Transitioning from Micro to Nano: Unlocking the Potential of Cellulose Nanomaterials

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Wednesday, June 4, 2025 (online)

Laboratory of Sustainable Materials and Product Design

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Sustainable practices in papermaking and fiber-based products

Biocomposite materials

Bio-based nanomaterials

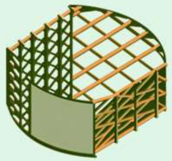
Product ecodesign & modelling

Research lines

14 professors/tenured researchers
2 emeritus
14 PhD candidates and postdocs
2 laboratory technicians
25 undergraduate students

Staff

Papermaking



Biocomposites

Packaging

Biorefinery

Advanced materials

Industrial sustainability

Main sectors

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Content

- Cellulose nanomaterials (CNMs): categorization, applications, and complexity.
- Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment.
- Understanding the transition from micro to nano: energy and property implications.
- Concluding remarks.

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Cellulose nanomaterials (CNMs): categorization, applications, and complexity

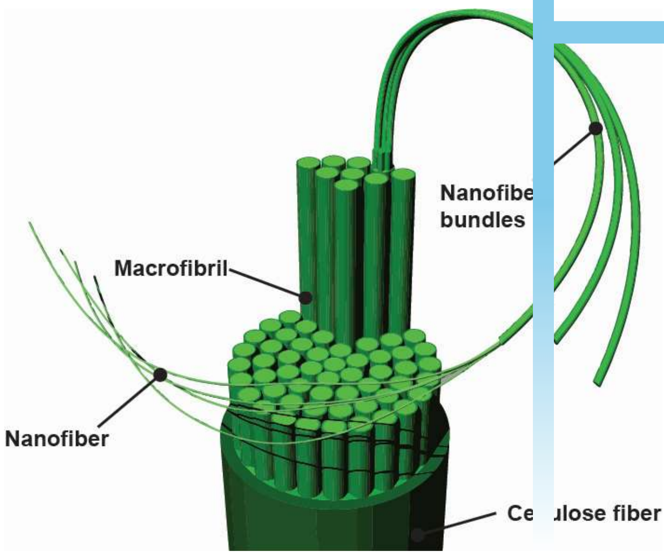
Cellulose nanomaterials (CNMs)

Top-down ← → *Bottom-up*

- Cellulose nanofibers (CNF)
- Cellulose nanocrystals (CNC)
- Bacterial cellulose (BC)

Cellulose nanofibers (CNF)

- Fibers with diameters ranging from 5 to 100 nm.
- High aspect ratio (length of few microns) and huge surface area.
- Contain both amorphous and crystalline regions.



Schematic representation of CNF, from micro to nano.
Delgado-Aguilar et al. (2015). Environmental Science and Technology, 49, 12206-12213.

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Cellulose nanomaterials (CNMs): categorization, applications, and complexity

Cellulose nanomaterials (CNMs)

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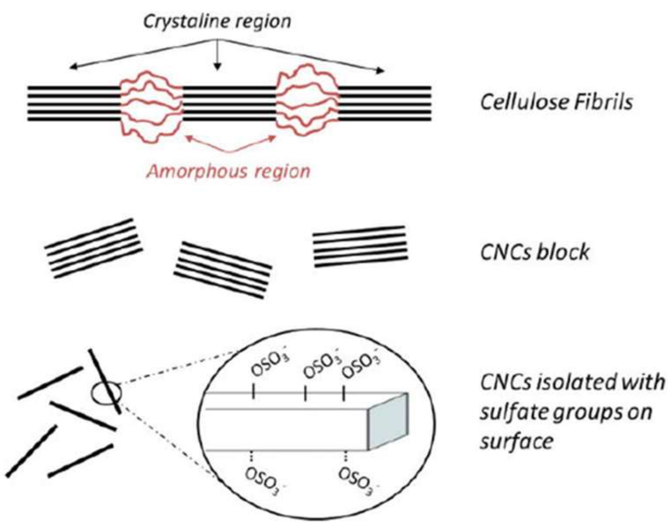

- Cellulose crystals at nano-domain.
- Shorter than CNF and diameters of the same magnitude.
- They contain mainly crystalline regions.

Schematic representation of CNC, from micro to nano.
Le Gars et al. (2019). Cellulose Nanocrystals: From Classical Hydrolysis to the Use of Deep Eutectic Solvents, in Smart Nanosystems for Biomedicine, Optoelectronics and Catalysis

Cellulose nanomaterials (CNMs): categorization, applications, and complexity

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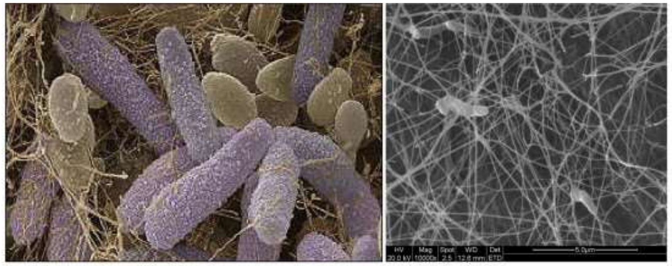
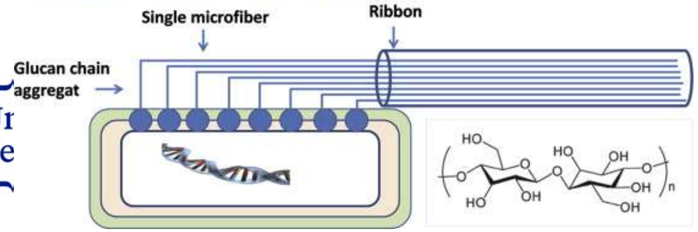
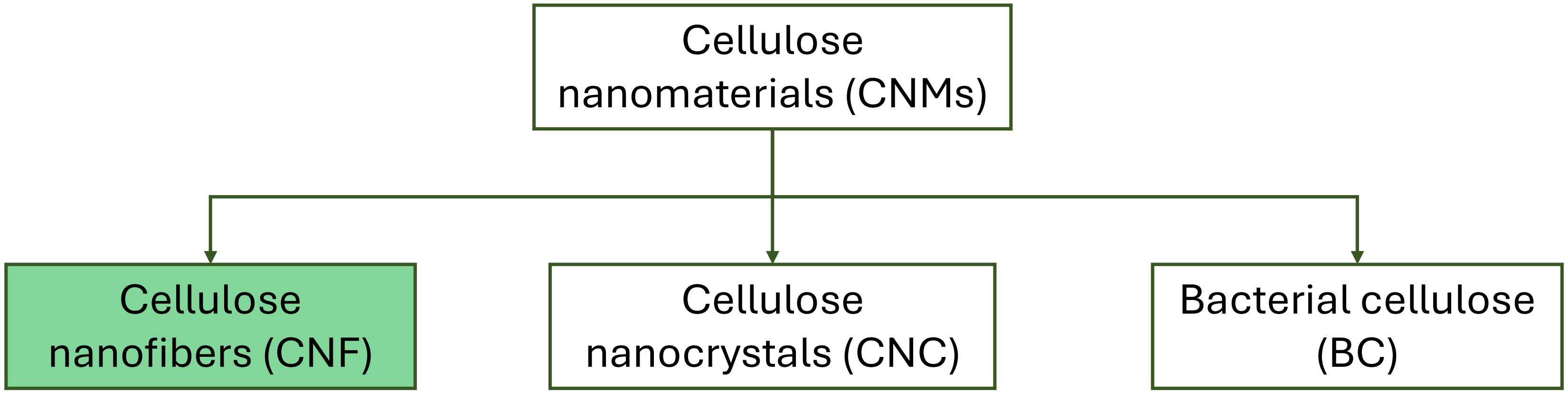


- Organic compound grown from bacteria.
- Cellulose is polymerized from glucose (cellobiose).
- Polymerization can be easily stopped at the desired DP.



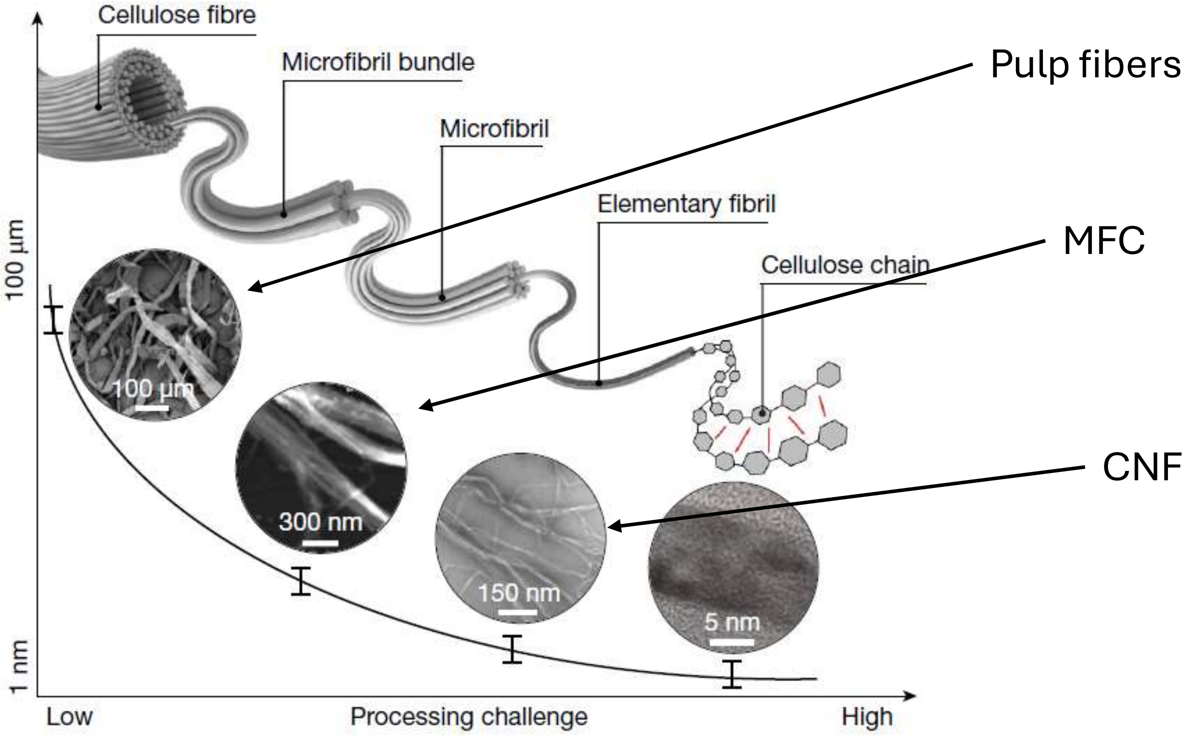
Schematic representation of BC production.
Shi et al. (2014). Food Hydrocolloids, 35, 539-545

Cellulose nanomaterials (CNMs): categorization, applications, and complexity



Cellulose nanomaterials (CNMs): categorization, applications, and complexity

Cellulose nanofibers (CNF)



Main attributes & properties:

- High aspect ratio and SSA.
- Tunable rheology.
- Functionalization capacity.
- Mechanical properties.
- Biodegradability & biocompatibility.
- Tunable surface.

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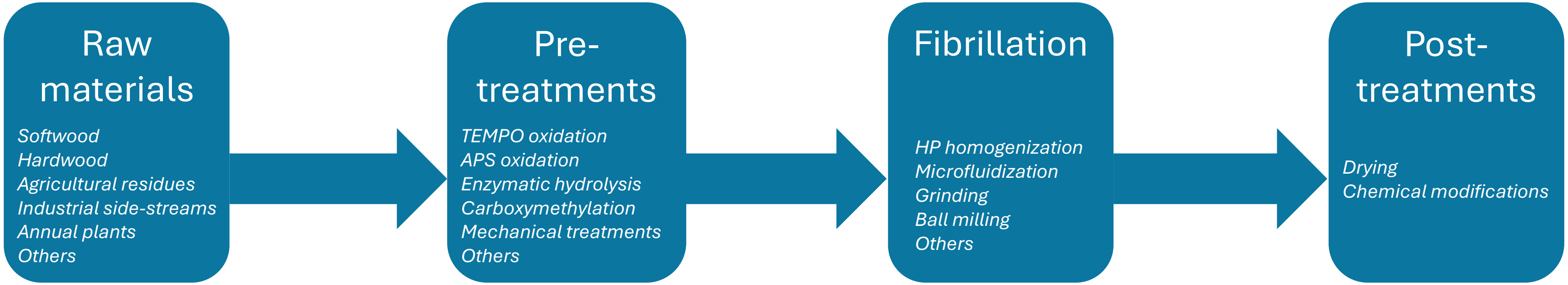
Li et al. (2021). Nature 590, 47-56.

Cellulose nanomaterials (CNMs): categorization, applications, and complexity



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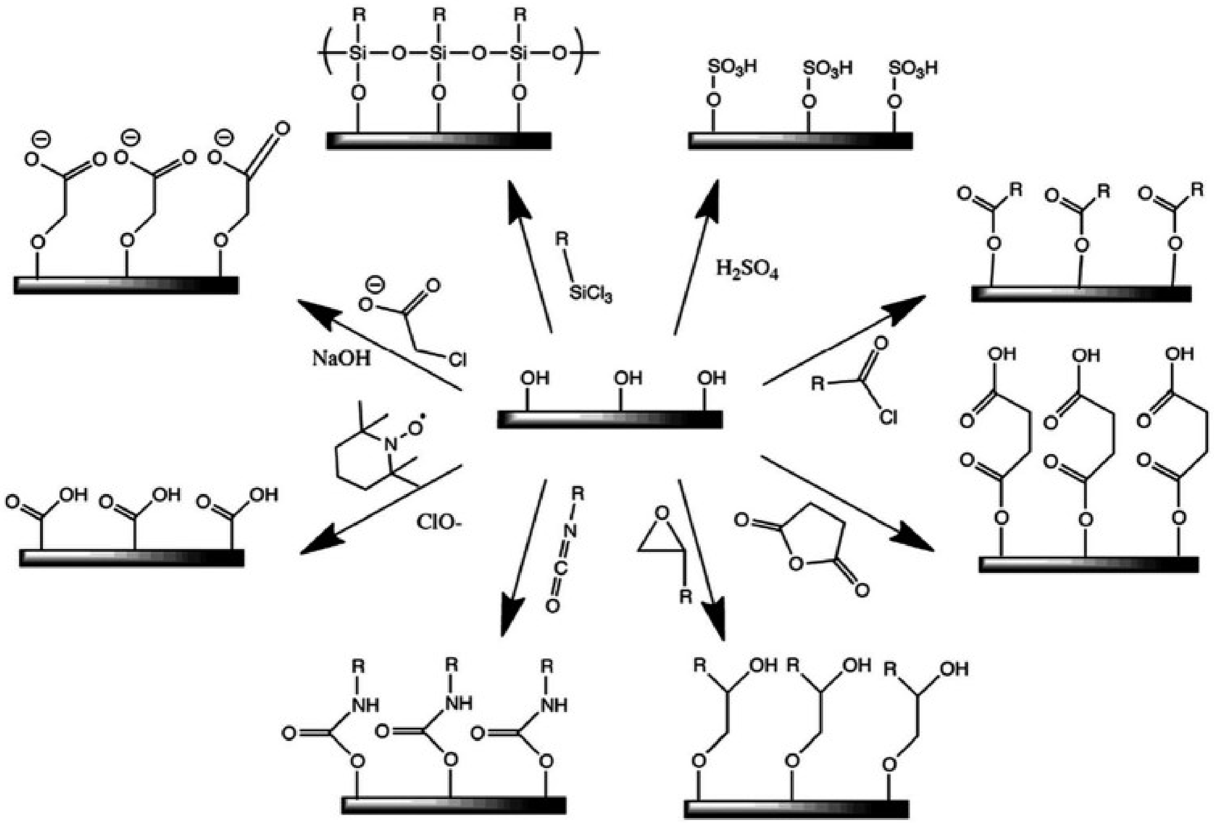
Cellulose nanomaterials (CNMs): categorization, applications, and complexity



Thakur et al. (2021), Mater. Adv. 2, 1872-1895

Cellulose nanomaterials (CNMs): categorization, applications, and complexity

Pre-treatments

≈ 300 – 400 µeq/g

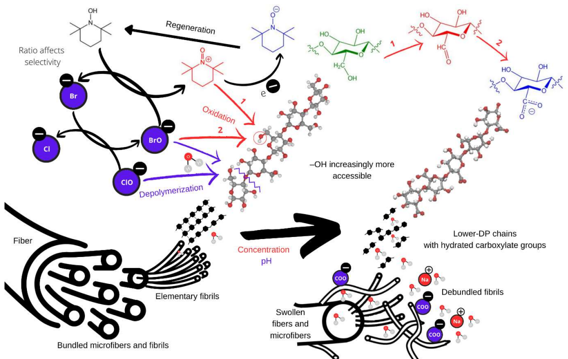
≈ 70 µeq/g

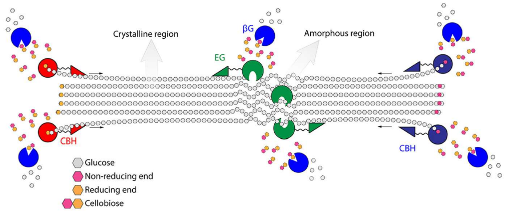
≈ 300 – 400 µeq/g

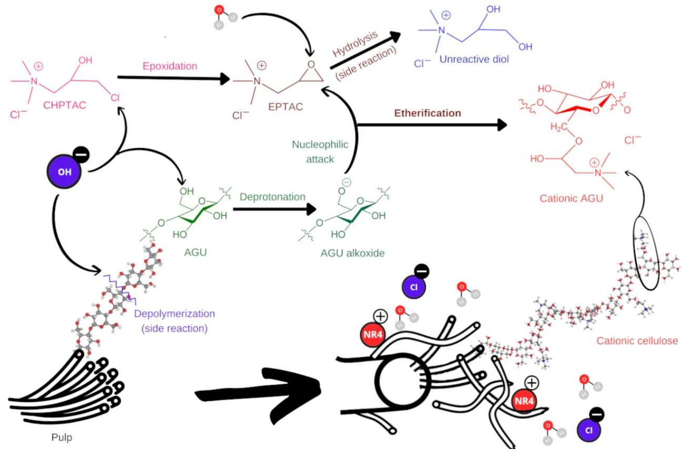
Moderately anionic

Close to the isoelectric point

Moderately cationic







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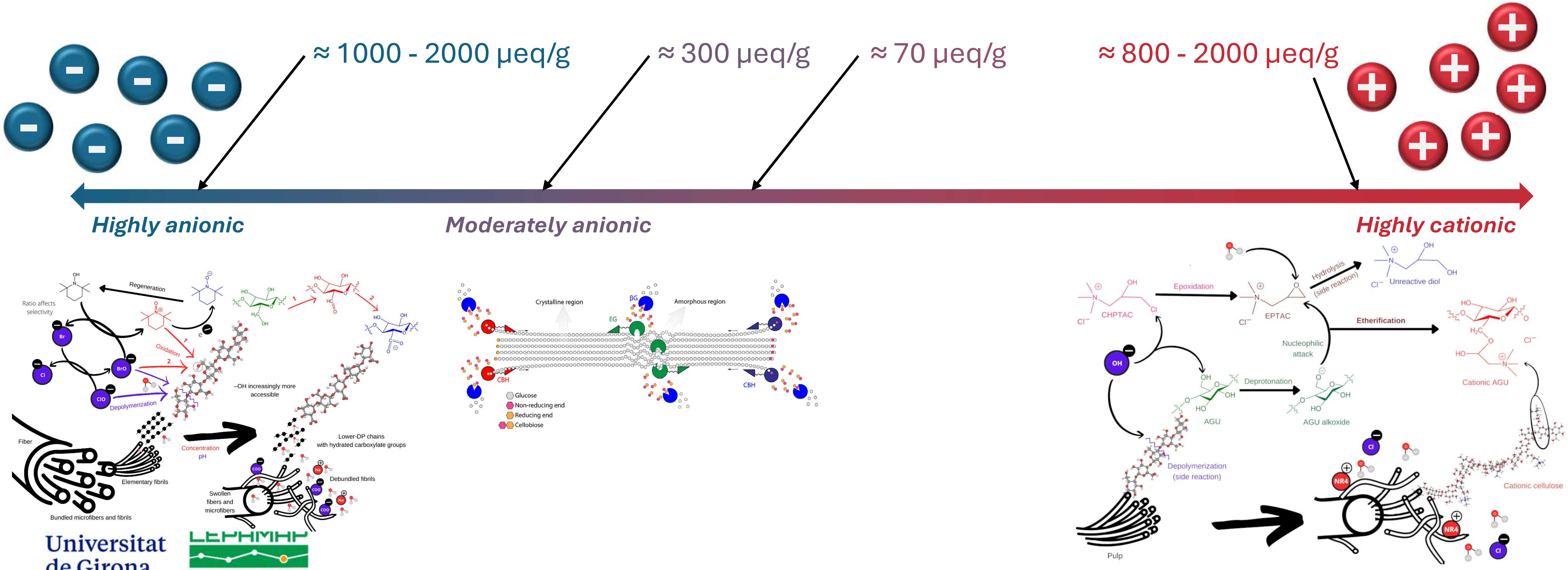
Cellulose nanomaterials (CNMs): categorization, applications, and complexity

Pre-treatments + Fibrillation



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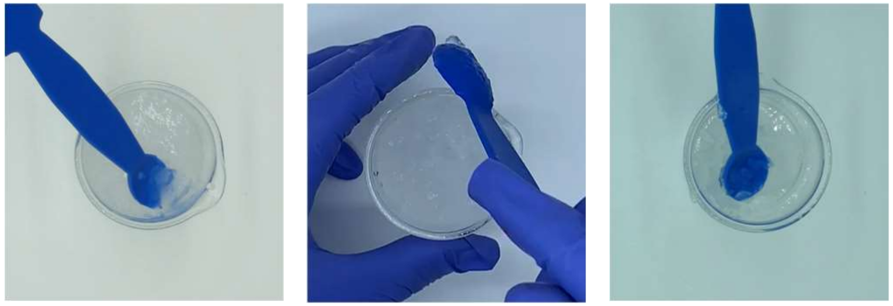
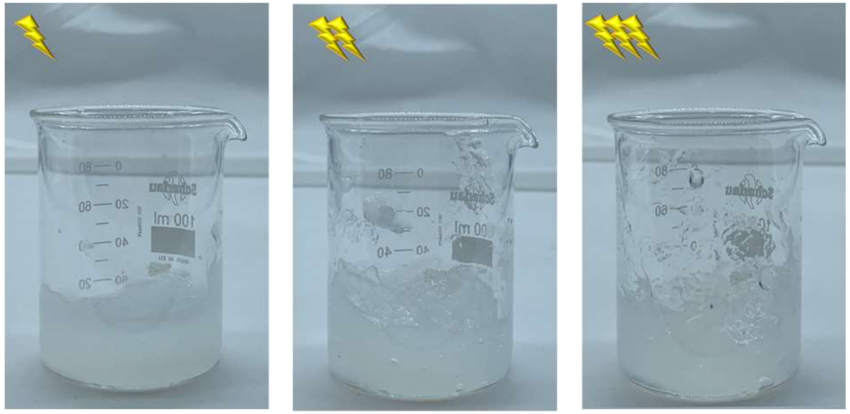
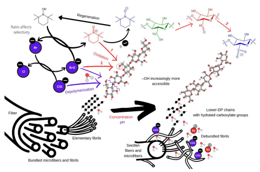
Cellulose nanomaterials (CNMs): categorization, applications, and complexity



Pretreatment intensity: increasing
Fibrillation intensity: constant



Pretreatment intensity: constant
Fibrillation intensity: increasing



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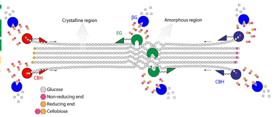
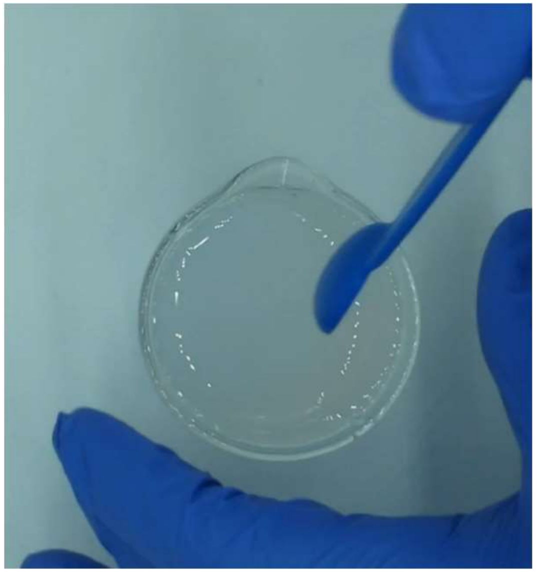


Cellulose nanomaterials (CNMs): categorization, applications, and complexity



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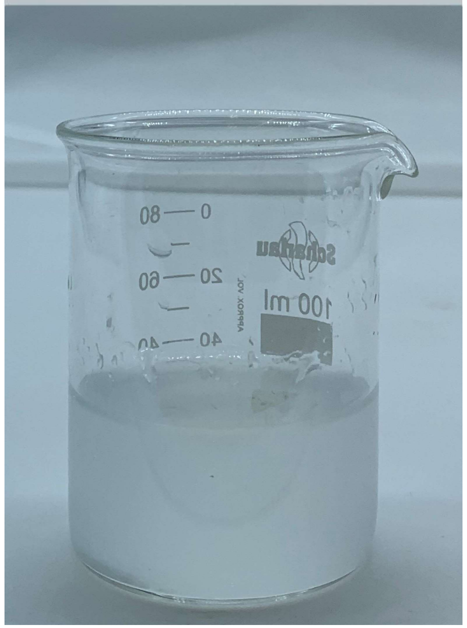
Cellulose nanomaterials (CNMs): categorization, applications, and complexity

Starting material: eucalyptus pulp
Consistency: 0.5 wt%



Starting material: eucalyptus pulp
Consistency: 1.5 wt%

Starting material: eucalyptus pulp
Consistency: 3.0 wt%

Credits to Gabriela Bastida and Giulia Herbst


Strength additives
• (Nano)composites
• Construction materials
• Paper and board
• Textiles
Emulsions & Dispersions
• Food industry
• Cosmetics and pharma
• Paints and coatings
• Drilling fluids
Coatings & Surface treatments
• Barrier layers
• Functional surfaces
• Optical coatings
• Paints and varnishes
Films & Membranes
• Flexible electronics
• Batteries
• Packaging films
• Separation membranes
Aerogels
• Thermal insulation
• Sound absorption
• Filtration
• Drug delivery
• Oil absorption
Hydrogels
• Biomedical scaffolds
• Wound dressings
• Drug delivery
• Sensors
• Separation media

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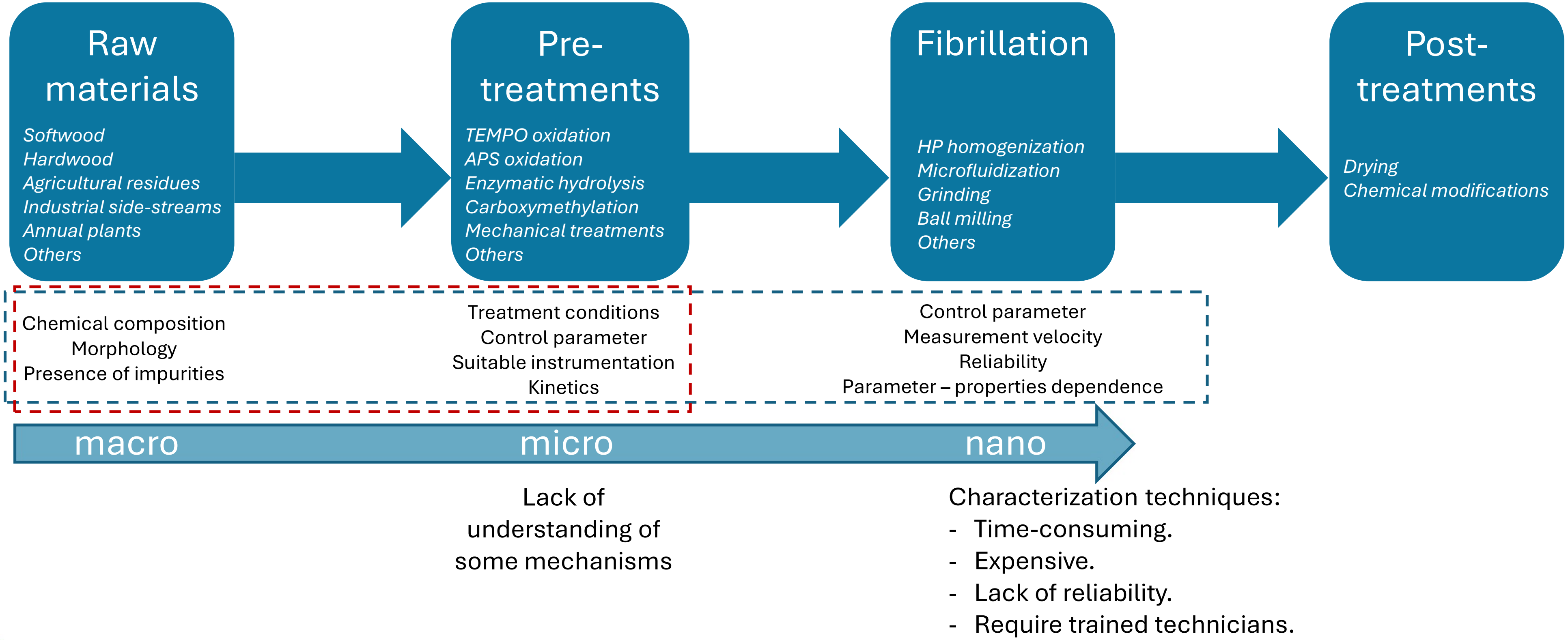
Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment



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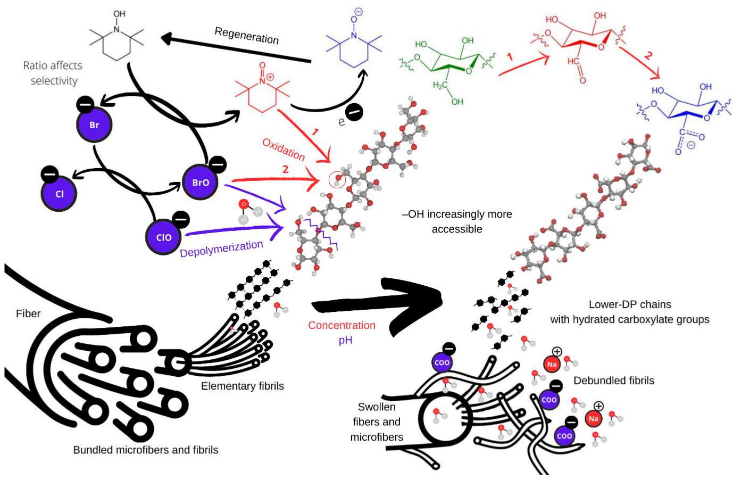
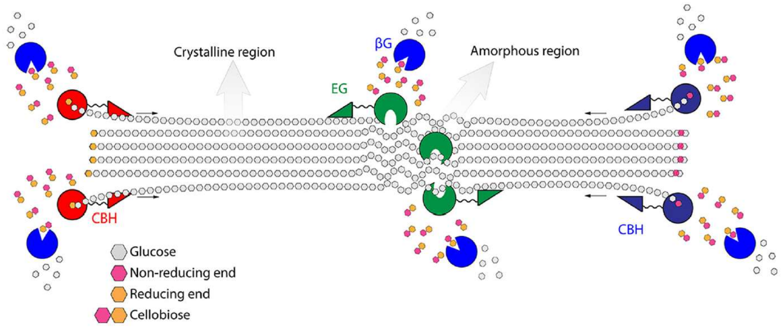
Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment

TEMPO-mediated oxidation



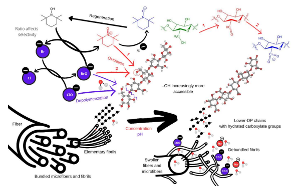
- CC as parameter for extent of oxidation.
- Offline measurement and time consuming.
- Delay between process and characterization.

Enzymatic treatment



- Low effect over fiber morphology.
- Reducing sugar concentration is low.
- Delay between process and characterization.

Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment



1. HBrO formation from NaClO:

$$OCl^- + H_2O \leftrightarrow HClO + OH^- \quad (1)$$

$$HClO + Br^- \rightarrow HBrO + Cl^- \quad (2)$$

$$HBrO + OH^- \leftrightarrow OBr^- + H_2O \quad (3)$$

$$OCl^- + Br^- \leftrightarrow OBr^- + Cl^- \quad (4)$$

2. TEMPO$^+$ formation:

$$(H)BrO + 2TEMPO^{\cdot} \rightarrow 2TEMPO^+ + OH^- + Br^- \quad (5)$$

$$(H)BrO + TEMPOH \rightarrow TEMPO^+ + Br^- + H_2O \quad (6)$$

$$TEMPO^+ + TEMPOH \rightarrow 2TEMPO^{\cdot} \quad (7)$$

3. Oxidation of the C6 from the primary hydroxyl into carboxyl group::

$$\boldsymbol{R - CH_2OH + TEMPO^+ + OH^- \xrightarrow{k_1} R - CHO + TEMPOH + H_2O} \quad (8)$$

$$R - CHO + H_2O \leftrightarrow [R - CHO - H_2O] \quad (9)$$

$$[\boldsymbol{R - CHO - H_2O}] + (\boldsymbol{H})\boldsymbol{BrO + OH^- \xrightarrow{k_2} R - COOH + Br^- + 2H_2O} \quad (10)$$

Pseudo-first order reaction:

$$\boldsymbol{k_2} \gg \boldsymbol{k_1}$$

$$\ln([R - CH_2OH]_0 - [R - COOH]_t) = -\boldsymbol{k_1} t + \ln([R - CH_2OH]_0)$$

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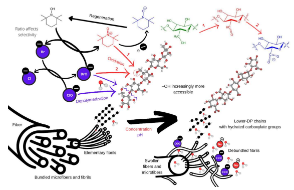
Reaction kinetics

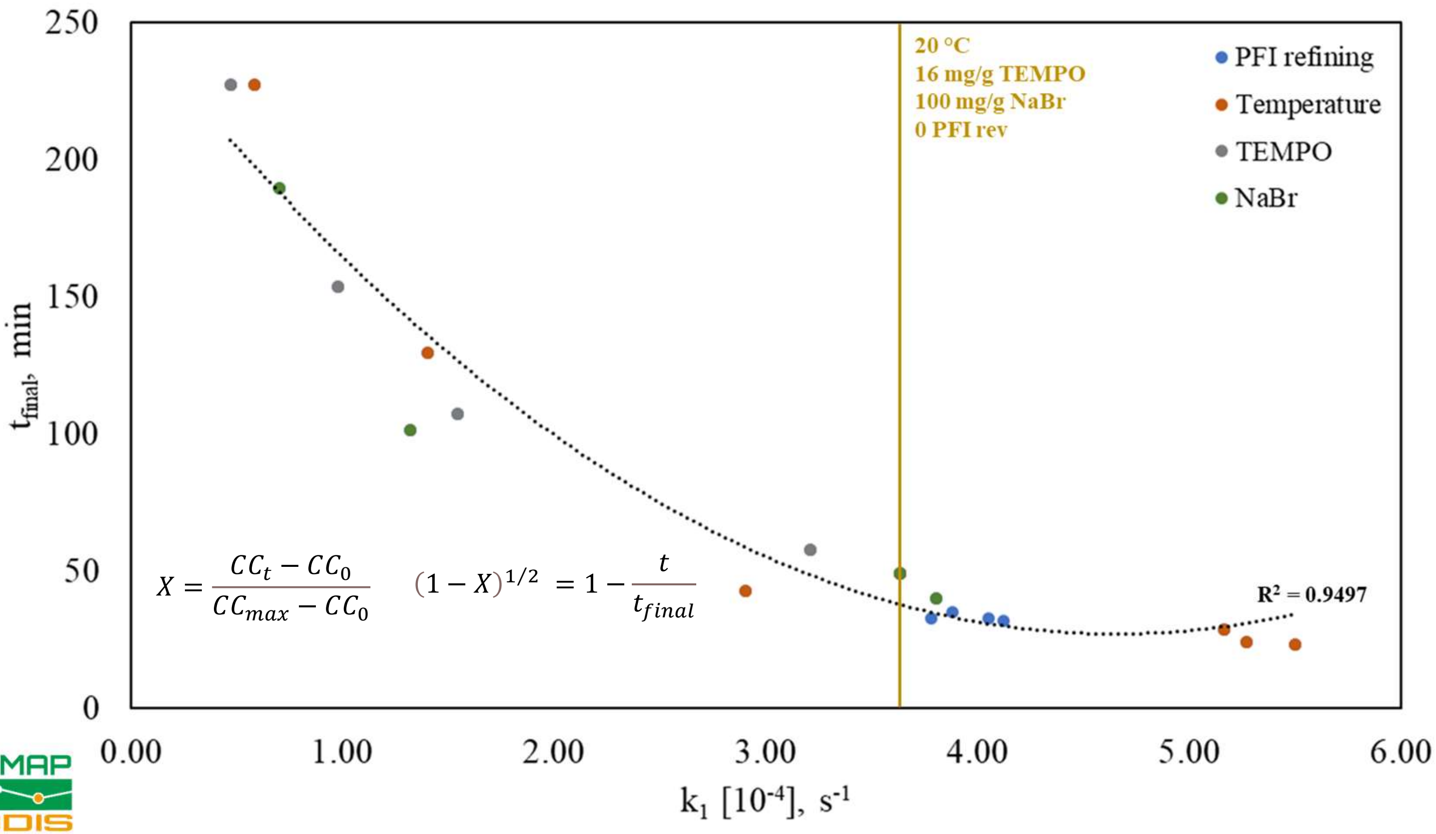
Chemometrics

Mazega et al. (2023). Cellulose 30(3), 1421-1436

Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment



$$\ln([R-CH_2OH]_0-[R-COOH]_t)=-\boldsymbol{k_1}t+\ln([R-CH_2OH]_0)$$



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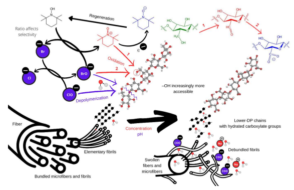
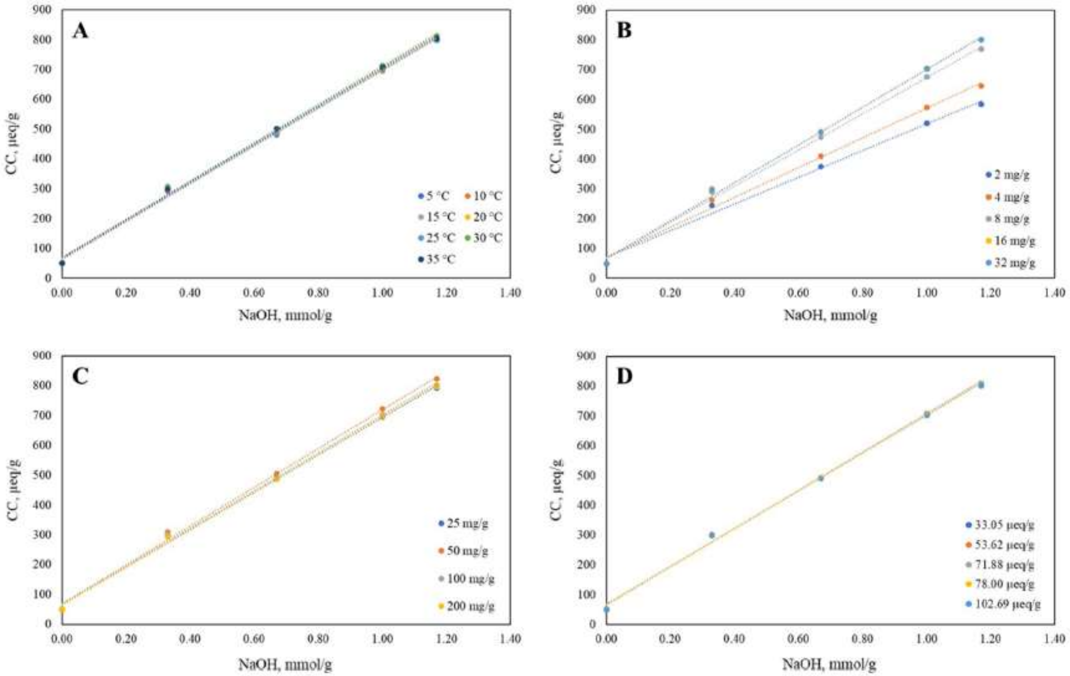
Mazega et al. (2023). Cellulose 30(3), 1421-1436

Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment





- CC can be estimated based on experience, correlating CC with oxidizer dosage.
- CC can be estimated based on its correlation with NaOH consumption.

We would be overlooking at:

1. Structural and chemical composition effects over reaction performance and CNF properties.
2. Possibility to rapidly identify substrates and CC.
3. Real-time measurements for industrial application.

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Mazega et al. (2023). Cellulose 30(3), 1421-1436

Reaction kinetics

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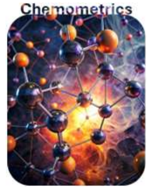

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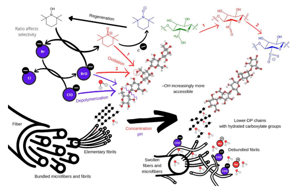
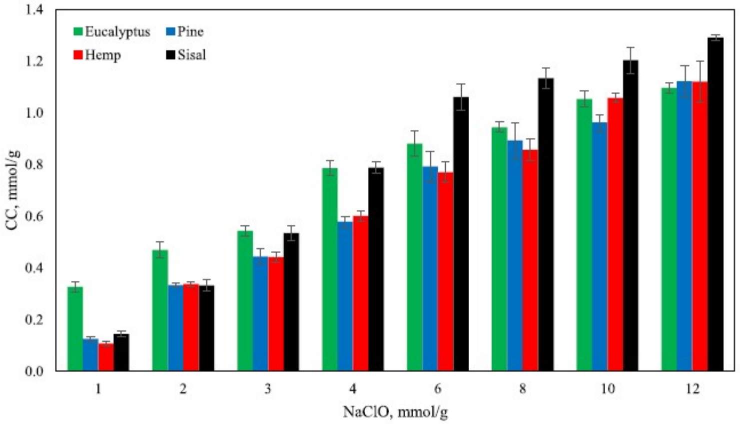
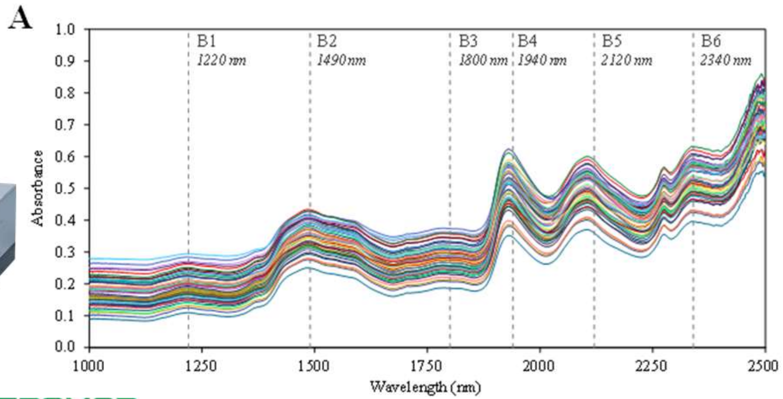


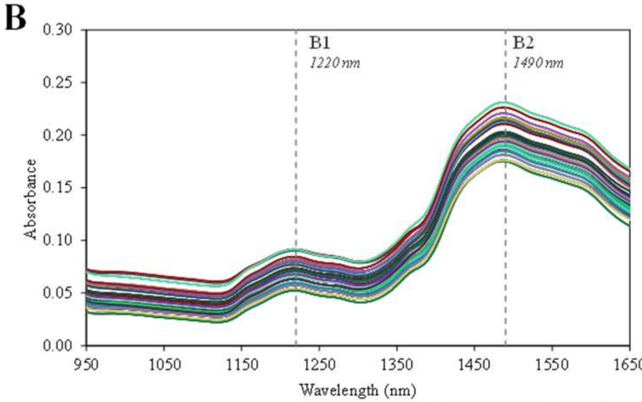


- No aparent influence of the starting material.
- Slight differences can be observed:
  - At low oxidizer dosages, eucaliptus provides higher CC.
  - At higher oxidizer dosages, sisal provides higher CC.
  - Similarities between hemp and pine.

Benchtop NIR equipment



Portable MicroNIR equipment



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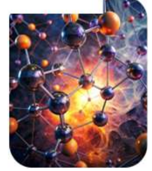
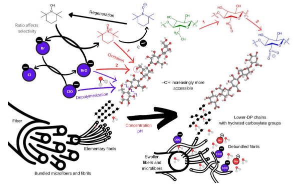
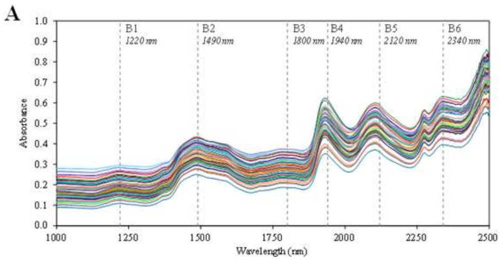
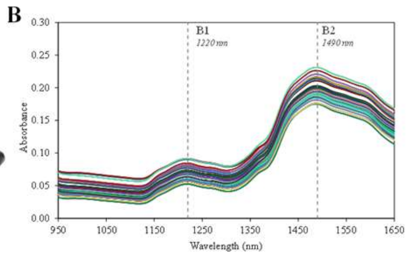
Mazega et al. (2024). Cellulose 31(6), 3465-3482



Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment

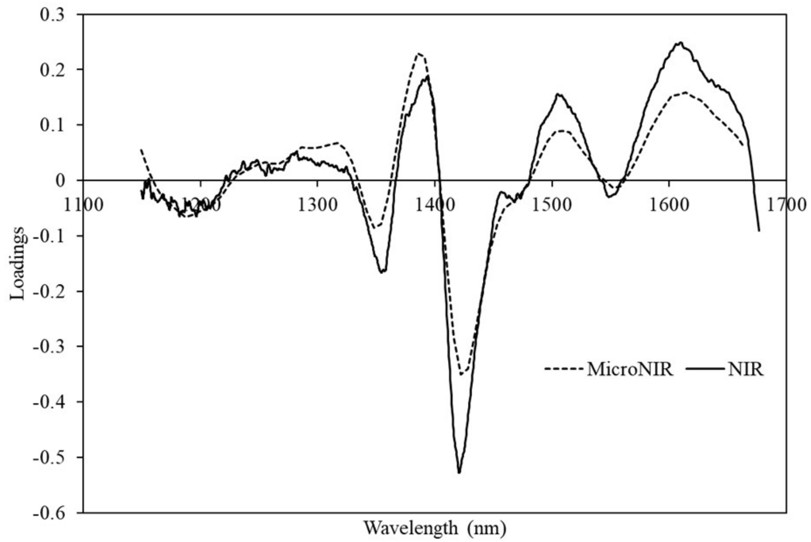






Calibration Model between NIR spectra and CC (Partial Least Squares, PLS)

Equipment	Spectral Range (nm)	LV	R_C^2	R_{CV}^2	RMSEC	RMSECV
NIR	1000-2500	5	0.9901	0.9694	0.0340	0.0614
NIR	1150-1676	3	0.9900	0.9737	0.0344	0.0570
MicroNIR	908-1676	3	0.9895	0.9816	0.0353	0.0486
MicroNIR	1150-1676	3	0.9846	0.9779	0.0428	0.0531



Peaks belonging to band **B1**:
- 1357 nm
- 1391 nm

Peaks belonging to band **B2**:
- 1422 nm
- 1509 nm
- 1614 nm

High similarity between loadings for the first LV.

We can proceed with MicroNIR

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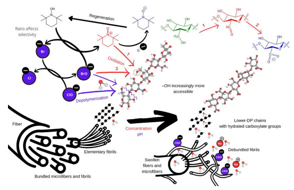
Reaction kinetics

Chemometrics

Mazega et al. (2024). Cellulose 31(6), 3465-3482



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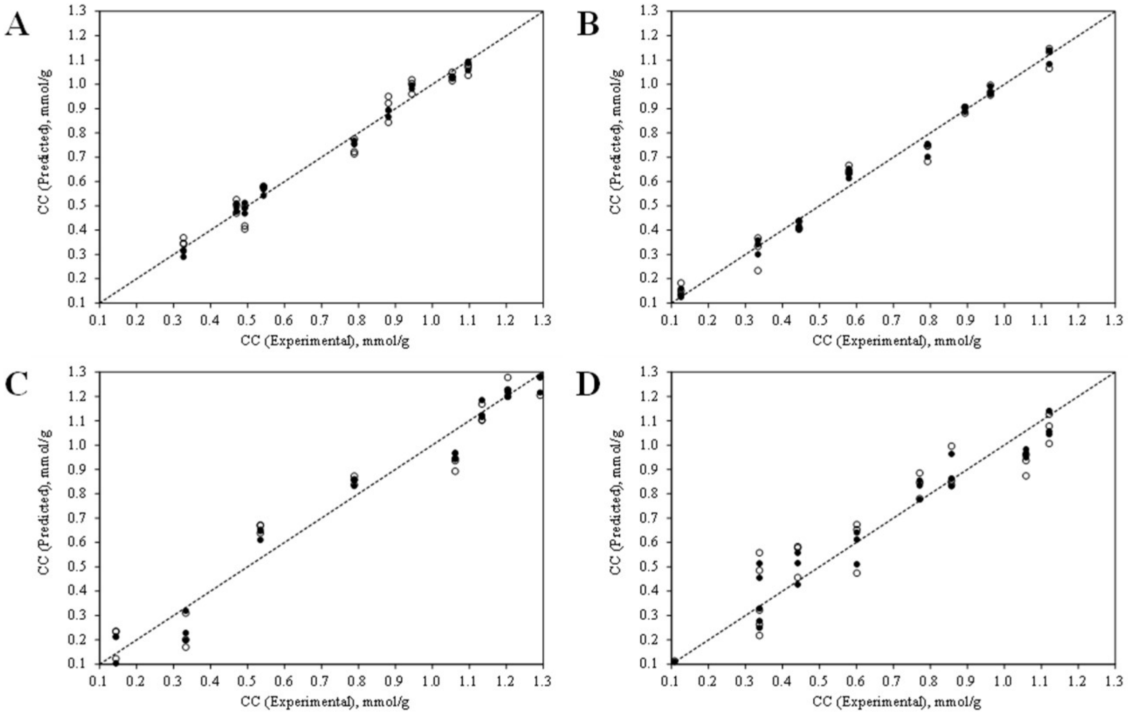
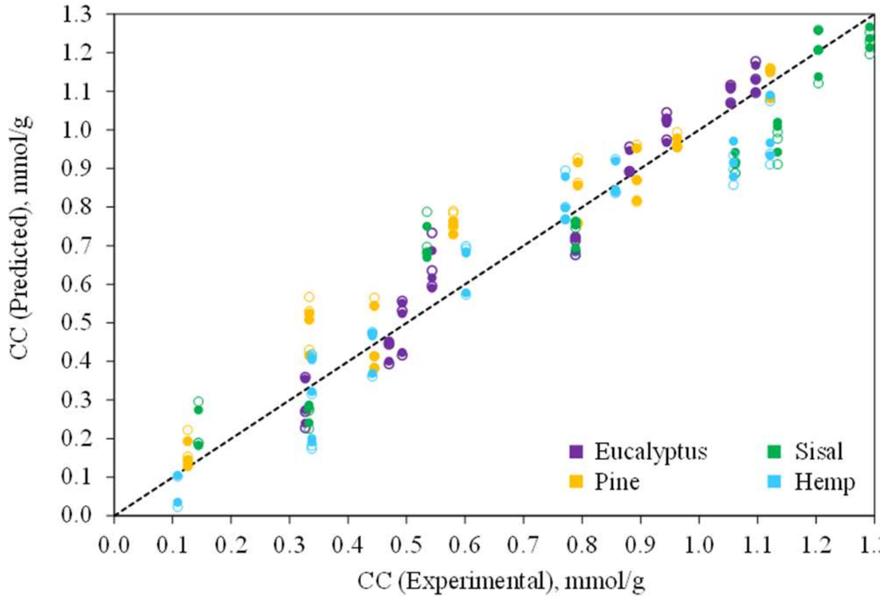
Calibration Model between NIR spectra and CC (Partial Least Squares, PLS)



Fiber	LV	R_C^2	R_{CV}^2	RMSEC	RMSECV	RPD
Eucalyptus	3	0.9895	0.9816	0.0353	0.0486	5.74
Pine	3	0.9883	0.9796	0.0528	0.0728	6.65
Sisal	3	0.9731	0.9494	0.0812	0.1167	4.34
Hemp	3	0.9466	0.9096	0.1199	0.1621	3.10
All	5	0.9292	0.9069	0.1271	0.1471	1.00



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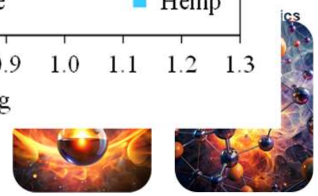
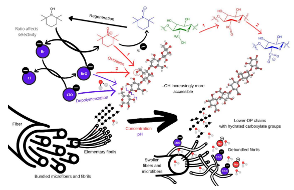
A. Eucalyptus
B. Pine
C. Sisal
D. Hemp

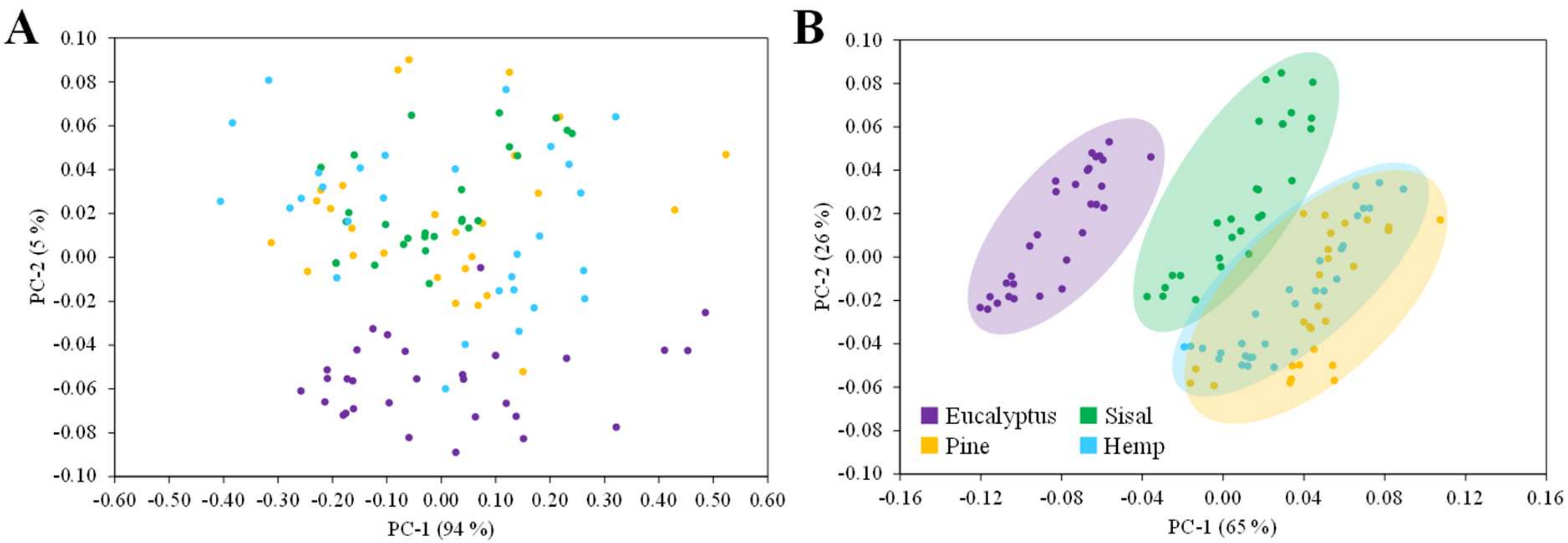
Mazega et al. (2024). Cellulose 31(6), 3465-3482





Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment

Principal Component Analysis (PCA)



A. Raw spectra (2 PCs): PC1 & PC2 cover 99% variance
B. SNV-processed spectra (4 PCs for RMSECV minimization): PC1 & PC2 cover 91% variance

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Reaction kinetics

Chemometrics

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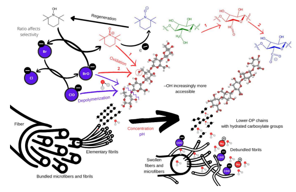
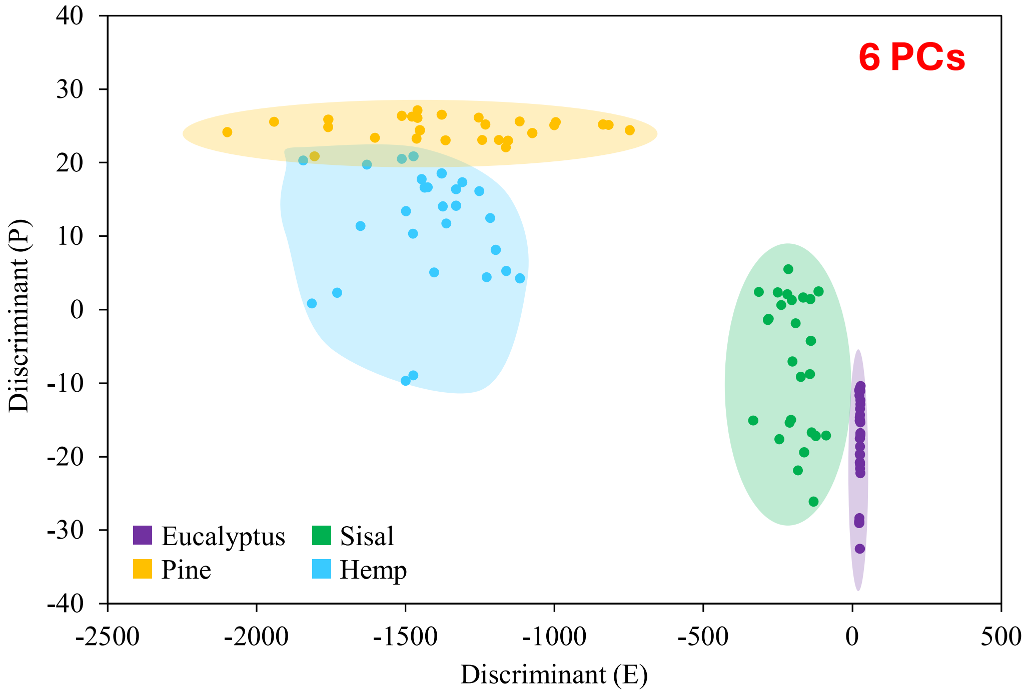
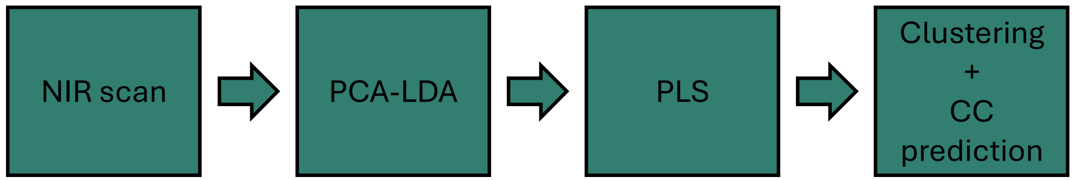


Principal Component Analysis – Linear Discriminant Analysis (PCA-LDA)



- ✓ A portable equipment can be used (MicroNIR) for CC determination.
- ✓ Appropriate data processing allow CC quantification and feedstock identification.



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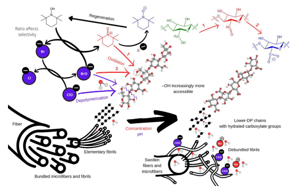
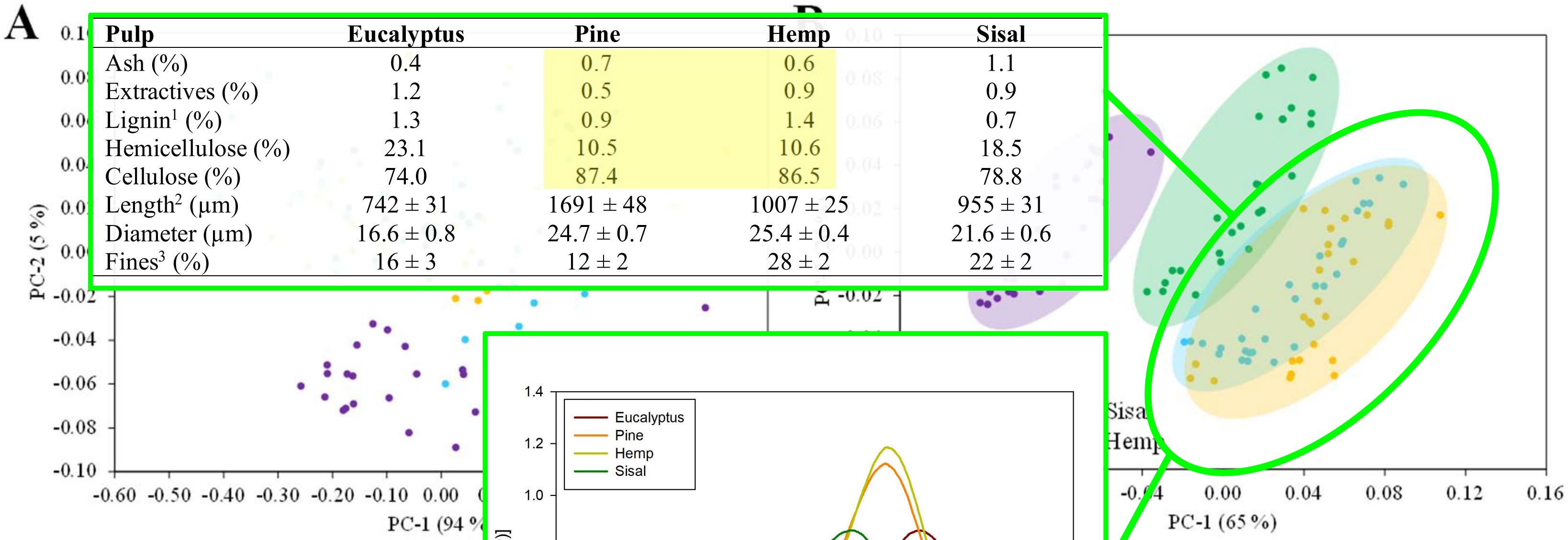
Reaction kinetics

Chemometrics

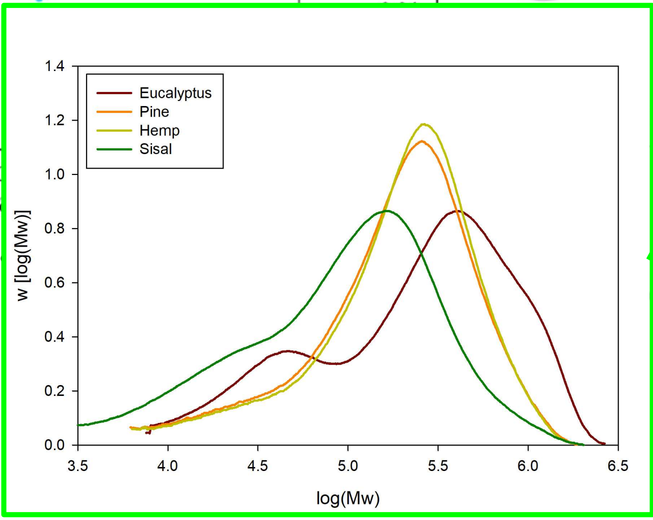
Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment



Principal Component Analysis (PCA)



Pulp	Eucalyptus	Pine	Hemp	Sisal
Ash (%)	0.4	0.7	0.6	1.1
Extractives (%)	1.2	0.5	0.9	0.9
Lignin[1] (%)	1.3	0.9	1.4	0.7
Hemicellulose (%)	23.1	10.5	10.6	18.5
Cellulose (%)	74.0	87.4	86.5	78.8
Length[2] (μm)	742 ± 31	1691 ± 48	1007 ± 25	955 ± 31
Diameter (μm)	16.6 ± 0.8	24.7 ± 0.7	25.4 ± 0.4	21.6 ± 0.6
Fines[3] (%)	16 ± 3	12 ± 2	28 ± 2	22 ± 2

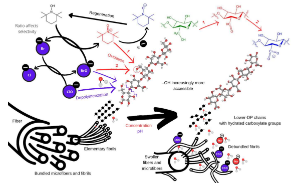


A. Raw spectra (2 PCs): PC1 …
B. SNV-processed spectra (4 … ver 91% variance

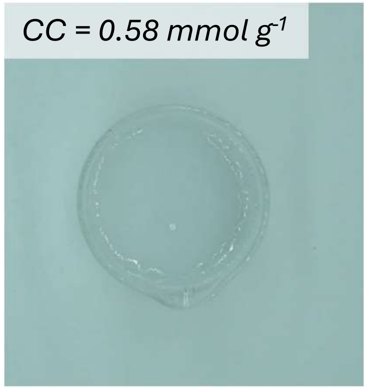
Mazega et al. (2024). Cellulose 31(6), 3465-3482

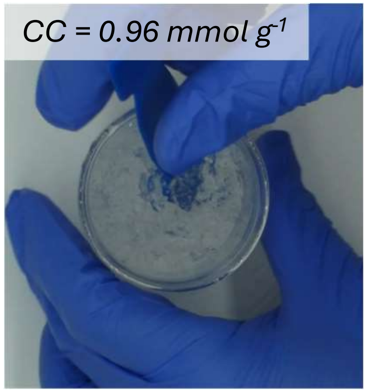
Mazega et al. (2025). Cellulose, Published online

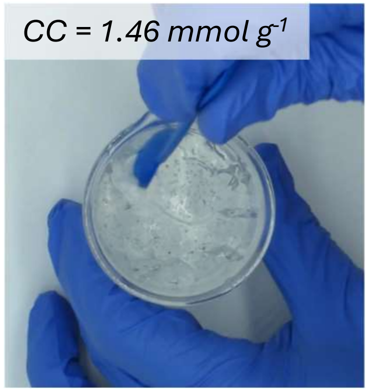
Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment



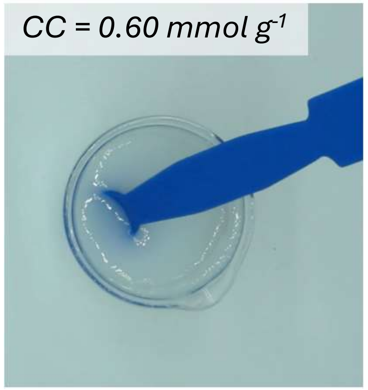
Bleached Kraft Softwood Pulp

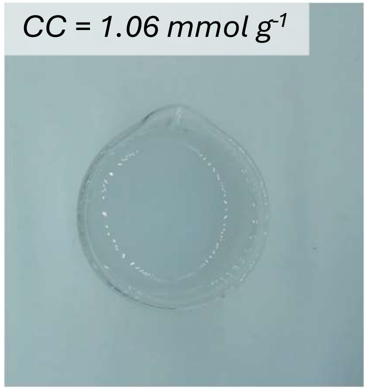


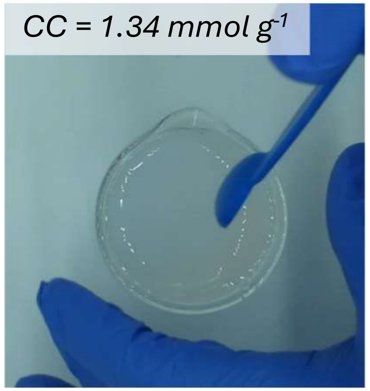




Bleached Hemp Pulp







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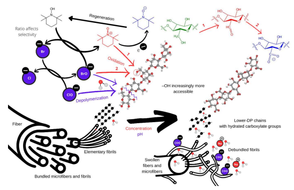

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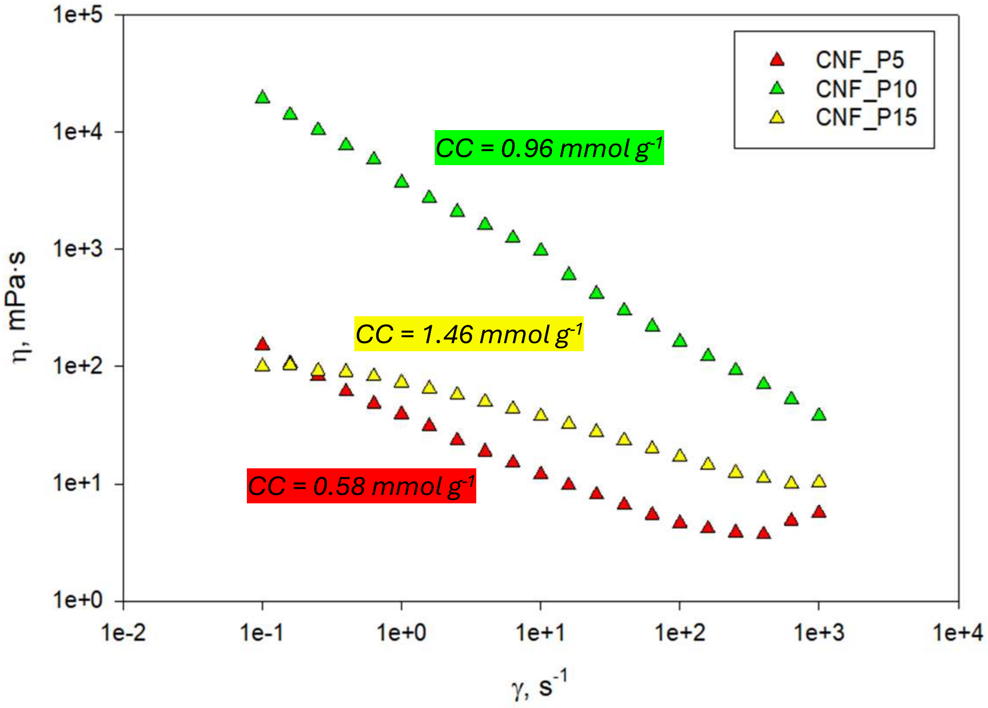

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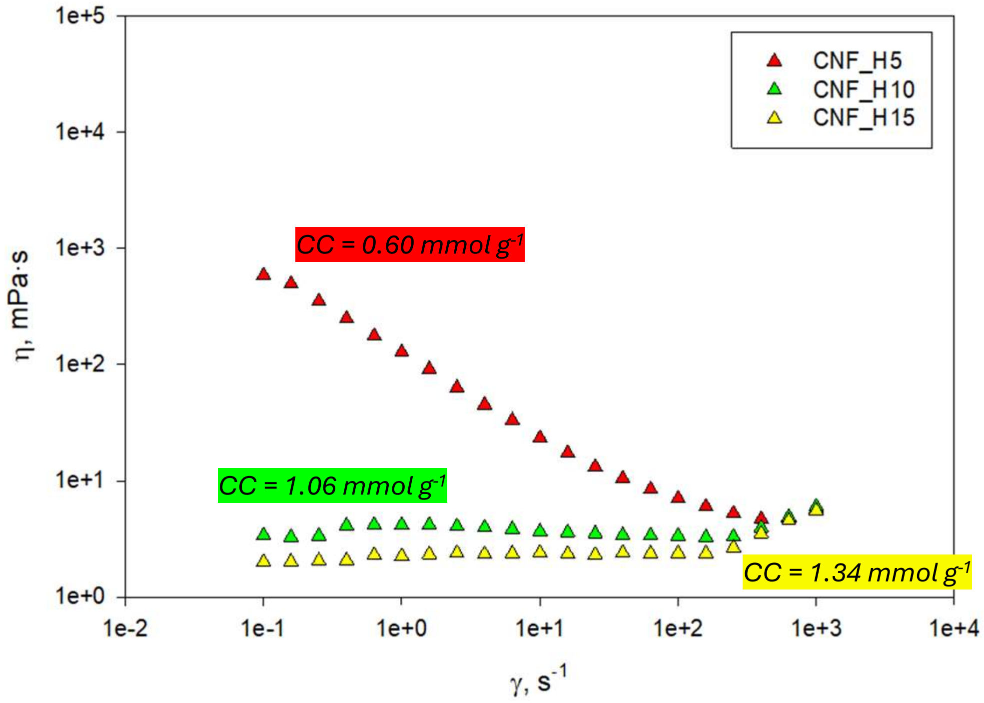

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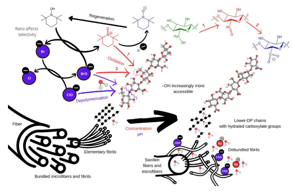

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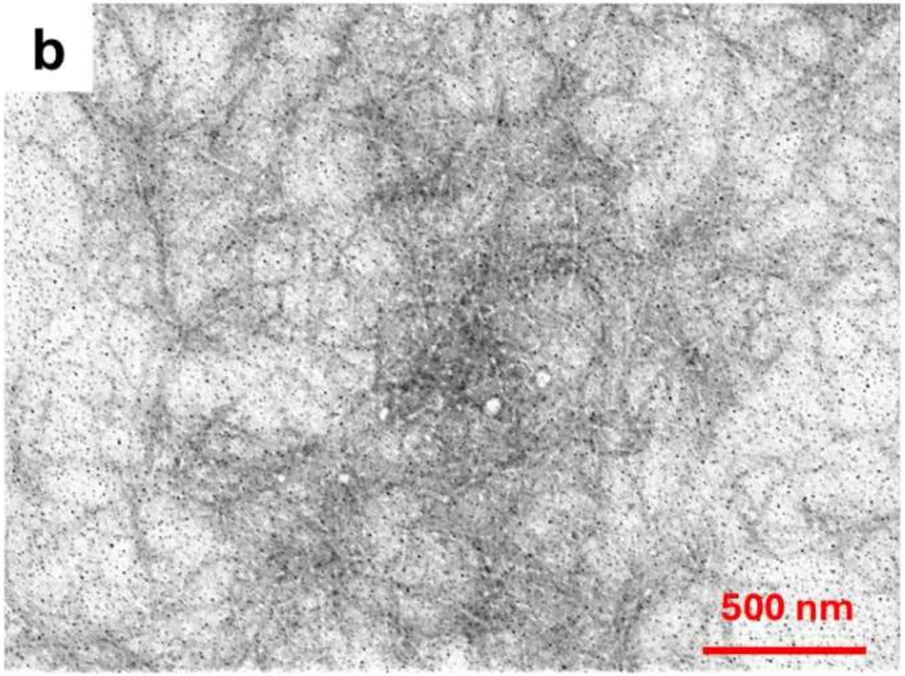

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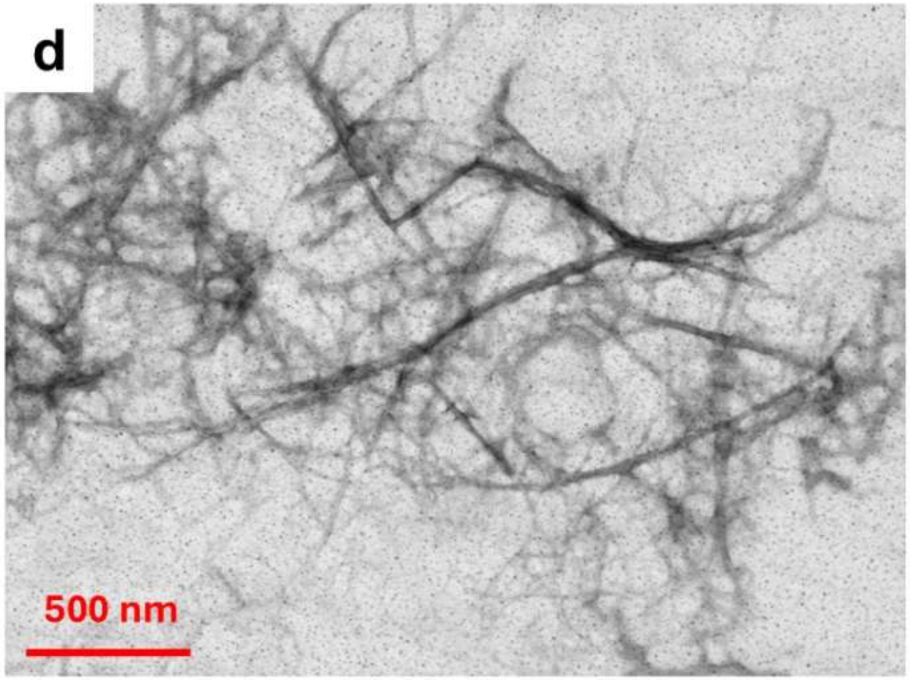

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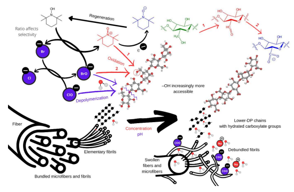
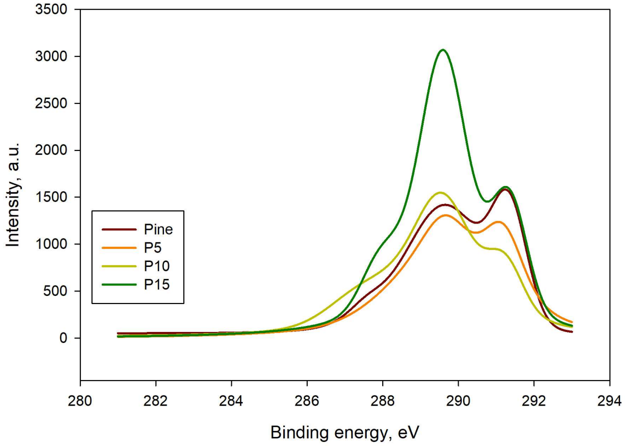
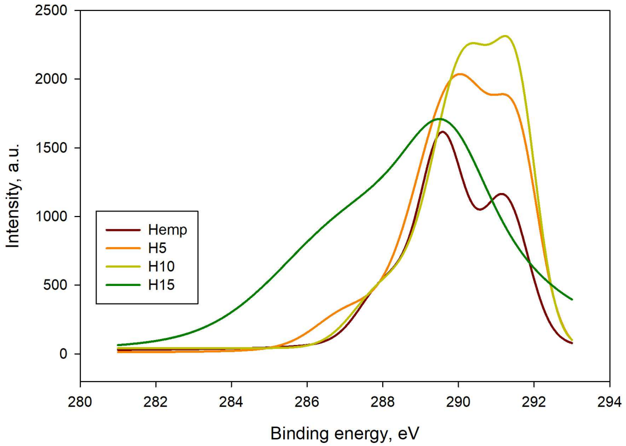
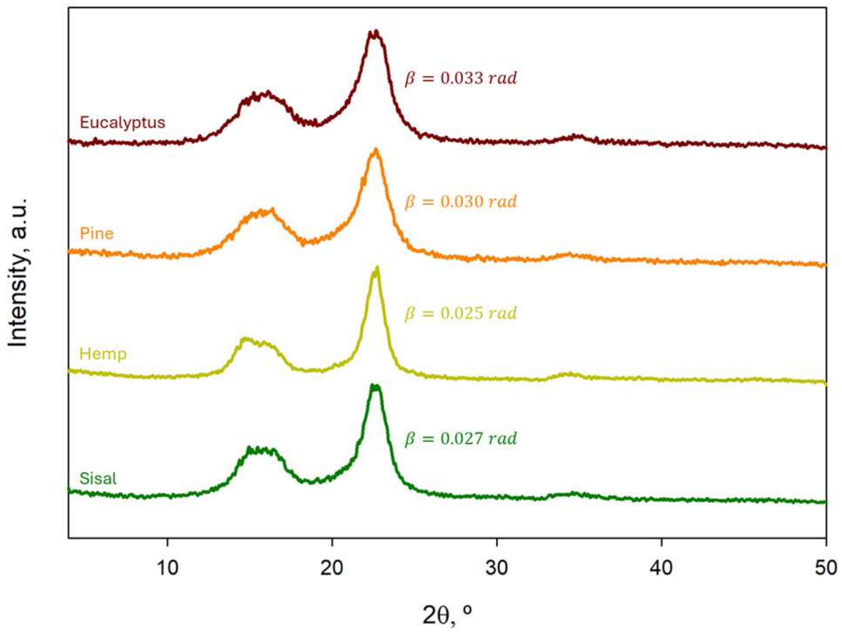






Starting material	D_{200} (nm)	CI			
		Non-oxidized	5 mmol/g	10 mmol/g	15 mmol/g
Eucalyptus	4.48	0.58	0.64	0.68	0.75
Pine	4.93	0.61	0.64	0.68	0.78
Hemp	5.92	0.78	0.85	0.87	0.89
Sisal	5.47	0.69	0.73	0.76	0.77



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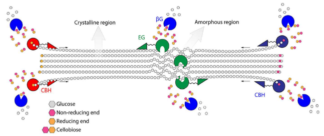

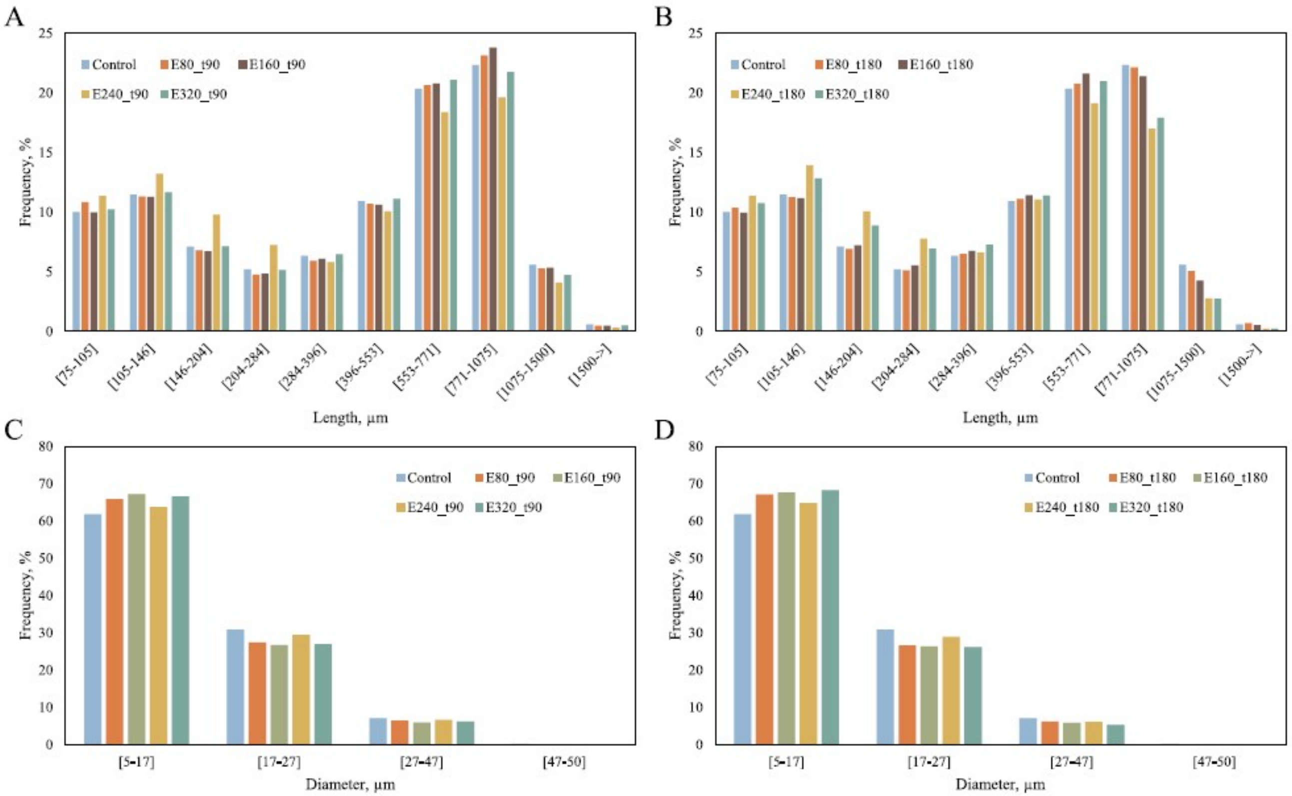

Enzyme dosage	Treatment time	
80 mg/kg	0 min	120 min
160 mg/kg	30 min	150 min
240 mg/kg	60 min	180 min
300 mg/kg	90 min	240 min

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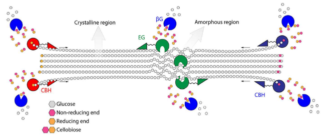

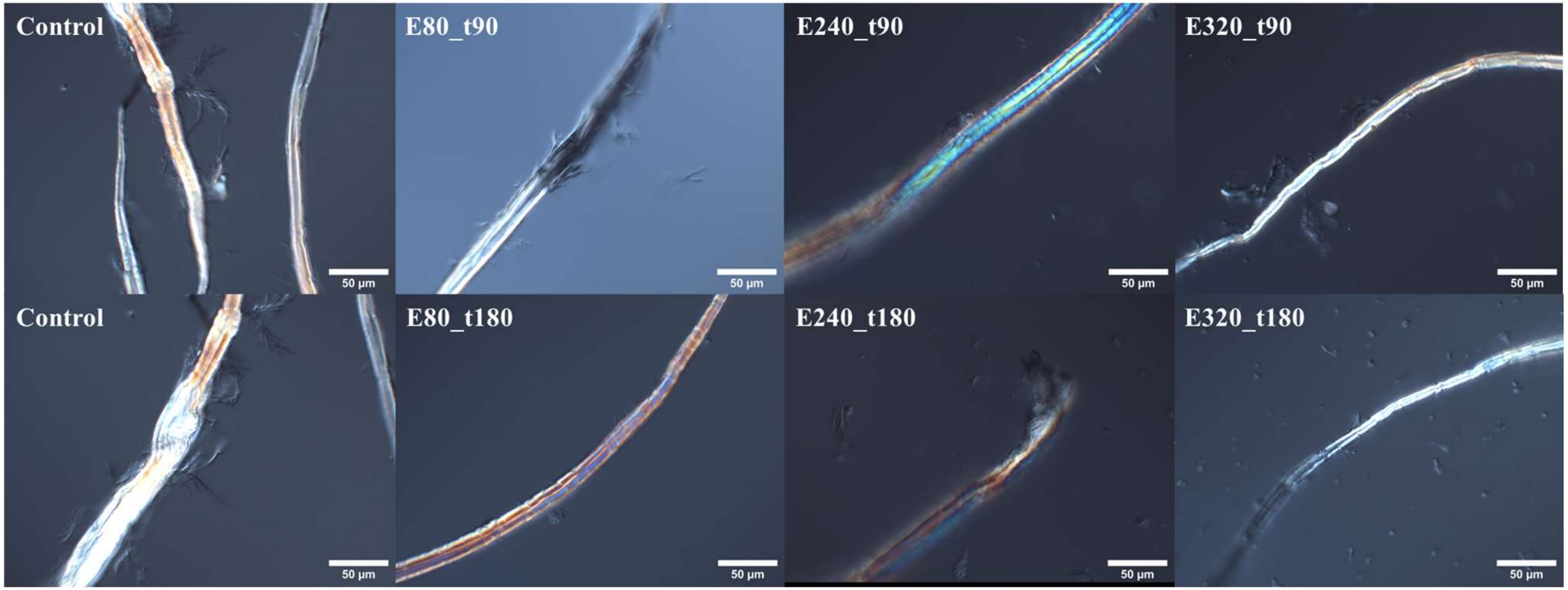

Effects on surface fibrillation and fines

Internal fibrillation is promoted

Fines generation. Stronger effects.

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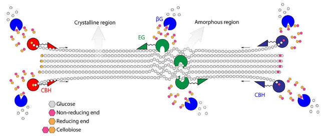

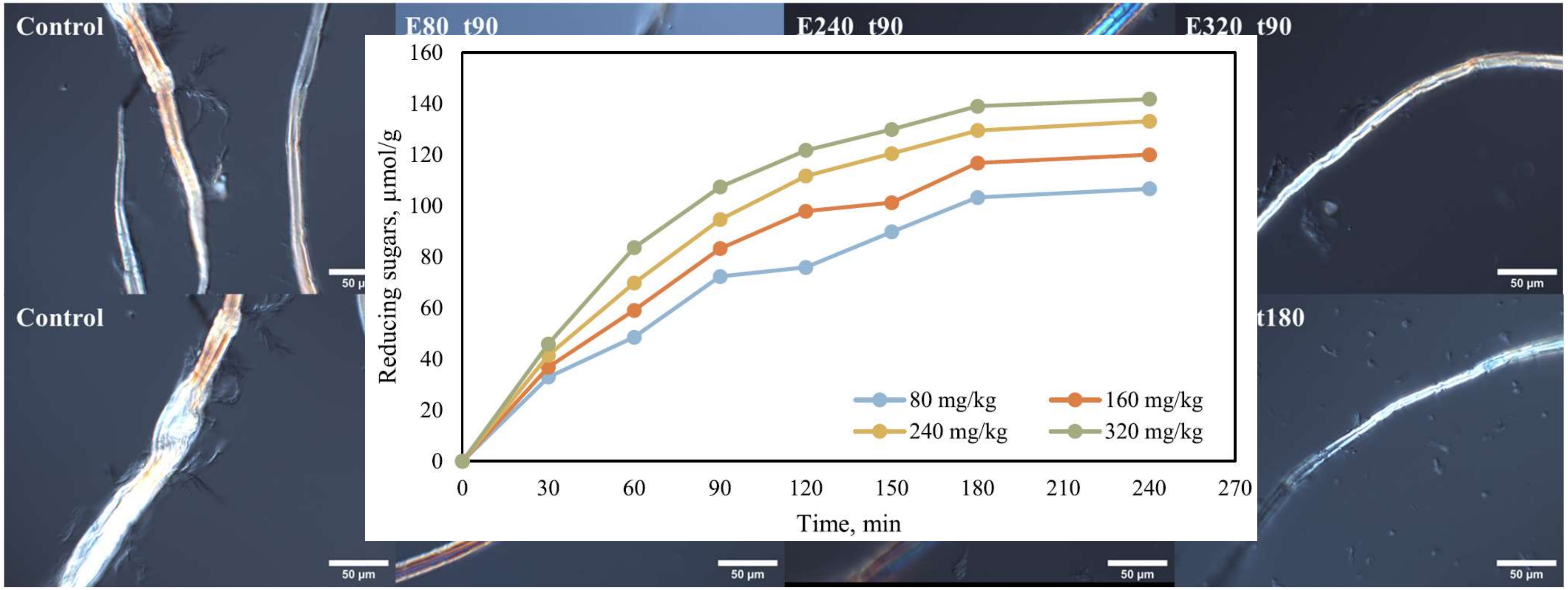

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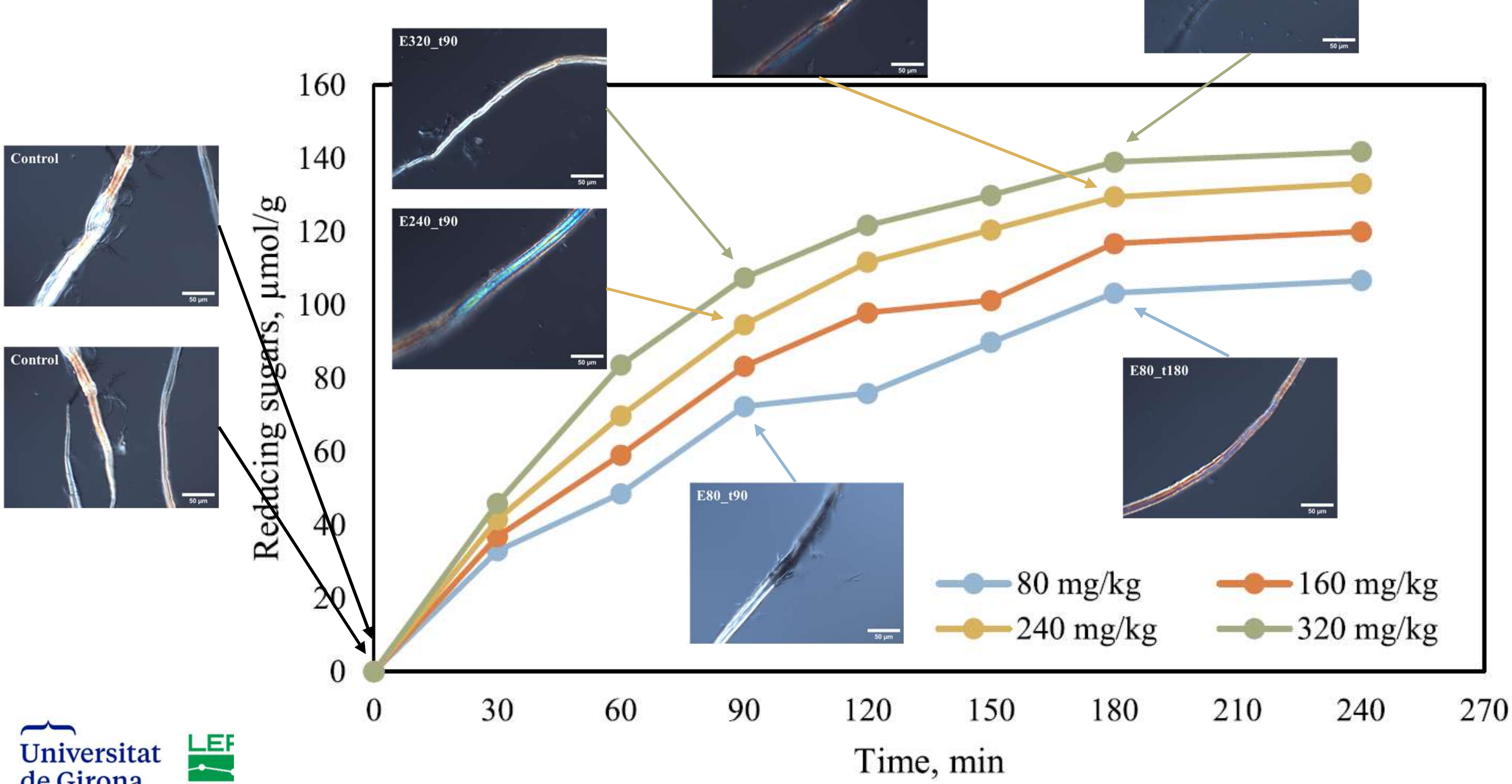

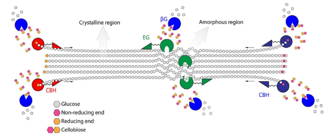

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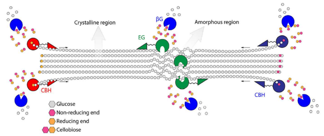

- MorFi does not provide relevant information on morphological changes.
- Optical microscopy requires sampling and can lead to some qualitative assessments.
- The determination of the reducing sugars concentration is time consuming.

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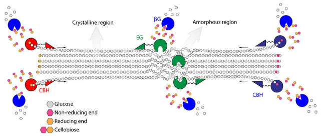

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A visual inspection reveals a significant decrease on viscosity.

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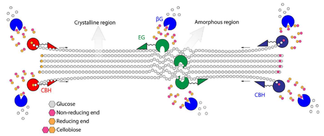

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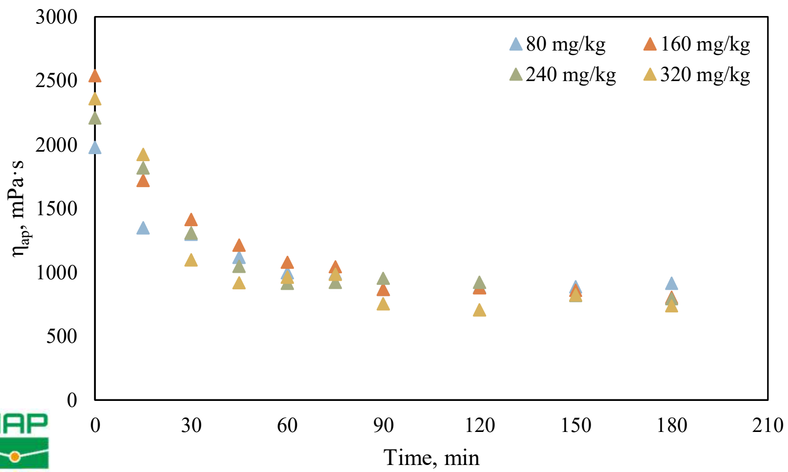

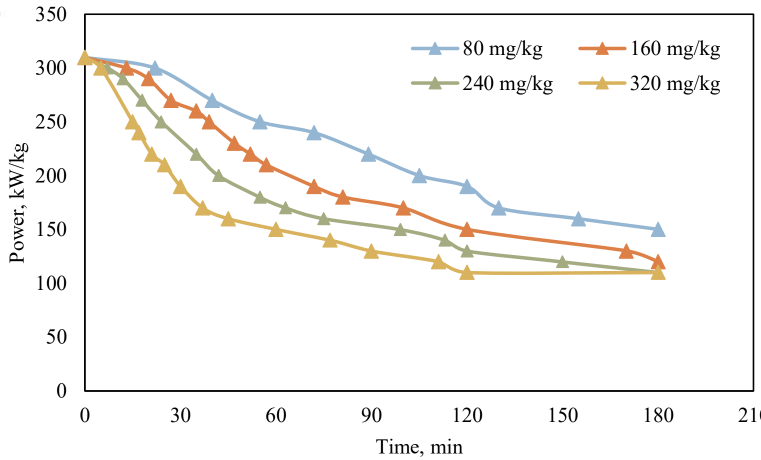

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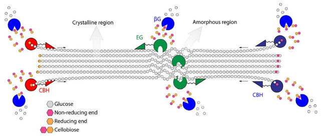
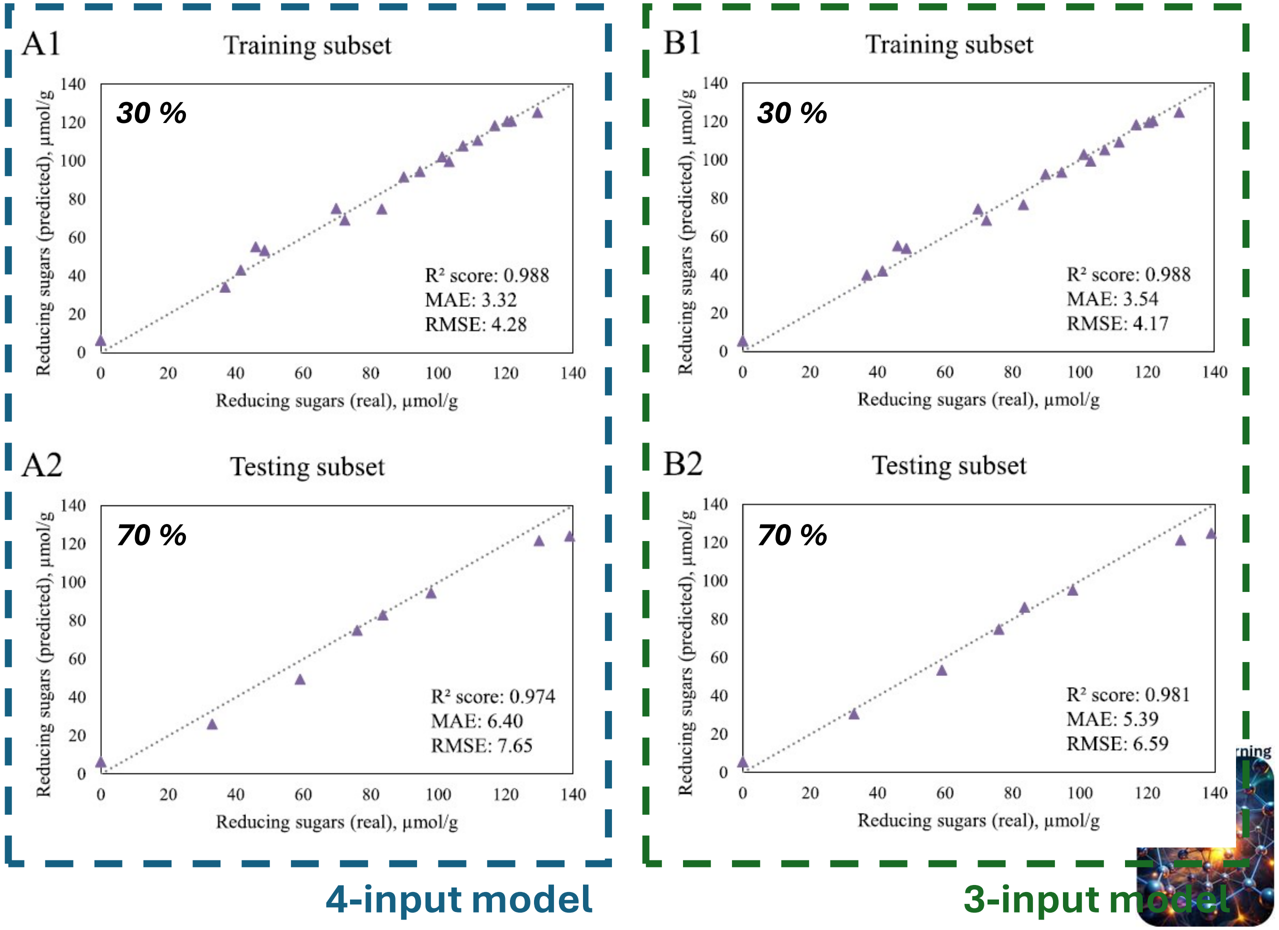


- Selected model: Random Forest.
- Input variables:
  - **First attempt:** (i) fiber length, (ii) apparent viscosity, (iii) fines content, and (iv) stirrer consumption.
- Output: Reducing Sugars concentration.



4-input model **3-input model**

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Content

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- Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment.
- Understanding the transition from micro to nano: energy and property implications.
- Concluding remarks.

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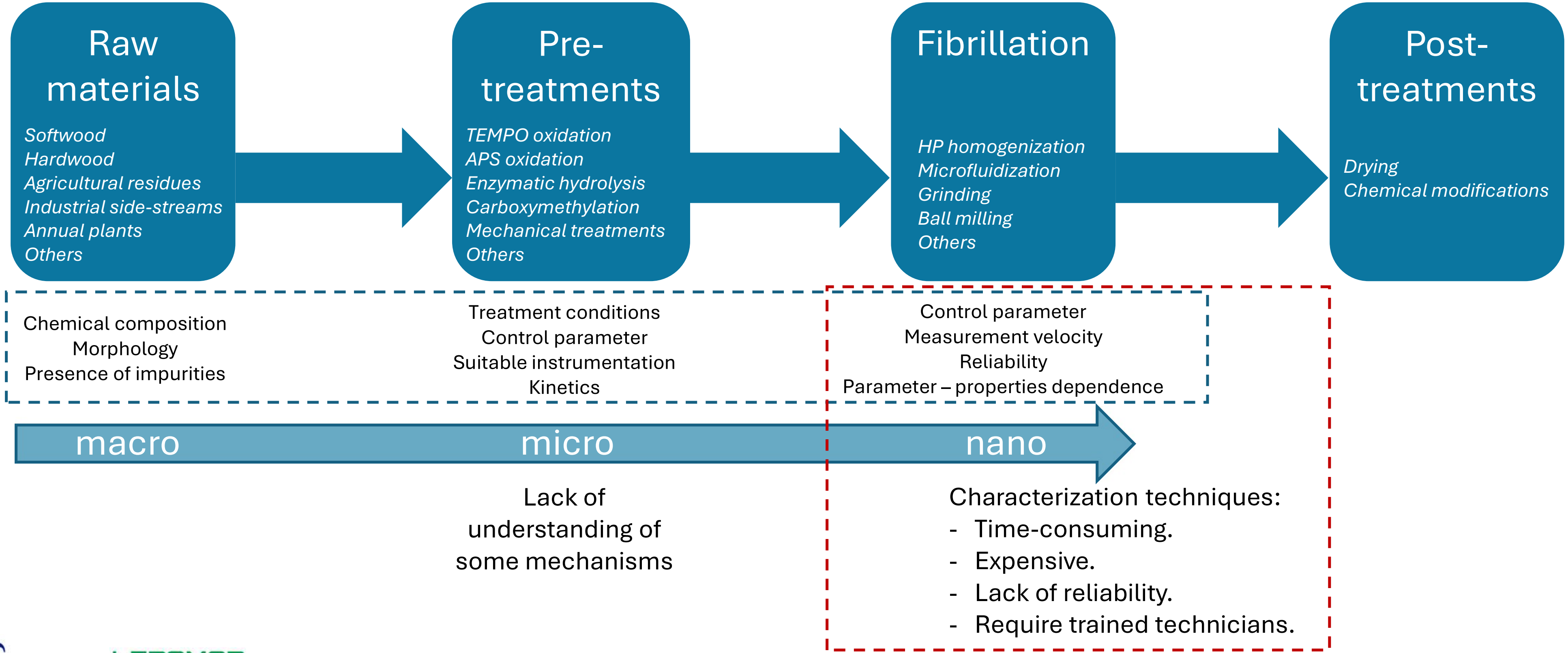

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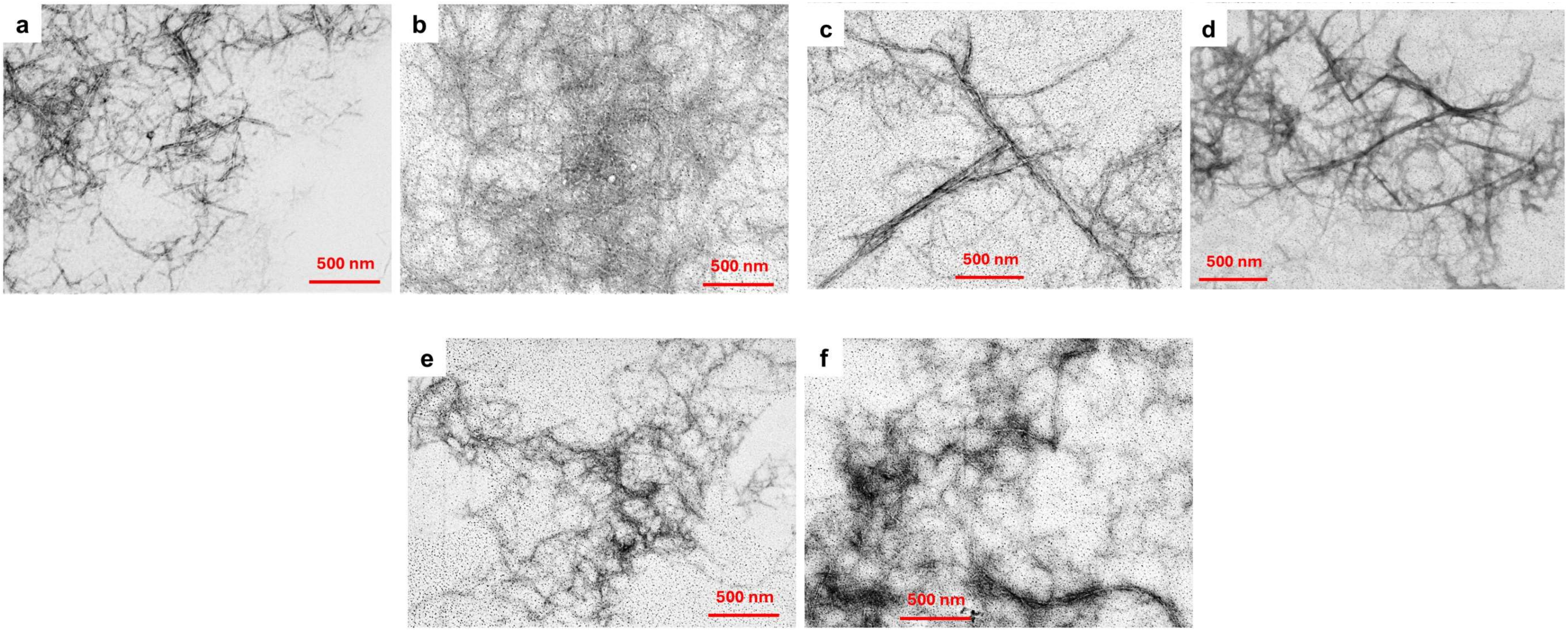

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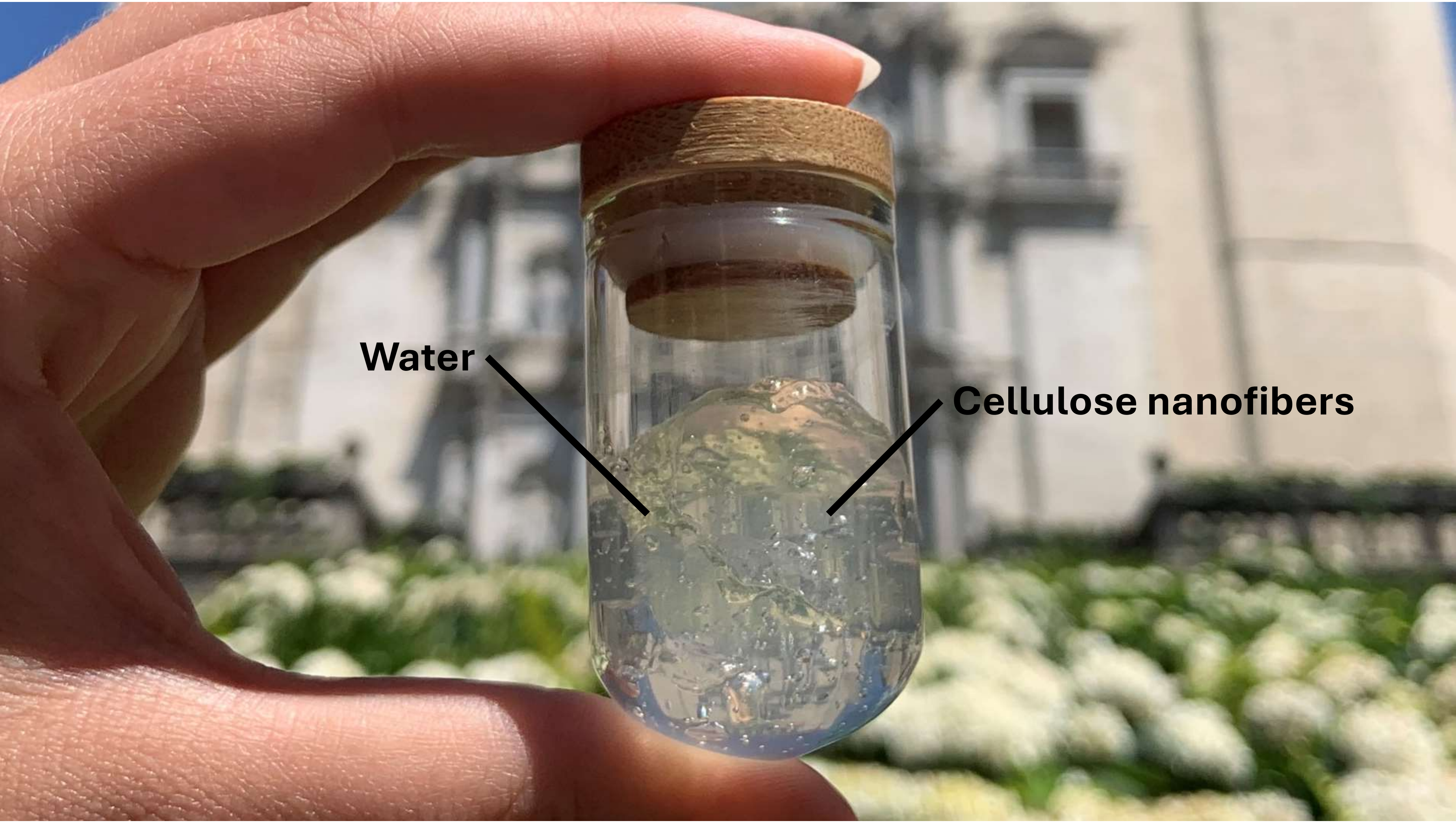
Credits to Gabriela Bastida and Giulia Herbst


Water
Cellulose nanofibers

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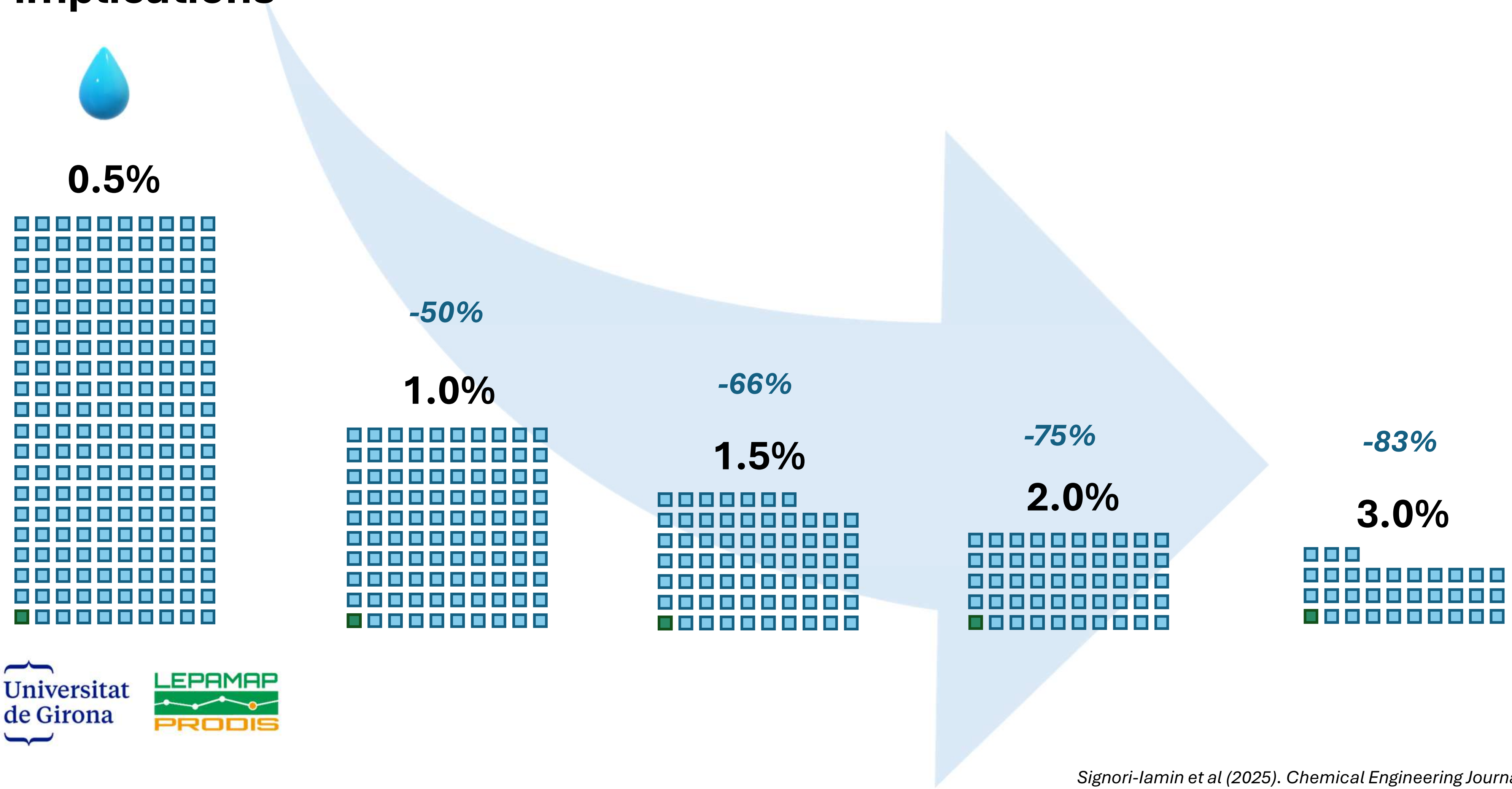

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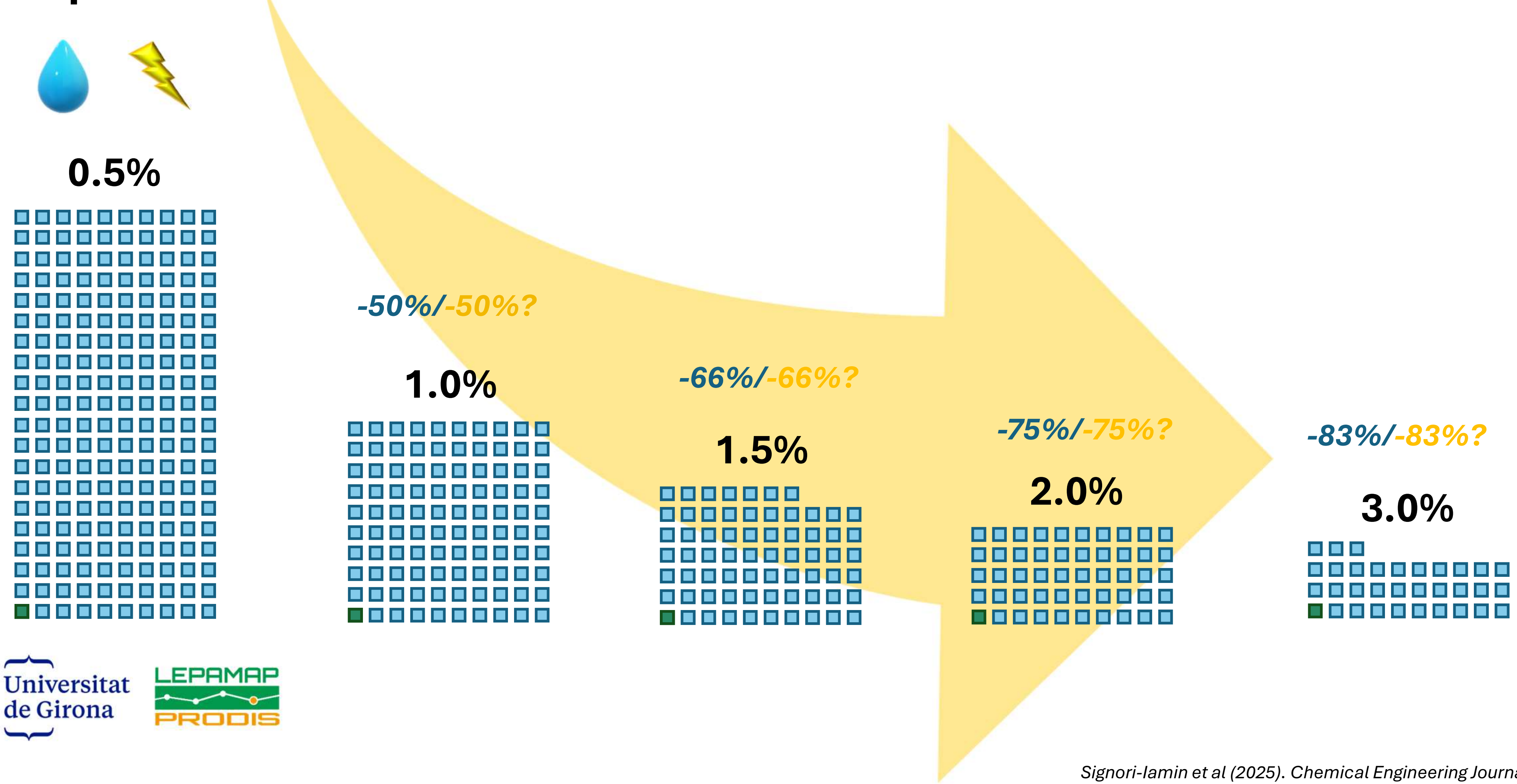

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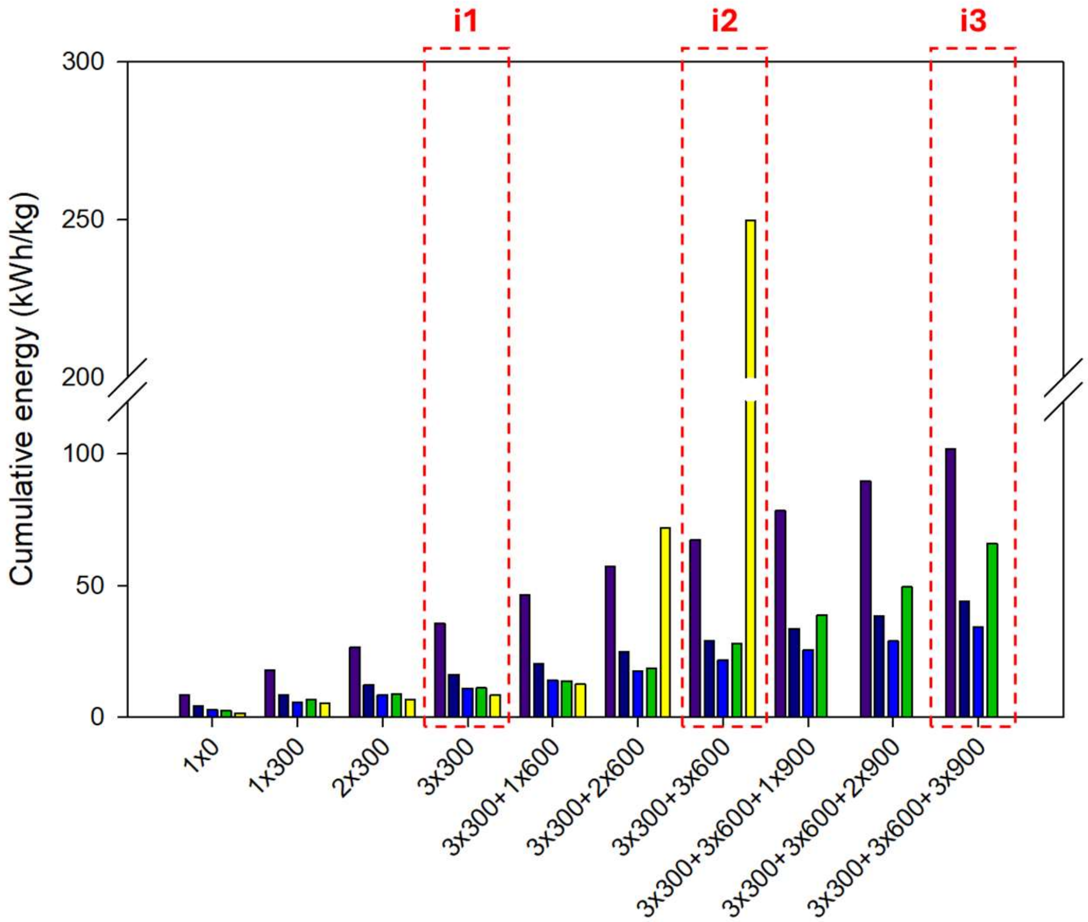
0.5%	
1.0%	-50%/-50%?
1.5%	-66%/-66%?
2.0%	-75%/-75%?
3.0%	-83%/-83%?



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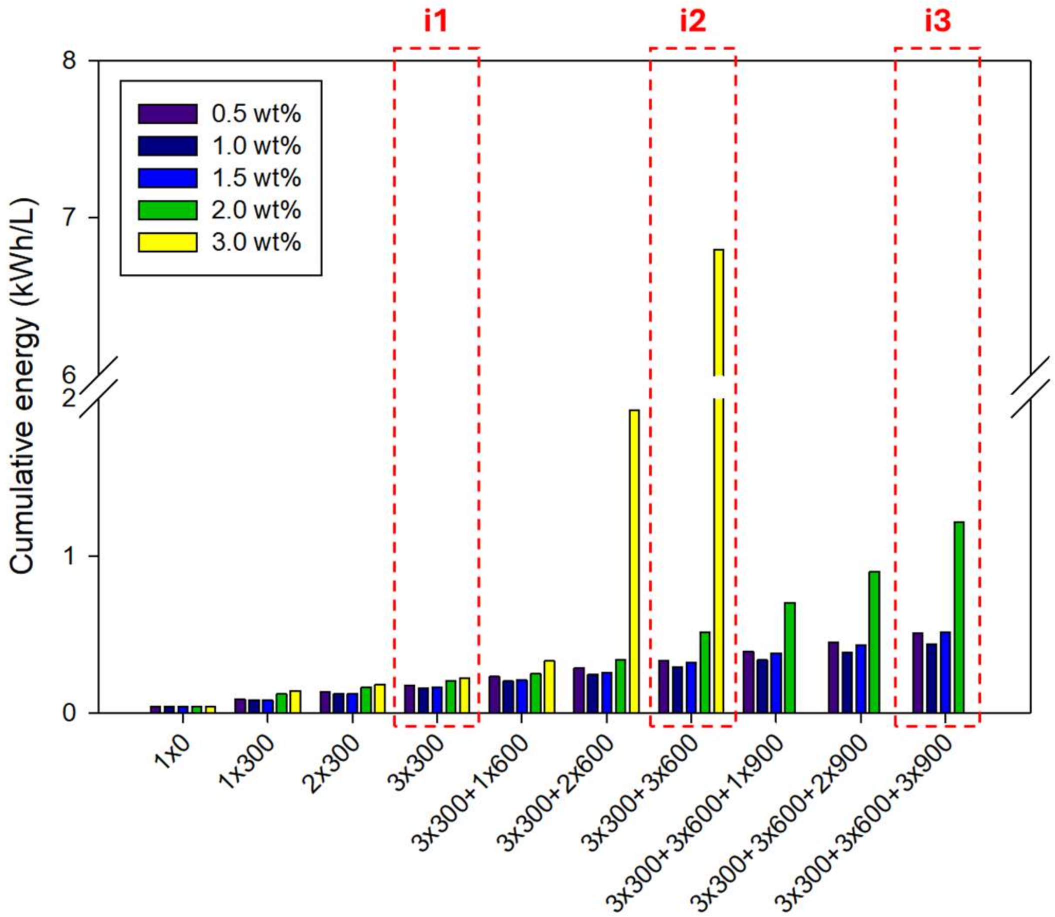

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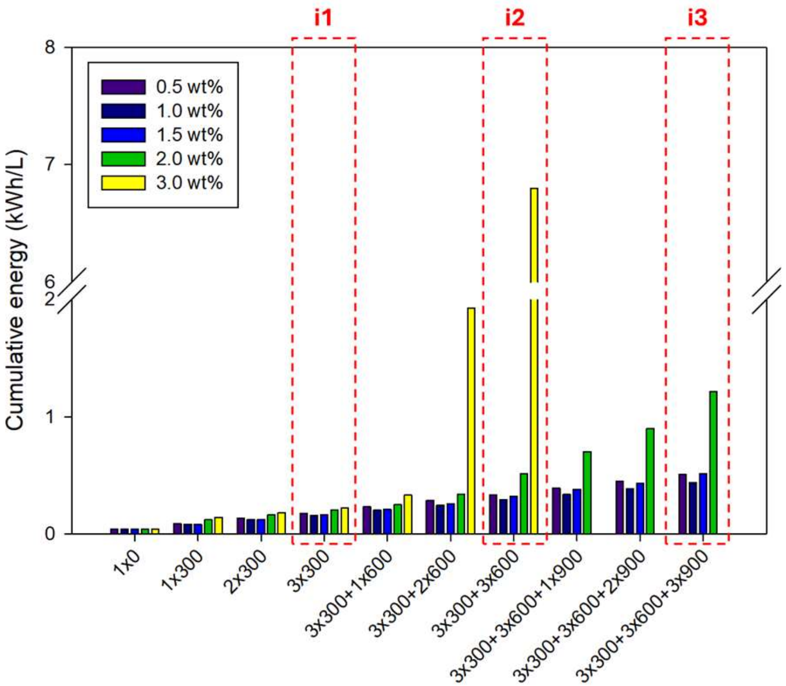

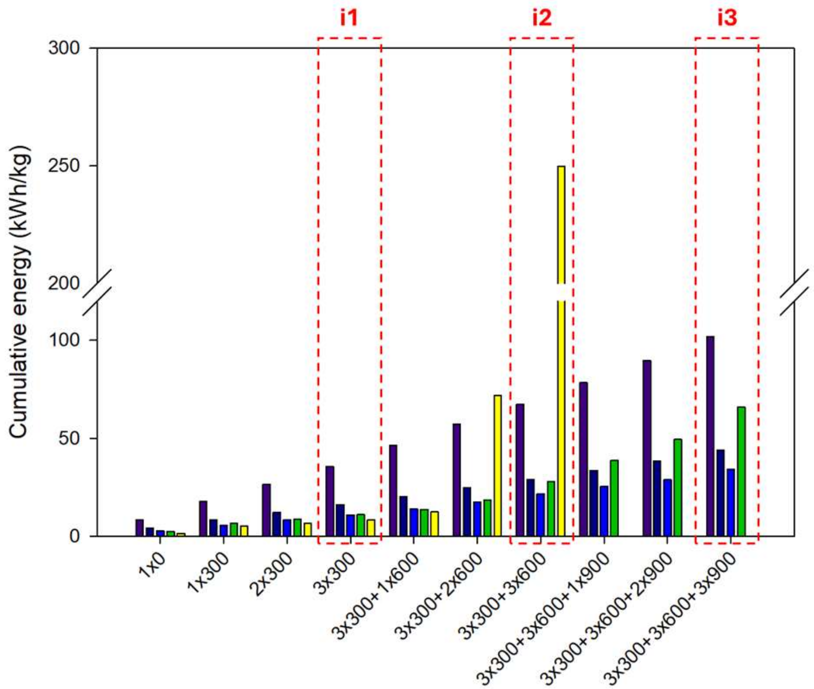

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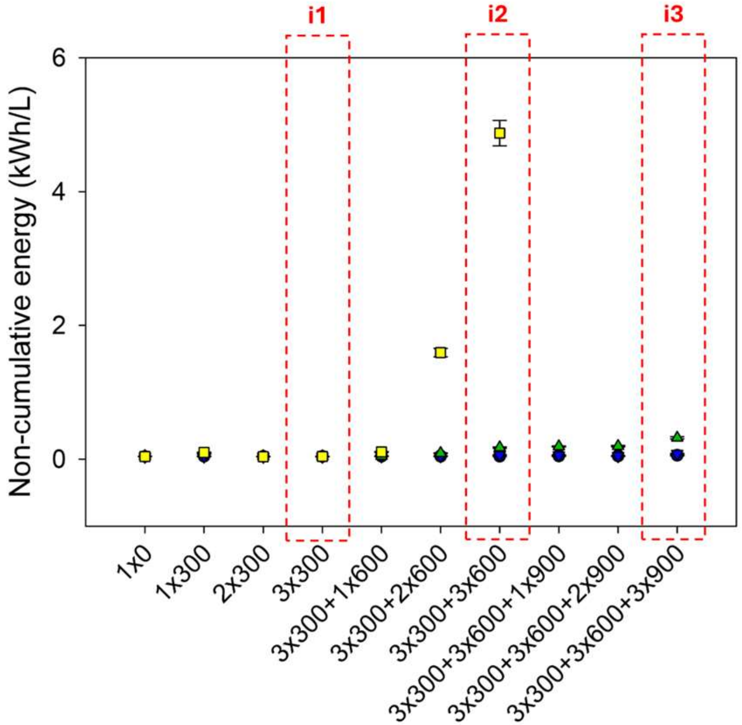

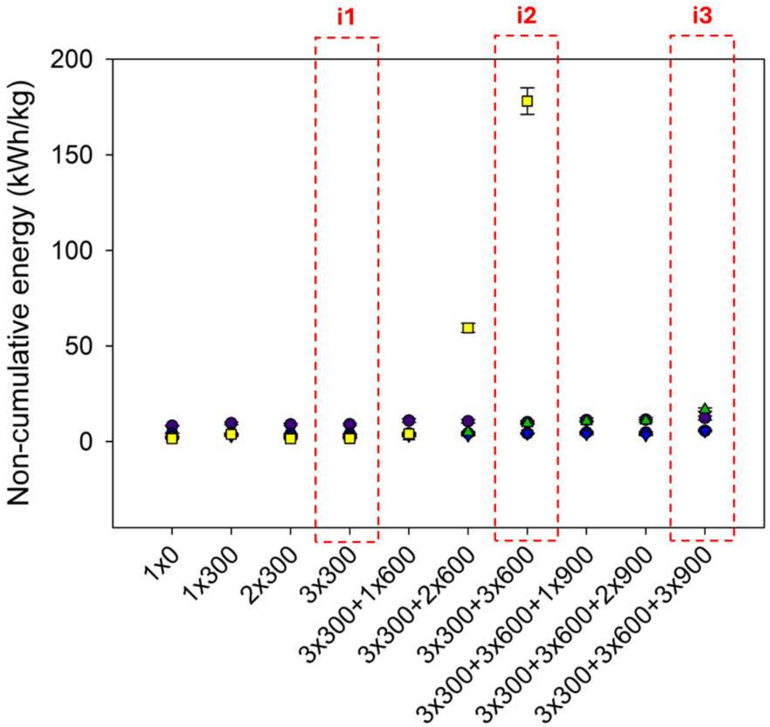

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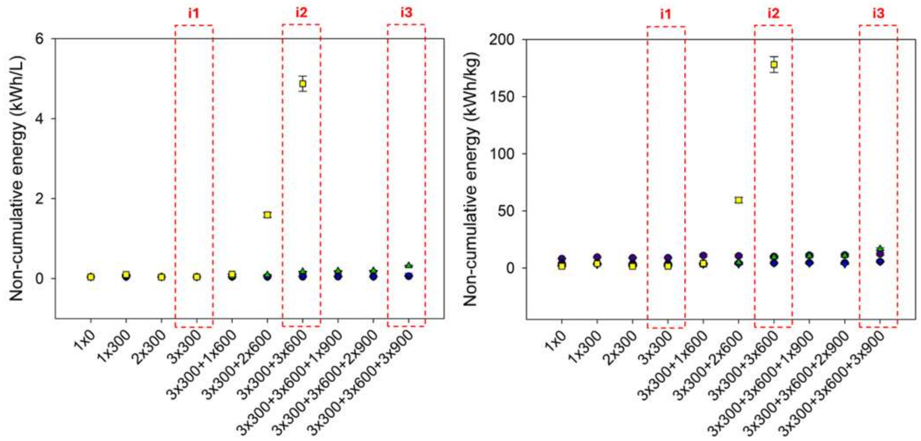

Relative non-accumulated energy consumption (kWh/kg)

	Fibrillation level	i1	i2	i3
Consistency (wt%)	0.5	100.0%	100.0%	100.0%
	1.0	45.4%	40.8%	42.9%
	1.5	31.0%	33.5%	36.4%
	2.0	26.2%	54.8%	108.2%
	3.0	17.4%	788.3%	n.p.

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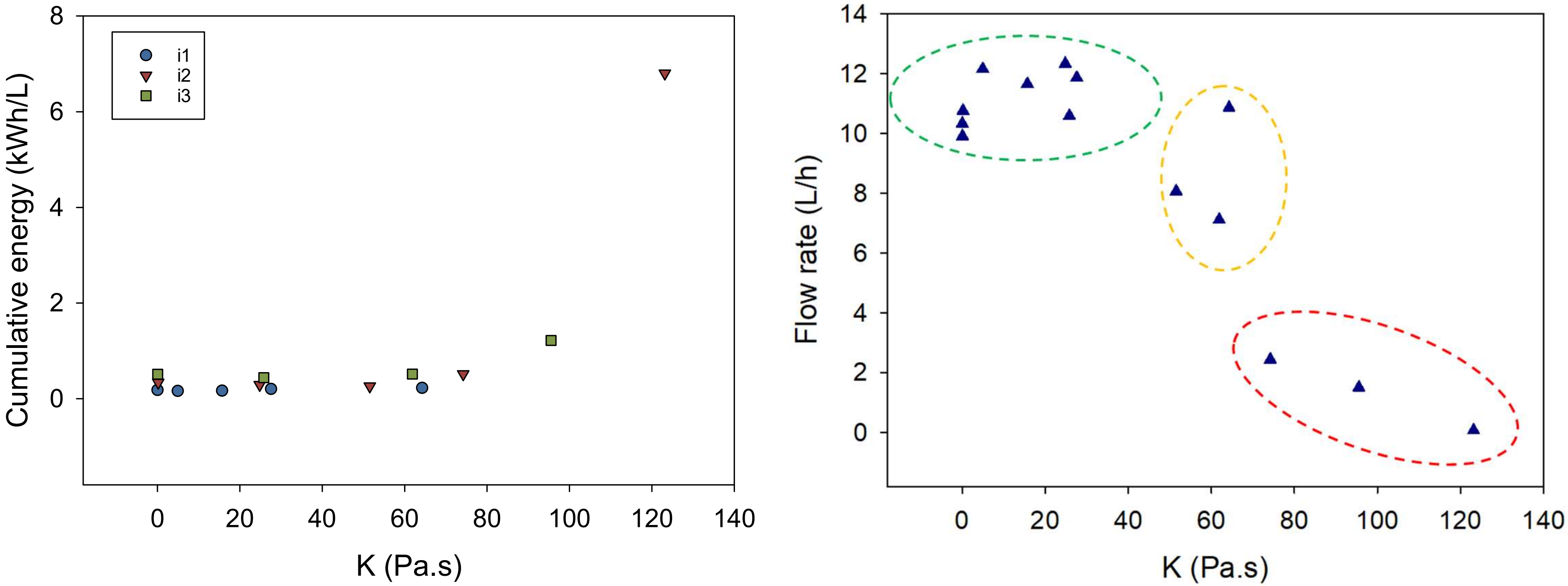

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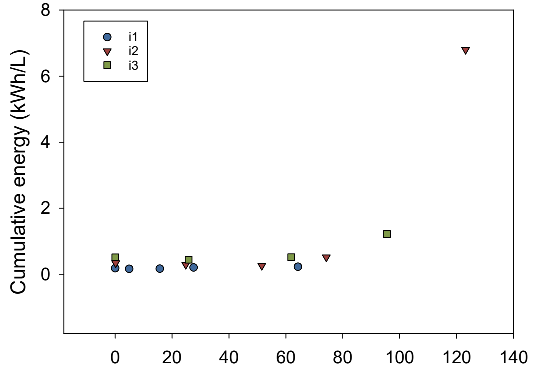

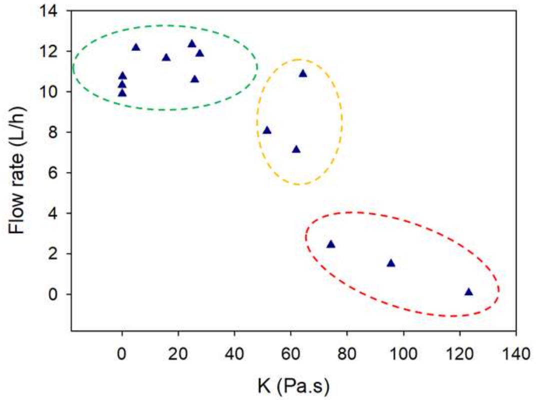

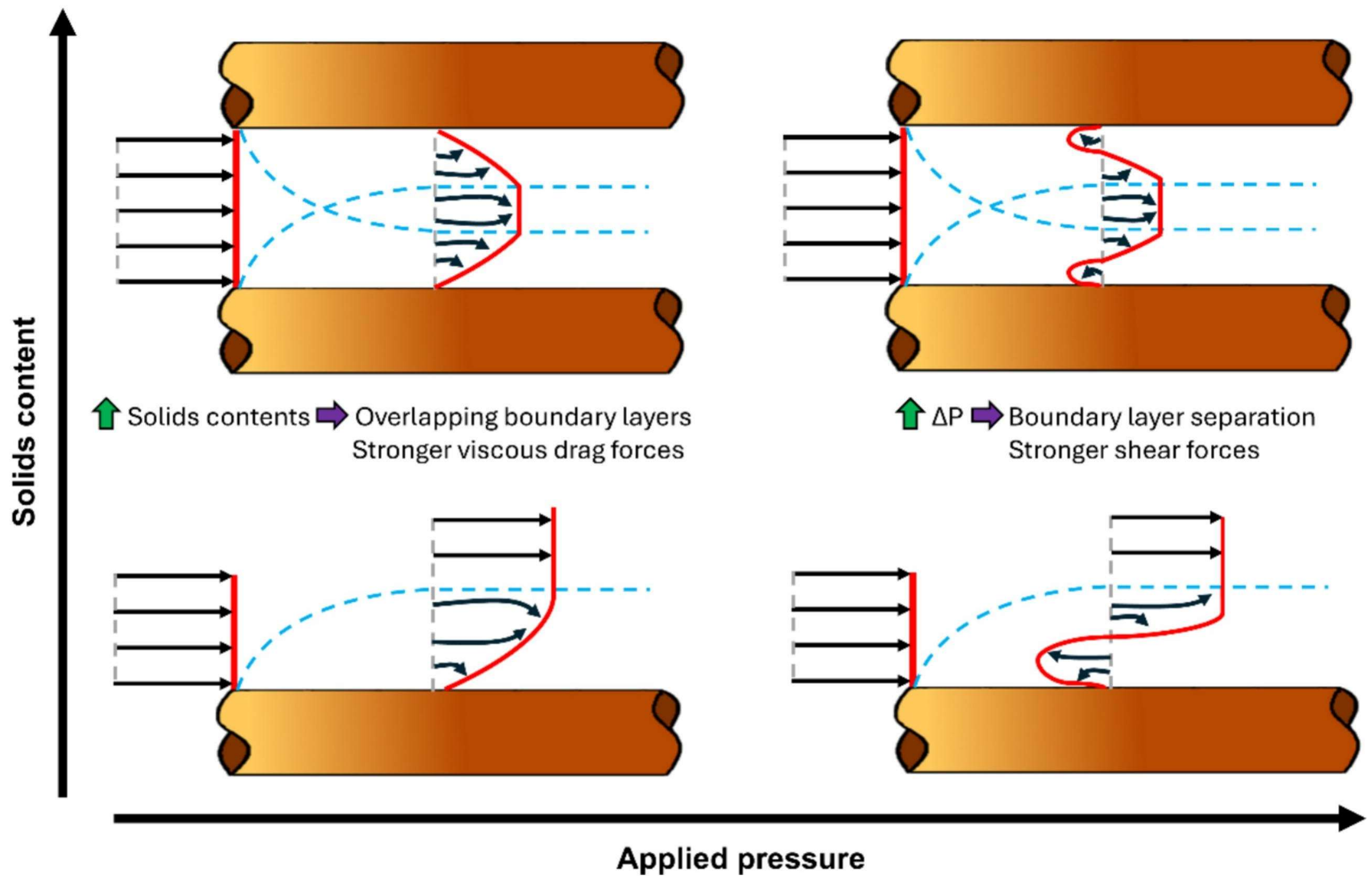

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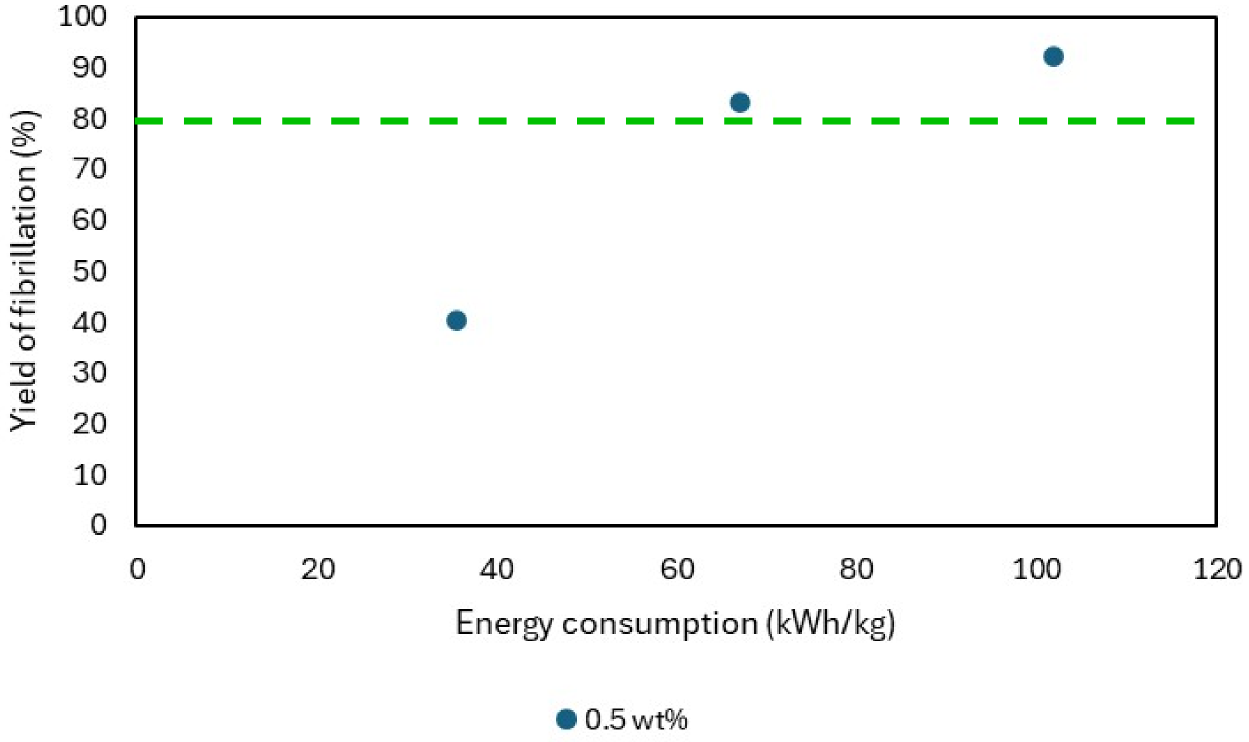
Signori-Iamin et al (2025). Chemical Engineering Journal 509, 161257

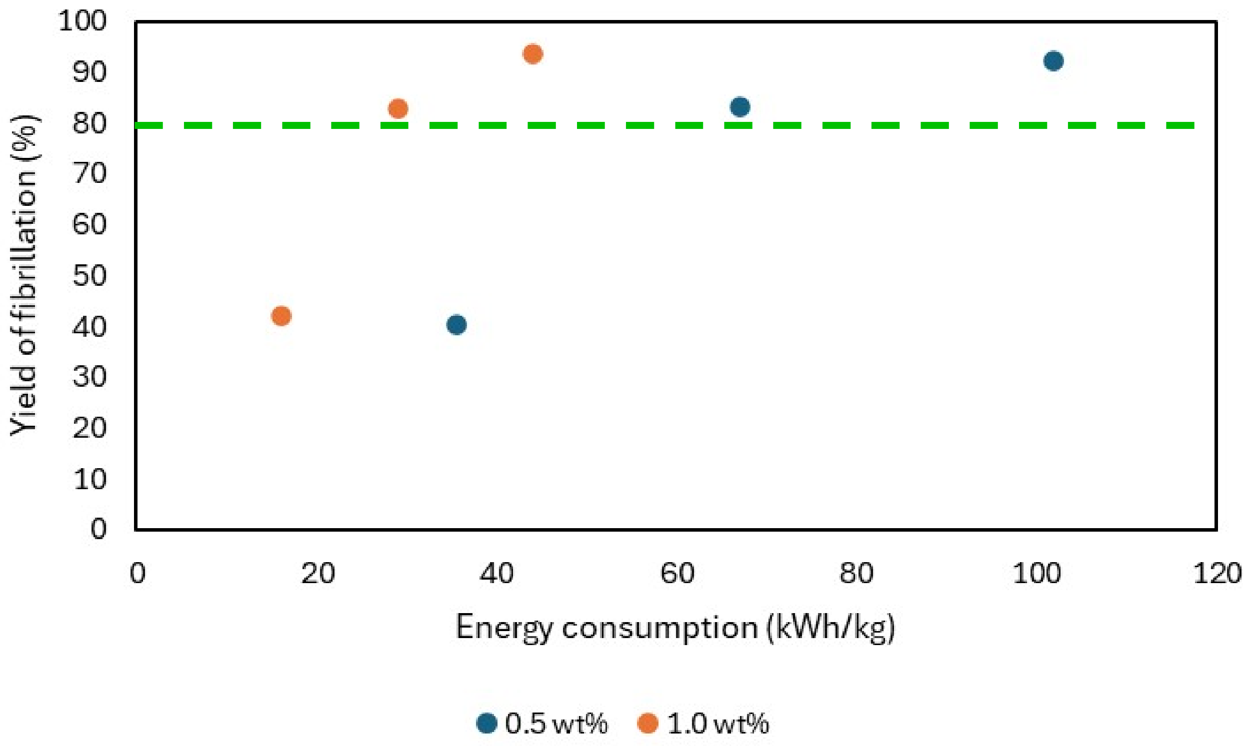
Understanding the transition from micro to nano: energy and property implications



Best: 0.5 wt%; i2 (67.15 kWh/kg)

Signori-Iamin et al (2025). Chemical Engineering Journal 509, 161257

Understanding the transition from micro to nano: energy and property implications



Best: ~~0.5 wt%; i2 (67.15 kWh/kg)~~
1.0 wt%; i2 (28.97 kWh/kg)

Signori-Iamin et al (2025). Chemical Engineering Journal 509, 161257

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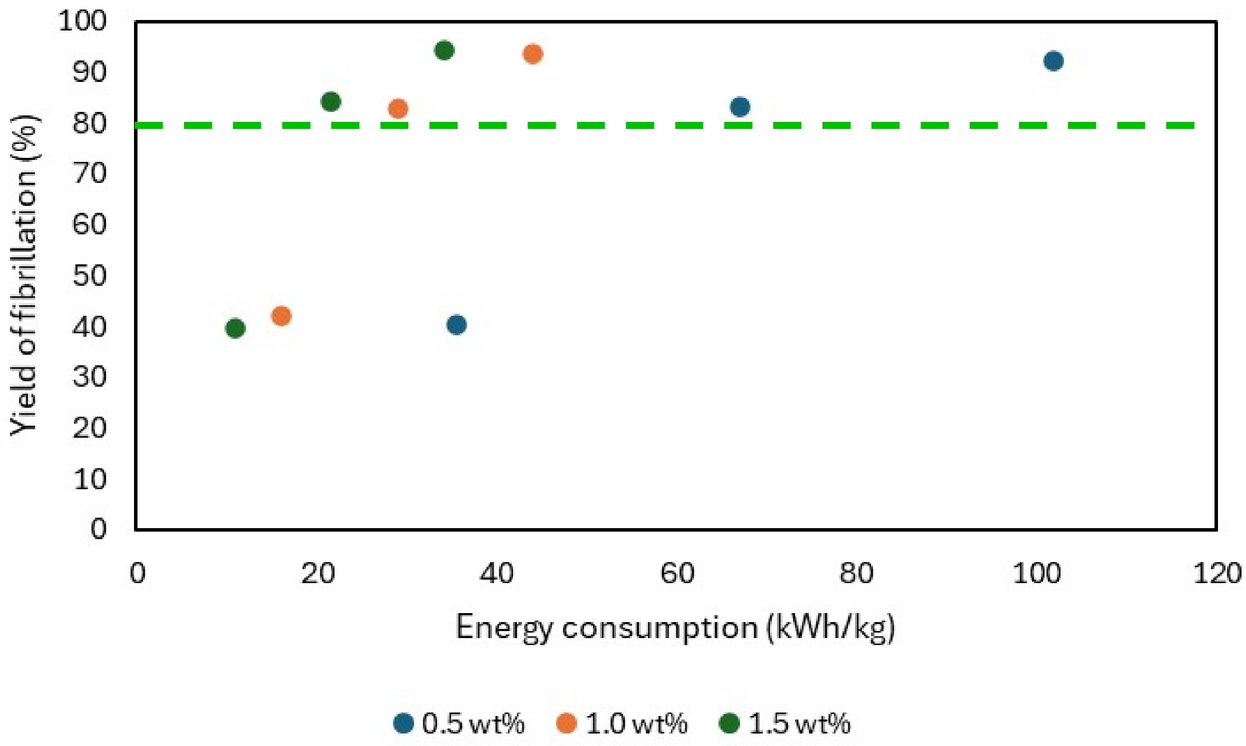

Best: ~~**0.5 wt%; i2 (67.15 kWh/kg)**~~
~~**1.0 wt%; i2 (28.97 kWh/kg)**~~
1.5 wt%; i2 (21.50 kWh/kg)

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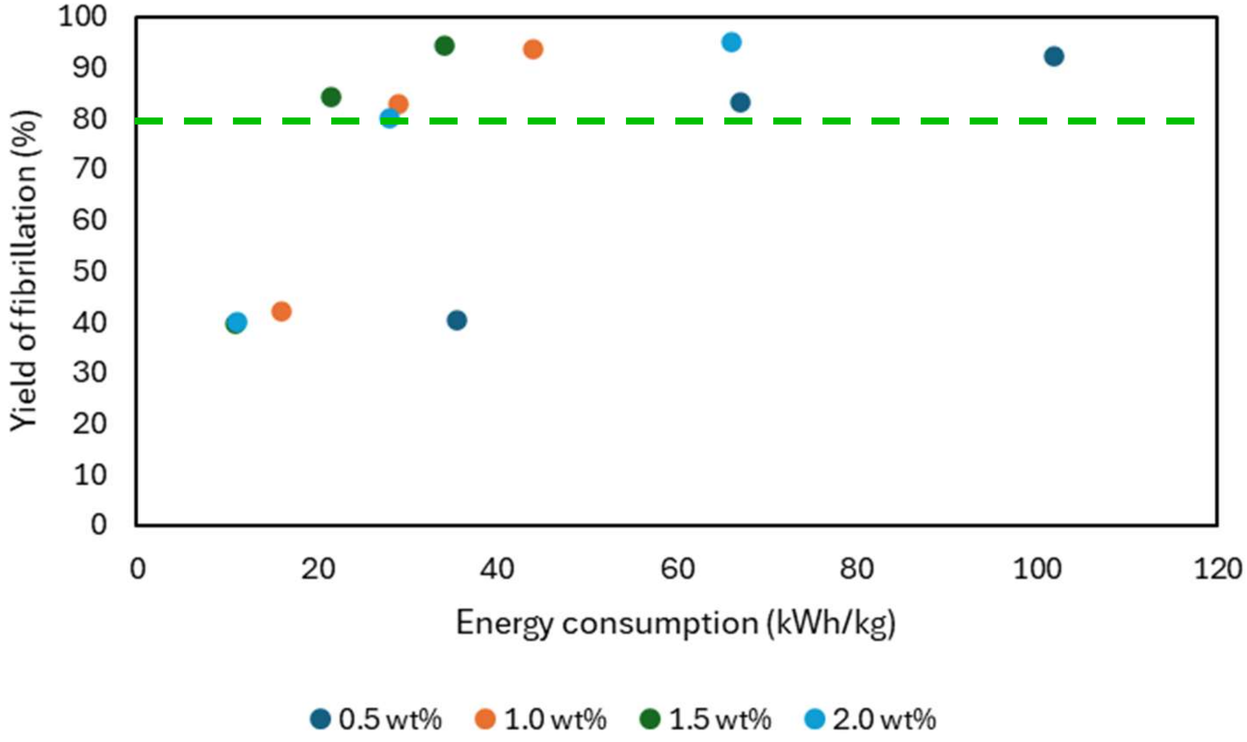

Best: ~~0.5 wt%; i2 (67.15 kWh/kg)~~
~~1.0 wt%; i2 (28.97 kWh/kg)~~
1.5 wt%; i2 (21.50 kWh/kg)

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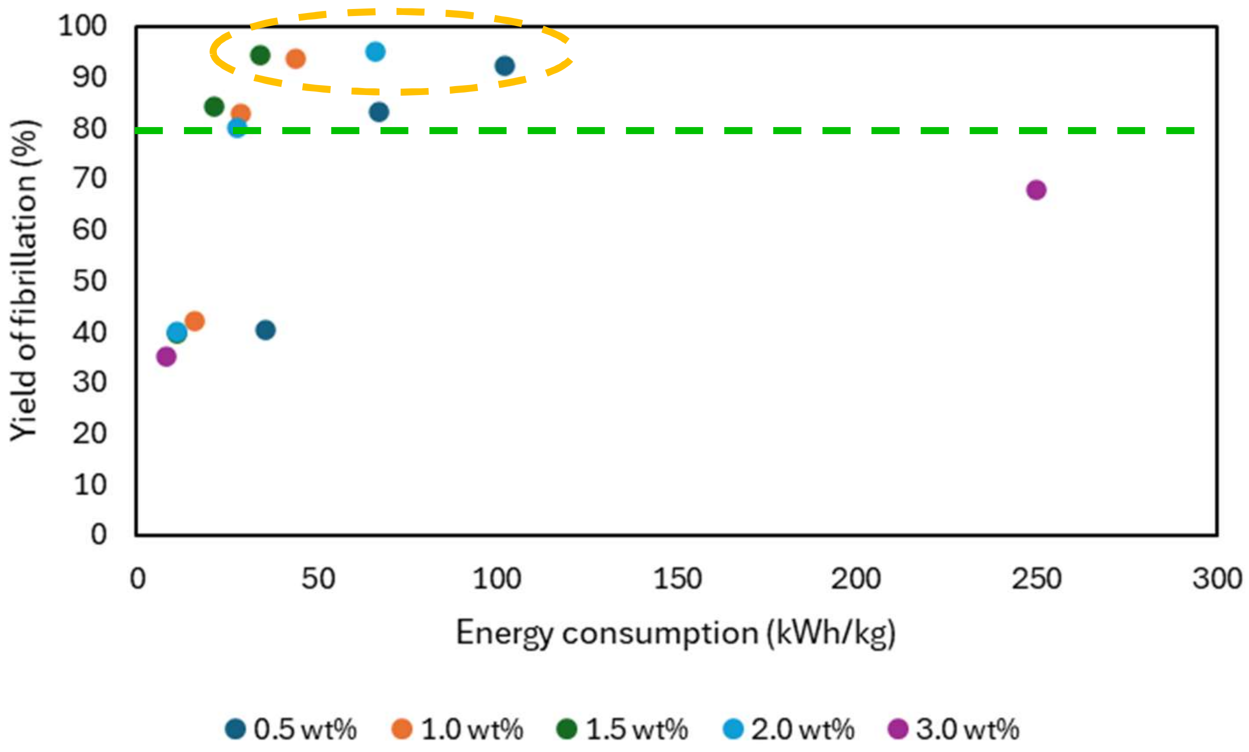
1.5 wt% also stands for the best option!



Best: ~~0.5 wt%; i2 (67.15 kWh/kg)~~
~~1.0 wt%; i2 (28.97 kWh/kg)~~
1.5 wt%; i2 (21.50 kWh/kg)

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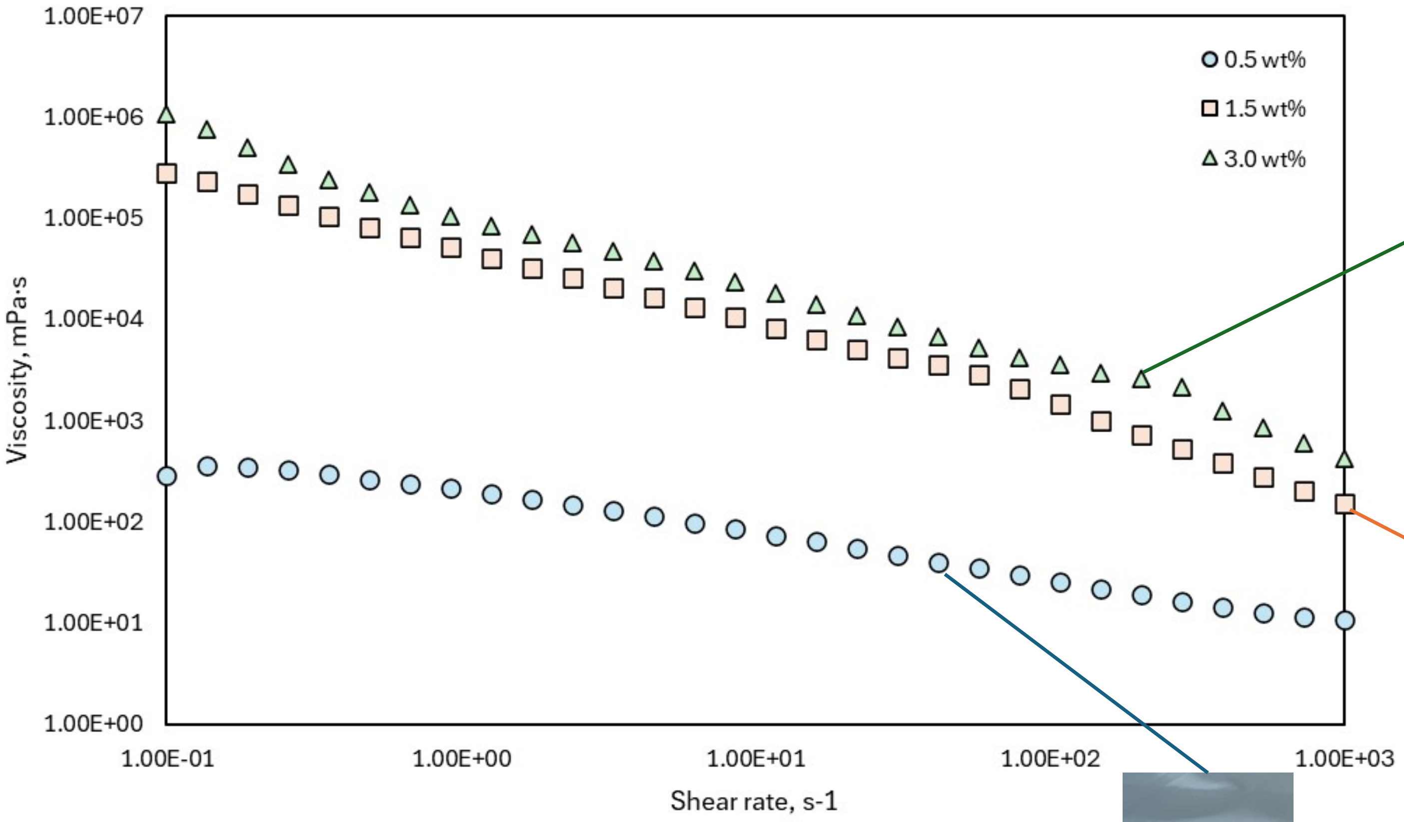

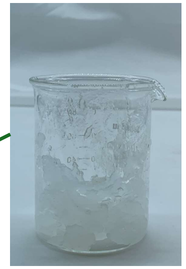

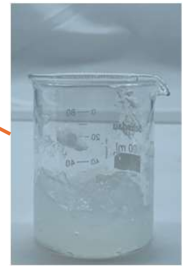

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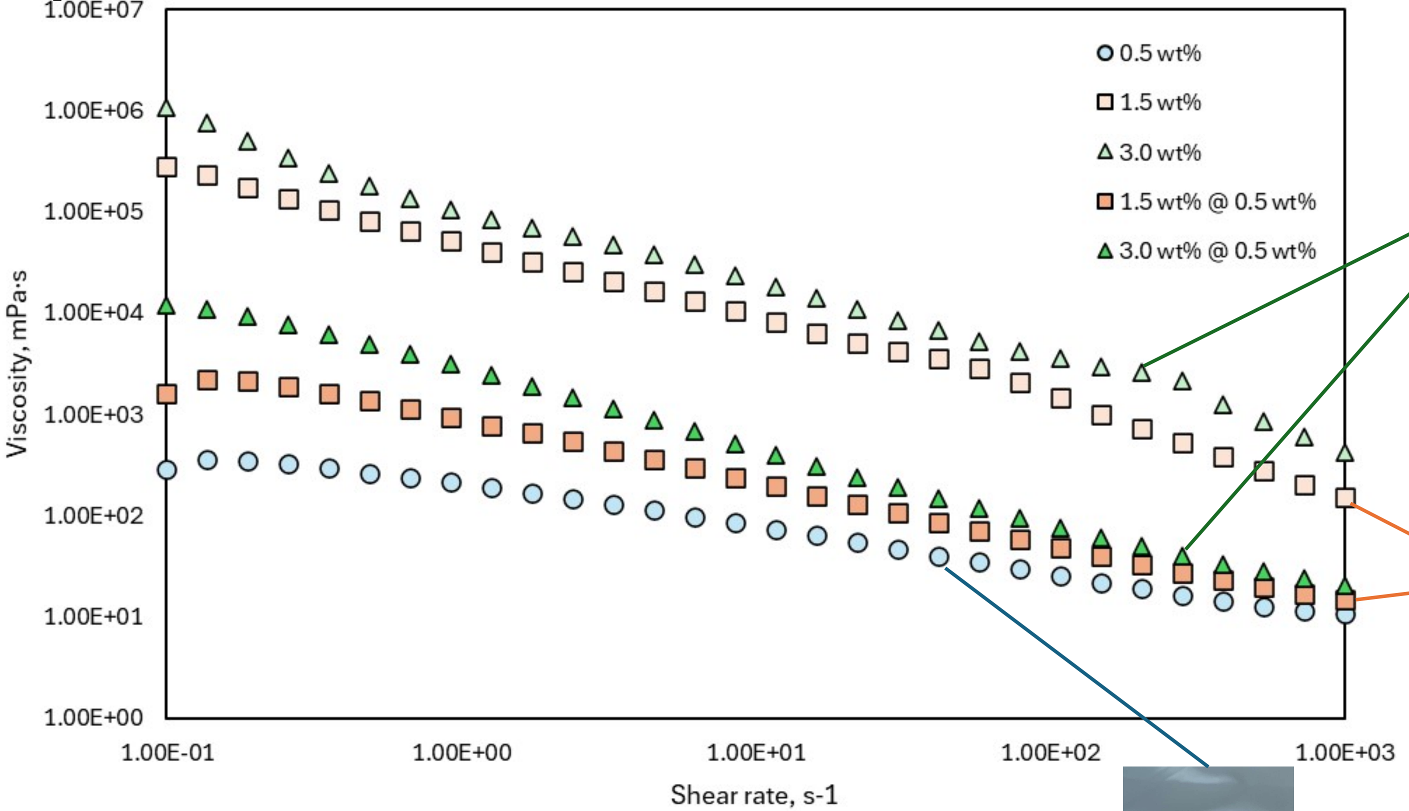

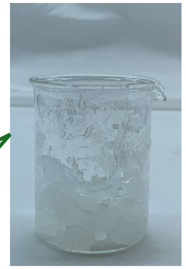

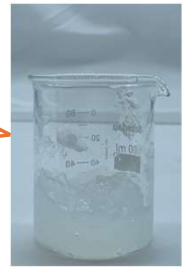

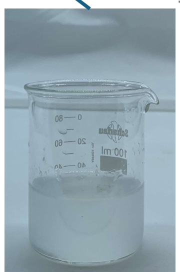

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Signori-Iamin et al (2025). Chemical Engineering Journal 509, 161257

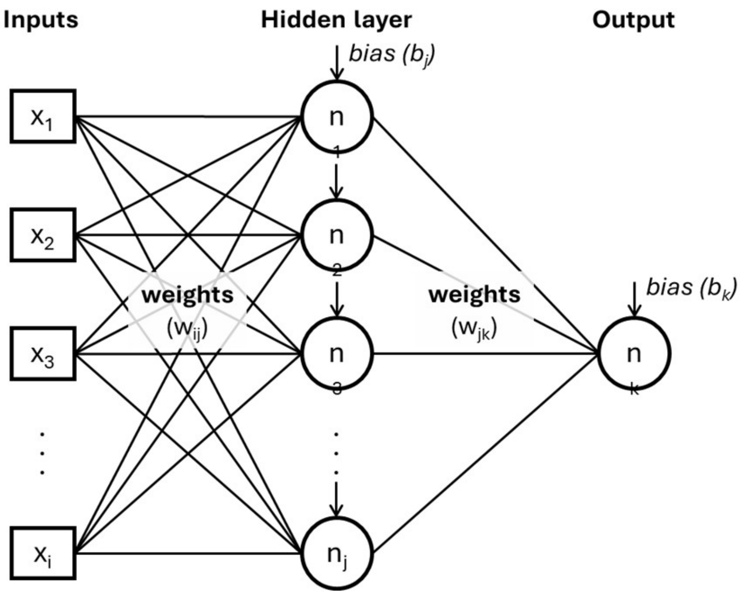
Credits to Gabriela Bastida and Giulia Herbst

TACIT KNOWLEDGE

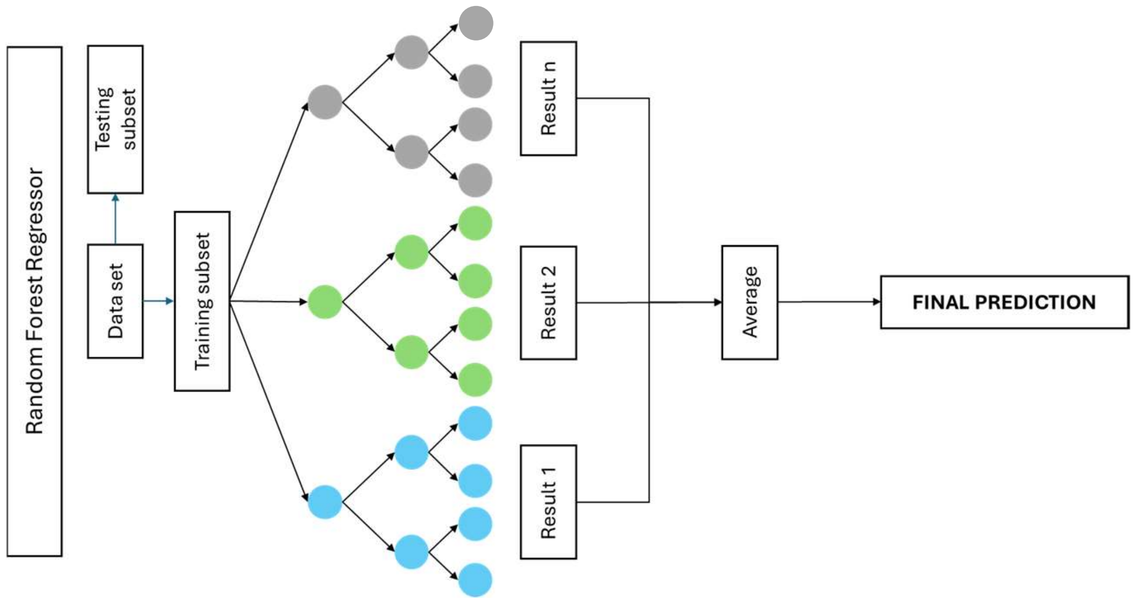
EXPLICIT KNOWLEDGE

Understanding the transition from micro to nano: energy and property implications

Artificial Neural Network
ANN



Random Forest
RF



Understanding the transition from micro to nano: energy and property implications

Selecting the outputs: **aspect ratio** & yield of fibrillation

Database (only mechanically obtained CMNFs):

- Pine TMP.
- Pine USKP.
- Pine BKSP.

Training

- Spruce BTMP.
- Eucalyptus BKHP.
- Aspen pulp.
- Hemp pulp.
- Sisal pulp.

Validation

Available inputs:

1	HPH - Energy consumption (kWh/kg)	11	Consistency (wt.%)
2	Length weighted in length (µm)	12	Cationic demand (µeq/g)
3	Diameter (µm)	13	Carboxyl content (µeq/g)
4	Fines (%)	14	Transmittance at 600 nm ()
5	Cellulose (wt.%)	15	Aspect ratio
6	Hemicellulose (wt.%)	16	Yield of nanofibrillation ()
7	Insoluble lignin (wt.%)		
8	Soluble lignin (wt.%)		
9	Consistency index "k"		
10	Flow index "n"		

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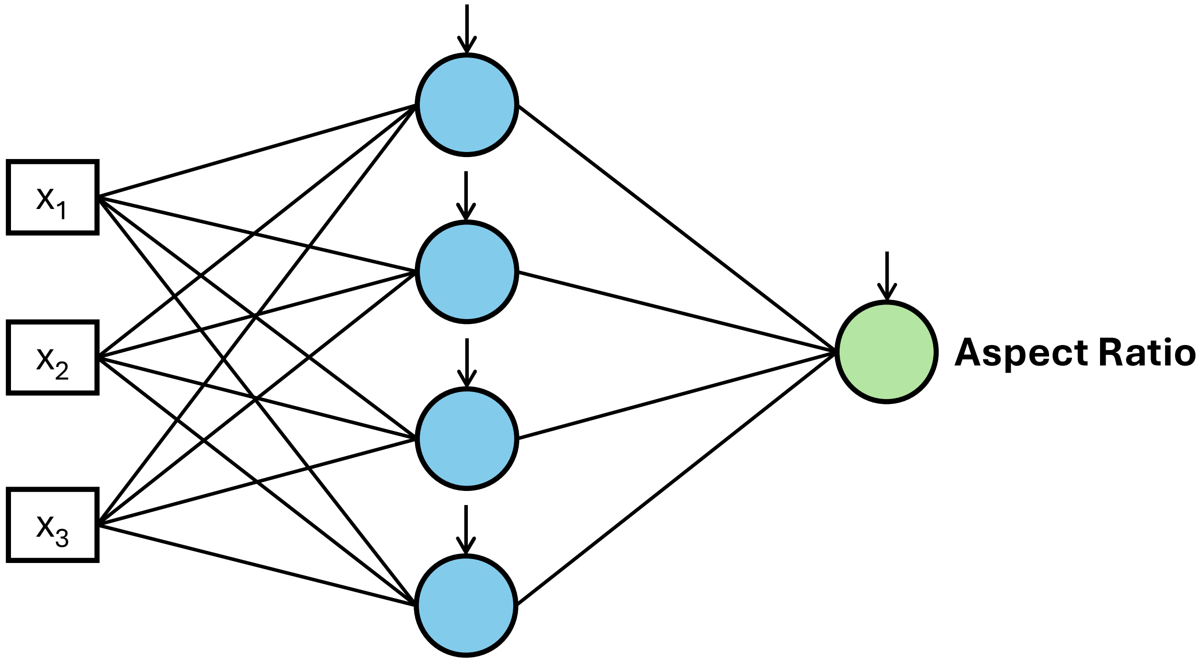
Santos et al (2022). Cellulose 29, 5609-5622

Understanding the transition from micro to nano: energy and property implications

Determining the relevance of each input:



Combinations of 3 inputs (out of 14) looking for the lowest MSE.

$$MSE = \frac{1}{N}\sum_{j=1}^{n}\left(y_j - \widehat{y_j}\right)^2$$

The best prediction results among 364 possibilities.

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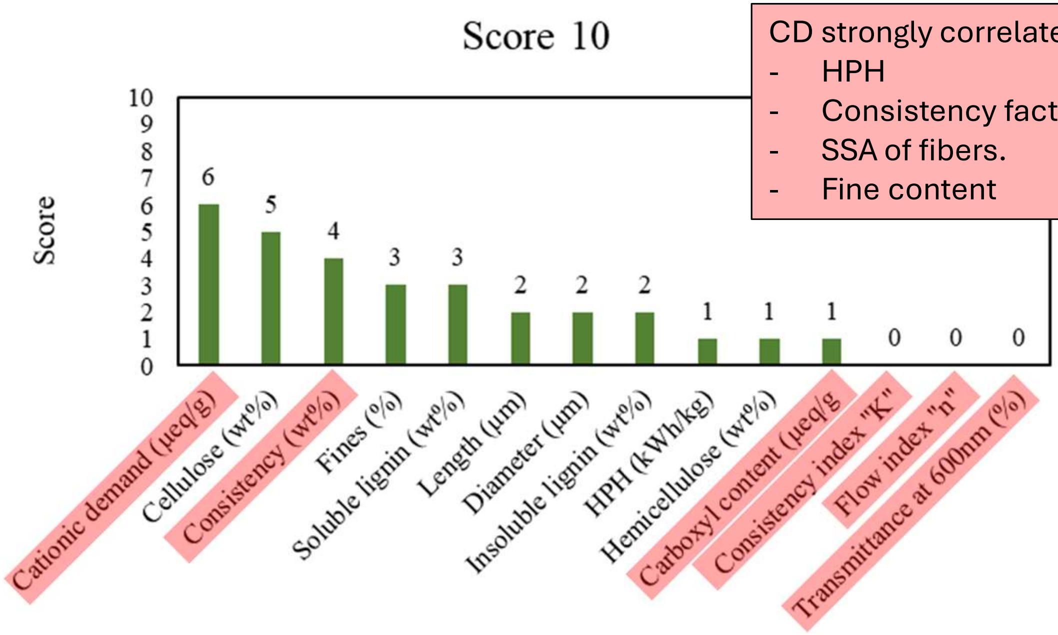
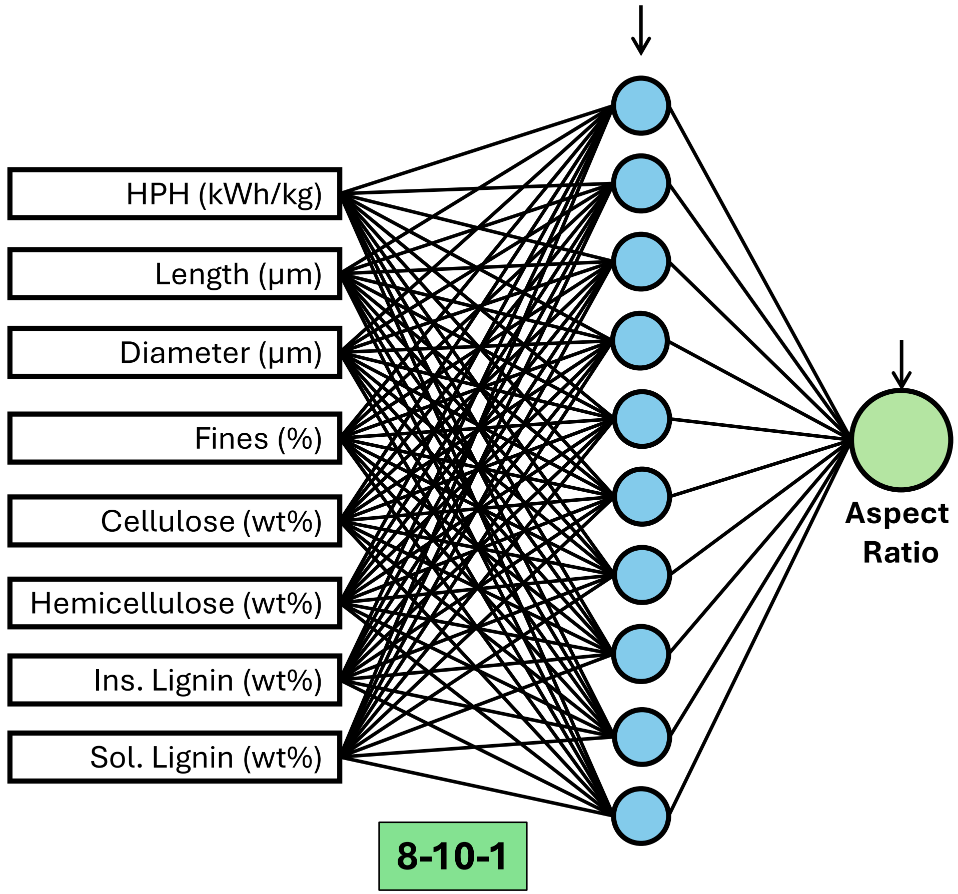


CD strongly correlated to:
- HPH
- Consistency factor “K”
- SSA of fibers.
- Fine content



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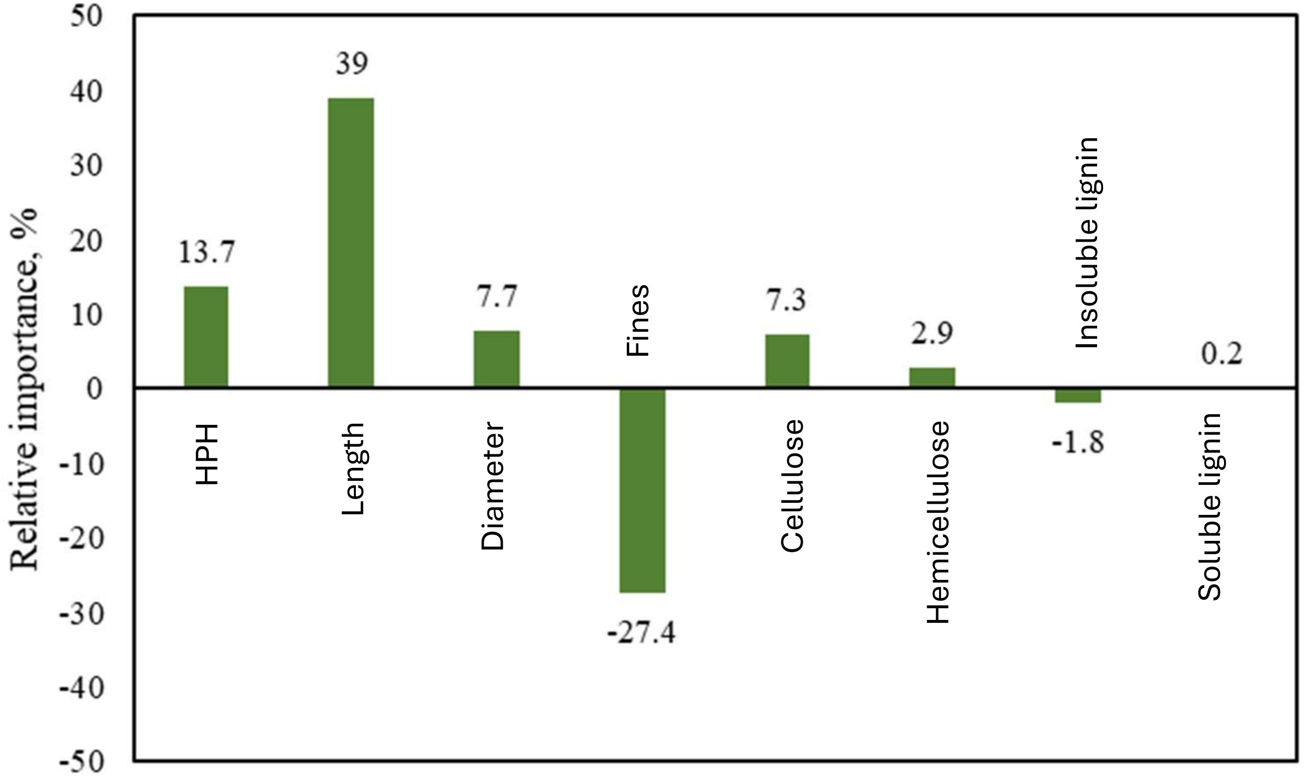

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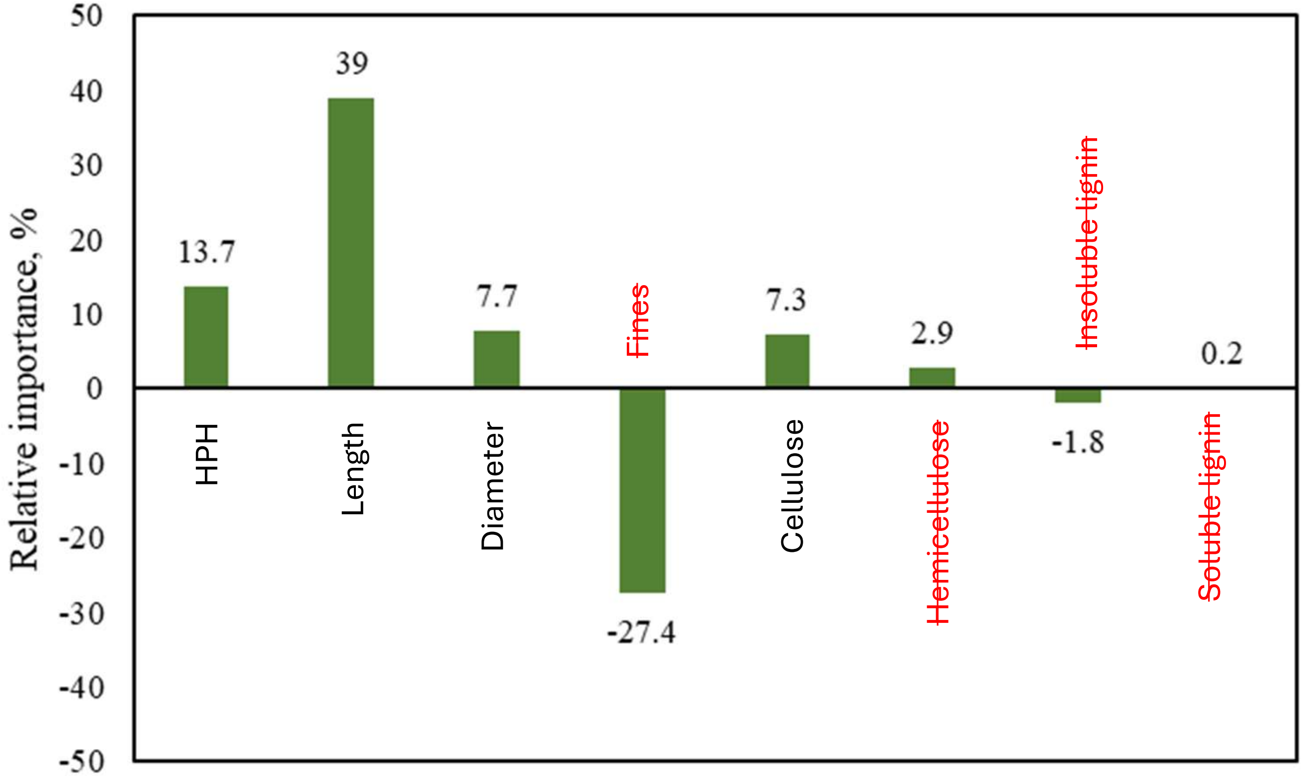

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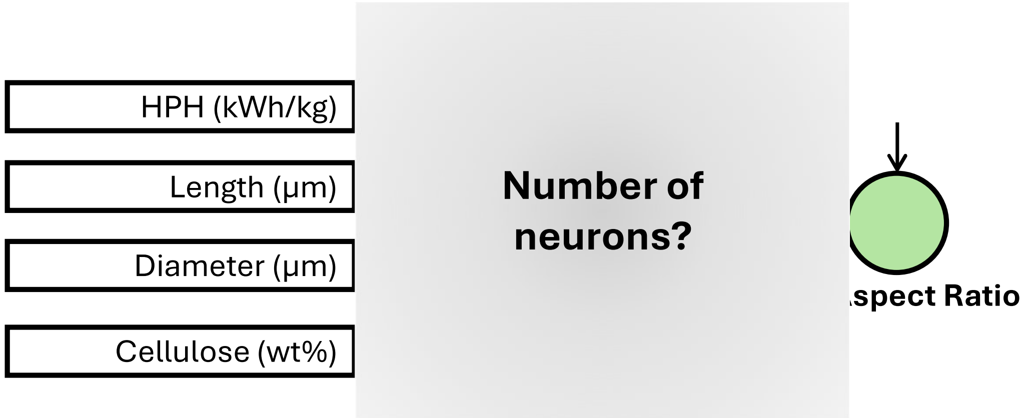

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Understanding the transition from micro to nano: energy and property implications

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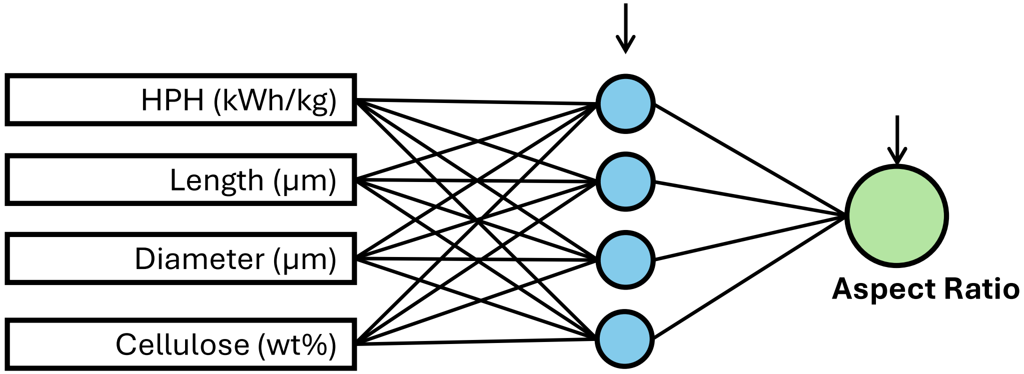


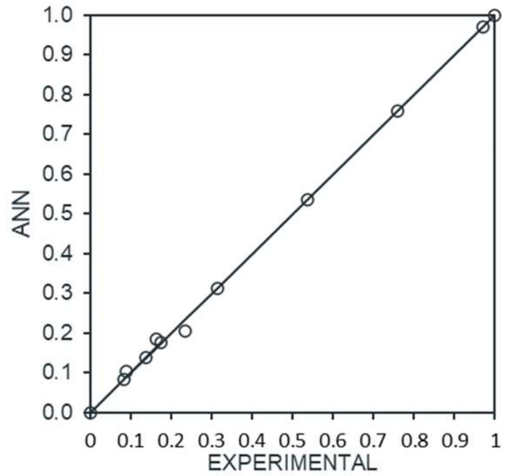
Model	MSE	R_train	R_val	R_test
4-6-1	$4.14 \cdot 10^{-3}$	0.9981	0.9918	0.9876
4-4-1	$5.43 \cdot 10^{-4}$	0.9993	0.9989	0.9984
4-3-1	$2.42 \cdot 10^{-5}$	0.9997	0.9995	0.9988
4-2-1	$4.72 \cdot 10^{-4}$	0.9979	0.9991	0.9986
4-1-1	$2.72 \cdot 10^{-3}$	0.9920	0.9946	0.9887

Heuristic rules and/or recommendations:

1. Neurons ≥ Inputs.
2. Minimize error.

Pine dataset

(training)



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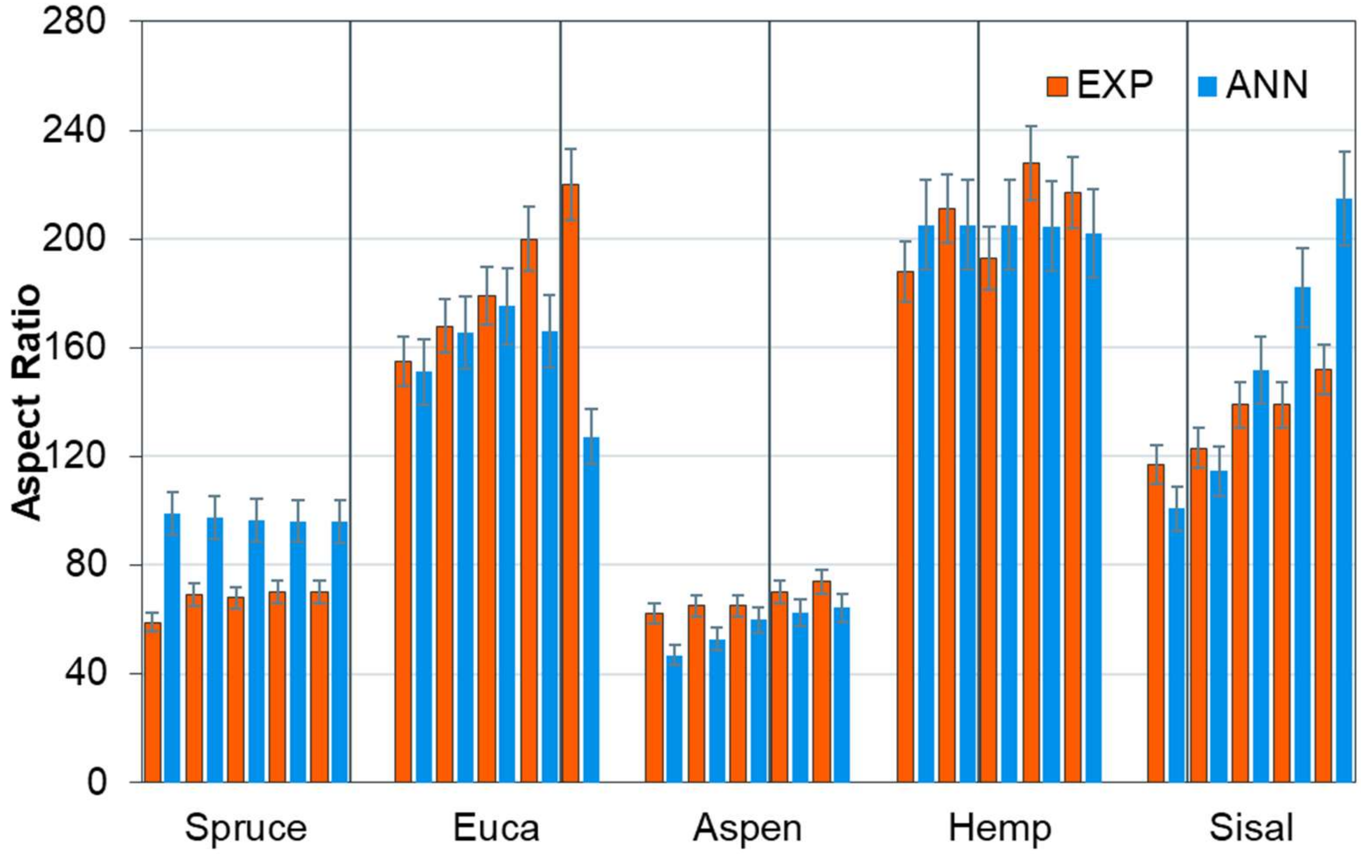

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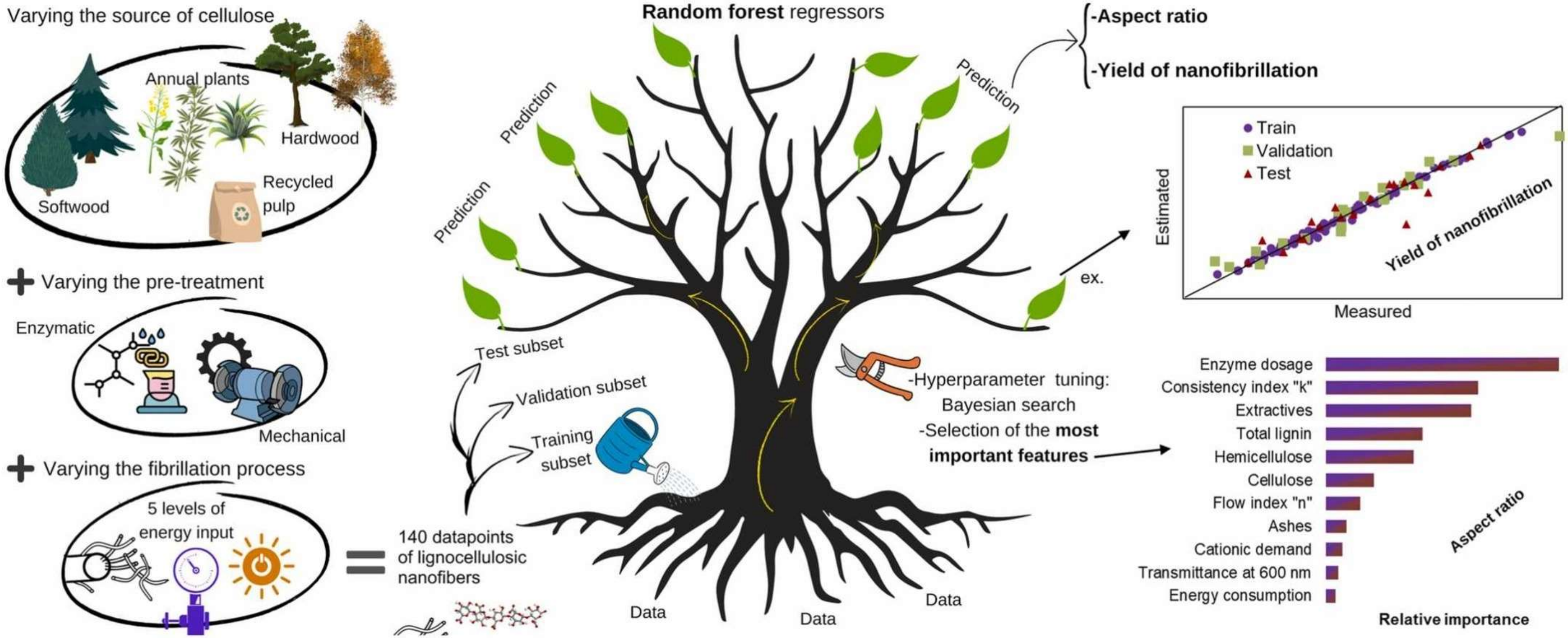

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Signori-Iamin et al (2023). Industrial Crops and Products 206, 117719

Understanding the transition from micro to nano: energy and property implications

Selecting the outputs: **aspect ratio** & **yield of fibrillation**

Database (only mechanically obtained CMNFs):

- Pine TMP.
- Pine UKSP.
- Pine BKSP.
- Spruce BTMP.

4 raw materials (20 datapoints)
+
Mechanical pretreatment
+
5 levels of high-pressure homogenization

Available inputs:

1	HPH - Energy consumption (kWh/kg)	11	Transmittance at 600 nm ()
2	Cellulose (wt.%)	12	Aspect ratio
3	Hemicellulose (wt.%)	13	Yield of nanofibrillation (%)
4	Total lignin (wt.%)		
5	Ashes (wt.%)		
6	Extractives (wt.%)		
7	Crystallinity index		
8	Consistency index "k"		
9	Flow index "n"		
10	Cationic demand (μeq/g)		

Limited to 3-5 inputs

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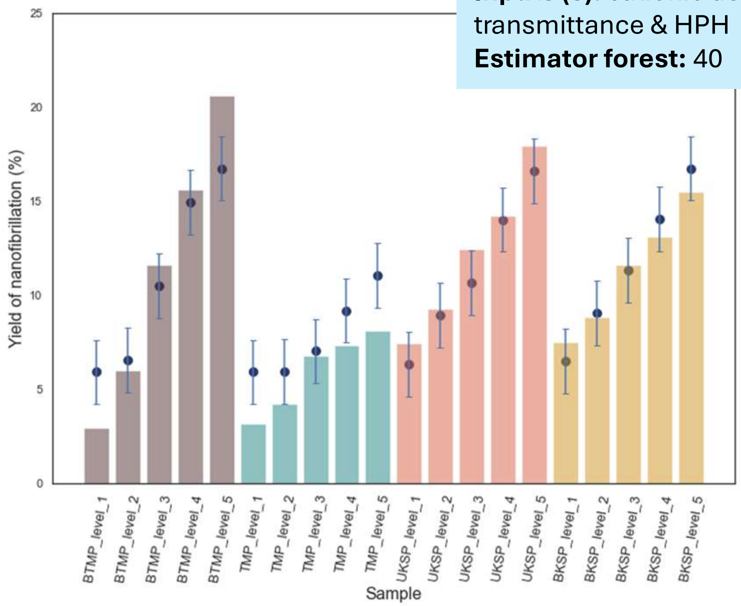
Signori-Iamin et al (2022). Cellulose 29, 9143-9162

Understanding the transition from micro to nano: energy and property implications

Yield of fibrillation

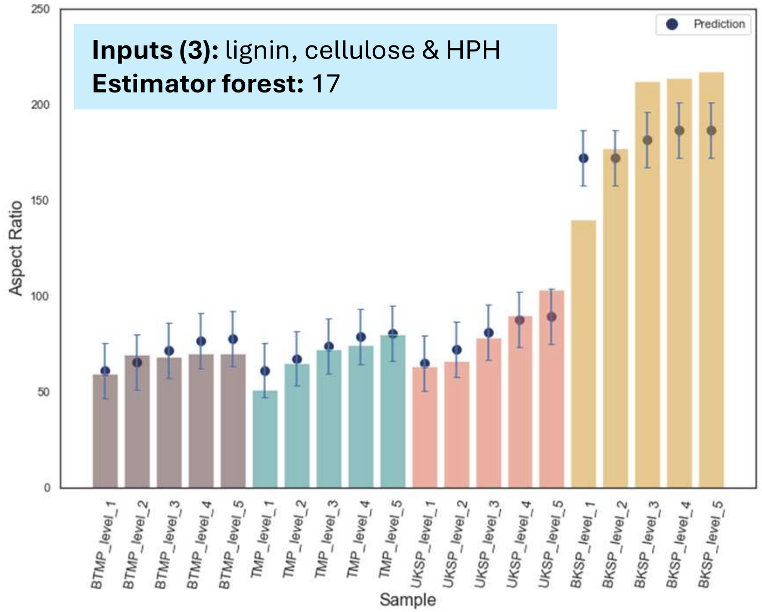
Inputs (3): cationic demand, transmittance & HPH
Estimator forest: 40



MAE	RMSE	MAPE	R^2
1,358	1,712	20,79%	0,8720

Aspect ratio

Inputs (3): lignin, cellulose & HPH
Estimator forest: 17



MAE	RMSE	MAPE	R^2
9,760	14,448	8,18%	0,9313

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Signori-Iamin et al (2022). Cellulose 29, 9143-9162

Content

- Cellulose nanomaterials (CNMs): categorization, applications, and complexity.
- Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment.
- Understanding the transition from micro to nano: energy and property implications.
- Concluding remarks.

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- Pre-treatment: real-time monitoring of TEMPO-mediated oxidation and enzymatic pretreatment.
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- Concluding remarks.

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Concluding remarks

- Cellulose (and lignocellulose) is an heterogeneous material with a myriad of opportunities.
- The complexity of its structure hinders the implementation of typical real-time monitoring strategies.
- Kinetics, chemometrics, and machine learning will play a key role in the industrial deployment of high-performance cellulose-based materials.

- Understanding the fundamentals is crucial for exploiting the full potential of cellulose-based materials.
- We need to approach these kind of processes holistically: fundamentals, process engineering, and product.

- Collaboration is a must: any of these works would have been possible without the implication of scientists from many disciplines.

- We keep advancing on three main lines:
    - Understanding how process parameters can further enhance cellulose nanomaterial properties.
    - Decreasing uncertainty in production processes (enabling scaling-up!).
    - Applying optimization strategies (e.g. recycling streams).

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Agència de Gestió d'Ajuts Universitaris i de Recerca

AGAUR

Generalitat de Catalunya

Transitioning from Micro to Nano: Unlocking the Potential of Cellulose Nanomaterials

Prof. Marc Delgado-Aguilar
m.delgado@udg.edu
https://lepamap.udg.edu

Nanotechnology Webinar, TAPPI International Nanotechnology Division
Wednesday, June 4, 2025 (online)