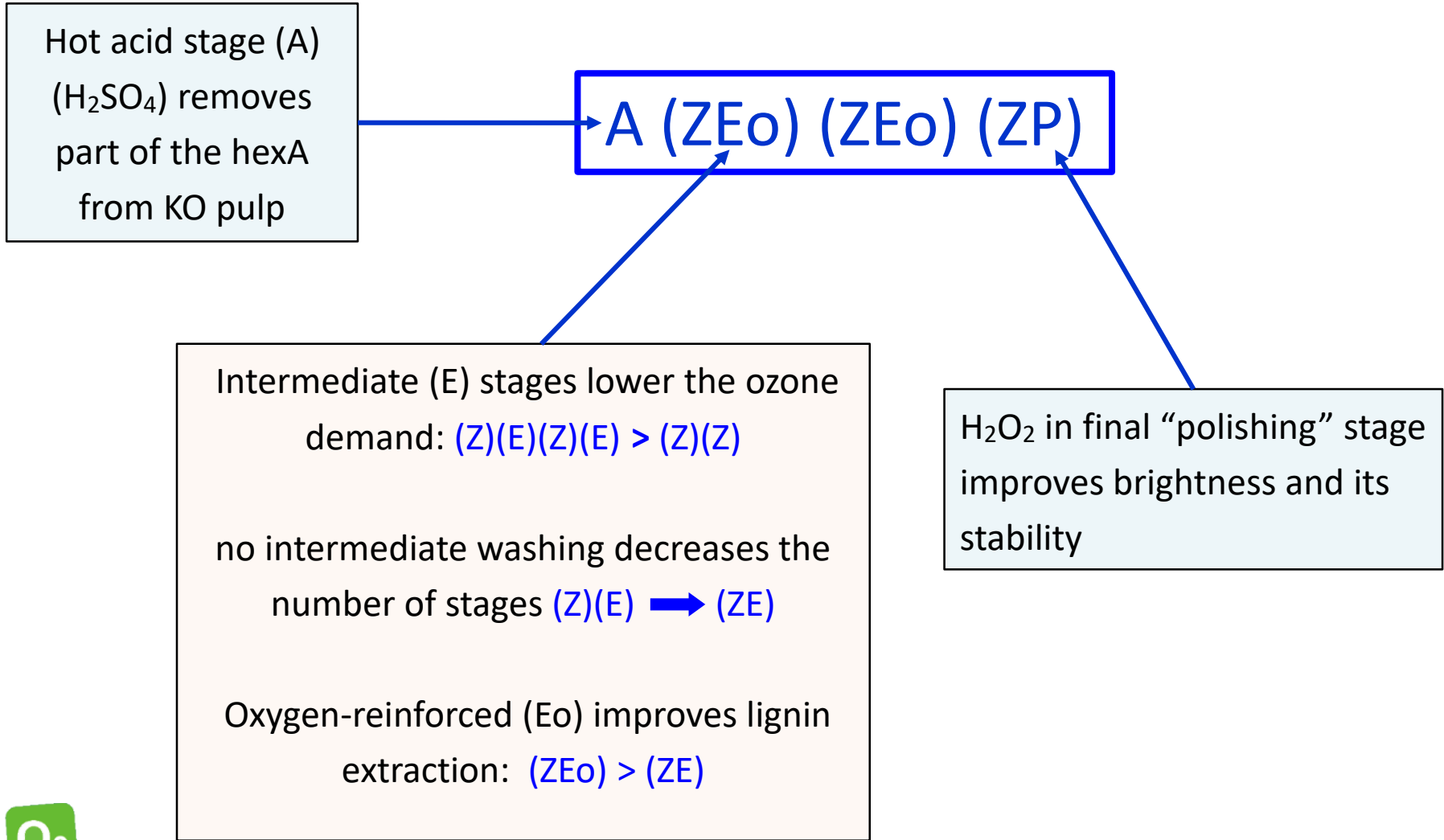
**Starting pulp = Oxygen-delignified  
hardwood Kraft pulp = “KO”**



Pulp	Brightness (%ISO)	Lignin (%)	HexA ( $\mu\text{mol/g}$ )
KO	48.3	1.1	58







❑ St-Gaudens prebleached kraft pulp “KO” was bleached with DEpDD (ECF) to **91.5 %ISO** brightness.

❑ **How much O<sub>3</sub>?** (*wt.% on dry pulp*)

⇒ finding the right recipe to obtain approx. 91.5 %ISO (+/- 0.5 %ISO)

**A(Z?%Eo)(Z?%Eo)(Z?%P)**

**Pulp bleaching**



**(Z)**

$T = T_{room}$   
 $t = \text{few min!}$   
35% dry matter

0.17% / 0.17% / 0.16%

**Total = 0.5% O<sub>3</sub>**

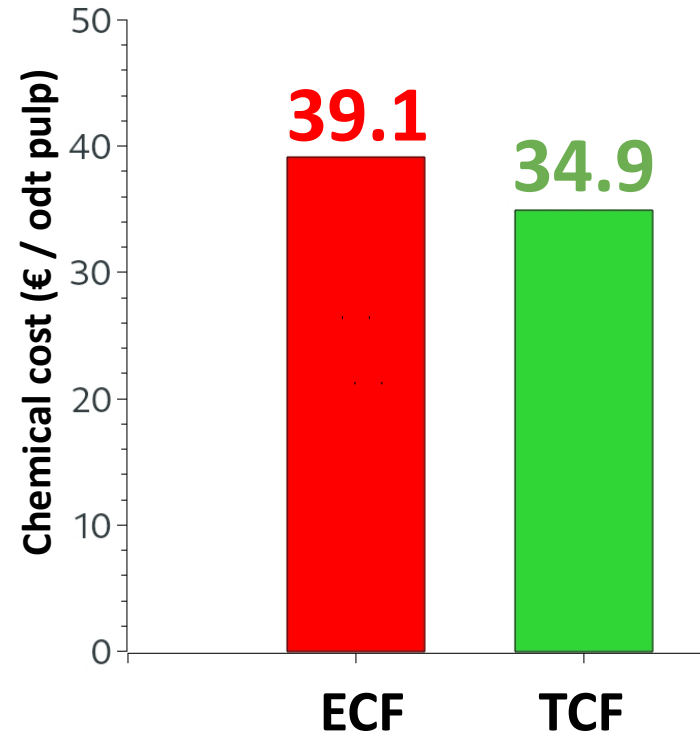
**brightness = 91 %ISO**



Pulp	Brightness (%ISO)
KO	48.3
ECF	91.5
TCF	91.0

TCF-ozone bleached pulp:

⇒ high brightness (= ECF brightness)



...at a lower chemical cost!



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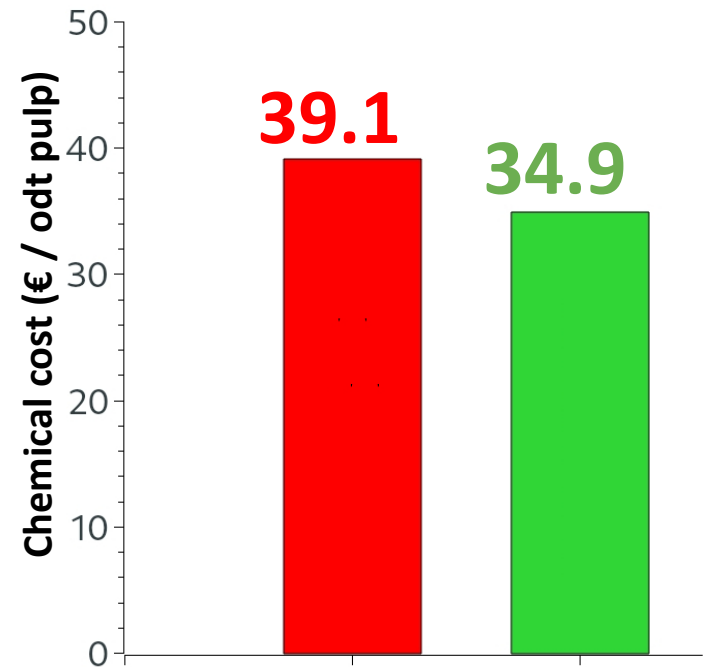
Heat used in the paper manufacturing process and pulp handling can provoke pulp yellowing.

⇒ High brightness is useless if it is unstable.

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KO	48.3
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TCF-ozone bleached pulp:

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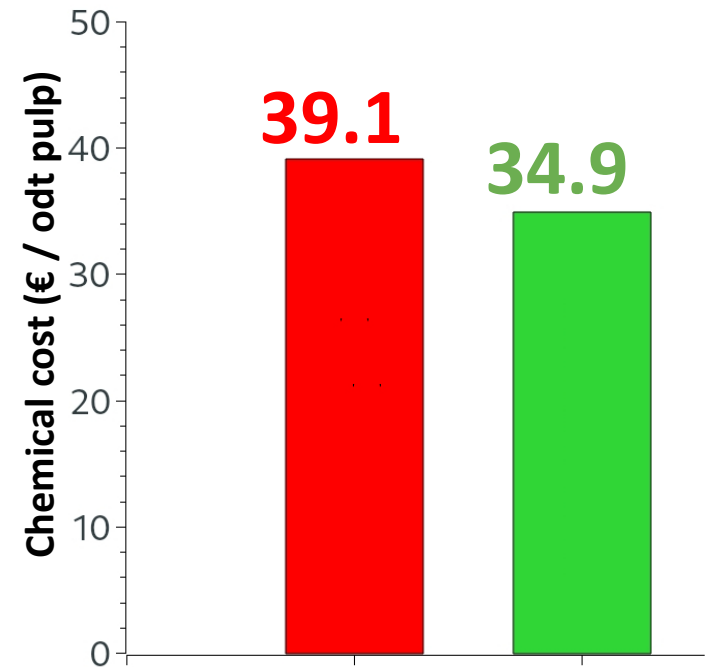
...at a lower chemical cost!



Heat used in the paper manufacturing process and pulp handling can provoke pulp yellowing.

⇒ High brightness is useless if it is unstable.

Pulp	Brightness (%ISO)	PCN (+/- 0.01)
KO	48.3	-
ECF	91.5	0.61
TCF	91.0	0.29



TCF-ozone bleached pulp:

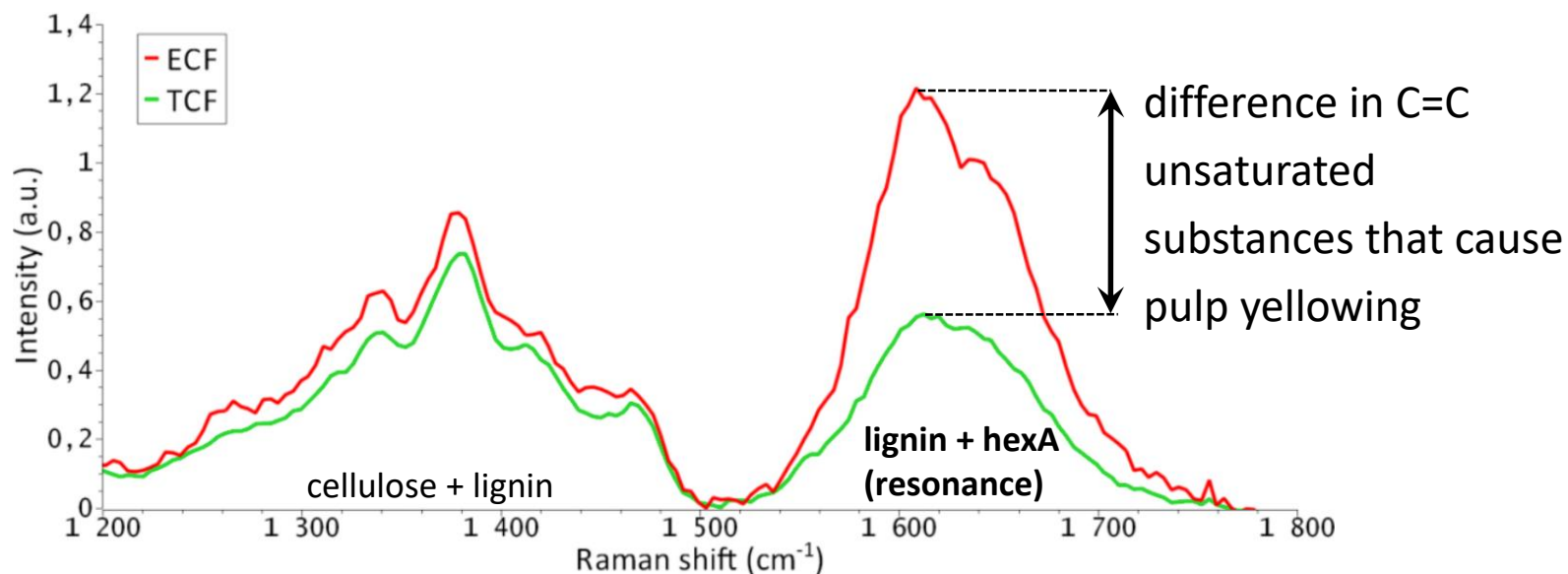
⇒ high brightness (= ECF brightness)

⇒ more stable brightness

...at a lower chemical cost!



UV Resonance Raman (UVR R) spectroscopy to detect the presence of C=C impurities (lignin and hexA) in bleached pulp.



*...special thanks to Prof. T. Vuorinen!*





Pulp	Brightness (%ISO)	PCN (+/- 0.01)
KO	48.3	-
ECF	91.5	0.61
TCF	91.0	0.29
BP	89.8	0.43

commercial “BP” pulp



DEpDD from St-Gaudens

**Post-bleaching  
treatment**  
(D), (E), (P), (Z),  
(ZE), (ZP)...

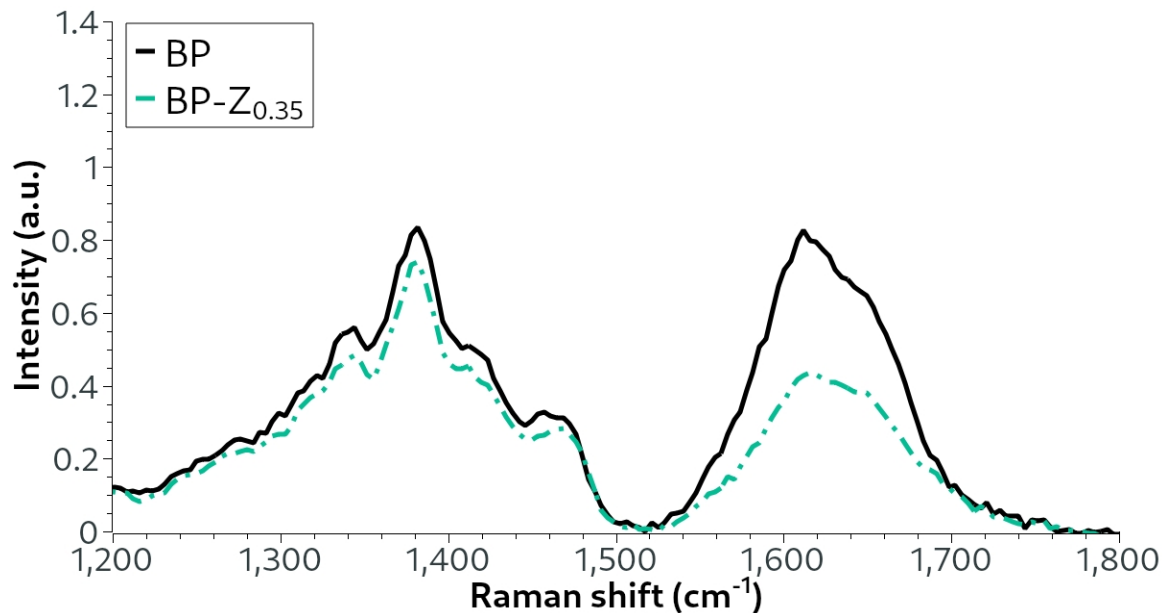
**brightness, PCN**

**UVRR spectroscopy**

⇒ Investigation of the effect of various bleaching chemicals on pulp brightness and brightness stability and understanding of their chemistry



**Ozone Days** towards residual lignin moieties



**BP**  
89.8 %ISO  
0.43 PCN

**BP-Z<sub>0.35</sub>**  
92.1 %ISO  
0.40 PCN

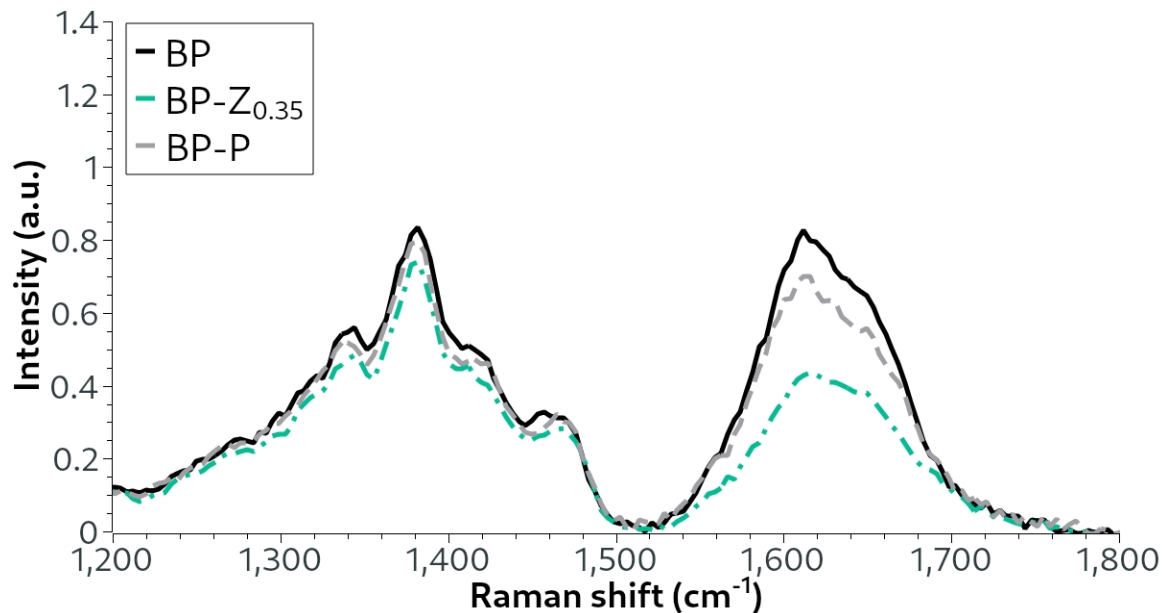


BP

**(Z)**

+ removes C=C  
- introduces C=O





**BP**  
89.8 %ISO  
0.43 PCN

**BP-Z<sub>0.35</sub>**  
92.1 %ISO  
0.40 PCN

**BP-P**  
91.3 %ISO  
0.23 PCN



BP

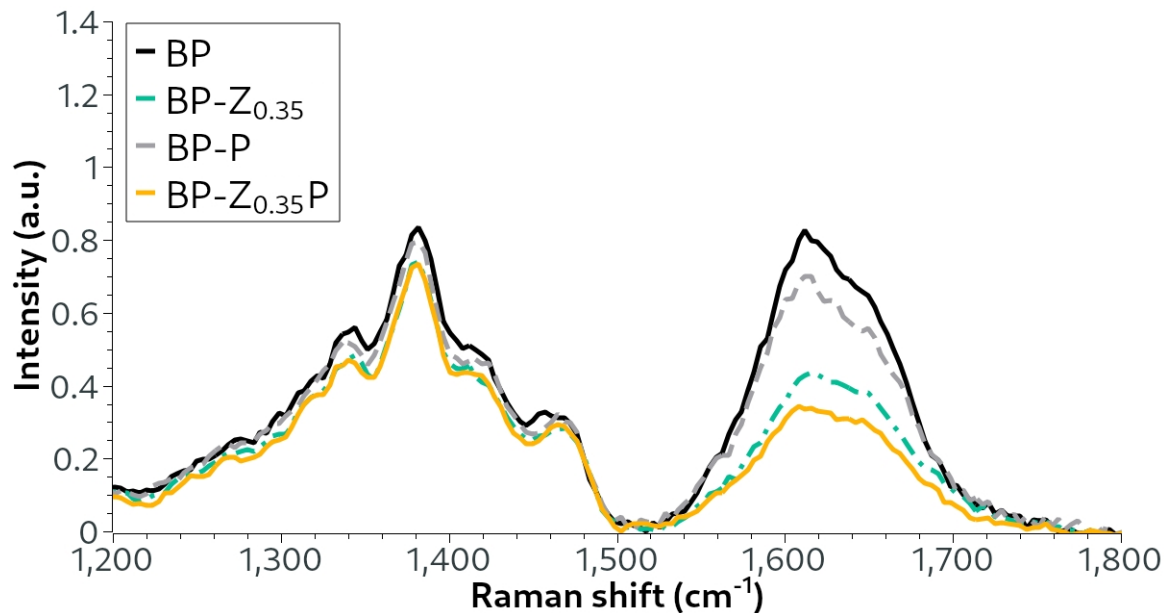
**(Z)**

+ removes C=C  
- introduces C=O

**(P)**

+ removes C=O  
- C=C almost unaffected

O<sub>3</sub>



**BP**  
89.8 %ISO  
0.43 PCN

**BP-Z<sub>0.35</sub>**  
92.1 %ISO  
0.40 PCN

**BP-P**  
91.3 %ISO  
0.23 PCN

**BP-Z<sub>0.35</sub>P**  
93.3 %ISO  
0.21 PCN



**BP**

**(Z)**

+ removes C=C  
- introduces C=O

**(P)**

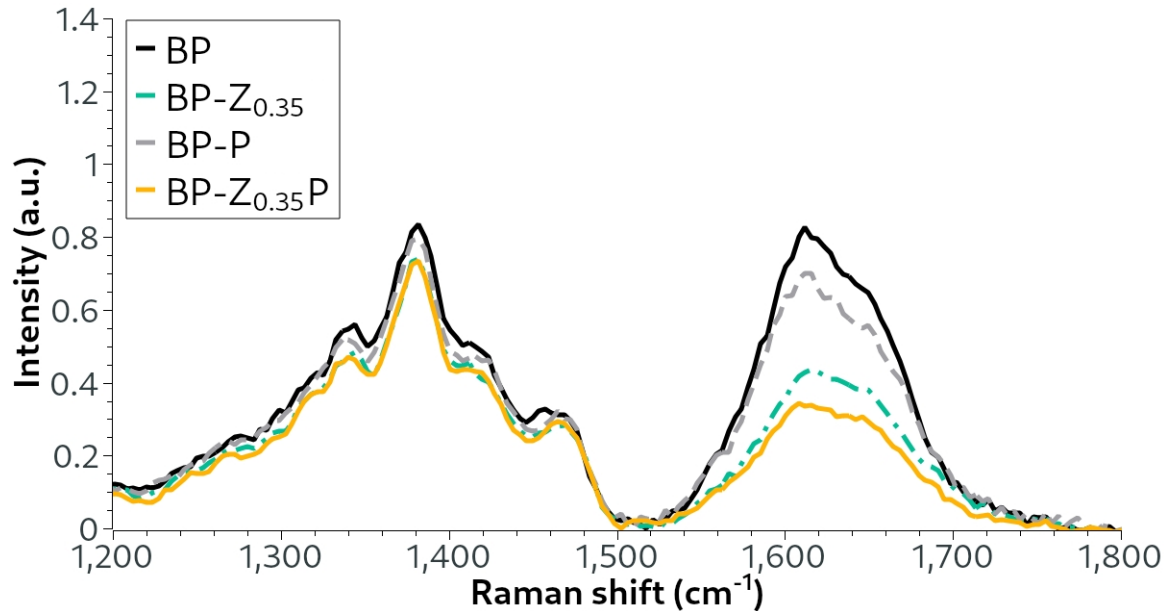
+ removes C=O  
- C=C almost unaffected

**(ZP)**

+ removes C=C  
+ removes C=O



**O<sub>3</sub>**



**BP**  
89.8 %ISO  
0.43 PCN

**BP-Z<sub>0.35</sub>**  
92.1 %ISO  
0.40 PCN

**BP-P**  
91.3 %ISO  
0.23 PCN

**BP-Z<sub>0.35</sub>P**  
93.3 %ISO  
0.21 PCN



BP

**TCF > ECF due to (Z) or (P)?**

**(Z)**

+ removes C=C  
- introduces C=O

**(P)**

+ removes C=O  
- C=C almost unaffected

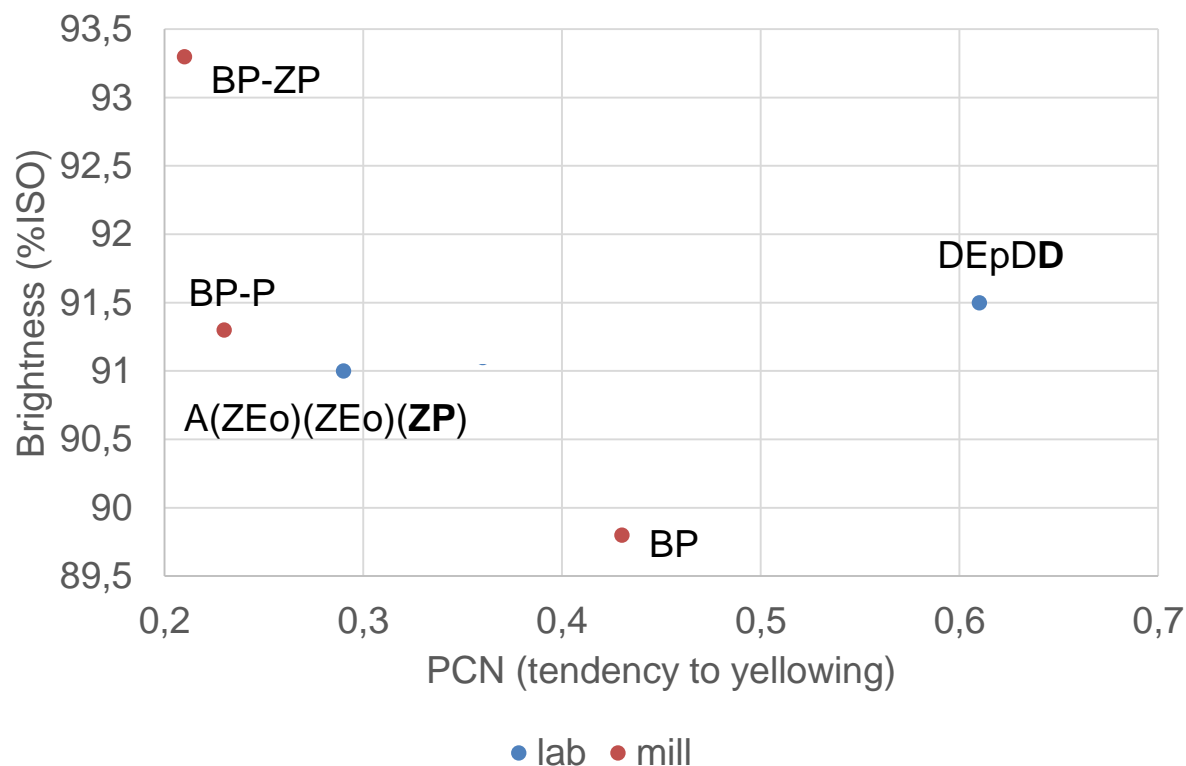
**(ZP)**

+ removes C=C  
+ removes C=O

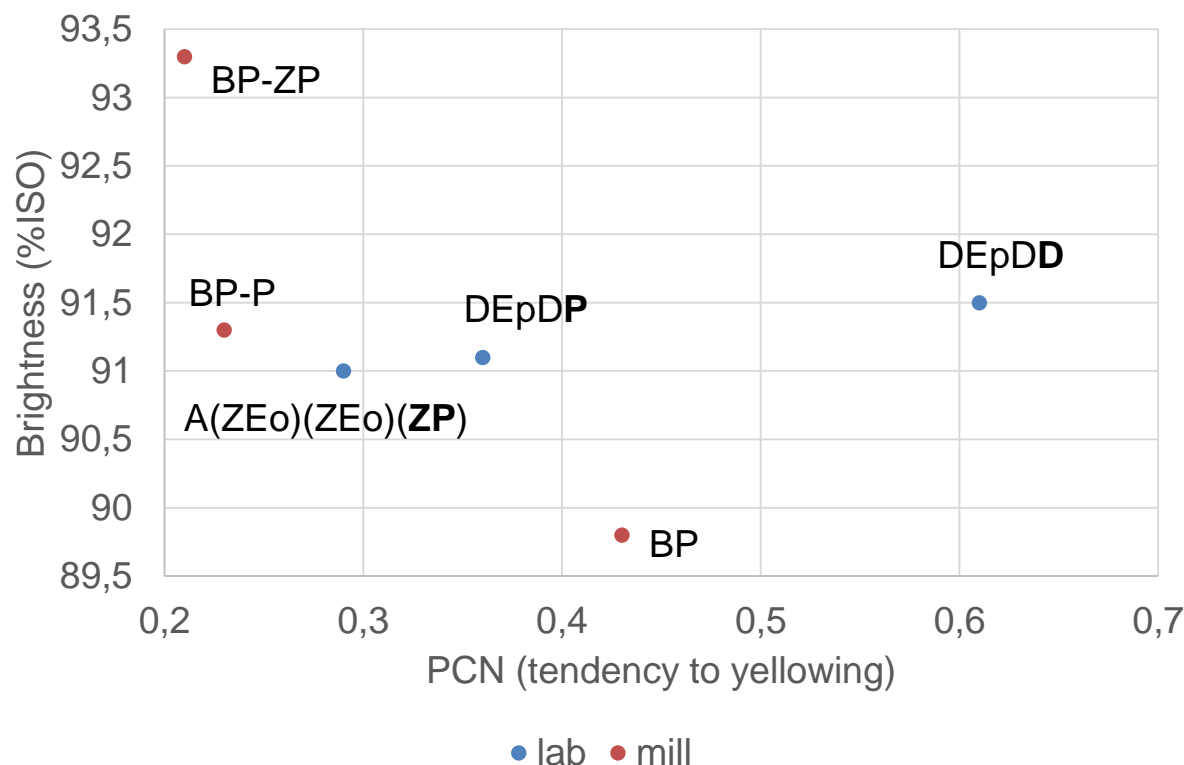


O<sub>3</sub>

Could a DEpDP (ECF) sequence perform as well as the TCF?



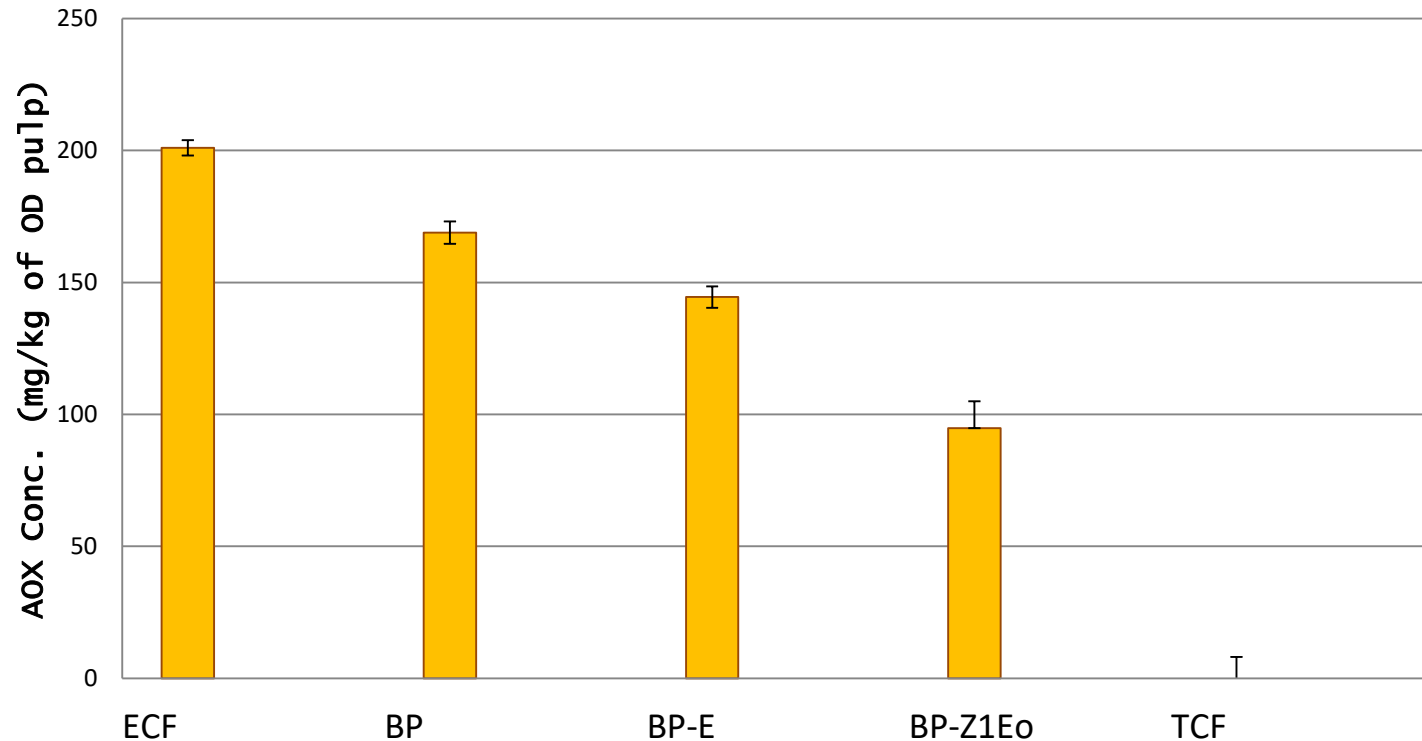
Could a DEpDP (ECF) sequence perform as well as the TCF?



**Only ozone** can eliminate stable C=C unsaturated substances that provoke bleached kraft pulp yellowing



### AOX content in various bleached pulp samples



Ozone is efficient at removing residual lignin (Cl-bearing stable moieties)





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*refining, fibre length, surface charge...*

*presence of weak points, **cellulose DP**...*

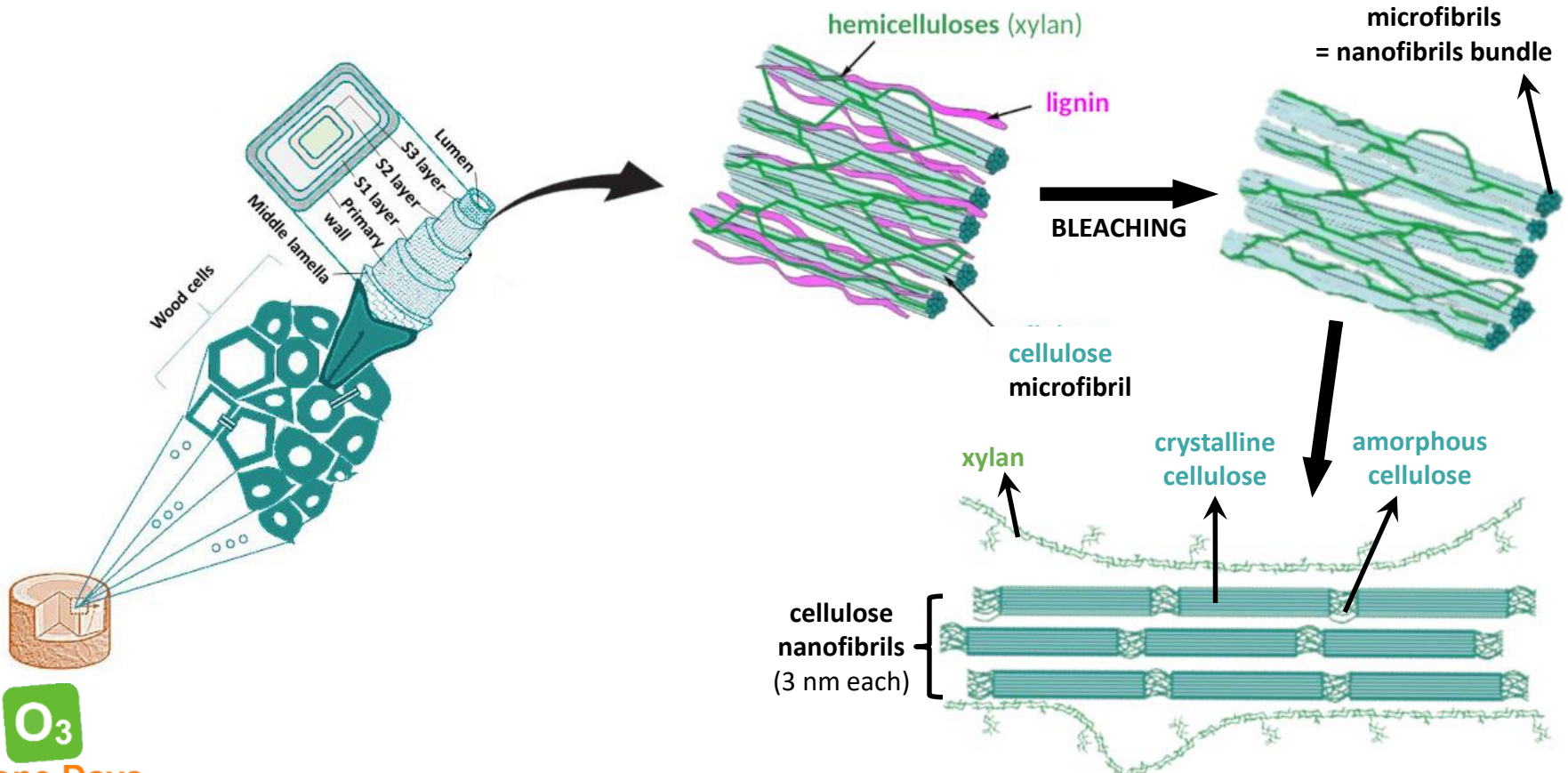
Paper strength = fibre-fibre bonding + **single fibre strength**



refining, fibre length, surface charge...

presence of weak points, **cellulose DP**...

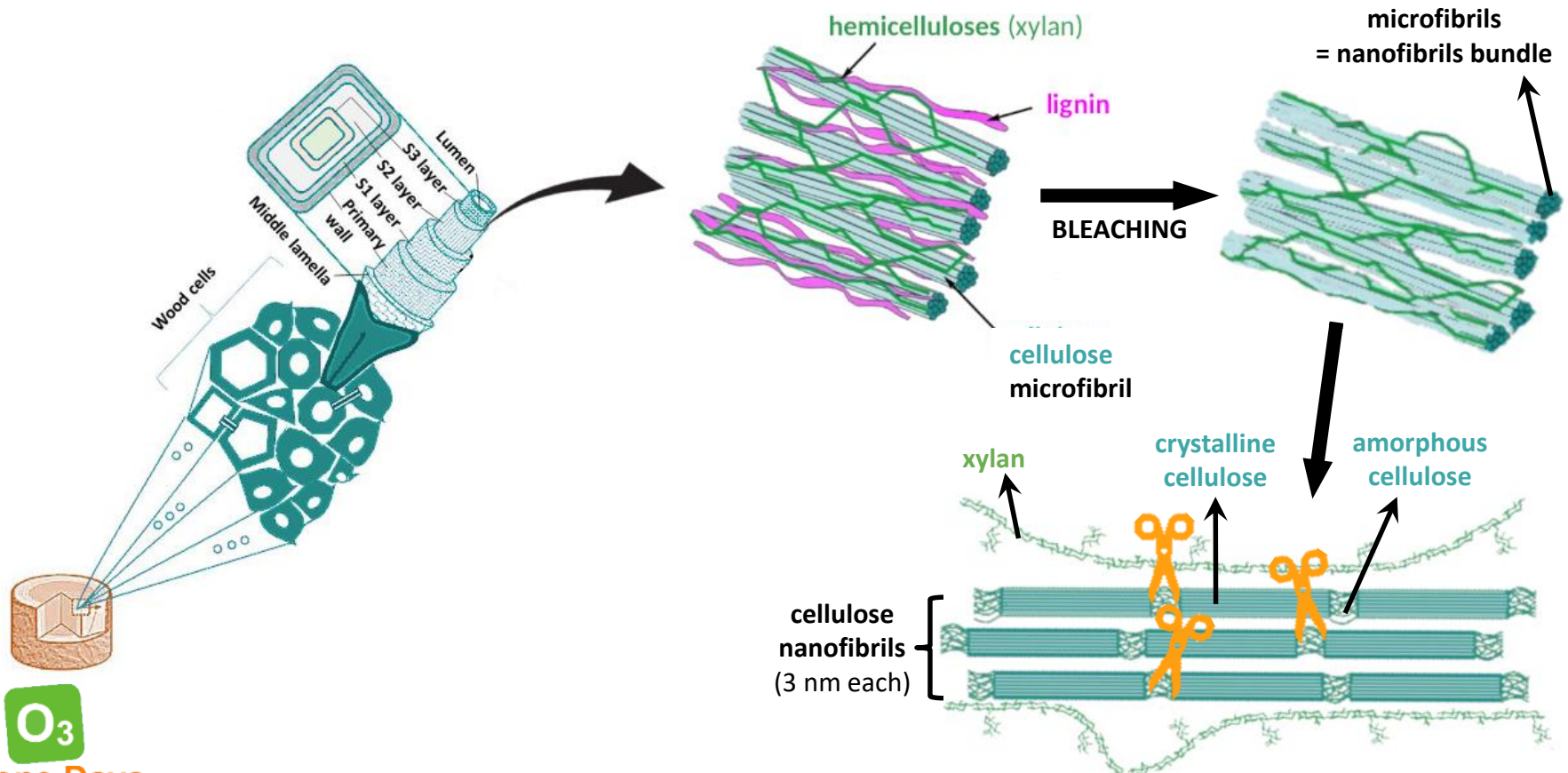
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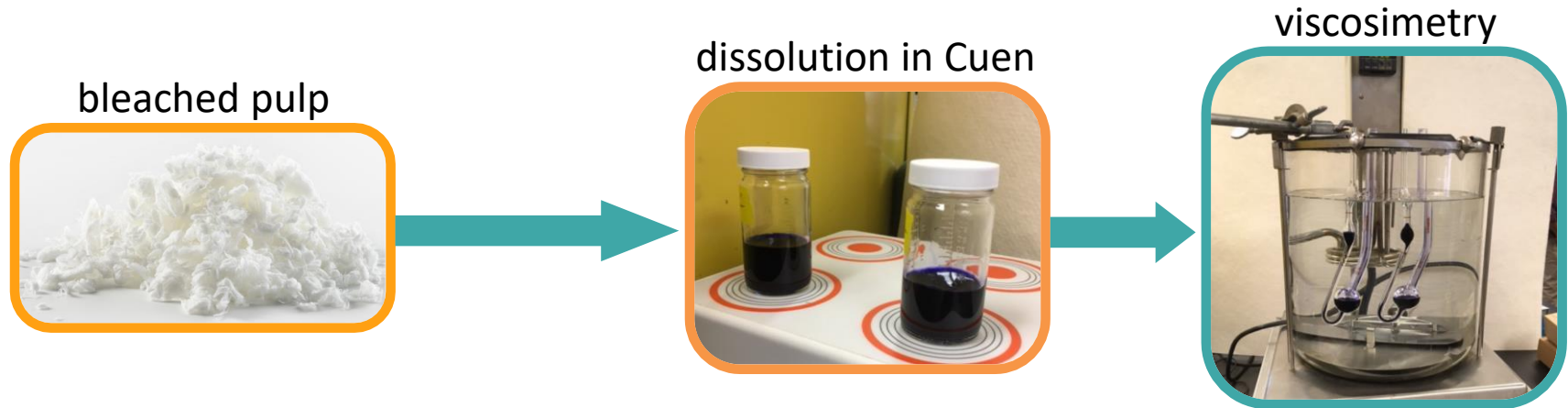
refining, fibre length, surface charge...

presence of weak points, **cellulose DP**...

Paper strength = fibre-fibre bonding + **single fibre strength**



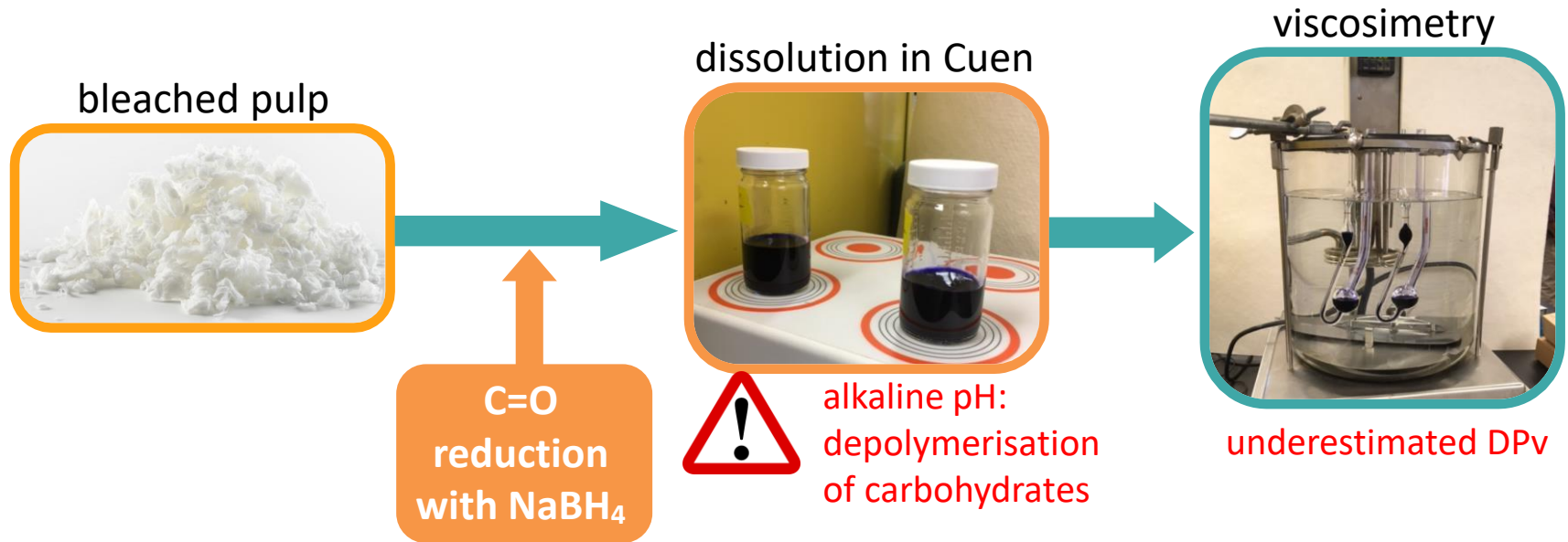
Paper strength is associated with the average DP of cellulose, commonly measured as the “**DPv**”:



- + cheap and quick method
- is influenced by hemicelluloses



Paper strength is associated with the average DP of cellulose, commonly measured as the “**DPv**”:



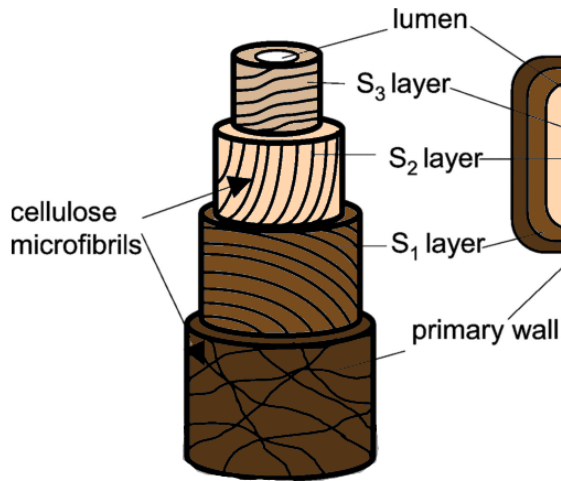
- + cheap and quick method
- is influenced by hemicelluloses
- oxidised pulps (O<sub>3</sub>, HOCl...) require an additional step for DPv (NaBH<sub>4</sub>)



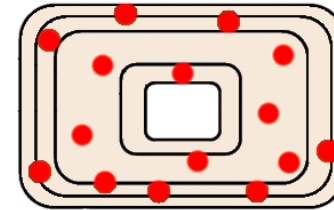
Any pulp DPv loss is commonly associated with paper strength loss

# Uniform vs. localised degradation

□ Theory:



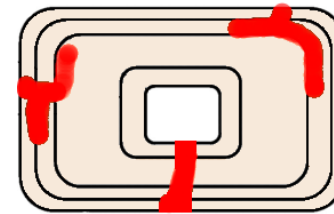
uniform degradation



strength  
⊖

*ex: hypochlorous acid (H)*

localised degradation



strength  
⊖ ⊖ ⊖

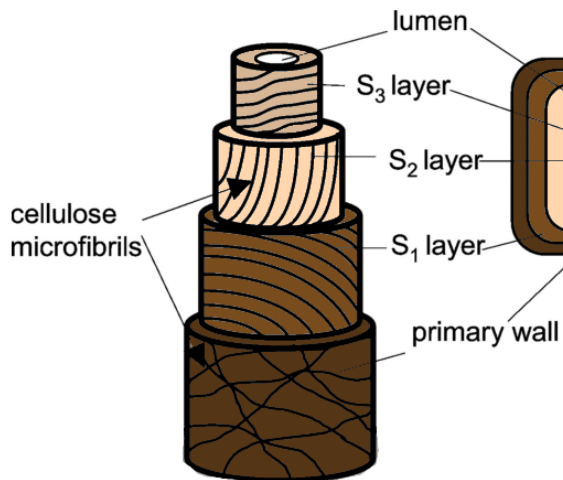
*ex: cellulase enzyme (C<sub>endo</sub>)*



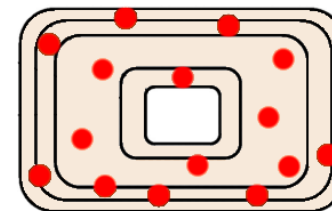


# Uniform vs. localised degradation

## □ Theory:



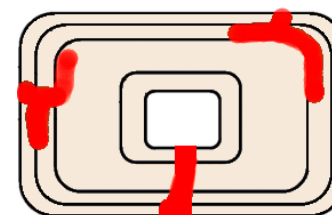
uniform degradation



strength  $\ominus$

*ex: hypochlorous acid (H)*

localised degradation

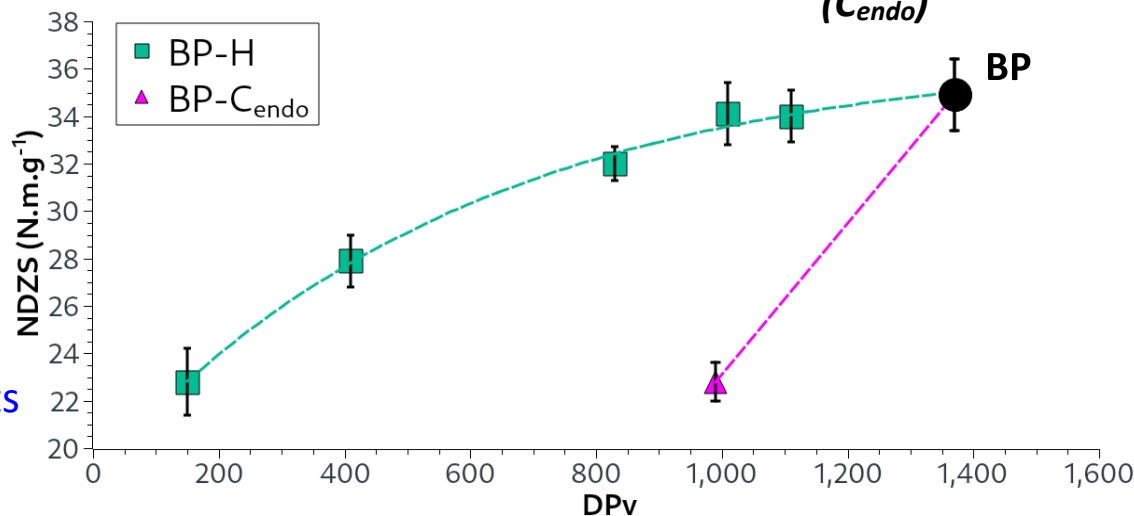


strength  $\ominus\ominus\ominus$

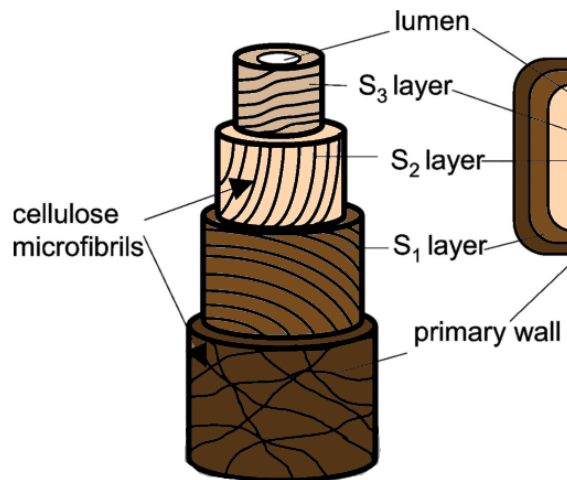
*ex: cellulase enzyme (C<sub>endo</sub>)*

□ Zero-span (ZS) tensile strength = intrinsic strength of single fibres

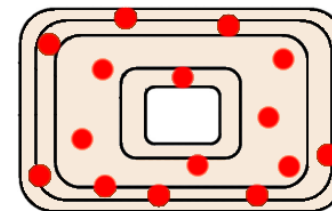
□ (never-dry) NDZS = chemical-induced weak points



□ Theory:



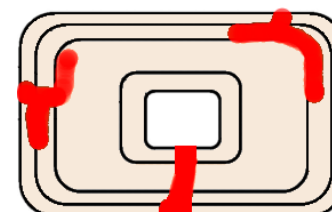
uniform degradation



strength  $\ominus$

*ex: hypochlorous acid (H)*

localised degradation

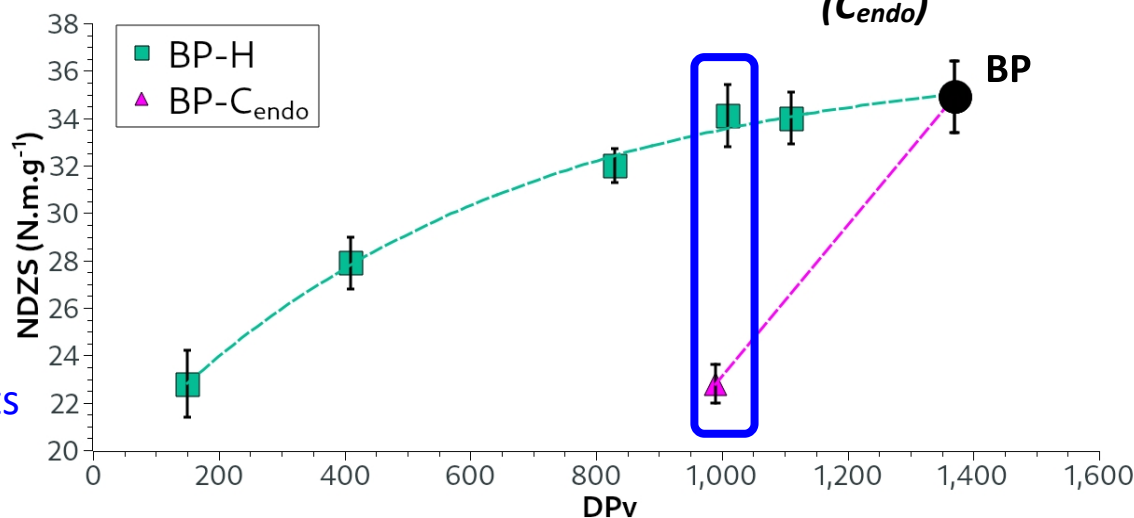


strength  $\ominus\ominus\ominus$

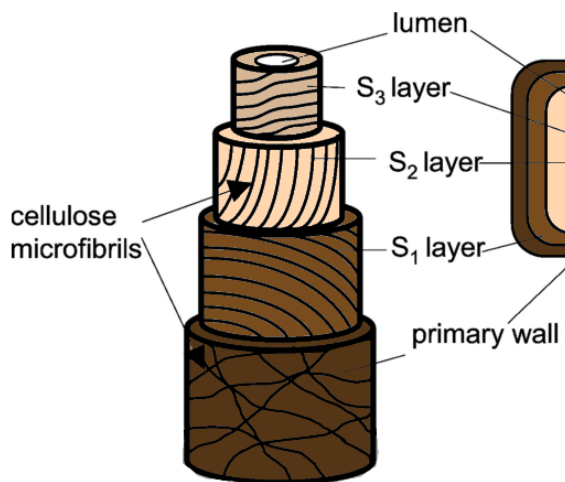
*ex: cellulase enzyme (C<sub>endo</sub>)*

□ Zero-span (ZS) tensile strength = intrinsic strength of single fibres

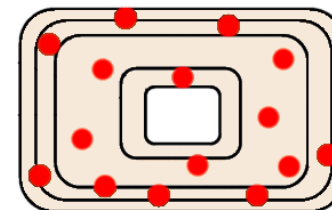
□ (never-dry) NDZS = chemical-induced weak points



□ Theory:



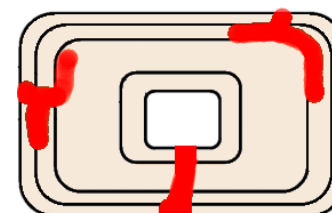
uniform degradation



strength  $\ominus$

*ex: hypochlorous acid (H)*

localised degradation

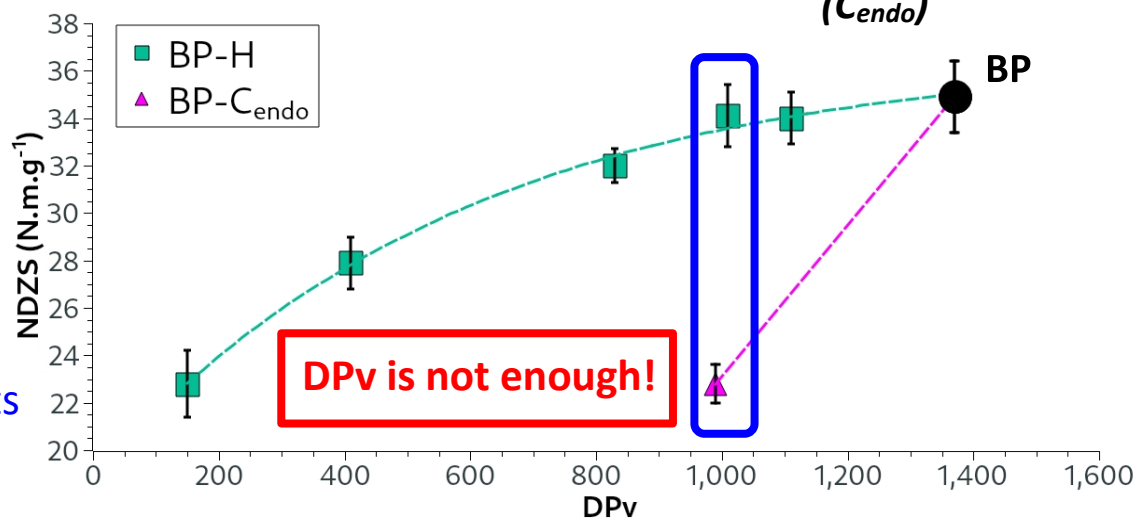


strength  $\ominus\ominus\ominus$

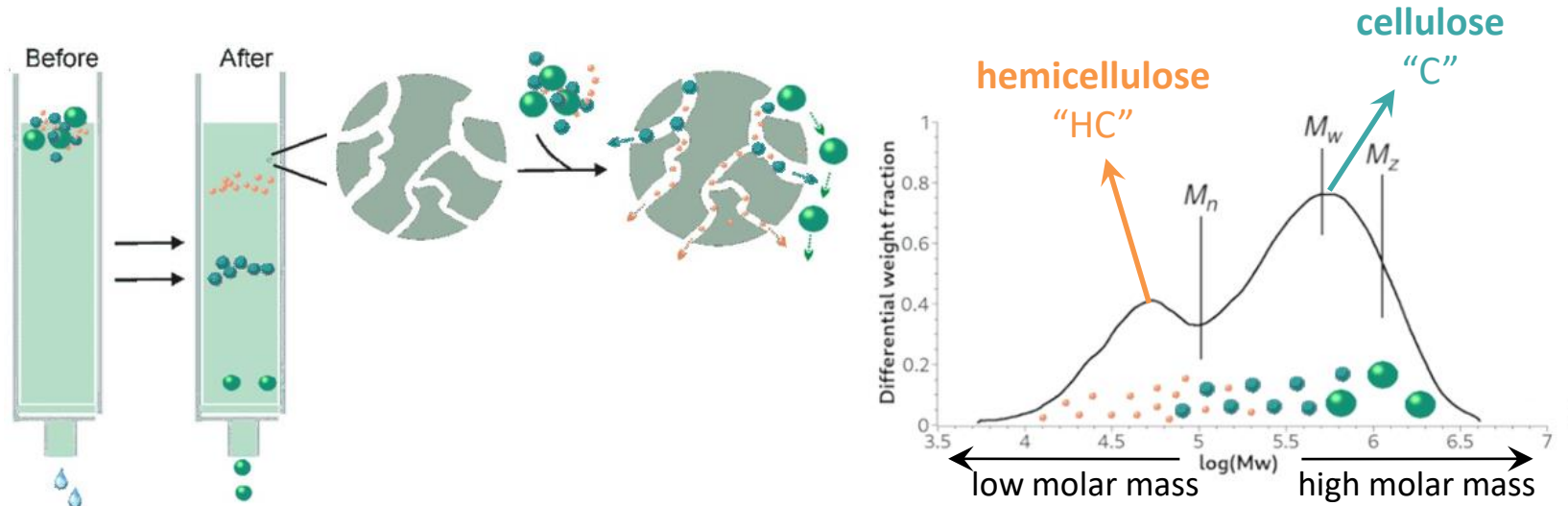
*ex: cellulase enzyme (C<sub>endo</sub>)*

□ Zero-span (ZS) tensile strength = intrinsic strength of single fibres

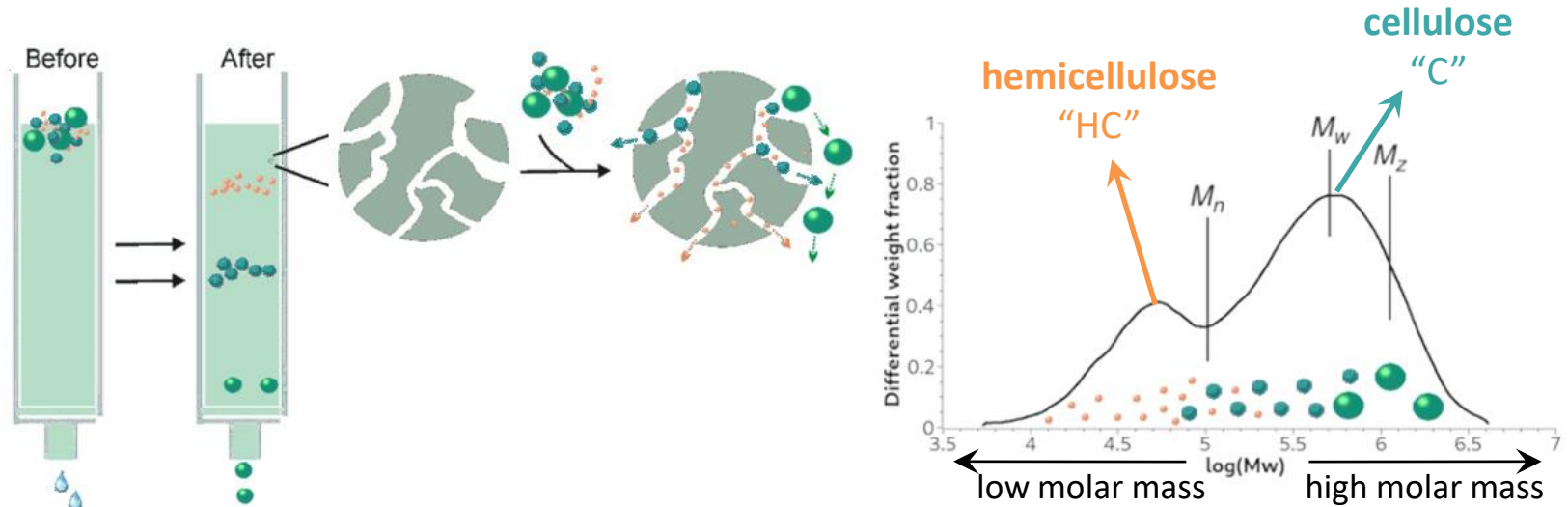
□ (never-dry) NDZS = chemical-induced weak points



□ Bleached pulp dissolved in DMAc / LiCl (8%) and injected in SEC to obtain molar mass distributions:

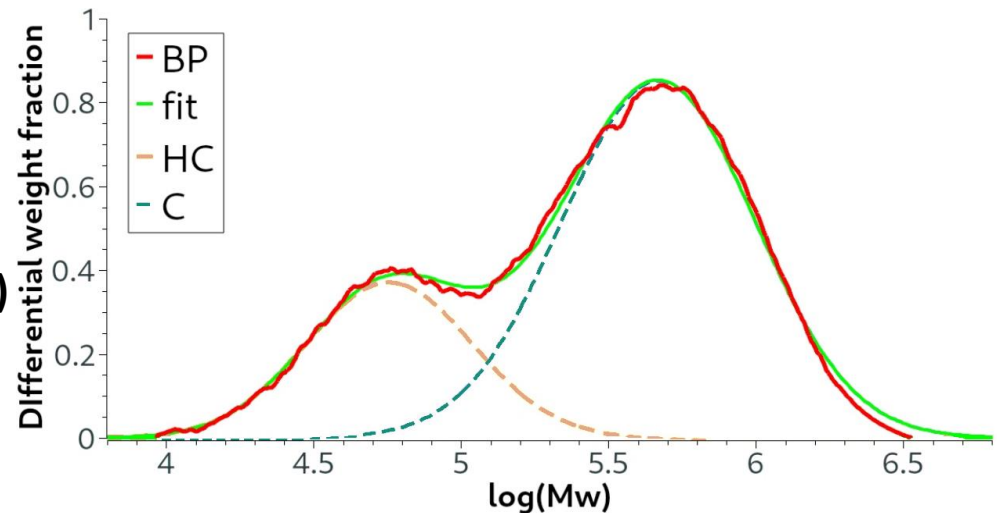


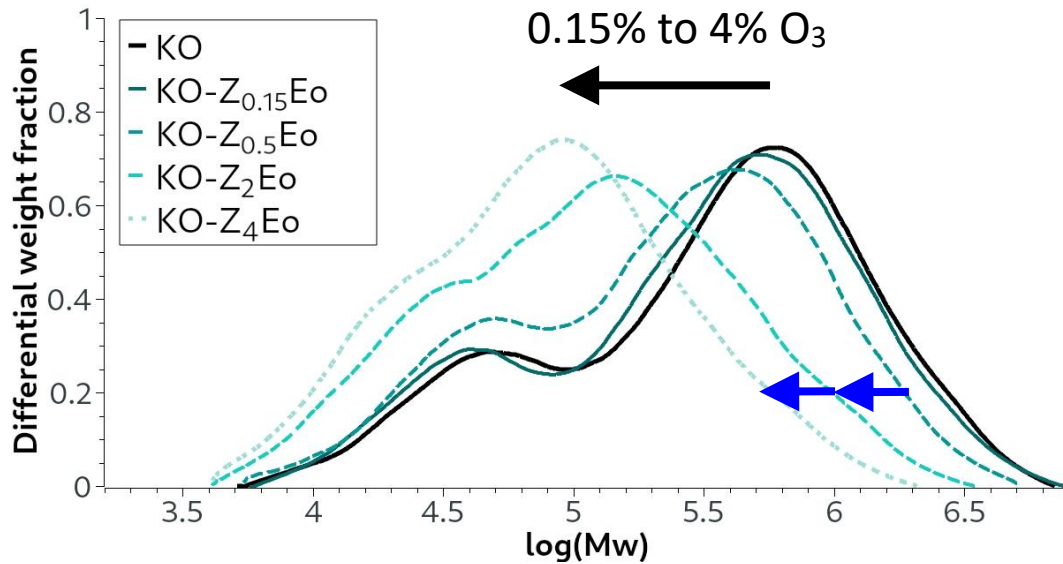
☐ Bleached pulp dissolved in DMAc / LiCl (8%) and injected in SEC to obtain molar mass distributions:



☐ SEC > DPv:

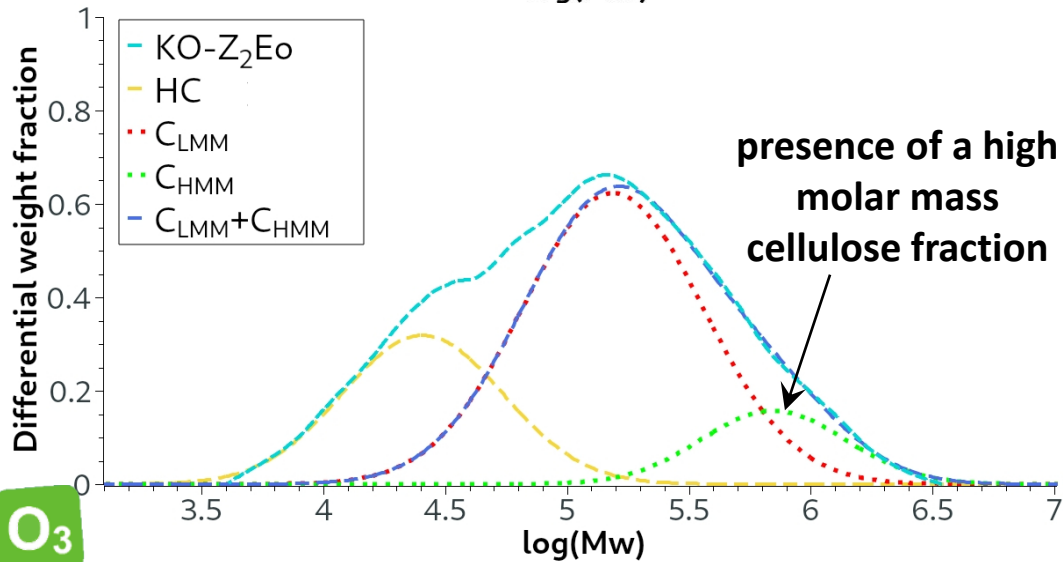
- no pretreatment needed for ozone-bleached pulps
- cellulose fraction average **DPw(C)** by deconvolution of the gaussian peaks





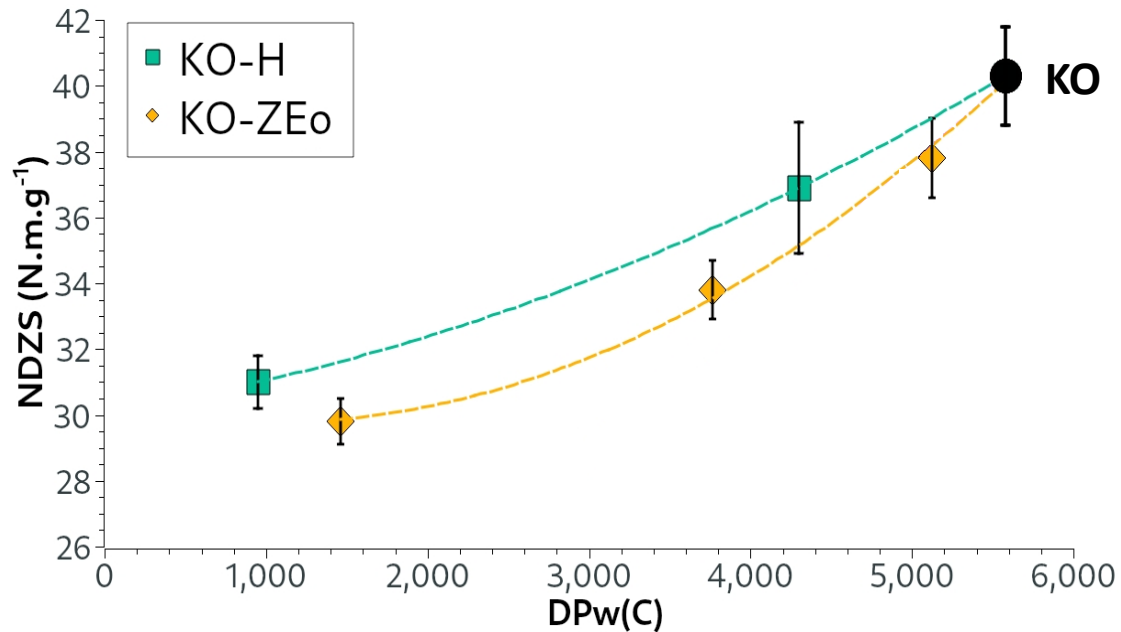
☐ Ozone indirectly depolymerises cellulose chains close to lignin

☐ All the cellulose microfibrils in the fibre are affected



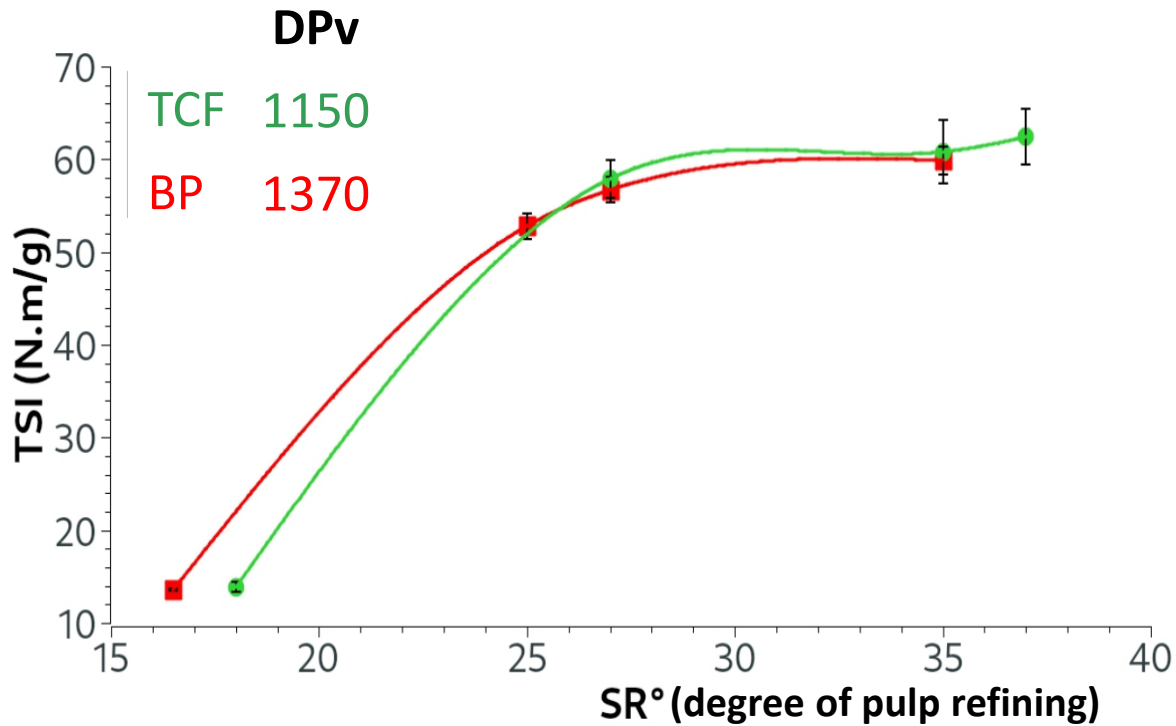
☐ Some parts of the fibres are less affected by ozone, possibly the fibre core (middle of S<sub>2</sub> layer)





- ❑ Fibre strength loss induced by (ZEo) is similar to the effect of (H)
- ❑ Overall, all the cellulose has been depolymerised within the (ZEo) stage: cellulose degradation by ozone is rather **uniform** within the fibres, as opposed to cellulase





Similar results were obtained for Tearing strength and Bursting strength

Equivalent paper strength in spite of the lower DPv of the TCF pulp

⇒ In this DPv range, paper strength and DPv are not correlated





**Introduction**

**TCFz bleaching potential and chemical cost**

**Residual impurities and pulp brightness stability**

**Cellulose preservation and paper strength**

**Conclusion and prospects**



**Introduction**

**TCFz bleaching potential and chemical cost**

**Residual impurities and pulp brightness stability**

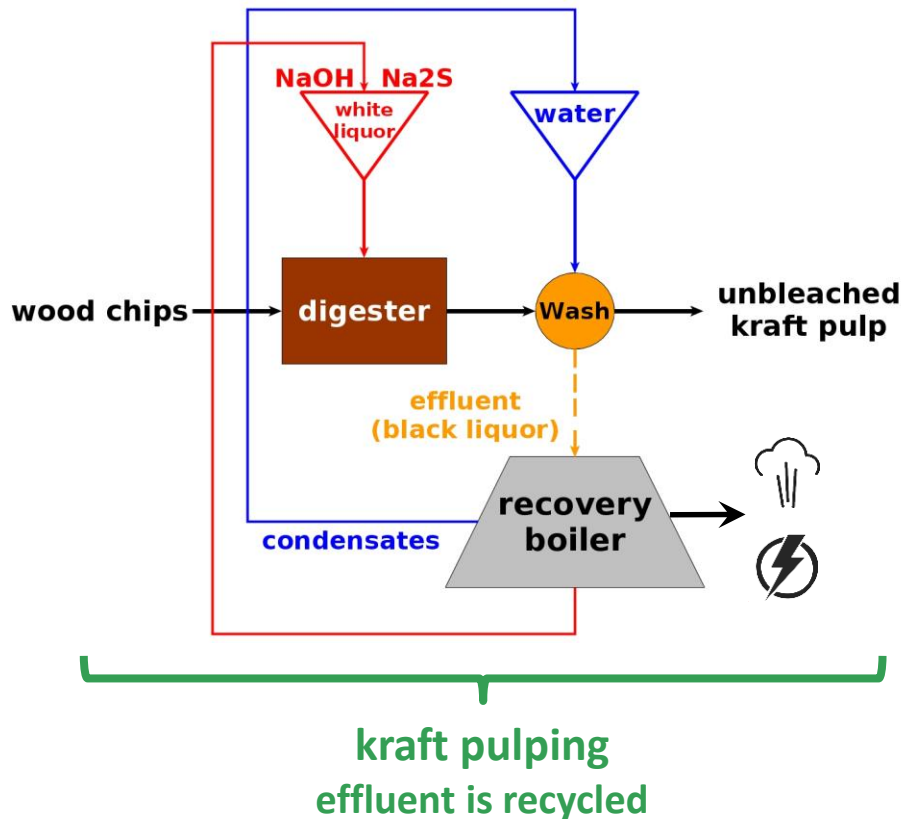
**Cellulose preservation and paper strength**

**Conclusion and prospects**



- ❑ A modern four-stages TCF-ozone bleaching sequence **A(ZEo)(ZEo)(ZP)** was designed.
- ❑ The TCF pulp was bleached to the brightness level of a conventional ECF pulp, with better brightness stability and lower chemical cost.
- ❑ UVRR spectro. study proved that  $(ZP) > (DP)$  and so that  $(Z) > (D)$  in terms of brightness stability.
- ❑ SEC shows that all the cellulose is affected by ozone within the fibres, thus with mild impact on fibre strength but no visible impact on paper strength.





❑ In ECF sequences, the effluent generated during pulp washing needs to go to the WWTP (**corrosion from Cl<sup>-</sup> ions**)

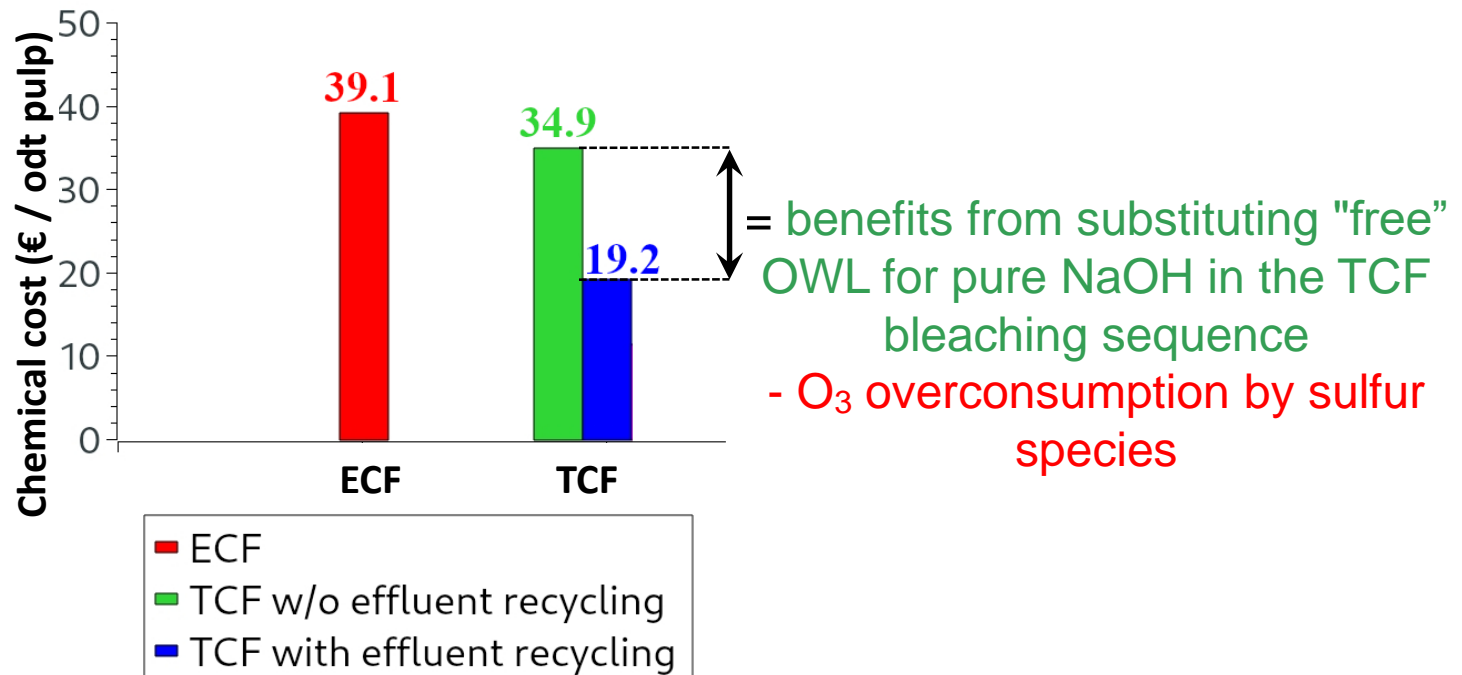
❑ In TCF sequences, alkaline effluent can be recirculated back to the brownstock washing and burnt in the mill recovery boiler

This implies using white liquor (or oxidised white liquor) as alkali source

❑ 99% of the white liquor is recycled (Na<sub>2</sub>S + NaOH) within the kraft process



- ❑ Recirculated organics, ie. eliminated lignin in a (ZEO) stage, had no observable impact on a fresh (ZEO) stage
- ❑ Oxidised white liquor (OWL) model-compounds had a negative impact on the (ZEO) stage... but:



## ECF *Elemental Chlorine Free*

- + no carbohydrates degradation
- + well-known chemistry and process based on  $\text{ClO}_2$  bleaching chemical
- + high brightness (over 90% ISO)
- AOX (in water streams and in pulp)
- No effluent recycling (corrosion from Cl): requires large waste-water treatment plant and high process water consumption)



## TCFz *Totally Chlorine Free with ozone*

- + carbohydrates mild and uniform degradation with no impact on paper strength
- + high brightness (over 90% ISO)
- + very stable brightness
- + no AOX
- effluent recycling might be feasible
- + TCF sequence is cheaper than ECF



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## Ozone Days

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Ozone Days

## Thank you for your attention

