In Situ Nanocellulose elaboration and modification using natural deep eutectic solvent

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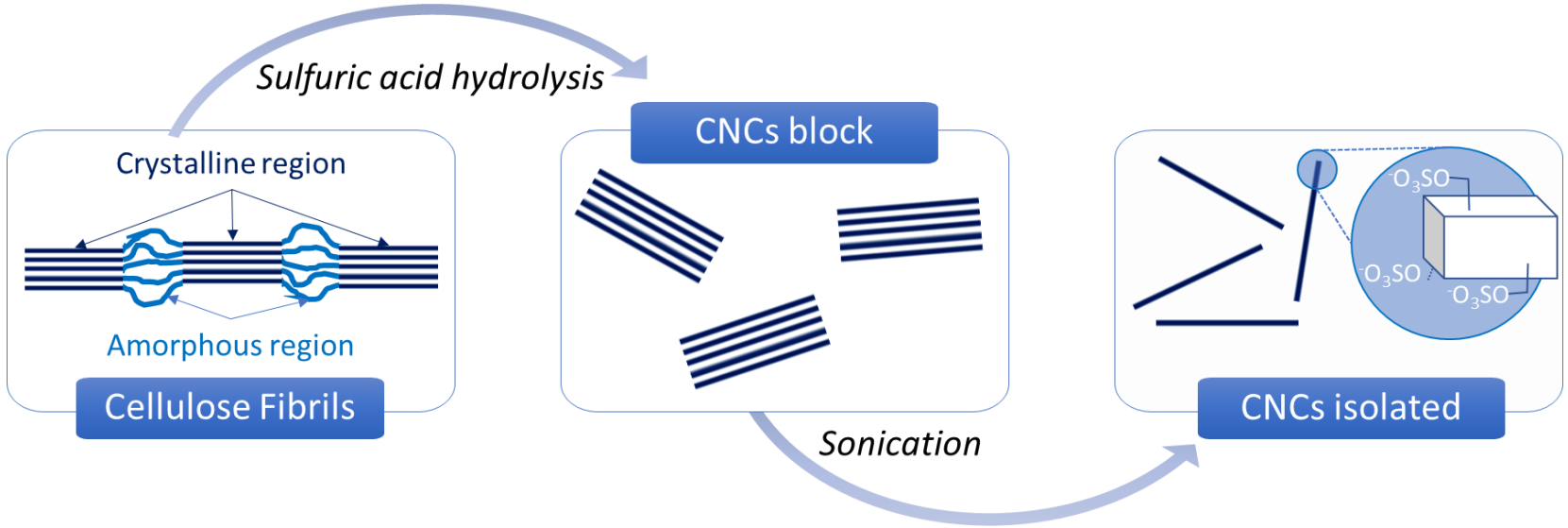
❑ Classical way of obtention and characterization: TOP-DOWN approach



Purified cellulose fibres

Length > 500 µm
Diameters ≈ 40 µm

Crystallinity Index ≈ 50%
Semi-crystalline
Cellulose I

- Sulfuric acid hydrolysis
  64 wt% sulfuric acid,
  40-45°C
  30 min
- Desintegration
  Ultra sonic probe

Isolated CNC

Length ≈ 200 nm
Diameters ≈ 15 nm

Crystallinity Index ≈ 80%
Cellulose I

Charges on the CNC Surface

❑ CNC Production

Production < 400 t/year [1]

Due to:

- Strong acid
- Batch process
- Washing process difficult
- Low yield [2]

[1] Le Gars *et al.*, 2020
[2] Mukherjee & Woods, 1953

❑ Applications <=> Surface Modification

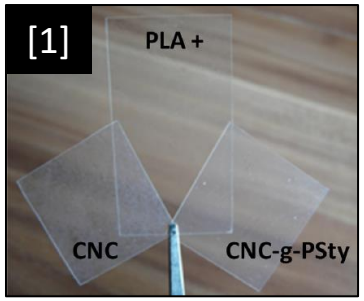
Numerous advantages:
- Biosourced
- Biodegradable
- Biocompatible
- Nanometric dimension

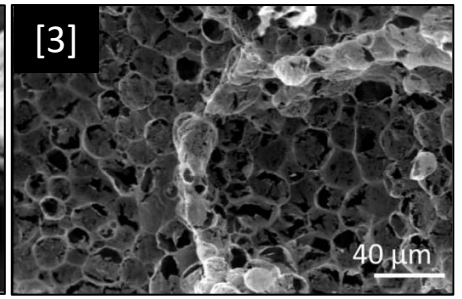
→

Large field of applications:
- Composite reinforcements
- Coating
- Rheological agents
- Etc..

→

Chemical surface modifications
→ Hydrophobic CNC
→ Charged CNC
e.g. TEMPO oxydation





Post treatment modification → **washing steps**
New approach consists on the *in situ* CNC modification during their extraction

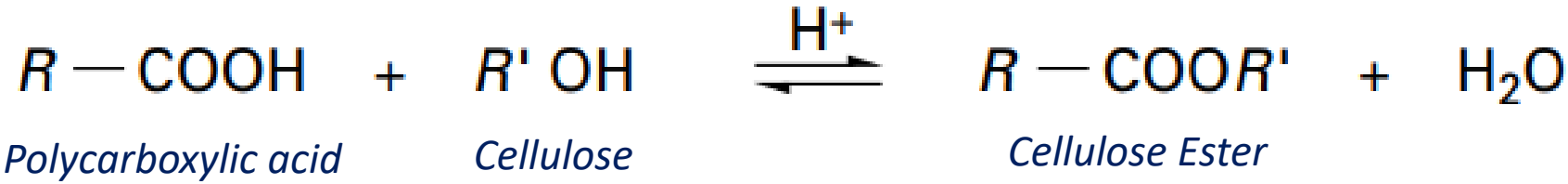
❑ Aims of this project

→ Extract CNC → Acid hydrolysis

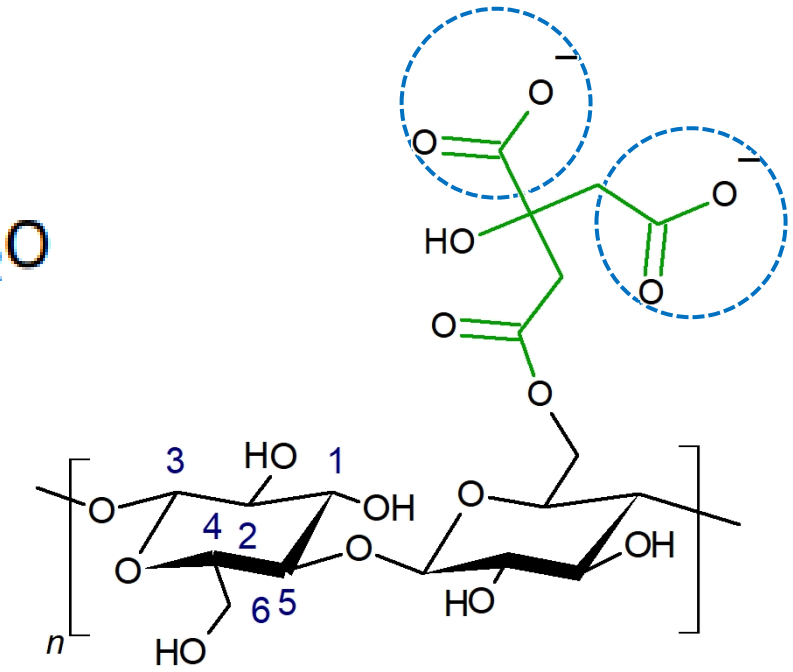
→ Bring charges on CNC surface → Esterification of *polycarboxylic acid* with hydroxyl groups

[1] E. Espino-Pérez *et al.*, 2016
[2] Mascheroni *et al.*, 2016

❑ Esterification



Polycarboxylic acid *Cellulose* *Cellulose Ester*



Limitations	*Solutions*	
Equilibrium	• ***Long time of reaction***	→ Study
Athermic reaction	• *Increase temperature to attend the equilibrium faster*	
Limiting step : Carboxylic acid protonation	• *Use of catalysis*	
	• ***Remove water to shift the equilibrium***	
Slow reaction	• ***Add an excess of carboxylic acids***	→ **NADES as reactive solvent**

❑ **Acidic Natural Deep Eutectic Solvents Type III**

Definition

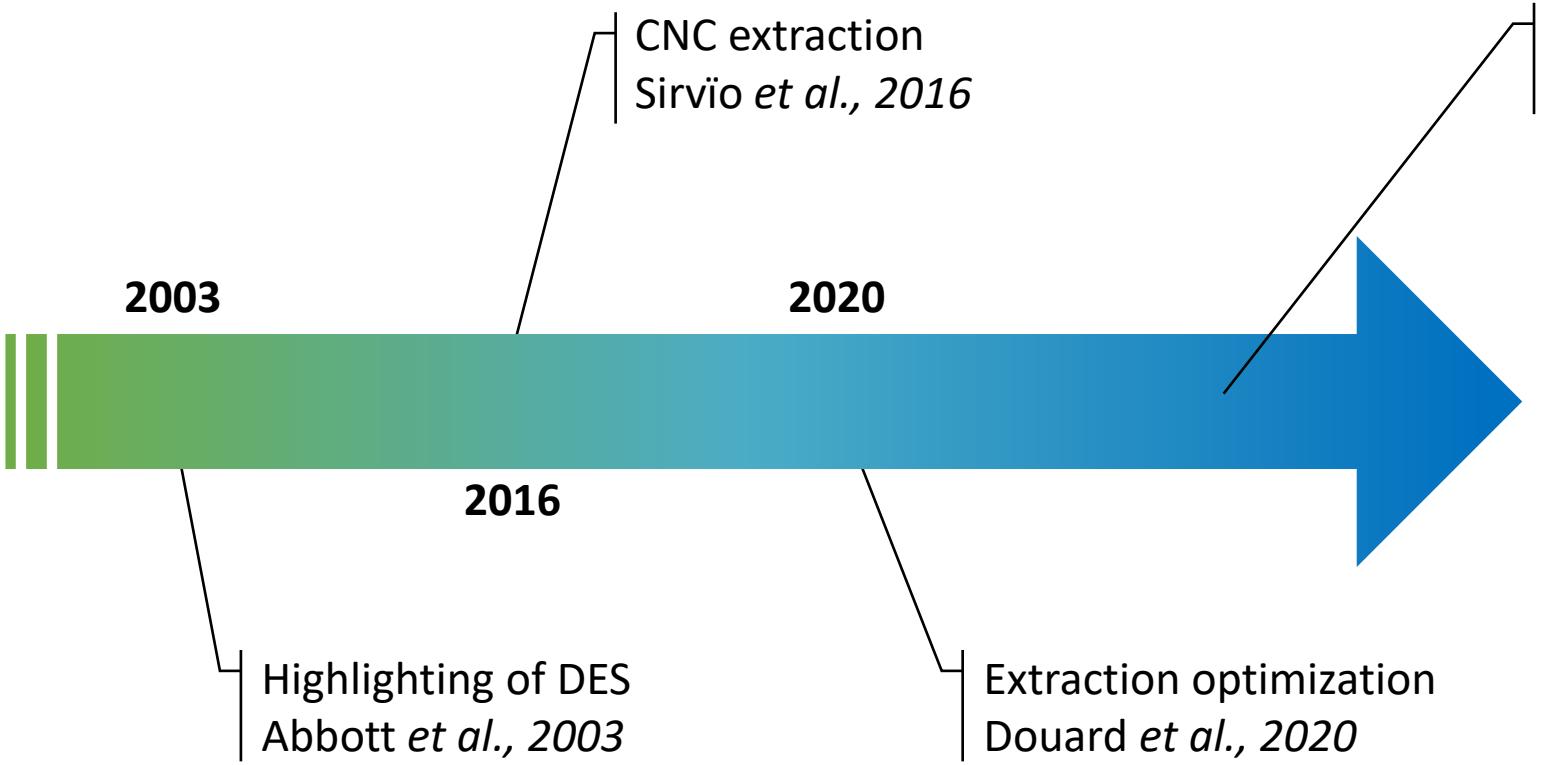
Organic Solvent

Quaternary ammonium salt (HBA) + HBD

Properties:

- Easy to obtain
- Low cost
- Reusable
- Simple condition for using
- « Design Solvent »

❑ CNC extraction using NADES



❑ ChCl:CAM NADES

In Situ CNC modifiction and extraction using Choline Clhoride:Citric Acid Monohydrate

❑ Why this solvent?

→ Acidic NADES can be used to extract CNC [1]

→ Molten citric acid can be used to obtain modified cellulose [2]

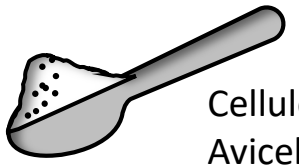
→ Production of esterified nanocellulose by CAM can be obtain by biorefinery concept [3]

→ **Acidic NADES as reactive solvent**

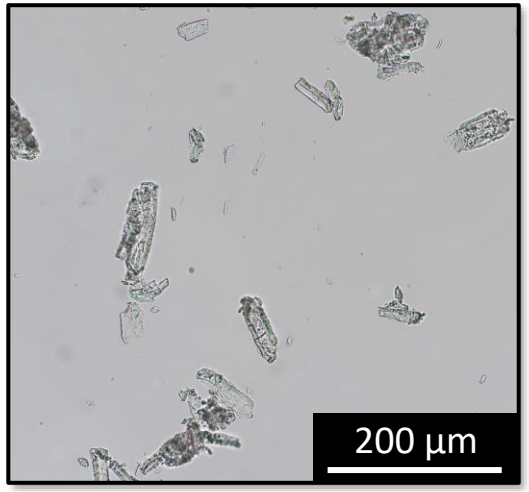
[1] Le Gars et al., IntechOpen, 2020
[2] Romeo et al., RSC adv., 2020
[3] Bondancia et al., Ind. Eng. Chem. Res. 2020

- Context
- Materials & Methods
- Results & Discussion
- Conclusion & Perspectives

❑ Cellulose Sources

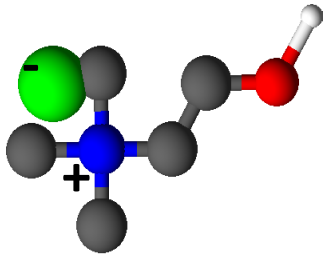


Cellulose Powder
Avicel PH-101



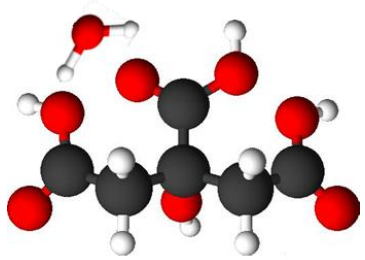
Fibre length:	145 ± 1 µm
Fibre width:	32 ± 0 µm
DP	225 ± 1
CI%	88%

❑ Choline Chloride: Citric acid monohydrate



Choline Chloride
n°CAS: 67-48-1

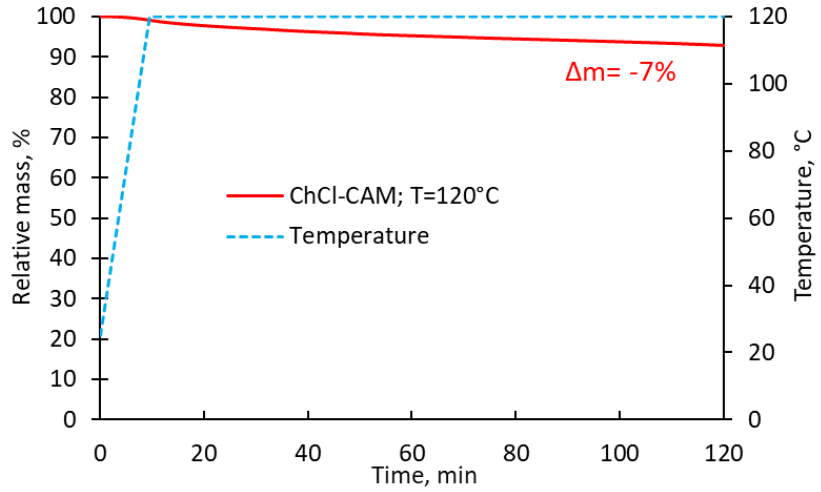
molar ratio 1:1



Citric Acid Monohydrate
n°CAS: 5949-29-1

Properties [1]:

- Viscous & dense liquid
- Biodegradable
- Low Toxicity
- Low vapor pressure



[1] Liu et al., Carbohydrate polymer, 2021

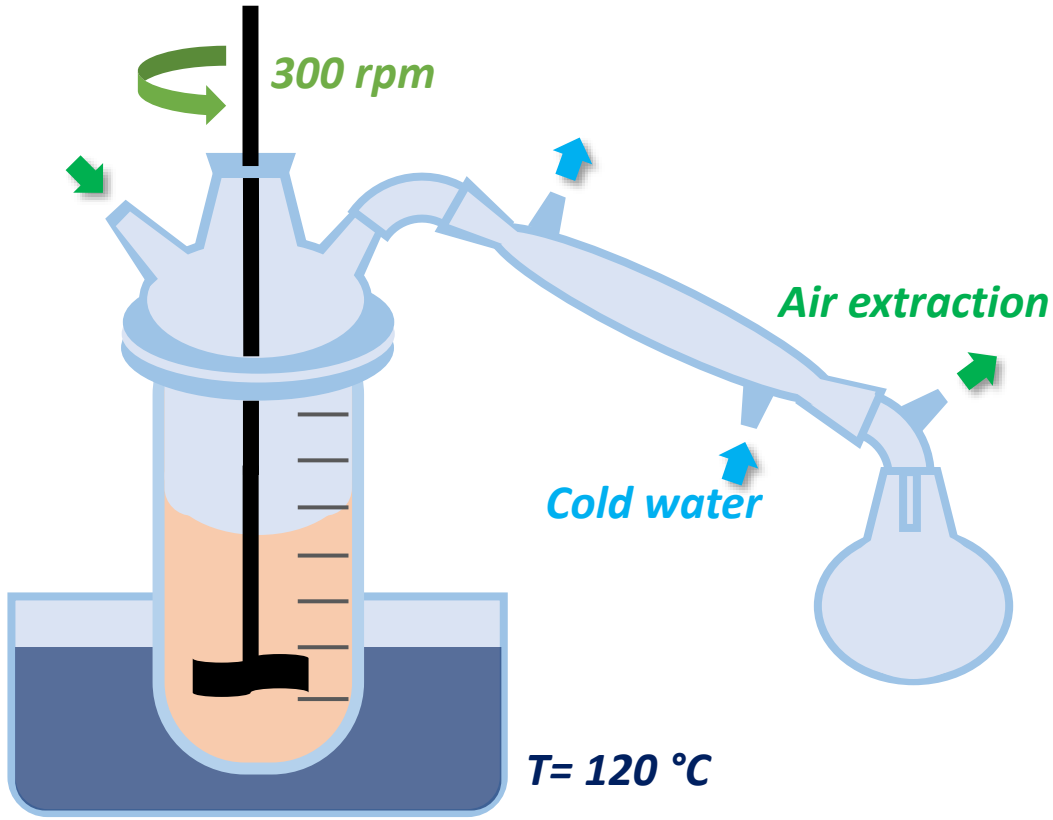
❑ Cellulose treatment

1. NADES preparation

   CC:CAM molar ratio 1:1
   T= 120°C

2. Cellulose treatment

   Cellulose: A, B or C
   c= 1%
   T= 120 °C
   t= 2 - 16 h



3. Washing steps

   Dionized water
   Centrifugation X3
   Dialysis: 1 week

4. Splitting step

   Centrifugation + sonication:
   → CNC
   Sedimentation 1 week

   → Light Particules: LP
   → Heavy Particules: HP

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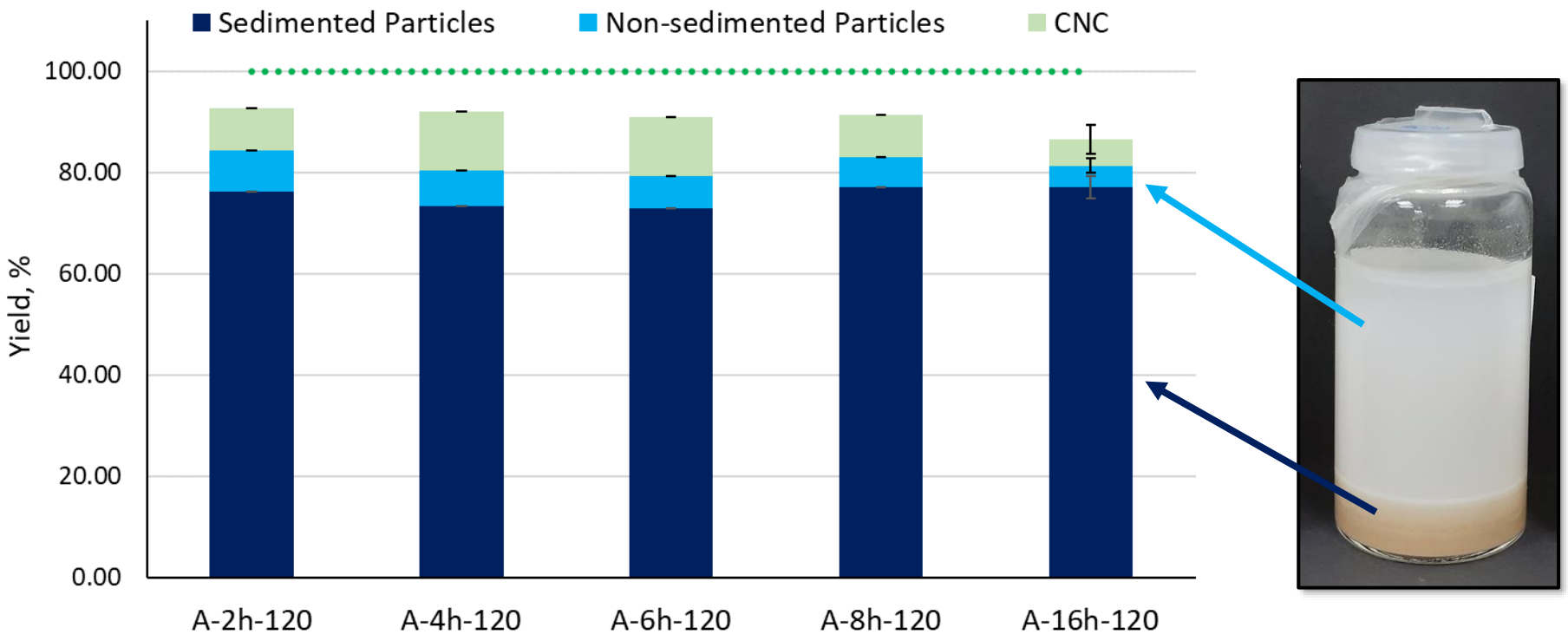
❑ Yields of CNC / WP /BP



Notation:
X – t – T ( )
e.g. A-8h-120 (CNC)

Conclusion:

→ Treatment time does not influence the CNC Yield

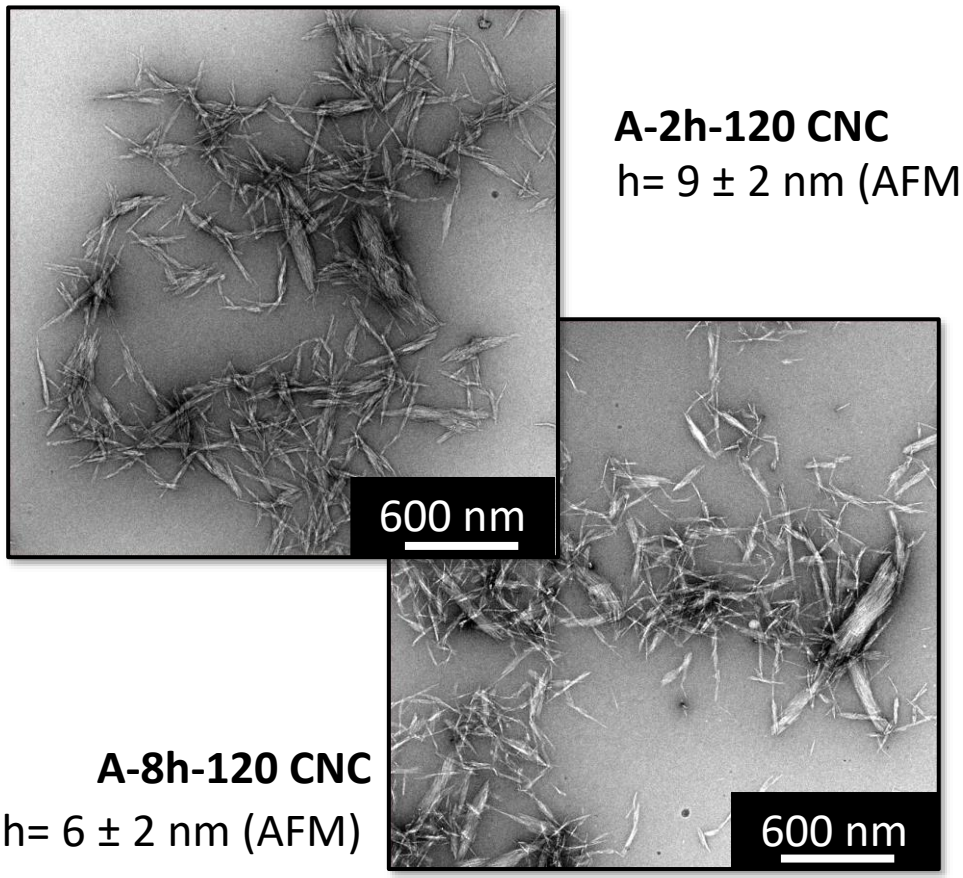
→ Yield $_{BP}$ > Yield $_{CNC}$ > Yield $_{WP}$

→ Focus on **CNC characterization**

❑ CNC morphology

Transmission electron microscopy

(c= 10^{-2}%, V= 10 ml, ultrasonication 1min)

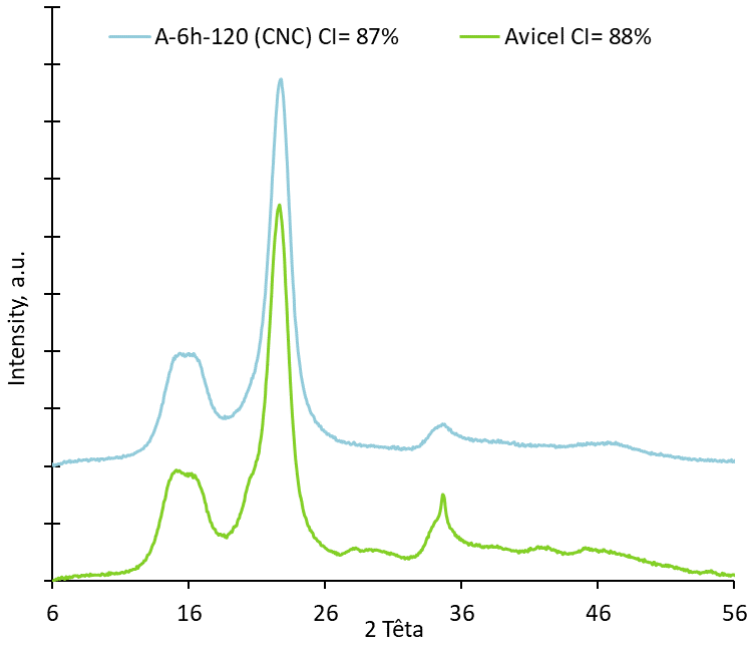


A-2h-120 CNC
h= 9 ± 2 nm (AFM)

A-8h-120 CNC
h= 6 ± 2 nm (AFM)

❑ CNC crystallinity

X-Ray Diffraction - Segal method [1]



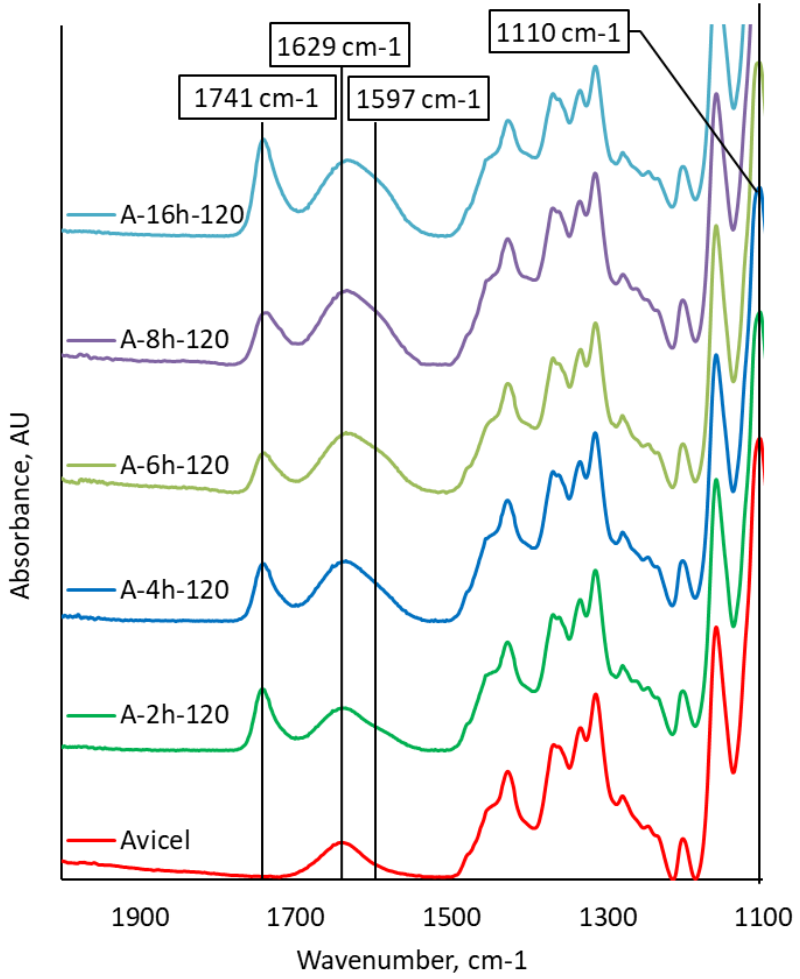
→ Cellulose I

	CI, %
Avicel	88
A-2h-120 – CNC	89
A-6h-120 – CNC	88
A-16h-120 – CNC	88

[1] Park et al. Biotechnology for Biofuels 2010

❑ Proof of grafting(CNC)

InfraRed Spectra - ATR



1110 cm^{-1}: Peak of normalisation

1600 cm^{-1}: Carboxylate ion

1629 cm^{-1}: Adsorbed Water

1741 cm^{-1}: C=O stretching

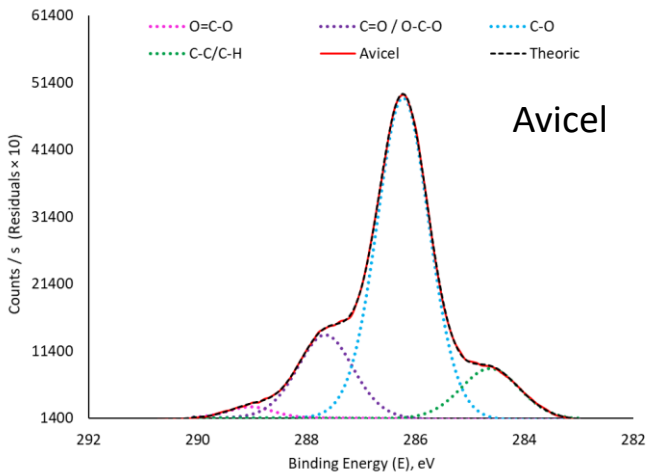
Conclusion:

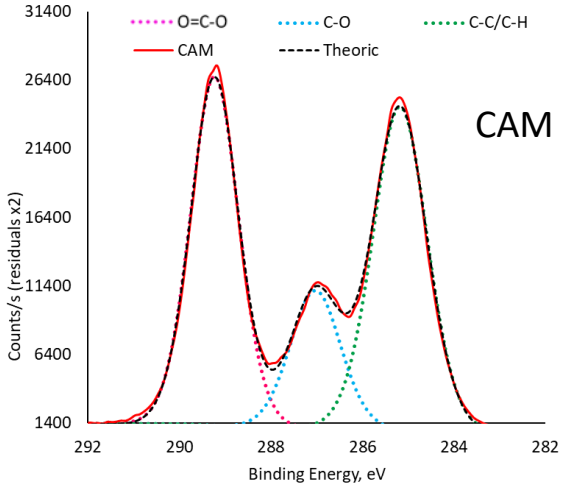
→ Grafted CNC are successfully obtained

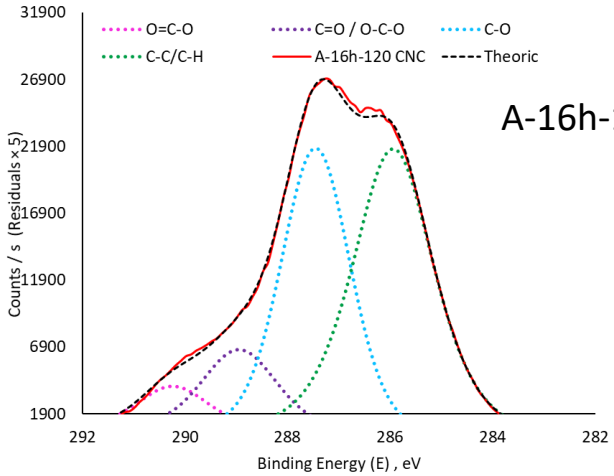
→ Treatment time ↗: C=O groups on CNC appears (esters and carboxylic acids)

I. II. III. Results: Effect of treatment time

X-ray photoelectron spectroscopy







Decomposition	% on total area		
	Avicel	CAM	CNC
C-C / C-H	12%	42%	46%
C-O	67%	17%	37%
C=O / O-C-O	19%	0%	11%
O-C=O	2%	41%	5%
Total carbon	100%	100%	100%
O/C	0.62 (0.8)	0.82 (1.1)	0.43

Conclusion:

→ Expected results:

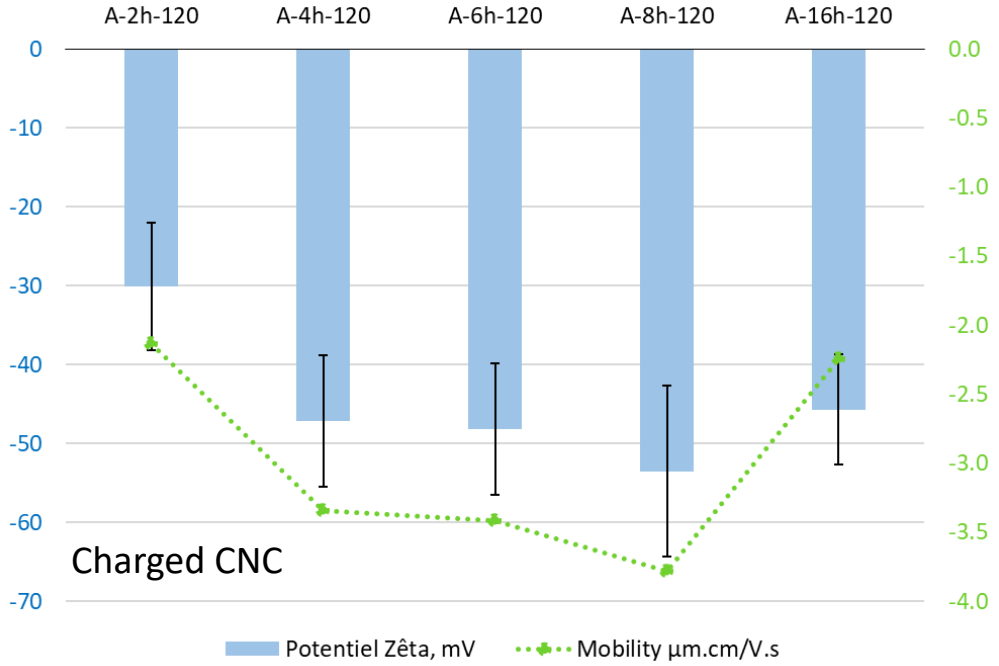
C-C and O=C-O ↗ (CAM+esterification) ✓

O-C-O ↘ (hydrolysis) ✓

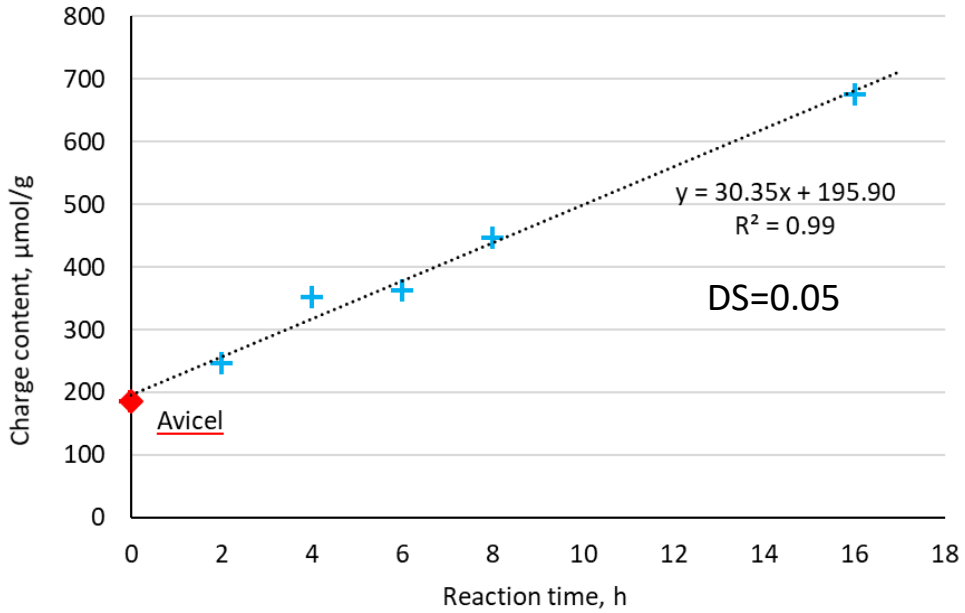
C-O → (cell -1 + CAM +1) ✗

❑ Modified CNC → Charged CNC

Zêta potential



Conductimetric titration



Conclusion:

→ Charged CNC are successfully obtained

→ Treatment time ↗: Surface charge content ↗ and stabilize after 4h

→ Total charged content ↗ continuously

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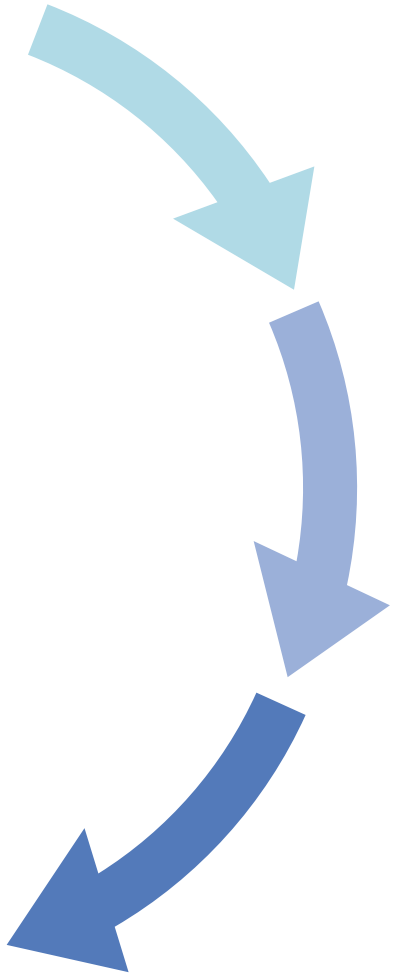


Aims

→ Extract CNC → Acid hydrolysis

→ Bring charges on CNC surface → Esterification with CAM using NADES

Results

→ Success of the CNC extraction

→ Success of the CNC *in situ* modification

→ High crystallinity of CNC

→ CNC charge content increase with treatment time

→ No influence of the treatment time on CNC yield (≈ 10%)

❑ Prospects

Increase CNC yield:

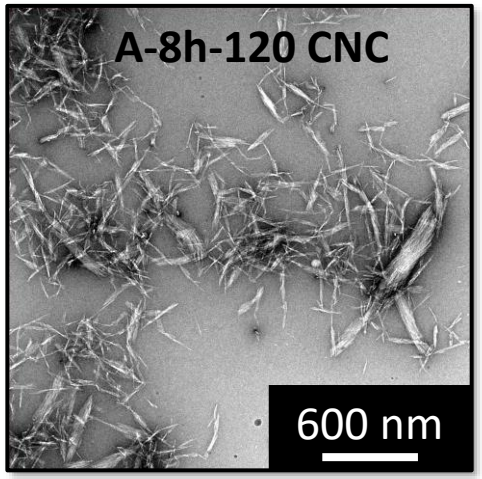
→ Increase acid hydrolysis with catalyst
→ Use different time of treatment

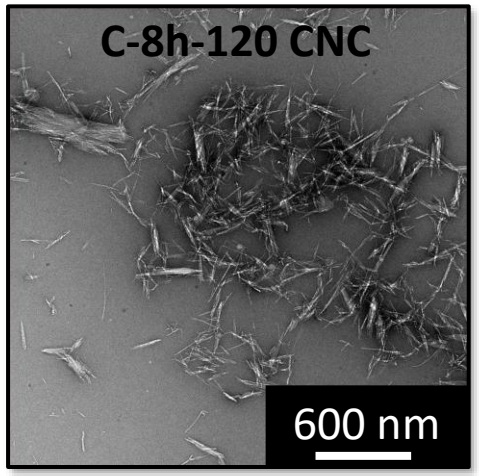
Valorized residual particles

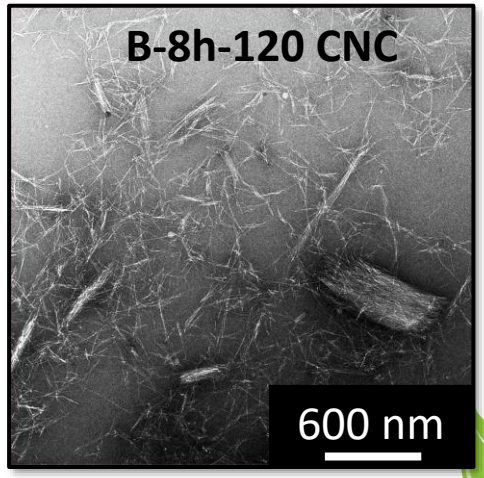
→ CNF production
→ Reinforcement in paper and composites

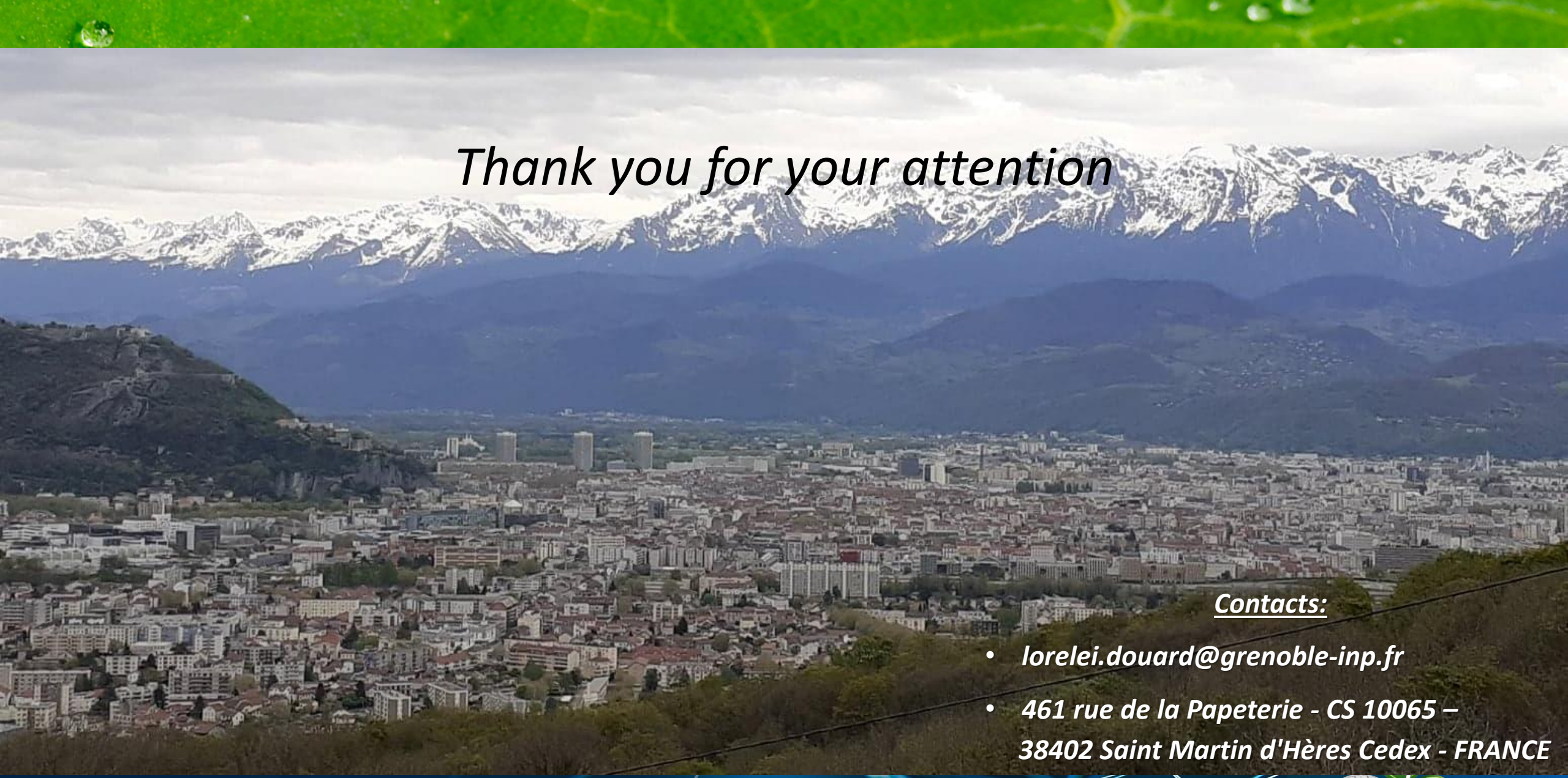
❑ Complementary results

Extract modified CNC form different raw materials









Thank you for your attention

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