3er Congreso Iberoamericano
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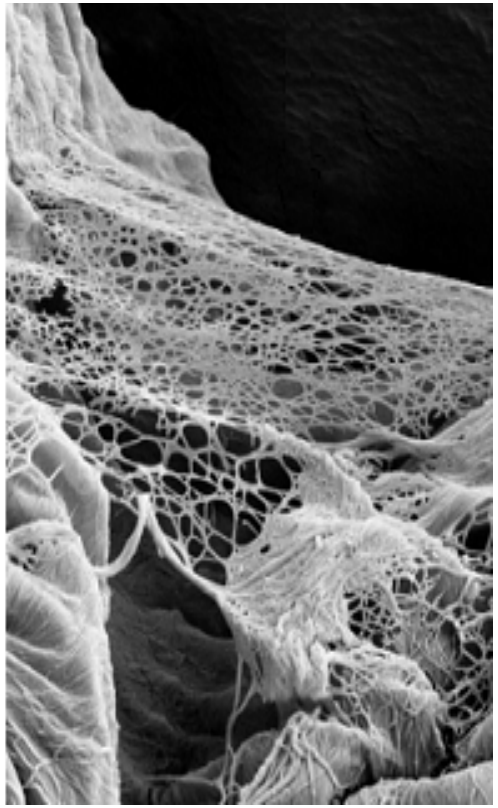
Biorrefinerías
Ciencia, Tecnología e Innovación para la Bioeconomía
23 al 25 de noviembre de 2015, Concepción - Chile

"CHARACTERIZATION OF EUCALYPTUS BARK AND ITS POTENCIAL USE FOR FIBER AND CELLULOSE NANOFIBRILS"



Bárbara Martínez, Carolina Puentes, Juan Pedro Elissetche, Regis Teixeira and **Miguel Pereira**.

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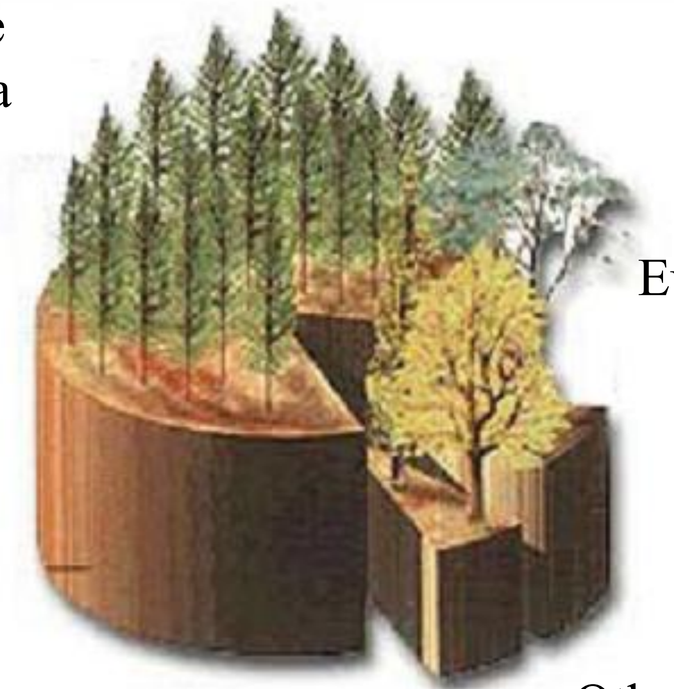
Departamento de Ingeniería Química
Facultad de Ingeniería
Universidad de Concepción

Forest Plantation in Chile

Radiata Pine
1.500.000 ha
64%



Eucalyptus spp.
650.000 ha
28%

65% *E. globulus*
422.500 ha

35% *E. nitens*
227.500 ha

Other Species
200.000 ha
8%

Total: 2.350.000 ha

INFOR

Quantification of Bark residues, available in Kraft pulp mill

Radiata Pine

594.000 ton/year

Uses

Biomass fuel

Compost

Tannins source

Eucalyptus spp

506.000 ton/year

Biomass fuel

Potential of Eucalyptus Bark Biorefinery

- **High value extractives**
- **Sugar source for biorefinery**
- **Fiber for paper and board**
- **Source of cellulose and cellulose nanofibril.**

Eucalyptus globulus biomass residues from pulping industry as a source of high value triterpenic compounds

R.M.A. Domingues[a], G.D.A. Sousa[b], C.S.R. Freire[a], A.J.D. Silvestre[a,*], C. Pascoal Neto[a]

Industrial Crops and Products 31 (2010) 65–70

Miscanthus x giganteus **Bark Organosolv Fractionation: Fate of Lipophilic Components and Formation of Valuable Phenolic Byproducts**

Juan José Villaverde,[*,†] Alberto De Vega,[‡] Pablo Ligero,[‡] Carmen S. R. Freire,[†] Carlos Pascoal Neto,[†] and Armando J. D. Silvestre[†]

The bark biorefinery: a side-stream of the forest industry converted into nanocomposites with high oxygen-barrier properties

Myriam Le Normand · Rosana Moriana · Monica Ek

Cellulose (2014) 21:4583–4594

Fractioning and chemical characterization of barks of *Betula pendula* and *Eucalyptus globulus*

Isabel Miranda, Jorge Gominho*, Inês Mirra, Helena Pereira

Industrial Crops and Products 41 (2013) 299–305

GENERAL PURPOSE

- To Characterize chemically and morphologically Eucalyptus bark to determine its potential use as a source of fibers, cellulose and cellulose nanofibers.

Goals

- Compare the performance of bark with wood from eucalypts during the kraft cooking and the pulp fiber characteristics.

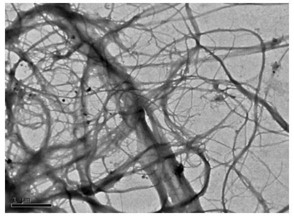
- Compare the performance of bark fibers with wood fibers from eucalyptus during a mechanical treatment of deconstruction of fiber: PFI refining.

Methodology

Eucalyptus Wood

Eucalyptus Bark

Kraft Pulping → Bleaching → Beating PFI → **CNF**



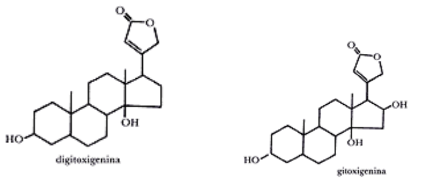
WOOD AND BARK ANALYSIS

Chemical Analysis

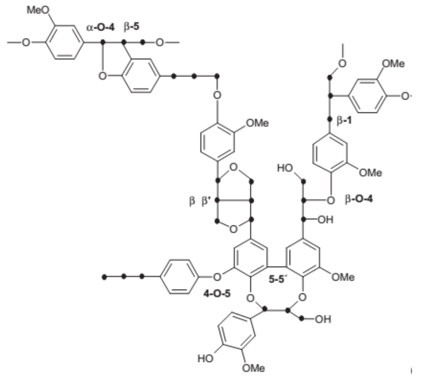
Morfological Analysis

Mechanical Properties

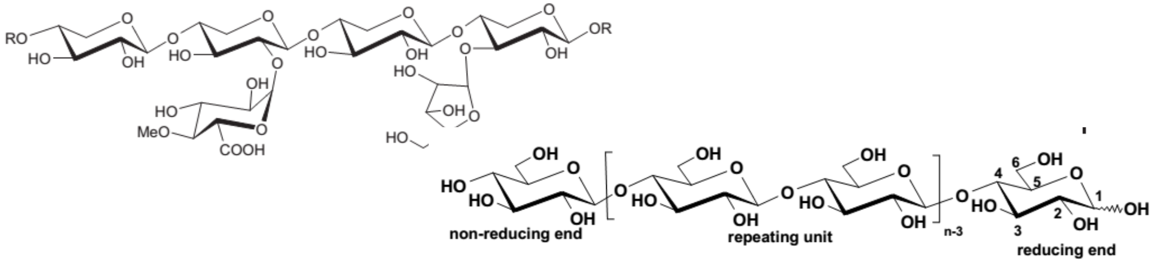
Extractable in acetone



Lignin



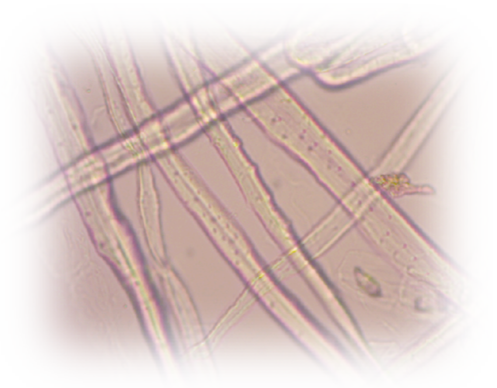
Carbohydrates



Mendoça, R., A. Guerra, and A. Ferraz, *Delignification of Pinus taeda wood chips treated with Ceriporiopsis subvermispora for preparing high-yield kraft pulps.* . Journal of Chemical Technology and Biotechnology, 2002. **77**: p. 411-418.

Wood and Bark Analysis

- Chemical Analysis
- **Morfological Analysis**
- Mechanical Properties

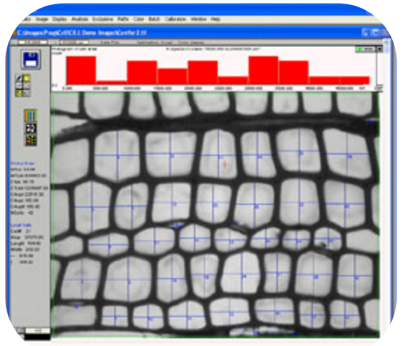


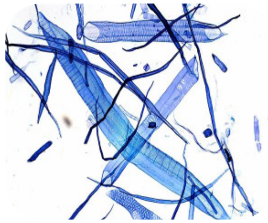
Fiber Quality (FiberTester)

- Fiber length distribution.
- Fiber width distribution.

Microscopy Analysis

Software WinCell





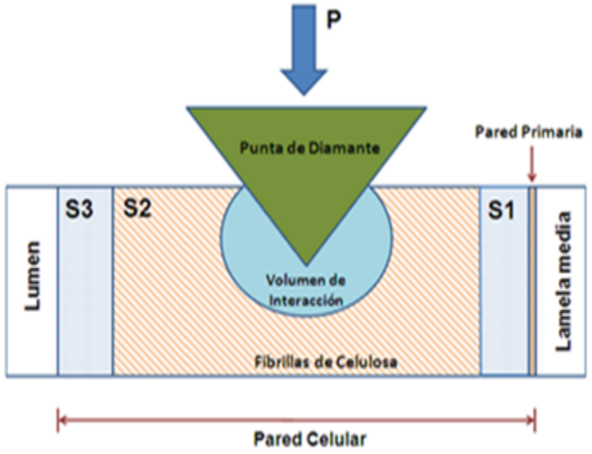
Wood and Bark Analysis

Chemical Analysis

Morphological Analysis

Mechanical Properties

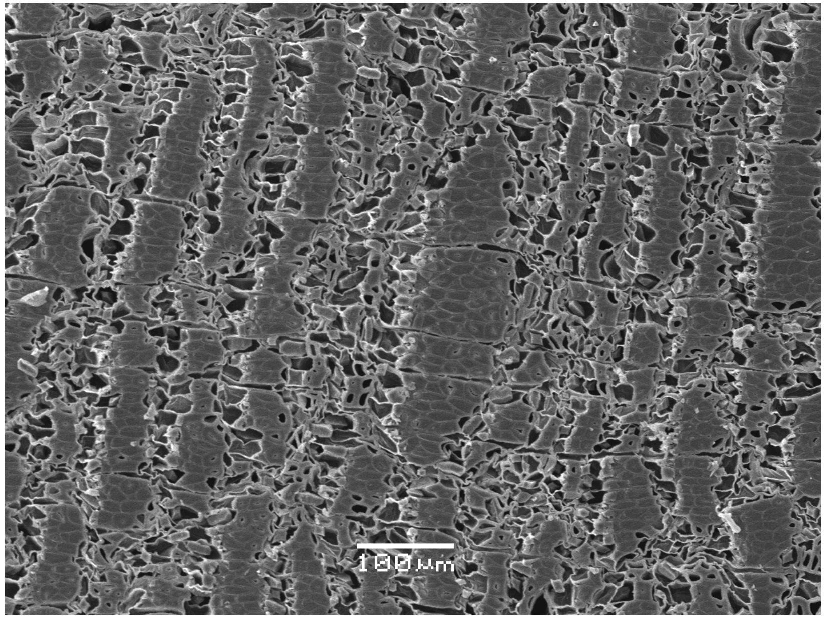
Hardness and modulus of elasticity of the cell wall: nanoindentation testing.



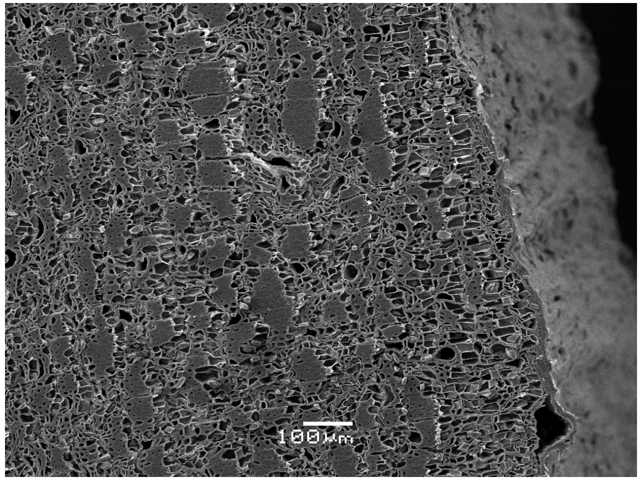
- Nanoindentación en *Centro de Biomateriales y Nanotecnología de la Universidad del Bío-Bío.*

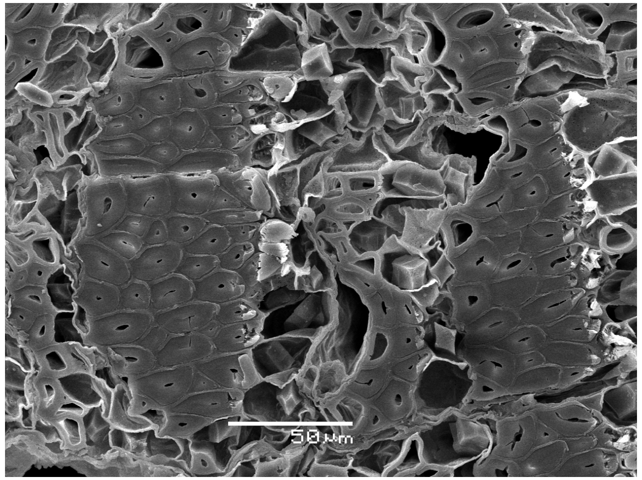
SEM Microscopy Bark

Eucalyptus hybrids
nitens × globulus

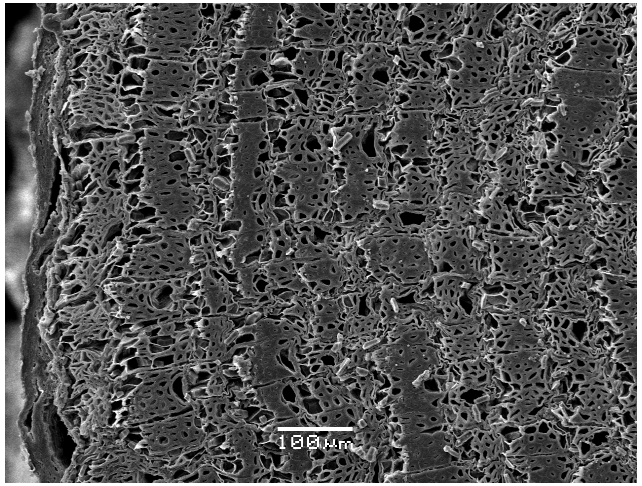


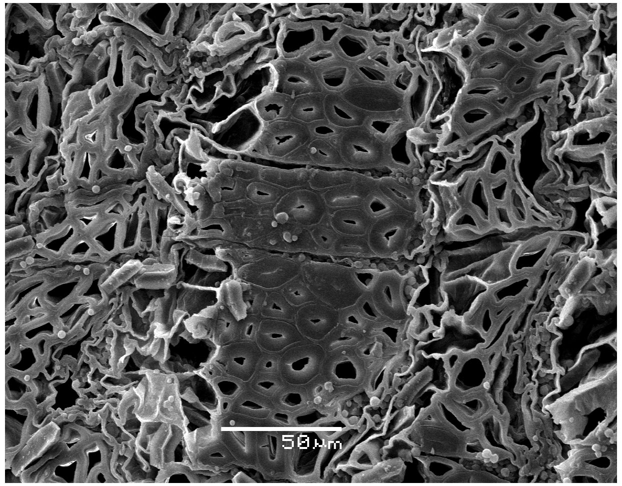
Eucalyptus globulus



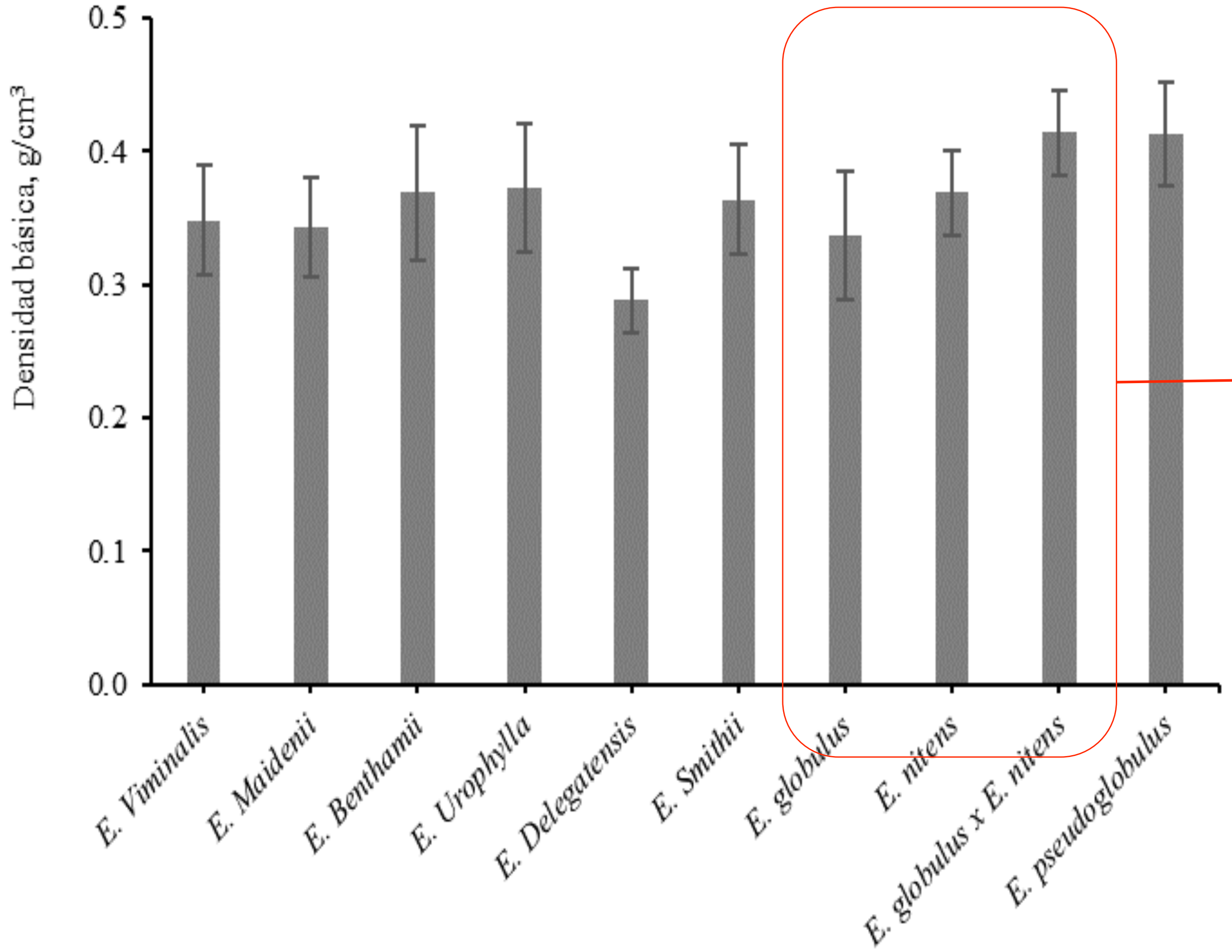


Eucalyptus nitens





Basic Density Of bark

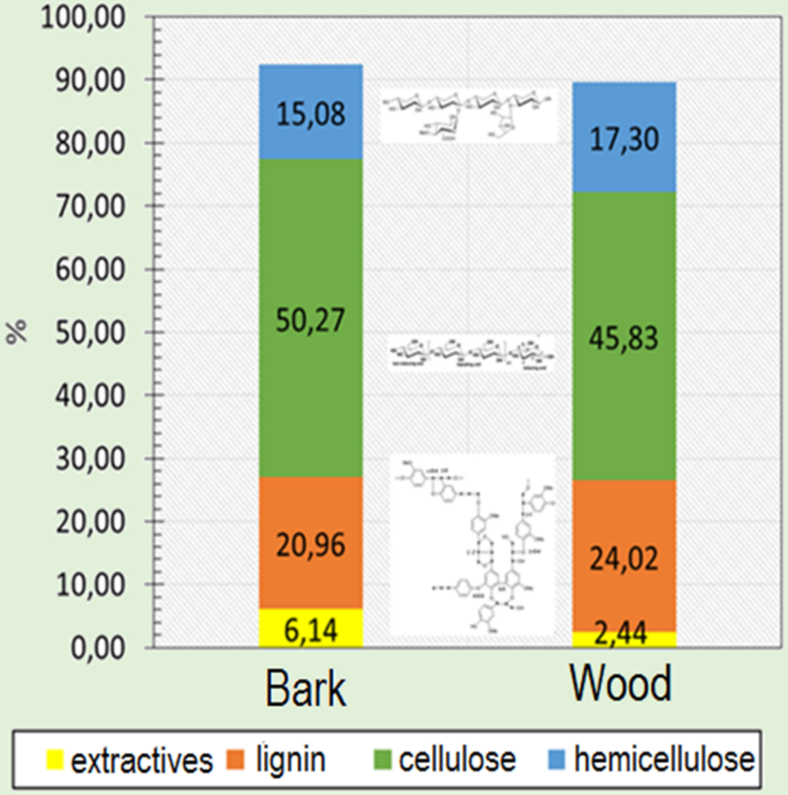


E. globulus	330 - 340 kg/m^3
E. nitens	370 - 385 kg/m^3
Hybrids En X Eg	400 - 415 kg/m^3

Chemicals Analysis

Eucalyptus globulus
Wood Chips

Eucalyptus globulus
Bark



Eucalyptus spp. Bark

Materia Prima	Extraíbles	Celulosa	Hemicelulosas	Lignina
E. viminalis	16,3 ± 0,6	51,5 ± 1,2	18,9 ± 0,8	13,1 ± 1,2
E. maidenii	7,3 ± 0,3	44,1 ± 3,3	18,6 ± 0,5	22,4 ± 0,3
E. benthamii	7,0 ± 0,1	41,6 ± 3,0	19,2 ± 0,7	16,9 ± 1,6
E. urophylla	3,1 ± 0,4	52,5 ± 1,1	17,8 ± 0,7	18,8 ± 0,5
E. delegatensis	10,1 ± 0,3	39,5 ± 2,1	19,5 ± 0,6	24,2 ± 0,2
E. smithii	1,5 ± 0,1	67,3 ± 2,2	16,7 ± 0,4	18,8 ± 1,0
E. globulus	1,5 ± 0,1	43,6 ± 2,5	21,6 ± 0,3	15,2 ± 0,5
E. nitens	3,3 ± 0,8	50,0 ± 1,7	22,7 ± 0,6	15,1 ± 1,1
E. nitens x E. globulus	3,1 ± 0,3	45,1 ± 2,5	23,4 ± 1,0	16,6 ± 1,2
E. pseudoglobulus	3,6 ± 0,5	50,4 ± 2,3	17,0 ± 0,4	17,0 ± 1,6

Morfological Analysis

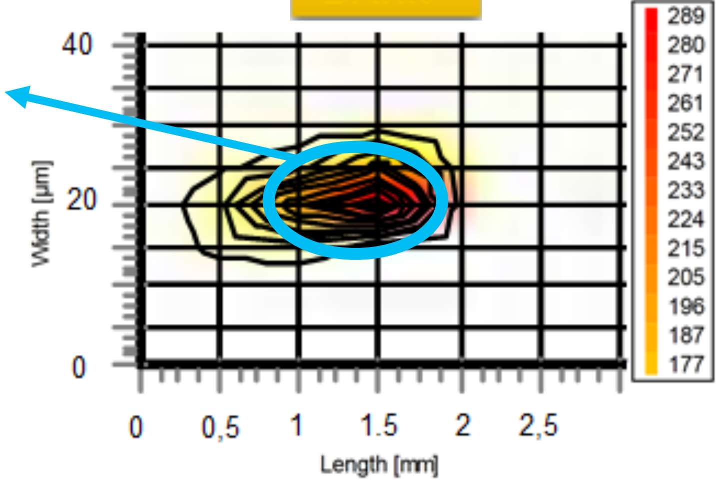
- **Cortex cells are 23% longer and 10% thinner than wood cells.**

	Unit	Wood	Bark
Length	mm	0,86	1,06
Width	µm	22	20
Fine	%	2,6	4,8

Bark has a greater number of cells of smaller dimensions (fine) with respect to the xylem.

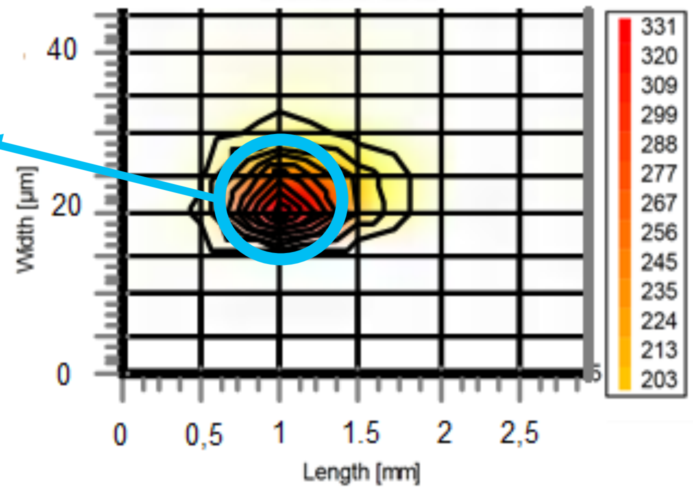
BARK

length : 0,8-1,9 mm
width : 15-28 µm

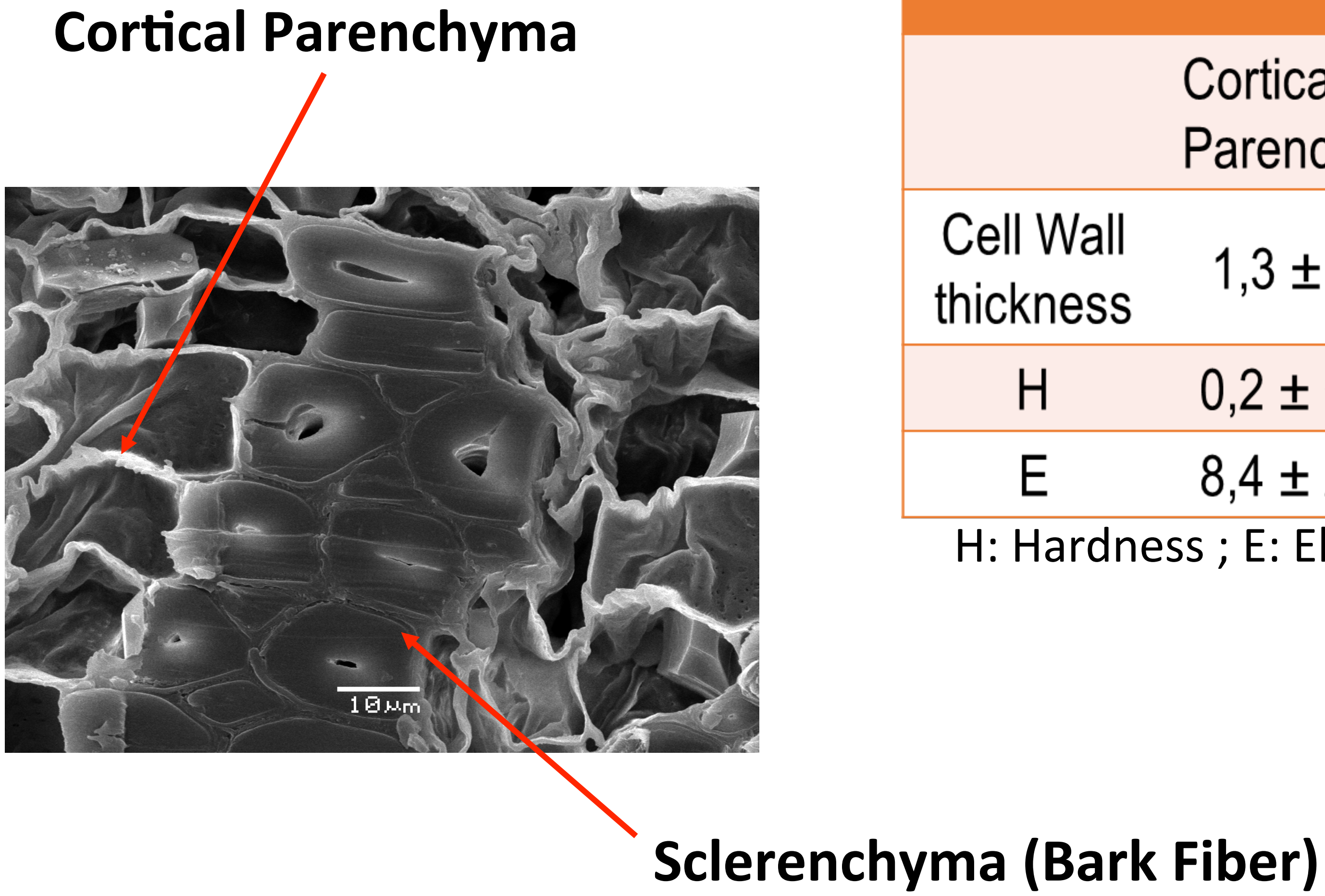


WOOD

length: 0,5-1,3 mm
Width: 15-33 µm



Nanoindentation



	Bark		Wood
	Cortical Parenchyma	Sclerenchyma	Fiber
Cell Wall thickness	1,3 ± 0,3 µm	3,2 ± 0,3 µm	1,3 ± 0,3 µm
H	0,2 ± 0,1 GPa	0,3 ± 0,1 GPa	0,3 ± 0,1 GPa
E	8,4 ± 2,8 GPa	11,3 ± 0,1 GPa	11,4 ± 2,3 GPa

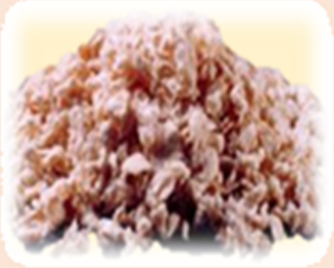
H: Hardness ; E: Elasticity modulus

Wood and Bark Kraft pulping

Liquor/Wood or Bark ratio: 4:1
Cooking Temperature: 170°C
Time to reach Temperature: 90 min
Time at Temperature: 60 min.
Effective álcali: 13% o.d.w. (as Na_2O)
Sulfidity 30%.

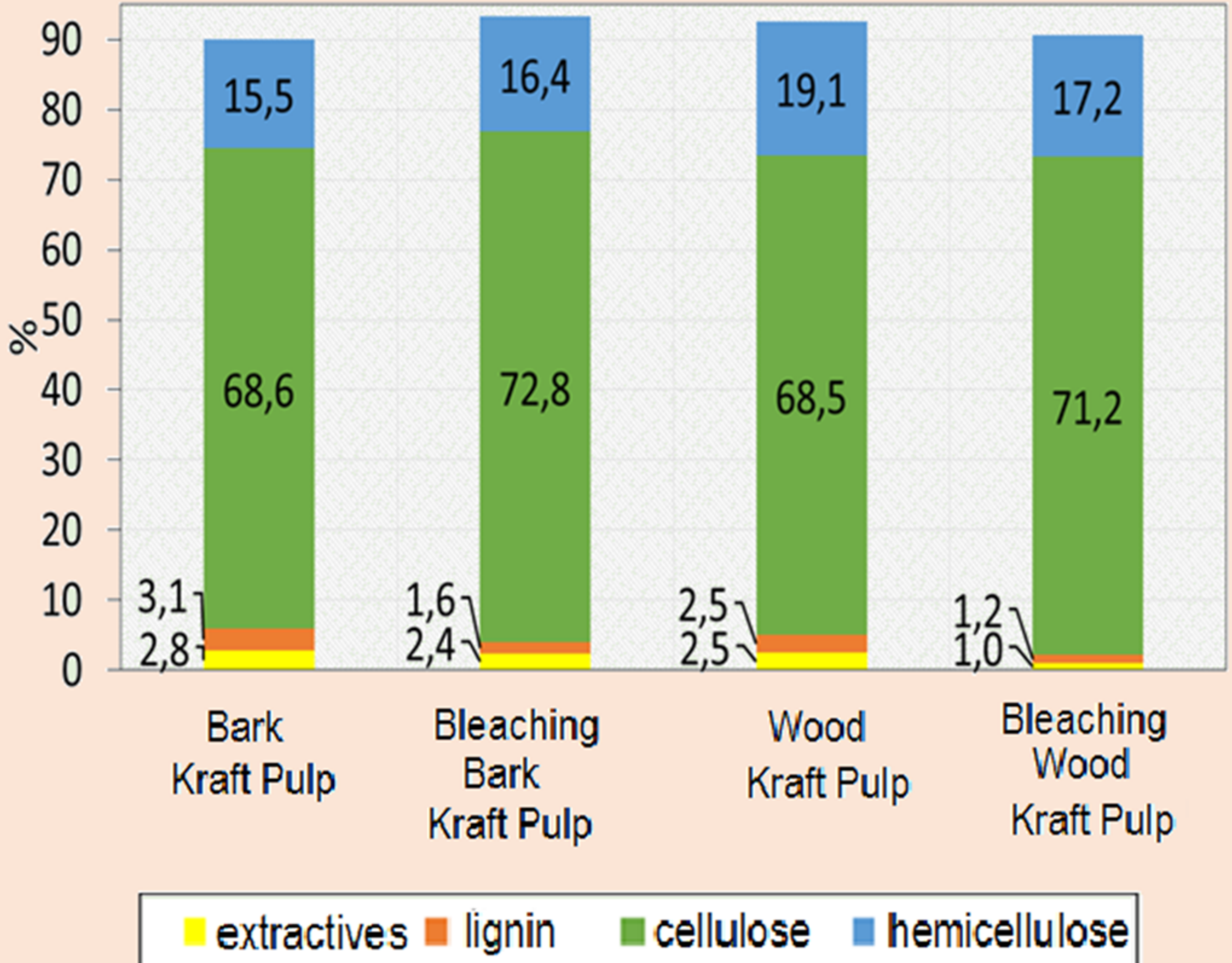
	Bark	Wood
Pulp yield (%)	46,4	52,9
Reject (%)	0,07	0,2
Kappa number (%)	28	15,1
Bleaching-yield (%)	83,7	95,7

Chemical Composition of Bark and Wood kraft pulp

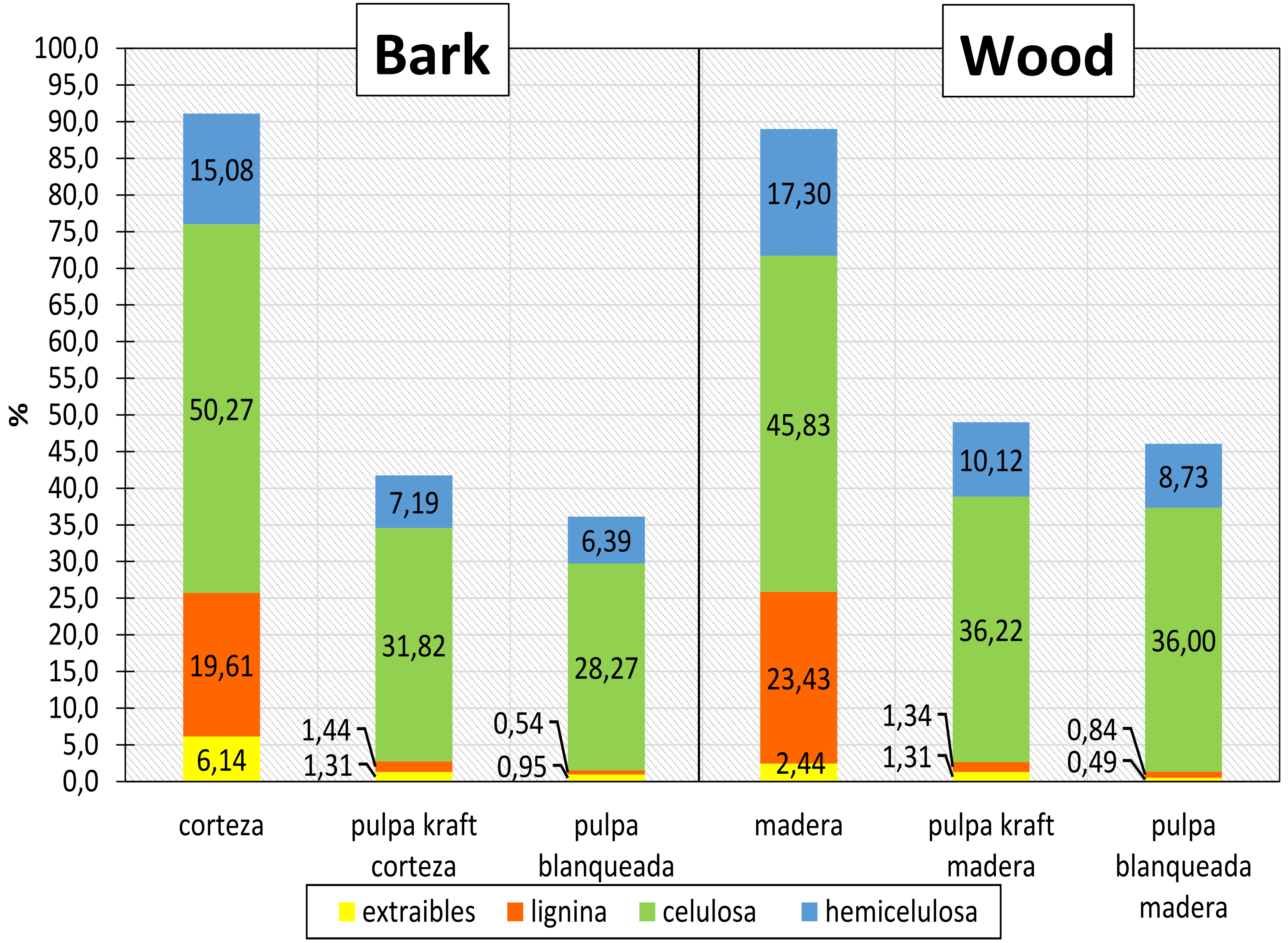


Eucalyptus globulus
Wood pulp

Eucalyptus glubulus
Bark pulp

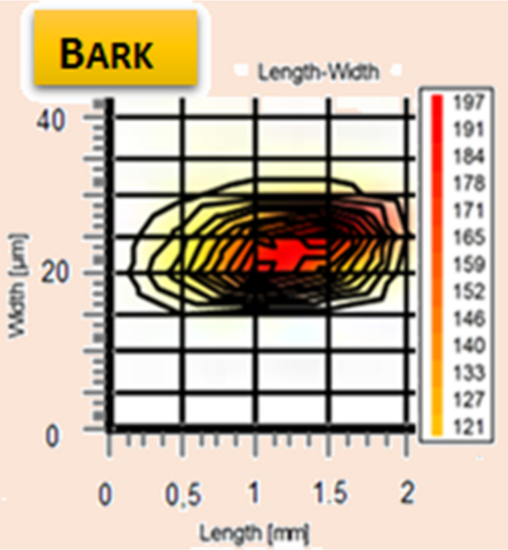


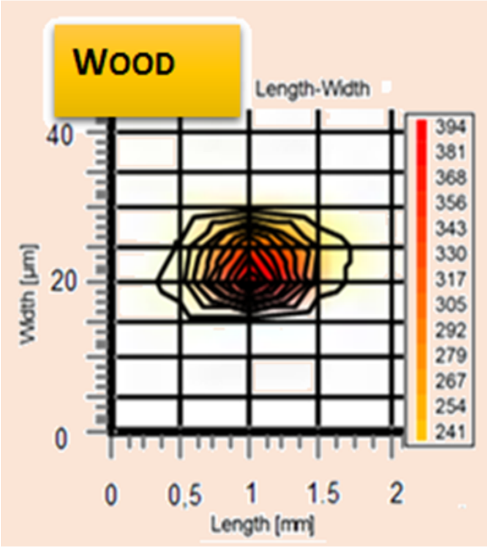
Yield of Chemical Composition of Bark and Wood kraft pulp



Morfological properties of Wood and Bark kraft pulp

	Wood	Bark
Lenght (mm)	0,86	1,06
Widht (µm)	22	20
Fine (%)	2,6	4,8





	Wood pulp		Bark pulp	
	Unbleaching	**Bleaching**	**Unbleaching**	**Bleaching**
Lenght (mm)	**0,79**	**0,79**	**0,94**	**0,94**
Widht (µm)	**20,1**	**19,9**	**21,9**	**21,1**
Fine (%)	**3,8**	**3,8**	**3,9**	**3,8**

Nanoindentation of kraft pulp.

- The wall thickness of bark fibers remain greater than the wood fibers.

	Unbleaching Bark pulp			Unbleaching Wood pulp		
	Width (μm)	H (GPa)	E (GPa)	Width (μm)	H (GPa)	E (GPa)
Average	2,9	0,3	10,7	1,86	0,28	10,6
SD	0,8	0,1	4,0	0,17	0,05	2,7
Average	1,9	0,2	9,1	1,82	0,2	9,4
SD	0,6	0,03	2,2	0,26	0,04	1,7

- The wood fibers and bark have the same modulus of elasticity and hardness.

Production of Cellulose nanofibrils CNF

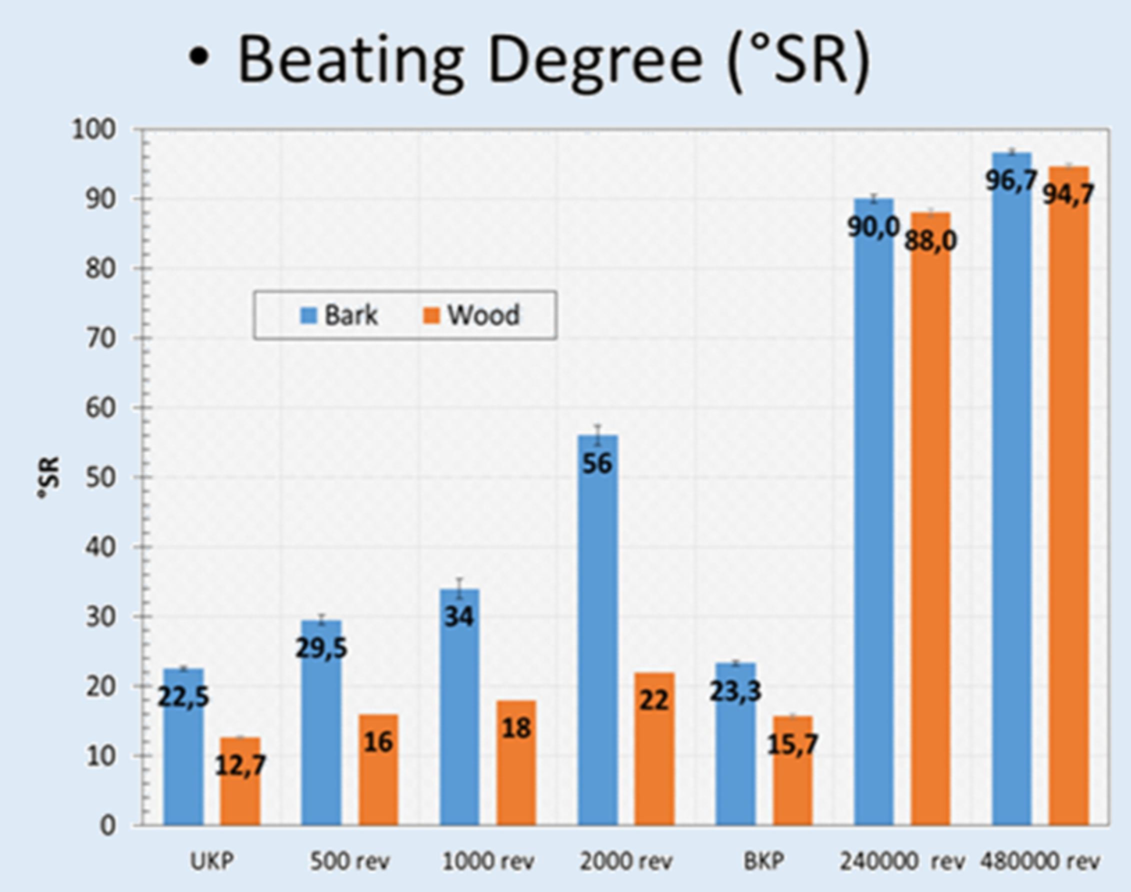
PFI Beating

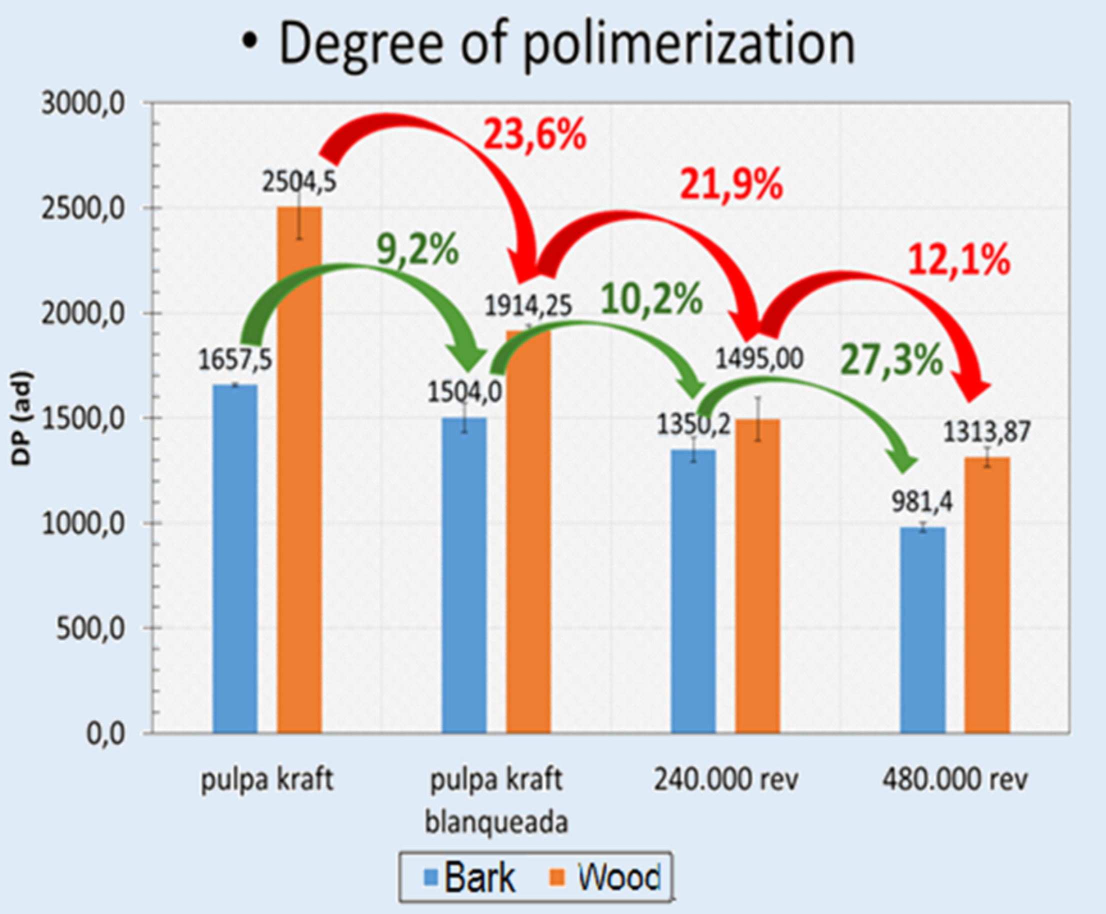
- 240000 rev
- 480000 rev

- 30 grams dry
- 10 % Consistency

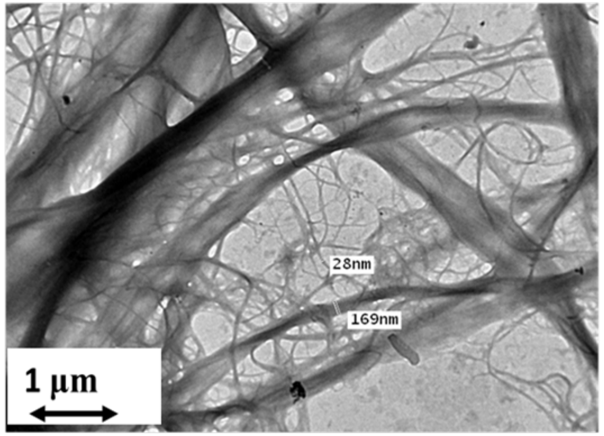
PFI - Mill

Production of Cellulose nanofibrils by PFI-Refiner

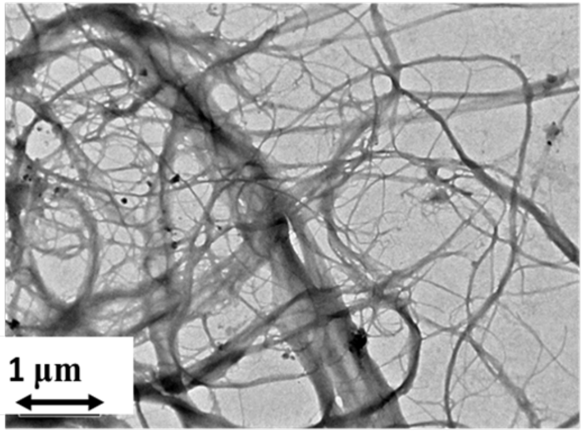




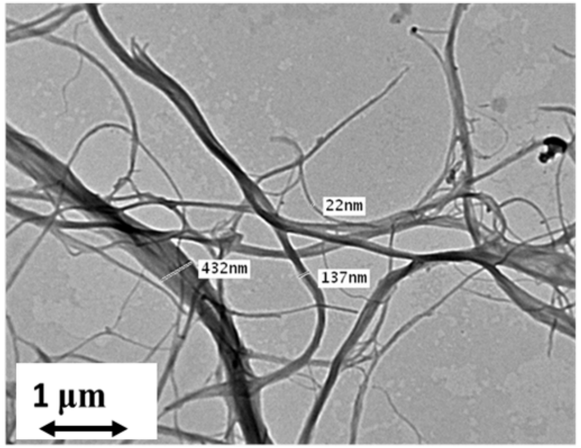
Production of Cellulose nanofibrils by PFI-Refiner



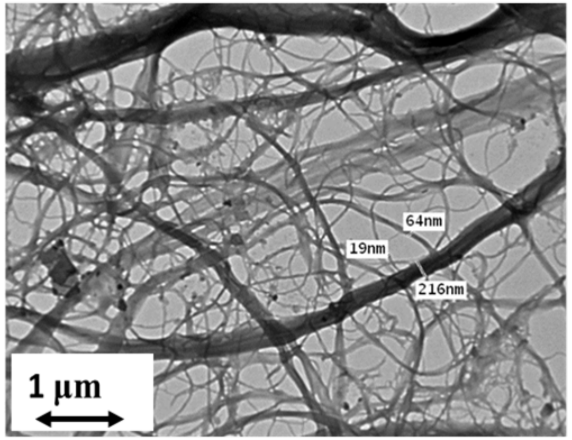
CNF from Bark pulp, 240.000 rev



CNF from Bark pulp, 480.000 rev



CNF from, Wood pulp 240.000 rev



CNF from Wood pulp 480.000 rev

- **Significant difference between NFC from Wood and bark pulp was not detected by TEM microscopy.**

- **The degree of fibrillation increased significantly between 240.000 and 480.000 PFI rev.**

Determination of rheological parameters of CNF suspensions

Measuring the apparent viscosity at constant temperature and consistency.

Power law:

$$\mu = K\gamma^{n-1}$$

Where:

μ: *is the* viscosity

γ: la shear rate

K : Consistency Index, and

n: performance index.

If:

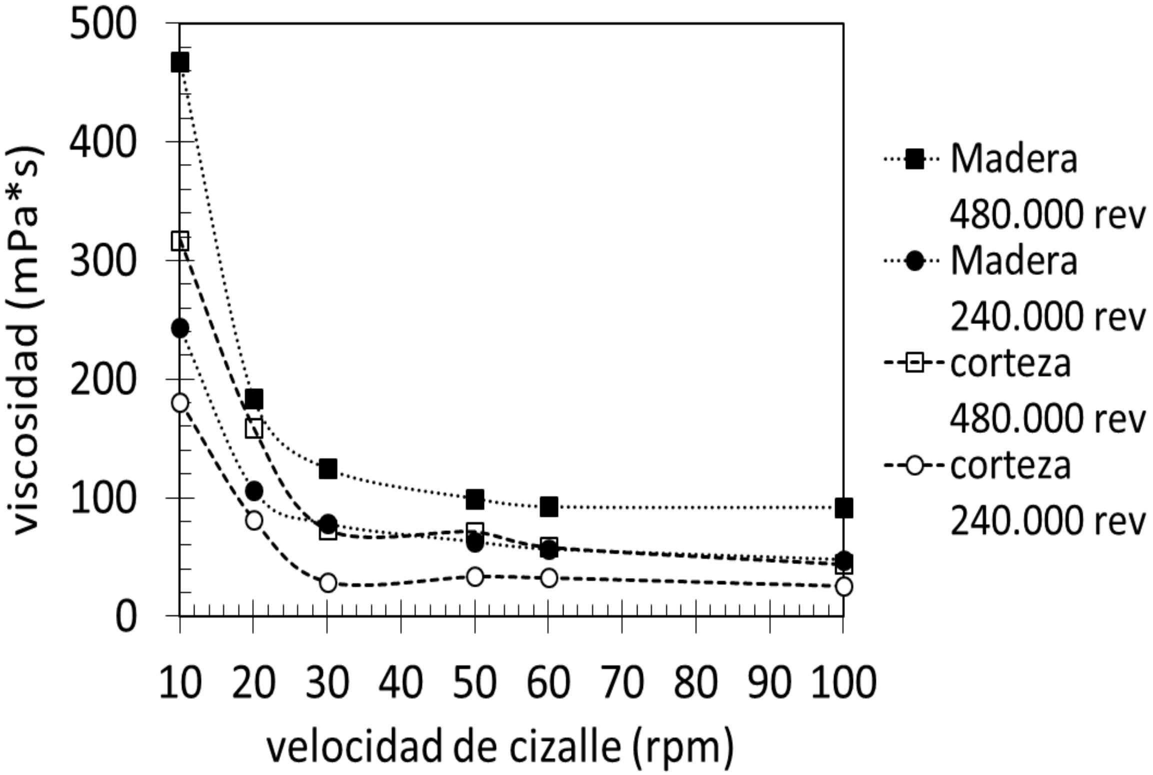
n = 1: Newtonian fluid,

n <1: pseudoplastic fluid

n> 1: Dilatant fluid

Rheological parameters of PFI- CNF suspensions

bark pulp become a high degree of fibrillation faster than wood fibers



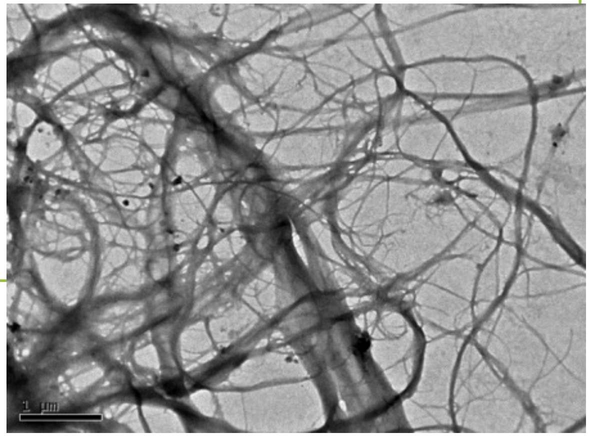
Muestra	Parámetros reológicos		R^2
	n	K	
Madera 480.000 rev	0,290	1797,5	0,861
Madera 240.000 rev	0,309	971,8	0,931
corteza 480.000 rev	0,147	1946,2	0,930
corteza 240.000 rev	0,162	940,6	0,816

pseudoplastic fluid

Lower performance index is associated with higher intensity of mechanical treatment and higher degree of fibrillation.

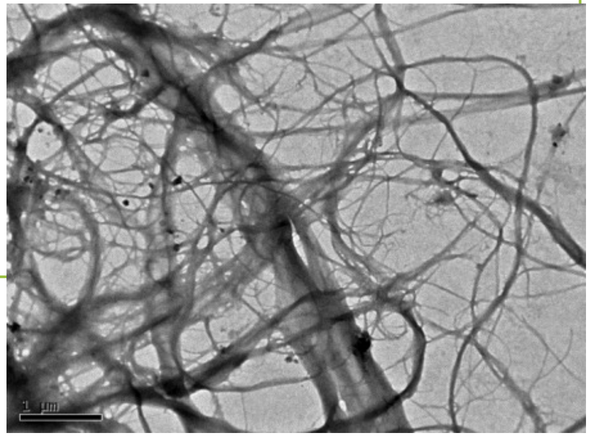
Conclusions

- Due its high cellulose content and its cell biometric characteristic, Eucalyptus bark represent a great opportunity for the production of a new products with higher add value like a paper grade fiber, cellulose derivatives products and/or for the production of nanofibrillated cellulose.



conclusions

- Biorefinery of Eucalyptus bark represent a great opportunity to take advantage of a side stream of the chain value of the chilean forestry industry.



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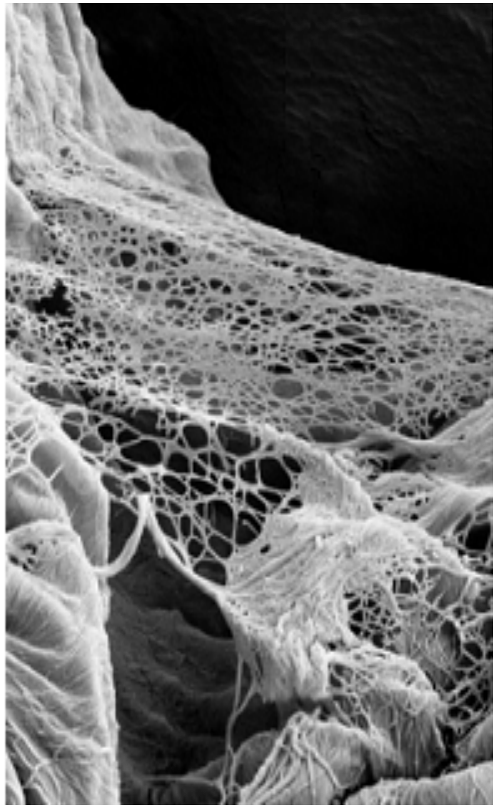

Bárbara Martínez, Carolina Puentes, Juan Pedro Elissetche, Regis Teixeira and **Miguel Pereira**.

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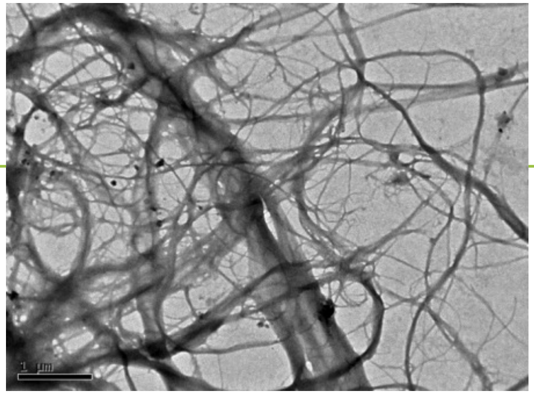
Departamento de Ingeniería Química
Facultad de Ingeniería
Universidad de Concepción

conclusions

- The performance of kraft pulp of Eucalyptus bark and its response during the beating and homogenizer mechanical suggest the use as fiber and/or for the production of nanofibrillated cellulose.



Acknowledgements

- The authors acknowledge the support of CORFO-Chile 13IDL2-18588 project and FPC (Forestal y Papelera Concepción) Company for financial support.
- The authors also acknowledge the support of the CBT and UDT research centers of the University of Concepción.

Production of Cellulose nanofibrils by TEMPO-Homogenizator

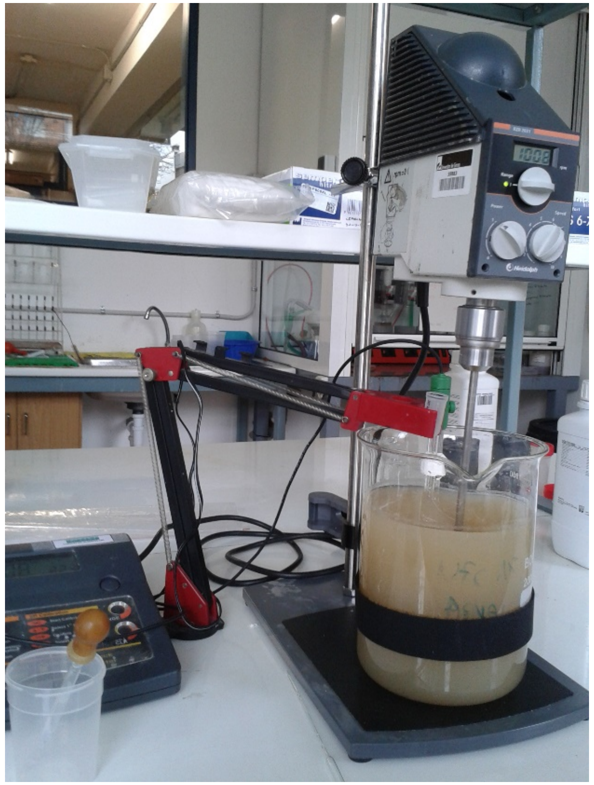
TEMPO mediated oxidation

- 3 mmol sodium hypochlorite / g and cellulose
- 5 mmol sodium hypochlorite / g and cellulose

TEMPO

- pH=10
- 0,016 gr TEMPO/g cellulose
- 0,1 gr NaBr/gr cellulose
- constant stirring.

pH control by NaOH 0,5 M addition.



Saito, T., Y. Nishiyama, and A. Isogai. Biomacromolecules, 2006. **7**(6): p. 1687-1691.

HOMOGENIZATION

Obtention of CNF

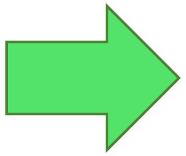
- 1 passed
- 4 passed

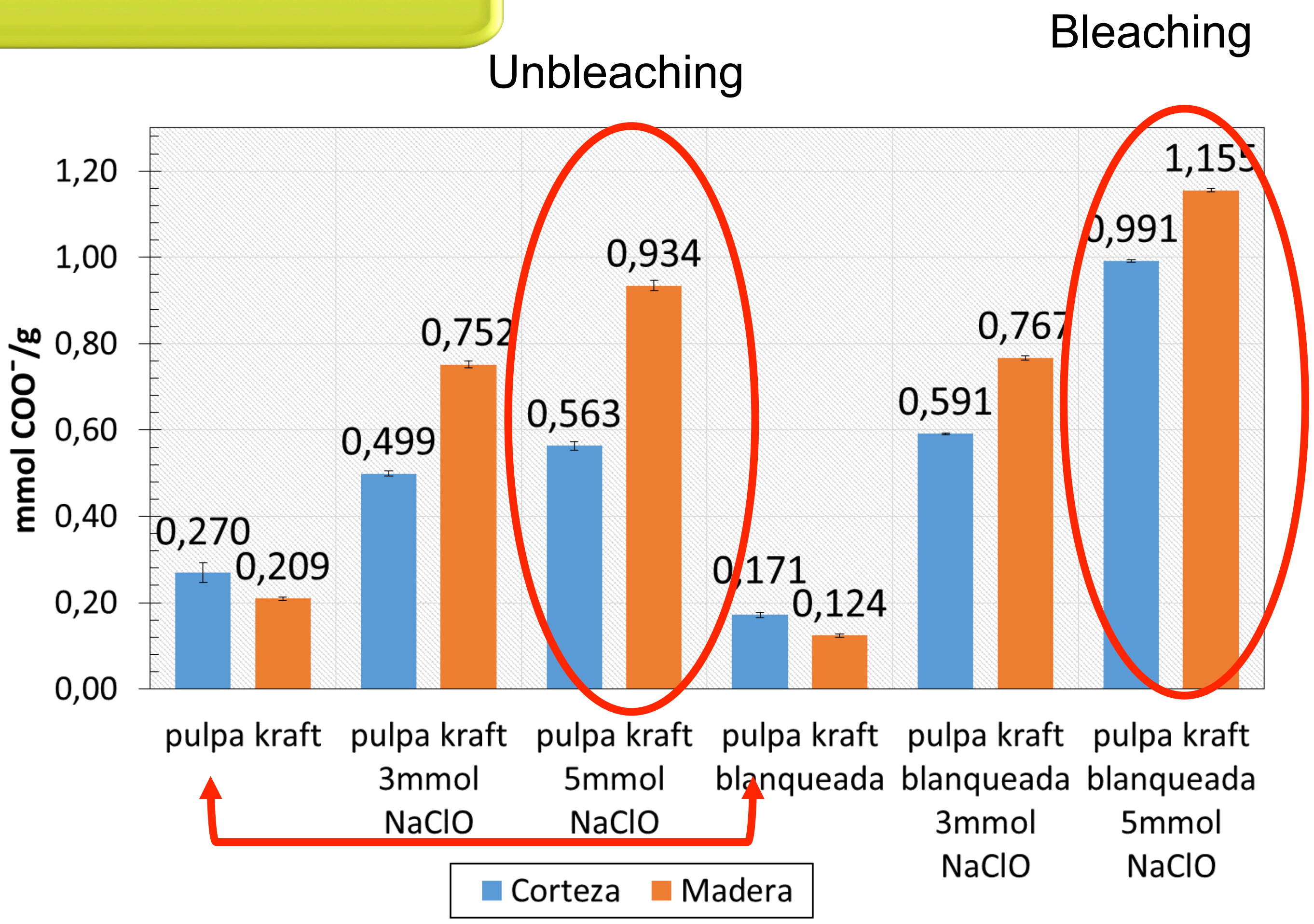
- 1% Consistency
- 600 - 800 bar

Carboxylic groups Determination

conductometric titration

(Saito,2006).





- **Unbleached pulp contains higher amount of carboxylate groups that bleached pulps.**
- **After oxidation, bleached pulp have higher amount of carboxylate groups that bleached pulps.**

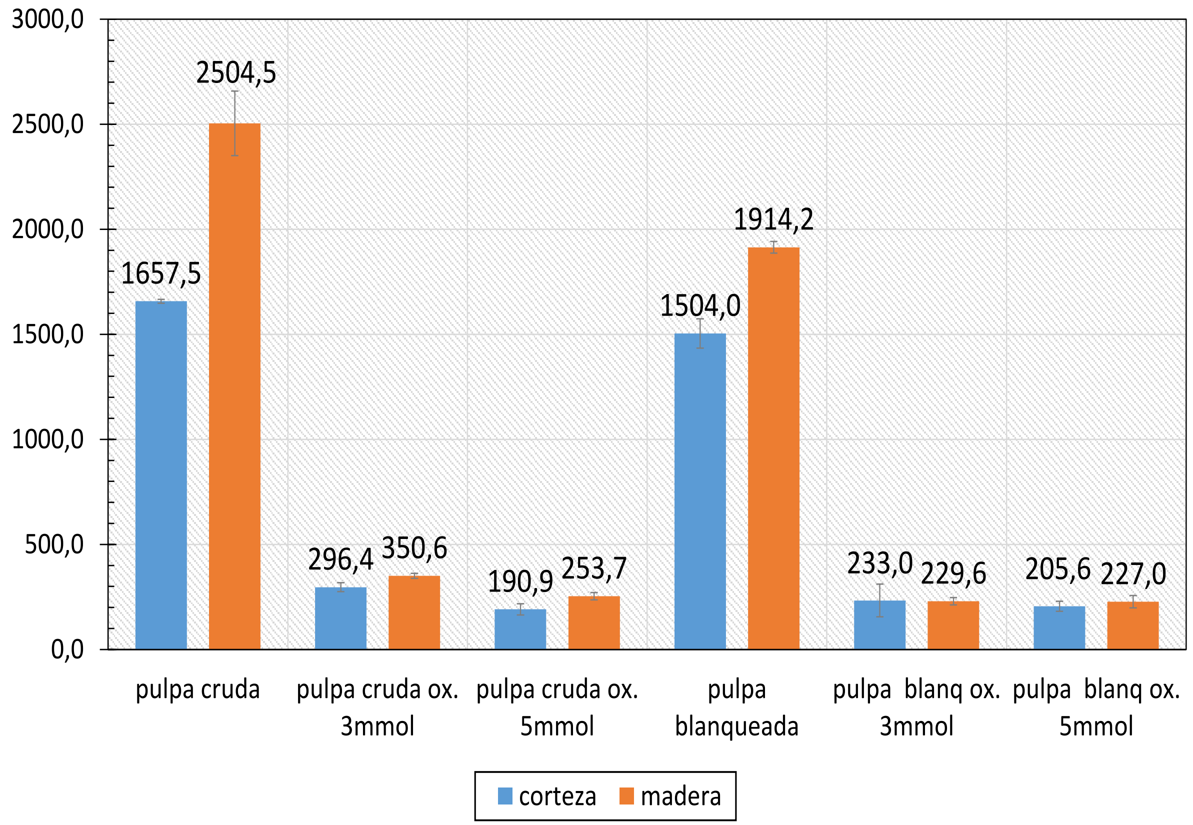
Saito, T., Y. Nishiyama, and A. Isogai,. Biomacromolecules, 2006. **7**(6): p. 1687-1691.

Degree of polymerization

From Henriksson (2007):

$$\eta = 2{,}28 \cdot DP^{0{,}76}$$

DP is related to the intrinsic viscosity, which is measured according to ISO 5351-2010. in a Ostwald type viscometer.

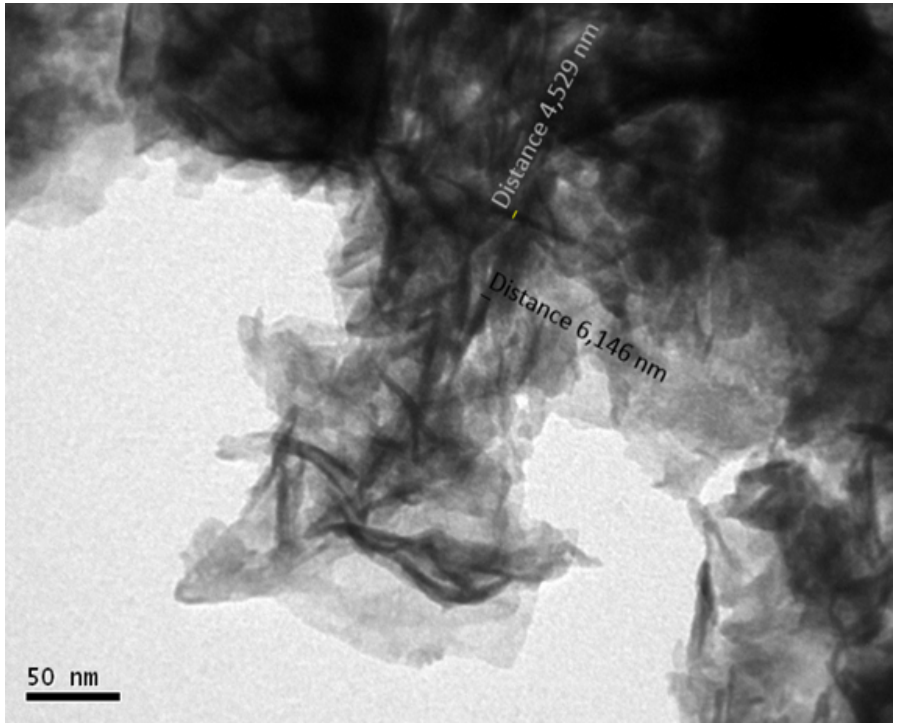


The degree of polymerization decreases drastically after TEMPO Oxidation reaction.

Henriksson, M., G. Henriksson, and T. Lindström, Europ. Polym, 2007. **43**: p. 3434-3441.

TEM microscopy of nanofibrils obteined by TEMPO

Imagen TEM



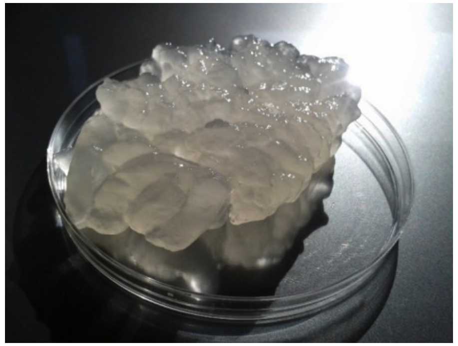


Figura 1: MCF pulpa corteza blanqueada oxidada con 5mmol de NaClO. 4 pasadas 600 bar

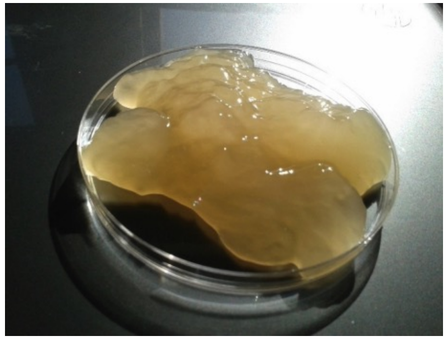


Figura 2: MCF pulpa corteza no blanqueada oxidada con 5mmol de NaClO. 4 pasadas 600 bar

Figura MCF pulpa madera blanqueada oxidada con 5mmol de NaClO. 4 pasadas 600 bar

Figura MCF pulpa madera no blanqueada oxidada con 5mmol de NaClO. 4 pasadas 600 bar

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