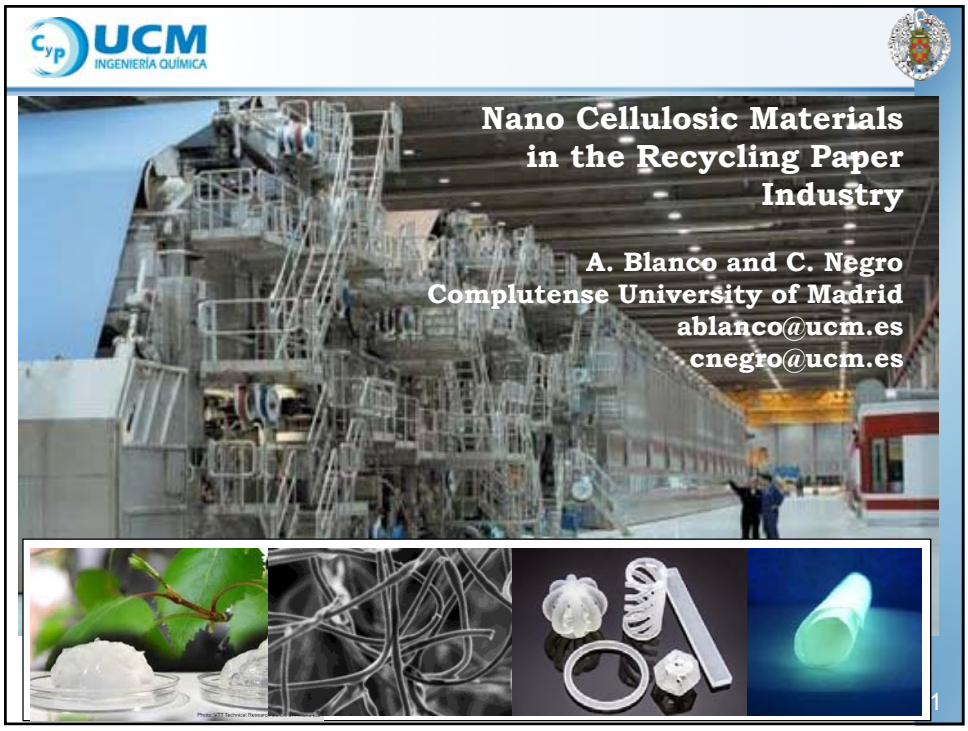
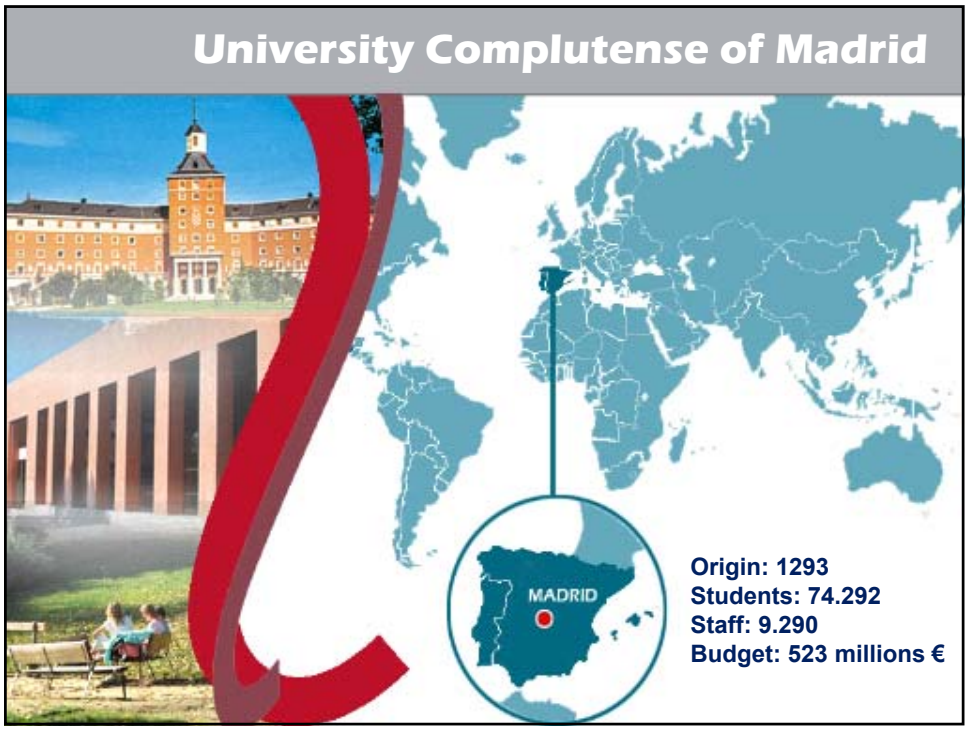
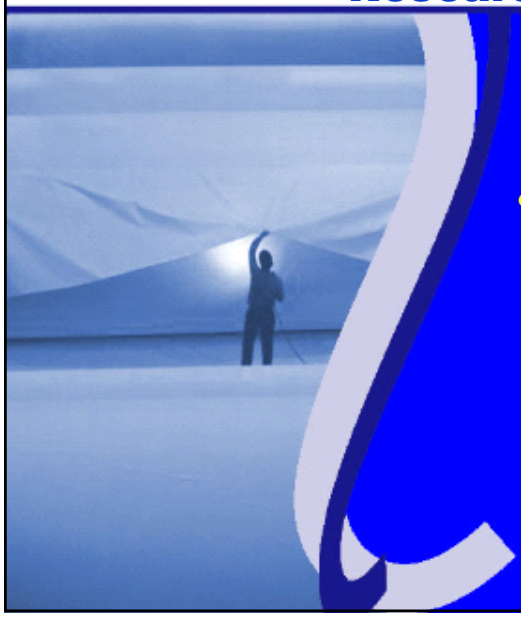

UCM
INGENIERÍA QUÍMICA
Nano Cellulosic Materials in the Recycling Paper Industry
A. Blanco and C. Negro
Complutense University of Madrid
ablanco@ucm.es
cnegro@ucm.es
1


University Complutense of Madrid
MADRID
Origin: 1293
Students: 74.292
Staff: 9.290
Budget: 523 millions €

Cellulose, Paper & Water Research Group



Its activities are conducted in two lines: Fundamental Research and the Applied Research, in order to enhance the technical and scientific expertise of the industry. The Fundamental Research is devoted to the acquisition of new knowledge and the fundamental understanding of the phenomena taking place during pulp and papermaking. On the other hand, the Applied Research is devoted to the application of these knowledge to solve the needs of the industry and suppliers.

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World is looking for more sustainable raw materials

Incentives for Manufacturing Industry

- New source of raw material with wide, largely unexplored range of applications
  - New products

Nano cellulose

A world of sustainable possibilities

Nature-based material

Huge applications

Monash, 28th August 2018

4

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NANO

CELLULOSE

Why nano?

The size reduction enables new opportunities for the development of innovative nano systems and nanostructured materials

Particle of any shape with dimensions < than 100 nm

- ❑ Very strong
- ❑ Large specific area
- ❑ Highly reactive
- ❑ Less Defect
- ❑ Thermal stability
- ❑ Unique optical, electrical, magnetic properties

Why cellulose?

A sustainable material: high availability, natural & renewable, economic, non-toxic, biocompatibility and biodegradability

- ❑ High strength & modulus
- ❑ Flexible
- ❑ Lightweight material
- ❑ Electrically charged
- ❑ Chemically reactive
- ❑ Dimension stability
- ❑ Water absorption
- ❑ Barrier properties
- ❑ High aspect ratio
- ❑ Transparent and translucent
- ❑ Builds network structures

5

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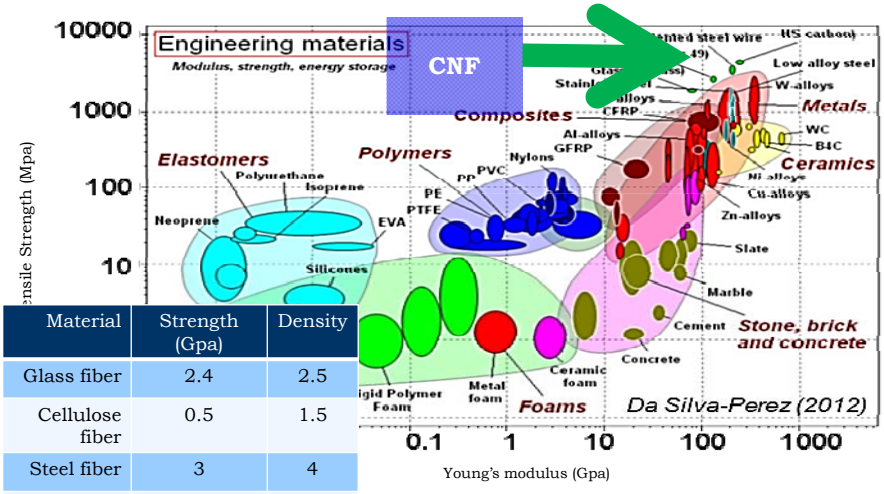
Nanocellulose Materials

At the nano-scale, the material has fewer defects, and is therefore stronger



Material	Strength (Gpa)	Density
Glass fiber	2.4	2.5
Cellulose fiber	0.5	1.5
Steel fiber	3	4
CNC	10	1.5
CNF	9-10	1.5

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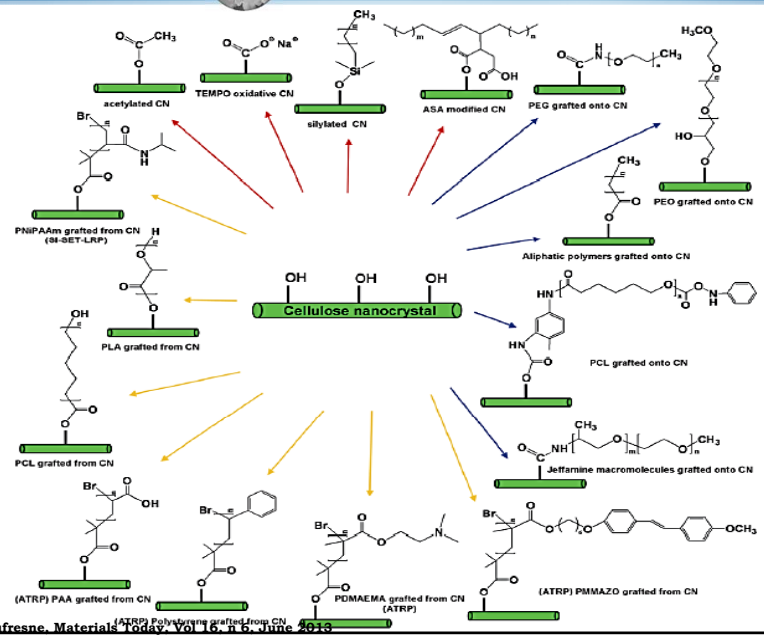
Nanocellulose Materials



Alain Dufresne. Materials Today. Vol 16. n 6. June 2013

Nanocellulose Materials

PULP SUSPENSION PRODUCTION

Chemical treatments:
- cooking
- bleaching

Mechanical treatments:
Recycling Treatments

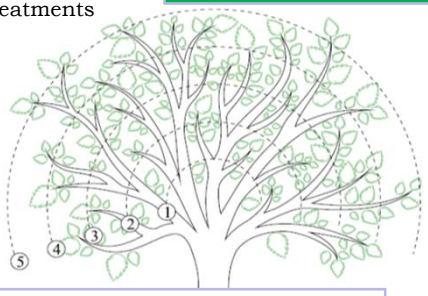
➢ **50 types of CNF**

CNF PRODUCTION

Pre-treatments:
TEMPO oxidation
carboxylation
carboxymethylation
sulfonation
enzymatic hydrolisis

Mechanical treatment:
- homogenization
- microfluidization
- refining
- grinding
- electrospinning
- cryocrushing
- ultrasonication
- steam explosion

Post-treatments:
- chemical modification
- fractionation



1 raw material
(wood, plants, agricultural wastes…)

Adapted from Nechyporchuk et al. Ind. Crops & Prod., 2016

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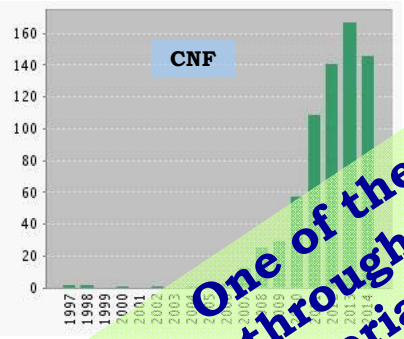
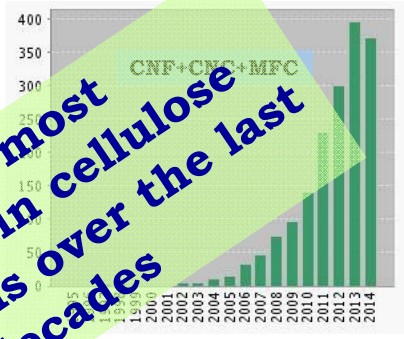
NANOCELLULOSE EVOLUTION
INTEREST OF SCIENTIFIC COMMUNITY





One of the most breakthrough in cellulose based materials over the last two decades

Increasing interest in nanocellulose can be seen from the exponential rise in the scientific reports dealing with nanofibrillated cellulose and cellulose nanocrystals since 2000

Nanocellulose is unique among nanomaterials due to it is bio-based, renewable, biodegradable, non-toxic.

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Source: ISI web of knowledge

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NANOCELLULOSE APPLICATIONS

MEDICINE

PHARMACEUTICAL INDUSTRY

BIOLOGY

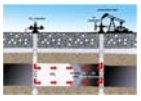
FOOD INDUSTRY

NANOCOMPOSITES

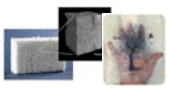
LABORATORY

PAINTS AND RESINS

OIL INDUSTRY



POROUS MATERIALS & FILMS



HYGIENE AND ABSORBENT PRODUCTS

PAPER & BOARD INDUSTRY

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10

Nanocellulose Materials

- Cellulose nano-objects
- Cellulose nanomaterials (CN)
- Nanofibrillated cellulose (NFC)
- Nanofibrillar cellulose (NFC)
- Microfibrillated cellulose (MFC)
- Microfibrillar cellulose (MFC)
- Cellulose microfibril (CMF)
- Cellulose nanofibre
- Cellulose nano
- Cellulose
- Cell aterials
- se (NCC)
- rticles (CNP)
- icrocrystal (CMC)
- se nanowhiskers (CNW)
- Bacteria Nanocellulose

ISO/TS 20477:2017 Nanotechnologies
Standard terms and their definition for cellulose nanomaterial

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Cellulose Nanofibril (CNF)

Cellulose (3.2.4) nanofibre (3.1.6) composed predominantly of cellulose and composed of at least one elementary fibril (3.2.5), containing crystalline (3.2.1), paracrystalline (3.2.3) and amorphous (3.2.2) regions, with aspect ratio usually greater than 10, which may contain longitudinal splits, entanglement between particles, or network-like structures

- **The dimensions are typically 3-100 nm in cross-section and typically up to 100 µm in length.**
- **The terms nanofibrillated cellulose (NFC), nanofibrillar cellulose (NFC), microfibrillated cellulose (MFC), microfibrillar cellulose (MFC), cellulose microfibril (CMF) and cellulose nanofibre (CNF) have been used to describe cellulose nanofibrils produced by mechanical treatment of plant materials often combined with chemical or enzymatic pre-treatment steps.**

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Cellulose Nanocrystal (CNC)

Nanocrystal (3.1.7) predominantly composed of cellulose (3.2.4) with at least one elementary fibril (3.2.5), containing predominantly crystalline (3.2.1) and paracrystalline (3.2.3) regions, with aspect ratio of usually less than 50 but usually greater than 5, not exhibiting longitudinal splits, inter-particle entanglement, or network-like structures

- **The dimensions are typically 3-50 nm in cross-section and 100 nm to several µm in length depending on the source of the cellulose nanocrystal.**
- **Historically cellulose nanocrystals have been called nanocrystalline cellulose (NCC), whiskers such as cellulose nanowhiskers (CNW), and microfibrils such as cellulose microfibrils; they have also been called spheres, needles or nanowires based on their shape, dimensions and morphology; other names have included cellulose micelles, cellulose crystallites and cellulose microcrystals.**

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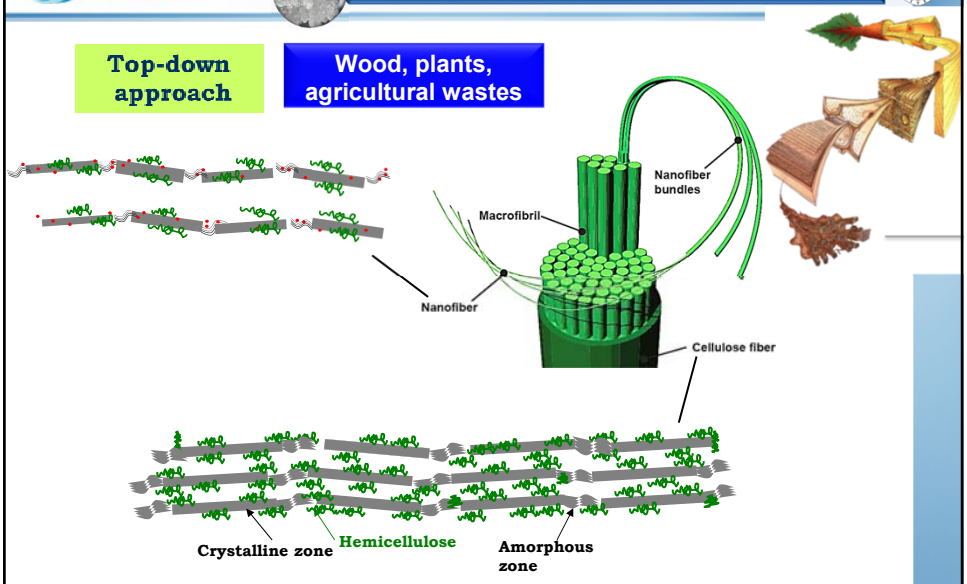
Nanocellulose Materials

Top-down approach

Wood, plants, agricultural wastes



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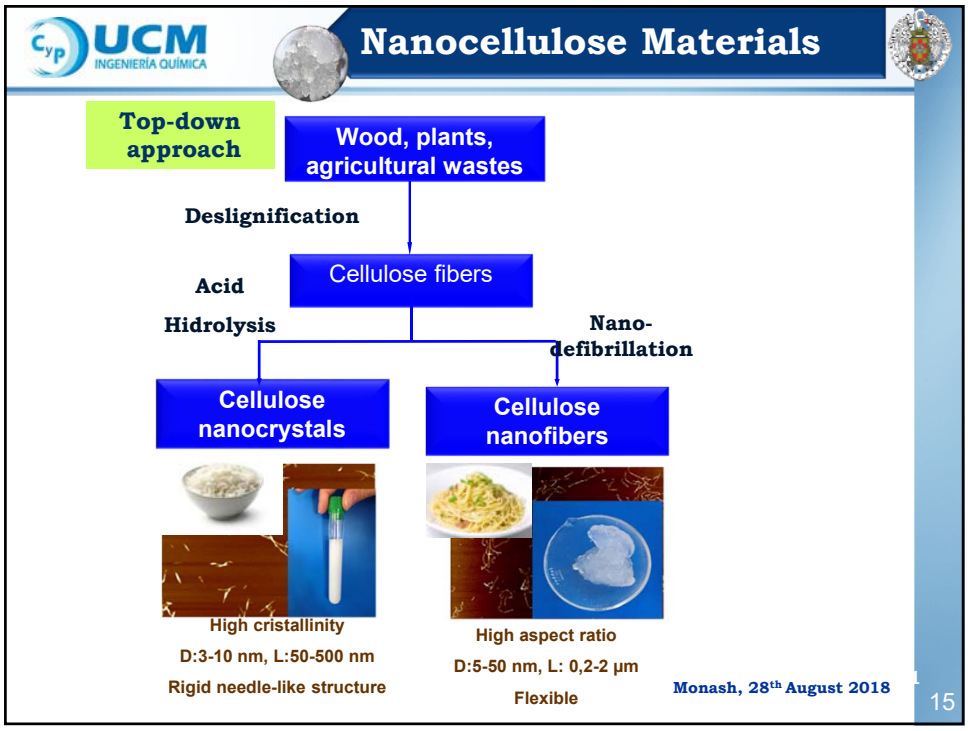
14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INGENIERÍA QUÍMICA
Nanocellulose Materials
Top-down approach
Wood, plants, agricultural wastes
Deslignification
Acid Hidrolysis
Cellulose fibers
Nano-defibrillation
Cellulose nanocrystals
Cellulose nanofibers
High cristallinity
D:3-10 nm, L:50-500 nm
Rigid needle-like structure
High aspect ratio
D:5-50 nm, L: 0,2-2 µm
Flexible
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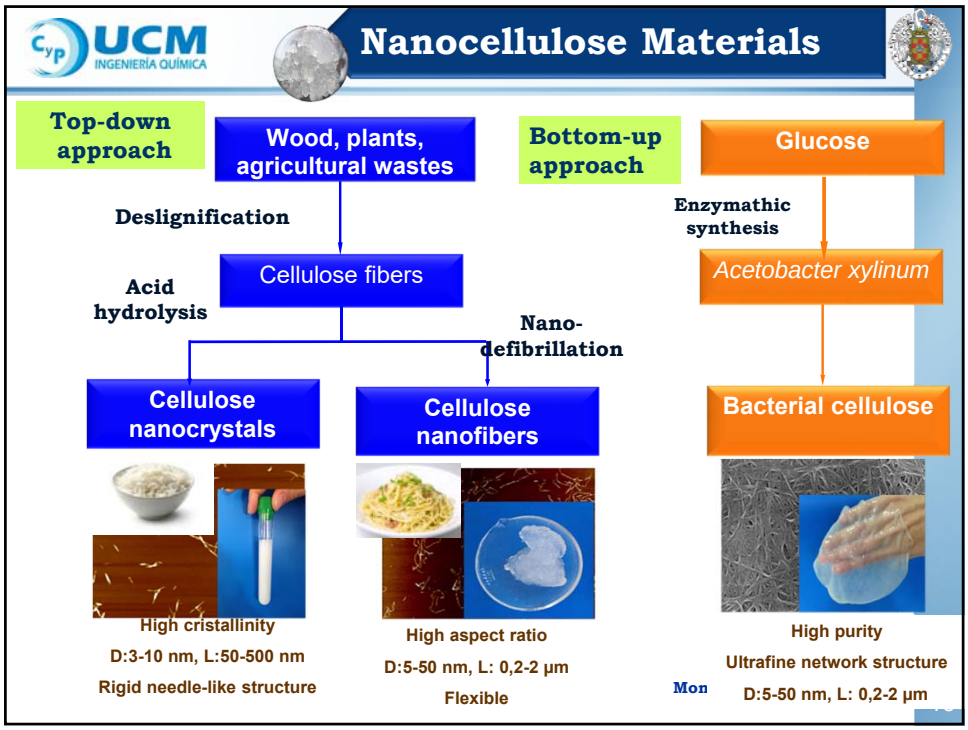
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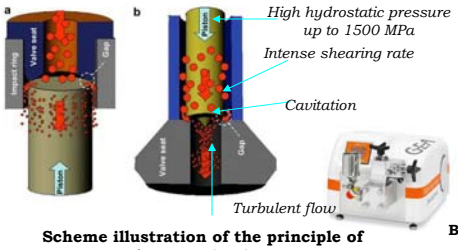
Nanocellulose Materials
Top-down approach
Wood, plants, agricultural wastes
Bottom-up approach
Glucose
Deslignification
Enzymathic synthesis
Acetobacter xylinum
Acid hydrolysis
Cellulose fibers
Nano-defibrillation
Cellulose nanocrystals
Cellulose nanofibers
Bacterial cellulose
High cristallinity
D:3-10 nm, L:50-500 nm
Rigid needle-like structure
High aspect ratio
D:5-50 nm, L: 0,2-2 µm
Flexible
High purity
Ultrafine network structure
D:5-50 nm, L: 0,2-2 µm
Mon

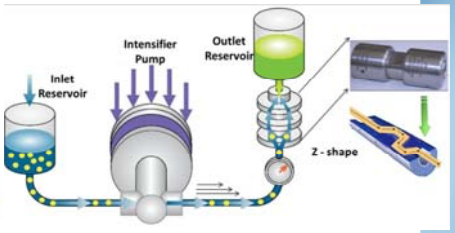
Top-down
Conventional Mechanical Treatments for CNF production

Homogenizer



Scheme illustration of the principle of homogenization lab-scale homogenizer (GEA niro-soavi),

Microfluidizer



Basic concept of the single pump microfluidizer functionning

Refining

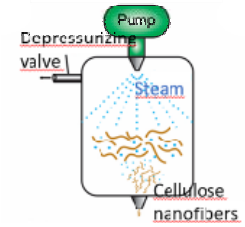
Grinding

Masuko

Blanco et al, Handbook of Nanomaterials for industrial applications. Chapter 5, Elsevier, 2018

Top-down
Non-conventional Mechanical Treatments for CNF production

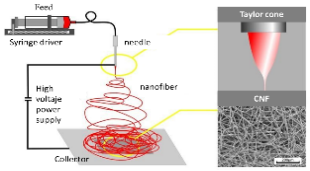
Steam Explosion



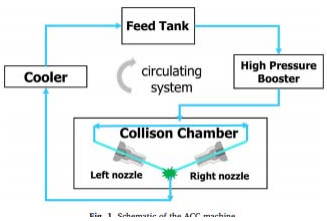
High power ultrasonication

High speed desintegration: Rotor-stator

Electrospinning



Aqueous counter collision

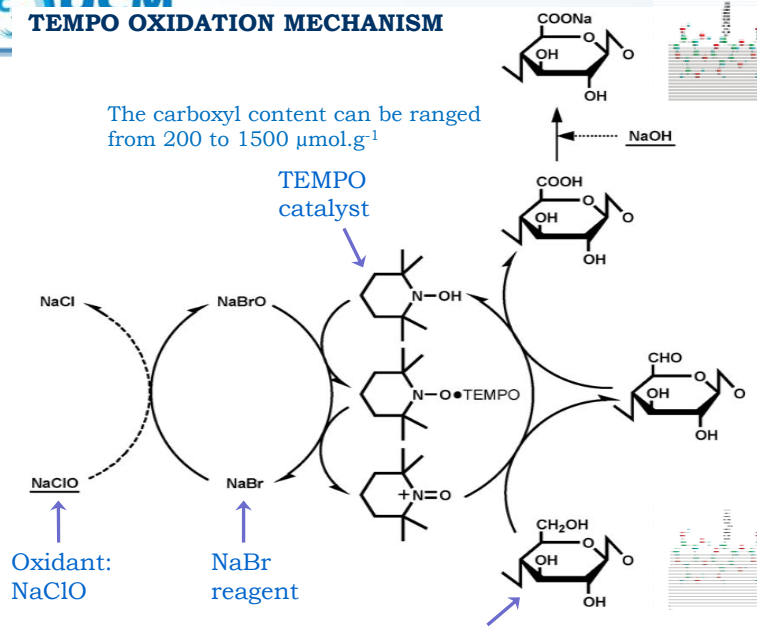


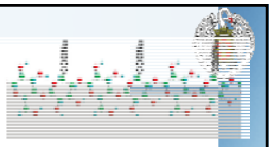
Easier approach but requires fibers preatrement

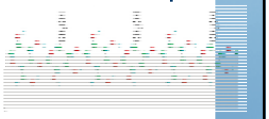
Blanco et al, Handbook of Nanomaterials for industrial applications. Chapter 5, Elsevier, 2018

TEMPO OXIDATION MECHANISM

The carboxyl content can be ranged from 200 to 1500 µmol.g^{-1}







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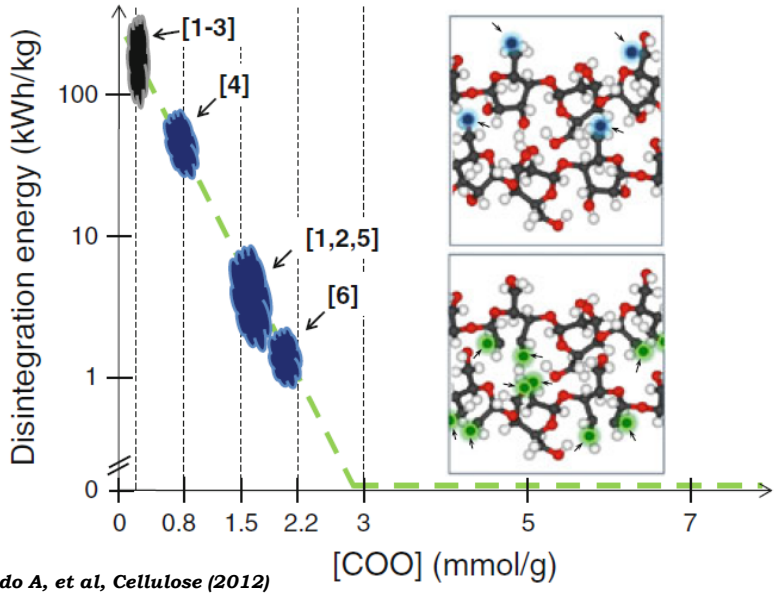

Tejado A, et al, Cellulose (2012)

20


2018
21

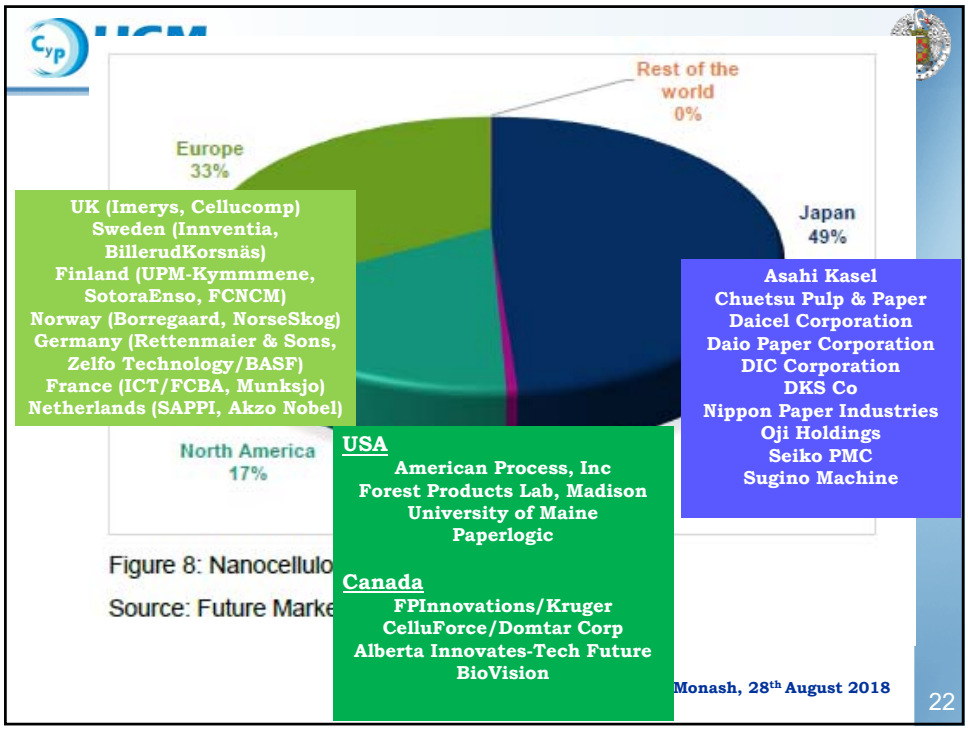
Rest of the world 0%
Europe 33%
Japan 49%
North America 17%
UK (Imerys, Cellucomp)
Sweden (Innventia, BillerudKorsnäs)
Finland (UPM-Kymmmene, SotoraEnso, FCNCM)
Norway (Borregaard, NorseSkog)
Germany (Rettenmaier & Sons, Zelfo Technology/BASF)
France (ICT/FCBA, Munksjo)
Netherlands (SAPPI, Akzo Nobel)
USA
American Process, Inc
Forest Products Lab, Madison
University of Maine
Paperlogic
Canada
FPInnovations/Kruger
CelluForce/Domtar Corp
Alberta Innovates-Tech Future
BioVision
Asahi Kasel
Chuetsu Pulp & Paper
Daicel Corporation
Daio Paper Corporation
DIC Corporation
DKS Co
Nippon Paper Industries
Oji Holdings
Seiko PMC
Sugino Machine
Figure 8: Nanocellulo
Source: Future Marke
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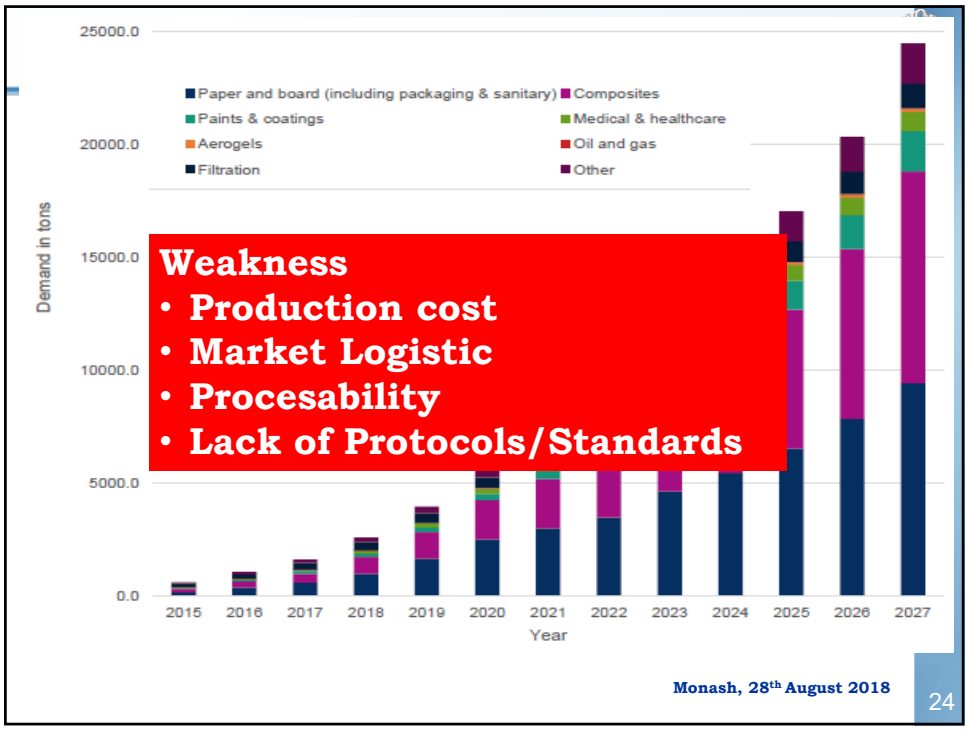
Table 4: Current and planned production capacities, by major suppliers, pilot/pre-commercial and commercial volumes.

	Pilot/Pre-commercial (tons)	Commercial (tons)
American Process	150	
Asahi Kasei		2,000
Borregaard	150	50,000
Cellucomp	150	2,000
Chuetsu Pulp & Paper Co.		100
Daio Paper	10	
Daicel Corporation	10	
DIC	150	
DKS		50
Kruger	250	
Innventia AB	1000	
Nippon Paper	10	500
Oji Paper	40	
Paper Logic		500
Seiko PMC	30	
Stora Enso	300	
Sugino Machine Limited		50
	2250	**55,200**

Source: Future Markets.

23



Weakness

- **Production cost**
- **Market Logistic**
- **Procesability**
- **Lack of Protocols/Standards**

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CNF Price

Company	NFC Gel/ NFC Slurry/MFC	Price range/kg	Main target markets
American Process	Gel	$100-$500	• Adhesives. • Rheology modifiers.
	Slurry	$100-$150	• Composites.
Asahi Kasei	Slurry	<$100	• Filters. • Films.
Borregaard Chemcell	MFC Slurry	<$100	• Adhesives. • Detergents. • Cosmetics. • Composites. • Paints and coatings. • Rheology modification.
Cellucomp	Slurry	<$50	• Paints and coatings
Chuetsu Pulp & Paper	Slurry	<$100	• Composites.
Daicel Corporation	Slurry	$100-$500	• Rheology modification. • Packaging.
Daio Paper Corporation	Slurry	$100-$500	• Packaging.
DIC Corporation	Slurry	<$100	• Packaging.
DKS Co.Ltd.	Slurry	$500-$1000	• Rheology modification.
Imerys	MFC slurry.	<$100	• Paper. • Packaging. • Composites.

CNF Price

Company	NFC Gel/ NFC Slurry/MFC	Price range/kg	Main target markets
Innventia	Slurry.	<$100	- Paper. - Packaging. - Composites.
Kruger Biomaterials, Inc.	Cellulose filaments	<$100	- Paper. - Packaging. - Composites. - Textiles - Rheology modification.
Nippon Paper Industries	Slurry	$500-$1000	- Paper. - Packaging. - Composites. - Rheology modification.
Oji Holdings	CNF slurries, CNF wet powder and CNF sheets	<$100	- Paper. - Packaging. - Composites. - Electronics. - Rheology modification.
Paperlogic	Slurry	<$100	- Paper. - Packaging. - Composites.
Seiko PMC	Slurry	<$100	- Composites. - Paper.
Stora Enso	MF/NFC slurry.	<$100	- Paper. - Packaging.
Sugino Machine	Slurry.	$1000/kg (export)	- Paper. - Packaging. - Composites. - Rheology modification.
University of Maine	Slurry	CNF slurry:<$100 Tempo CNF slurry: >$1000	- Paper. - Packaging. - Composites.
US Forest Service FPL	Slurry	CNF slurry:<$50 Tempo CNF slurry: $1200	- Packaging. - Composites. - Rheology modification.
VTT	Slurry Gel	Not known.	- Packaging. - Composites. - Rheology modification. - Electronics.
Zelfo Technology	Slurry	<$100	- Packaging.

Lab Prices

2018 Cellulose Lab Nano & Micro Products Price www.CelluloseLab.com

Product Series	Cellulose Lab Catalog Number	Product	Form	Small Package Order		Large Package Order		Extra Large Order
				Size (oven-dry weight basis)	Cost, USD per gram (oven-dry weight)	Size (oven-dry weight basis)	Cost, USD per gram (oven-dry weight)	
NFC series (Cellulose Nanofibrils or nano fibrillated cellulose) or MFC series (micro fibrillated cellulose)	CNF-Slurry	Cellulose Nanofibrils	Slurry, 3.0% solids	1 g — 500 g	$2.00	501 g —5 kg	$1.75	Please contact us
	CNF-FD	Cellulose Nanofibrils Freeze-dried	Dry	1 g — 200 g	$6.00	201 g — 2 kg	$5.50	
	CNF-CM-Slurry	Carboxymethylated Cellulose Nanofibrils	Slurry, 0.5% - 7% solids	1 g — 60 g	$15.00	61 g — 1 kg	$12.00	
	CNF-CM-FD-P	Carboxymethylated Cellulose Nanofibrils, Freeze-dried, Pulp material	Dry	1 g — 60 g	$15.00	61 g — 1 kg	$12.00	
	CNF-CM-SD-C	Carboxymethylated Cellulose Nanofibrils, Spray-dried, Cotton material	Dry	1 g — 30 g	$20.00	31 g — 1 kg	$15.00	
	CNF-CM-SD-S	Carboxymethylated Cellulose Nanofibrils, Spray-dried, Sisal material	Dry	1 g — 30 g	$25.00	31 g — 1 kg	$20.00	
	CNF-Cationic	Cationic type Cellulose Nanofibrils	Slurry, 0.5% - 7% solids	1 g — 60 g	$20.00	61 g — 1 kg	$17.50	
	CNF-TEMPO-FD	TEMPO (Anionic type) Cellulose Nanofibrils Powder	Dry	1 g — 30 g	$25.00	31 g — 1 kg	$20.00	
	CNF-TEMPO-S	TEMPO (Anionic type) Cellulose Nanofibrils Slurry	Slurry, 0.5% - 7% solids	1 g — 60 g	$20.00	61 g — 1 kg	$17.50	
NCC (or CNC) series (Nanocrystalline Cellulose or Cellulose Nanocrystals)	CNC-Slurry	Cellulose Nanocrystals, acid hydrolysis	Slurry, 11.8% solids	1 g — 500 g	$3.00	501 g —5 kg	$2.50	
	CNC-FD	Cellulose Nanocrystals Freeze-dried	Dry	1 g — 200 g	$6.00	201 g — 1 kg	$5.50	
	CNC-SD	Cellulose Nanocrystals Spray-dried	Dry	1 g — 200 g	$6.00	201 g — 1 kg	$5.50	
	CNC-CM-SD	Carboxymethylated Cellulose Nanocrystals, Spray-dried, Pulp material	Dry	1 g — 100 g	$10.00	101 g — 1 kg	$8.00	
	CNC-Cationic	Cationic type Cellulose Nanocrystals	Slurry, 1% - 7% solids	1 g — 30 g	$25.00	31 g — 1 kg	$20.00	
	CNC-TEMPO	TEMPO (Anionic type) Cellulose	Slurry, 1% - 7% solids	1 g — 30 g	$25.00	31 g — 1 kg	$20.00	

https://www.celluloselab.com/wp-content/uploads/2016/03/CelluloseLab-Product-Price-List-2018.htm

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Market – SWOT Analysis

Strengths
- Bio-Renewable
- Safety
- Outstanding properties
- Production

Weaknesses
- Not cost competitive
- Market
- Procesability
- Lack of protocols/standards

Opportunities
- Increase demand for environmental friendly products
- Wide end users market
- High volume end users market
- Development of new products

Threats
- Public aceptance
- Industry perception
- Production process, up scaling and product integration
- Slow progress in standard and legislation

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PROCESABILITY

MEDICINE

PHARMACEUTICAL INDUSTRY

BIOLOGY

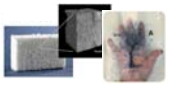
FOOD INDUSTRY

RECYCLING PAPER AND BOARD INDUSTRY

NANOCOMPOSITES

LABORAT

POROUS MATERIALS & FILMS



HYC ABS

- Strength enhacement, linting

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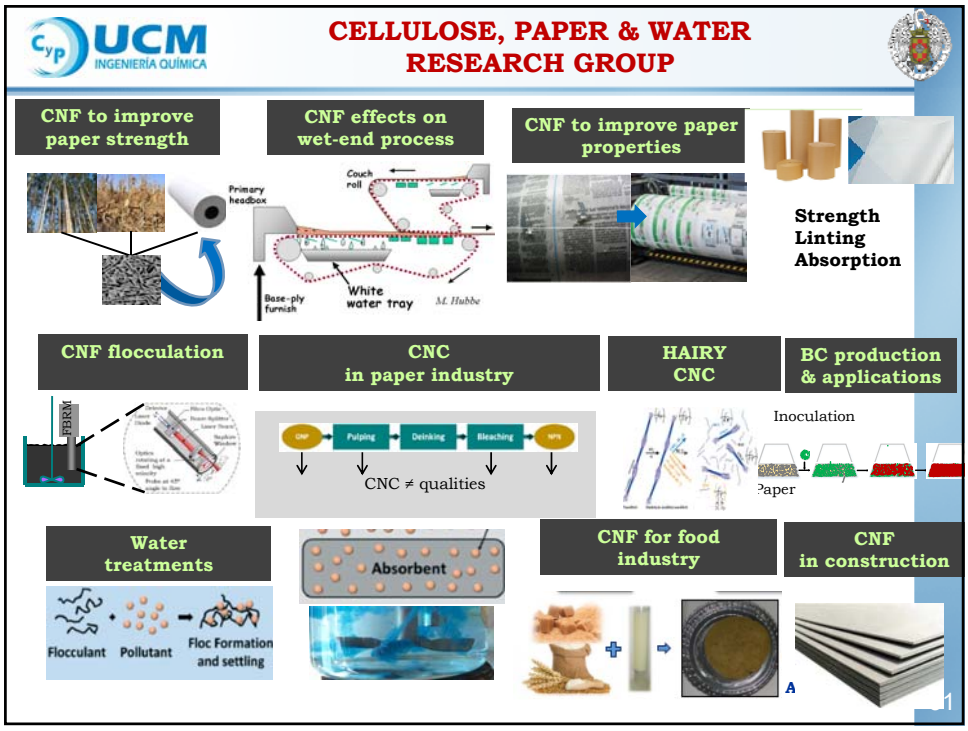
SPANISH PAPER SECTOR

Production (t/y)	Paper	Pulp
Total 2017	6.217.800	1.699.500
Total 2011	6.202.600	1.976.000

Consumption (t/y)	Paper	Pulp
Total 2017	6.802.900	1.876.900
Total 2011	6.427.700	1.770.500

	Collection	Utilisation	Collection rate	Utilisation rate	Recycling rate
Total 2017	4.560.100	5.020.000	67	80,7	73,8
Total 2011	4.722.500	5.093.800	73,5	82,1	79,2

Source: ASPAPEL, 2017


CELLULOSE, PAPER & WATER RESEARCH GROUP
UCM INGENIERÍA QUÍMICA
CNF to improve paper strength
CNF effects on wet-end process
CNF to improve paper properties
Strength
Linting
Absorption
Primary headbox
Couch roll
White water tray
Base-ply furnish
M. Hubbe
CNF flocculation
CNC in paper industry
HAIRY CNC
BC production & applications
Pulping
Deinking
Bleaching
CNC ≠ qualities
Inoculation
Paper
Water treatments
Absorbent
Flocculant
Pollutant
Floc Formation and settling
CNF for food industry
CNF in construction


UCM INGENIERÍA QUÍMICA
• CNF to improve paper strength
• CNF as linting control agent
• CNF effects on wet-end processes: flocculation-retention-drainage
• CNC in recycling paper industry
• BC production and application
• CNF for water treatments
• CNF-chitosan
• Conclusions
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CURRENT SITUATION OF THE PAPER INDUSTRY

Recovered paper

Fillers

Lower strength properties

Recycled paper

Refining

Strength additives

cPAM PVA MF starch GPAM

New alternatives

CNF

Board

Fit-for-use

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CELLULOSE NANOFIBRES

Virgin Pulps	Agroforestry Wastes		Recovered Papers
			
❑ Pine ❑ Eucaliptus	❑ Corn Stalk ❑ Rapessed Straw	❑ Pine Sawdust ❑ Eucaliptus Sawdust ❑ Triticale Straw	❑ NP
ECF	Organosolv	NaOH/AQ Bleached	

PULPS

PRETREATMENTS

Bleached NaClO

Refine

TEMPO NaBr + NaClO (pH=10)

TEMPO NaBr + NaClO (pH=10)

HOMOGENIZATION

CELLULOSE NANOFIBRE

- AFM
- Nanofibrillated Yield
- Transmittance
- Carboxilic Content
- Zeta Potenial
- Cationic Demand
- Polymerization Degree

Cellulose (2016) 24(2), Cellulose (2017); BioResources (2016) 11 (4), 8123; BioResources (2016) 11 (2), 3416; Industrial Crops and Products (2017) 97, 374

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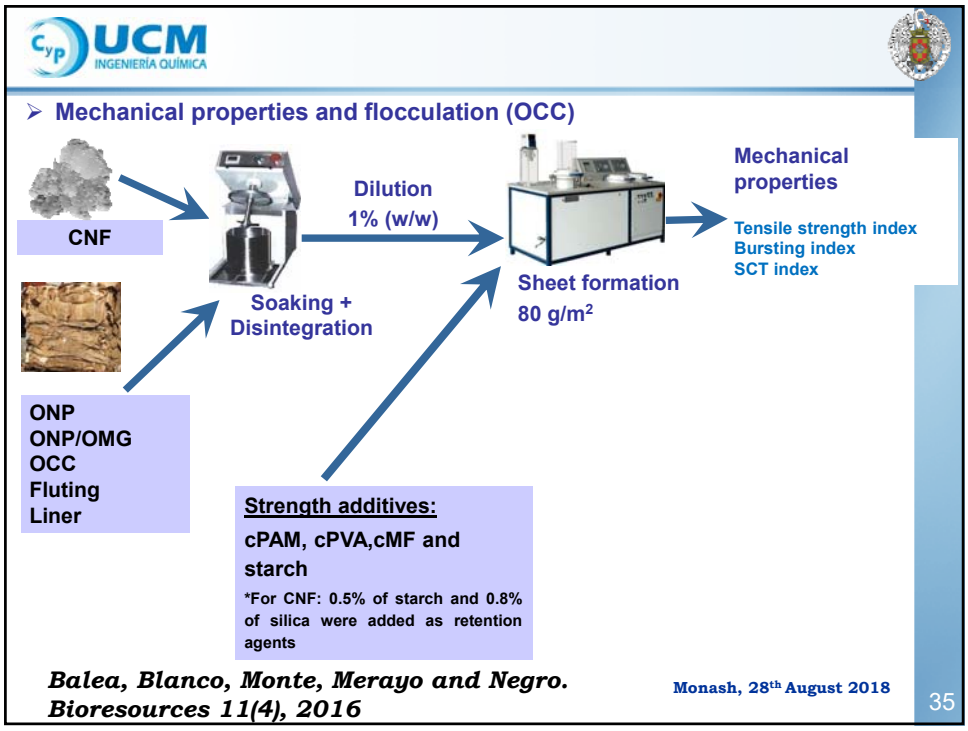
UCM
INGENIERÍA QUÍMICA
Mechanical properties and flocculation (OCC)
CNF
Dilution
1% (w/w)
Soaking +
Disintegration
Sheet formation
80 g/m2
Mechanical
properties
Tensile strength index
Bursting index
SCT index
ONP
ONP/OMG
OCC
Fluting
Liner
Strength additives:
cPAM, cPVA,cMF and
starch
*For CNF: 0.5% of starch and 0.8%
of silica were added as retention
agents
Balea, Blanco, Monte, Merayo and Negro.
Bioresources 11(4), 2016
Monash, 28th August 2018
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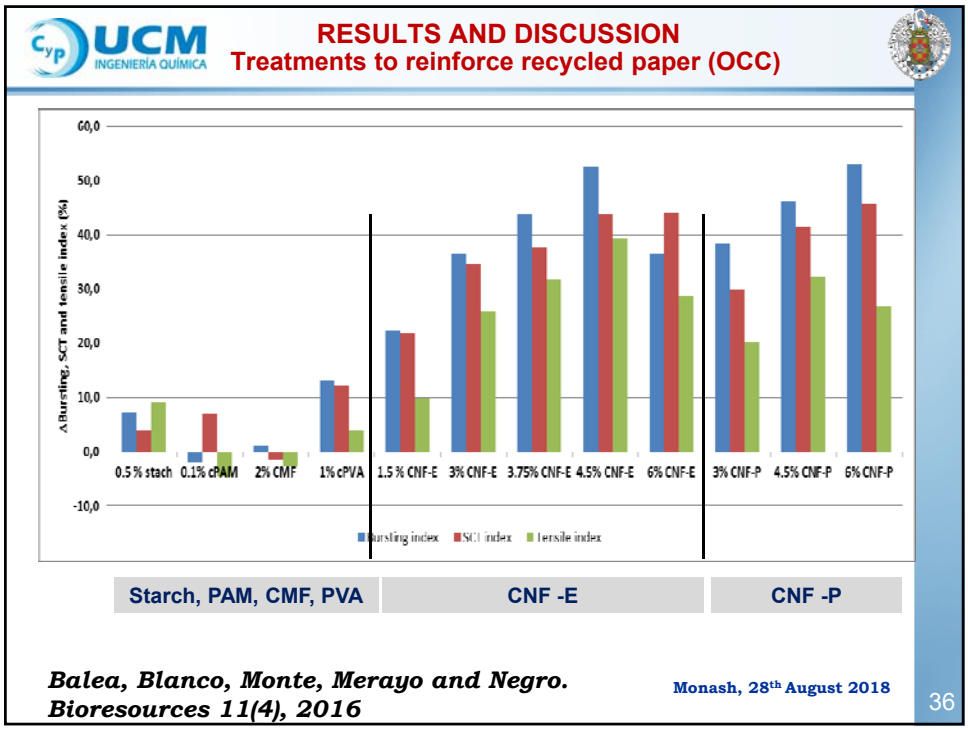
UCM
INGENIERÍA QUÍMICA
RESULTS AND DISCUSSION
Treatments to reinforce recycled paper (OCC)
Δ Bursting, SCT and tensile index (%)
60,0
50,0
40,0
30,0
20,0
10,0
0,0
-10,0
0.5 % stach
0.1% cPAM
2% CMF
1% cPVA
1.5 % CNF-E
3% CNF-E
3.75% CNF-E
4.5% CNF-E
6% CNF-E
3% CNF-P
4.5% CNF-P
6% CNF-P
Bursting index
SCT index
Tensile index
Starch, PAM, CMF, PVA
CNF -E
CNF -P
Balea, Blanco, Monte, Merayo and Negro.
Bioresources 11(4), 2016
Monash, 28th August 2018
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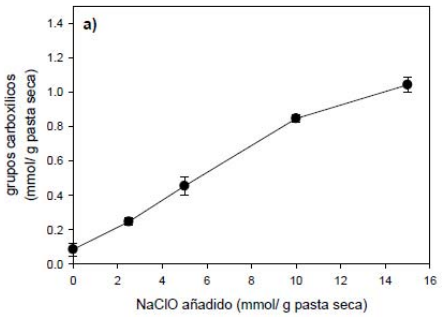
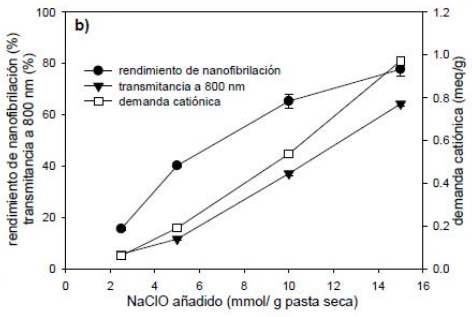
CNF obtained from NP 100% RP





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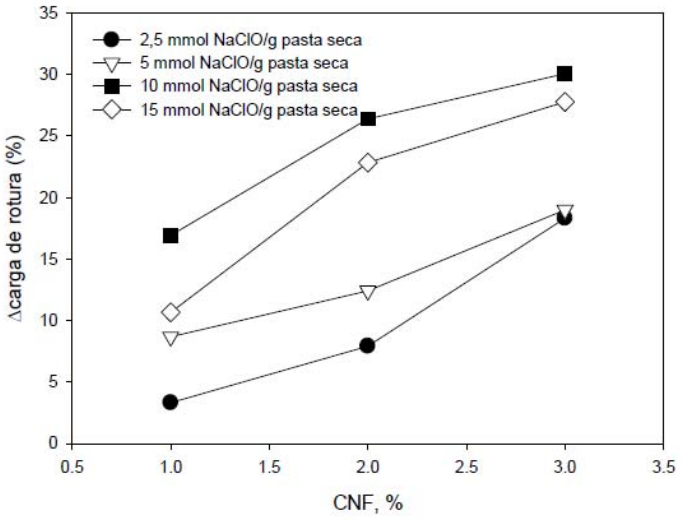
CNF obtained from NP 100% RP



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Onsite Production of NFC

- Screw Press Filtrate
- Broke System (wet/dry)
- Flotation Rejects

Mechanical Properties

Cost
Fit for Use
Quality of CNF

- Wet- End Chemistry
- Dispersion

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- CNF to improve paper strength
- **CNF as linting control agent**
- CNF effects on wet-end processes: flocculation-retention-drainage
- CNC in recycling paper industry
- BC production and application
- CNF for water treatments
- CNF-chitosan
- Conclusions

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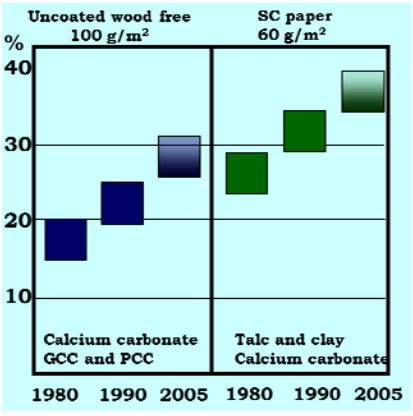
Linting material

Low specific surface particles

Low bonding potential

Ray cells
Fibre fragments
Fines
Fillers

- **Linting problems:**
  - Product quality
  - Operational (pressroom): shut-downs and cleaning



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Linting

Offset printing

Build up on the impression cylinder

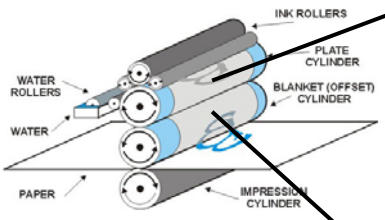

Image degradation caused by linting

High build up on blanket (flakes)

Linting collection: application of tape to the blanket

Strategies to solve linting:
- Raw material
- Printing-press adjustments
- Paper machine
  - Mechanical treatment
  - Chemical treatment

New strategies: nanocellulose

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Methodology

Recycled pulp: 100 % ONP
1.5 wt% consistency

E-CNF
(0.5-1.5 wt%)

PCC
(20-60 wt%)

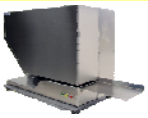
CNF-PCC
suspension

Retention system:
Coagulant: 1.25 mg/g
cPAM: 0.75 mg/g
Bentonite: 1.7 mg/g

Hand-sheets 60 g/m²

Mechanical and physical characterization

Linting propensity (LintView)



Drainage measurements

Dynamic drainage analyser (DDA)

A. Balea, A. Blanco, N. Merayo and C. Negro
Appita J.,Vol 69, No 2, June 2016

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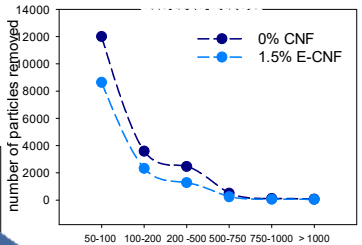
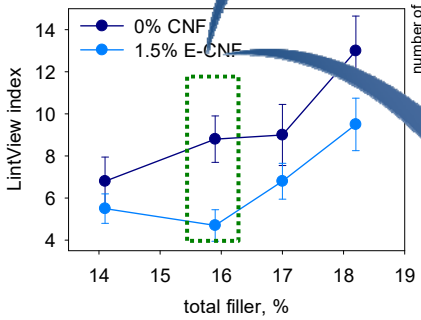
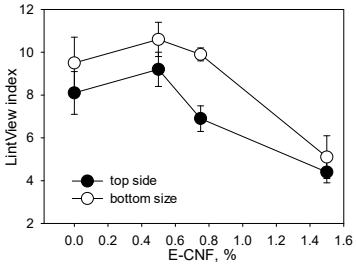
Number of linting particles and their particle size





Effect of E-CNF dose on linting



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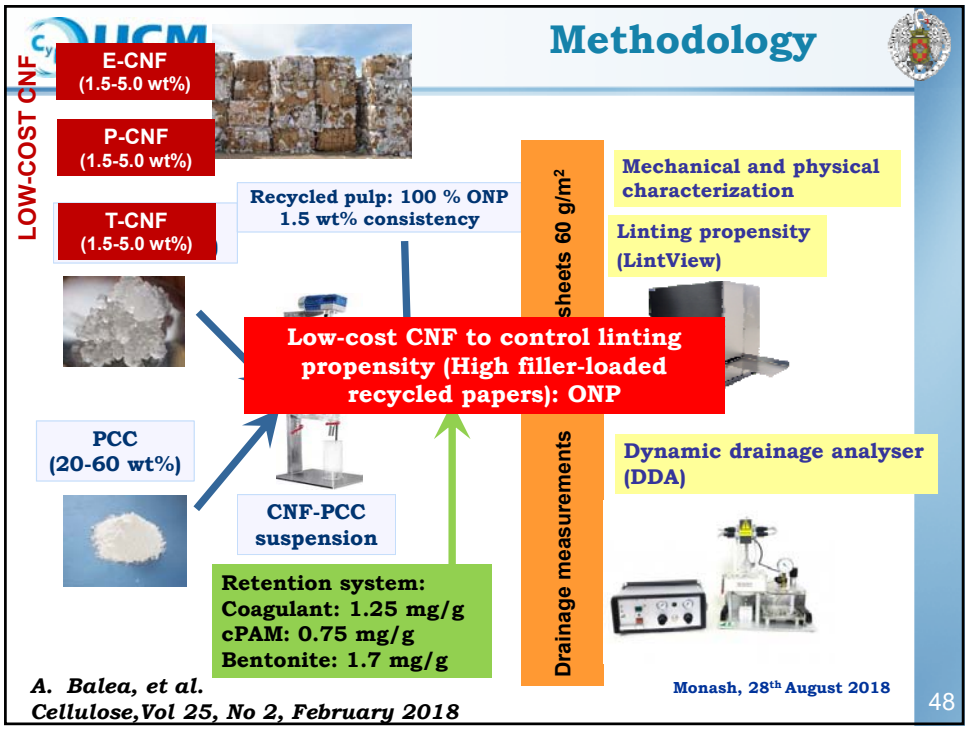
Methodology
LOW-COST CNF
E-CNF (1.5-5.0 wt%)
P-CNF (1.5-5.0 wt%)
T-CNF (1.5-5.0 wt%)
Recycled pulp: 100 % ONP
1.5 wt% consistency
PCC (20-60 wt%)
CNF-PCC suspension
Retention system:
Coagulant: 1.25 mg/g
cPAM: 0.75 mg/g
Bentonite: 1.7 mg/g
Low-cost CNF to control linting propensity (High filler-loaded recycled papers): ONP
sheets 60 g/m²
Drainage measurements
Mechanical and physical characterization
Linting propensity (LintView)
Dynamic drainage analyser (DDA)
A. Balea, et al.
Cellulose,Vol 25, No 2, February 2018
Monash, 28th August 2018
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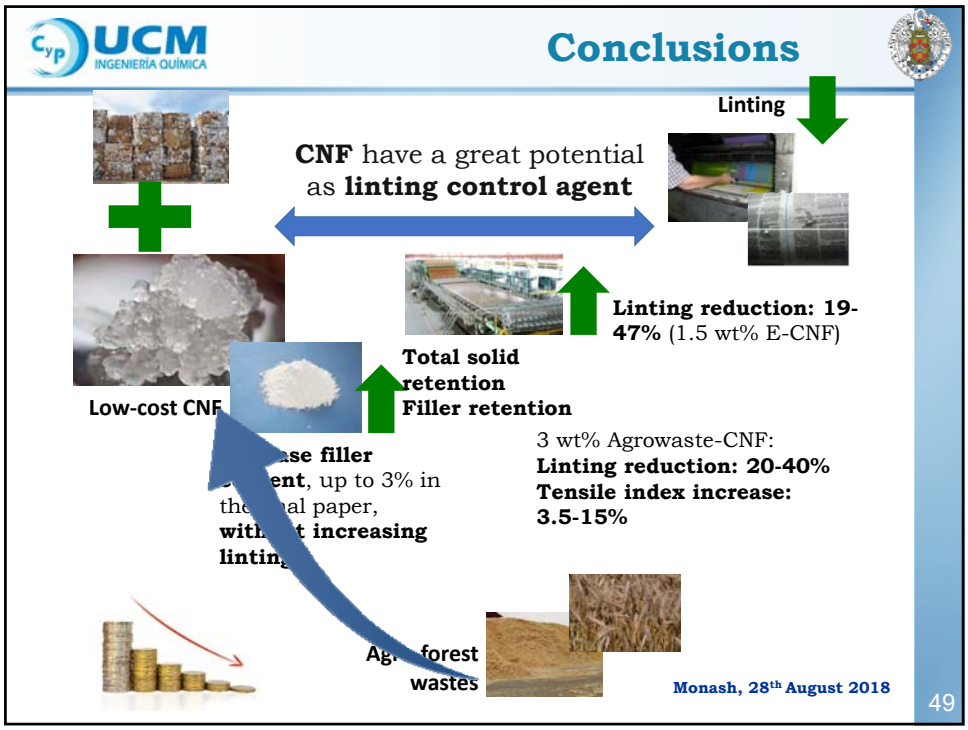
Conclusions
Linting
CNF have a great potential as linting control agent
Linting reduction: 19-47% (1.5 wt% E-CNF)
Total solid retention
Filler retention
Low-cost CNF
3 wt% Agrowaste-CNF:
Linting reduction: 20-40%
Tensile index increase: 3.5-15%
forest wastes
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- CNF to improve paper strength
- CNF as linting control agent
- **CNF effects on wet-end processes: flocculation-retention-drainage**
- CNC in recycling paper industry
- BC production and application
- CNF for water treatments
- CNF-chitosan
- Conclusions

Use of NC products in papermaking

1. HIGH PRODUCTIVITY

- **Formation**
- **Retention**
- **Drainage**

New products

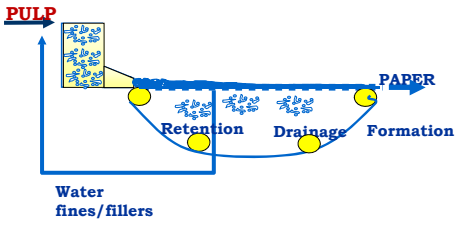
Max. production
Without breaks
Minimum cost

NC APPLICATION

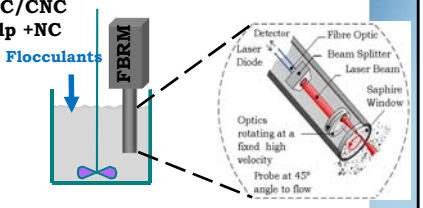
2. HIGHER QUALITY PRODUCTS

Strength, absorption, printability,...

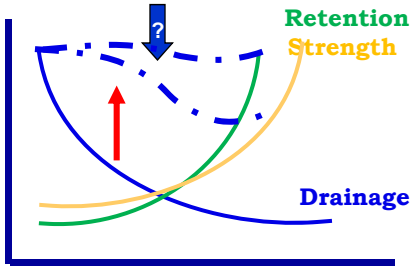
Wet-end optimization



- NFC/CNC
- Pulp +NC



NC characteristics
ZP, CD, adsorption, gel point
Floc properties: size, number, characteristics



DFR tester

0.5 wt% pulp/NC
+ Retention system

Total retention
Drainage curve
W250 / W300
(time/250 g water)

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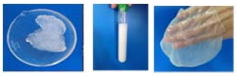
CNF effects on wet-end

Soaking
Disintegration

Mixing

Sheet formation

MFC/CNF/CNC/
HCNC/BC



- Recovered paper
- Agro-wastes: corn stalk, rapeseed stalk
- Eucalyptus
- Pine

Wet-end systems:

- Cationic starch (CS)
- Single systems: PEI, PAM, Polyvinylamine (PVA)
- Dual-system: coagulant (C) + C-PAM
- Three-component system: coagulant (C) + C-PAM + bentonite (B)
- Chitosan
- ....

Properties:
- ✓ Physical
- ✓ Mechanical
- ✓ Optical

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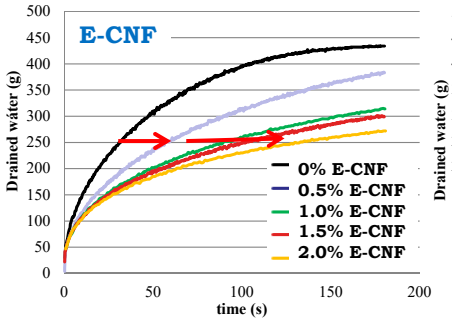
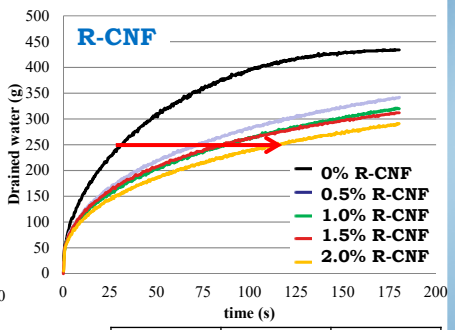
CNF effects on wet-end

Effect of E-CNF and R-CNF on drainage of recycled pulp (60/40) without retention system





- **Retention: 90%**
- **E-CNF: drainage time increases from 31s to 57-133s**
- **R-CNF: drainage time increases from 70 to 114s**

% CNF	E-CNF (s)	R-CNF (s)
0	31	
0.5	57	70
1.0	100	86
1.5	100	85
2.0	133	114

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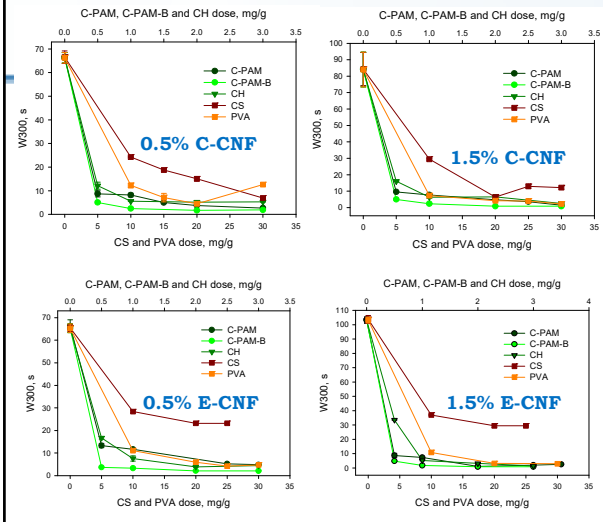
CNF effects on wet-end



C-PAM: PDADMAC + PAM (HWW, 1,2 meq/g)
C-PAM-B: polyamine+PAM (HMW, 3,7 meq/g))
CH: 4,8 meq/g LMW
CS: 0.02-0.17, 0.5 meq/g
Pplyvinylamine: HMW, 11meq/g

Merayo et al. Synergies between CNF and retention additives.... Cellulose (2017) 24:2987-3000.

- **CNF + CS presents drainage problems, specially with E-CNF**
- **Negative drainage effect of CNF can be compensated by re-optimizing the wet-end chemistry.**
- **Effect of CNF depends on its interaction with polymers.**
- **Strong interactions may affect formation, tensile index and drainage.**

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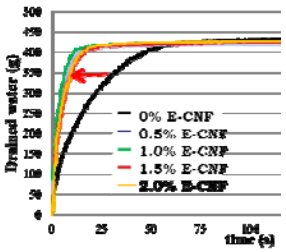
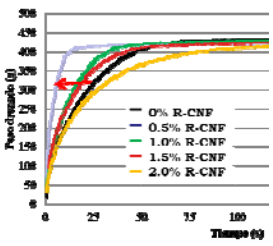
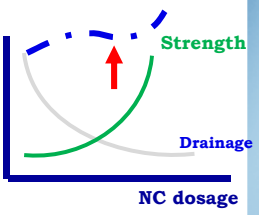
CNF effects on wet-end
Recycled pulp with chitosan







E-CNF	No RS W250, s	Chitosan W250, s	R-CNF	No RS W250, s	Chitosan W250, s
0	30.86	15.34	0	30.86	15.34
0.5	57.12	4.15	0.5	70.25	3.60
1.0	99.67	3.29	1.0	86.37	9.88
1.5	100.02	4.28	1.5	85.53	10.80
2.0	133.03	3.80	2.0	113.65	17.30

Decoupling Strength-drainage

- ✓ 0% CNF + chitosan: Drainage time ↓ 50% W250
- ✓ E-CNF (0.5, 1.0, 1.5, 2%) + chitosan: Drainage time ↓ 75%
- ✓ R-CNF (0.5, 1, 1.5) + chitosan: Improve drainage >30%

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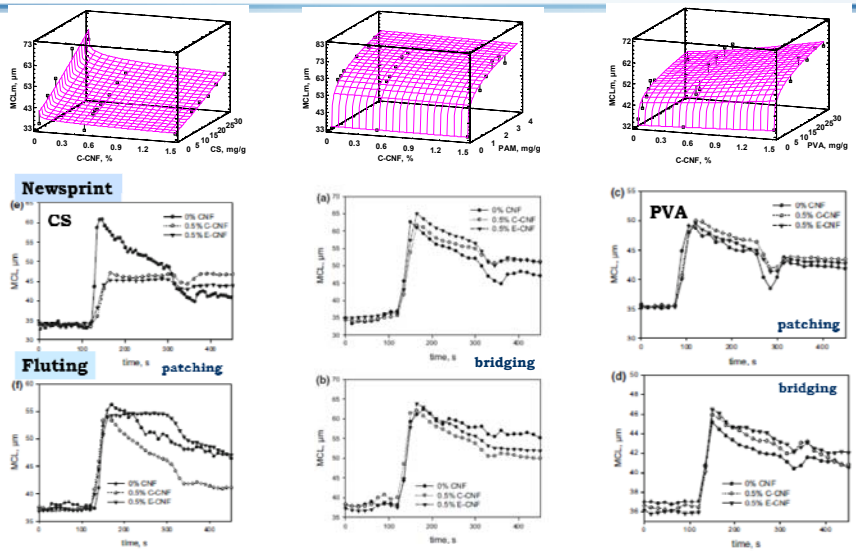
Renponse surface methodology to assess the influence of CNF, RS and type of pulp on MCLm



- CS: MCLm decreases with CNF
- PAM: MCLm ≠ (type CNF, dosage, type of pulp)
- PVA: MCLm = (type CNF, dosage, type of pulp)

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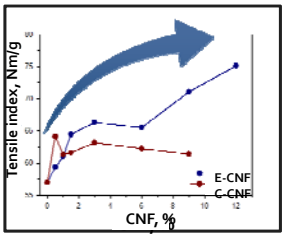
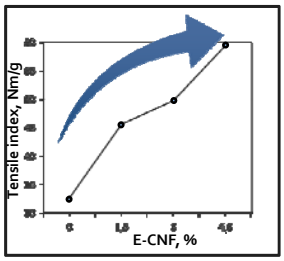
CNF effects

E-CNF: CNF from Eucalyptus bleached pulp
C-CNF: CNF from corn **stalk** pulp

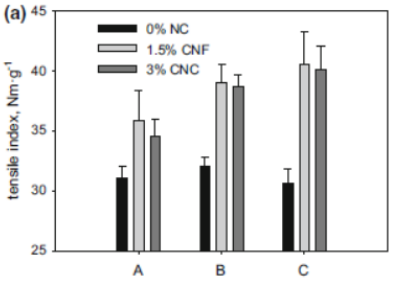


Balea et al. BioResources (2016) 11 (2), 3416



Delgado-Aguilar et al. Cellulose (2015) 22 (1), 789

....but the curves are different...



A: 10 min pulping, ~50 °C
B: 60 min pulping, ~50 °C
C: soaking, 60 min pulping, ~20 °C

- ✓ **Pulping has an important impact on the homogeneous mixture of NC in the pulp ➔ effects**
- ✓ **Dispersants reduce time**

CNF effects on wet-end

- **CNF produced from recycled paper mills pulps and agro-wastes improve mechanical properties and do not reduce drainage if retention systems are optimized adequately.**
- **Compatibility with traditional RS is possible.**
- **Chitosan has a synergic effect with CNF improving drainage while retention is maintained ➔ ↑ machine speed.**
- **Minimum CNF quality must be defined for each mill goal ➔ cost efficiency = CNF fit4use**

- CNF to improve paper strength
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- Conclusions

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CNC production

- Recoverd paper
- Corn stalk
- MCC

Cellulose

Pretreatment

- Bleaching: 2% NaOH 80ºC and 2%w/v $NaClO_2$
- Pulping chemistry: 1%NaOH; 1% H_2O_2; 2% Na_2SiO_3

60% H_2SO_4, 13.5 mL H_2SO_4/g pulp, 45ºC, 90 min and continuous stirring

Acid hydrolysis

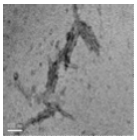
Purification

- Washing
- Dialysis
- Sonication

Characterization:

- Yield
- Lignin content
- Ash content and composition
- Sulfur content
- Polymerization degree
- Crystallinity
- Thermogravimetric Analysis

CNC



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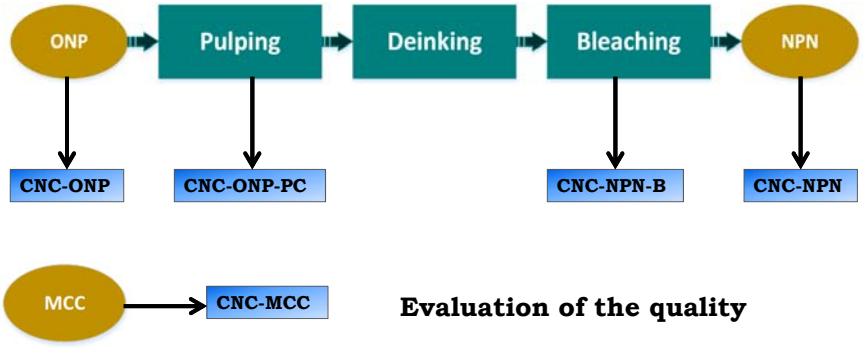
CNC production & application

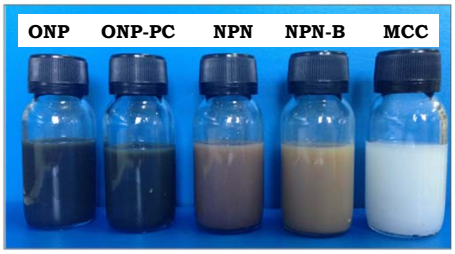
CNC from different pulps of the recycled paper industry



Evaluation of the quality

Direct production of CNC from ONP. Campano et al.
Carbohydrate Polymers (2017) 173: 489-496

CNC production

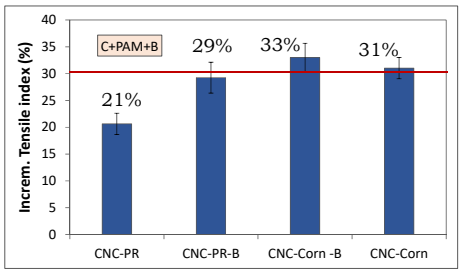


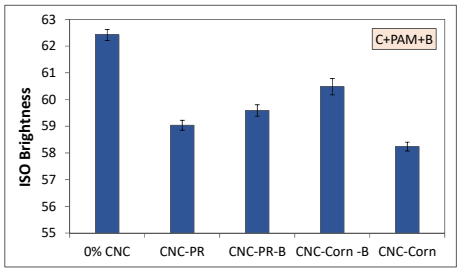
- Higher yield → Low pretreatment.
- Higher CNC quality → Aggressive pretreatment.

➢ **Compromise between yield and quality**
➢ **CNC fit for use**

Experiment	Cristalinity index (%)	Polimerization degree
ONP	92.6	182
ONP-PC	93.0	186
NPN	94.4	181
NPN-B	94.6	200
MCC	95.2	226

CNC effects on RP quality





Tensile index
Oil absorbance
Linting

CNC-PR and CNC-PR-B

- High differences in TI → 21-29%
- Similar brightness 59

CNC-Corn and CNC-Corn-B

- Low differences in TI → 31-33%
- Brightness is affected: from 62.5 to 60.5 (CNC-Corn-B) and 58 (CNC-Corn).

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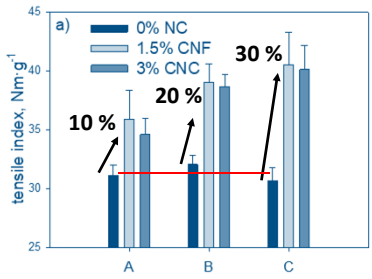
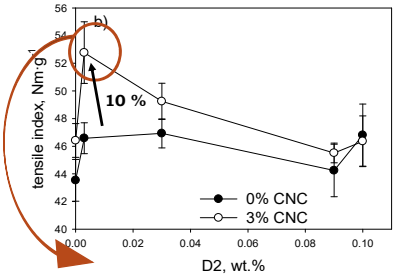
Effect of CNC dispersion

C-PAM-bentonite



A: 10 min pulping, ~50 °C
B: 60 min pulping, ~50 °C
C: soaking, 60 min pulping, ~20 °C

D2: Moisturizing agent (coatings formulations)



20% increase with 3 %CNC+0.003% D2

Campano, Merayo, Balea, Tarrés, Delgado-Aguilar, Negro, Blanco. Cellulose (2018)25;269-280

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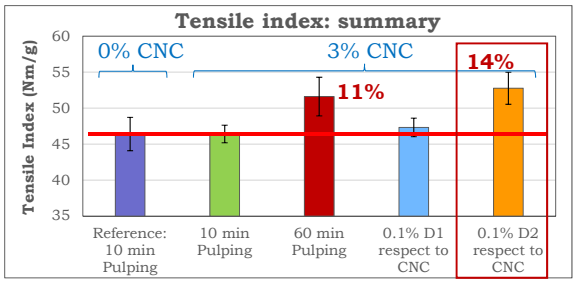
Effect of CNC dispersion



✓ **Bad dispersion hides the effect of NC**

Pulping conditions:
60 min and ~50°C

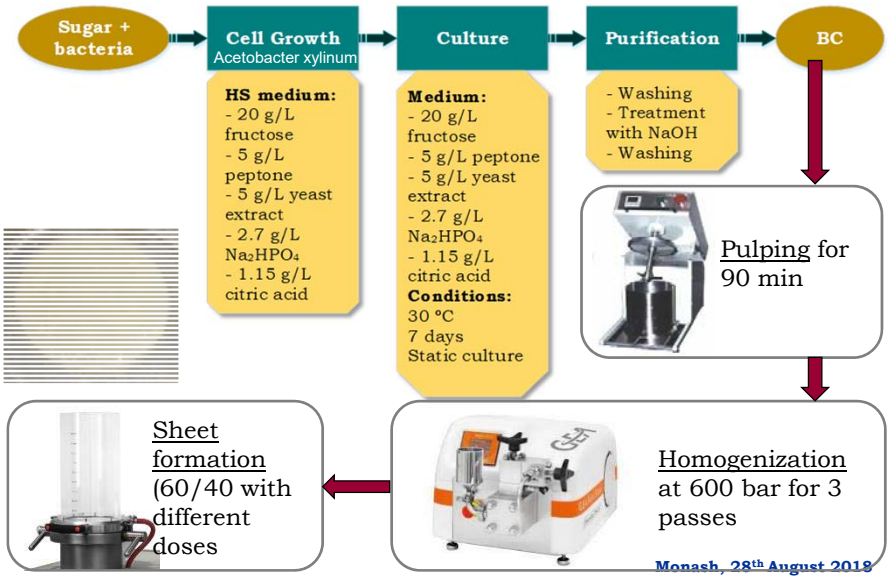
Objective: reduce pulping time to **10 min** (ind. pulping).

With D2 at low dosage (0.1% respect to CNC):

- **Increment of 14% TI**
- **Pulping time was reduced to 10 min**

- CNF to improve paper strength
- CNF as linting control agent
- CNF effects on wet-end processes: flocculation-retention-drainage
- CNC in recycling paper industry
- **BC production and application**
- CNF for water treatments
- CNF-chitosan
- Conclusions

2. Mass addition of BC



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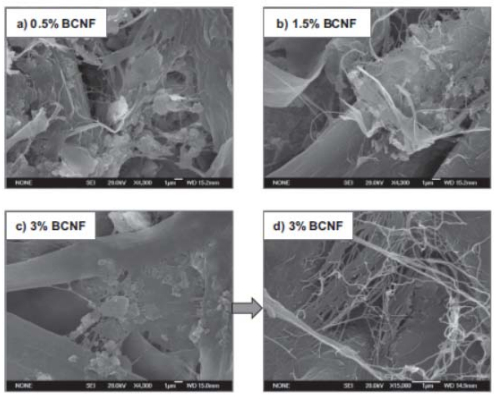
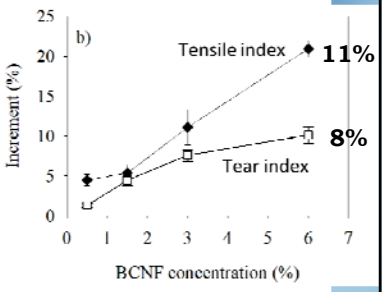
Bacterial cellulose nanofibers Papermaking

- **BCNF by soft homogenization of BC pellicles=low fibrillation 35%**
- **3% BCNF applied to recycled pulp**



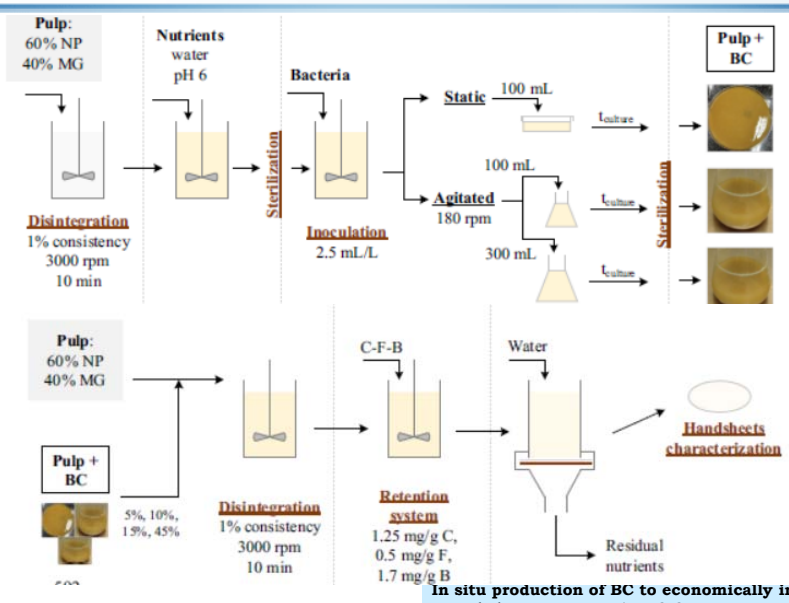
NF + small clusters



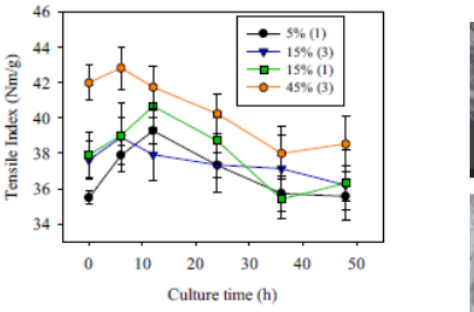
Decoupling tensile index & tear index
✓ Flexible paper

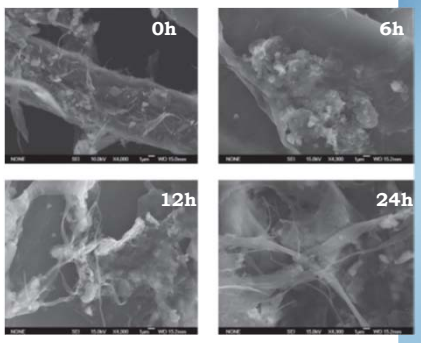
...lated bacterial cellulose nanofibers as a sustainable additive to enhance recycled paper quality. C. Campano et al. Int. J. of Biological Macromolecules. 114(2018) 1077-1083

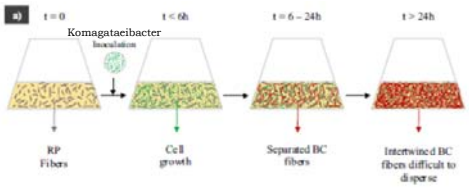
In situ production of BC

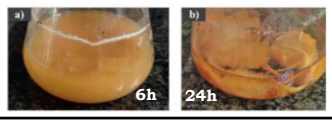


In situ production of BC to economically improve recycled paper properties. C Campano, Int J. Biological Macromolecules DOI: 10.1016/j.ijbiomac.2018.06.201









Improved mechanical properties

6-12 h → 25% increase of tensile index

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- CNF to improve paper strength
- CNF as linting control agent
- CNF effects on wet-end processes: flocculation-retention-drainage
- CNC in recycling paper industry
- BC production and application
- **CNF for water treatments**
- CNF-chitosan
- Conclusions

Deinking flexographic papers

- **Water-based flexographic inks are one of the main problems in paper and plastics recycling industries.**

- **They are more environmental favorable than organic solvents-based inks but conventional deinking technologies do not effectively remove them ➔ colored process water**

CNF to treat process water in PR mills

- **CNF-E** TEMPO-oxidation eucalyptus bleached pulp (0.8% pulp, 5mmol NaClO/g, 6 steps at 600 bar).
- **Flexographic ink solutions:** Copper phthalocyanine blue (Blue), Carbon Black, Yellow 12.
- **cPAM** 0.5 g/L Snowflake (lineal, 50% charge hensity, HMW (13MDa).

Inks	Concentration (ppm)	pH	λ (µS/cm)	CD (µeq/L)	Turbidity (NTU)
Blue ink	4.5 ± 0.05	5.73 ± 0.06	13.67 ± 0.21	10.93 ± 1.28	10.60 ± 0.46
Black ink	2.0 ± 0.05	5.71 ± 0.03	22.80 ± 0.10	9.33 ± 0.32	31.30 ± 0.03
Yellow ink	24.0 ± 0.21	4.26 ± 0.01	40.90 ± 0.10	-36.17 ± 1.5	30.69 ± 1.31

Jar test

Application of CNF to remove water-based flexographic inks from wastewater. A. Balea et al. 2017 ESPR 24(5):5049-5059

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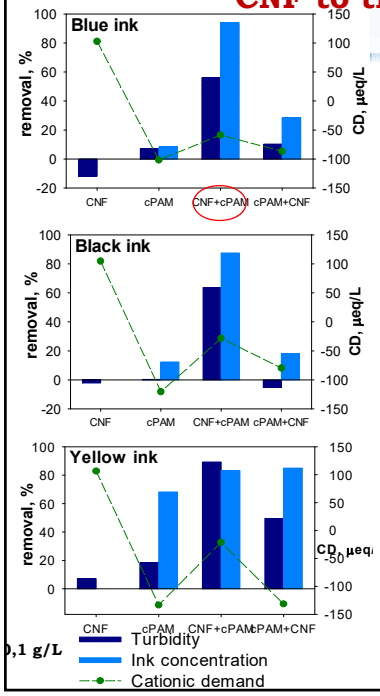
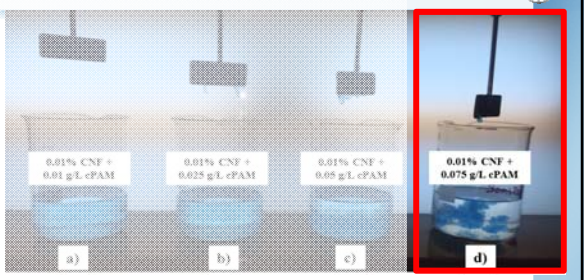
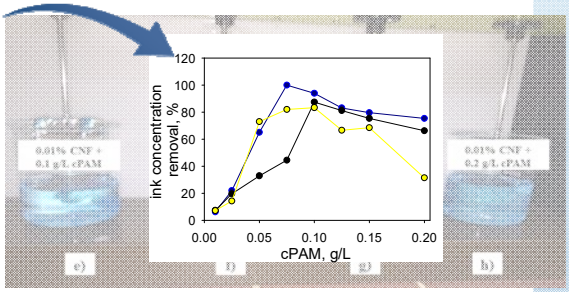
CNF to treat process water in PR mills







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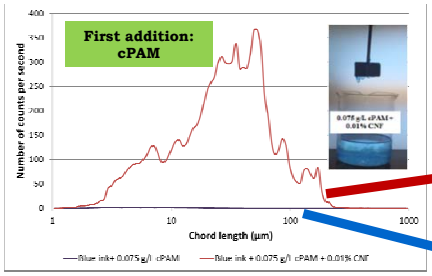
CNF to treat process water in PR mills

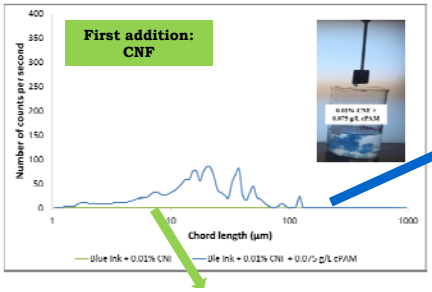


1. First the ink is adsorbed on the CNF (no increase of the size particle).
2. CNF with the ink adsorbed flocculates due to cPAM addition, removing totally the ink.

The size of the flocs and the number of counts increase when CNF is added due to the CNF flocculation.

The blue ink particles are not flocculated due to the cPAM addition.

✓ 24 % ink removal



When cPAM is added, the number of counts is lower than in the last case and few and big flocs are formed.

✓ 100% ink removal

The blue ink particles are not flocculated due to the CNF addition.

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CNF to treat process water in PR mills

Tratamientos cPAM – CNF from RP

		R-CNF (g/L)	cPAM (g/L)	Ink removal (%)	Turbidity removal (%)
R-CNF + cPAM	Blue ink	0,100	0,100	72,64 ± 0,44	91,07 ± 1,09
		0,100	0,050	29,98 ± 0,74	91,31 ± 0,70
	Black ink	0,150	0,075	38,75 ± 0,27	15,63 ± 0,13
		0,050	0,075	60,42 ± 0,62	50,69 ± 1,36
	Yellow ink	0,100	0,100	45,70 ± 0,83	58,25 ± 0,51
		0,050	0,100	87,89 ± 0,19	95,88 ± 0,81
cPAM + R-CNF	Blue ink	0,100	0,100	46,39 ± 0,81	90,21 ± 0,55
		0,100	0,050	76,06 ± 0,96	90,72 ± 0,19
	Black ink	0,150	0,075	89,45 ± 1,21	83,47 ± 0,63
		0,050	0,075	25,43 ± 0,52	7,76 ± 1,04
	Yellow ink	0,100	0,100	92,22 ± 0,60	97,12 ± 0,29
		0,050	0,100	30,16 ± 0,97	32,95 ± 0,88

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CNF to treat process water in PR mills

Tratamientos Chitosan – R-CNF

		R-CNF (g/L)	Chitosán (g/L)	Eliminación tinta (%)	Reducción turbidez (%)
R-CNF + Chitosán	Tinta azul	0,200	0,100	100,00 ± 0,00	66,16 ± 0,00
		0,050	0,100	66,08 ± 1,05	12,67 ± 6,34
	Tinta negra	0,200	0,100	86,43 ± 0,00	80,81 ± 0,41
		0,050	0,100	59,38 ± 0,38	47,29 ± 0,63
	Tinta amarilla	0,200	0,100	83,46 ± 0,49	91,07 ± 1,98
		0,050	0,100	66,20 ± 1,41	78,53 ± 0,83
Chitosán + R-CNF	Tinta azul	0,200	0,100	30,39 ± 1,01	0,00 ± 0,00
		0,050	0,100	18,24 ± 0,97	0,00 ± 0,00
	Tinta negra	0,200	0,100	1,36 ± 0,85	17,84 ± 0,99
		0,050	0,100	0,00 ± 0,00	0,00 ± 0,00
	Tinta amarilla	0,200	0,100	48,76 ± 2,65	54,76 ± 0,81
		0,050	0,100	16,18 ± 2,01	10,30 ± 1,12



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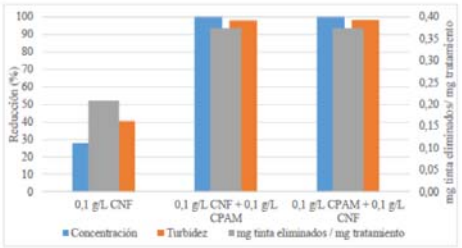
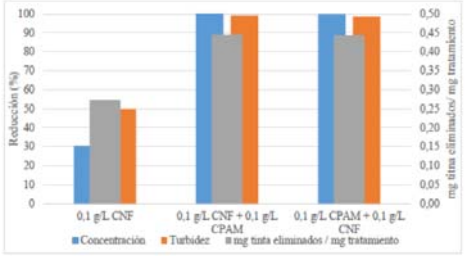
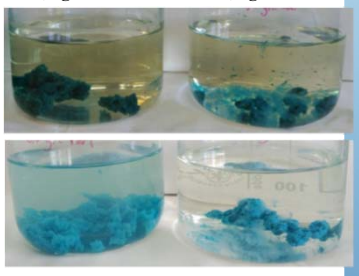
CNF to treat process water in PR mills

White water treatment of OCC/newsprint





0,1 g/L CNF + 0,1 g/L CPAM | **0,1 g/L CPAM + 0,1 g/L CNF**



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CNF to treat process water in PR mills

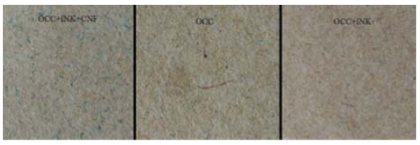
Recycling CNF-ink sludge

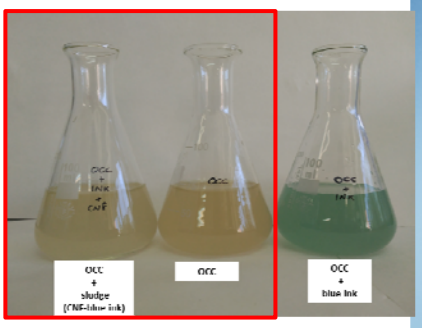
100% OCC
+ sludge (CNF+blue ink flocs)

↓

Disintegration

↓





- **Flexographic ink and CNF are retained in the paper**
- **Clean process water.**
- **Sludge can be re-used in the middle layer.**
- **Mechanical properties are no affected.**

	OCC+TINTA+CNF	OCC	OCC+TINTA
Gramaje (g/m²)	70,2	67,9	71,1
Porosidad (mm/Pa·s)	34,02	30,03	26,72
C. Rotura CD (kN/m)	1,84	1,70	1,75
Índice C. Rotura (Nm/g)	26,48	25,02	24,66
Alargamiento CD (%)	1,03	0,97	0,92
Desgarro MD (mN)	342	336	343
Índice desgarro (mN·m²/g)	4,93	4,96	4,83

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- CNF to improve paper strength
- CNF as linting control agent
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- **CNF-chitosan**
- Conclusions

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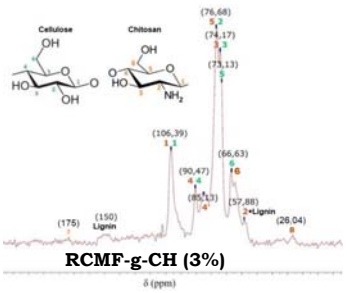
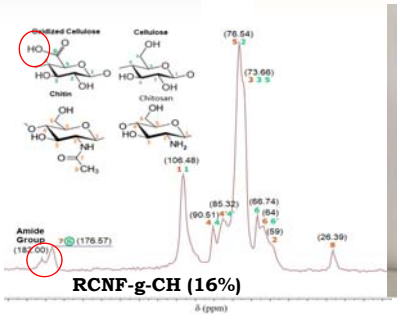
Nanocellulose-graft-chitosan polymer

NANO	CELLULOSE	CHITOSAN
< 100 nm	Sustainable	Abundant
Strength High specific surface Good reactivity No defects Thermal stability Unique intrinsic properties	Nenovable Biodegradability Biocompatibility Non-toxic Surface charge Chemically reactive	Abundant Biodegradability Biocompatibility Bioresorbable Non-toxic Antibacterial properties



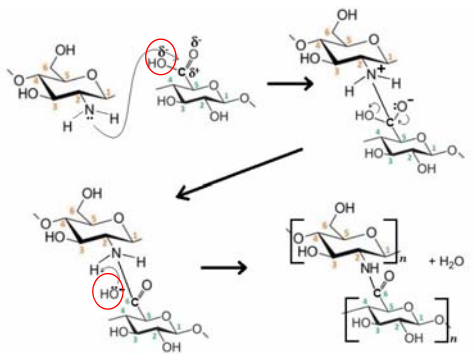


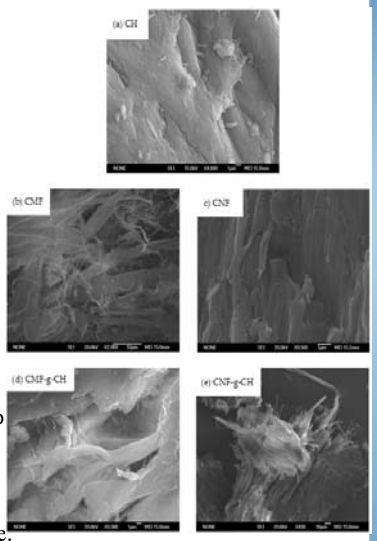
^{13}C NMR specter after copolymerization

Determination of the reaction mechanism to produce Nanocellulose-Graft-Chitosan polymer. JL Sanchez-Salvador et al. Sent to Nanomaterials.

Nanocellulose-graft-chitosan polymer

Copolymerization reaction mechanism of CNF-g-CH





1. Microwave heat to induce that the amino group of CH attacks the carboxylic group of NC ➔ nucleophilic substitution reaction➔ grafing to
2. The OH^- departs with an electron pair and carboxylic bond is formed in the principal molecule.
3. A water molecule is formed.

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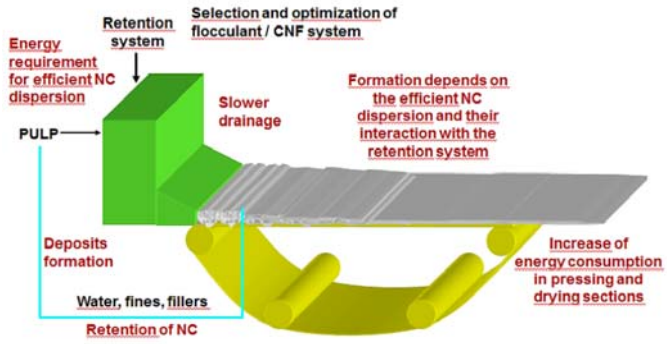
- CNF-chitosan
- **Conclusions**

Up-scaling the use of NC in papermaking

- **NC have a great potential to improve paper properties BUT they are not implemented yet at industrial scale**



- **Better knowledge of NC-polymers-furnish+water interactions**
- **In-situ production of NC fit4use to improve paper quality and develop new paper products + NC for local market**
- **Recyclability**

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MICROCELLULOSE CTQ 2012-36868-C02-01)
NANOSOLPAPEL-REC (CTQ2013-48090-C2-1-R)
NANOPROSOST (CTQ2017-85654-C2-2-R).

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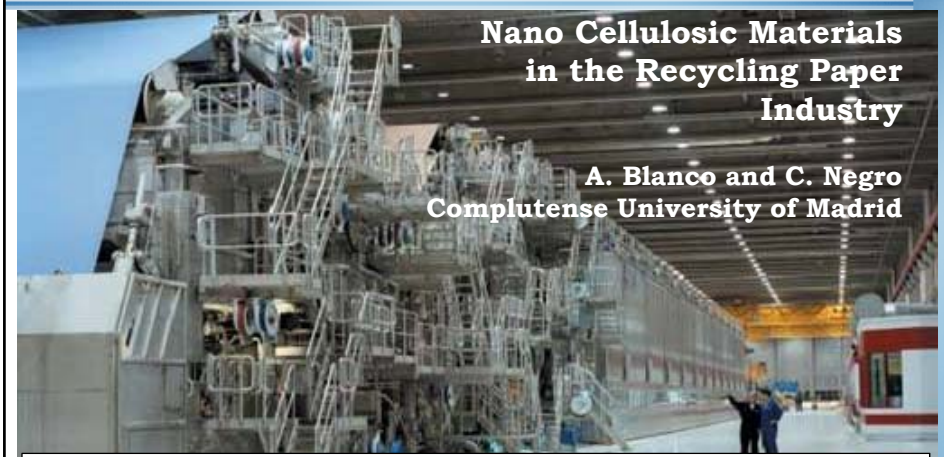
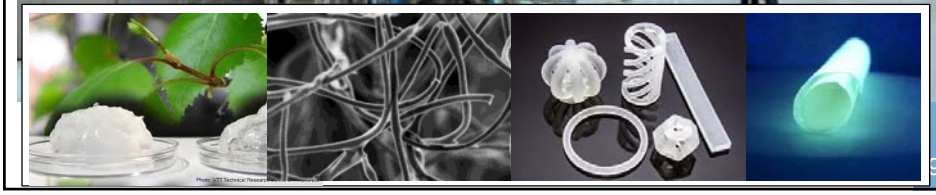


Nano Cellulosic Materials in the Recycling Paper Industry

A. Blanco and C. Negro
Complutense University of Madrid



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