# Production of various hydrolyzed cellulosic materials in a gas/solid reactor utilizing pressurized HCl

**CO-AUTHORS:**

Panagiotis Spiliopoulos, * Nonappa,** Katri S. Kontturi,*** Eero Kontturi *

*** Aalto University, Department of Bioproducts and Biosystems, Finland**

**** Aalto University, Department of Applied Physics, Finland**

***** VTT Technical Research Centre of Finland**

**PRESENTED BY:**

**Timo Pääkkönen**

**Postdoctoral Researcher**

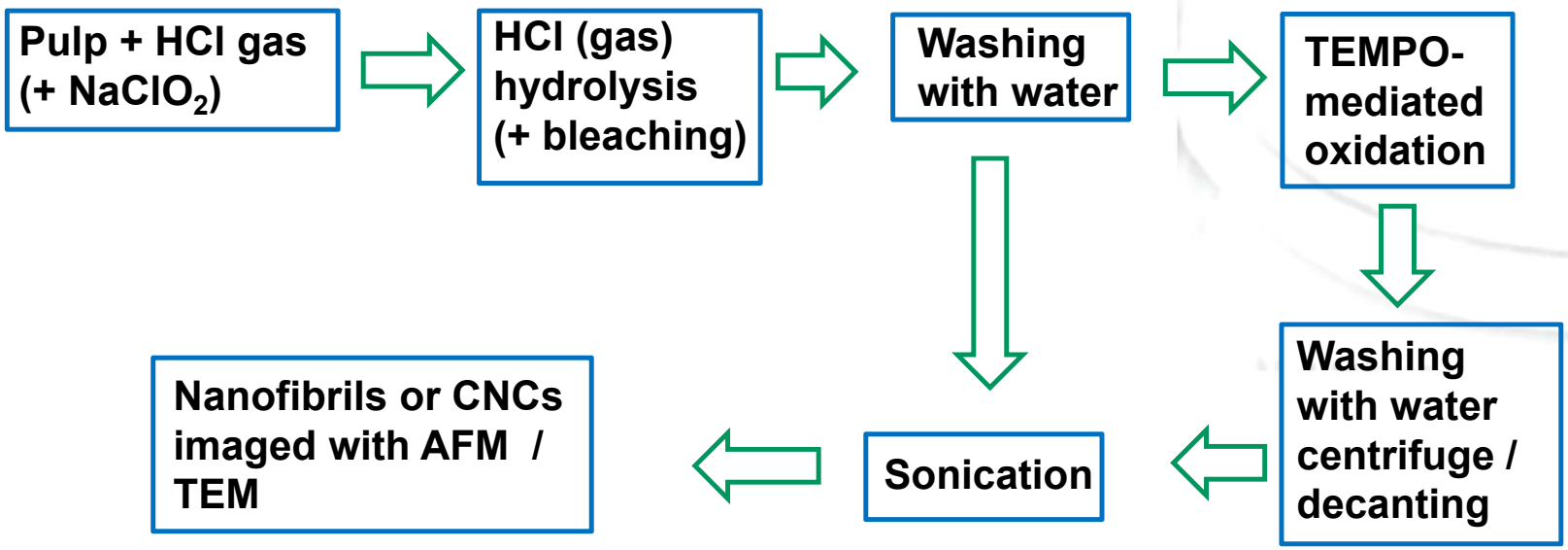
**Aalto University**

Aalto University

TAPPI

# Outline

- Background
- Production of BC-CNCs with HCl hydrolysis and TEMPO-mediated oxidation
- Production of CNCs and nanofibrils with $NaClO_2$ / HCl hydrolysis and TEMPO-mediated oxidation
- Summary

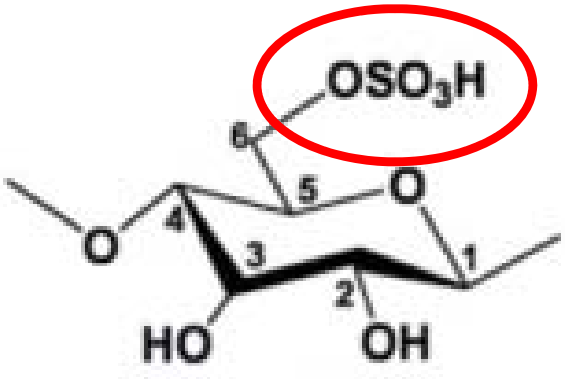


# Present situation: Production of Cellulose NanoCrystals (CNCs)

- Acid hydrolysis
- Liquid acid:
  - $H_2SO_4$
  - CelluForce manufacturing facility (300 t / year)
  - Pilot scale productions
    - Madison, Forest Products Laboratory
    - The University of Maine

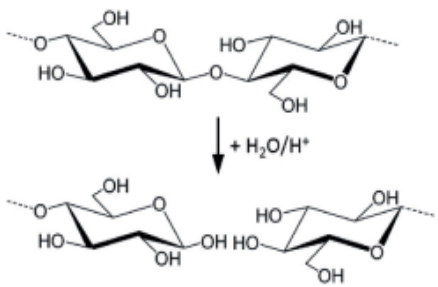
# The advantages and challenges of $H_2SO_4$ hydrolysis with cellulose

- Major process steps of CNC production:
  - [1] Acid hydrolysis
  - [2] Dispersion of cellulose
- Advantages
  - The introduction of $OSO_3^-$ groups on the surface on of CNC`s
  - **Dispersion of CNCs is effortless due to the $OSO_3^-$ groups**
- Challenges
  - Low yield
  - High water consumption
  - Acid (in the fiber mixture) is hard to recycle
  - Purification of product

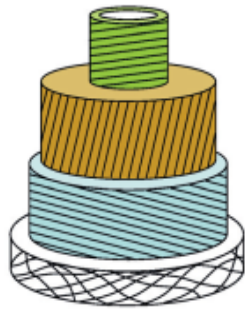


# Structure of cellulose and its chain cleavage by acid hydrolysis

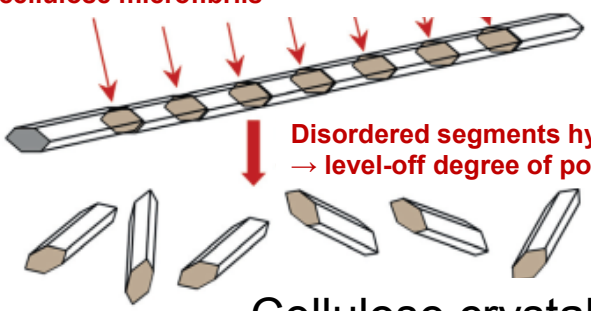
Cellulose molecule




Plant cell

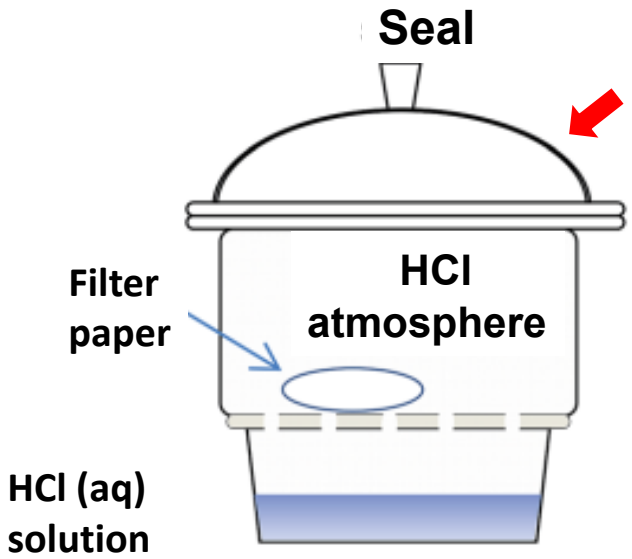


Acid hydrolysis targets the dislocations in cellulose microfibrils



Disordered segments hydrolyzed → level-off degree of polymerization

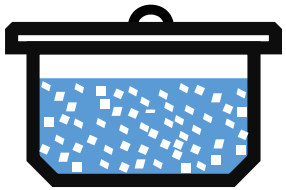
Cellulose crystallites






E. Kontturi, A. Meriluoto, P. A. Penttilä, N. Baccile, J. Malho, A. Potthast, T. Rosenau, J. Ruokolainen, R. Serimaa, J. Laine and H. Sixta, *Angewandte Chemie International Edition*, 2016, 55, 14455-14458

# CNCs from alkaliextracted Bacterial cellulose (BC)



**Alkaliextraction** (Nata De Coco)
**0.1 M NaOH / 2h / 80 °C**

**Washing with water**

**Freeze drying**

[1] Acid hydrolysis of cellulose

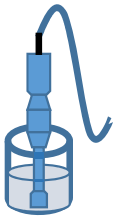
**HCl (gas) hydrolysis**

**Washing with water**

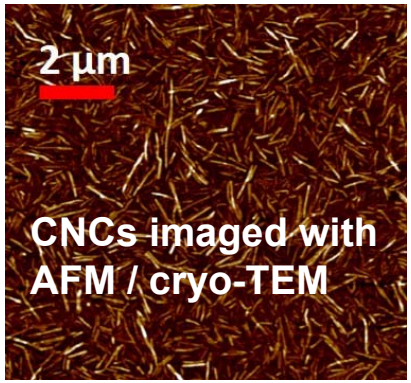
**TEMPO-mediated oxidation**

[2] Dispersion of CNCs

**Washing with water (centrifuge)**



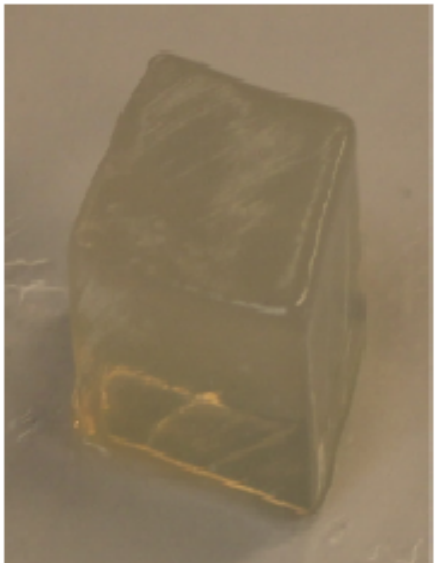
**Sonication**




- Combined yield of hydrolysis and TEMPO-mediated oxidation was 80.8 %
- Reduction of DP with HCl gas hydrolysis (1 bar / 21 h) was from 2590 to 219

# Nata De Coco - purification and freeze drying

**Purity**



Untreated BC

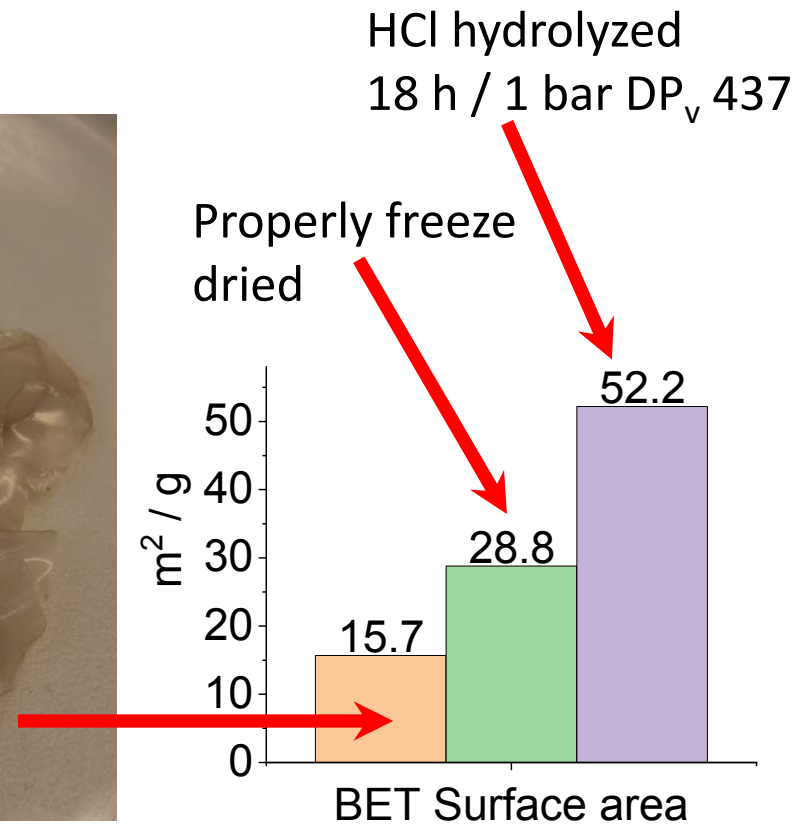
BC with NaOH

Washed BC

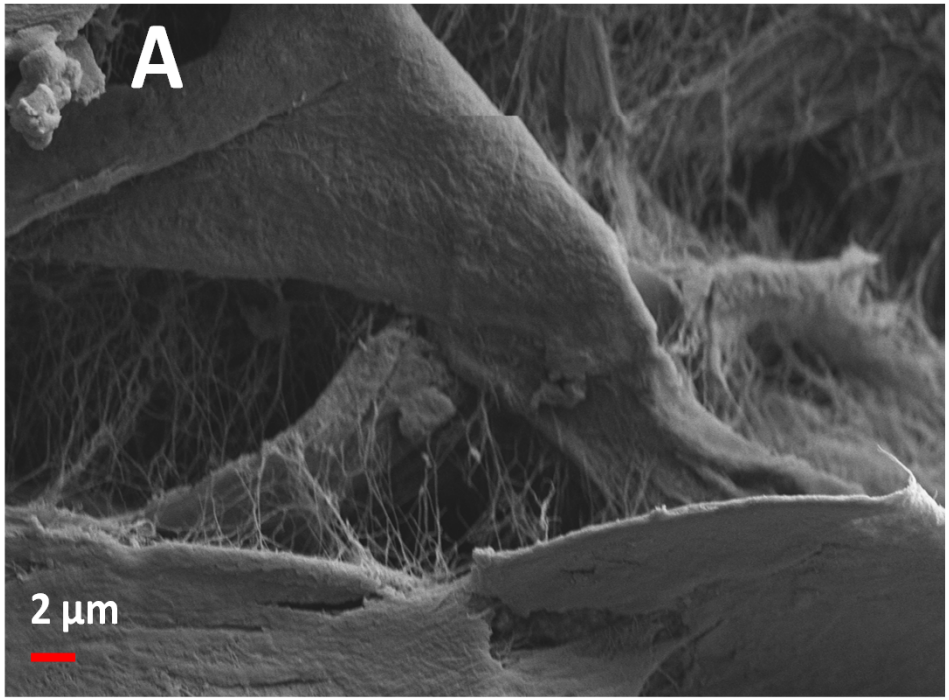
Freeze dried BC

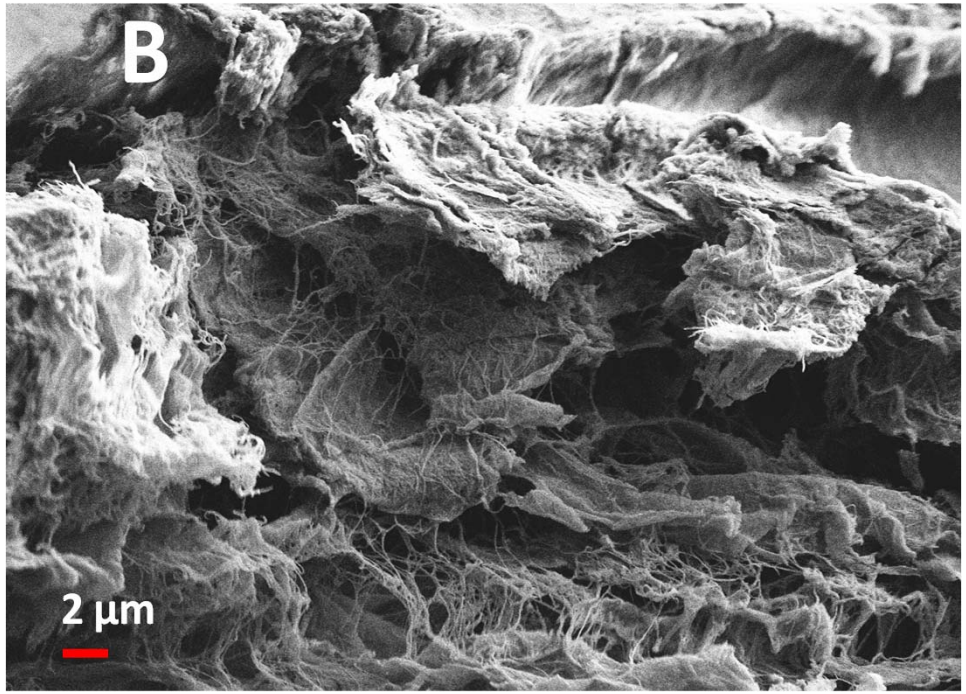
# Nata De Coco - poor freeze drying

## Hornification of bacterial cellulose impairs both hydrolysis and TEMPO-mediated oxidation



# SEM imaging of (A) alkaliextracted bacterial cellulose and (B) HCl gas hydrolyzed (1 bar / 18 h) bacterial cellulose



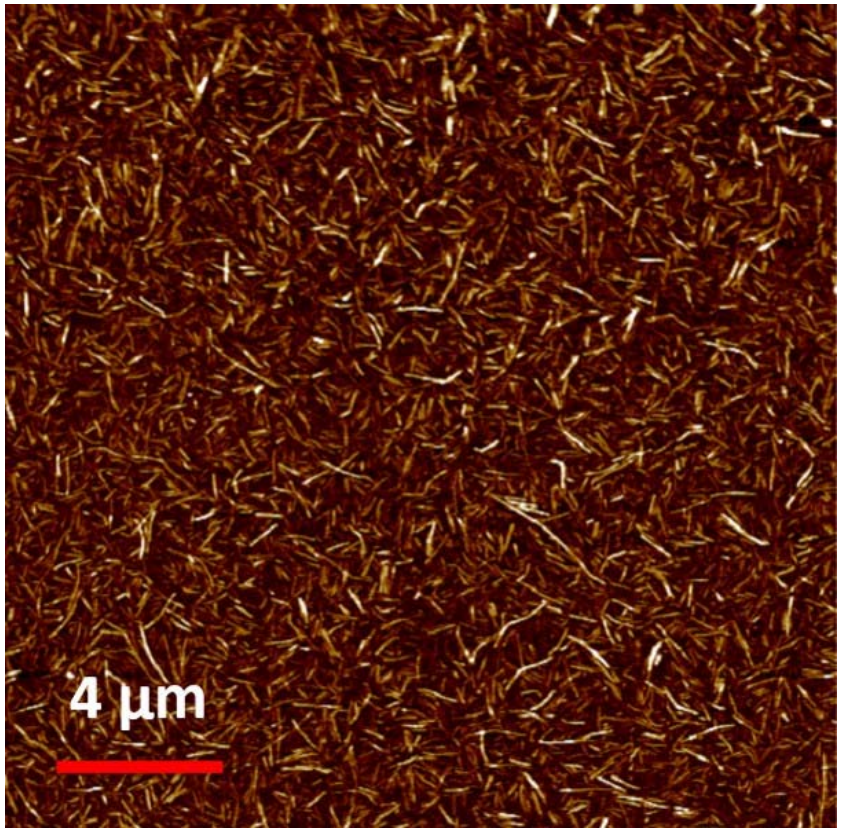



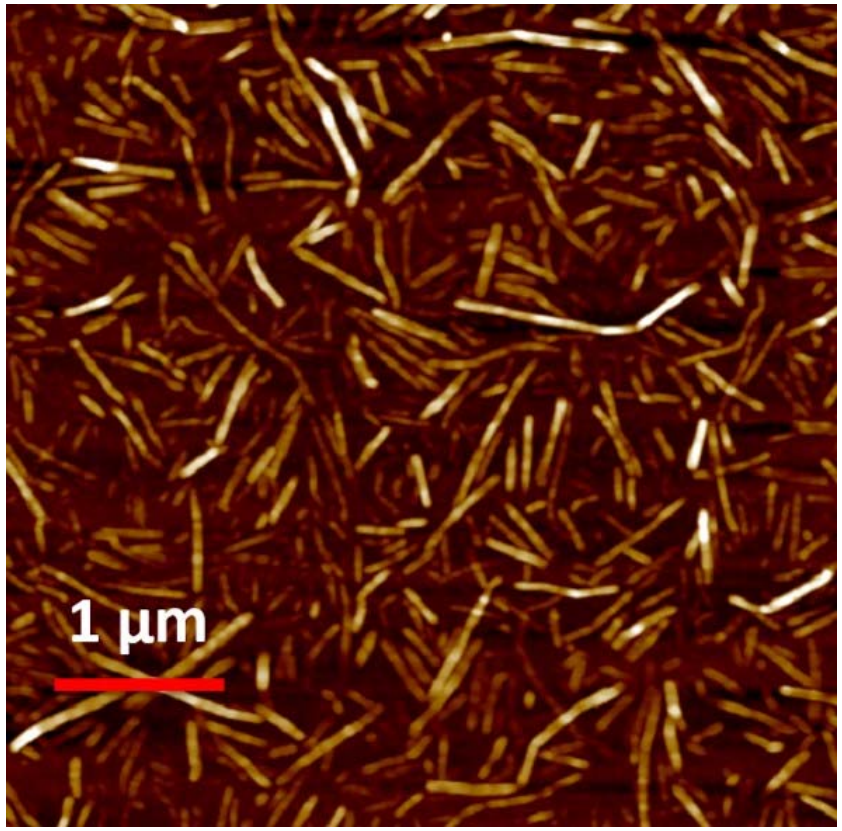
# Hydrolysis of BC / comparison of freeze drying

| | Hydrolysis reaction time (h) | DPv | Yield (%) | Carboxylate content mmol COOH / g BC |
|---|---|---|---|---|
| Mixed with blender, dried in fumehood | 4 | 886 | 77.9 | 0.55 |
| Pressed, freeze dried | 7 | 641 | 86.4 | 0.63 |
| Freeze dried | 3 | 260 | | 0.80 |
| Freeze dried | 21 | 219 | 80.8 | 1.02 |

# CNCs from bacterial cellulose (BC) / AFM

## Alkaliextraction - HCl hydrolysis - TEMPO-mediated oxidation

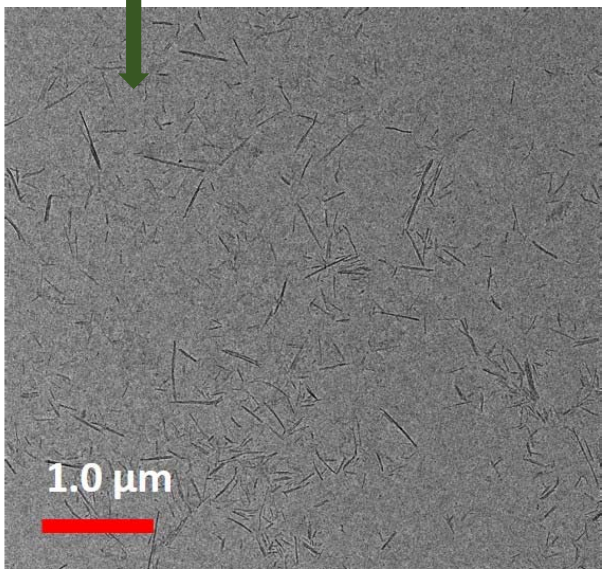


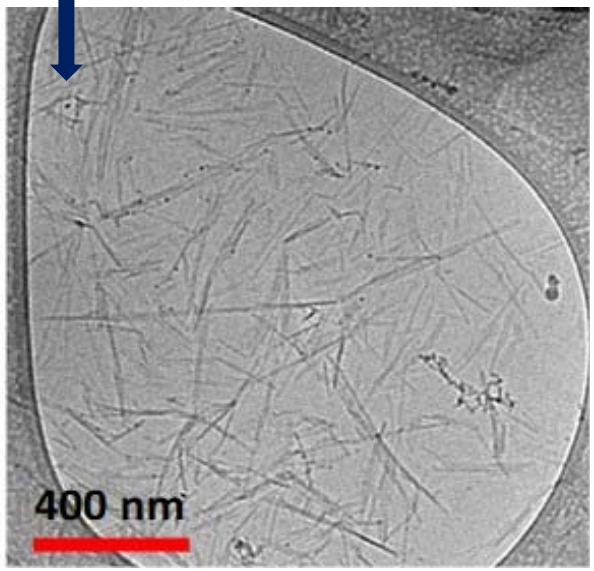



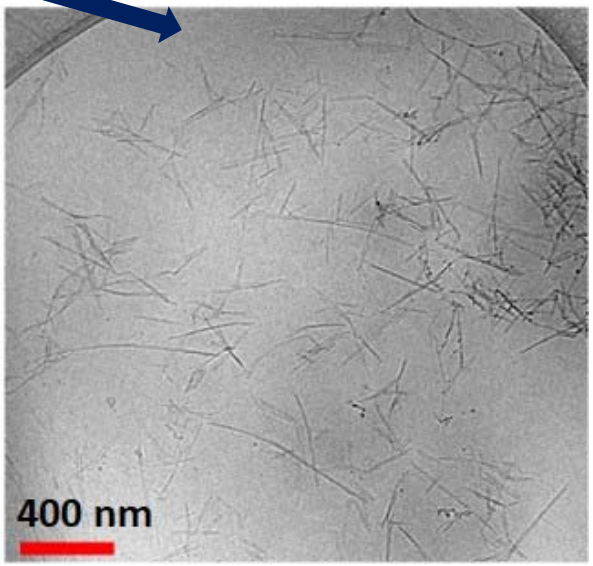
# CNCs from bacterial cellulose (BC)

## Alkaliextraction - HCl hydrolysis - TEMPO-mediated oxidation

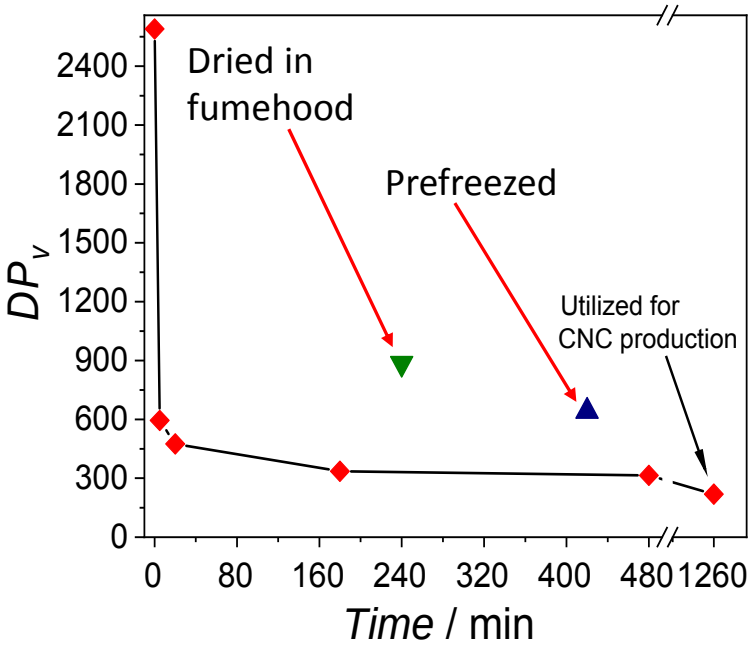
TEM and cryo-TEM



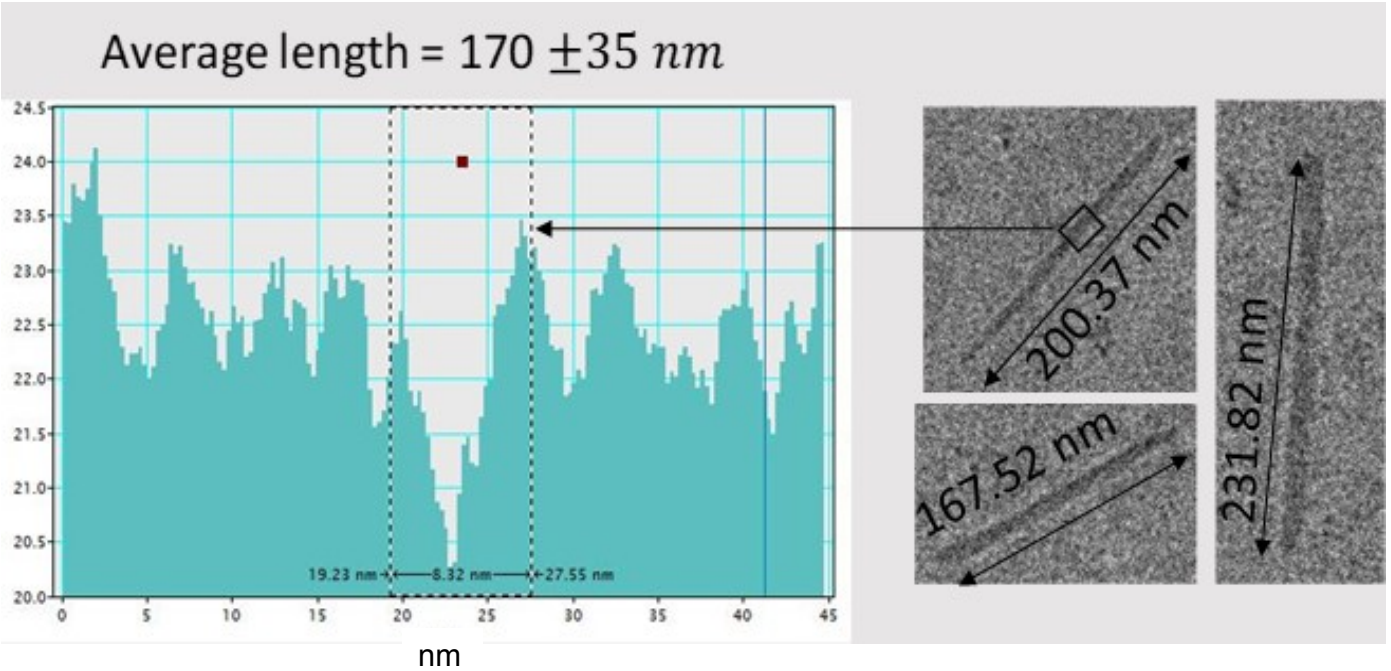



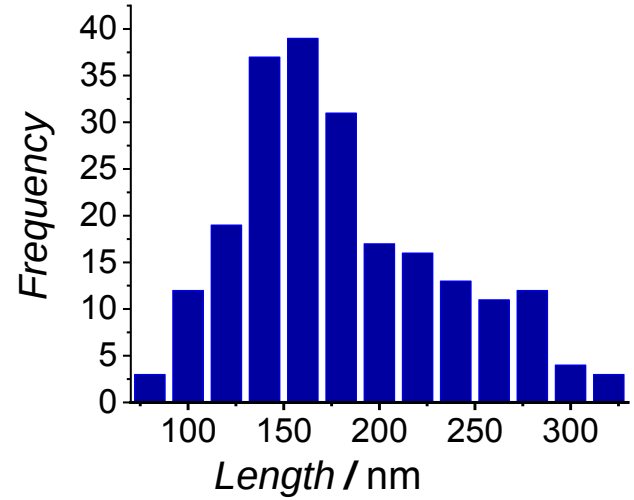



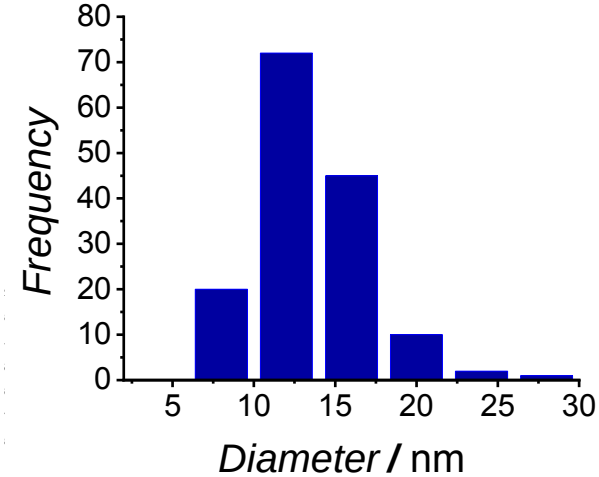
# $DP_V$ values of HCl gas hydrolysed (1 bar) BC as a function of time (3.5 g freeze dried BC / 1 $dm^3$ bottle)



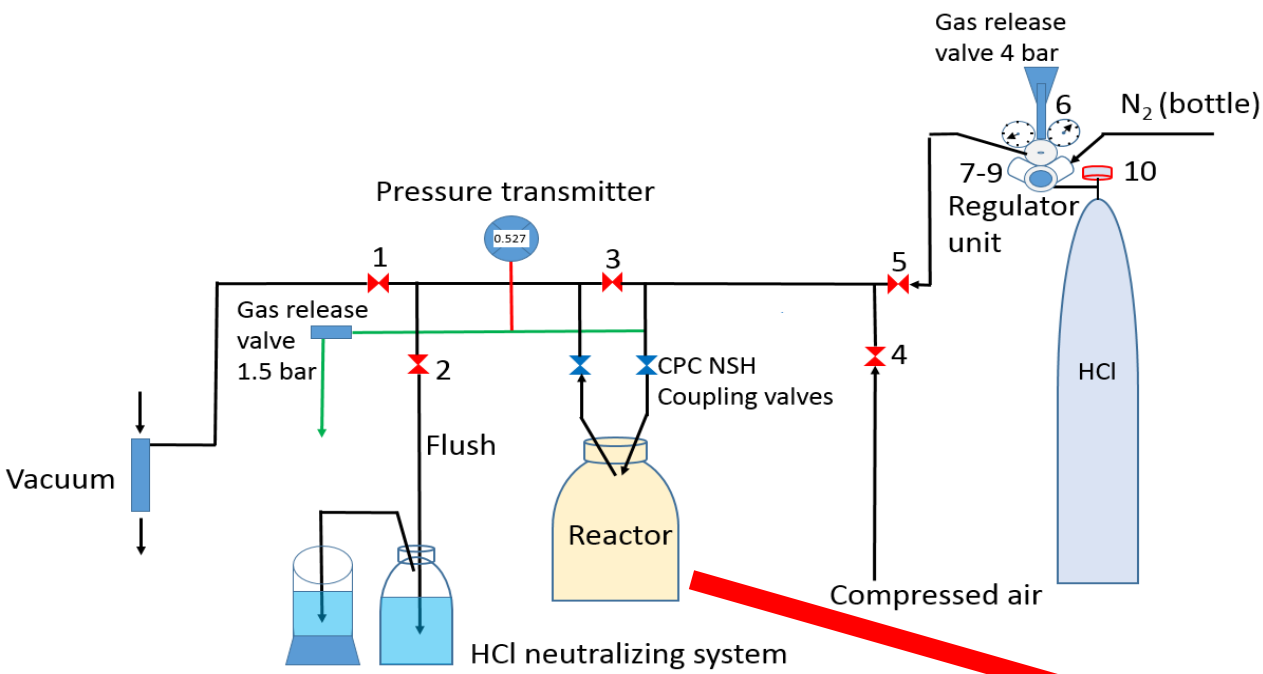
# CNC distribution of dimensions - TEM

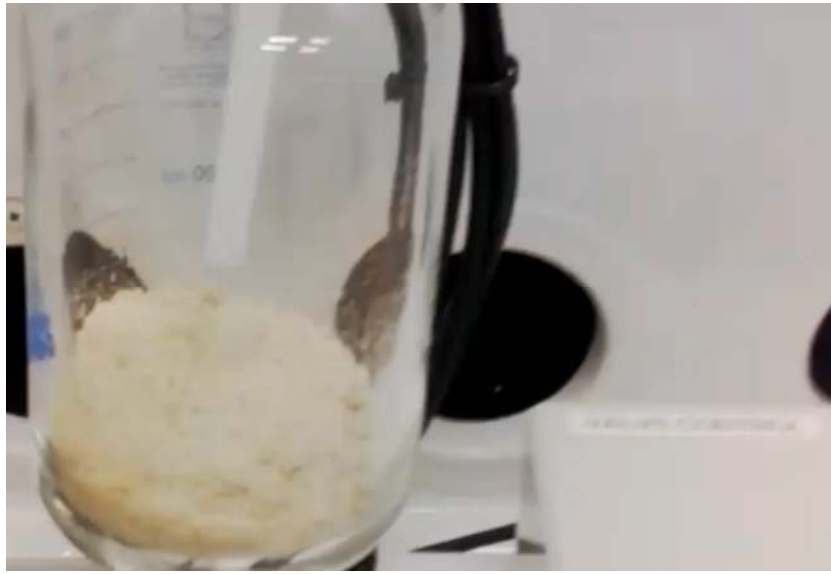


# Humin-free HCl gas hydrolysis

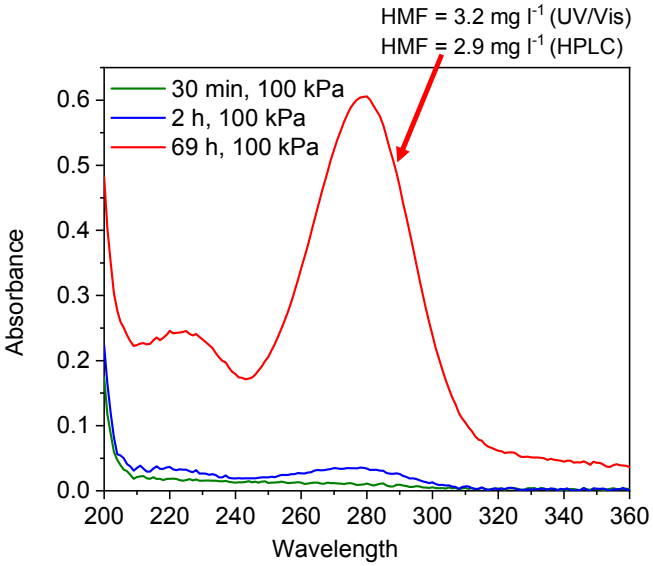


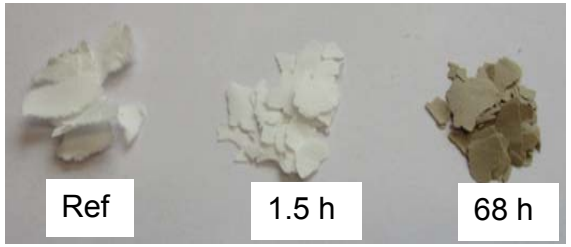



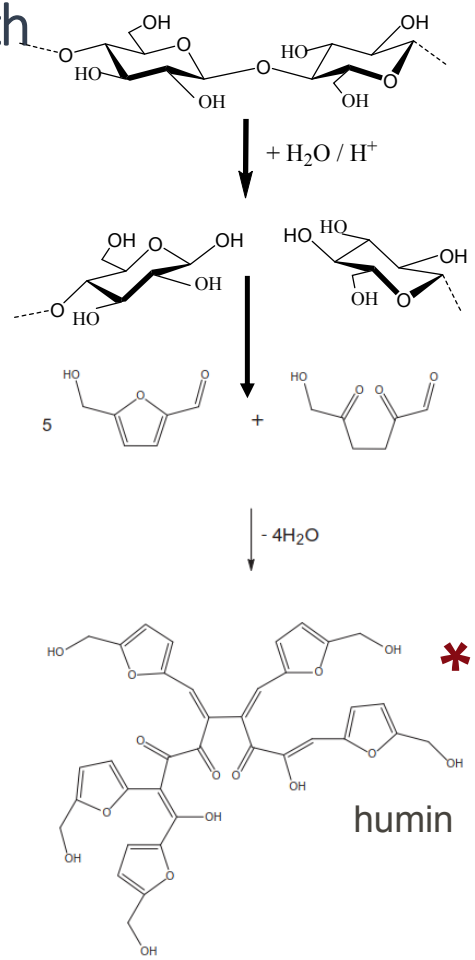
Aalto University
School of Chemical
Engineering

**HCl gas hydrolysis reactor:**
T. Pääkkönen, P. Spiliopoulos, A. Knuts, K. Nieminen, L.-S. Johansson, E. Enqvist, E. Kontturi, Reaction Chemistry & Engineering, 2018

# Background: Formation of humins / acid degradation with HCl gas (intense degradation conditions)



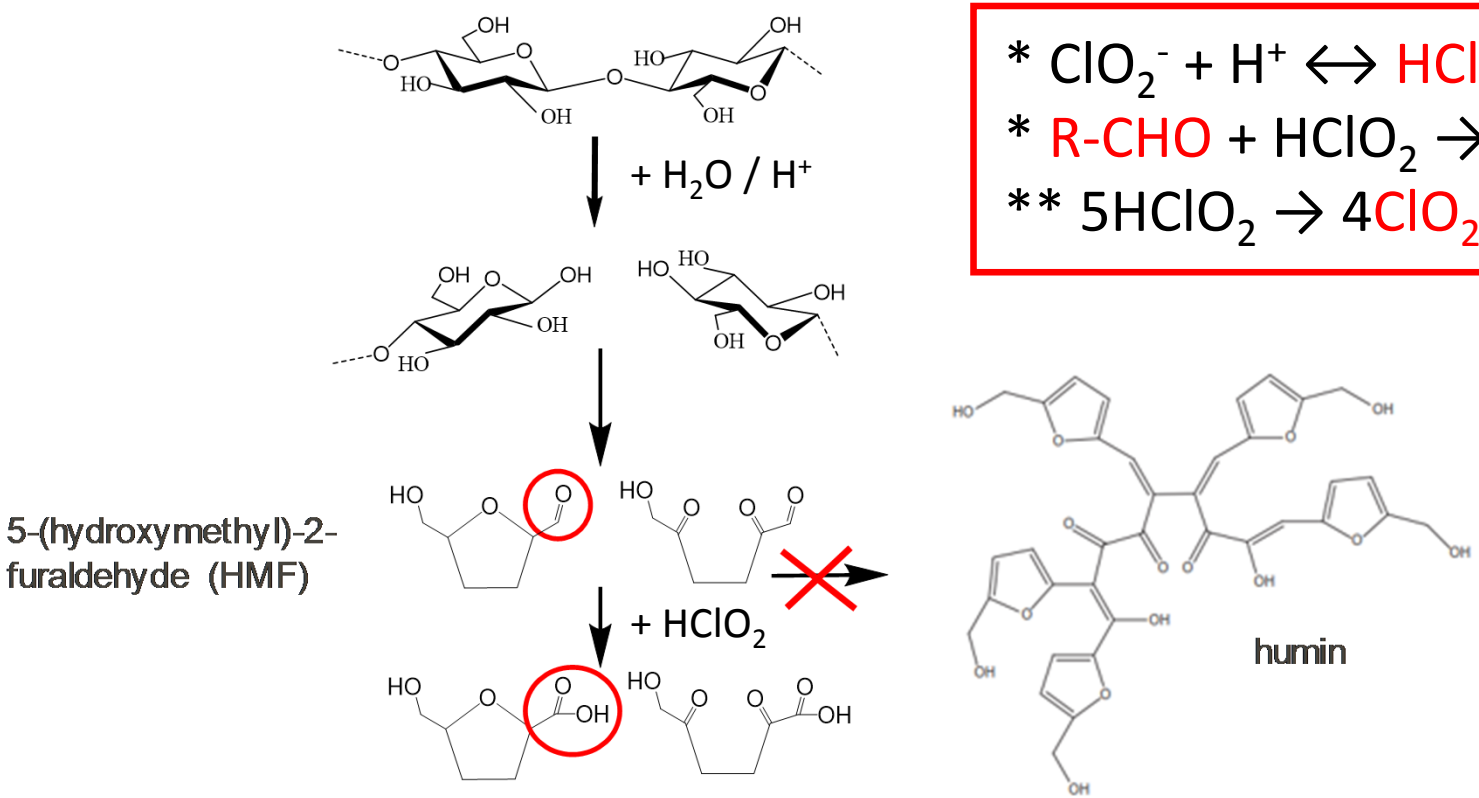




5-(hydroxymethyl)-2-furaldehyde (HMF)

Aalto University
School of Chemical Engineering

* H. Rasmussen, H. R. Sørensen and A. S. Meyer, *Carbohydrate Research*, 2014, **385**, 45-57.

# Blocking of humin formation with aldehyde oxidation

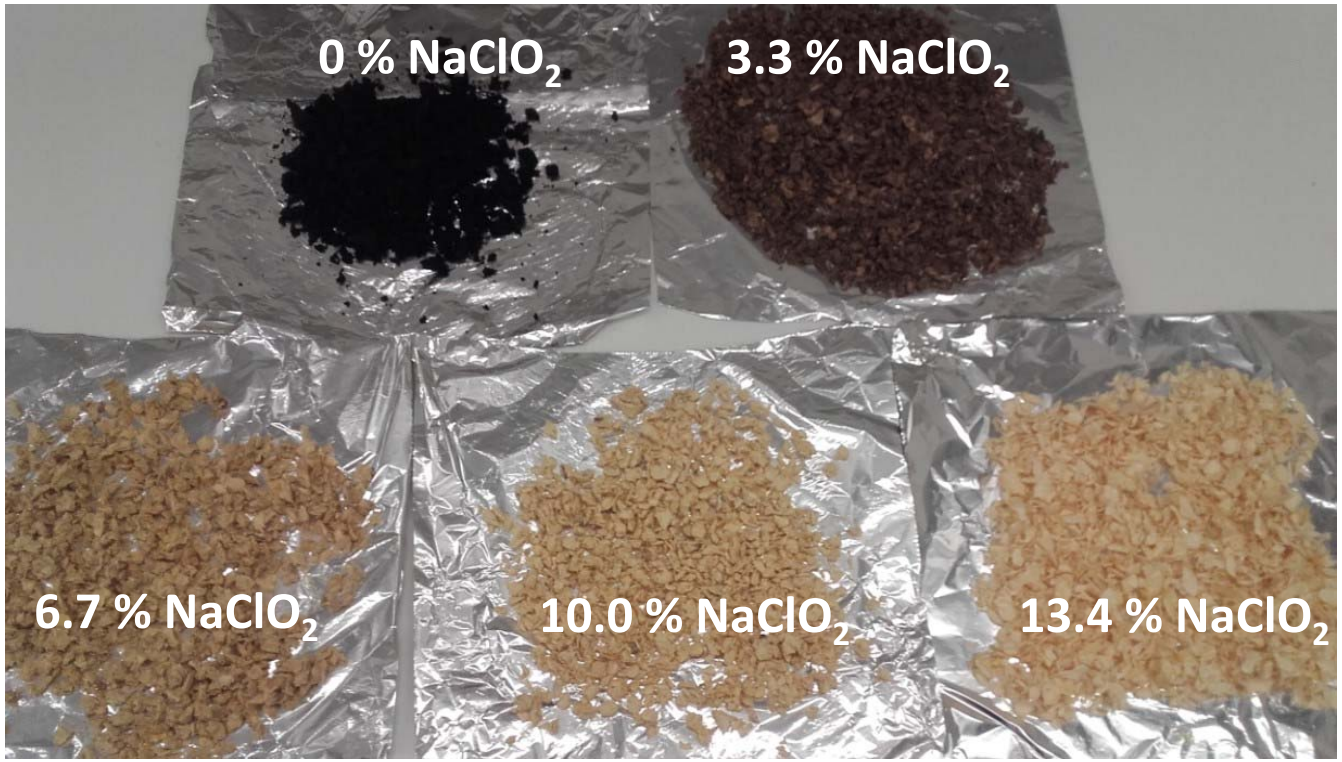



* $ClO_2^- + H^+ \leftrightarrow HClO_2$
* $R\text{-}CHO + HClO_2 \rightarrow R\text{-}CO_2H + HOCl$
** $5HClO_2 \rightarrow 4ClO_2 + Cl^- + 2H_2O + H^+$



*Ind. Eng. Chem. Res. 2010, 49, 2688-2693
**Ind. Eng. Chem. Res. 2008, 47, 5284–5290

# Acid hydrolysis (1 bar / 1.5 h) of unbleached softwood pulp as a function of added $NaClO_2$ (0 – 13.4 %) – high moisture content (dry matter content - 23 %)




**3 effects of $NaClO_2$/HCl process:**

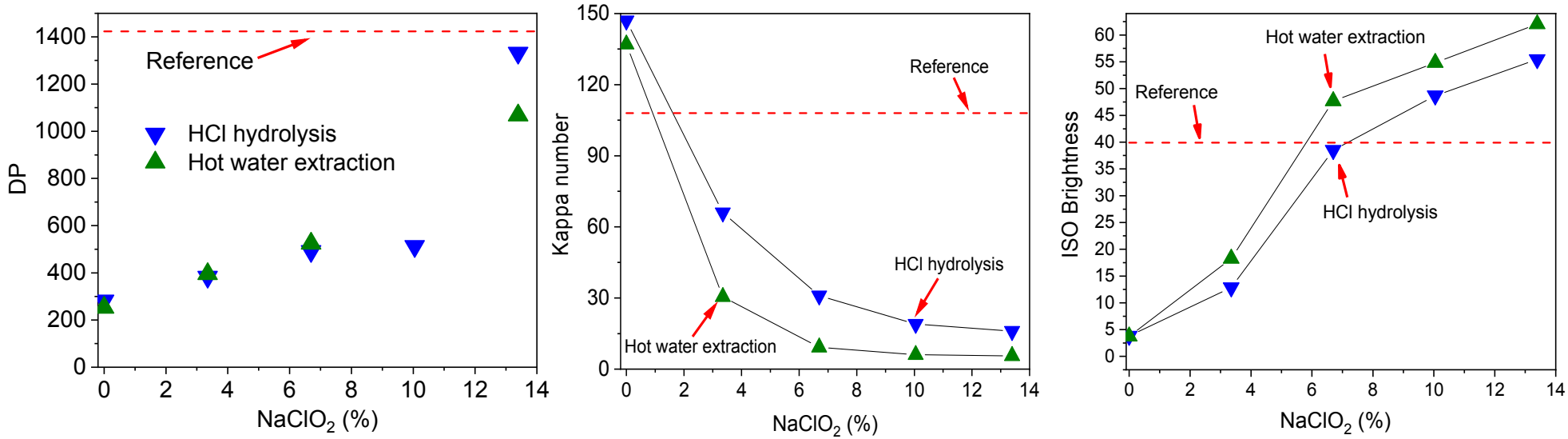
**[1] Acid hydrolysis**

**[2] Blocking of humin formation**

**[3] Bleaching of cellulose**

# Acid hydrolysis (1 bar / 1.5 h) of unbleached softwood pulp as a function of added $NaClO_2$ (0 – 13.4 %) – high moisture content (dry matter content - 23 %)

Hot water extraction - purification step (6 h with soxhlet extractor) after acid hydrolysis



# CNCs from alkaliextracted potatofiber (Vitacel)

Alkaliextraction
1 M NaOH / 2h / 80 °C

Washing with water

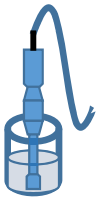
Addition of $NaClO_2$

HCl/ $NaClO_2$ hydrolysis

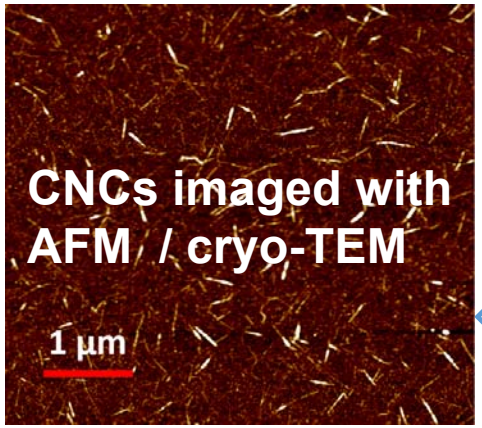
Washing with water

TEMPO-mediated oxidation

Washing with water (centrifuge)

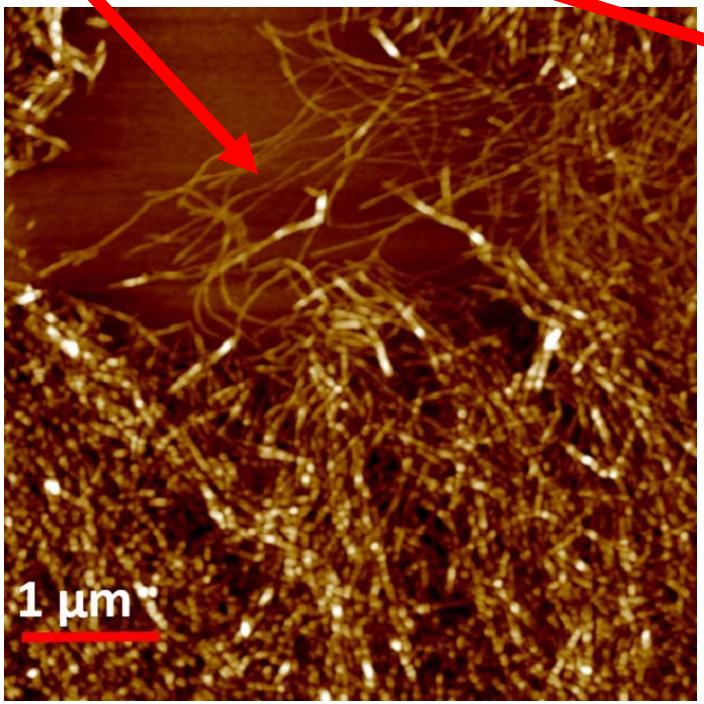


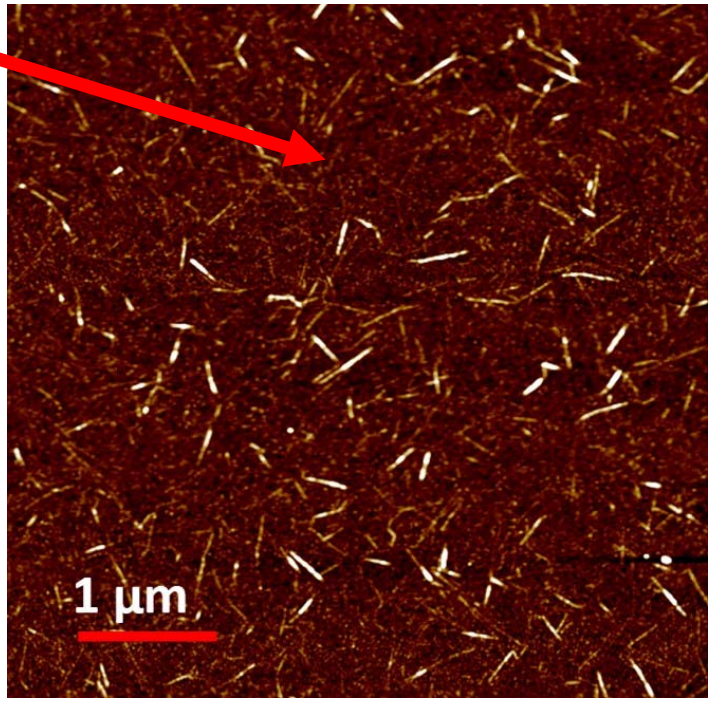
Sonication




- Combined yield of hydrolysis and TEMPO-mediated oxidation was 66.1 %
- Reduction of DP with HCl/$NaClO_2$ (3.4 %) hydrolysis (1 bar / 6 h) was from 3670 to 770 (422 after TEMPO oxidation)
- Both nanofibers and CNCs can be produced with same process

Fibrils and CNCs from potatofiber - AFM
Alkaliextraction - HCl / $NaClO_2$ hydrolysis - TEMPO-mediated oxidation
Without and with sonication

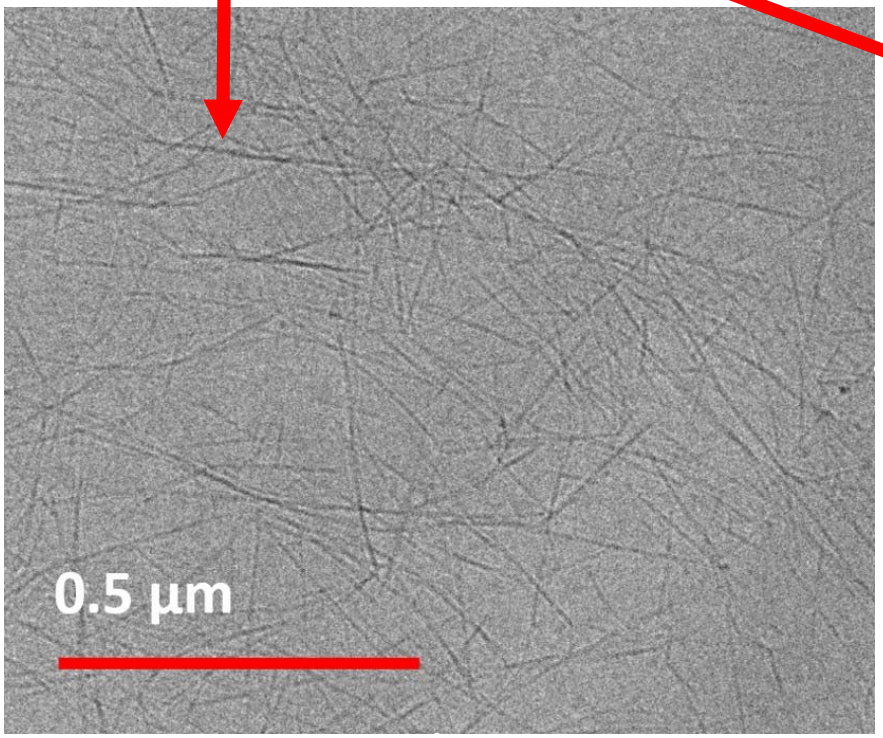


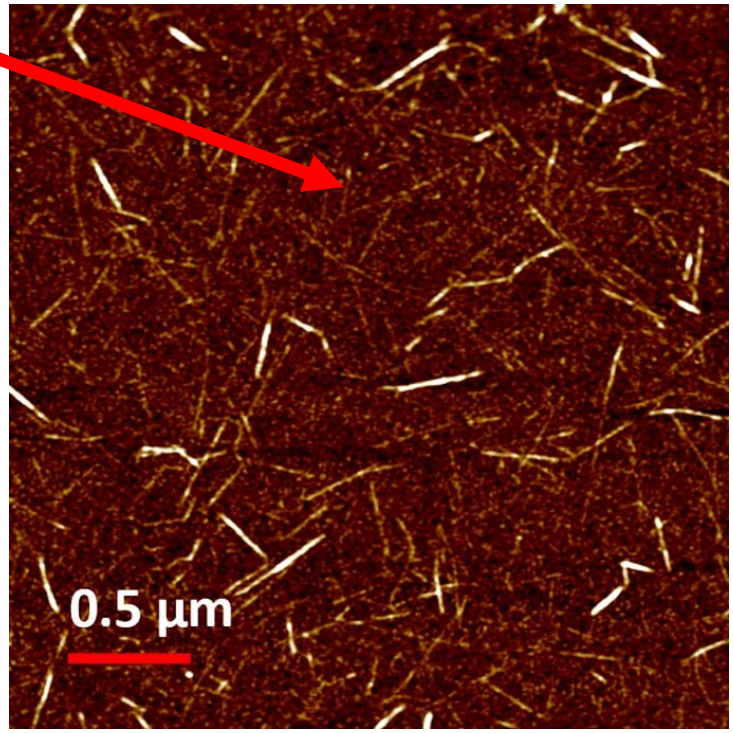



## CNCs from potatofiber (sonicated)

## Alkaliextraction - HCl / $NaClO_2$ hydrolysis - TEMPO-mediated oxidation

## Cryo-TEM and AFM

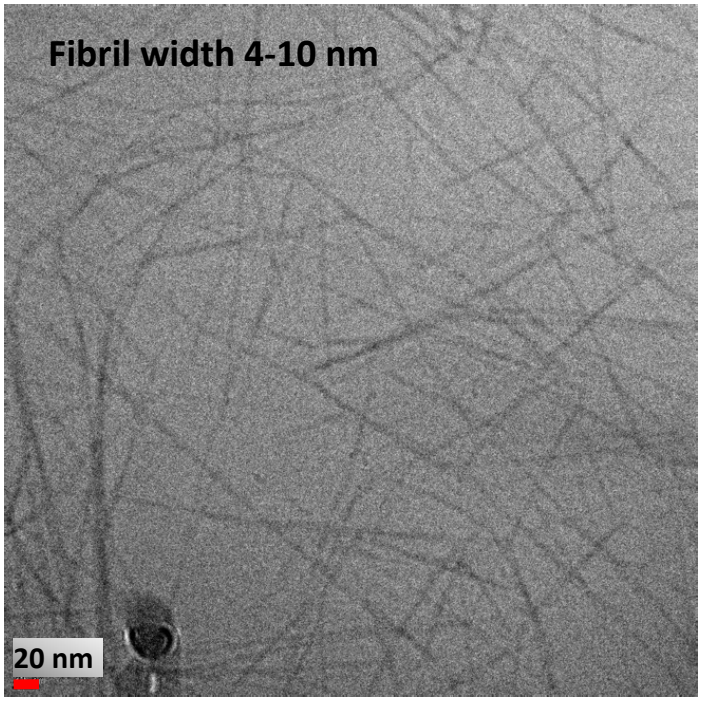


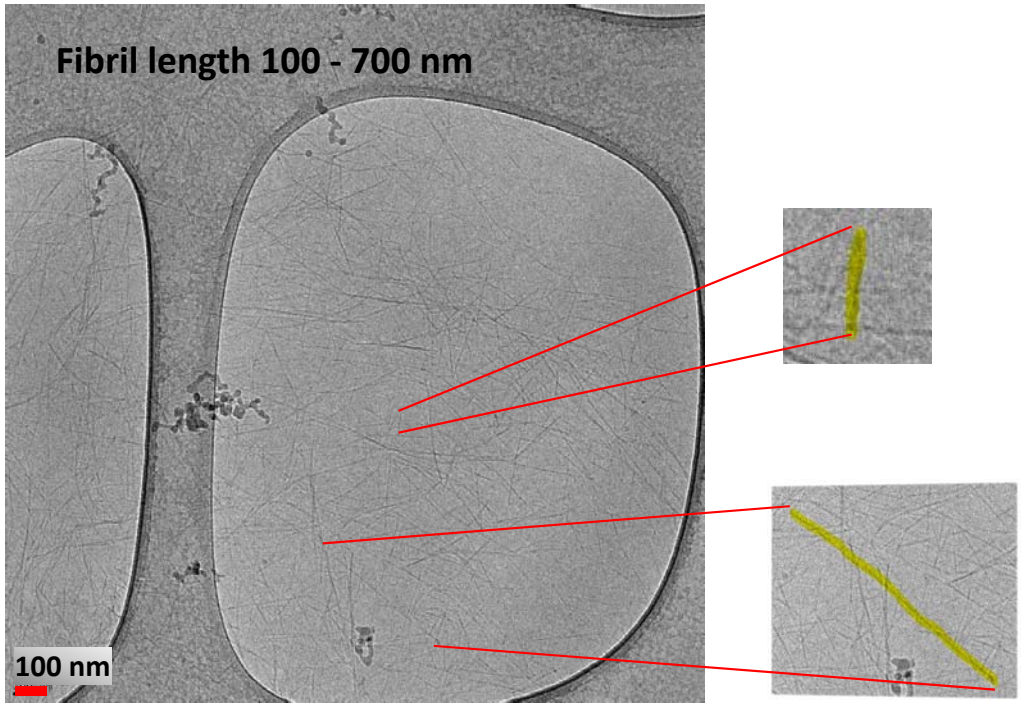



# CNCs from potatofiber (sonicated) - Cryo-TEM

## Alkaliextraction - HCl / $NaClO_2$ hydrolysis - TEMPO-mediated oxidation

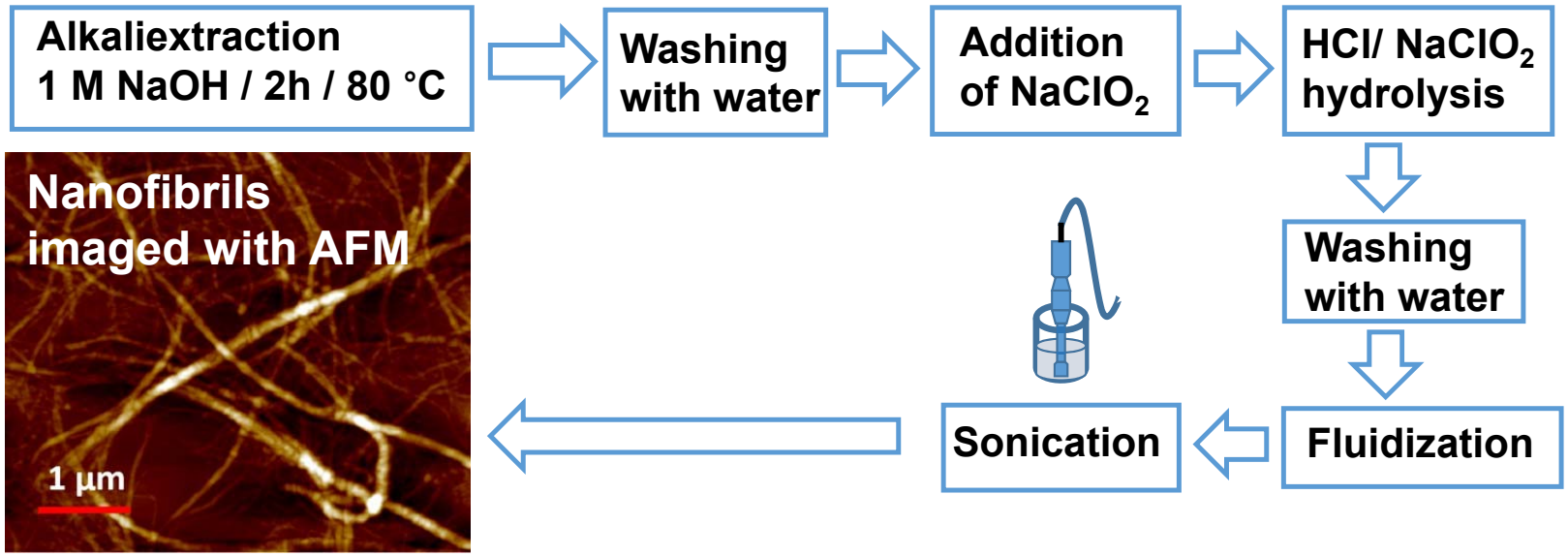
## Aspect ratio (L/D) ~ 10 - 175



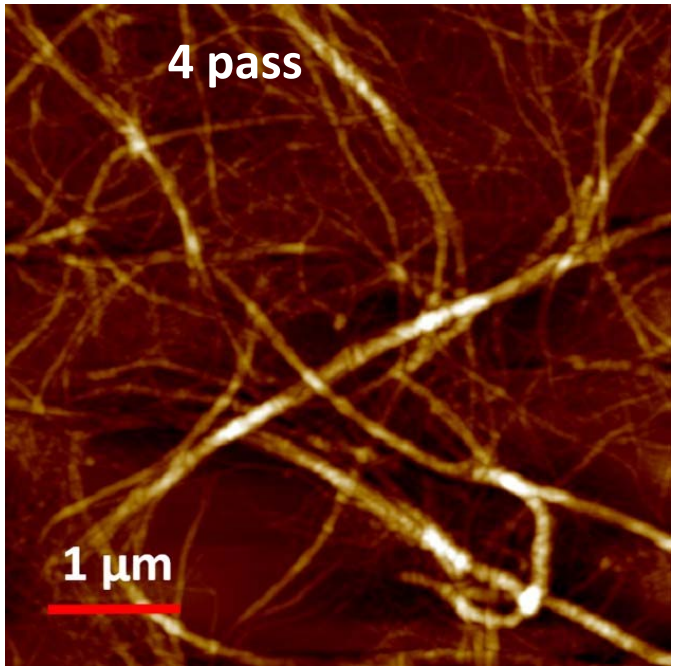
# Nanofibrils from alkaliextracted Potatofiber (Vitacel)

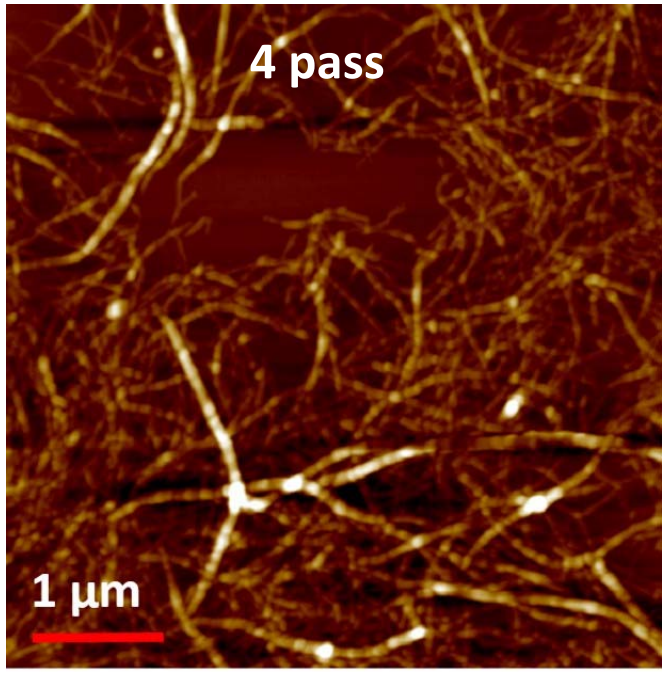
- Yield of hydrolysis was 67.4 %
- Reduction of DP with HCl/$NaClO_2$ (3.4 %) hydrolysis (1 bar / 4 h) was from 3670 to 781
- Nanofibrils are produced without TEMPO-mediated oxidation

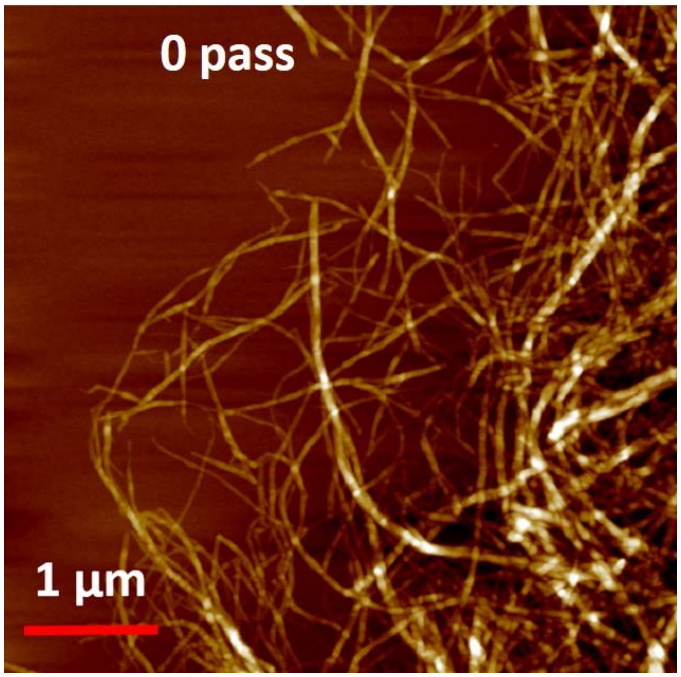


# Nanofibrils from alkaliextracted potatofiber (Vitacel) – AFM

## Alkaliextraction - HCl / $NaClO_2$ hydrolysis - fluidization - Sonication



# Summary

Acid hydrolysis with pressurized HCl gas is a platform for production of nanocellulosic materials with multiple processes and raw materials

CNCs produced with HCl hydrolysis + TEMPO-mediated oxidation

Bacterial cellulose

+ $NaClO_2$ not needed
+ High yield
- High raw material cost, risk of hornification

Potatofiber

+ Moderate yield, low raw material cost
+ Both nanofibers and CNCs can be produced with same process
+ Nanofibrils can be produced without TEMPO-mediated oxidation
- $NaClO_2$ needed

# Thank you

PRESENTED BY

**Timo Pääkkönen**

**Postdoctoral Researcher**

**Aalto University**

**timo.paakkonen@aalto.fi**

FinnCERES Materials Cluster

SciTech-Service

Aalto University

**Suvi Muukka and Xuetong Shi are acknowledged for additional experimental work**

TAPPI