



Les belles promesses des Nanocellulose

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Paris, France*

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agefpi



institut
universitaire
de France





AT THE CROSSROAD OF LEADING DISCIPLINES
CHEMISTRY, MATERIALS, PROCESSES

www.pagora.grenoble-inp.fr

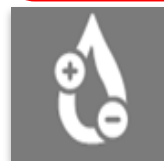


3 research departments



**Biorefinery: wood
chemistry and eco-
process**

**Multi-scale bio-
based materials**



**Surface
functionalization
by printing**



10 Permanent researchers, 5 technical staff, 25 PhD & Post-doc

1. Nanocellulose : un contexte favorable
2. Production des Nanocellulose
3. Vers des applications de plus en plus évoluées

Nanocelluloses

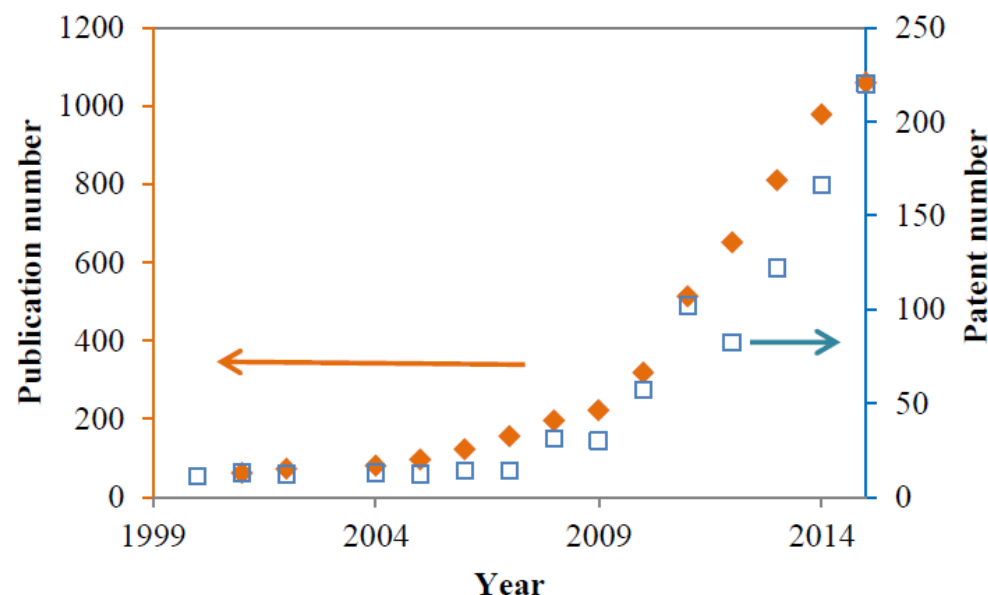
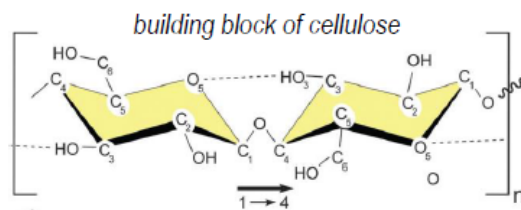
Nanomaterials

- 1 dimension < 100 nm
- high surface area (>100 m² /g)
- novel characteristics



Cellulose

- most available biopolymer on earth
- 200 billion tons / year (3 % used)
- many sources available

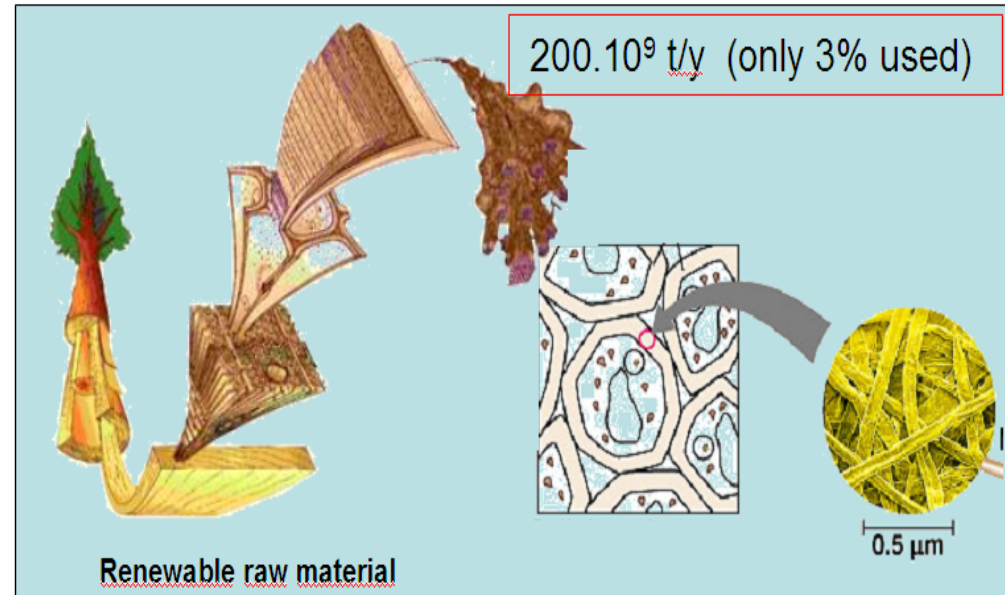
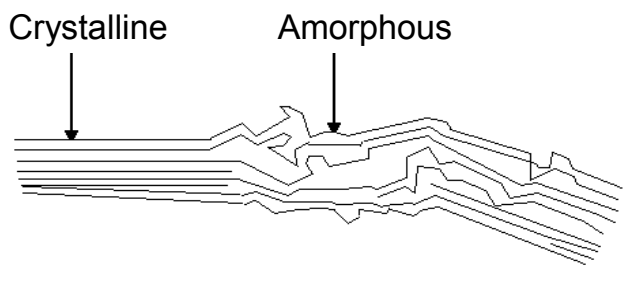
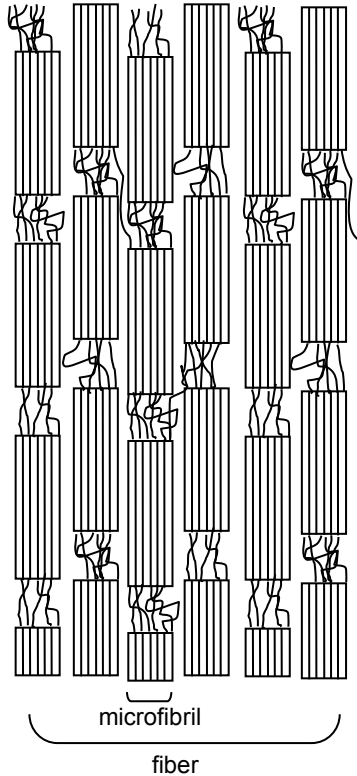


Evolution of annual non-cumulative number of publications and patents on nanocellulose

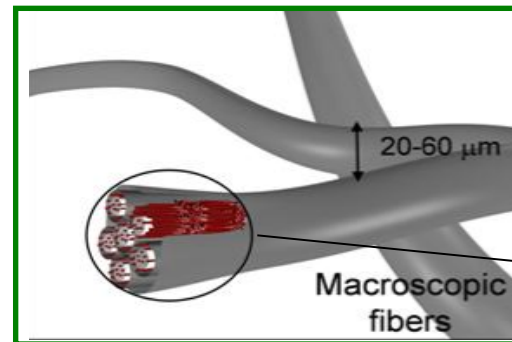
(Source: SciFinder, July 2016 –

descriptors : cellulose nanofibrils, cellulose microfibrils, cellulose nanocrystals, cellulose nanowhiskers, microfibrillated cellulose)

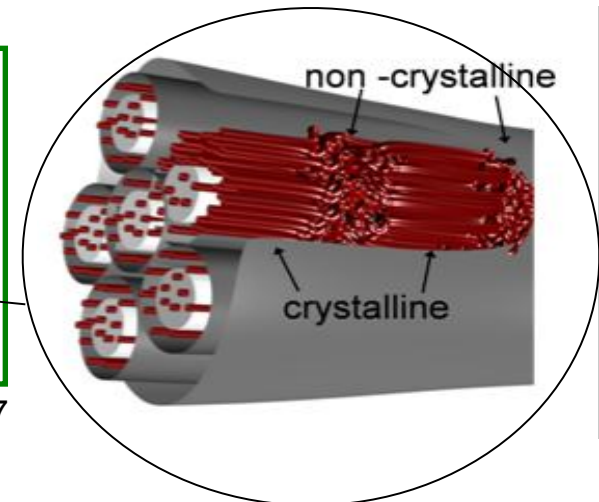
Hierarchical Structure

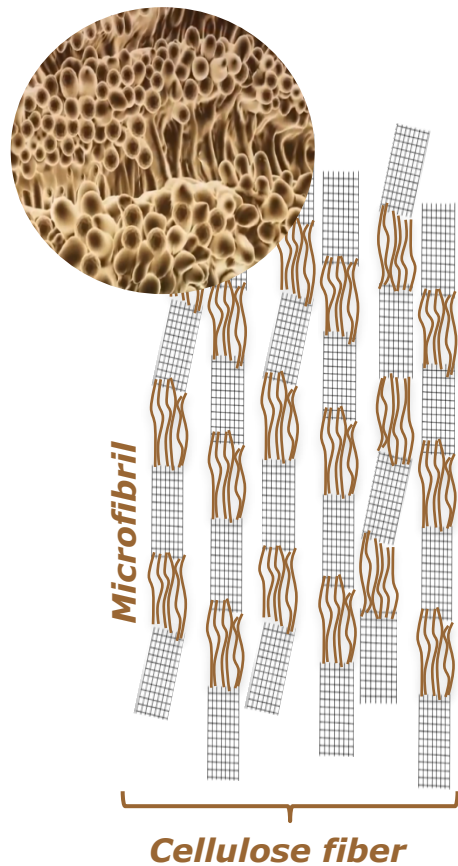


Multi-level Organization



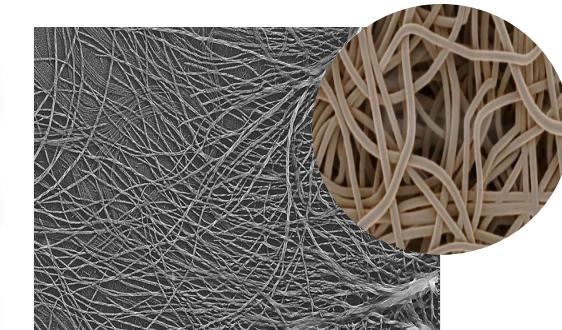
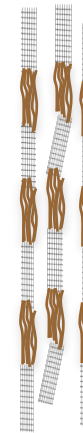
Adapted from Pääkkö, et al. 2007





2. Mechanical
Homogenization
1. Defibrillation

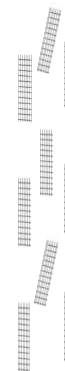
Microfibrillated cellulose (MFC)



D 2-20 nm
L > 1000 nm

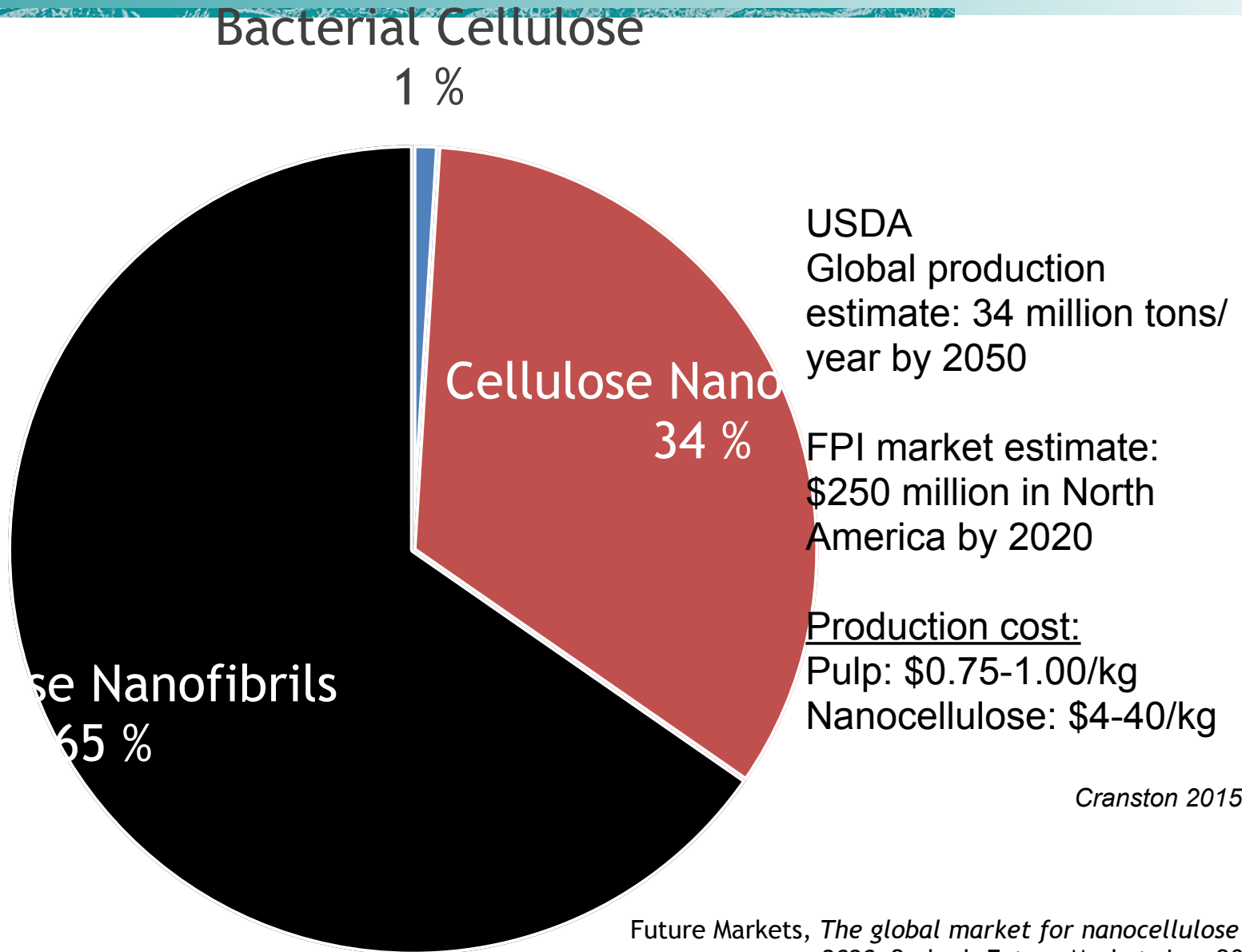
1. Hydrolysis
2. Dialysis / UF

Cellulose Nanocrystals (CNC)



D 2-10 nm
L 150-1000 nm







Flagships in Call 2016

Objective: deployment of a technology, which has been already demonstrated leading to a system, which is complete and qualified (TRL8) for successful commercial operation (large scale production facility in Europe)

TOPIC	FOCUS
BBI.VC1.F1	BIOETHANOL : second generation bioethanol production built on lignocellulosic non-food feedstock (straw)
BBI.VC2.F2	Microfibrillar Cellulose (MFC) : large-scale supply and market creation of MFC to demonstrate an industrial symbiosis between the biomass and the forest industry
BBI.VC1.F1	CELLULOSIC ETHANOL : Cellulosic ethanol from unused crop residues and crops grown on marginal lands



Borregaard / News / EUR 25 million in EU funding for Exilva

Borregaard Receives EUR 25 million for Commercialization of Microfibrillar Cellulose from the EU



Borregaard Receives EUR 25 million for Commercialization of Microfibrillar Cellulose from the EU

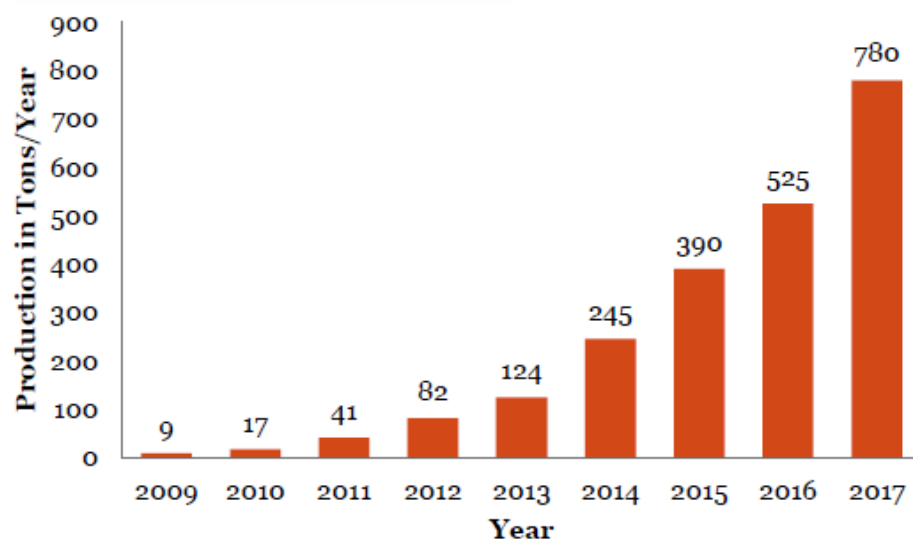
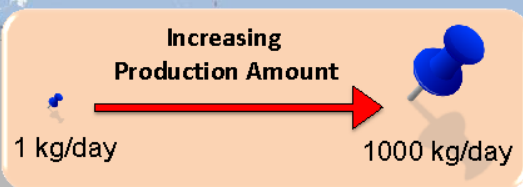
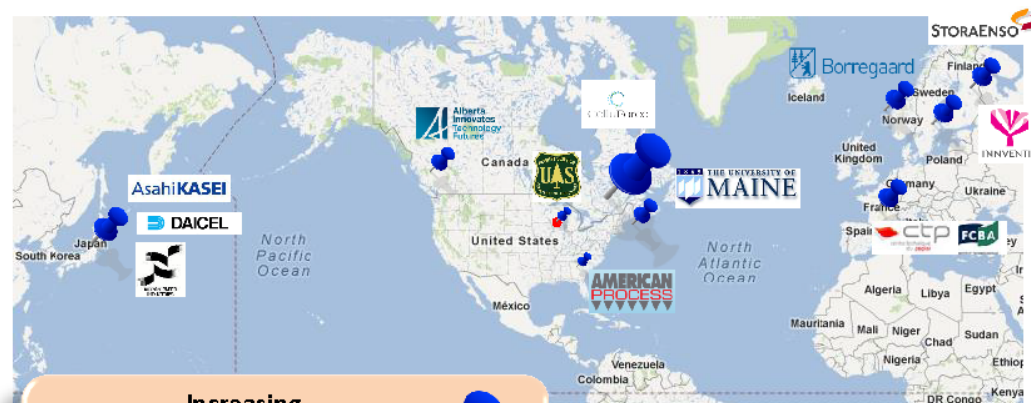
Borregaard has received a funding commitment of EUR 25 million (NOK 232 million), for the development and commercialization of

⇒ Nanocellulose = 2nd **priority** of european Bioeconomy

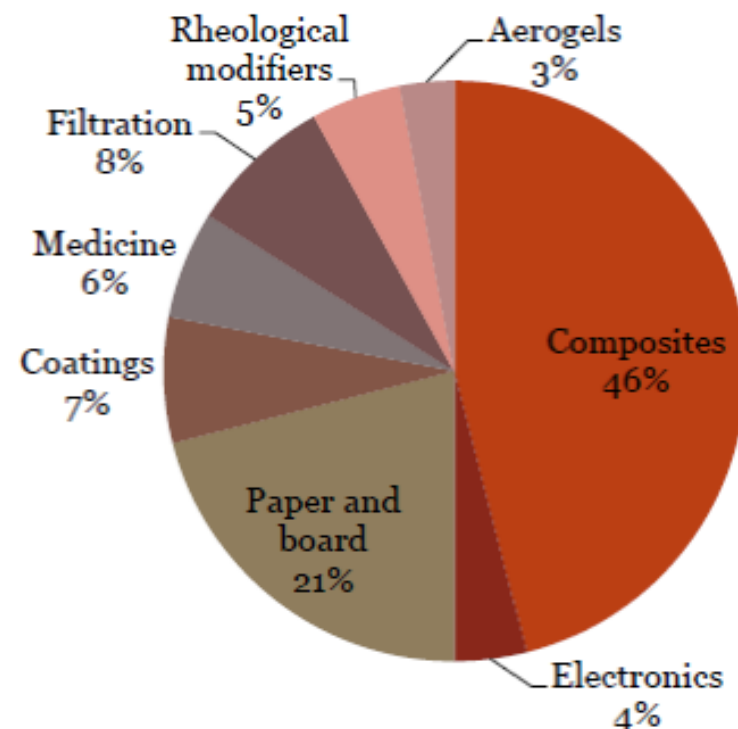
⇒ Not only fashionable but already **sustainable**

CNF – Production status



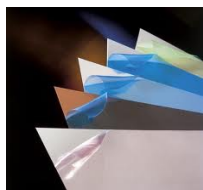


Nanocellulose toward industrialization



Future Markets, *The global market for nanocellulose to 2020*, 2nd ed. Future Markets Inc, 2012

23 million tonne potential (figure in ktons)

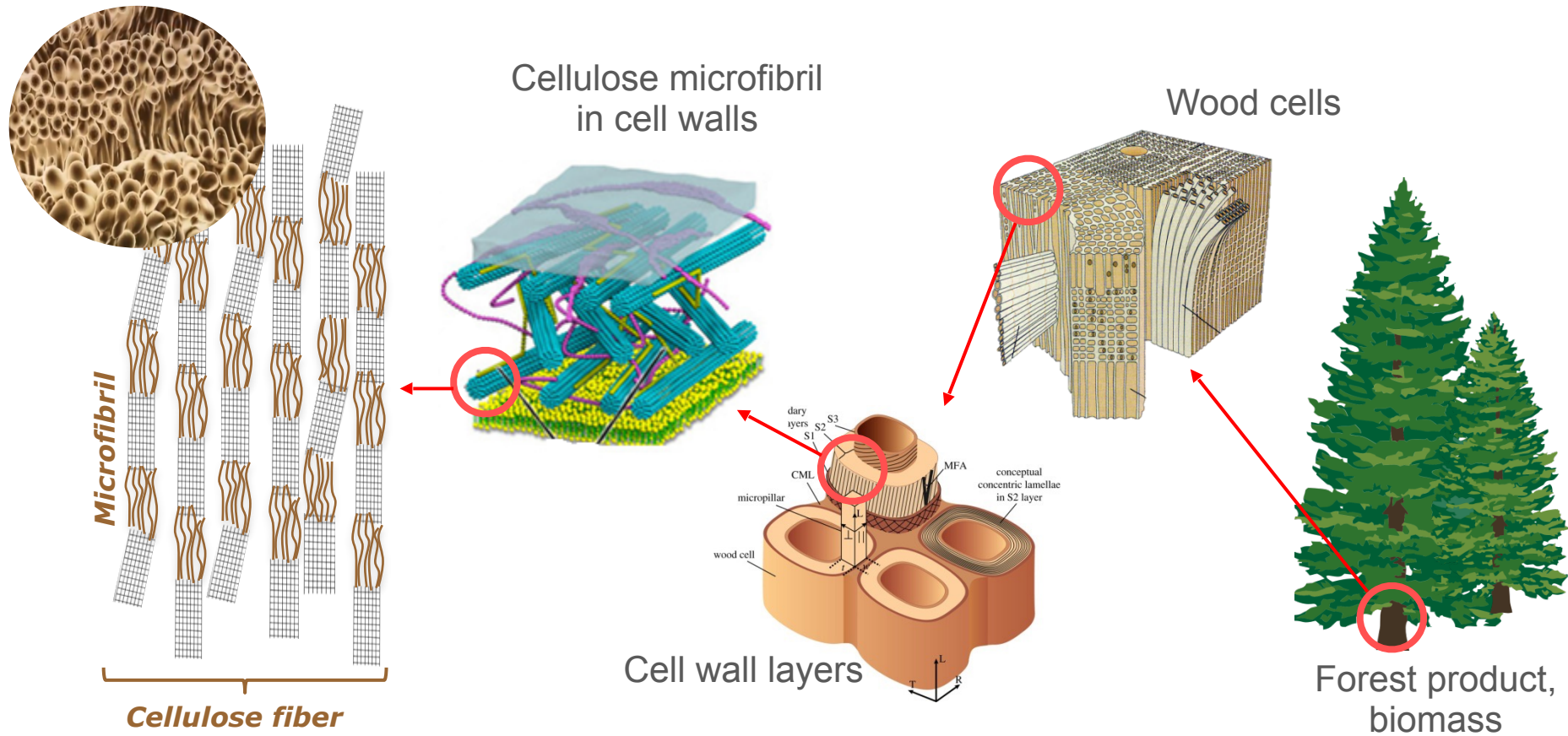


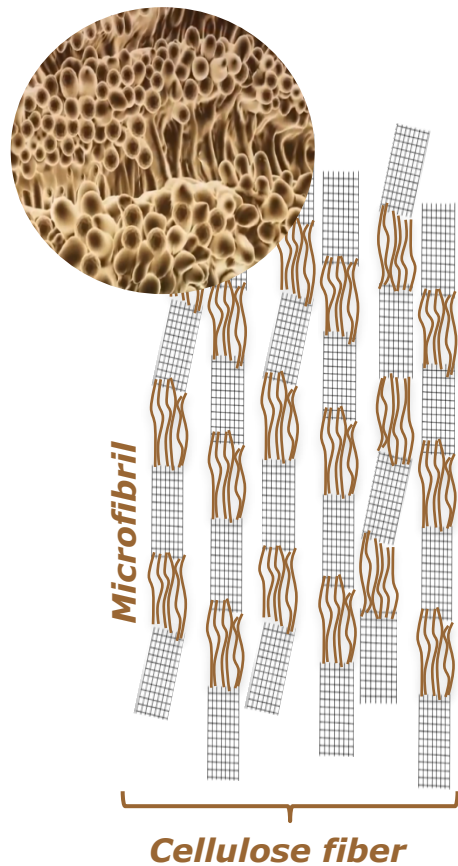
	Market Size	Potential Loading	Nano Cellulose Potential	Potential @ 5% Market Penetration	CNF Potential	CNC Potential	CNF	CNC
					95%	5%	950	10*
Paper and Paperboard	400,000	5.0%	20,000	1,000				
Paints and Coatings	40,000	2.0%	800	40	5%	95%	2	38
Composites	9,000	2.0%	180	9	5%	95%	0	9
Films and Barriers	9,670	2.0%	193	10		100%	0	10
Excipients	4,600	2.0%	92	5	10%	90%	0	4
Natural Textiles	34,500	2.0%	690	35		100%	0	35
Manufactured Textiles	56,300	2.0%	1,126	56		100%	0	56
Cement	15,000	0.5%	75	4	5%	95%	0	4
Oil and Gas	17,500	1.0%	175	9	10%	90%	1	8
Nonwovens	7,000	2.0%	140	7		100%	0	7
Adhesives	4,000	2.0%	80	4	5%	95%	0	4
TOTAL			23,551	1,178			954	184



Source: RISI, *Nanocellulose: Technology Applications, and Markets*

1. Nanocellulose : un contexte favorable
2. Production des Nanocellulose
3. Vers des applications de plus en plus évoluées





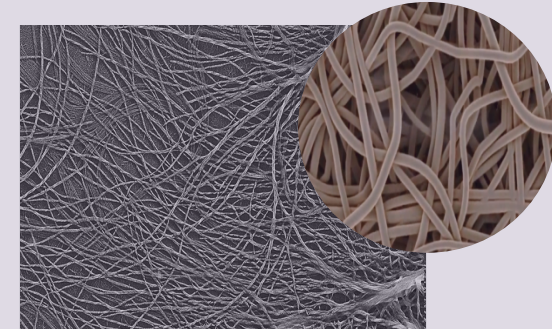
2. Mechanical Homogenization

1. Defibrillation

1. Hydrolysis

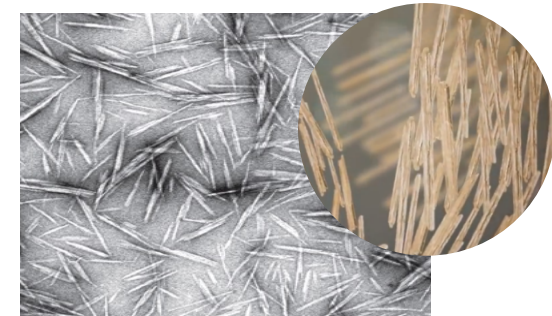
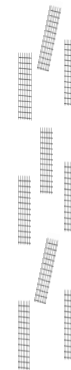
2. Dialysis

Microfibrillated cellulose (MFC)

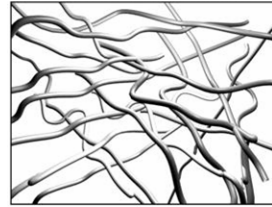


D 2-20 nm
L > 1000 nm

Cellulose Nanocrystals (CNC)



D 2-20 nm
L 200-1000 nm



> 50 types of CNF

① Purification
cooking and bleaching

② Mechanical pretreatment
– blending;
– refining;
– grinding.

③ Biological/chemical pretreatment
– enzymatic hydrolysis;
– carboxylation;
– carboxymethylation;
– quaternization;
– sulfonation;
– solvent-assisted pretreatment.



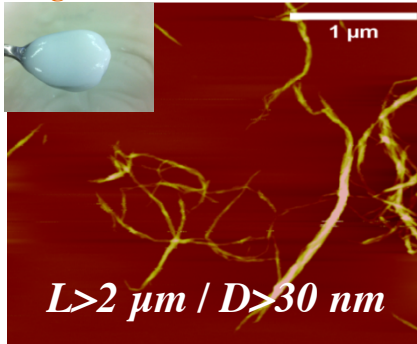
1 raw material
wood, plants etc.

④ Principal mechanical treatment
– homogenization;
– grinding;
– refining;
– extrusion;
– blending;
– ultrasonication;
– cryocrushing;
– steam explosion;
– ball milling;
– aqueous counter collision.

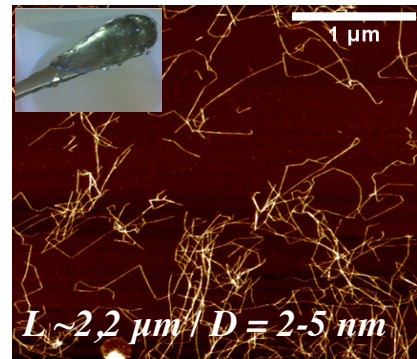
⑤ Post-treatment
– chemical modification;
– fractionation.

Mechanical Treatment

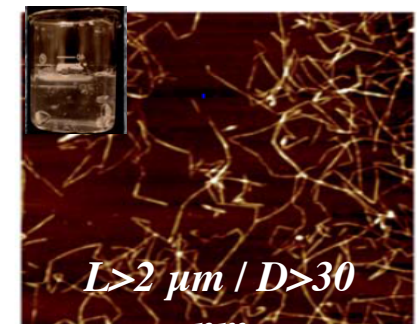
(Homogeniser, Microfluidiser, Grinding)



*Siqueira et al. (2009) Biomacromolecules



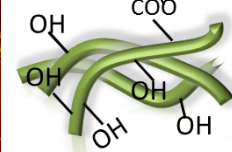
*Saito et al. (2006) Biomacromolecules



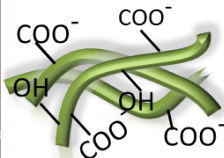
*Pei et al. (2013) Soft matter

Pretreatment

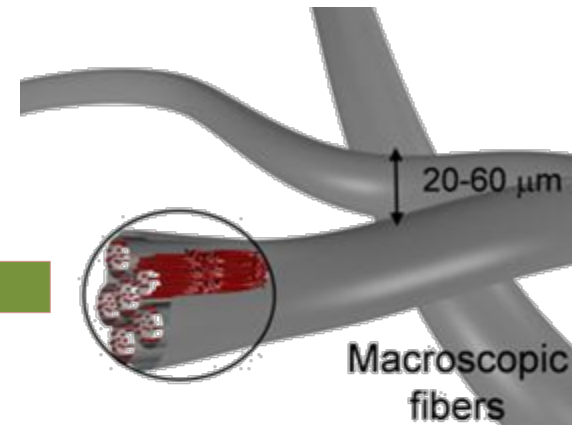
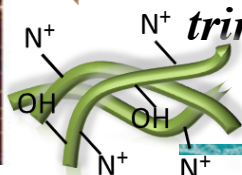
Enzymatic Hydrolysis
(Cellulase or endoglucanase)



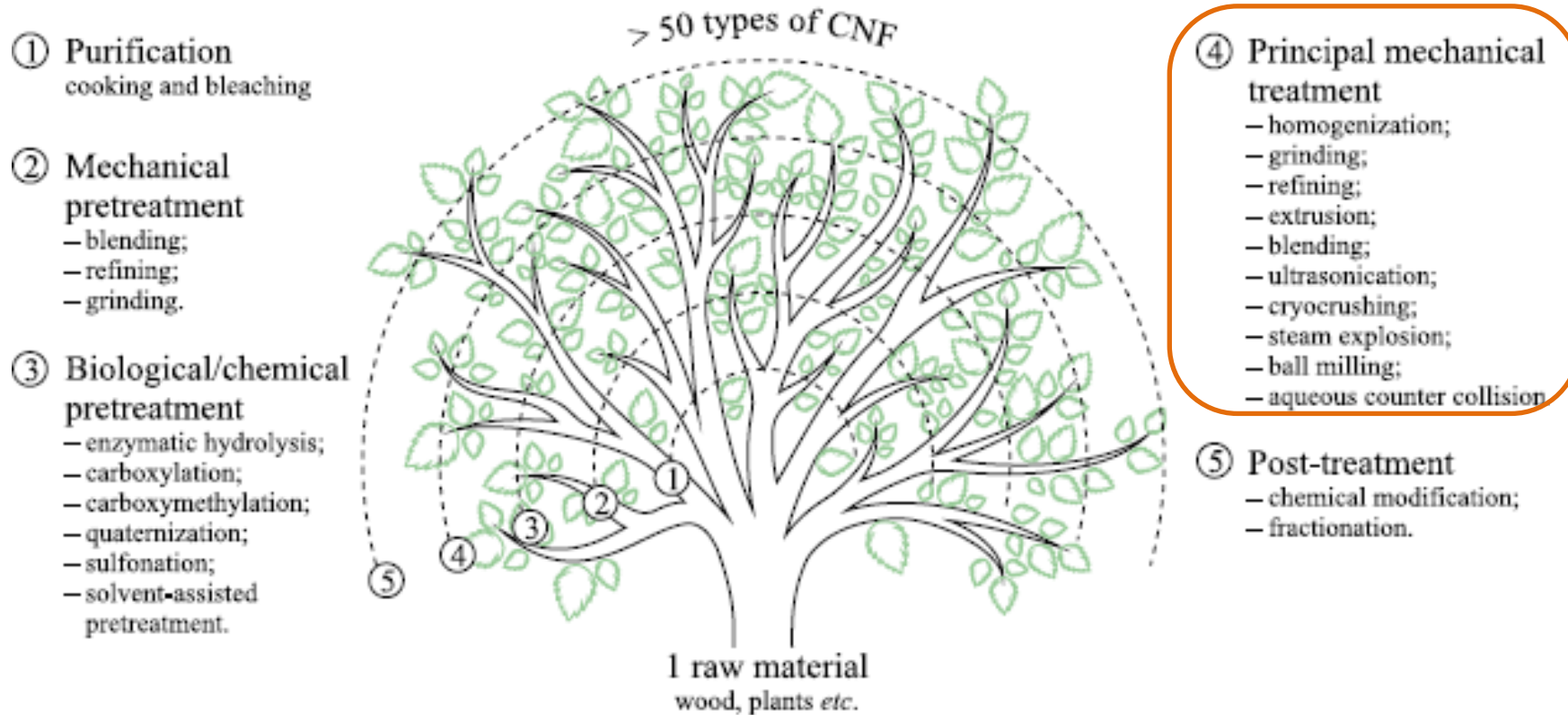
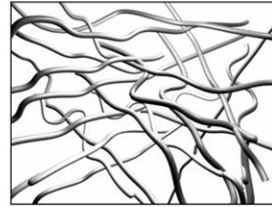
*Tempo oxidation (Tempo/
NaBr/NaClO)*



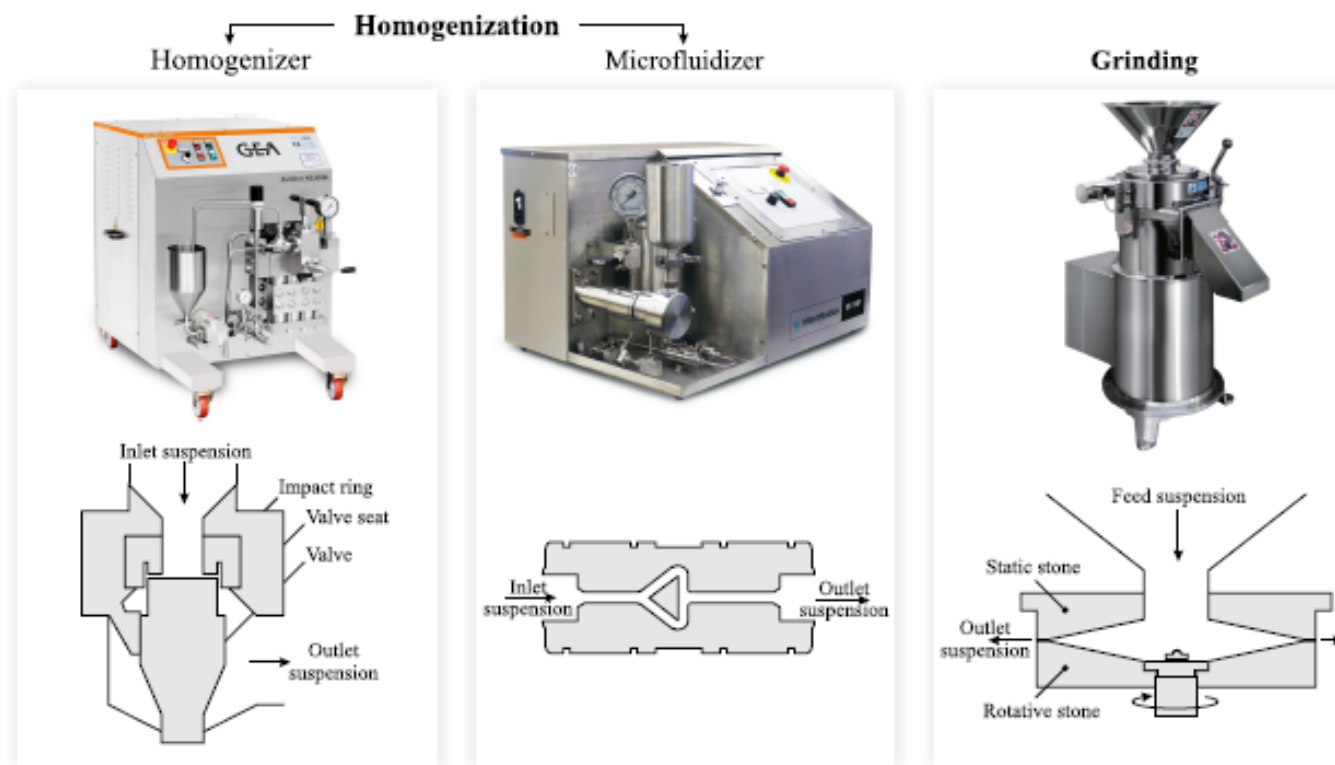
Cationization
(2,3-epoxypropyl
trimethylammonium chloride or
chlorocholine chloride)



*Pääkkö et al. (2007) Biomacromolecules



Nanofibrils & fibrillation process



Conventional

Mechanical processes for CNF production

Non-conventional

Extrusion

Blending

Ultrasonication

Cryocrushing

Refining*

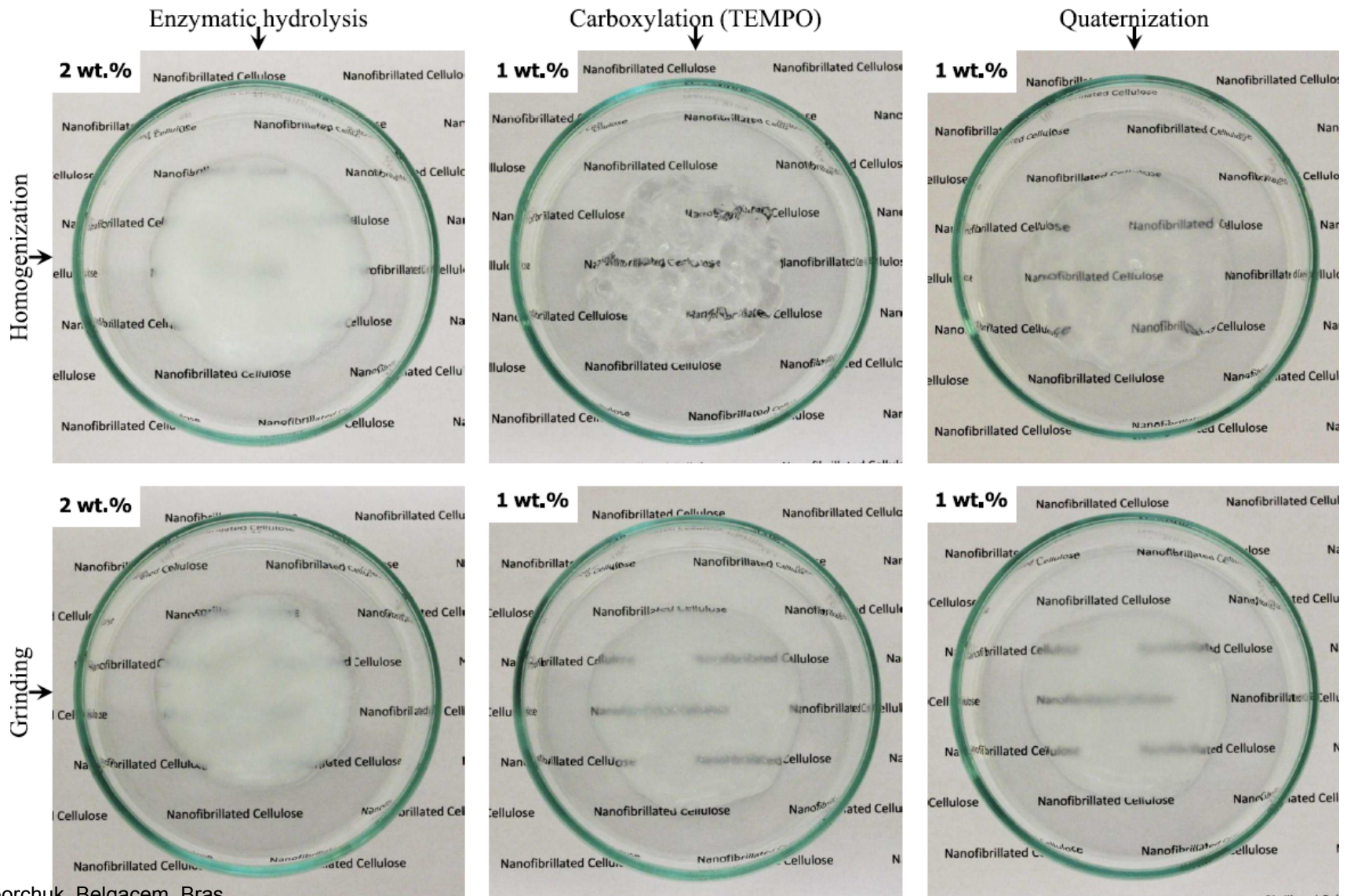
Steam explosion

Ball milling

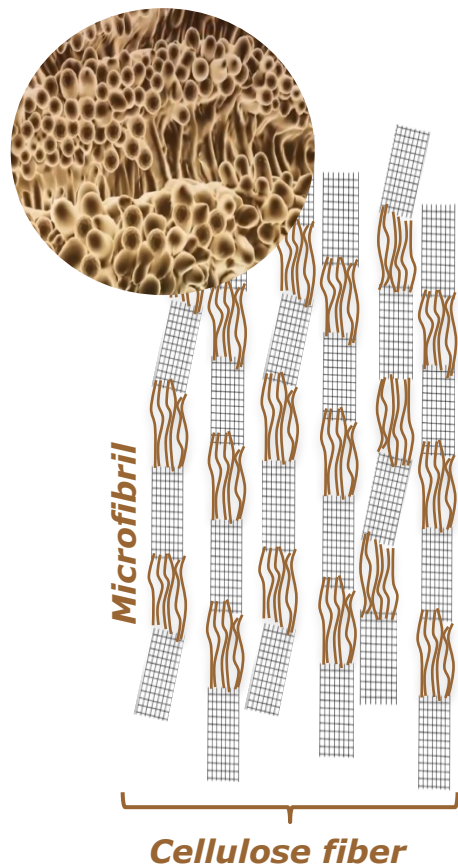
Aqueous counter collision

* as a principal mechanical process

Nechyporchuk, Belgacem, Bras
Production of cellulose nanofibrils: a review of
recent advances,
Ind crops (2016), in press



Nanocrystals and sustainable process



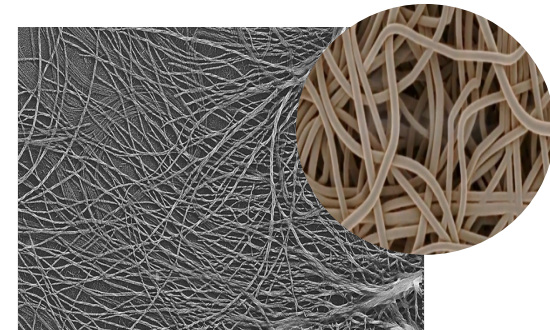
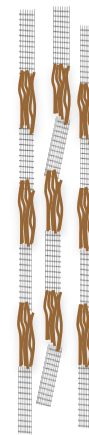
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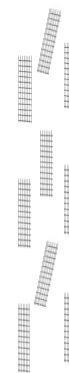
2. Dialysis / UF

Microfibrillated cellulose (MFC)



D 2-20 nm
L > 1000 nm

Cellulose Nanocrystals (CNC)



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Nanocrystals and sustainable process

One issue is the presence of acids => washing and thermal stability

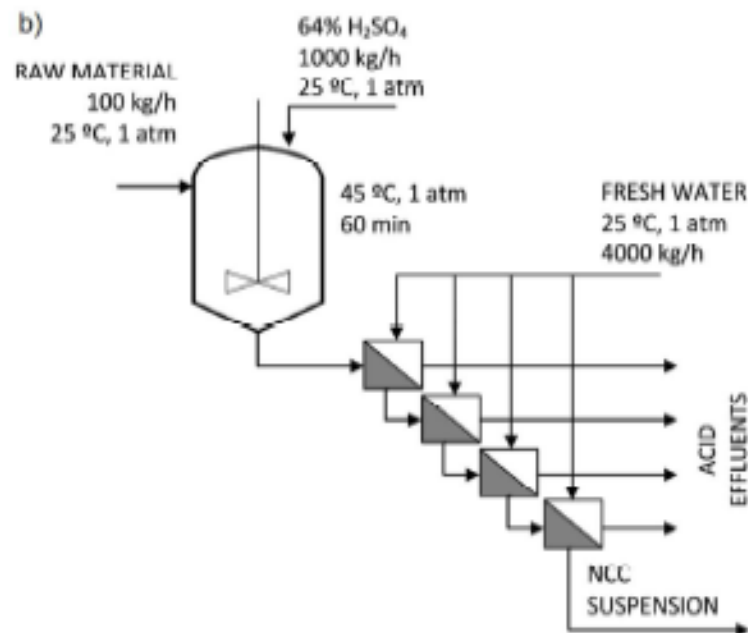


Figure S2. Flowsheet diagrams describing the evaluated nanocrystals production processes by (a) subcritical water and (b) conventional acid hydrolysis method.

Nanocrystals and sustainable process

One issue is the presence of acids => washing and thermal stability

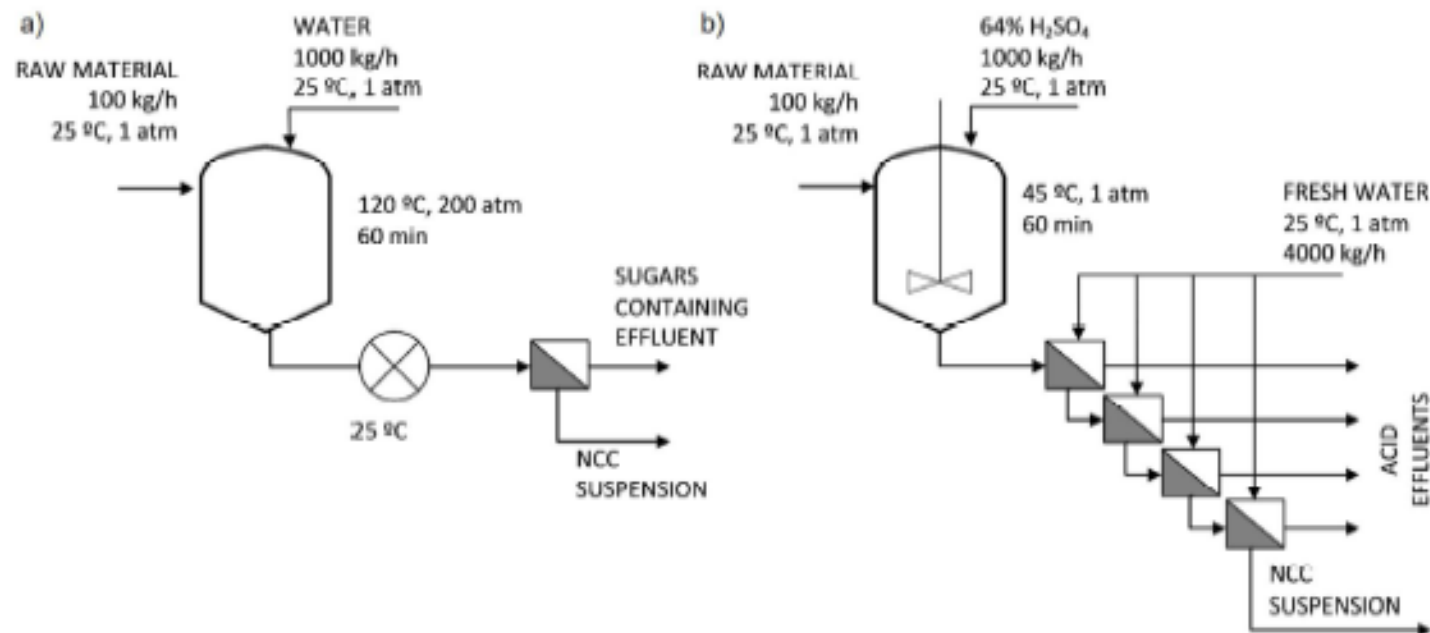
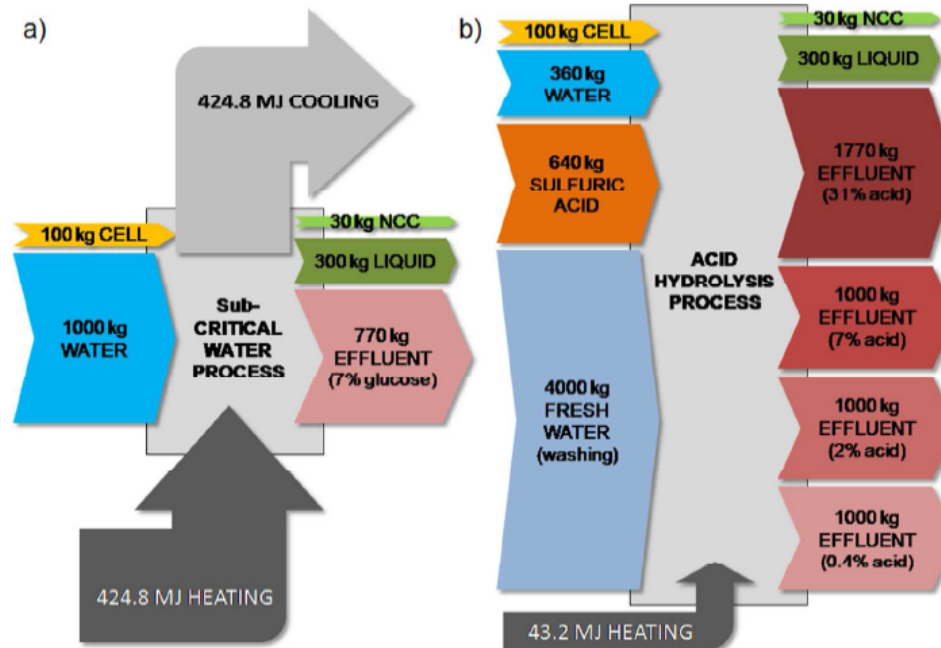


Figure S2. Flowsheet diagrams describing the evaluated nanocrystals production processes by (a) subcritical water and (b) conventional acid hydrolysis method.

Nanocrystals and sustainable process

	unit cost (\$/kg)	SC-NCC		H-NCC	
		consumption (kg)	cost (\$)	consumption (kg)	cost (\$)
process water	0.0003	1000	0.3000	4360	1.3080
sulfuric acid	0.070			640	44.80
cooling water ^a	0.00001	5059	0.0506		
low pressure steam ^b	0.002	193	0.3857	19.7	0.0390

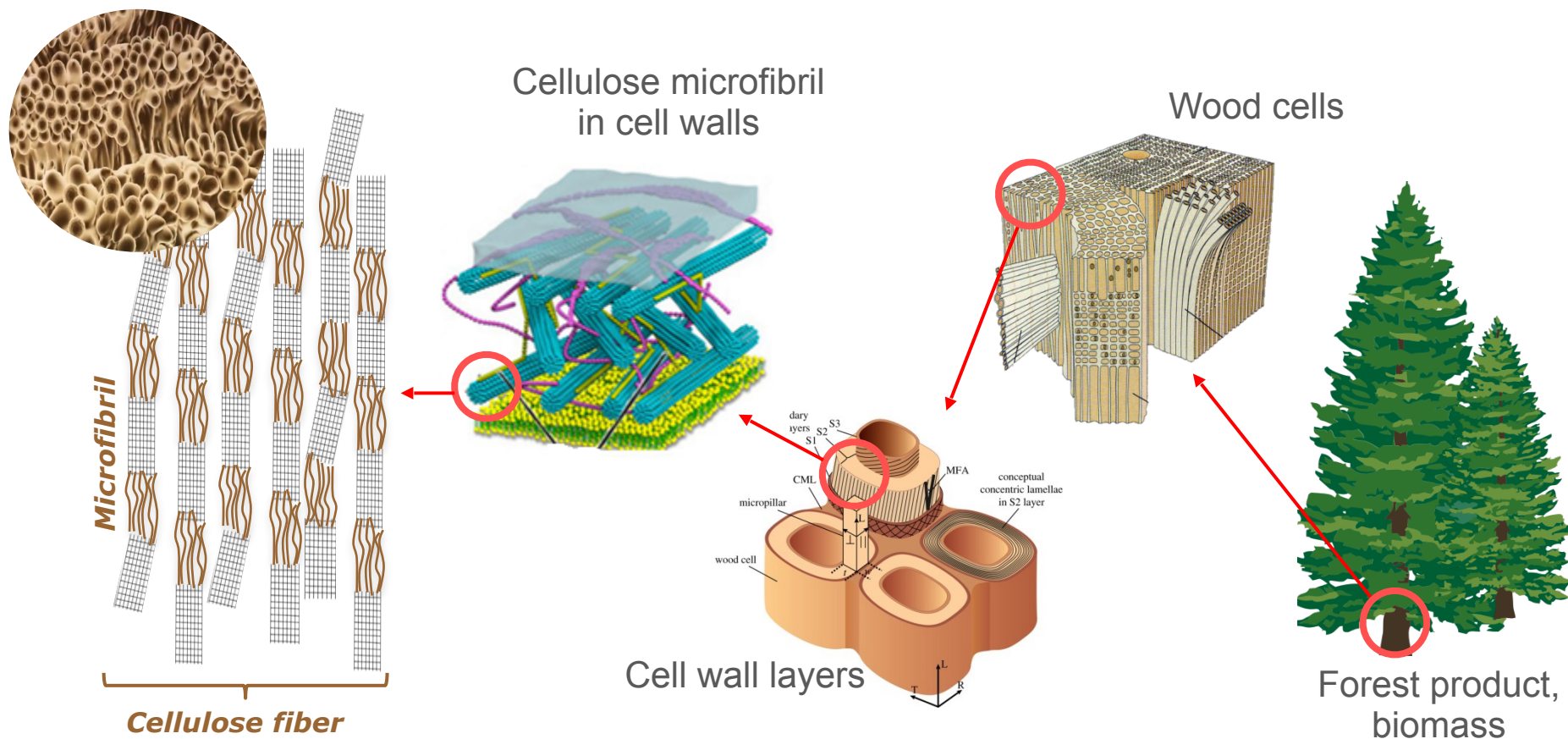
^aCooling water temperature input and output specifications: 10 and 30 °C, respectively. ^bLow pressure steam of 200 kPa, 2201.56 kJ/kg heating value.



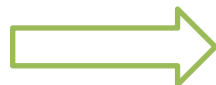
Conventional NCC cost = 1.54 \$/kg of NCC,

>>> NCC using the proposed subcritical treatment : 0.02 \$/kg of NCC

Cellulose or Wood



Long process for obtaining
INTACT cellulose fiber



Why not starting
directly from WOOD ?

Cellulose Nanocrystals

Abushammala, Krossing, Laborie, Ionic liquid-mediated technology to produce cellulose nanocrystals directly from wood/ Carbohydrate Polymers 134 (2015) 609–616

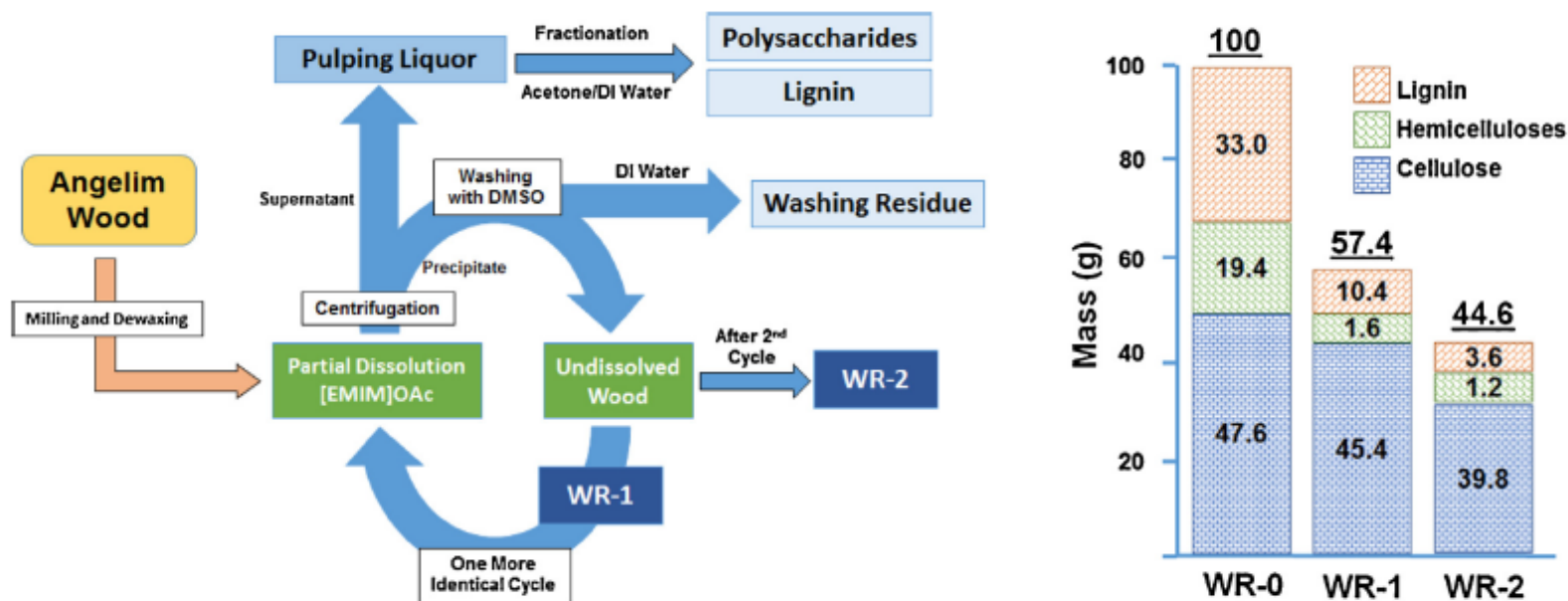
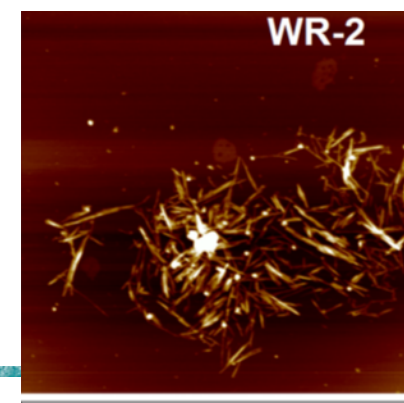
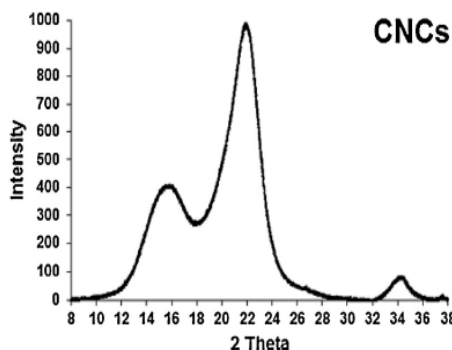
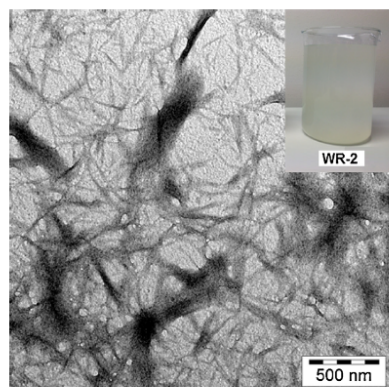
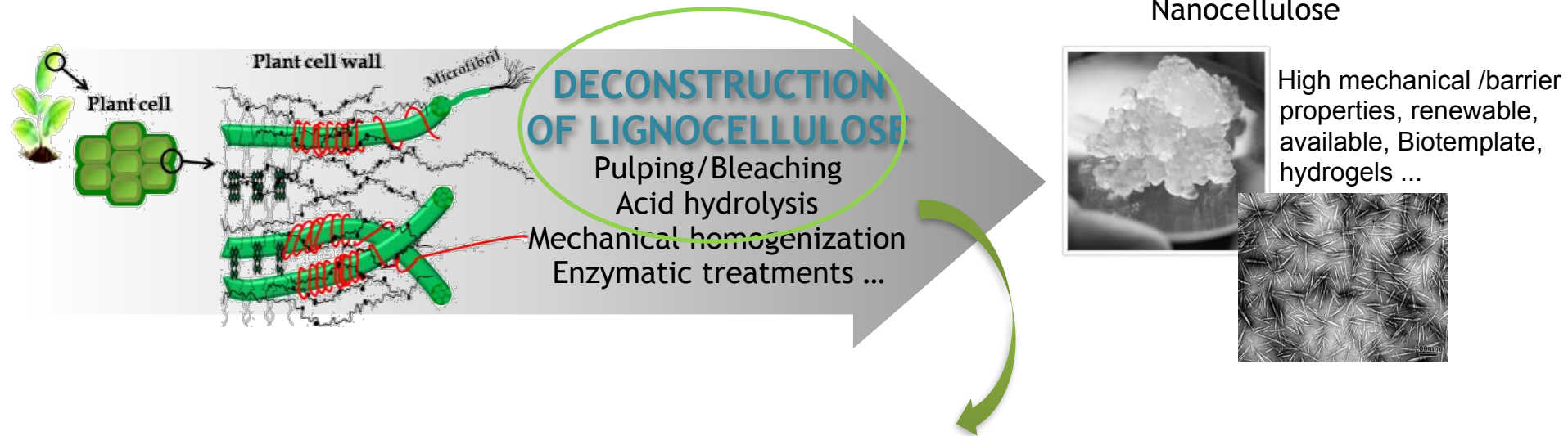


Fig. 1. The pulping procedure of Angelim Vermelho using [EMIM][OAc] (Left). The mass balance for the two pulping cycles including the wood residues starting with 100 g of Angelim vermelho wood (Right).

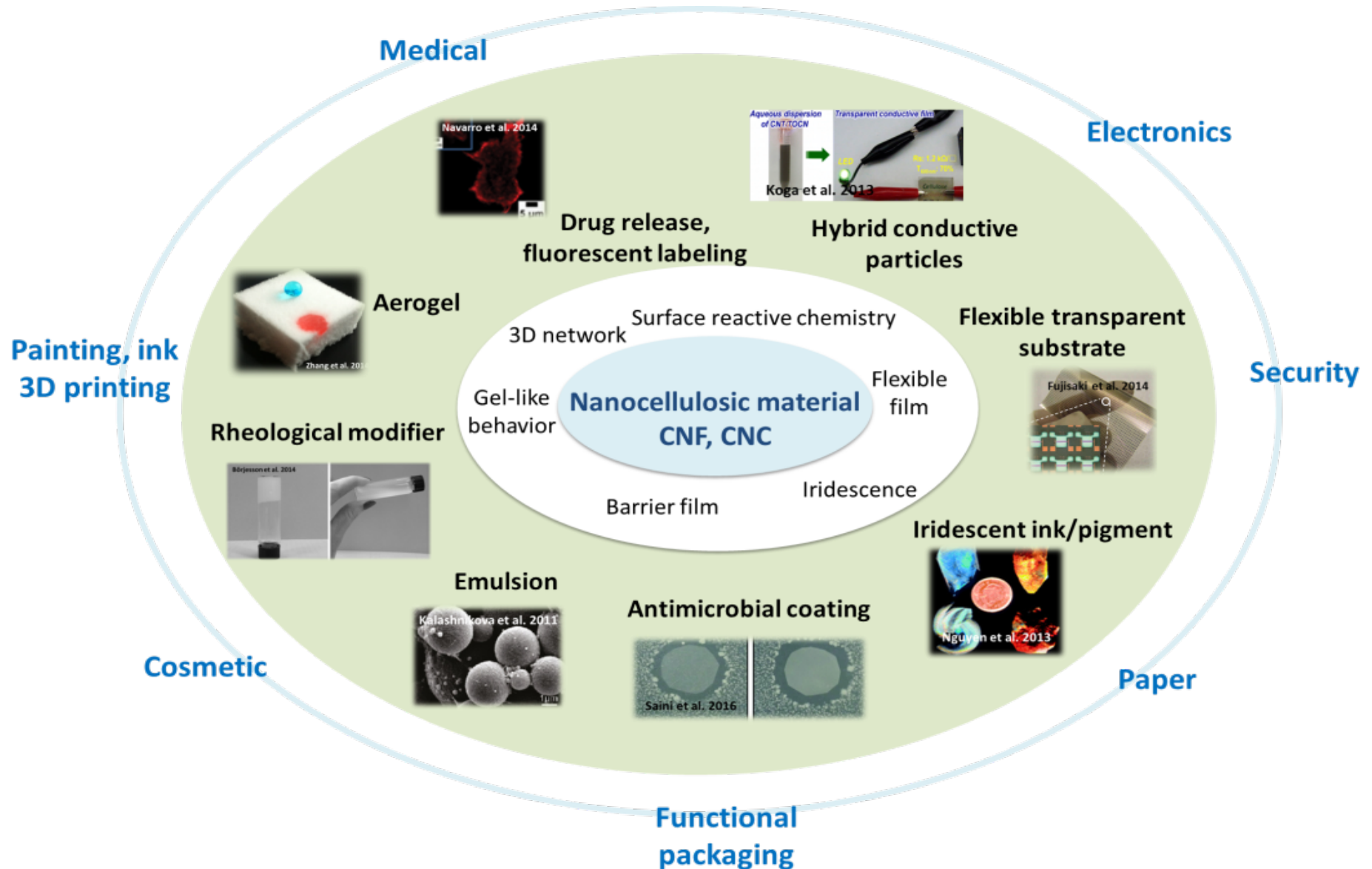




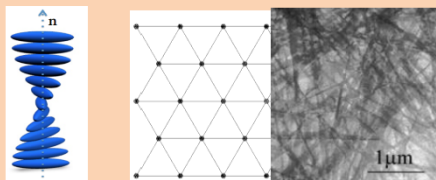
Look for more sustainable solutions

- New solution to increase fibre wall porosity
- New swelling solvents
- New mechanical pretreatment
- New fibers or industrial waste
- Start directly from wood

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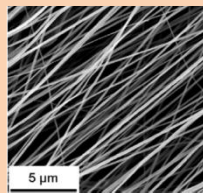


Self-Assembly



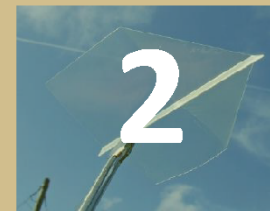
Noichiki et al., J. Appl. Poly. Sci., 2002, 86, 3425-3429

Continuous Fibers



Dong et al., Carb. Poly., 2012, 87, 2488-2495

Films



Nogi et al., Adv. Mater, 2009

Foams/Aerogels



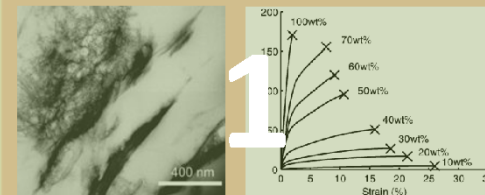
Paakko et al., Soft Matter, 2008, 4, 2492-2499

Hydrogels



Abe et al., Carb. Poly., 2011, 85, 733-737

Polymer Fillers



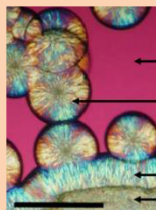
Bondeson et al., Comp. Inter., 2007, 14, 617-630
Svagan et al., Biomacromolecules, 2007

Rheology Modifier



T Lindström/STFI

Nucleation Agent



Gray, Cellulose, 2008, 15, 297-301

Reaction Pathway

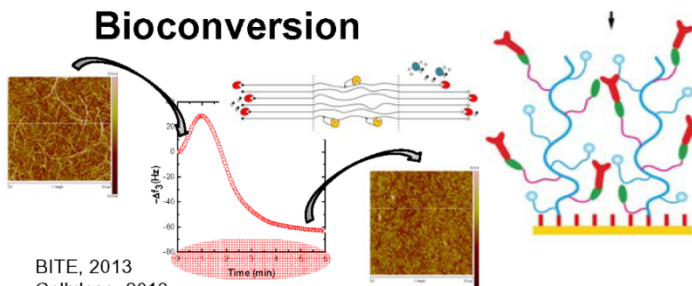


cement

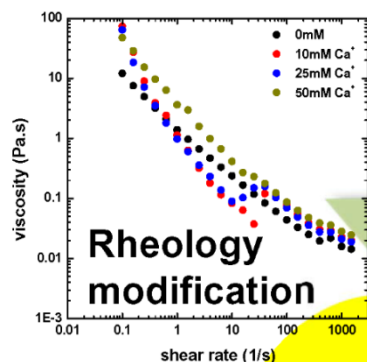
Cao et al.

Nanocellulose application

Bioconversion

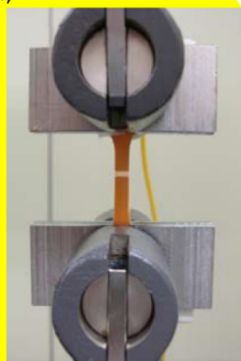


BITE, 2013
Cellulose, 2013
ACS Macro Letters, 1, 1321 (2012)
Biomacromolecules, 13, 3228 (2012)
Biomacromolecules, 14, 1637-1644 (2013)

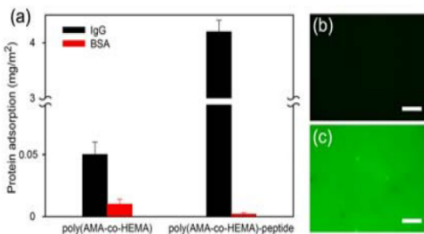


Composites

(reinforced materials)

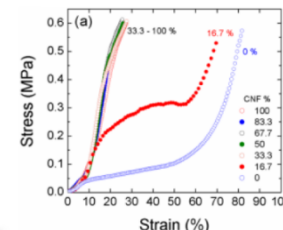


Bioactive materials



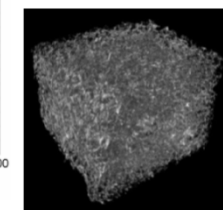
Anal. Chem, 2013
Biointerphases, 7, 61 (2012)
Biomacromolecules, 12, 4311 (2011)
Biomacromolecules, 13, 2802 (2012)
Carbohydrate Polymers,
doi:10.1016/j.carbpol.2012.11.063

Super-strong Hydrogels & Aerogels



Cellulose 20, 2417 (2013)

Appl. Mater. Interfaces
2012, 4, 636



Cellulose Nanofibrils NFC and BC

J. Renewable Resources, 2013, 1, 195
Carbohydrate Polymers, 89,1033-1037 (2012)

Nanopaper

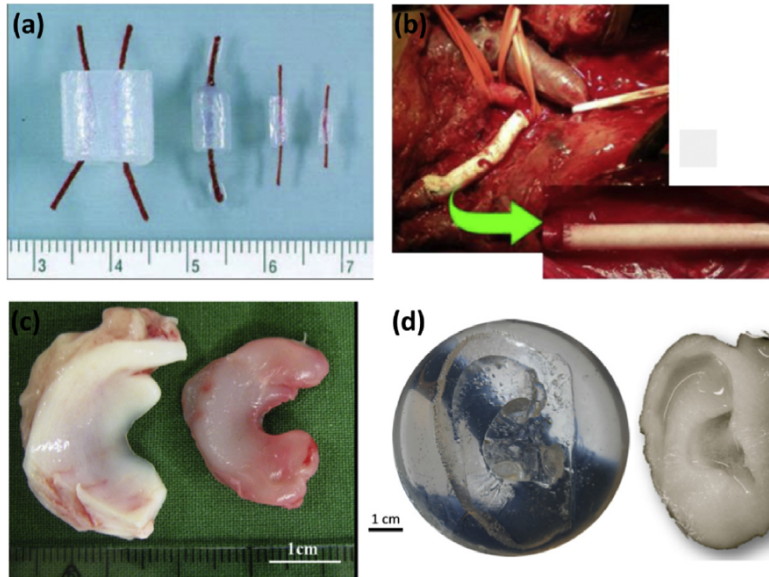


Appl. Mat. Interfaces, 2013

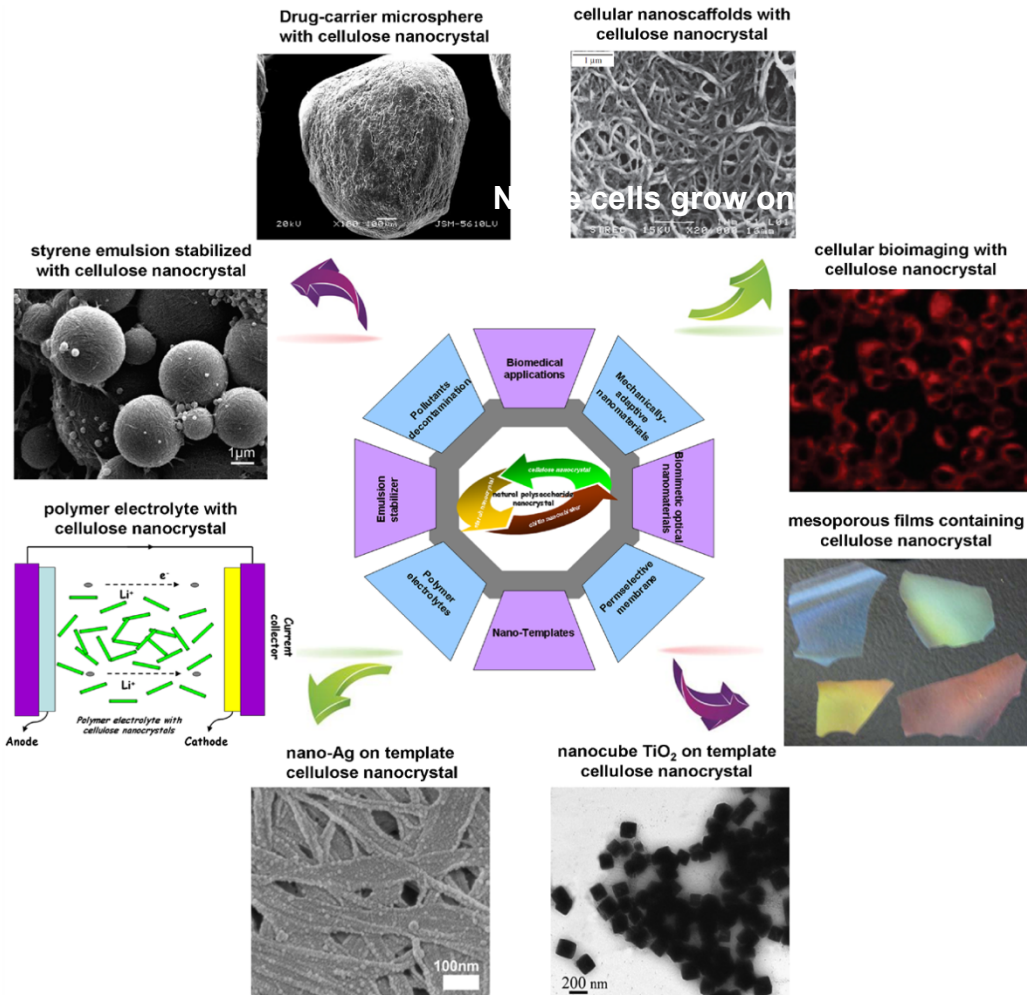
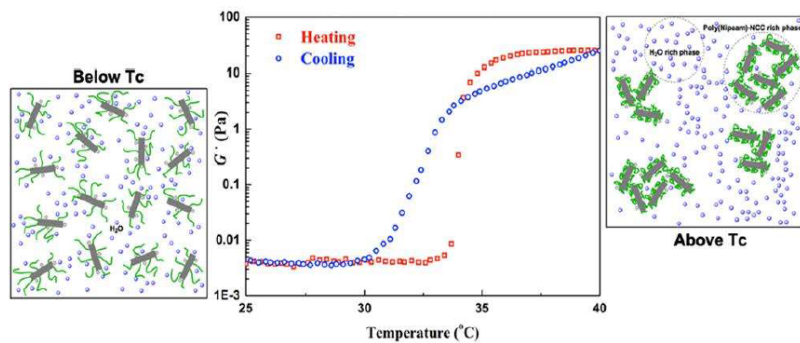
BITE 125, 249 (2012)
Cellulose, 19, 2179 (2012)
Bioresources, 6, 4370 (2011)
Cellulose, 18,1097 (2011)
Cellulose, 17, 835 (2010)
BITE 101, 5961 (2010)

Conductive nanopaper (+ Pyrrole, click chemistry): $37.4 \cdot 10^{-3} \text{ S/cm}$

Nanocellulose application



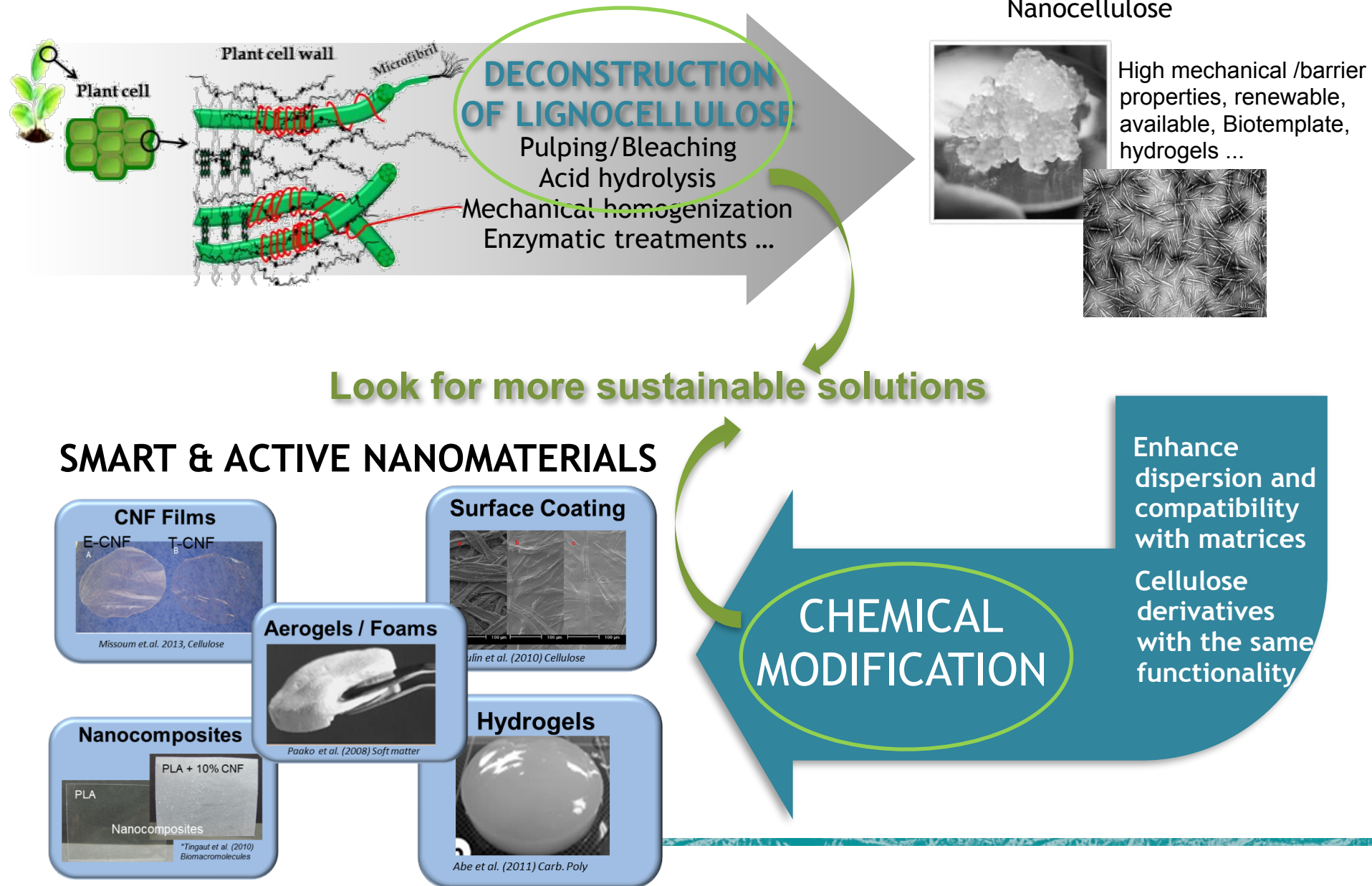
Cellulose Nanocrystals grafted with Poly(N-isopropylacrylamide)



Nanocellulose topic	Review/Publication
CNF production	Production of cellulose nanofibrils: A review of recent advances <i>Nechyporchuk et al. 2016</i>
CNC properties	Cellulose nanocrystals: chemistry, self-assembly, and applications <i>Habibi et al. 2010</i>
Surface modification	Key advances in the chemical modification of nanocelluloses - <i>Habibi et al. 2014</i>
CNF and CNC colloids and interactions	Nanocellulose properties and applications in colloids and interfaces <i>Salas et al. 2014</i>
	Electrostatic or steric? – preparations and characterizations of well-dispersed systems containing rod-like nanowhiskers of crystalline polysaccharides <i>Araki et al. 2013</i>
	Tuning supramolecular interactions of cellulose nanocrystals to design innovative functional materials – <i>Moreau et al. 2016</i>
Patents on nanocellulose	Nanocellulose patents trends: a comprehensive review on patents on cellulose nanocrystals, microfibrillated and bacterial cellulose - <i>Charreau et al. 2013</i>
TEMPO oxidation	TEMPO-oxidized cellulose nanofibers- <i>Isogai et al. 2011</i> TEMPO-mediated surface oxidation of cellulose whiskers - <i>Habibi et al. 2006</i>
CNF for paper	Cellulose nanofibers and their use in paper industry – <i>Bardet et al. 2014</i>
CNF and CNC for medical	Recent advances in nanocellulose for biomedical applications <i>Jorfi et al. 2015</i>
CNF barrier properties	Impact of different coating processes of microfibrillated cellulose on the mechanical and barrier properties of paper - <i>Lavoine et al. 2014</i>
CNF and CNC for composites	Microfibrillated cellulose and new nanocomposite materials: a review <i>Siro et al. 2010</i>
	Cellulose nanocrystals and related nanocomposites: Review of some properties and challenges - <i>Mariano et al. 2014</i>
CNF and CNC for electronics/metallic particles	Use of nanocellulose in printed electronics: A review - <i>Hoeng et al. 2016</i> Review: nanocelluloses as versatile supports for metal nanoparticles and their applications in catalysis – <i>Kaushik et al. 2016</i>

1. Nanocellulose : un contexte favorable
2. Production des Nanocellulose
3. Vers des applications de plus en plus évoluées

Conclusion et perspectives



Nanocellulose - Futucell *IUF*

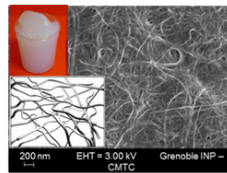
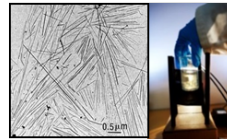
BIOMASS



T1: Nanocellulose preparation process optimization
(Deconstruction)



NANO-CELLULOSE



T2: Nanocellulose surface functionalization
(activation)

MATERIALS

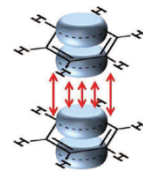
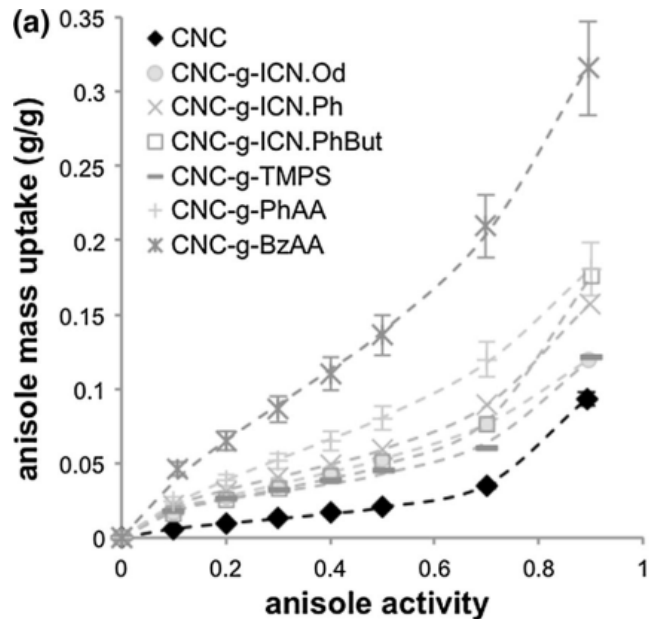


T3: Material preparation processes for Transfer and interactions
(reconstruction)

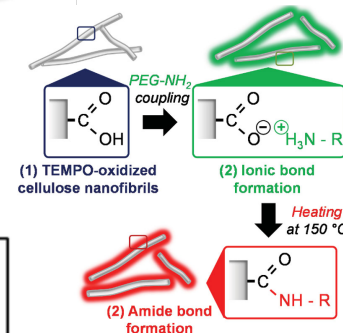
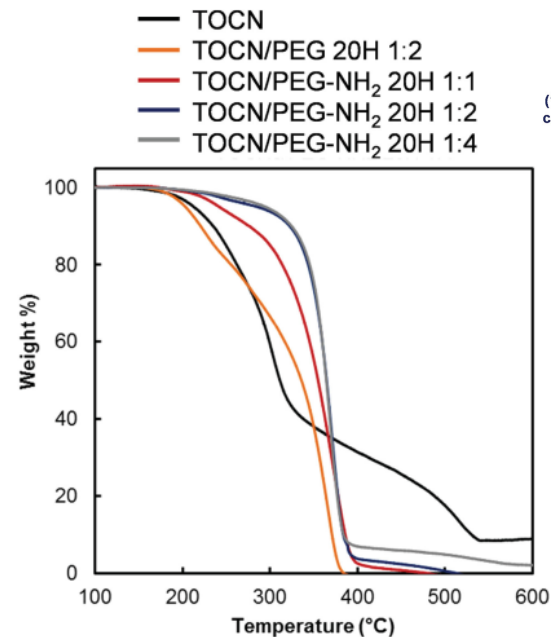


APPLICATIONS

Adsorption



T resistance



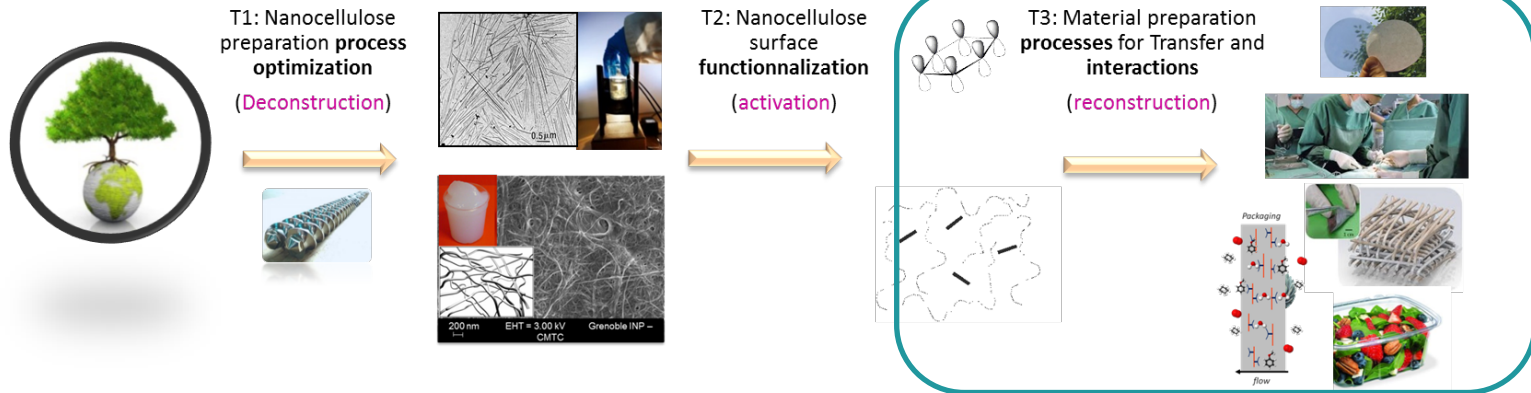
Nanocellulose - Futucell IUF

BIOMASS

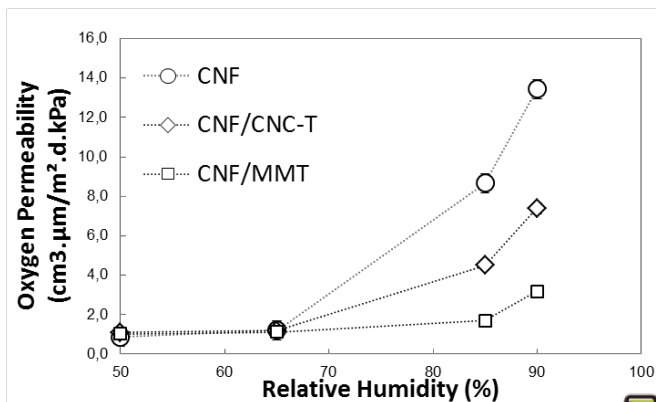
NANO-CELLULOSE

MATERIALS

APPLICATIONS



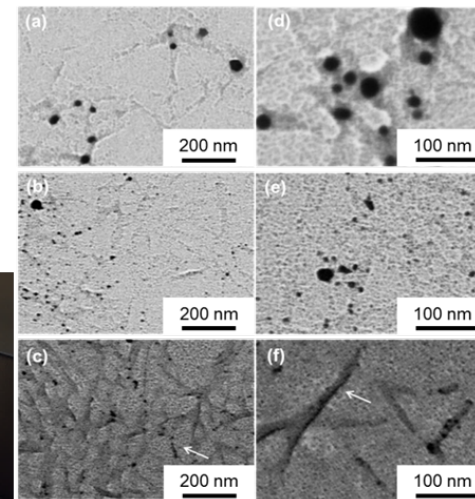
Barrier



ActInPak
NewGenPak

Bardet, Reverdy, Belgacem, Leirset, Syverud, Bras, J
(2015) Cellulose, 22(2), 1227-1241

Conductivity



STEM images of CNC-silver nanoparticles network

Hoeng F, Denneulin A, Neuman C and Bras J,
J. Nanoparticle Res. 17 244, 2015

CELLULOSE MEDICAL

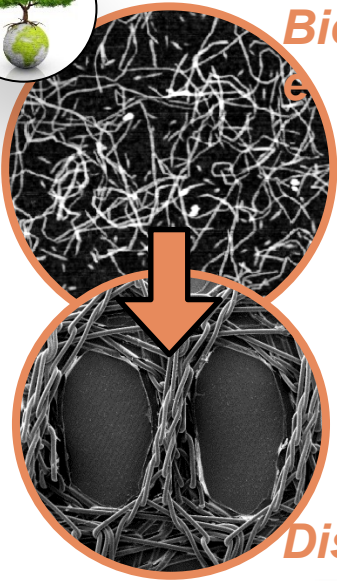
Les **microfibrilles de cellulose** comme nouveaux matériaux biosourcés pour designer des dispositifs bio-actifs de chirurgie réparatrice de tissus mous



Référence **ANR-15-CE08-0033**
Budget **597 042 €**
Durée **48 mois (2016 – 2020)**



Biomasse



Dispositif Medical



Porteur

LGP2

THANK YOU FOR YOUR ATTENTION

Julien.Bras@grenoble-inp.fr

Acknowledgement to my collaborators in this work:
Seema, Oleksander, Blagoj, Fleur, Lisias, Aracelli

Join us in the LinkedIn group « Nanocellulose Materials »



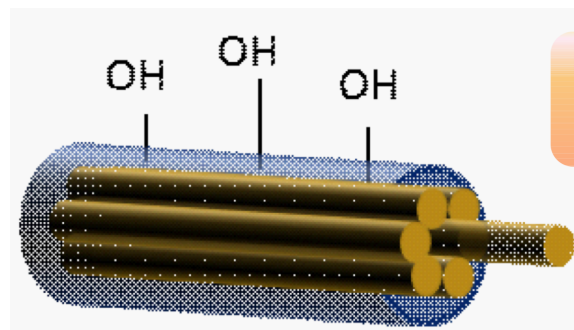
institut
universitaire
de France



tec21
the engineering
of complexity

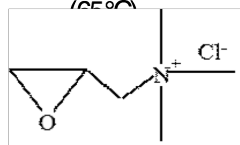


2,3-epoxypropyl trimethylammonium chloride (EPTMAC)

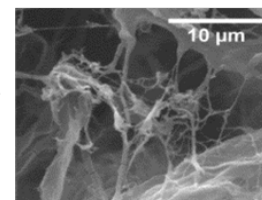
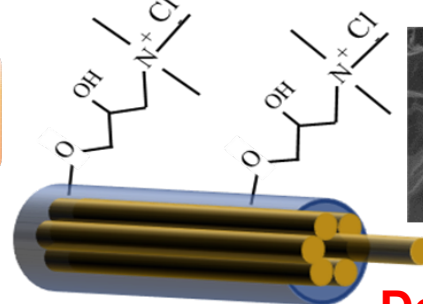


Step 1: Optimisation of pretreatment for different DS

NaOH, EPTMAC (65%)



Cationized cellulose



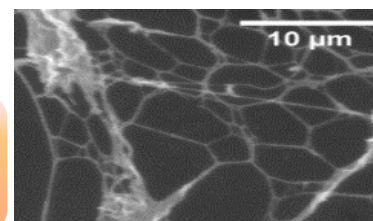
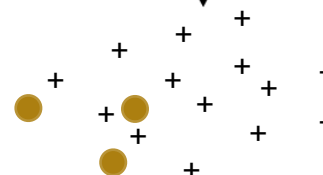
Degree of substitution

Masuko®Grinder



Fibrillation of cationized cellulose

Energy consumption

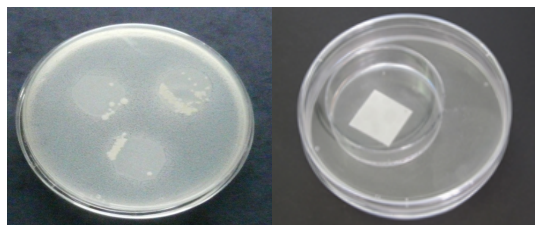


Morphology

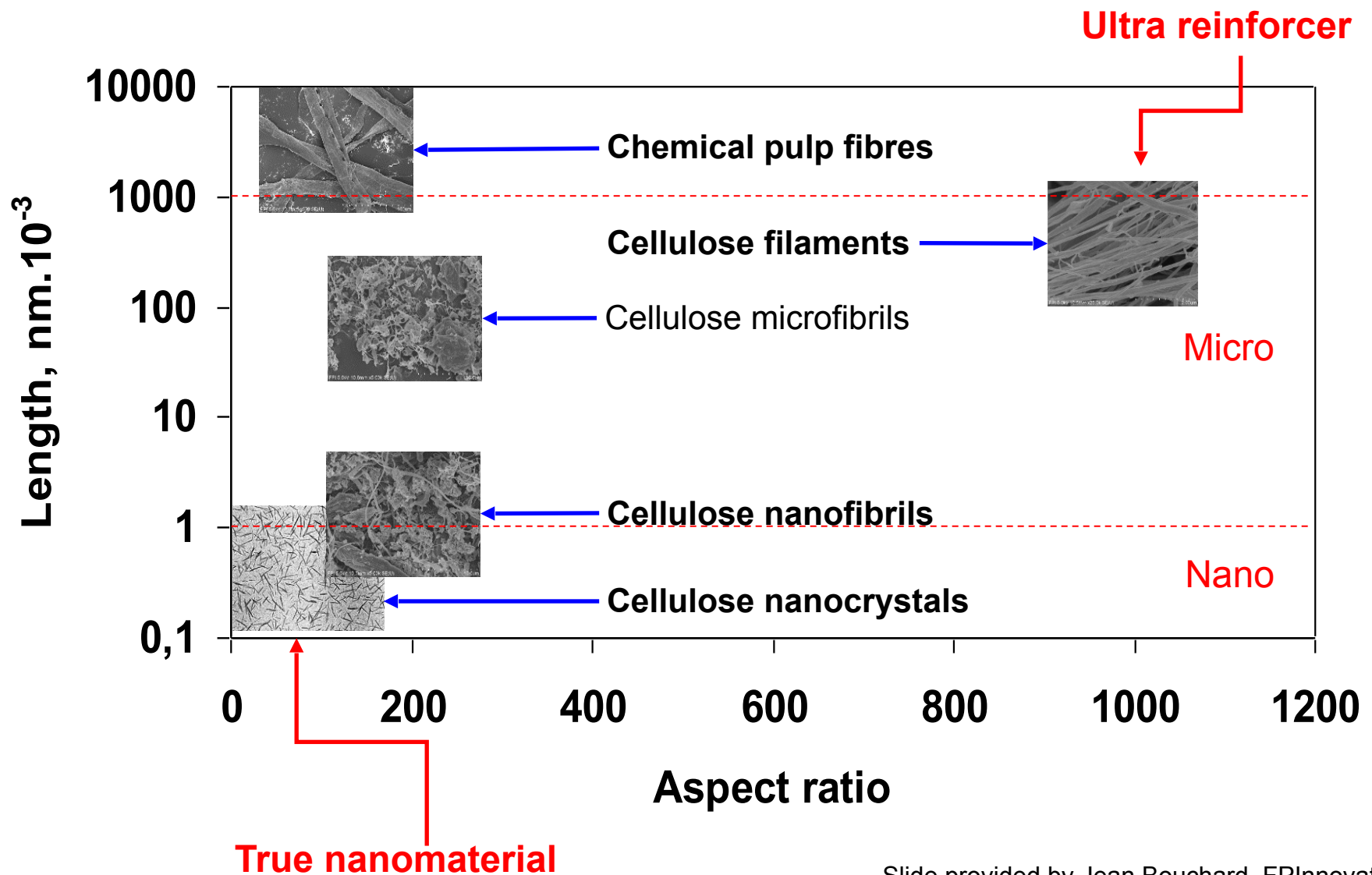
Cationized nanofibrils

Qualitative and quantitative antimicrobial activity

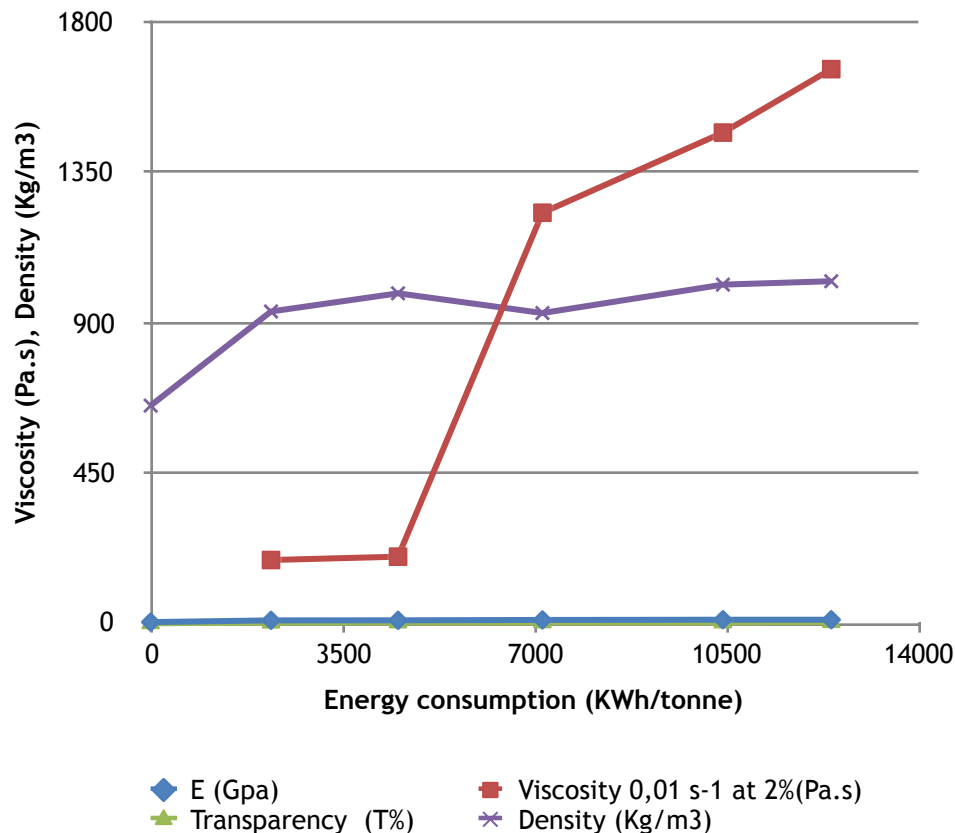
Activity against Gram +ve and Gram -ve bacteria



Step 2: Antibacterial activity evaluation of cationic CNF

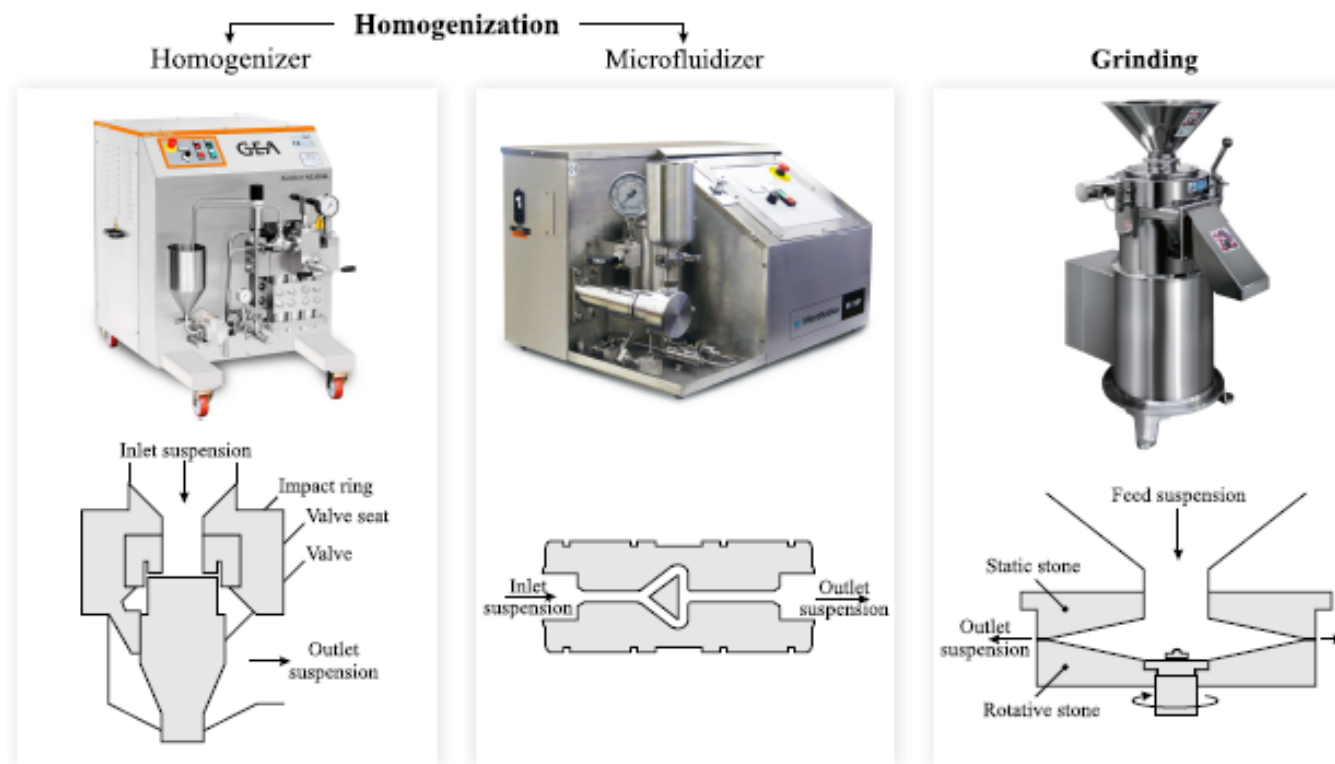


- **Main issues for the industries:**
High Costs & Energy consumption



Mechanical method	Total energy consumption for the MFC production	Reference
Homogenizer	70 000kWh/t	(Eriksen et al., 2008)
Microfluidizer	11 230 kWh/t	(Spence et al., 2011)
Grinder	12 810 kWh/t	(Spence et al., 2011)

Nanofibrils & sustainable process



Conventional

Mechanical processes for CNF production

Non-conventional

Extrusion

Blending

Ultrasonication

Cryocrushing

Refining*

Steam explosion

Ball milling

Aqueous counter collision

* as a principal mechanical process

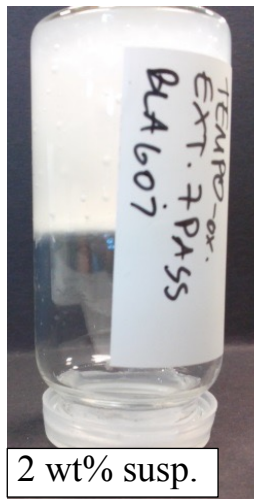
Nechyporchuk, Belgacem, Bras
Production of cellulose nanofibrils: a review of
recent advances,
Ind crops (2016), in press

Nanofibrils & sustainable process

NABEX (Nanocellulose composite by Extrusion) Project

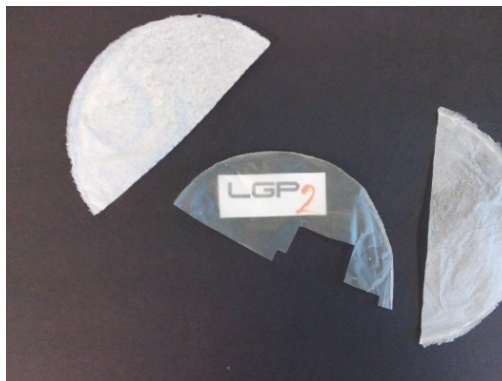
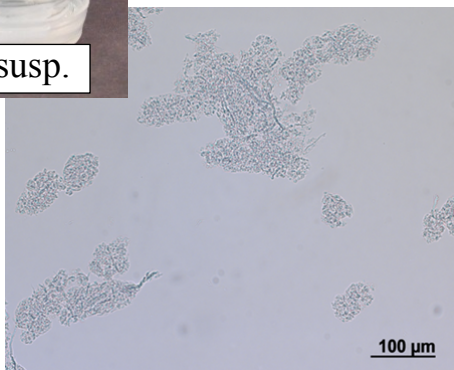
Blagoj Karabashov
(O.Nechyporchuk)
Julien Bras

Tec 21
Post-Master Trainee

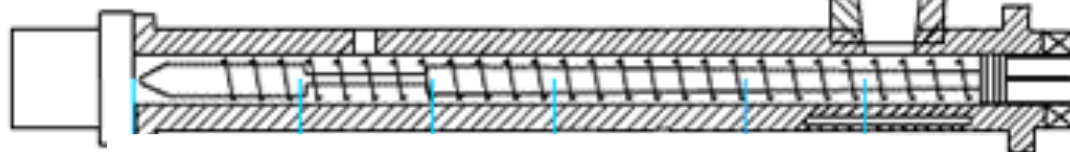


Nanocellulose

2 wt% susp.

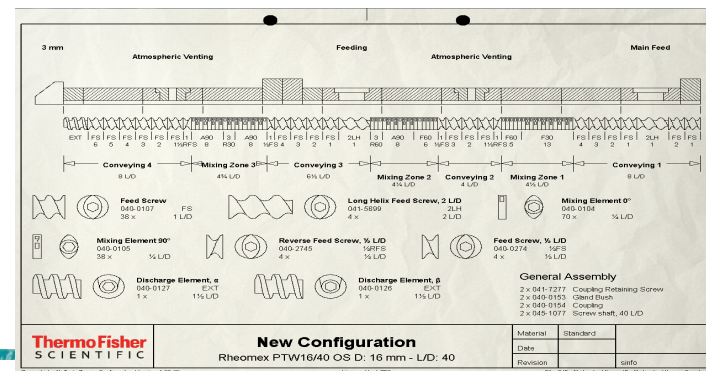
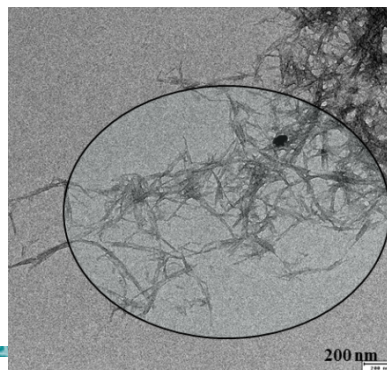


Enzymatic/ TEMPO/ Cationic
treated pulp



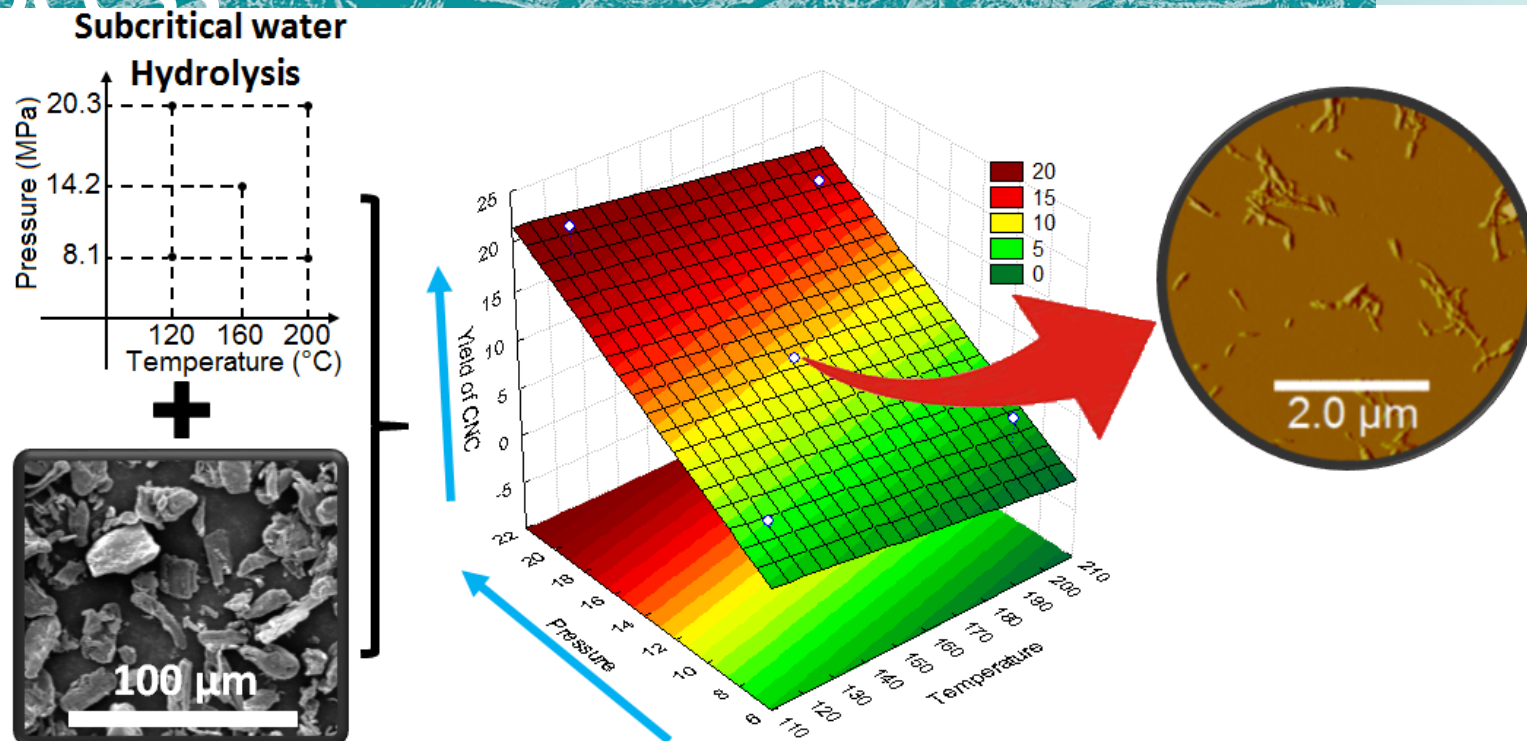
Melt compounding

In-situ Fibrillation



Industry or University	Country	Announced production (dry)	MFC characteristic and processes	Scale of process /trade Name
JRS	Germany	n.a.	Ultra refined fiber - not completely nanofibers	Commercial grade - Arbocell UFC
Booregaard- Exilva	Norway	1000 t/y	Enzymatic MFC	Pilot Plant
UPM Kymmene Ltd.	Finland	n.a.	Enzymatic MFC with Masuko	Commercial grade: Biofibrils
Stora Enso Ltd.	Sweden	own consumption	Enzymatic MFC with Masuko	Pre-commercial plant at Imatra (Fi)
Oji Paper	Japan	n.a.	High quality (films, wet powder, gel)	Pilot scale
Nippon Paper	Japan	30t/y	Tempo treated MFC	Commercial name: CSNF
Imerys	Swiss	n.a.	Enzymatic treated MFC with pigments in Masuko	Fiberlean
Kruger Canada	Canada	n.a.	Ultra refined fiber - not completely nanofibers	Ind scale
Betulium	Finland	n.a.	Different high quality grades	Pilot-ind scale
Sappi	UK	n.a;	n.a.	Ind scale?
Weidman Fiber Technology	Swiss	n.a.	Enzymatic MFC	Ind/Pilot scale
CelluComp	UK / Scot.	n.a.	NanoCellulose fibres from root vegetables (e.g. carrots)	Start-up
InoFib	France	n.a.	2 grades: classic MFC / functionalized or redispersable MFC	Start-up launch in 2012
Innventia*	Sweden	100 Kg/day	Enzymatic &/or functionalized with Microfluidizer or GEA	Pilot Plant / R&D purpose only
FCBA/CTP*	France	70 Kg/day	Enzymatic &/or functionalized with Microfluidizer or GEA	Pilot Plant / R&D purpose only
Univ Maine*	USA	300 Kg/day	Larger MFC	Pilot Plant / Commercial grade ready to order
EMPA*	Swiss	15 kg/day	Enzymatic and functionalized MFC with Microfluidizer	Lab scale
VTT*	Finland	15 kg/day	Enzymatic pretreated with Masuko grinder	Lab scale
LGP2 / Grenoble INP*	France	2 kg/day	Enzymatic or Tempo with Masuko grinder	Lab scale

Nanocrystals and sustainable process



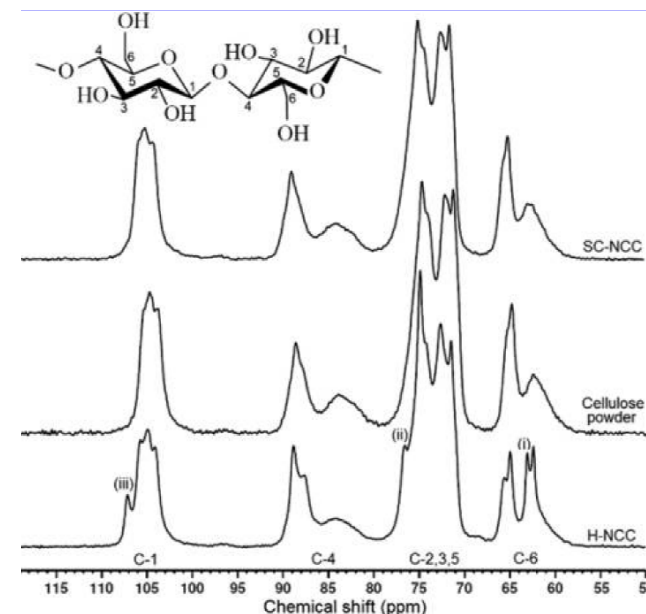
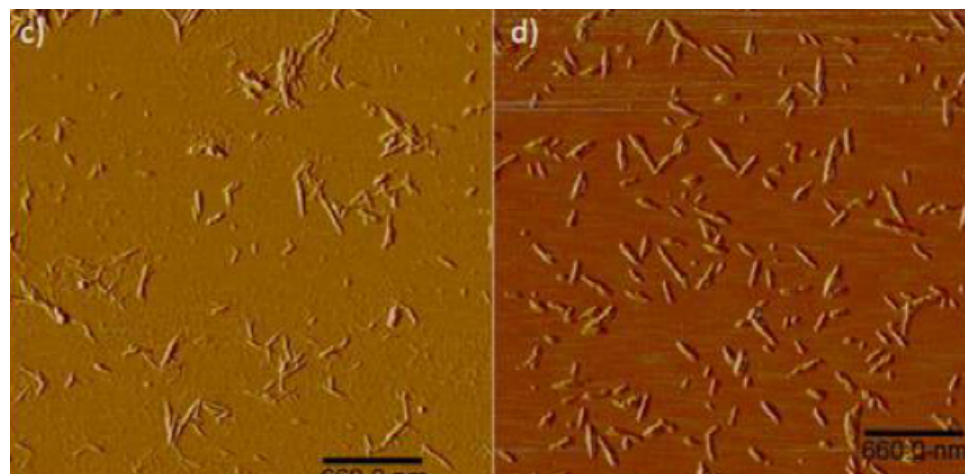
Levels of the factors and the responses of the 2^2 experimental design.

$T(^{\circ}\text{C})$	$P(\text{MPa})$	$Y(\%)$	$C_1(\%)$	$Z_D(\text{nm})$	$L(\text{nm})$	$W(\text{nm})$	L/W	$B(\%)$	$\text{DTG}(^{\circ}\text{C})$
120	8.1	5.5	80.83	822	249 ± 163	62 ± 36	4.0	79.73	348.2
200	8.1	4.0	82.18	371	247 ± 93	51 ± 14	4.8	12.30	339.4
120	20.3	21.9 ^a	79.01 ^a	503 ^a	242 ± 98^a	55 ± 20^a	4.4 ^a	79.21	344.7
200	20.3	16.2	81.32	305	189 ± 68	40 ± 11	4.7	13.64	340.0
160	14.2	6.6	81.68	606	221 ± 78	47 ± 13	4.7	81.64	349.1
160	14.2	6.5	81.43	507	258 ± 95	46 ± 15	5.6	77.79	347.8

^a Novo et al. (2015).

Novo, L., Bras, J.; Garcia, A.; Belgacem, N.; Curvel Aprigio da Silva A study of the production of cell nanocrystals through subcritical water hydrolysis, Industrial Crops and Products (2016),in press.

Nanocrystals and sustainable process



	cellulose powder	SC-NCC	H-NCC
Z_D (nm)		503 ± 82	224 ± 58
PDI		0.13 ± 0.06	0.35 ± 0.06
colloidal behavior		low birefringence	high birefringence
length	$23.1 \pm 14.2 \mu\text{m}$	$242 \pm 98 \text{ nm}$	$191 \pm 58 \text{ nm}$
width	$13.9 \pm 9.0 \mu\text{m}$	$55 \pm 20 \text{ nm}$	$37 \pm 16 \text{ nm}$
aspect ratio (L/W)	1.7	4.4	5.2
agglomerates	yes	yes	no
cellulose pattern	cellulose I β	cellulose I β	mainly cellulose I β
C_I^{XRD}	80.0	79.0	78.7
C_I^{NMR}	55	56	66

Nanocrystals and sustainable process

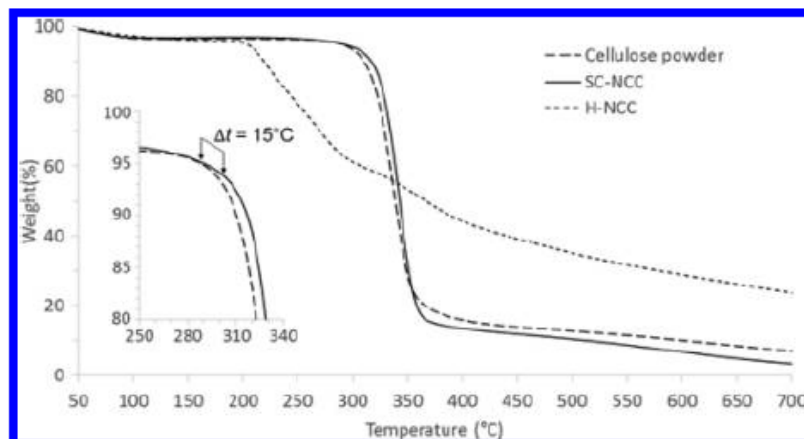


Figure 4. TGA thermograms of the cellulosic materials.

- The acid treated nanocrystal starts to degrade around 200 °C,

Vs

- The SC nanocrystals started to degrade only over 300 °C

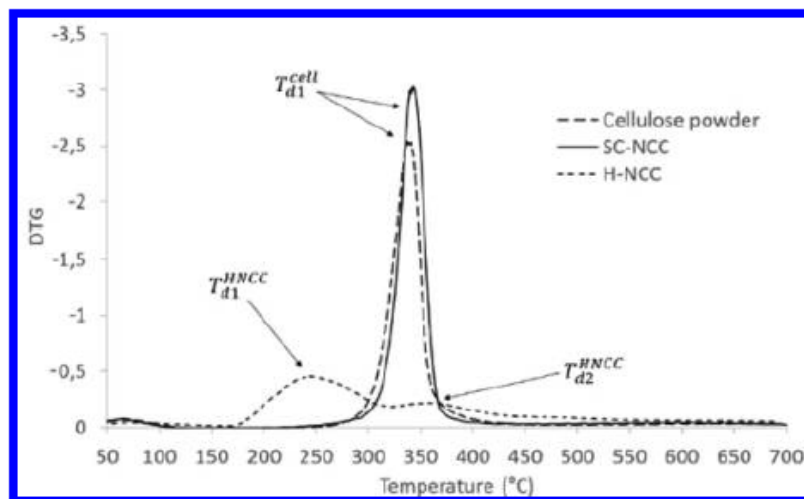


Figure 5. Differential thermogravimetry of the cellulosic materials.