Pickering emulsions from Norway spruce bark

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TAPPI Nano Conference 2023

Outline

Introduction

Objectives

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Conclusion

Introduction

Introduction

https://www.un.org/en/sustainable-development-goals

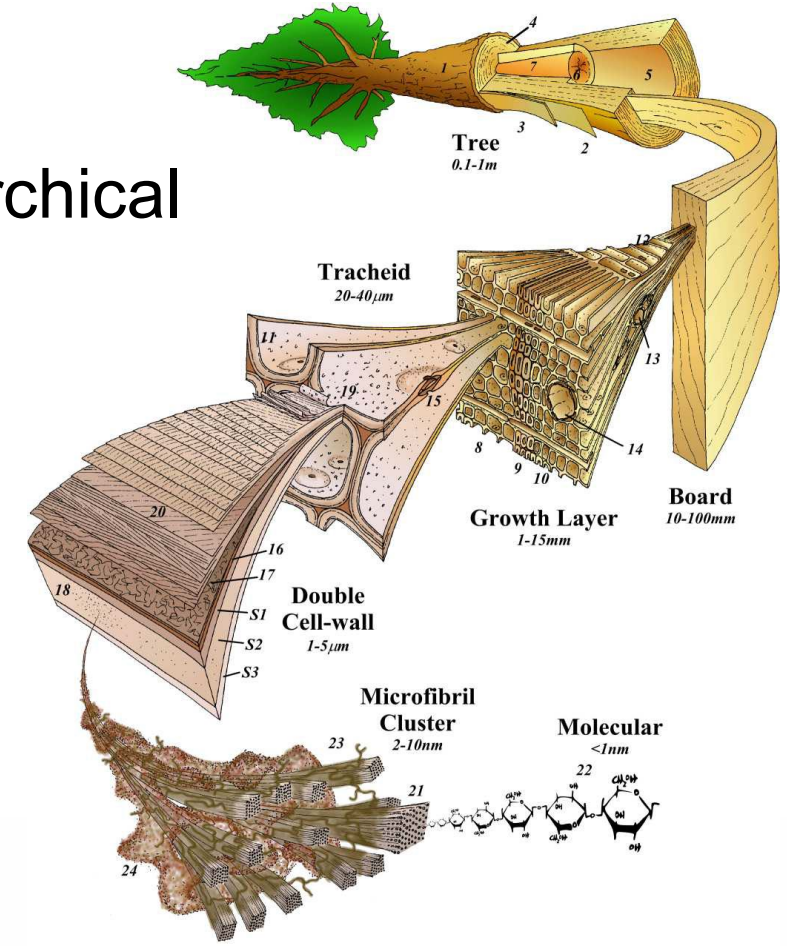
Introduction

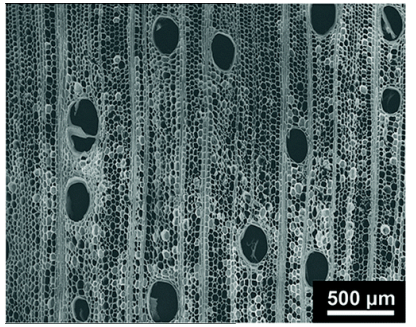
- Sweden: >70% forest
- Deforestation = Reforestation
  - 380 million trees per year

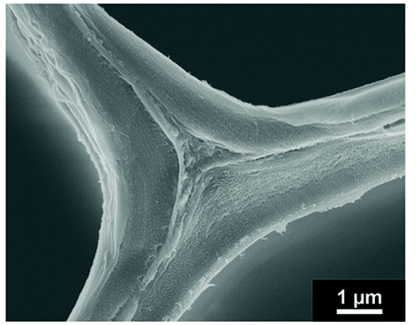
https://www.forestindustries.se/forest-industry/facts-and-figures/

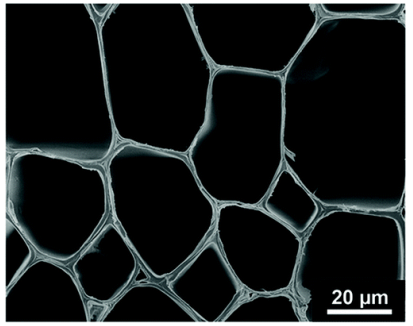
Introduction

- Complex hierarchical structure
- Cellulose
- Hemicellulose
- Lignin
- Extractives





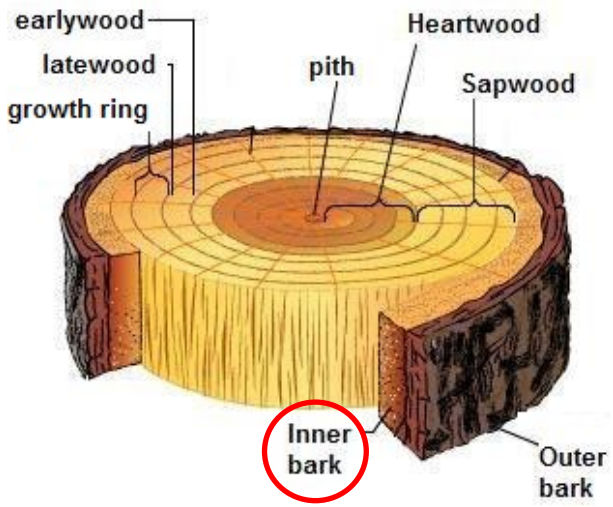




Montanari et al. 2020

Harrington, J. J. (2002). Hierarchical modelling of softwood hygro-elastic properties.

Bark



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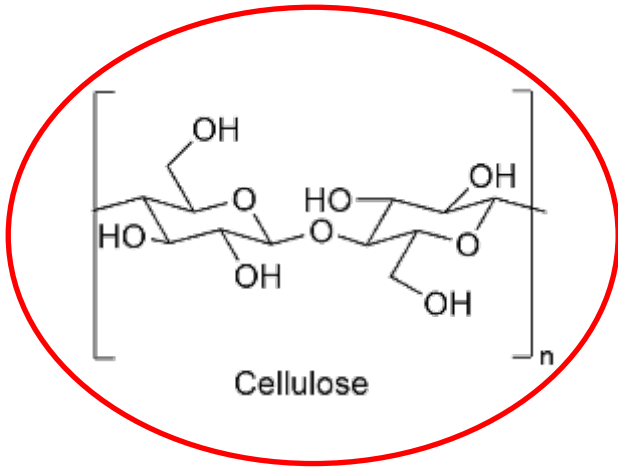
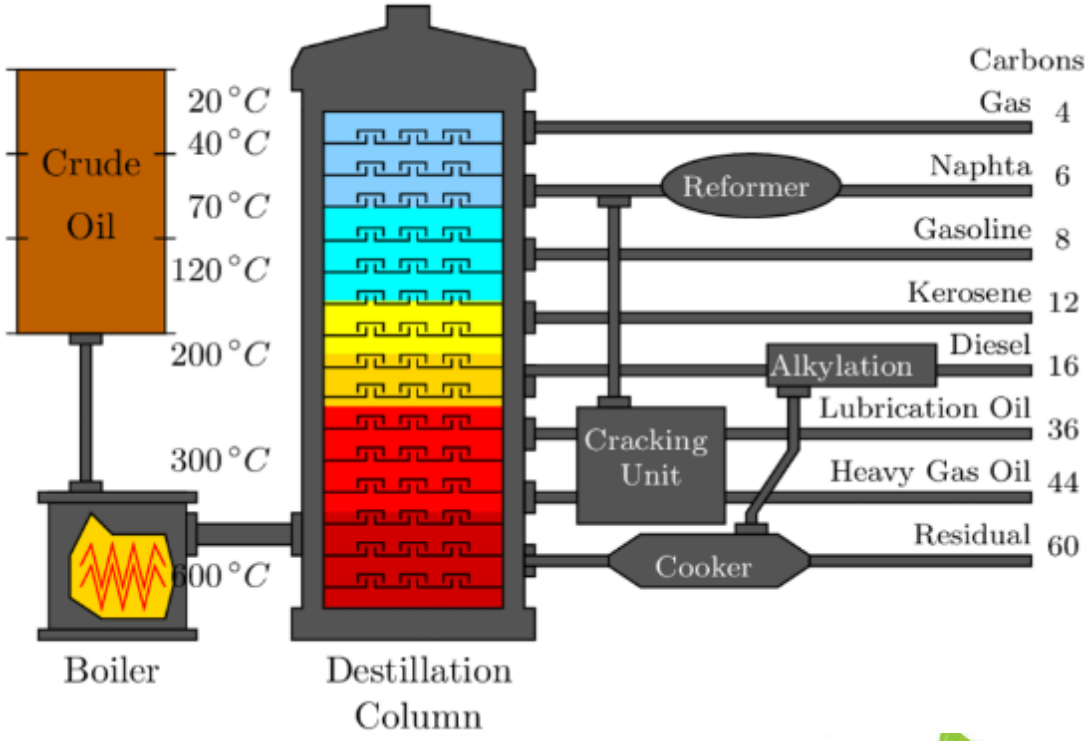
- **Cellulose (20%)**
- Hemicellulose (20%)
- Lignin (20%)
- **Extractives (20%)**
- Other (20%)

Norway spruce
(*Picea abies*)



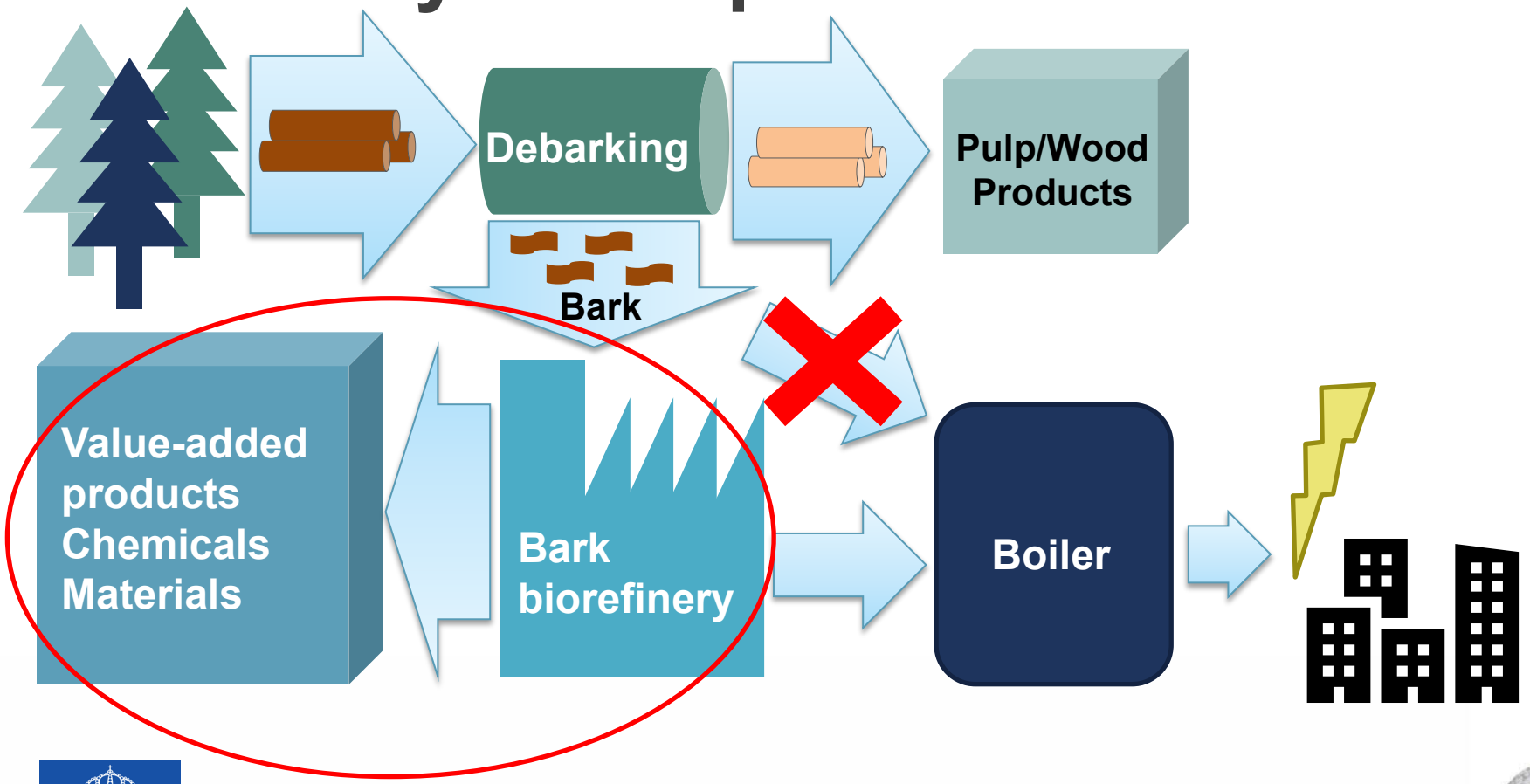
Refinery concept

https://www.forbes.com/sites/davidblackmon/2020/07/25/first-new-us-oil-refinery-since-1977-targets-bakken-shale-crude/?sh=6a2ce7e51a9f



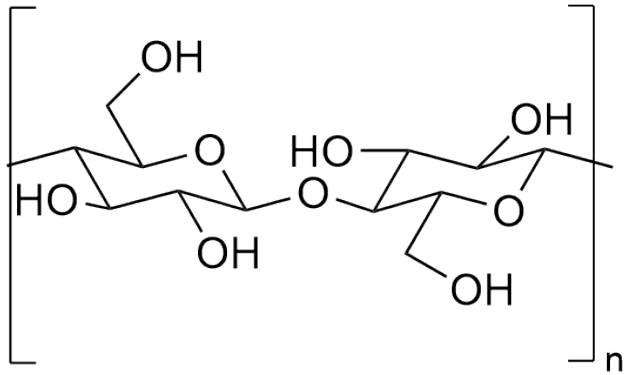
www.howstuffworks.com

Bark biorefinery concept

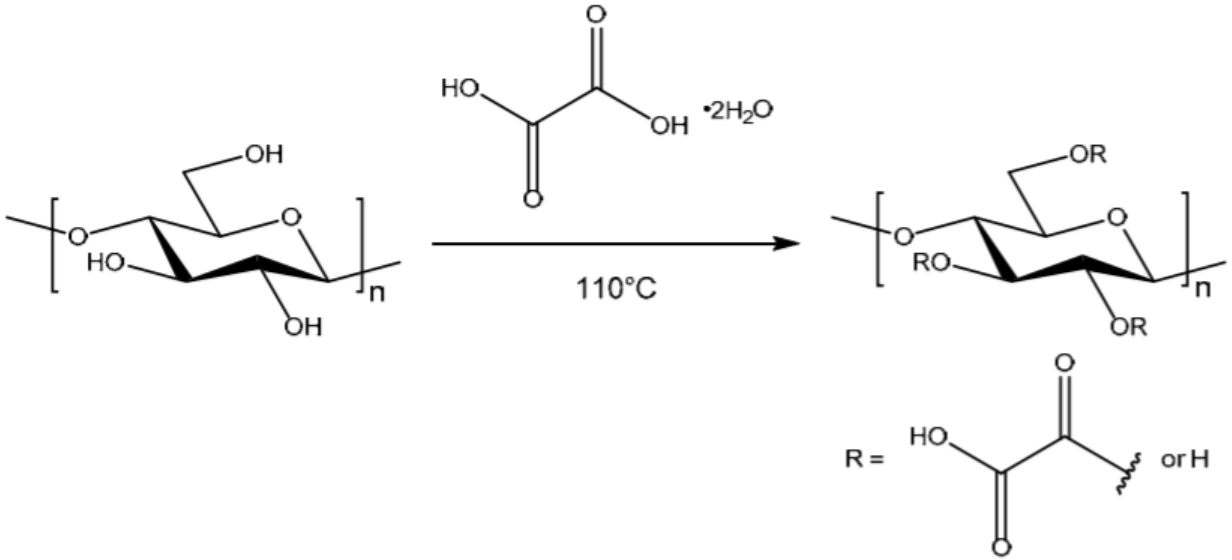


Cellulose oxalate (COX)

- Cellulose derivate
- Oxalic acid dihydrate
- One-pot esterification reaction



Cellulose



Li, D., Henschen, J., & Ek, M. (2017). Esterification and hydrolysis of cellulose using oxalic acid dihydrate in a solvent-free reaction suitable for preparation of surface-functionalised cellulose nanocrystals with high yield. *Green Chemistry*, *19*(23), 5564-5567.

Henschen, J. (2019). *Bio-based preparation of nanocellulose and functionalization using polyelectrolytes* (Doctoral dissertation, KTH Royal Institute of Technology).

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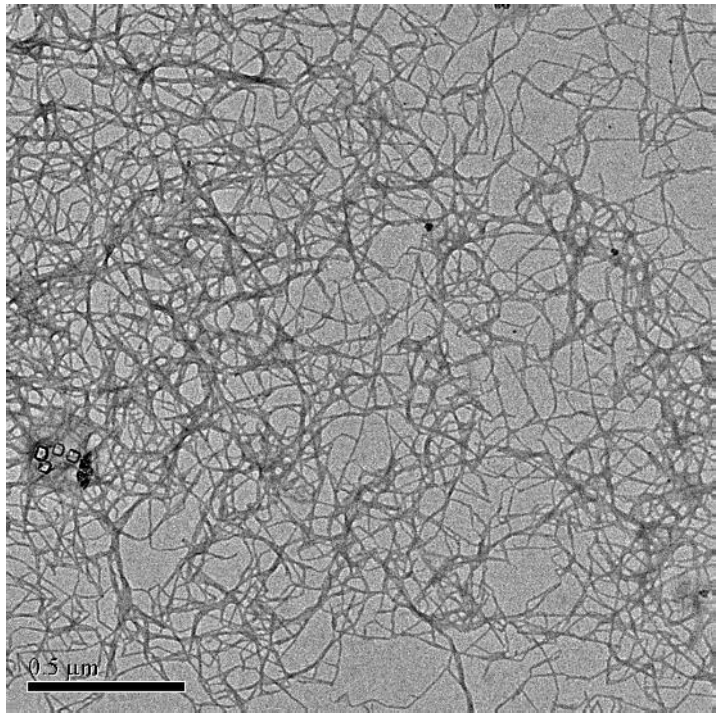
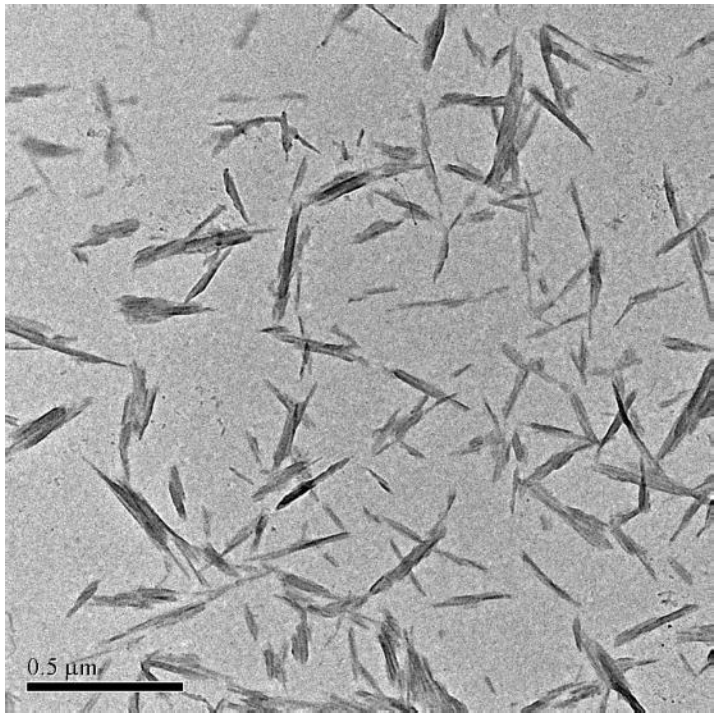
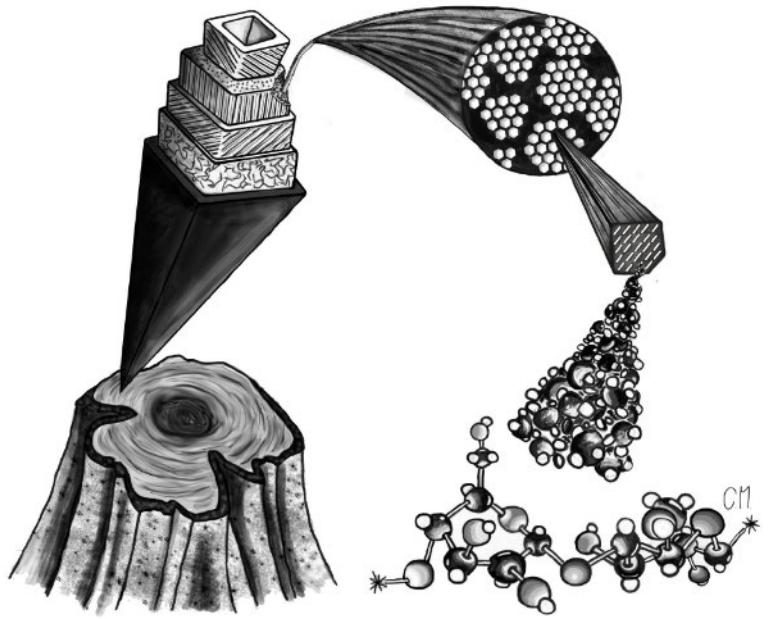
Nanocellulose



Cellulose Nanofibril (CNF)
Aspect ratio: 50-100 or above



Cellulose Nanocrystal (CNC)
Aspect ratio: 6-70



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www.celluloselab.com

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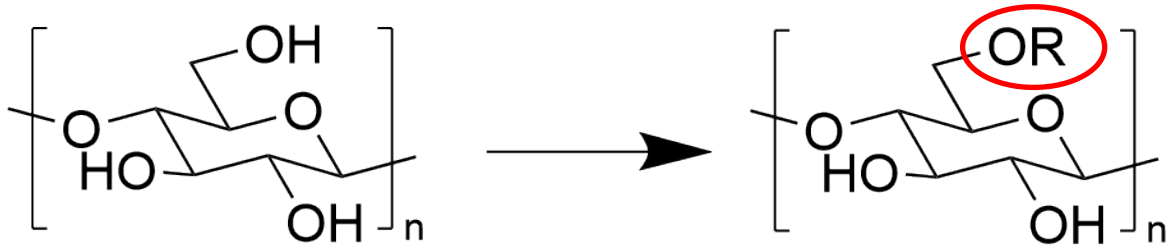
Nanocellulose production

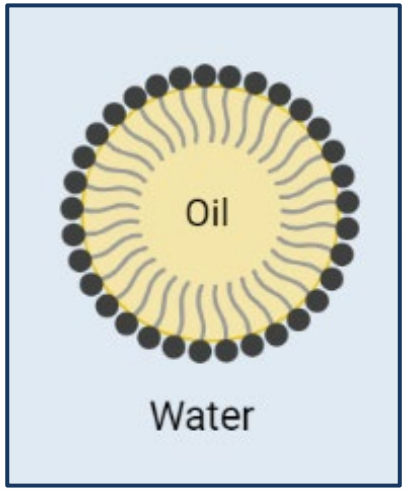
- Mechanical process
  - Energy consumption: 27 000 kWh/t (Ankerfors et al. 2014)
- Chemical + mechanical
  - Energy consumption: 2200 kWh/t
- Chemical pretreatment
  - Eases the fibrillation process
  - Charged group on C6

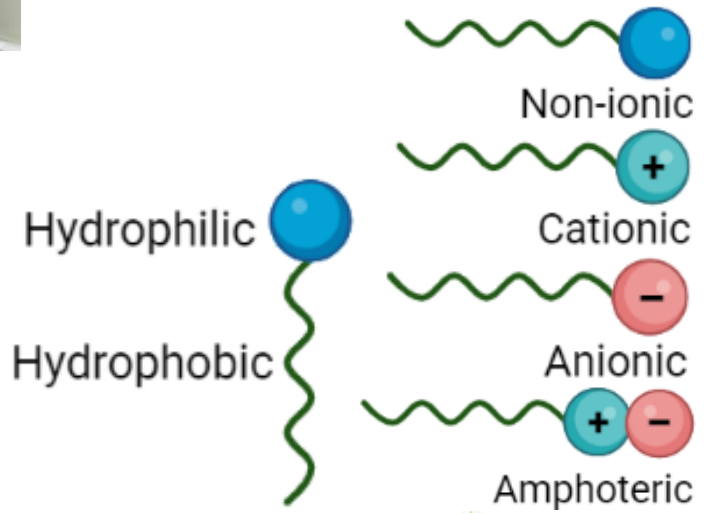


Emulsions

- Ice cream, beer, mayonnaise, cosmetic products…
- Surfactant = phospholipid
- Petroleum-based surfactants/emulsifying agents
- Sustainability → renewable resource





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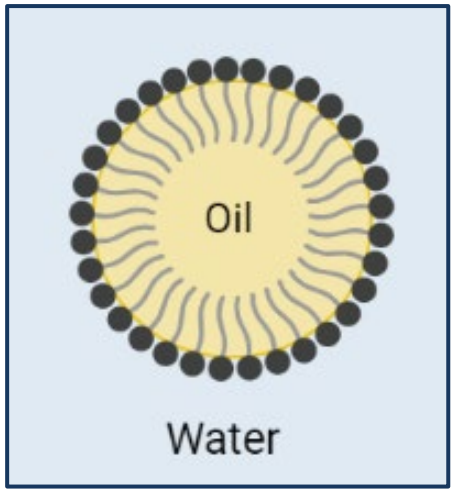
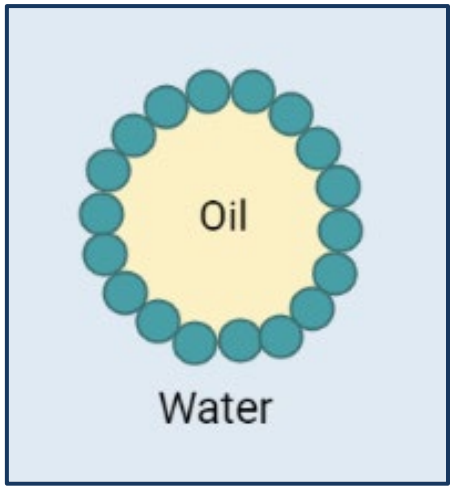
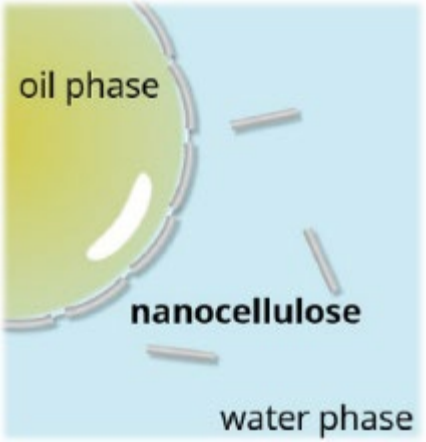
Pickering emulsions

- Solid particles
  - Silica
  - Clay
  - …
- Biomass
  - Nanocellulose
  - Lignin nanoparticles
  - …



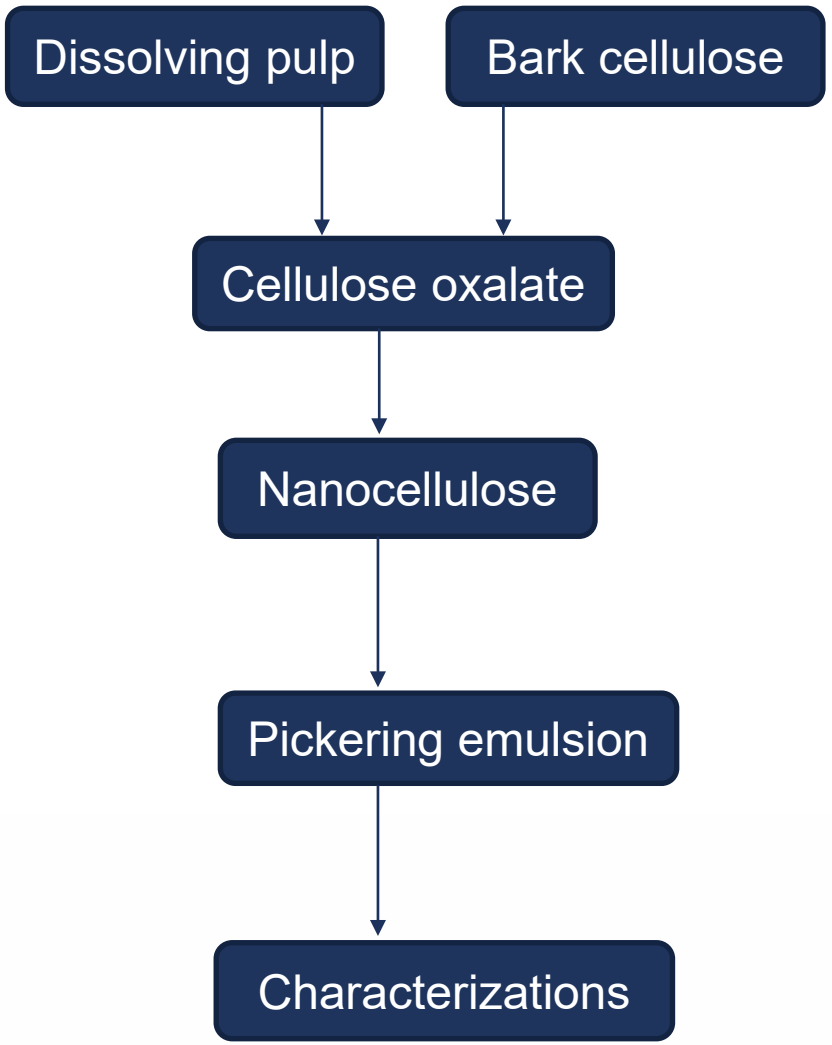




Fujisawa et al. 2017

Project objective

- Cellulose isolation from spruce bark
- Cellulose oxalate for Pickering emulsions
- Comparison with carboxymethylated CNF – reference



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Experimental

Bark biorefinery on lab scale

Rietzler, B., & Ek, M. (2021). Adding value to spruce bark by the isolation of nanocellulose in a biorefinery concept. *ACS Sustainable Chemistry & Engineering*, *9*(3), 1398-1405.

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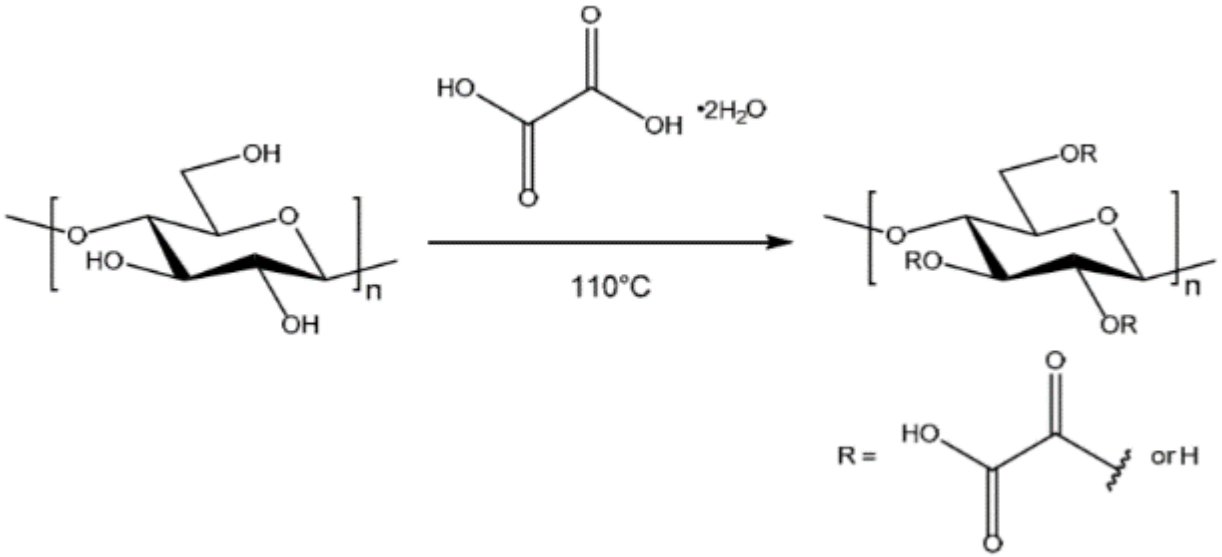
Producing cellulose oxalate and nanocellulose



Micro-fluidizer

Nanocellulose

Henschen, J. (2019). *Bio-based preparation of nanocellulose and functionalization using polyelectrolytes* (Doctoral dissertation, KTH Royal Institute of Technology).

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Characterizations

Cellulose oxalate

FTIR

Conductometric titration

Nanocellulose

Cone-and-plate viscometer

AFM

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Pickering emulsions production

- Nanocellulose concentrations: 0.1, 0.5, 1 wt%
- Almond oil (crude oil) and hexadecane (pure oil)
- Ratio 14:6 v/v (water:oil)

$CH_3(CH_2)_{14}CH_3$

Emulsion characterization

- Light microscopy
- Stability
  - Emulsion Index (EI)
    - Ability to resist structural changes over a defined time period
    - Gravitation: 0, 1, 7, and 27 days
    - Centrifugation

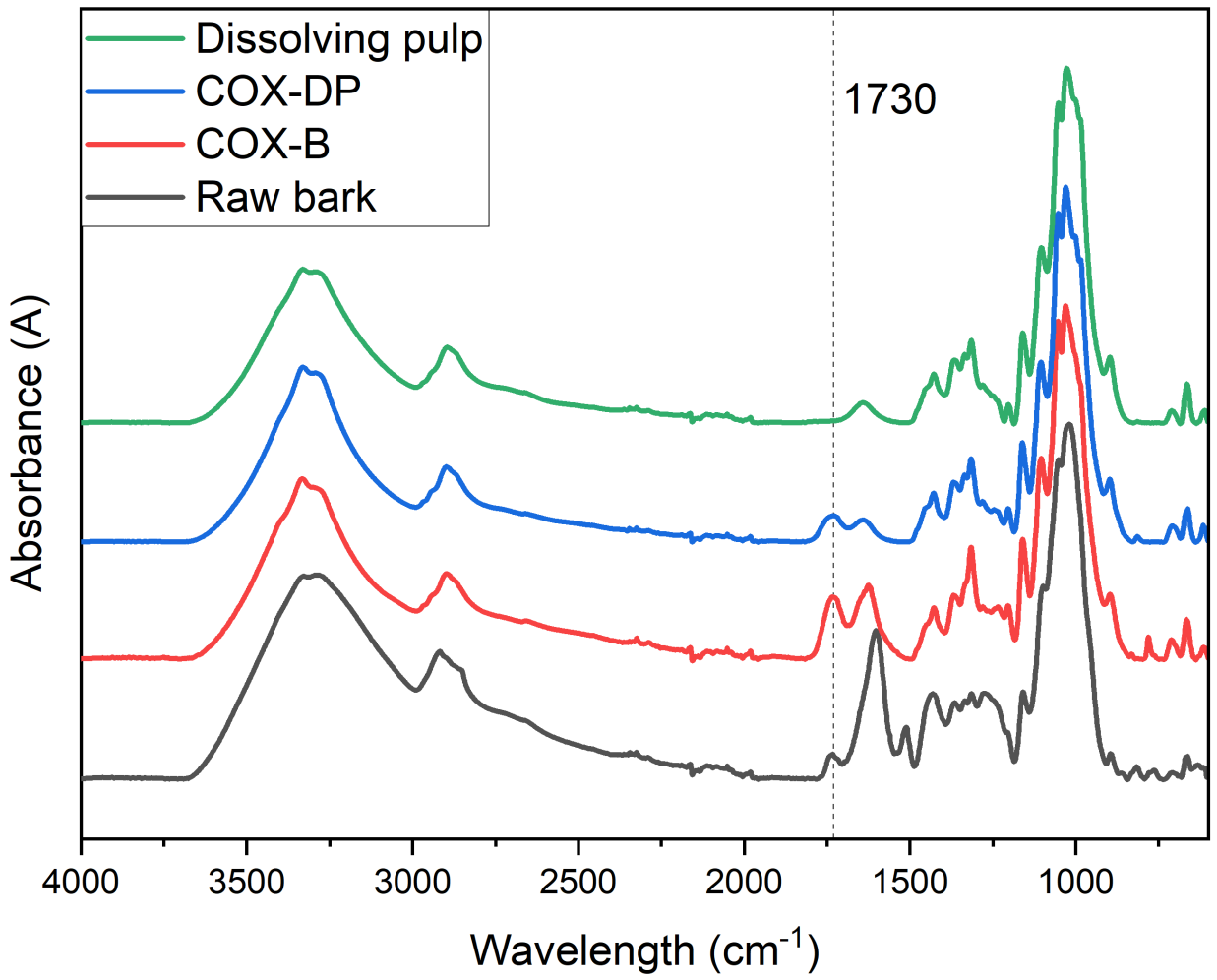
$$EI\ (\%) = \frac{Hc}{Ht} * 100$$

Hc = height of cream layer
Ht = total height of emulsion

Results and Discussion

FTIR

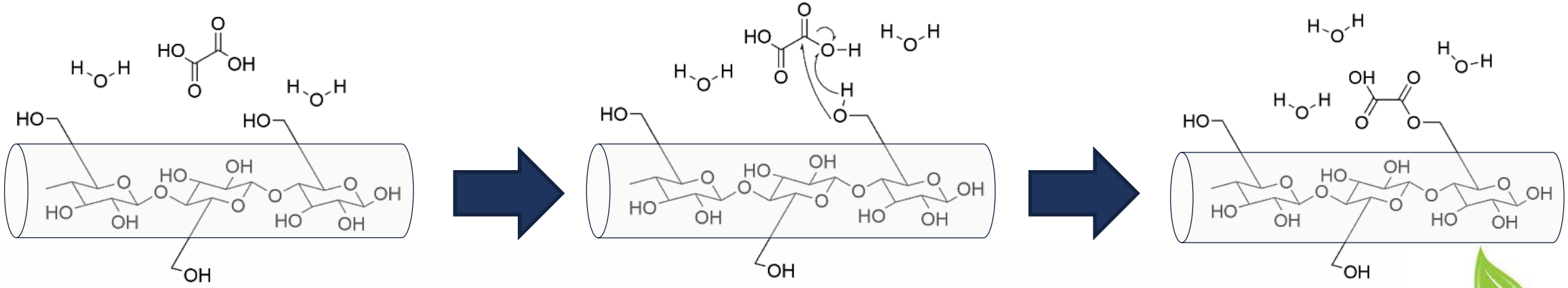
- C=O stretching of esters and carboxyl groups
- Raw bark → extractive compounds present in bark



DP – dissolving pulp
B – bark

Free carboxyl content (fiber charge)

Sample	Charge [mmol g^{-1}]
COX bark	1.6 ± 0.004
COX dissolving pulp	0.7 ± 0.005



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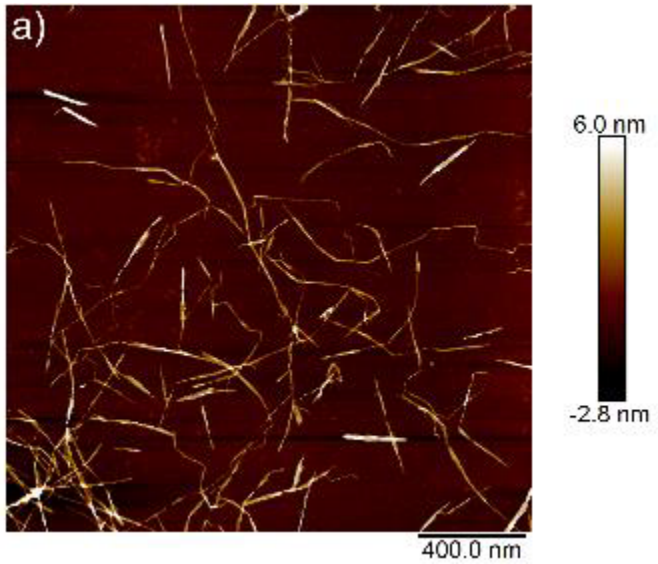
Viscosity

Sample	Viscosity [mPa.s]
Almond oil (crude oil)	80.1 ± 1.3
Hexadecane (pure oil)	10.9 ± 2.3
COX bark	10.2 ± 0.9
COX dissolving pulp	16.1 ± 1.2
CNF	54.3 ± 2.4

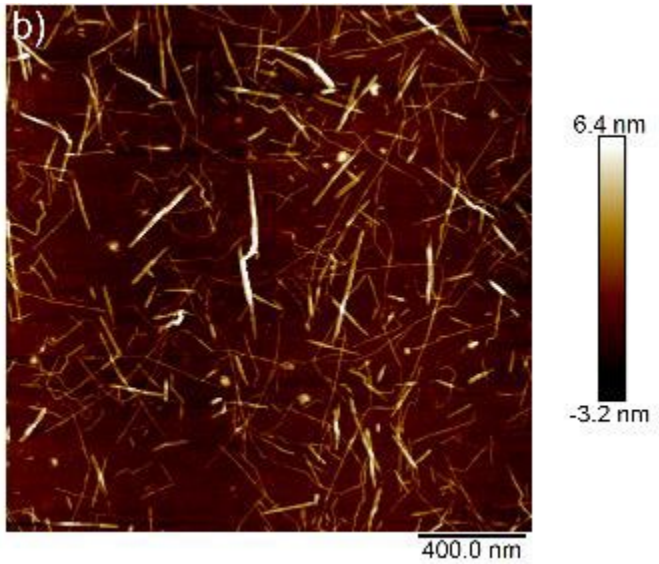
Nanocellulose concentration: 1 wt%

AFM



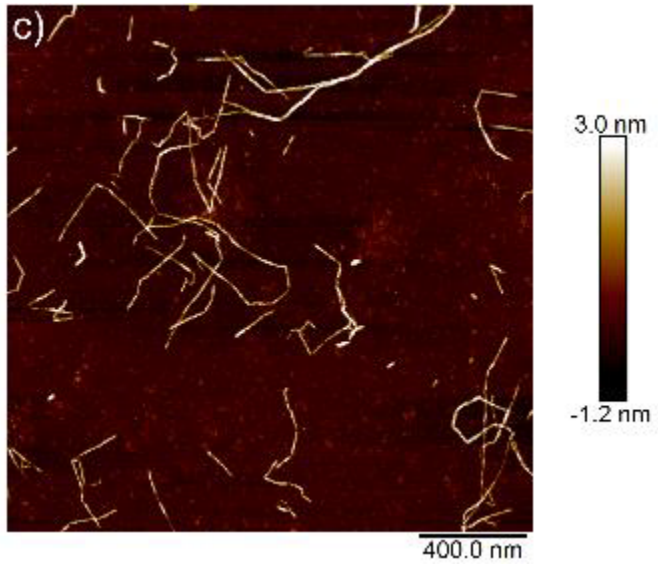
COX dissolving pulp

- Aspect ratio ~68
- Major part CNF



COX bark

- Aspect ratio ~66
- Major part CNC



CNF

- Aspect ratio ~230

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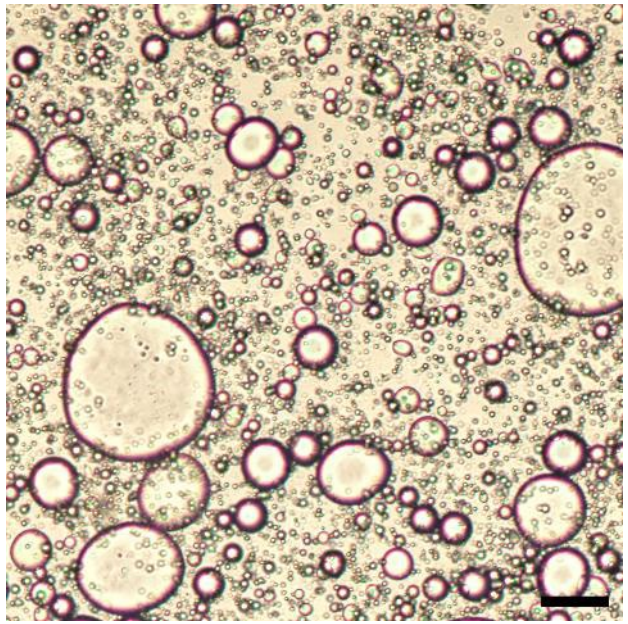
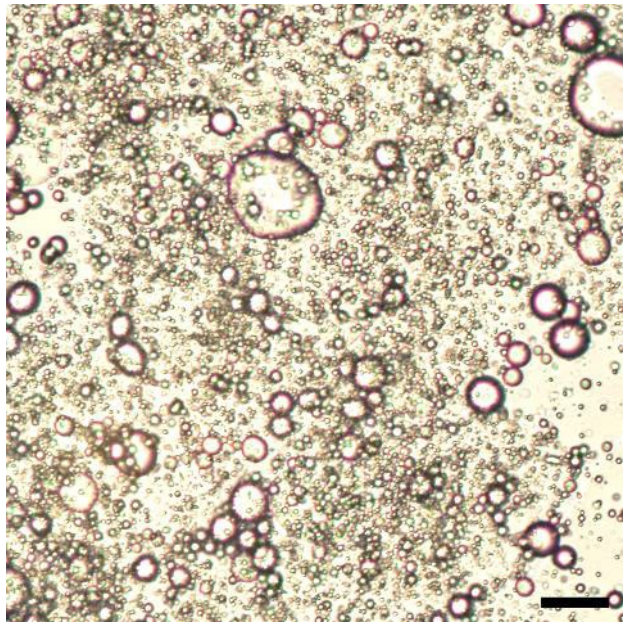
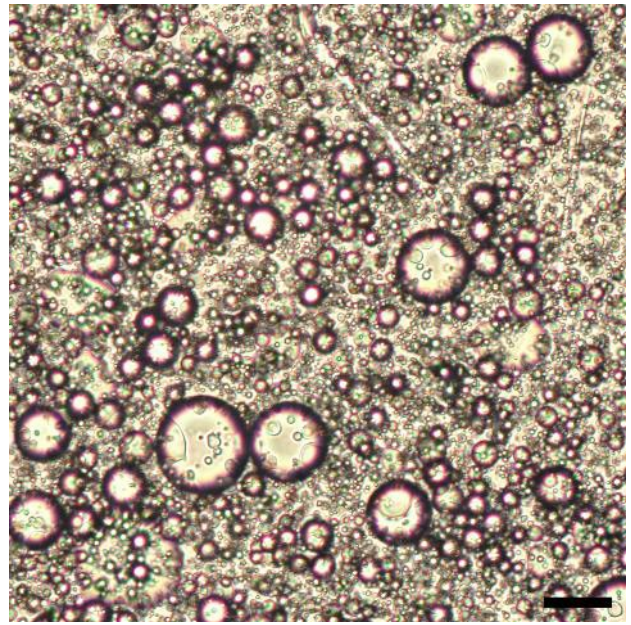
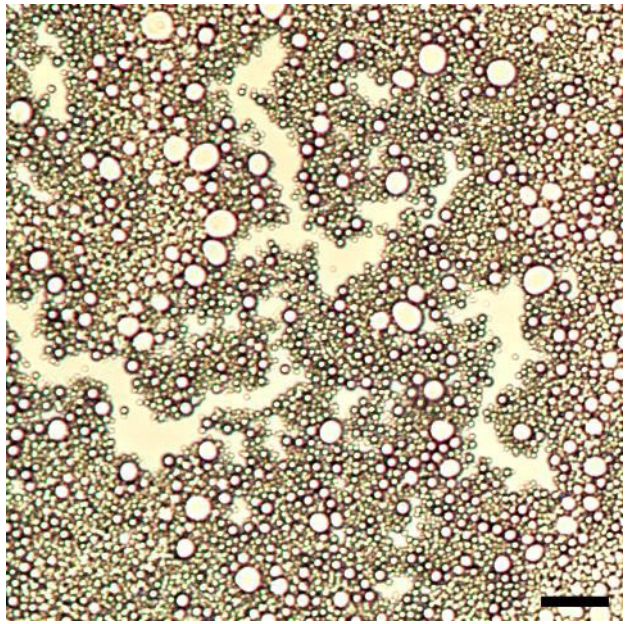
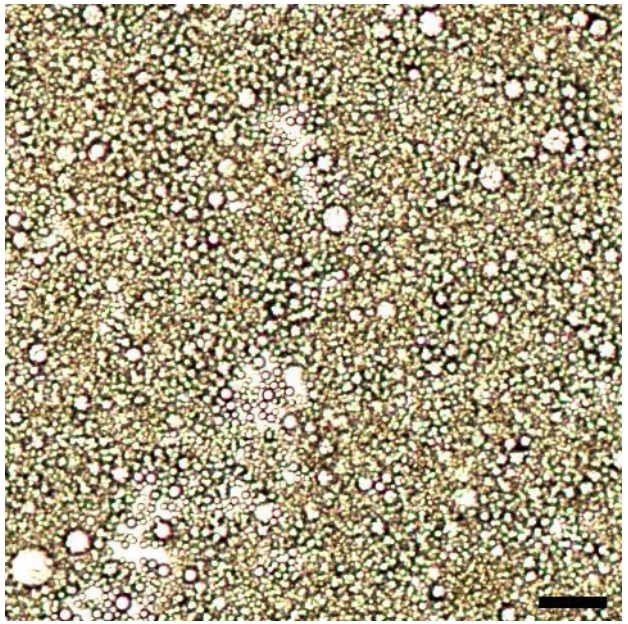
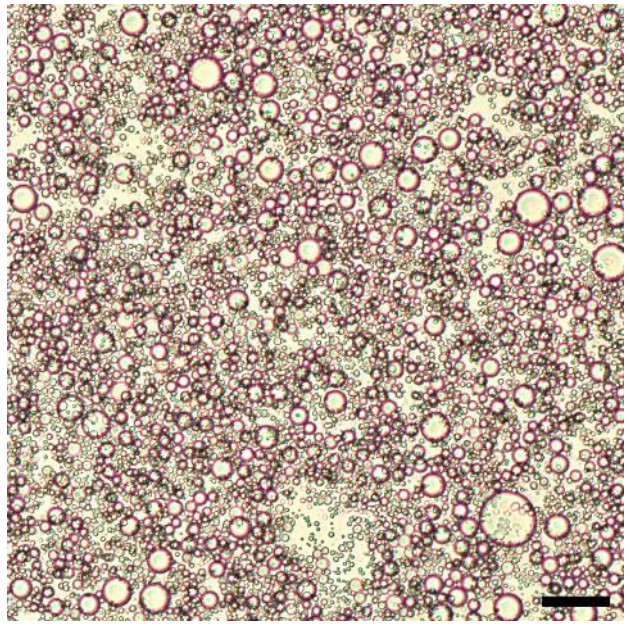
Light microscopy

	COX bark	COX dissolving pulp	CNF
Almond oil (crude oil)			
	Droplet size: 0.3-10 µm	Droplet size: 0.3-7 µm	Droplet size: 0.4-7 µm

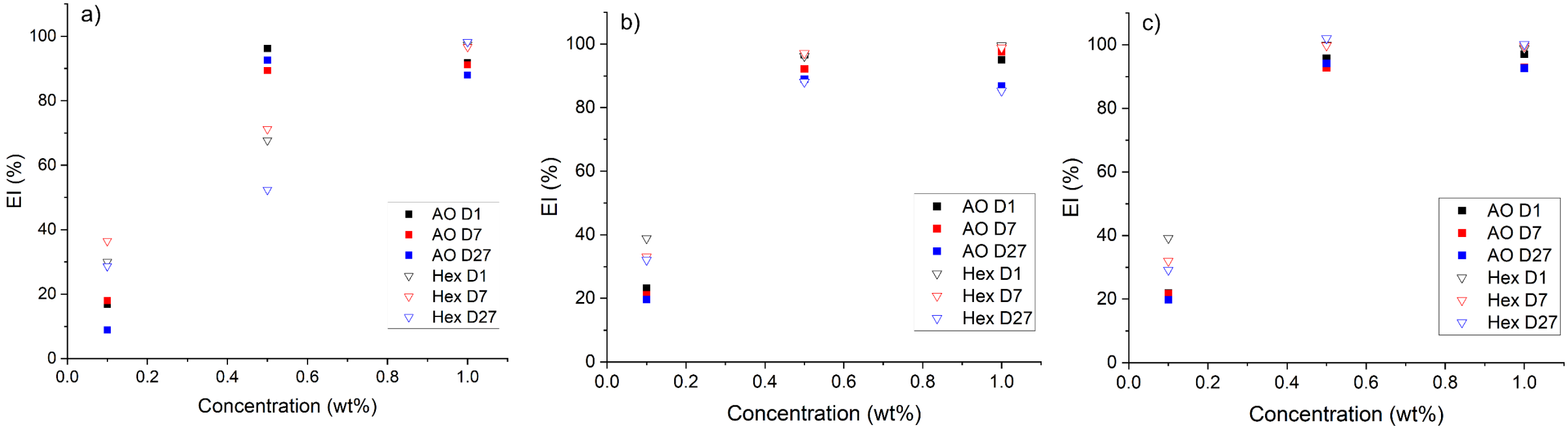
Scale bar: 5 µm
Images captured with 10x magnification and particle concentration of 1 wt%

Light microscopy

	COX bark	COX dissolving pulp	CNF
Hexadecane (pure oil)			
	Droplet size: 0.3-2 µm	Droplet size: 0.3-2 µm	Droplet size: 0.2-6 µm

Scale bar: 5 µm
Images captured with 10x magnification and particle concentration of 1 wt%

Emulsion stability – gravity



- Higher particle concentration → more stable emulsion
- Aspect ratio important
  - Fiber entanglements

a) COX bark
b) COX dissolving pulp
c) CNF
D# – day number
AO – Almond oil
Hex – Hexadecane

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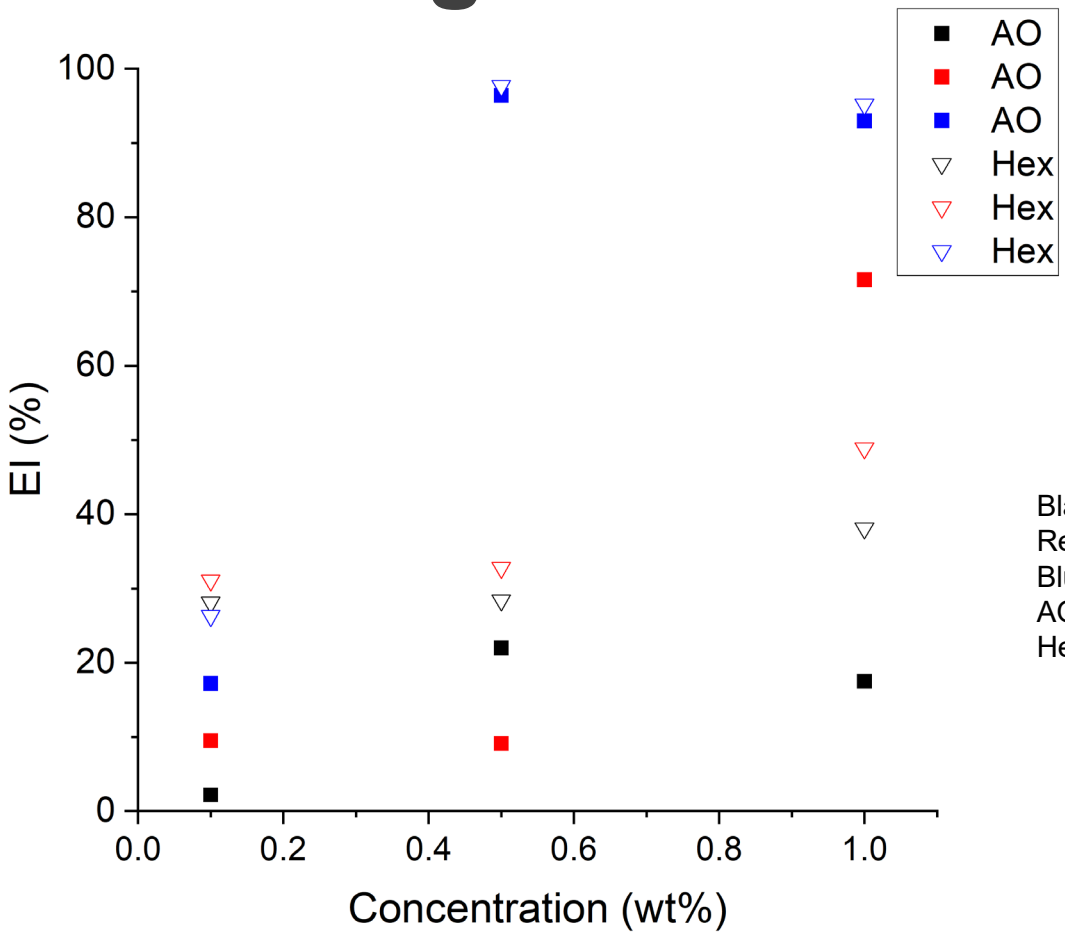
Emulsion stability – centrifugation

- Particle concentration, aspect ratio, and oil purity important
- For both AO and Hex, CNF most stable
  - Emulsion gel formation



Black – COX bark
Red – COX dissolving pulp
Blue – CNF
AO – Almond oil
Hex – Hexadecane

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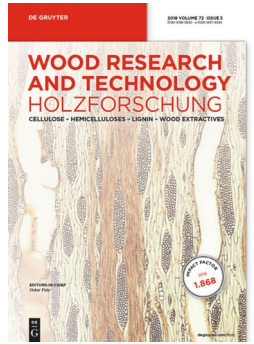
Conclusion

Conclusion

- Cellulose oxalate → greener processing route
- Spruce bark nanocellulose → sustainable alternative
- Stability affected by:
  - Nanocellulose aspect ratio
  - Particle concentration
  - Oil phase purity
- Suitable as an emulsifying agent → replacement for petroleum-based emulsifying agents



Kwan, I.; Rietzler, B.; and Ek, M. "Emulsions of cellulose oxalate from Norway spruce (*Picea abies*) bark and dissolving pulp" *Holzforschung*, 2023. https://doi.org/10.1515/hf-2022-0191

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Thank you!

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