PRETREATMENTS OF KRAFT PULPING
Experiences on the application of Steam Explosion to Eucalyptus Kraft Pulping

ABTCP 2012
45º CONGRESSO E EXPOSIÇÃO INTERNACIONAL DE CELULOSE E PAPEL
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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
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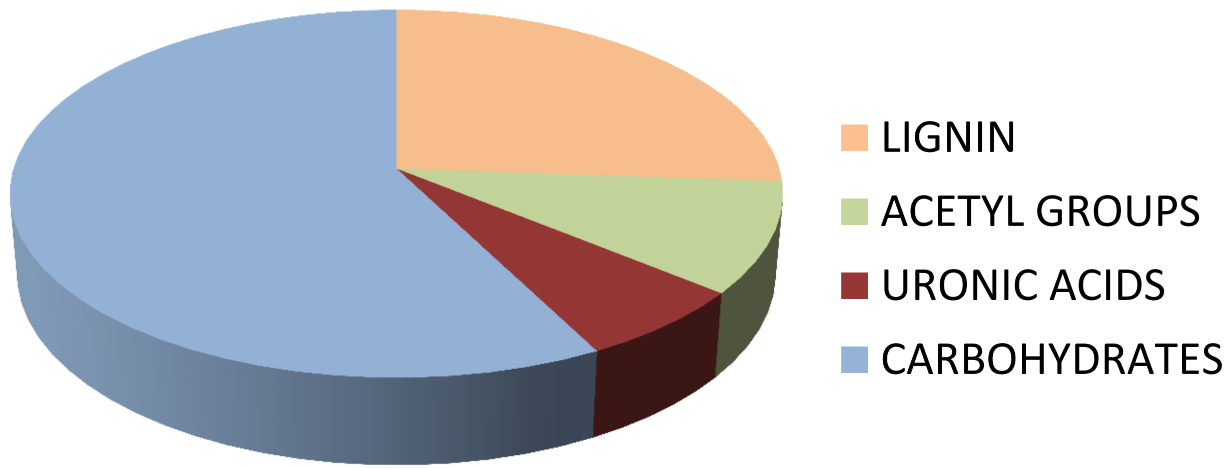
BRIEF **INTRODUCTION TO KRAFT COOKING**

THE STEAM EXPLOSION TREATMENT OF WOOD

COMBINATION STEAM EXPLOSION-KRAFT IN EUCALYPTUS COOKING

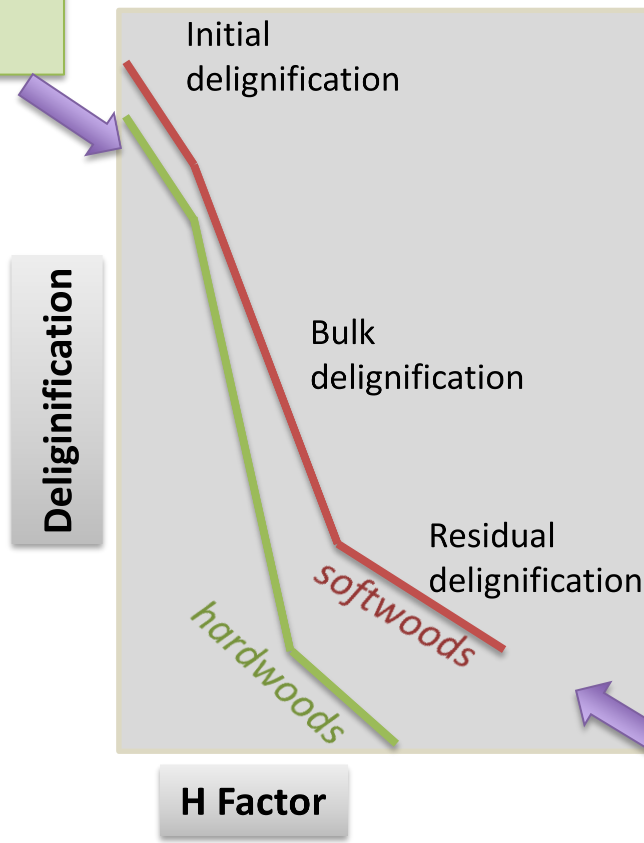
Alkaly Consumption Distribution (%)
Total Alkaly: c.a. 150 Kg NaOH/t.

Low yield: c.a. 50%



Quick chemical consumption at before delignification begins

High chemical consumption (40%) at 100-110ºC, and only 10% delignification



Low Selectivity at the end of cooking

Recovery is fundamental in Kraft Pulping

Hemicelluloses only suppose a half of the heat capacity of lignin and can be used for chemicals production

Recovery boiler could be a bottleneck in kraft pulping

Pre-Treatments to selectively remove carbohydrates would permit:

- Increase yield (improved selectivity)
- Reduce time of cooking (improved chemicals impregnation, more available chemicals for delignification)
- Removal of extractives and carbohydrates has a minor effect on the energy balance and improves recovery boiler performance

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Acid hydrolysis

Use diluted (0.5-4%) mineral acids. Temperature: 120-200ºC. Adequate for sugars production. Hemicellulose hydrolysis increases porosity and favors saccharification.

Alkaline hydrolysis

Use sodium, potassium or calcium hydroxides. Temperature < 120ºC. Cause delignification. Moderately efficient to remove hemicelluloses

Hot Water hydrolysis

Pressurized hot water at 120-220ºC. Lower temperatures cause poor hydrolysis (hemicelluloses) . Cellulose hydrolysis occurs above 220º.

Steam Explosion

Saturated Steam at 160-250ºC. Rapid decompression after a few minutes. High hemicelluloses hydrolysis while cellulose remains unaltered.

PRE-TREATMENTS OF LIGNOCELLULOSE

Steam Explosion

Initially used for defibration of wood chips to produce the board *masonite* (Mason, 1925).

Used to promote lignin softening and fiber separation in mechanical pulping methods with questionable results

Decompression origins a quick transformation of liquid water into steam causing wood destructuration

Chemical changes or mechanical modifications of the material has been proposed as the cause of wood/lignocelulose modification. Probably a combination of both take place.

HEMICELLULOSE REDUCTION

PARTIAL DELIGNIFICATION

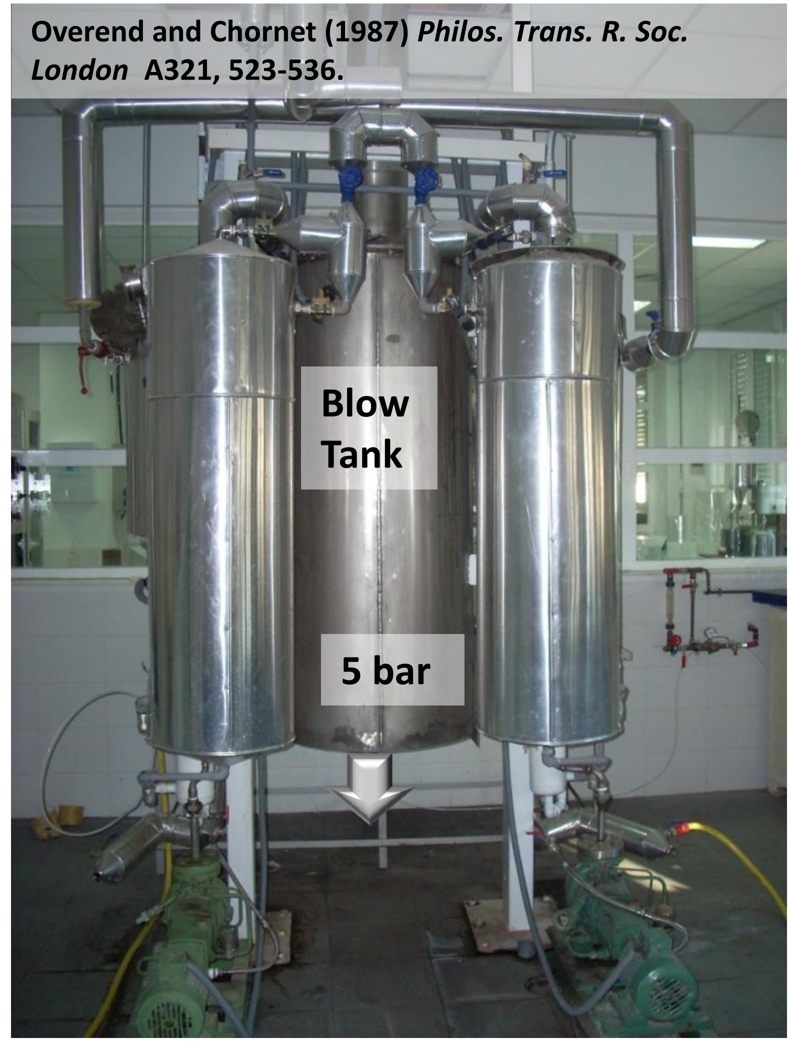
CELLULOSE CONSERVATION

PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION OBJECTIVES:

Improve diffusion of chemicals and enzymes into (eucalyptus) wood chips

Separate use of hemicelluloses and lignin as raw materials and fuel


Steam Explosion
Steam
183 ºC
10 bar
Chips
So range 3.14 – 3.56


Overend and Chornet (1987) *Philos. Trans. R. Soc. London* A321, 523-536.
Blow
Tank
5 bar

PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION
Changes in chemical composition of wood chips

Holocellulose content was reduced from the 76% down to 61-65%.
Similar reduction of holocellulose took place for all the treatments and suggest a "minimum" of severity above which the treatments reach a constant degree of holocellulose degradation.

Cellulose degradation is minimum

About a half of **xylans** (47%) are hydrolyzed by SE treatments of moderate severity (3.56)

SE liquor	% extracted on wood
Acetyl groups	4.6%
Glucose	0.5%
Xylose	8.0%
Arabinose	0.1%
Total	13.2%

PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION
Changes in chemical composition of wood chips:

Lignin
Most of the lignin (92-97%) remains in wood chips.
Darkening of the SE chips suggests that they undergone some kind of reaction.

Inhibitors of sugar fermentation
Neither furfural nor HMF was detected in the liquid phase of SE.
Mild SE conditions probably favor hydrolysis vs. degradation reactions.

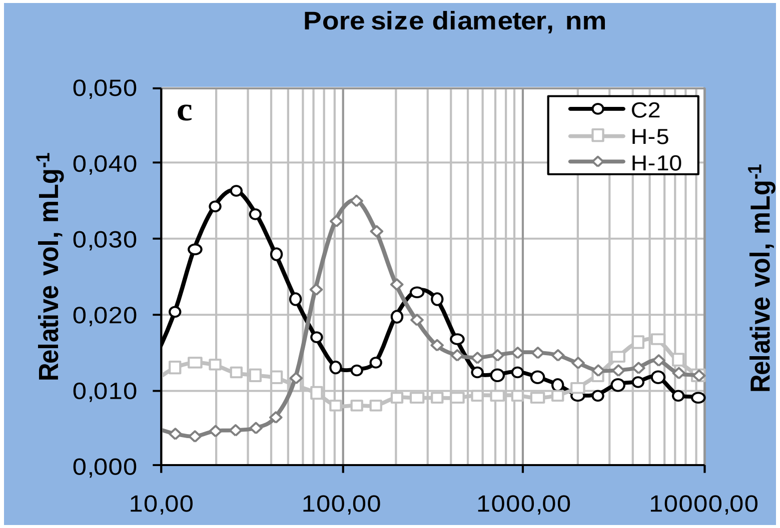
PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION
Changes in Structural properties of wood chips

Results of mercury intrusion porosimetry (MIP) have revealed a ***redistribution of the pore network*** in the SE material:

Decrease of volume of small pores

Increase of volume of bigger pores

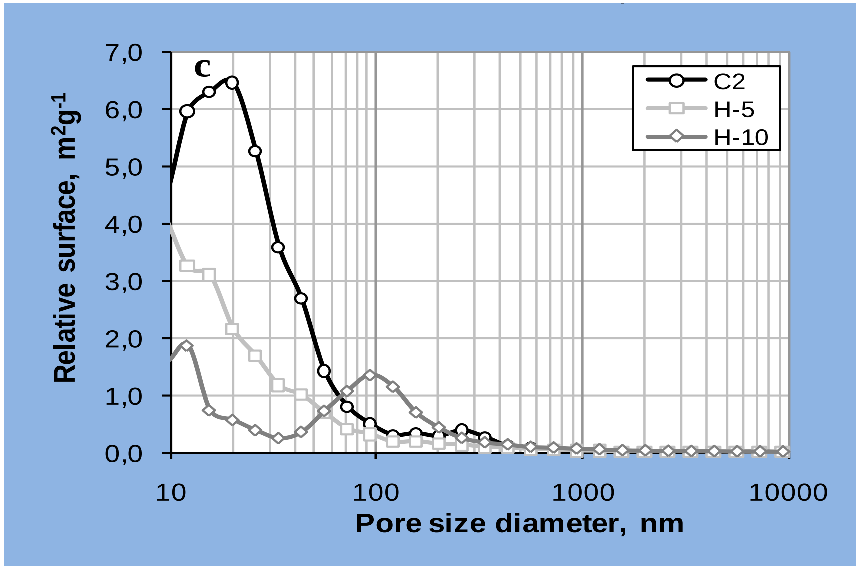
Since there was not an increase of the total pore volume (pore size range 10 - 10,000 nm) it is assumed the formation of pores of longer diameters derived from small pores.



PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION
Changes in Structural properties of wood chips:

There was a clear decrease in the relative surface in all the treated samples.

These phenomena is coherent with the disappearance of small pores to form bigger ones, because the ratio surface/volume decreases as pore volume increases.

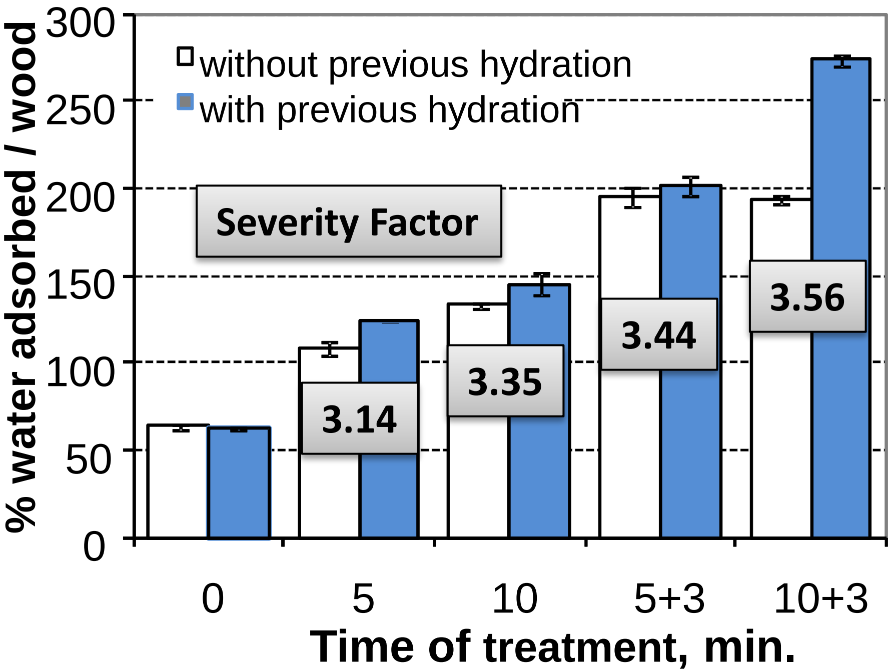


PRE-TREATMENT OF EUCALYPTUS CHIPS WITH STEAM EXPLOSION
Changes in Structural properties of wood chips

Analysis of the hydration capacity revealed greater water absorption for SE samples.

As there is no increase of the total pore volume, a relationship: new pore matrix - water penetration kinetics must exits.

The increase in water hydration capacity of the SE chips is explained if the water absorption lasts long enough for water to fill the new bigger pores, but not to penetrate into the smaller pores of the non exploded chips.



KRAFT COOKING OF STEAM EXPLODED CHIPS

Kraft Cooking

160 ºC
Liquor/Wood :4 L/Kg

AA= 16%
S= 20%

$$\left(\frac{}{}\right)\ dt$$

H Factor: 180 – 400 (24-56 min at max. T)

KRAFT COOKING OF STEAM EXPLODED CHIPS

Kraft Pulp (control)

kappa 49

separated fibers + bundles

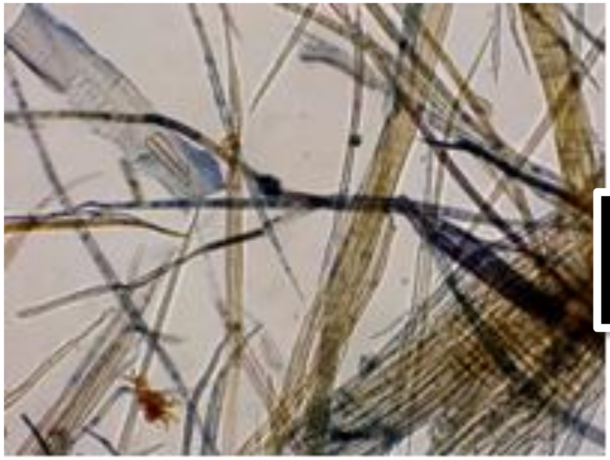
Semichemical type

Steam Exploded Kraft Pulp

kappa =15

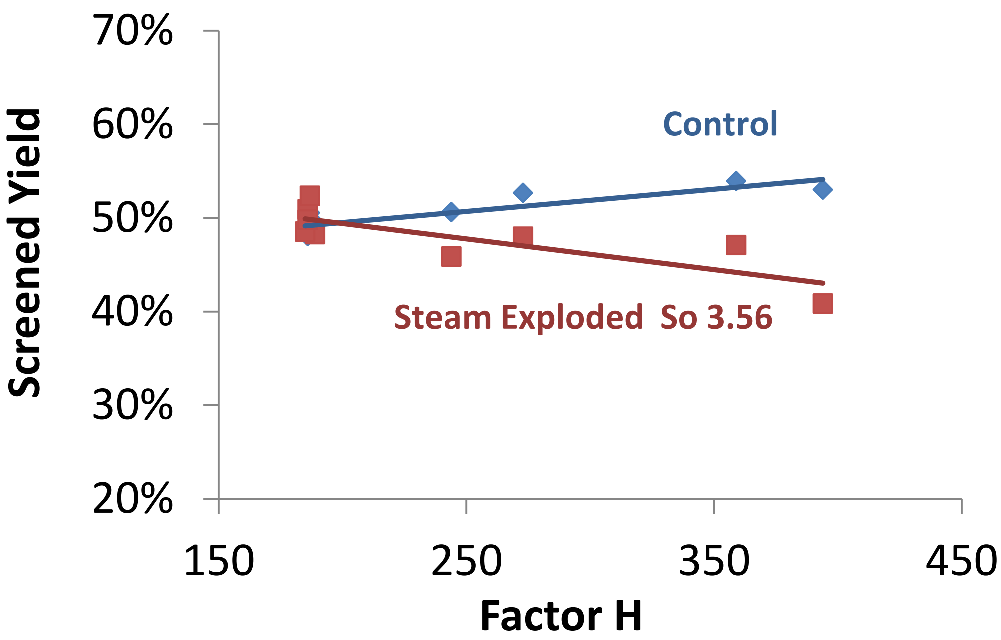
Individualized fibers

crude chemical



So 3.56
H-Factor 180

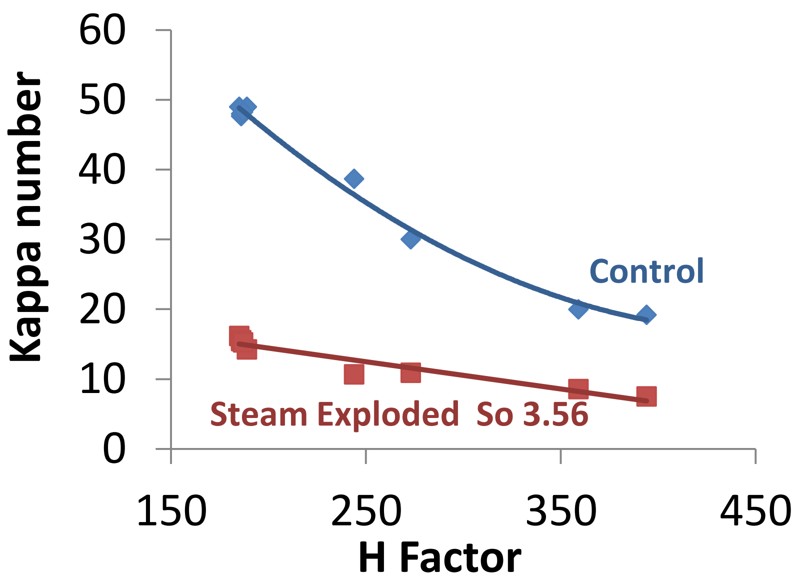
KRAFT COOKING OF STEAM EXPLODED CHIPS



Steam Explosion Pre-treatment cause:

- **Reduction of pulp yield**
- **Increase of chemicals consumption**
- **Reduction of Cooking time (25 vs 60 min)**

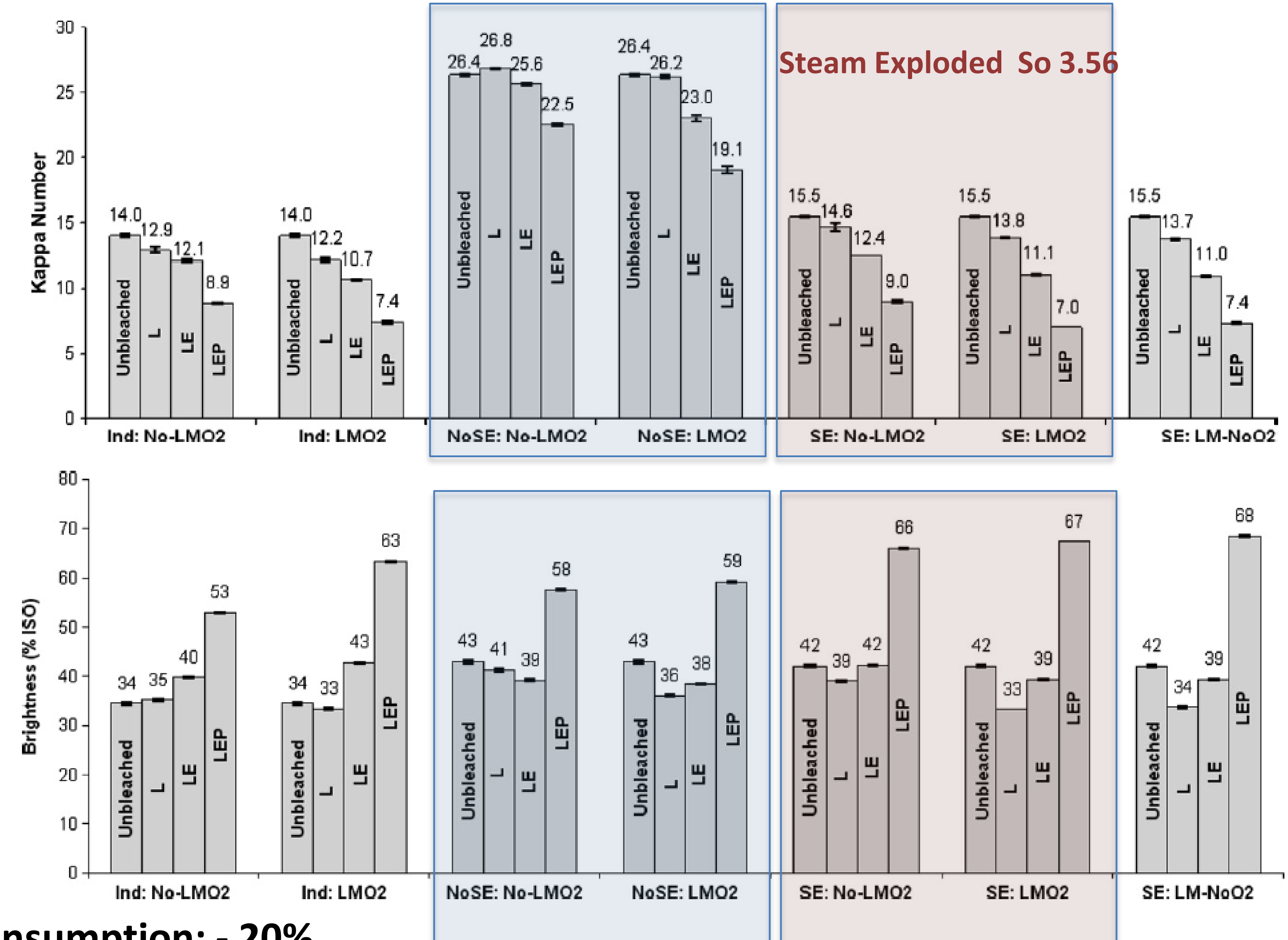
KRAFT COOKING OF STEAM EXPLODED CHIPS



Steam Explosion Pre-treatment cause:

- **Kappa number reduction (-70%)**
- **Hexenuronic Acids reduction: 88%**
- **Maintains viscosity**

KRAFT COOKING OF STEAM EXPLODED CHIPS

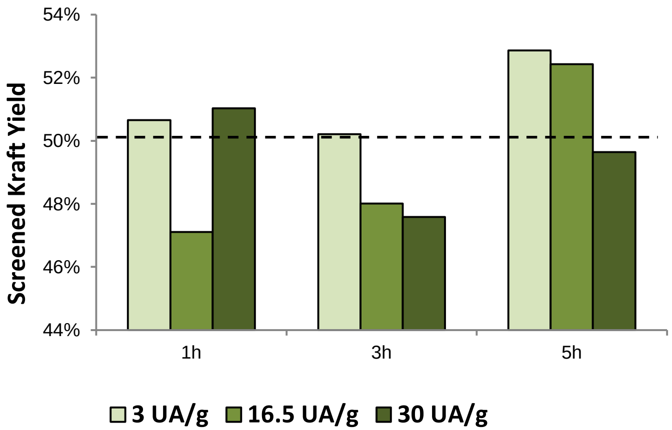


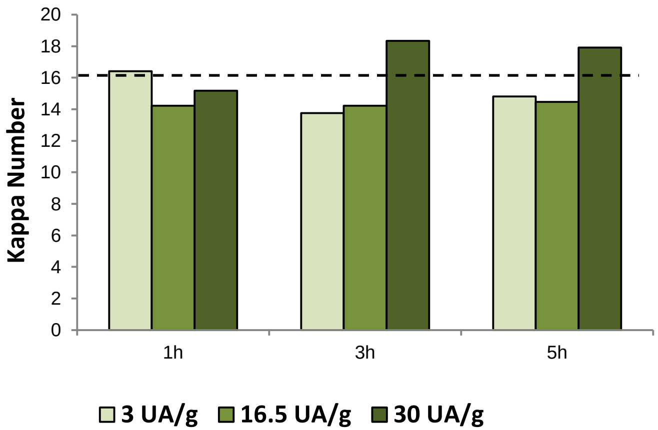
H_2O_2 consumption: - 20%

Bioresource Technology. 201 (102): 4530-4535.

KRAFT COOKING OF STEAM EXPLODED CHIPS

Application of a Laccase Delignification Stage to the Steam Explode Pulps

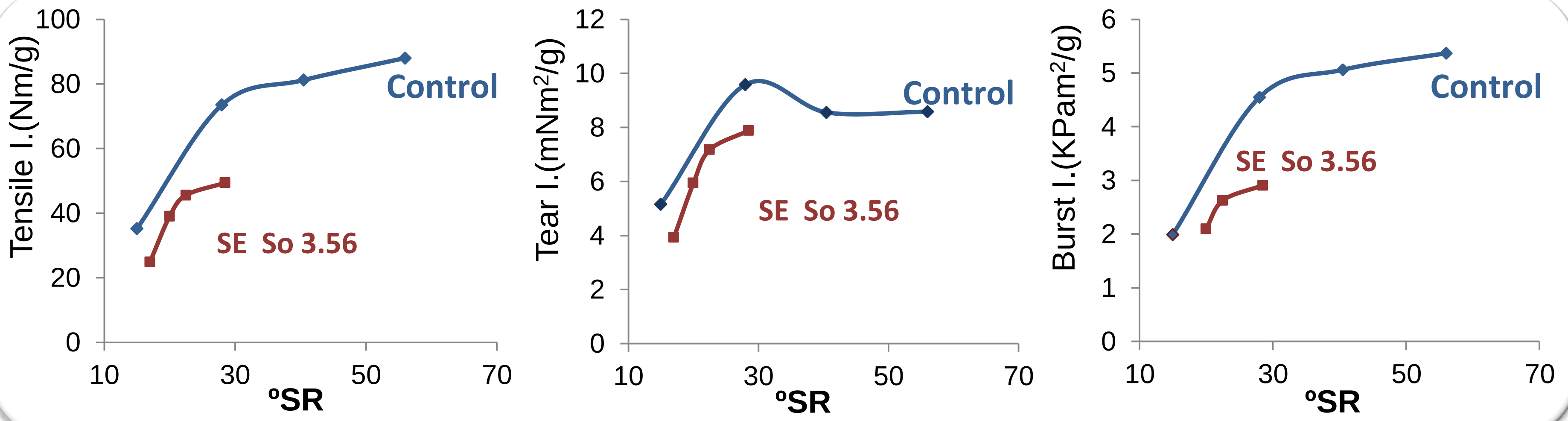




- Laccase application to Steam Exploded chips are effective to increase yield and reduce kappa in a further kraft cooking
- Laccase is only effective if a low dose is applied for more than 3 hours
- Pulp viscosity, drainability (ºSR) and mechanical properties were not affected by the laccase addition

KRAFT COOKING OF STEAM EXPLODED CHIPS

Development of mechanical properties



CONCLUSIONS

Steam Explosion pretreatment cause chemicals and structural modifications on eucalyptus chips

- Selective: remove xylans maintaining cellulose and lignin
- Reorganize the pore distribution into the chips. Small pores are combined into bigger pores but maintaining the global pore volume.

Steam Explosion favors kraft delignification:

- Lower kappa
- Lower reaction time
- Higher Brightness and lower bleaching chemical consumption

And has the drawbacks:

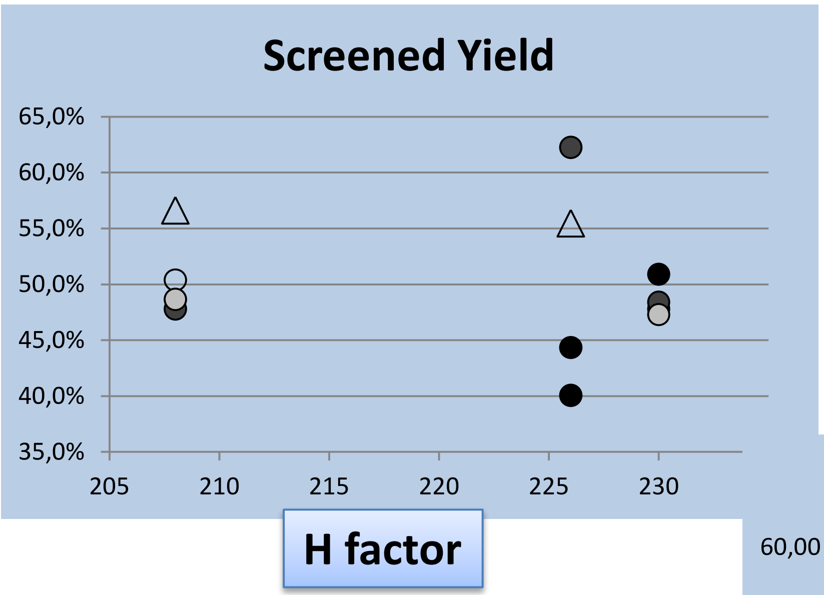
- Lower global yield (SE + Kraft)
- Poor refinability and lower mechanical properties

Steam Explosion permit enzyme (laccase) penetration in the chips boosting the selectivity of a further kraft cooking

FUTURE (AND PRESENT) WORK

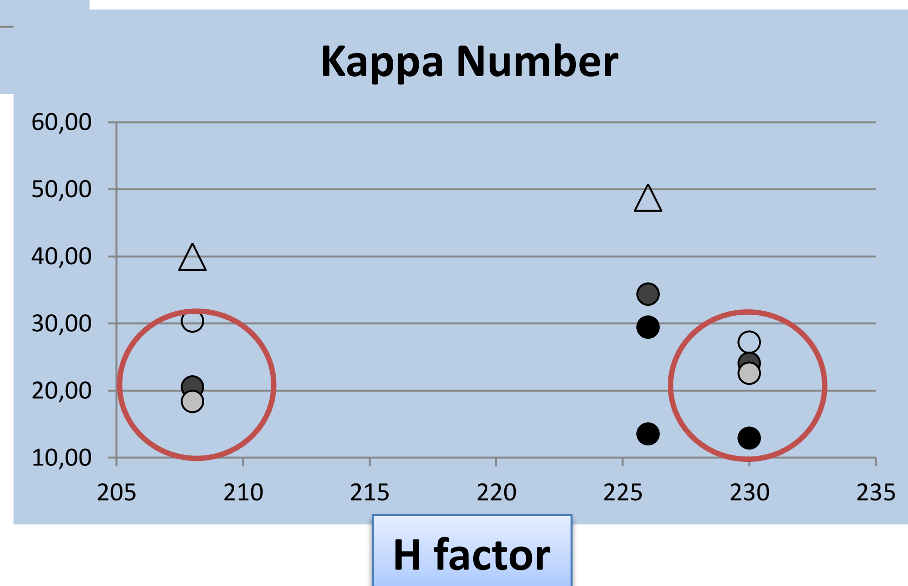
Steam Explosion has been applied at **moderate – high severity** (3.56) to favor enzyme penetration into the chips

- Could milder SE conditions maintain the advantages and improve yield and refinability?



△ Control (no SE)

○ Severity (3.14 – 3.56) a darker circle means more severe SE

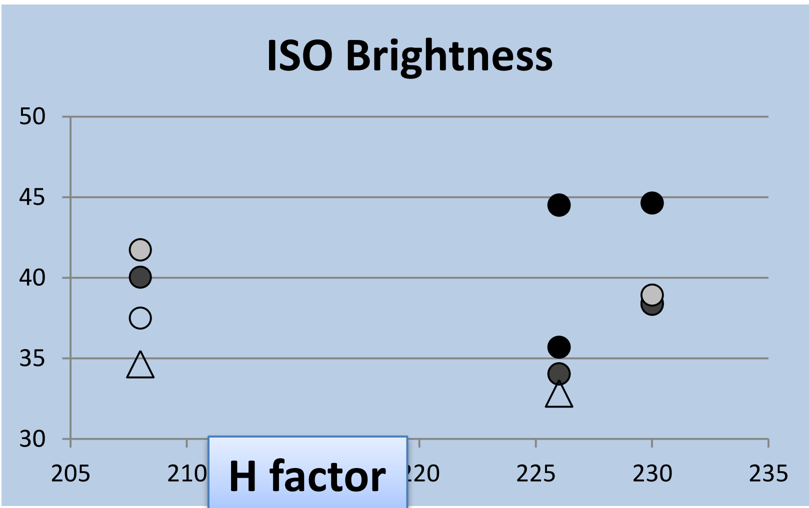


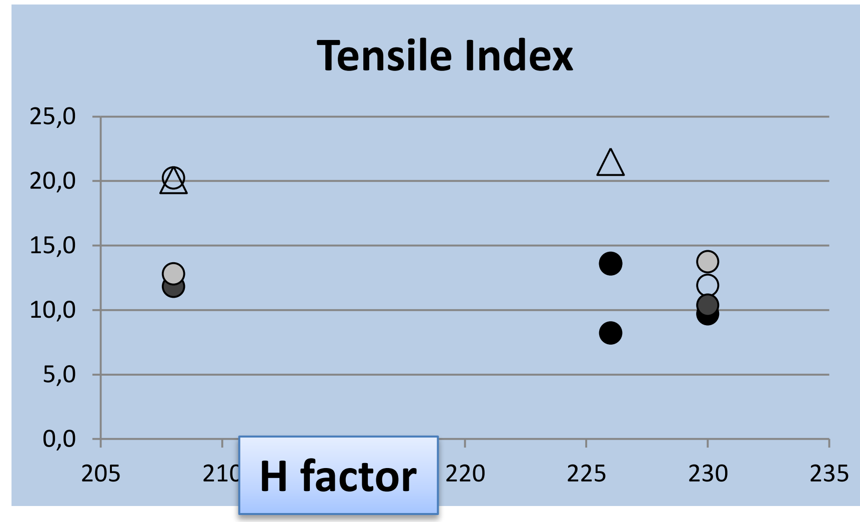
Delignified eucalyptus pulps (ready to bleaching) could be obtained from SE chips with low severity-low H-factor combinations.

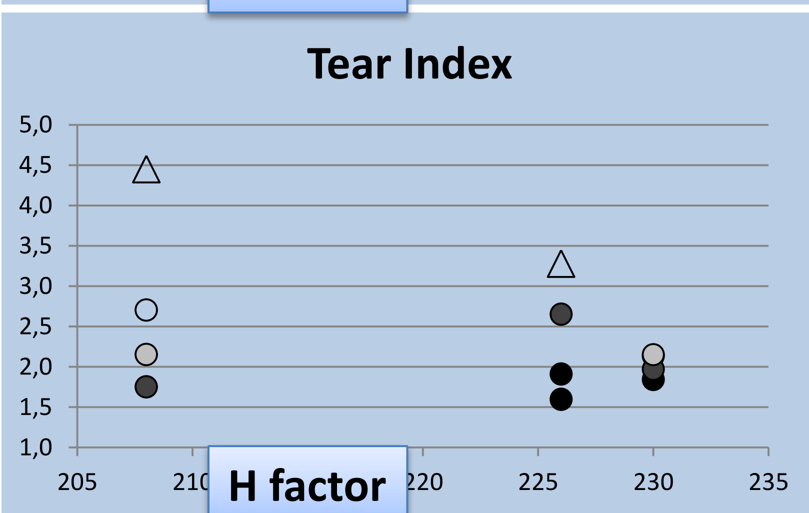
Equivalent cooking conditions on non SE chips produce a kraft liner pulp

△ Control (no SE)

○ Severity (3.14 – 3.56) a darker circle means more severe SE







Low severity-low H-factor combinations of SE-Kraft treatments also cause a improvement of bleaching, and maintain mechanical properties (except tear) Refinability experiments are actually been performed o compare the development of properties in SE pulps

BALANCES

Scenario. Medium SE severity; So= 3.56 (13 min.)

Cooking time: 60min (25 min. for SE) at 160ºC

Balance	Kraft	SE + Kaft
Pulp produced by batch (Kg)	50	40
Solids in Black Liquor (Kg)	50	40
Sugars production: xil + glu (Kg)	0	21
Pulp production(1) (%)	100	128
Calorific value(2) of black liquors (%)	100	68
Energy(3) in cooking + SE (%)	100	64

(1) Assuming a 60% more of batches by a given period of time

(2) Assuming: initial lig/hemic ratio: 1; calorific value hemic= ½ calorific value Lig; hemic. Removal 50%

(3) Calculated as directly proportional to reaction time

Acknowledges

<u>Spanish Ministry of Science and Technology</u>

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A more detailed information can be found in:

Integration of the kraft process for cellulose pulp production into a biorefinery process flow

Ph. D. thesis of Raquel Martín-Sampedro.

Obrigado pela sua atençao

Thanks for your attention

articles

Steam explosion treatment of *Eucalyptus globulus* wood: Influence of operational conditions on chemical and structural modifications. BioResources. 2011. 6 (4): 4922-4935

Lignin changes after steam explosion and laccase-mediator treatment of eucalyptus wood chips. J. of Agricultural and Food Chemistry. 2011. 59 (16): 8761-8769

Steam explosion and enzymatic treatments as pre-treatments to improve enzymatic hydrolysis of Eucalyptus globulus. Biomass and Bioenergy

Integration of kraft pulping on a forest biorefinery by the addition of a steam explosion pretreatment. BioResources. 2011. 6 (1): 513-528

Biobleaching of Eucalyptus globulus kraft pulps: Comparison between pulps obtained from exploded and non-exploded chips. Bioresource Technology. 201 (102): 4530-4535.

Combination of steam explosion and laccase-mediator treatments prior to Eucalyptus globulus kraft pulping. Bioresource Technology. 2011 (102): 7183-7189.