Cellulose Nanomaterials Isolated via Subcritical Water Treatment

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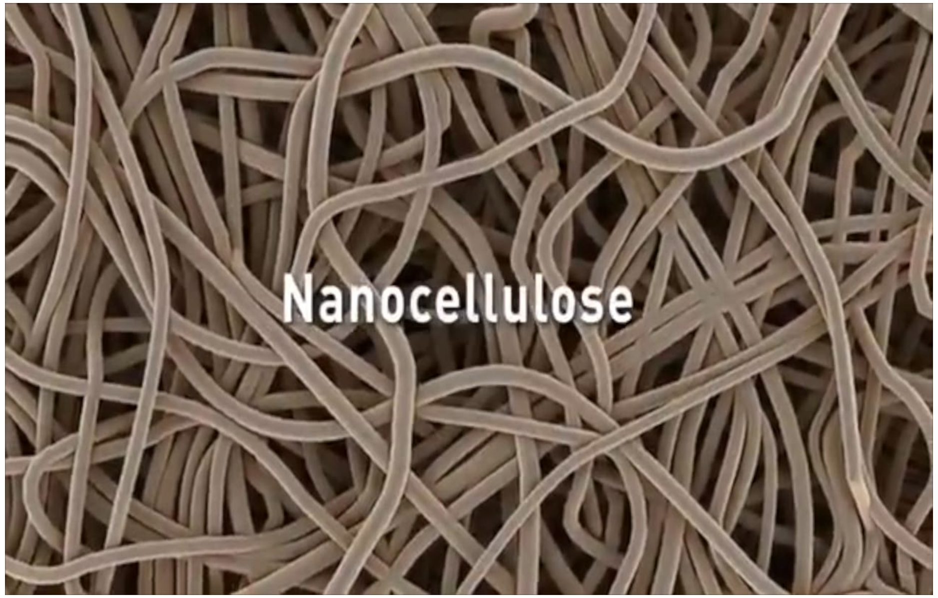
TAPPI NANO DIVISION

Nanocellulose: Sources and Applications

Plants

Tunicates

Bacteria



Biomedical industry

Chemical industry

Papermaking industry

Cellulose sources → **Nanocellulose isolation** → **Industrial applications**

K. Dhali, M. Ghasemlou, F. Daver et al. *Science of the Total Environment* 775 (2021) 145871, N. Lin, A. Dufresne ,*European Polymer Journal* 59 (2014) 302–325, https://www.youtube.com/watch?v=R3HH4iN8aDM

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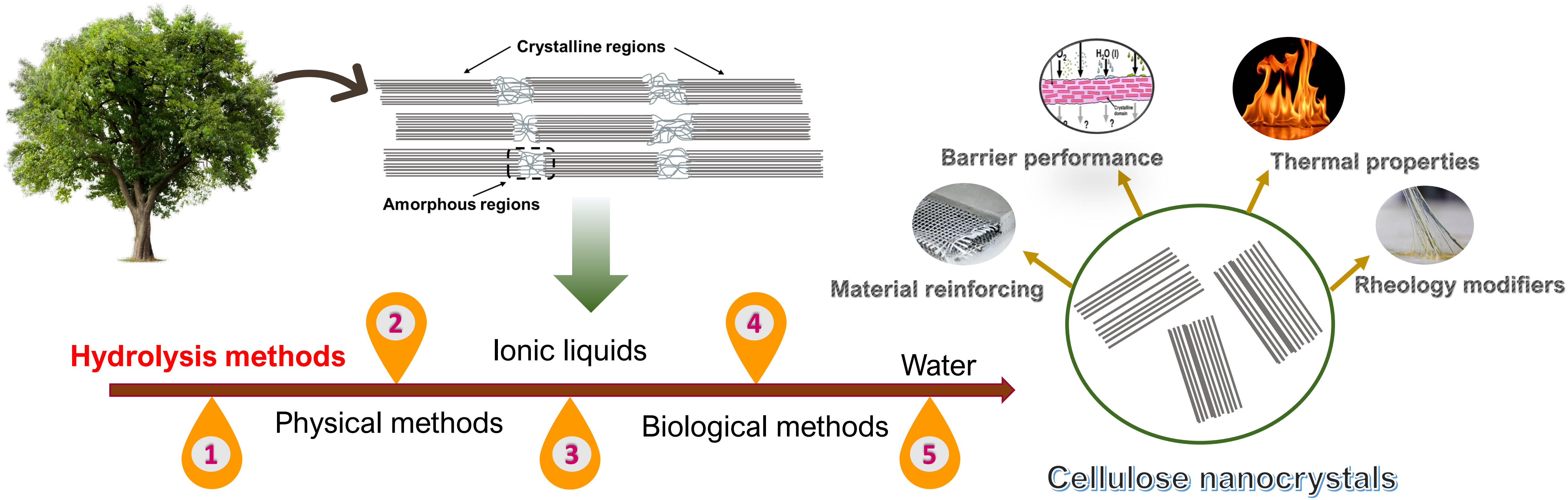
Nanocellulose Production



Recent production routes for cellulose nanocrystals

J. Wang et al.,*Journal Of Biomaterials Science*, Polymer Edition 2019, Vol. 30, No. 11, 919–946

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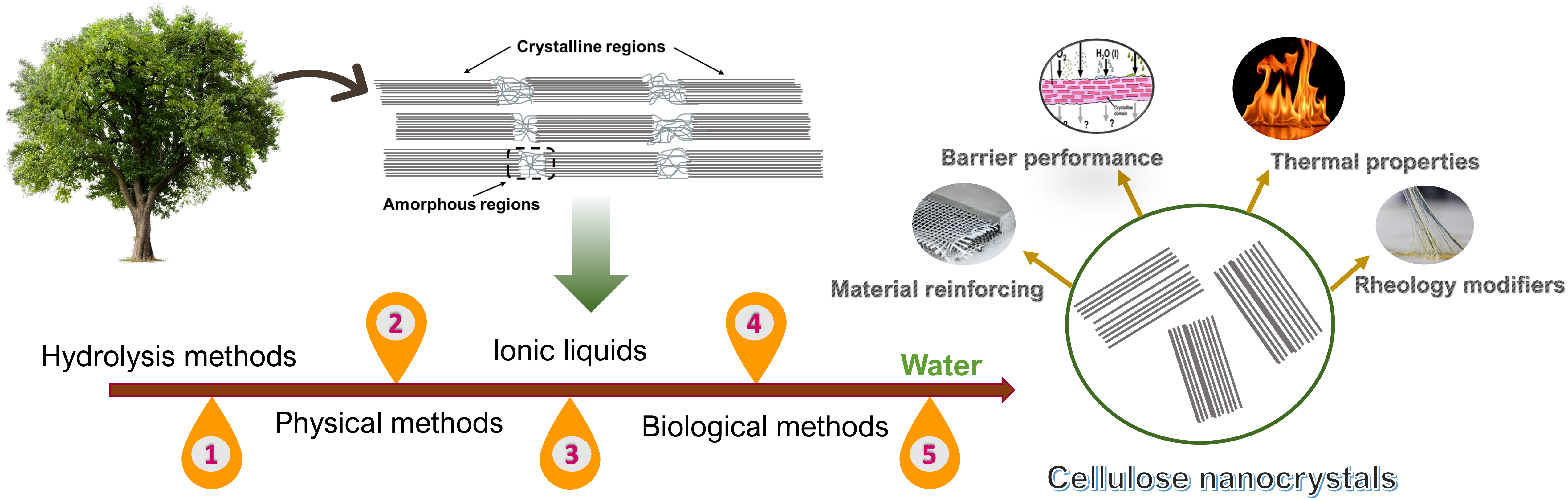
Nanocellulose Production



Recent production routes for cellulose nanocrystals

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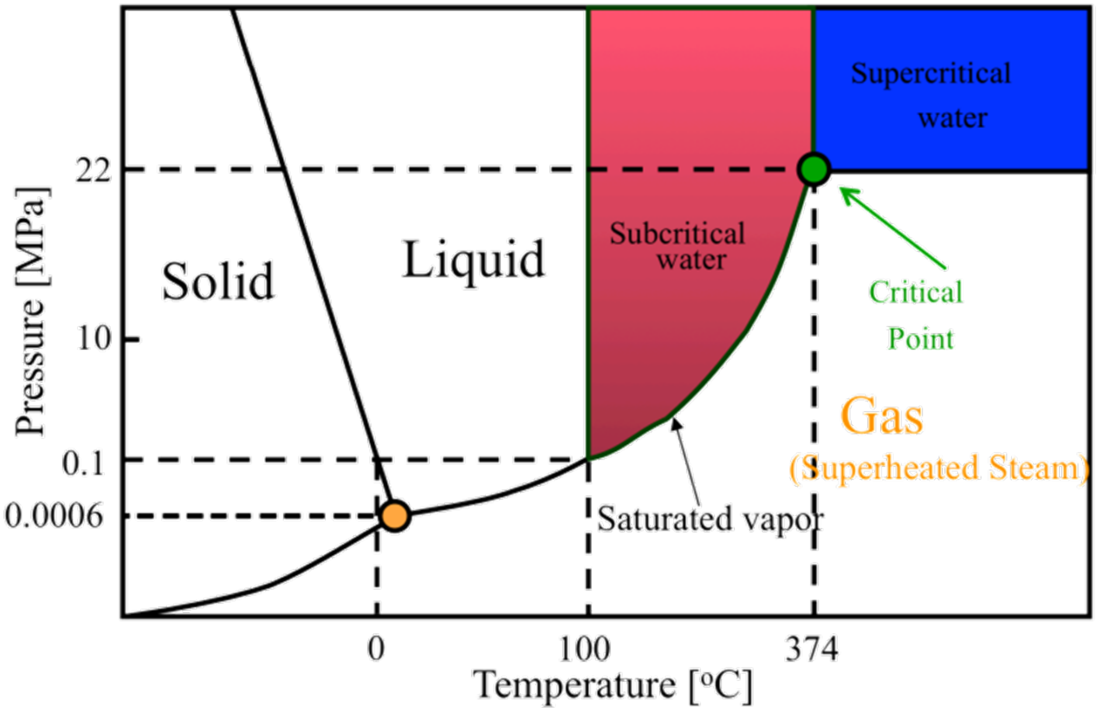
Subcritical Water Technology

- ➢ Hydrothermal treatment – uses hot water
- ➢ Requires sufficient pressure to maintain water as liquid (0.1- ~30 MPa)
- ➢ Temperatures < 374 ℃ - subcritical water
- ➢ Temperatures > 374 ℃ - supercritical water

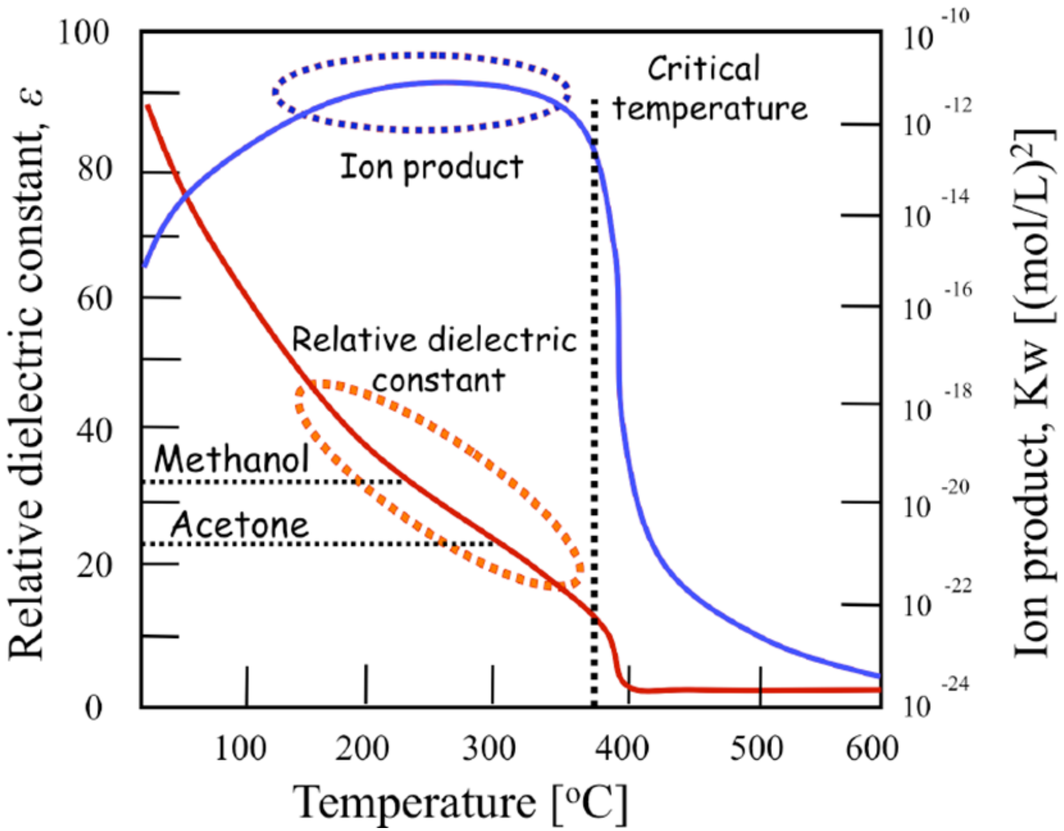
Several advantages

- ➢ Green process
- ➢ Relatively cheap
- ➢ Process is recoverable



W Yang. Thesis 2015 , Okayama University

Subcritical Water Properties



Physical properties of subcritical water

Dielectric constant

- Dissolve organic compounds
- Extract several components

Ion product

- Improves absorption proportion
- Improves absorption rate

W Yang. Thesis 2015 , Okayama University

Subcritical Water Conversion of Biomass


Plastic waste


Paper industry

Agricultural and Industrial waste


Food waste


Textile industry


Wood industry


Food and feed


Pharmaceuticals

Value added products

Biofuel

Bioenergy and heat


Bioplastics

A. Shitu et al., *Global J. Environ. Sci.* Manage., 1(3): 255-264, Summer 2015

Research Objectives

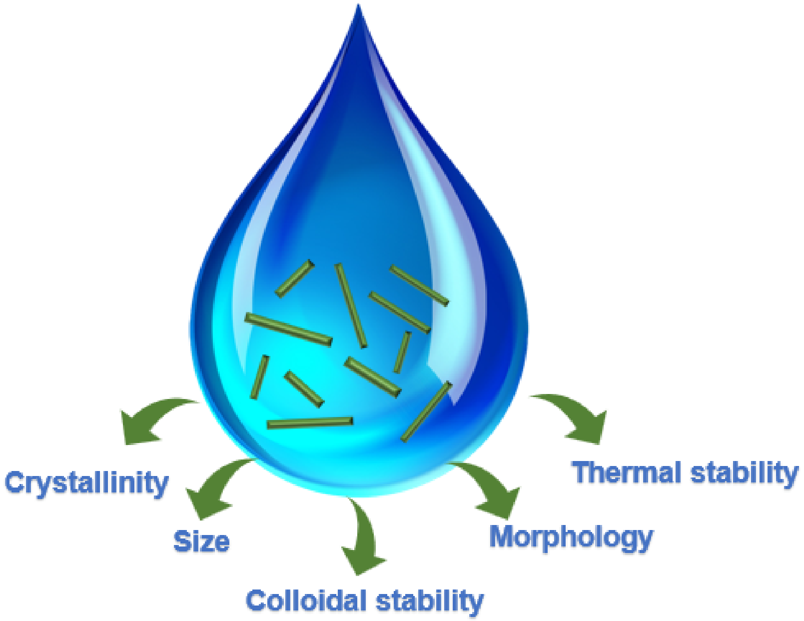
Main aim

To produce cellulose nanocrystals from controlled digestion of woody biomass using subcritical water as the solvent

Objectives

Investigate the tunability of the nanocellulose properties produced with varying subcritical water conditions (temperature and time)

Benchmark these properties against conventionally acid hydrolyzed nanocellulose



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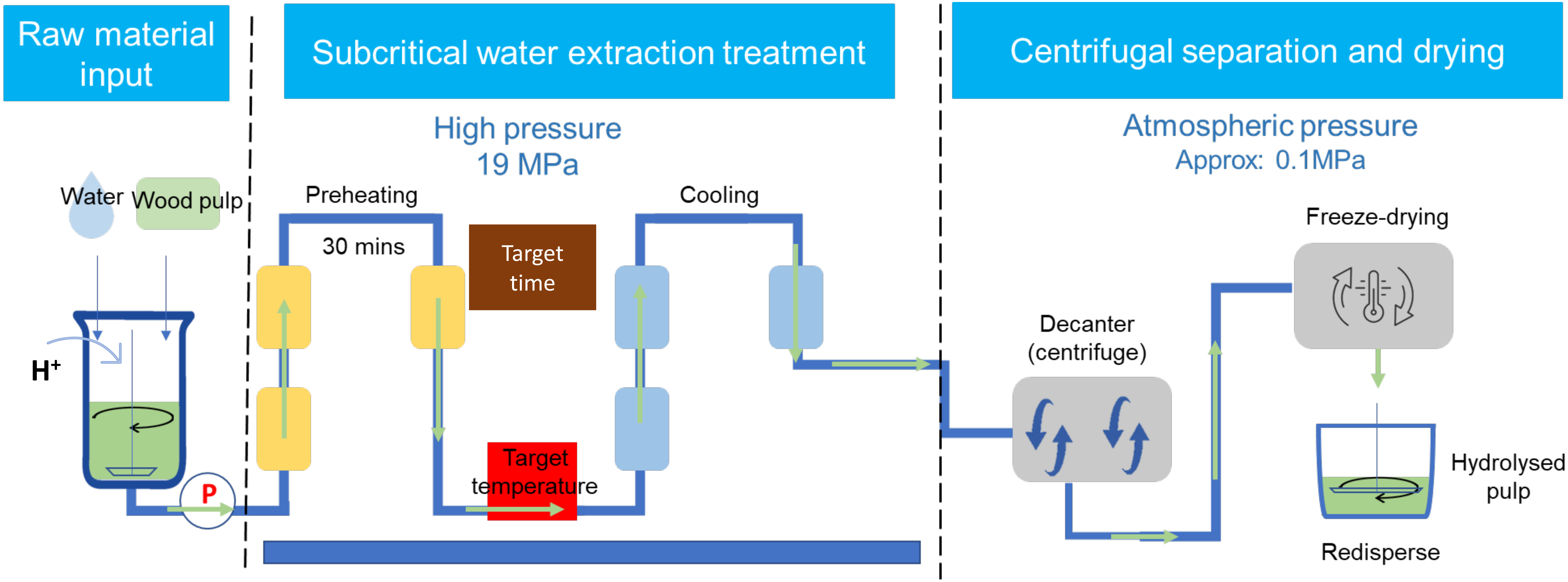
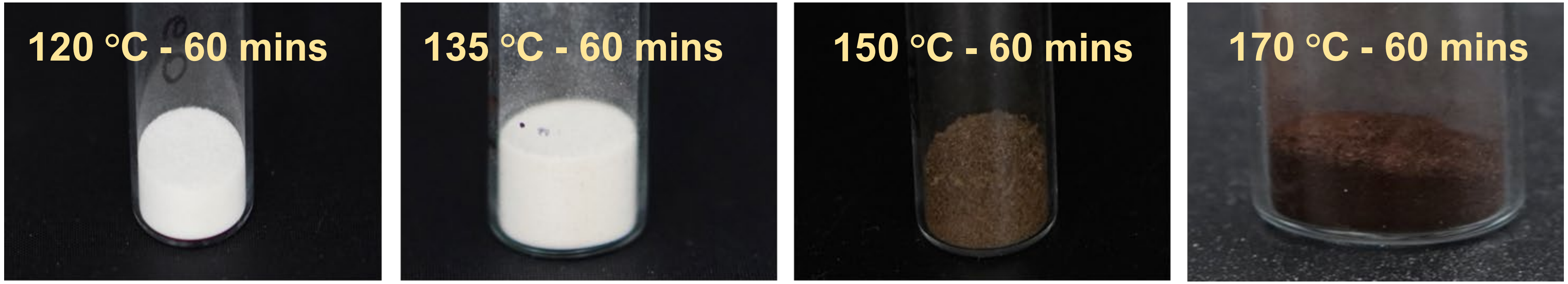
Experimental Method



Physical Observation

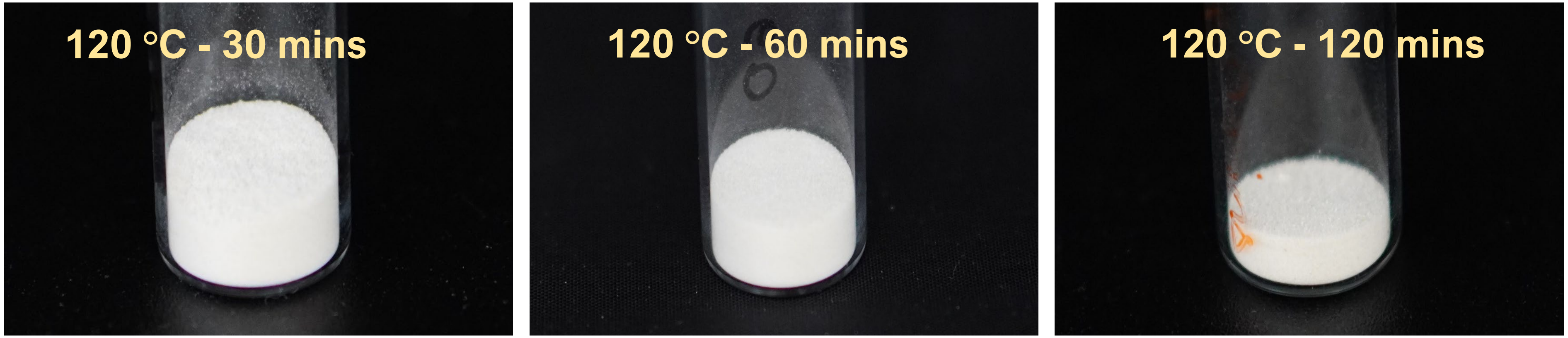
Change in whiteness with increasing temperature

SC treatment at constant time



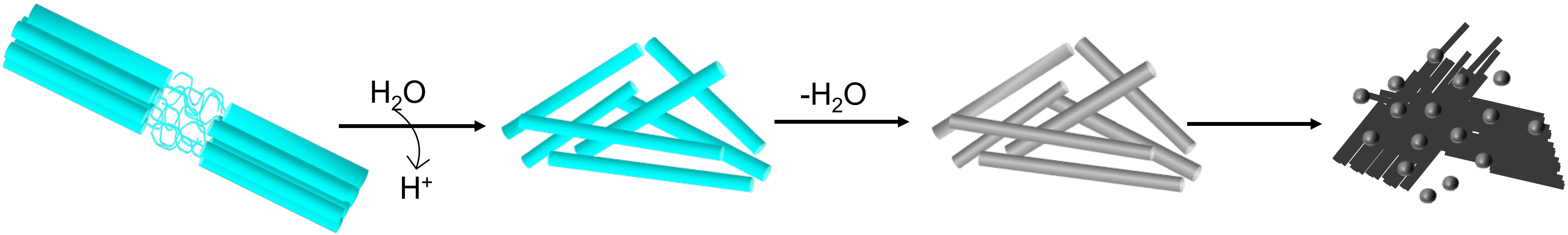
No visible change in coloration at low temperature

SC treatment at constant temperature



Subcritical Water Cellulose Digestion

1 **Hydrolysis** 2 **Dehydration** 3 **Fragmentation**



- Glycosidic bond breaking
- Dissolution of amorphous regions
- Increase in crystallinity

- Loss of water molecules from fibre
- Formation of water-soluble saccharides
- Reduced crystallinity

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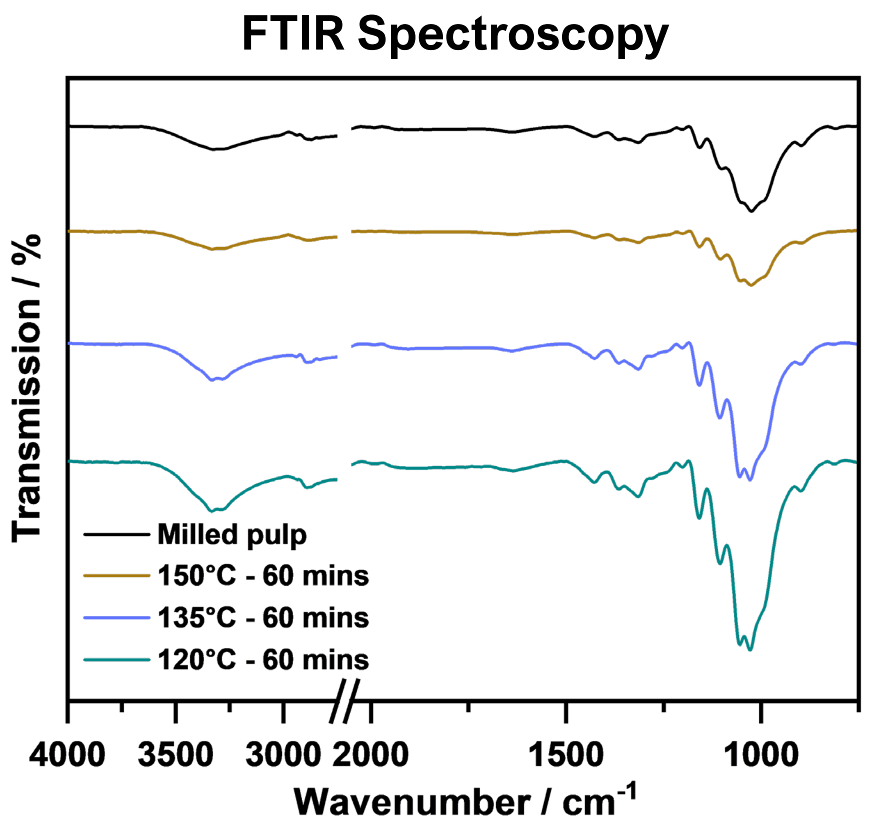
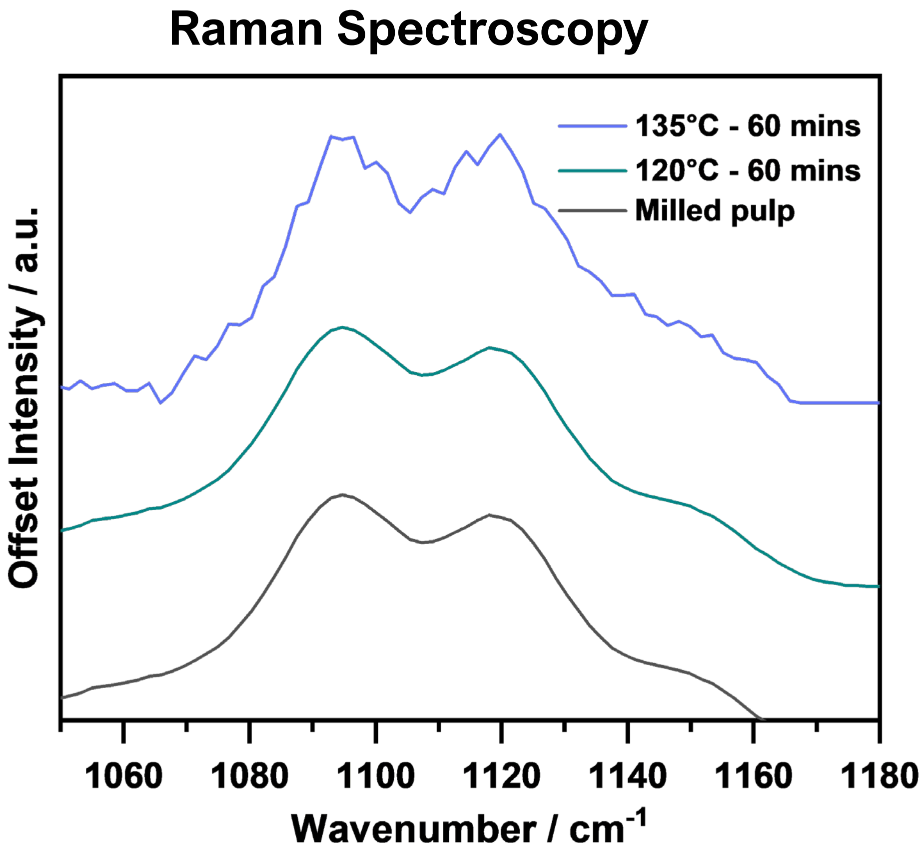
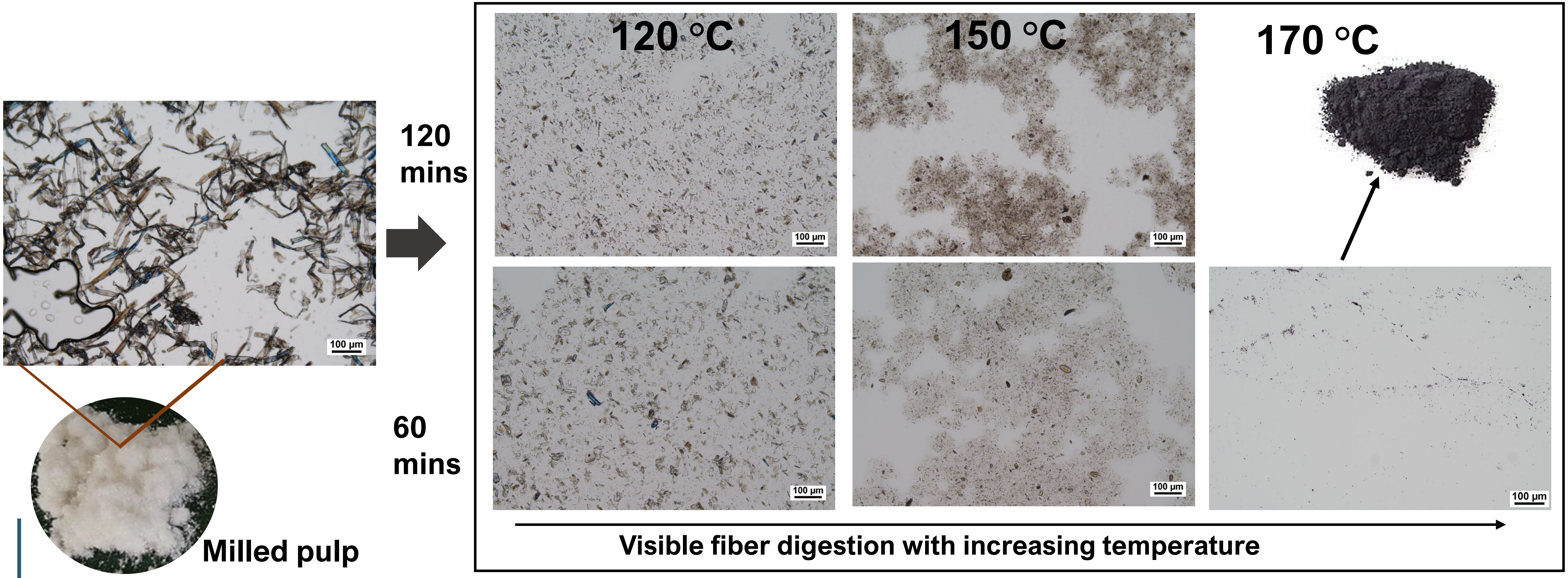
Chemical Characterization



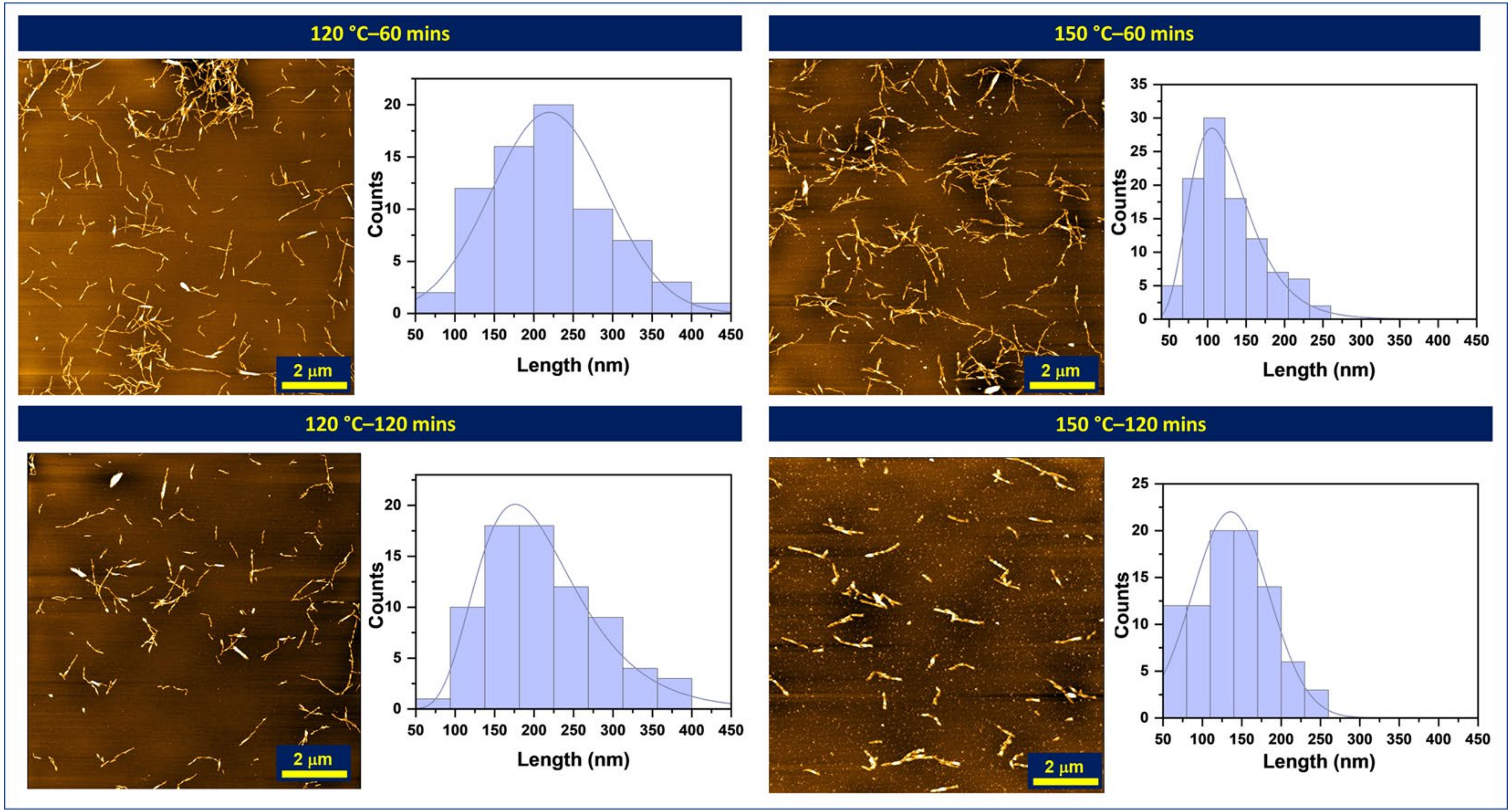


- No visible change in the chemical composition of cellulose

Fiber Digestion in Subcritical Water



Particle Size Distribution



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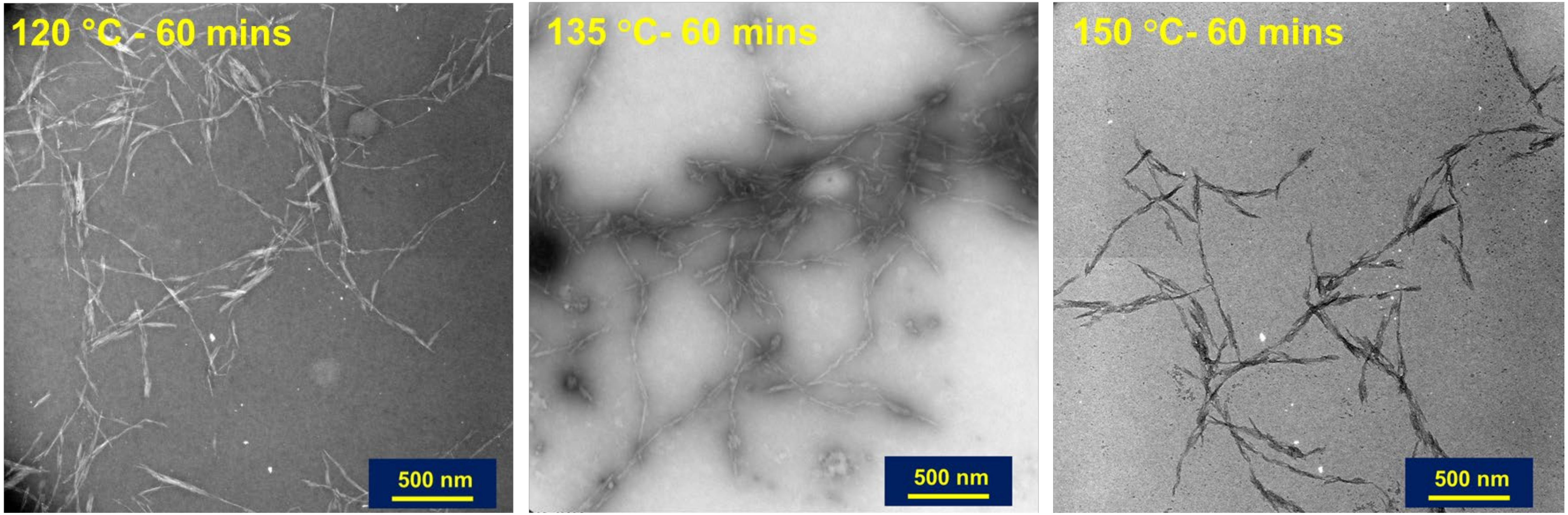
Particle Morphology



- All particles are rod-like regardless of reaction condition
- Homogeneous particle sizes observed at higher temperatures

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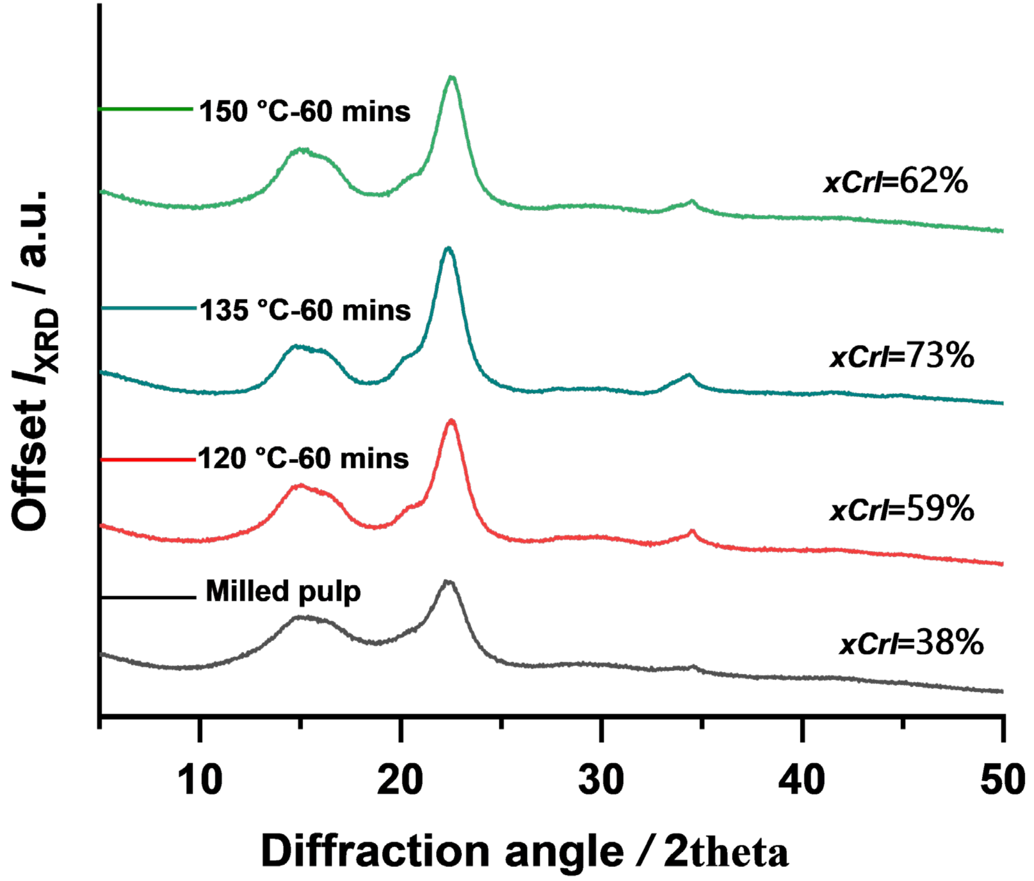
Bulk Properties-X-ray Diffraction

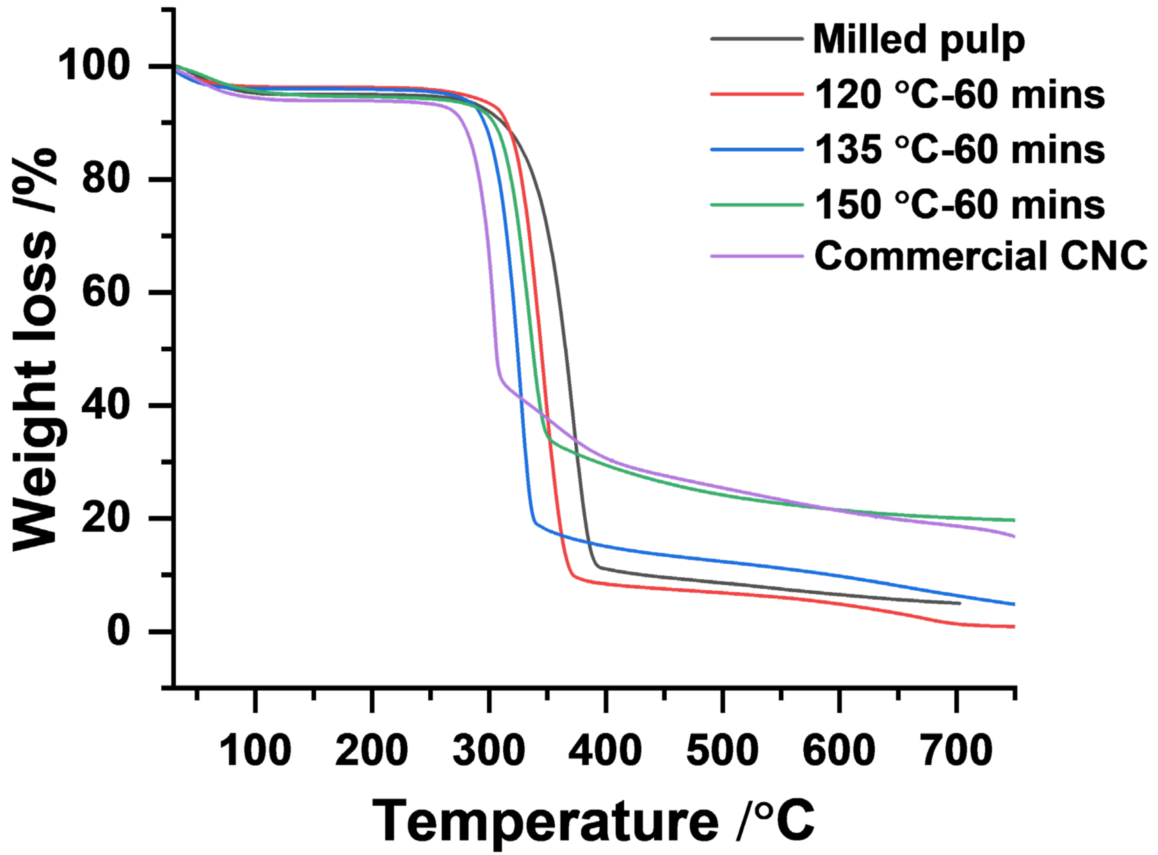
- Crystalline structure is cellulose I
- Apparent crystallinity:

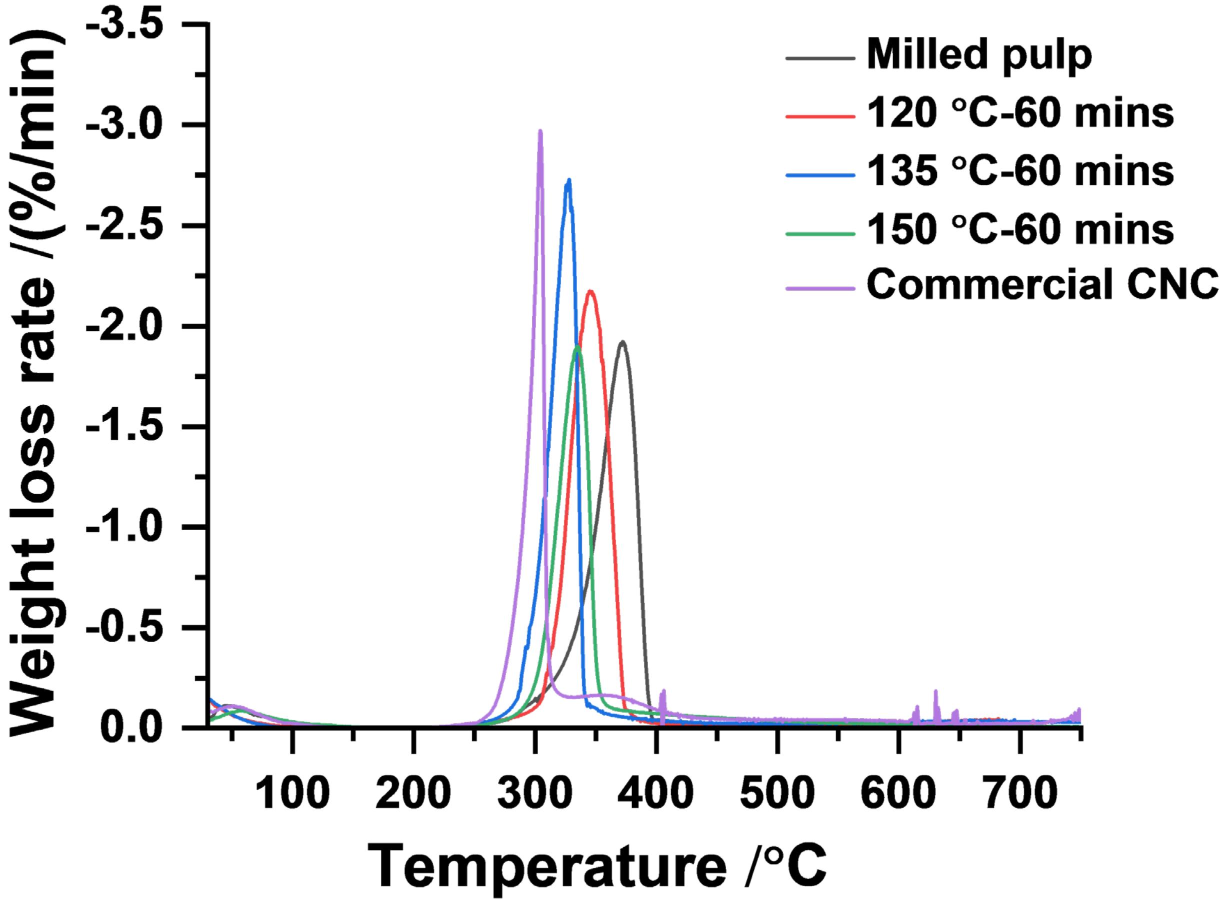
$$CI = \frac{I_{200} - Iam}{I_{200}} \times 100\%$$

- Overall increase in pulp crystallinity after subcritical water treatment
- Crystallinity influenced by subcritical water temperature



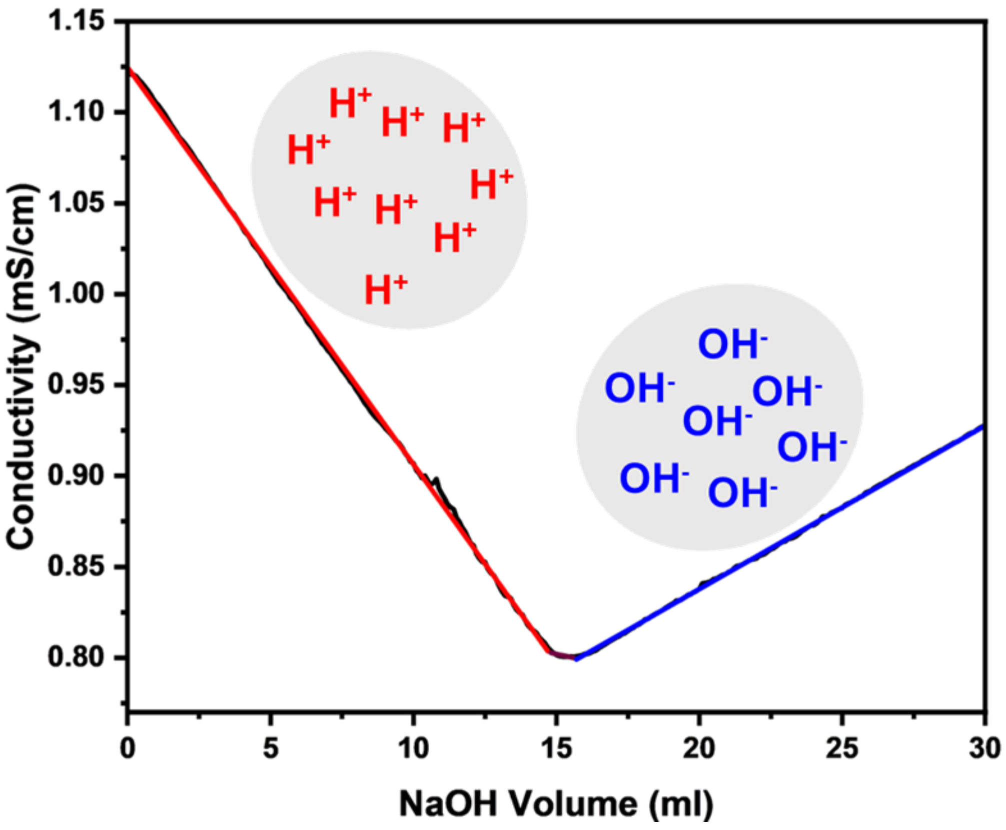
Bulk Properties-Thermogravimetric Analysis





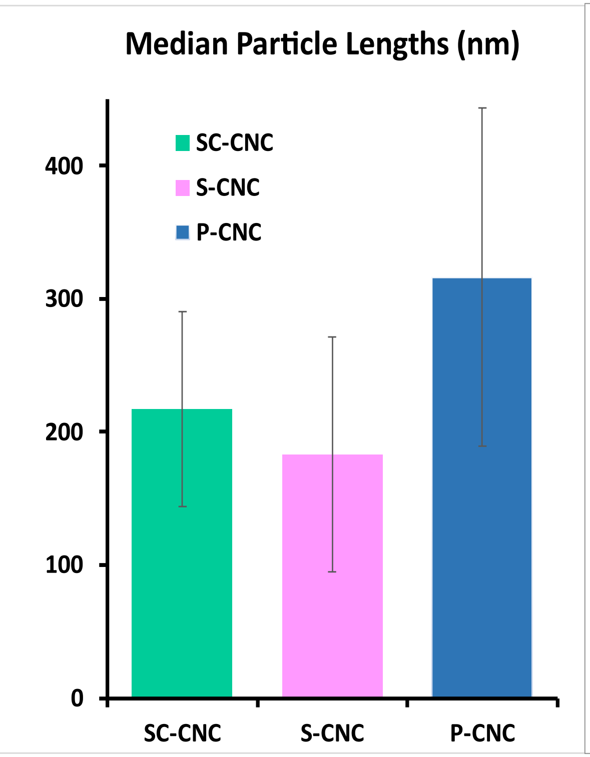
Surface Charge Measurement

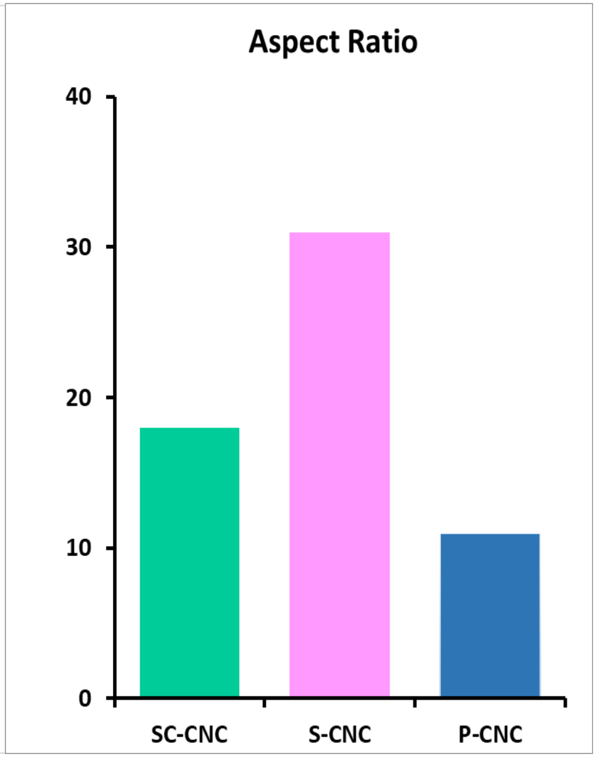
- Dictates the dispersibility of CNCs in composite applications
- Little or no surface groups observed for SC-CNCs
    - Very low amounts of acid used
    - Large water volume
- Charged density may be improved through:
    - Post hydrolysis surface modifications
    - Perform hydrolysis with acid blends



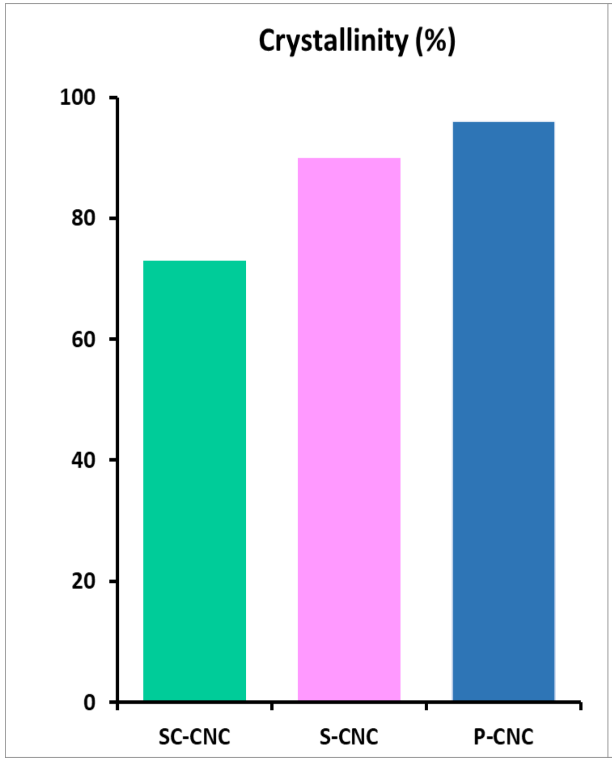
Benchmarking Properties of SC-CNCs

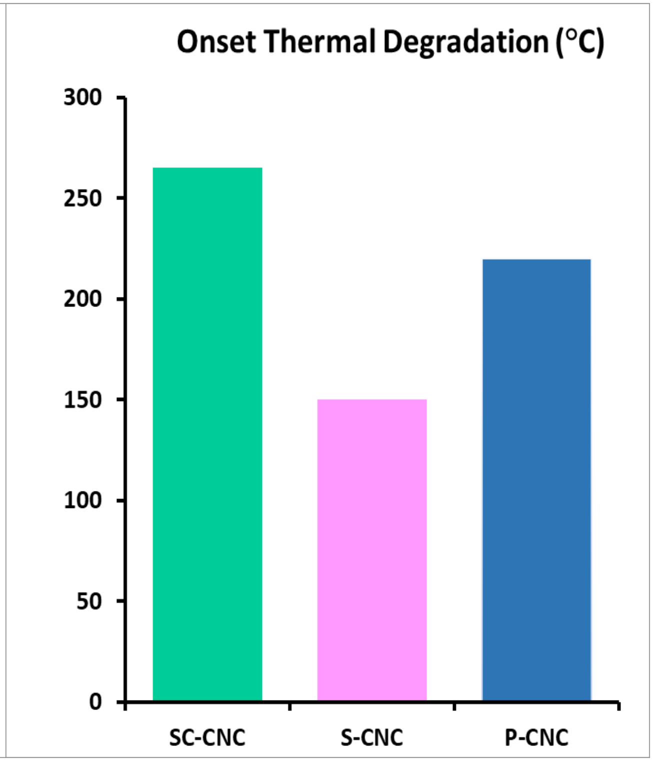
Physical Properties of CNCs





Bulk Properties of CNCs



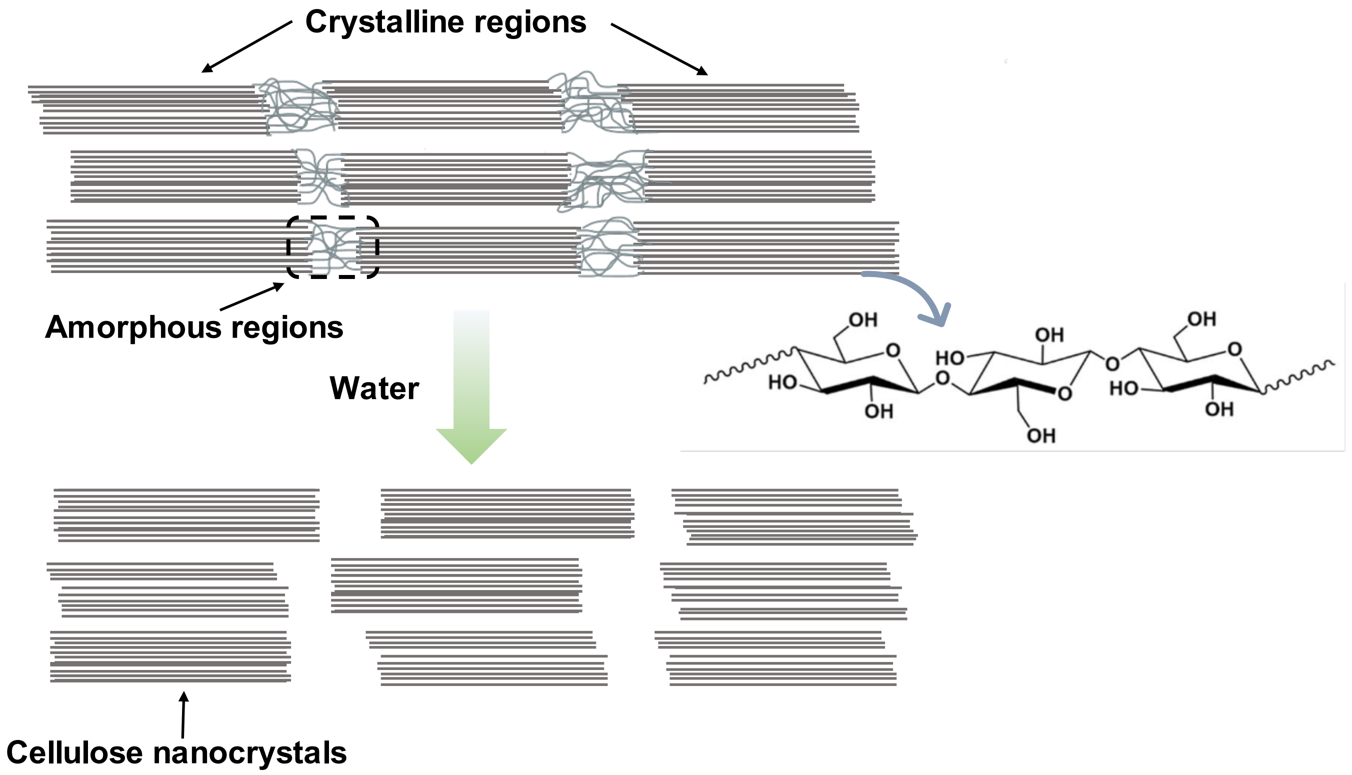


SC: Subcritical water hydrolyzed ; S: Sulfuric acid hydrolyzed ; P: Phosphoric acid hydrolyzed

S. Camarero et al, *Biomacromolecules* 2013, 14, 1223–1230, O. Vanderfleet et al., *Phil. Trans. R. Soc.* A 376: 20170041, M. Reid et al., *Langmuir* 2017, 33, 7, 1583–1598

Conclusions

- Investigated subcritical water technology for CNC production
- Isolated CNCs properties are comparable to acid hydrolyzed CNCs
- Improve colloidal stability with esterifying agents
- Water as the main reaction reagent:
  - reduces use of toxic chemicals
  - produces cleaner effluents
  - reduces cost of chemicals
  - presents a cost-effective process



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THANK YOU!!

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