Laboratório Nacional de Ciência e Tecnologia do Bioetanol

CNPEM

Pretreatment interactions with the multiscale architecture of sugarcane bagasse

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Workshop on Second Generation Bioethanol and Biorefining 2017
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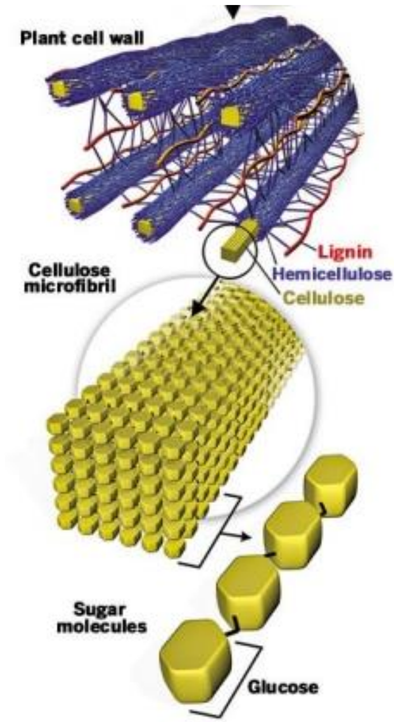
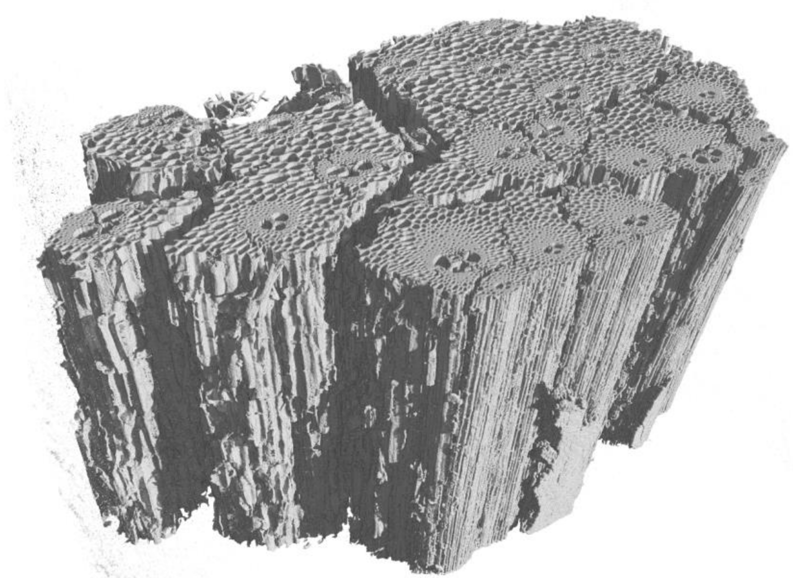
From macro to nano

100 μm – 1 cm	particle
100 μm – 1 mm	cell: length
5 – 100 μm	cell: diameter
1 – 4 μm	**cell wall:** thickness

≈3 nm: width of cellulose crystal, the cell wall building block.

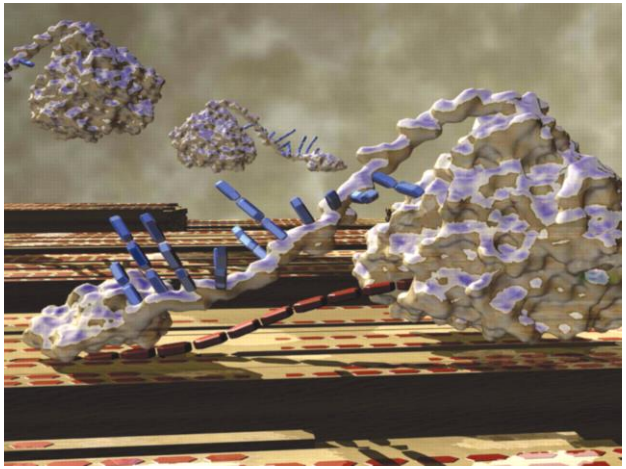




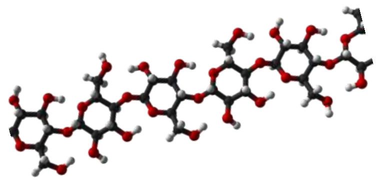
Microtomography of a bagasse particle

(Isaac, Sket, Driemeier & Rocha, 2013)

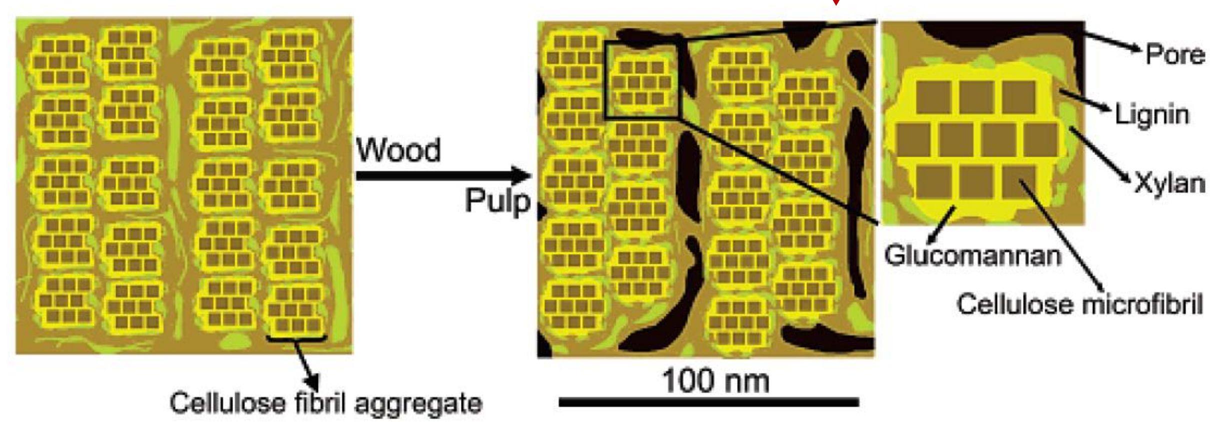
≈5 nm: enzyme



Lignocellulose hierarchical nanostructure

- molecule 
- cellulose crystal (3-5 nm width)
- fibrillar aggregate (10-40 nm width)
- lamella (10-40 nm thickness)
- cell wall thickness
- cell
- particle

How to deconstruct?



Fahlén and Salmén, 2005

Outline

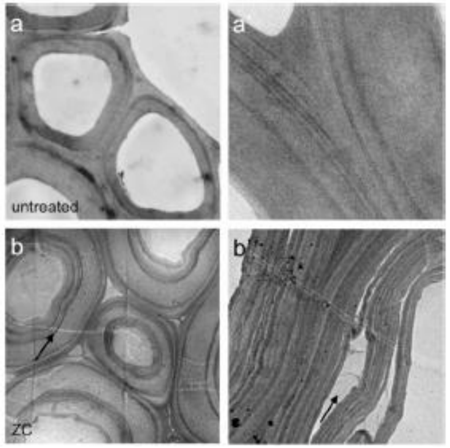
- Nano changes in hydrothermal pretreatments
- Nano changes in mild alkaline pretreatments
- Mineral particles observed by microtomography

Nano changes in hydrothermal pretreatments

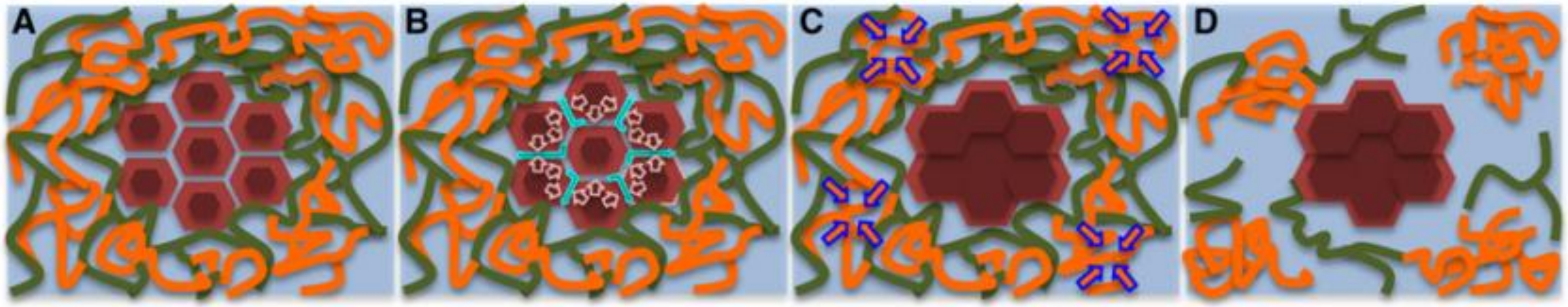
Opening of nanoscale pores

Cellulose co-crystallization

Lignin aggregation

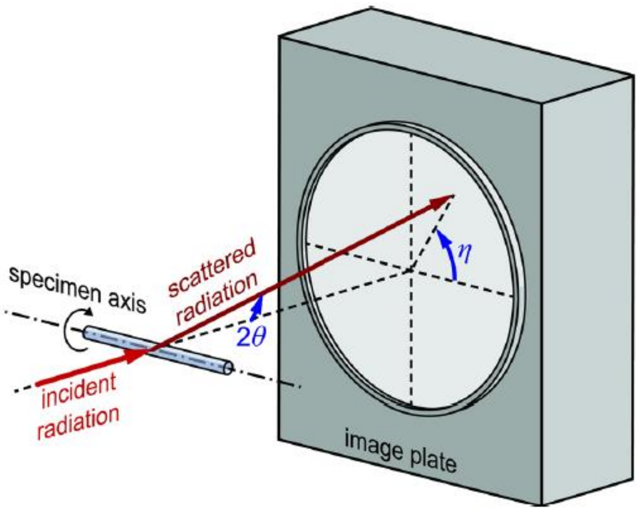


Ciesielski et al. 2014



Langan et al. 2014; Pingali et al. 2014

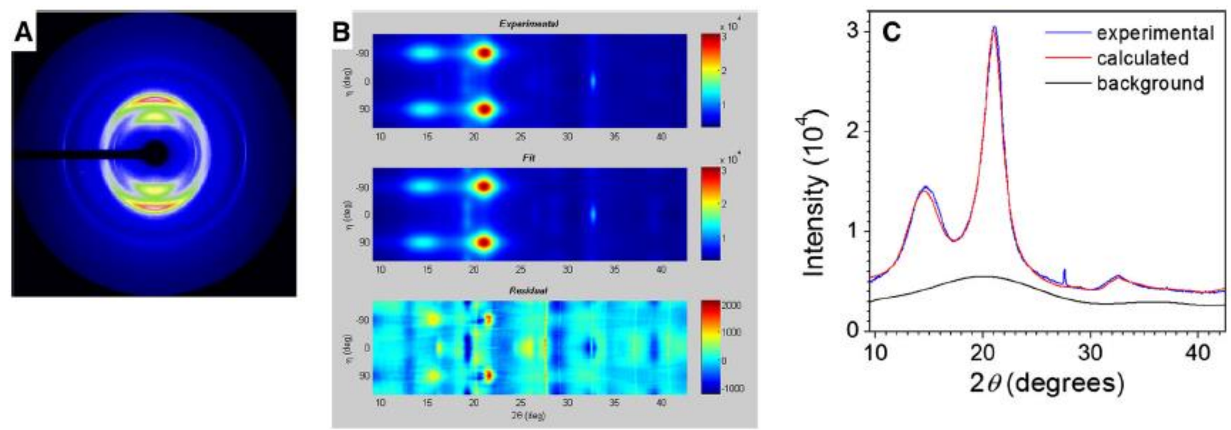
X-ray diffraction of sugarcane bagasse



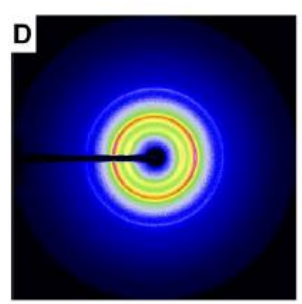
experimental
set-up

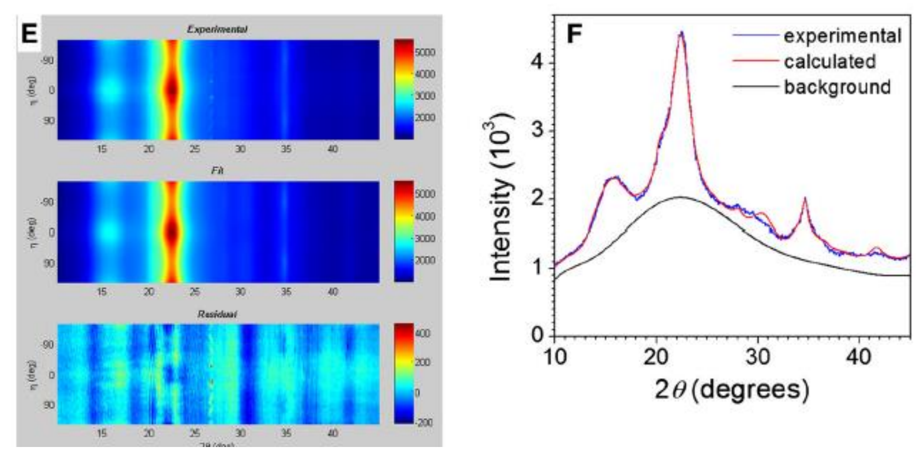
2D modelling

isolated particle



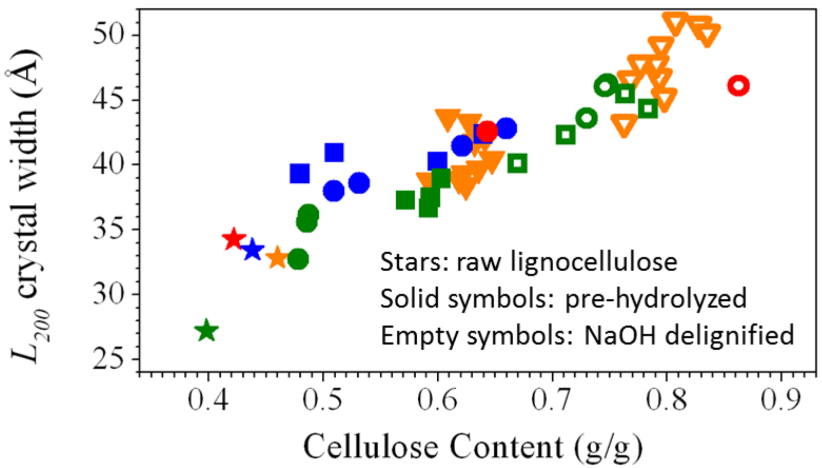
powder in capillary tube



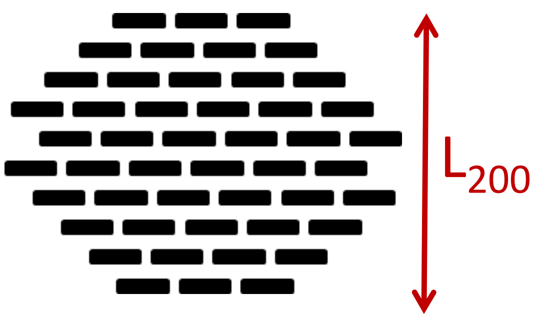


Driemeier 2014; Driemeier et al. 2015

Increasing cellulose crystal width (co-crystallization)

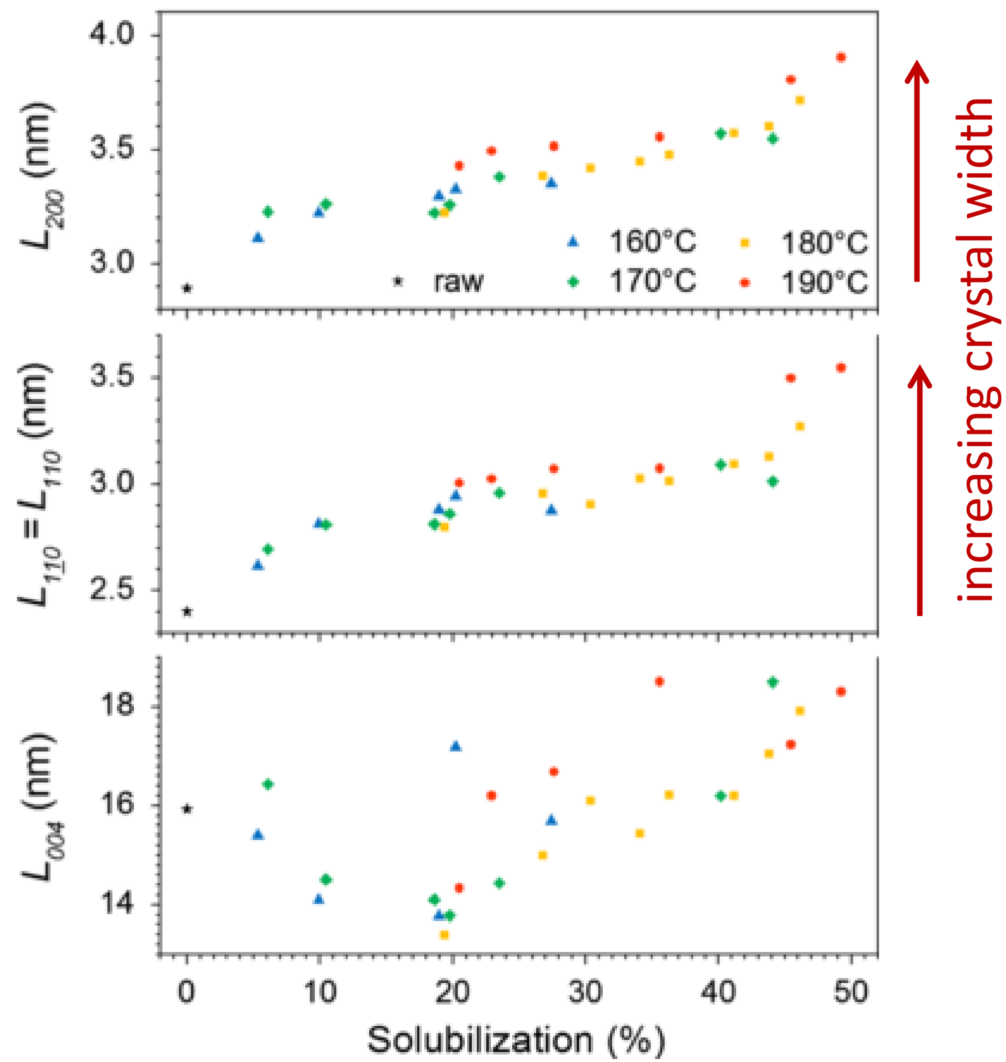


Driemeier, Pimenta, Rocha, et al. 2011



>width ⇒ >#cellulose chains

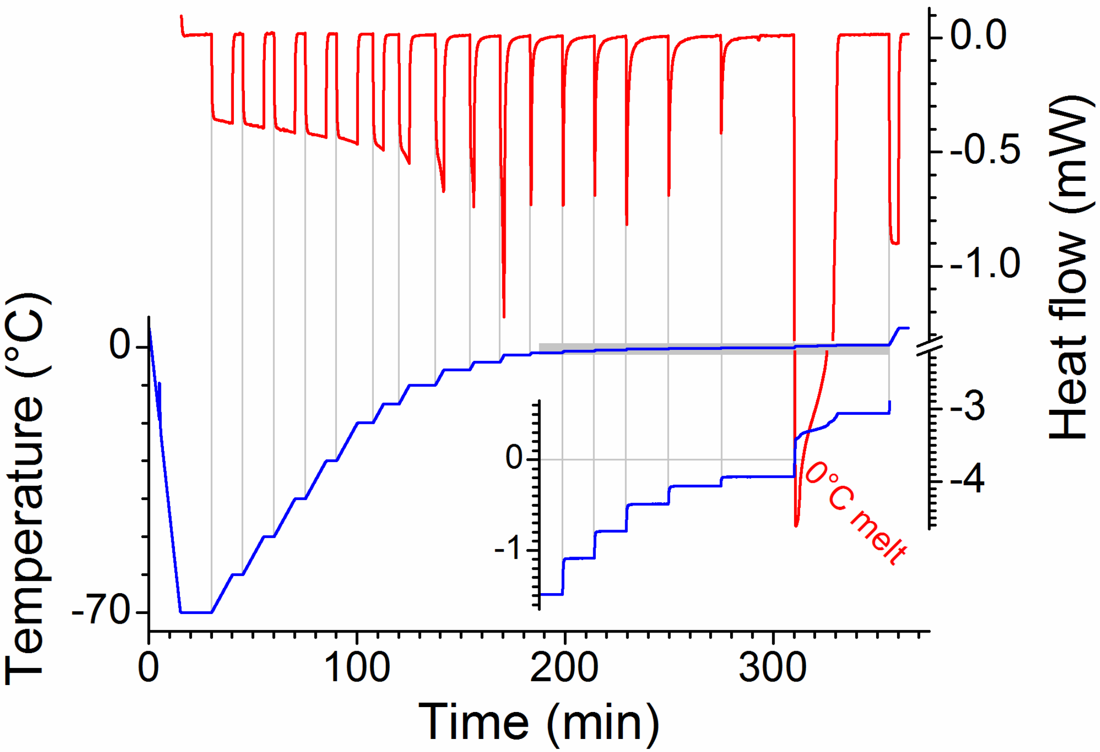
Hydrothermal treatments (160-190°C)



Driemeier, Mendes, Santucci, Pimenta 2015

Calorimetric thermoporometry determination of water in nano-confinement

Driemeier, Mendes, Oliveira 2012

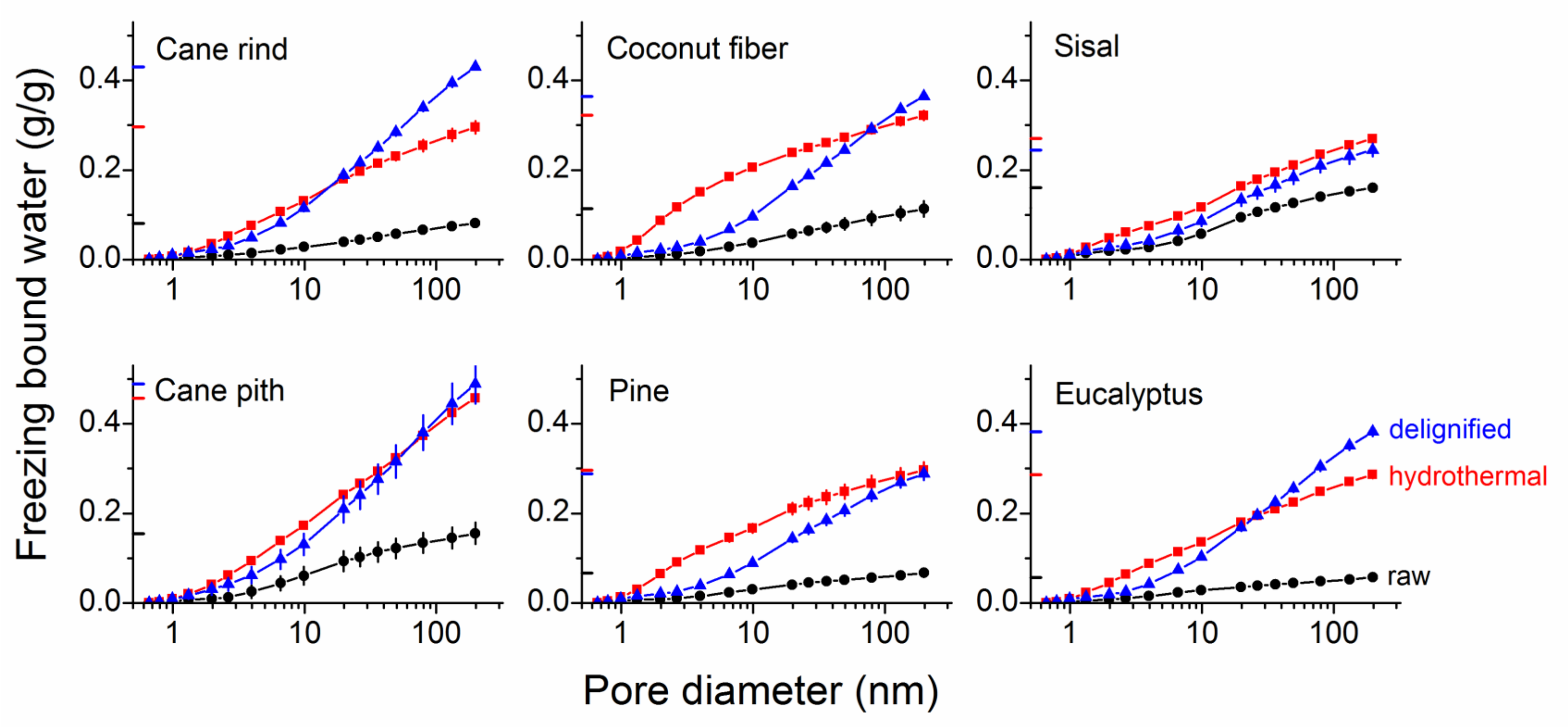


Principle: melting of confined ice

temperature → pore diameter

heat → mass of confined ice

Hydrothermal, delignification, and porosity



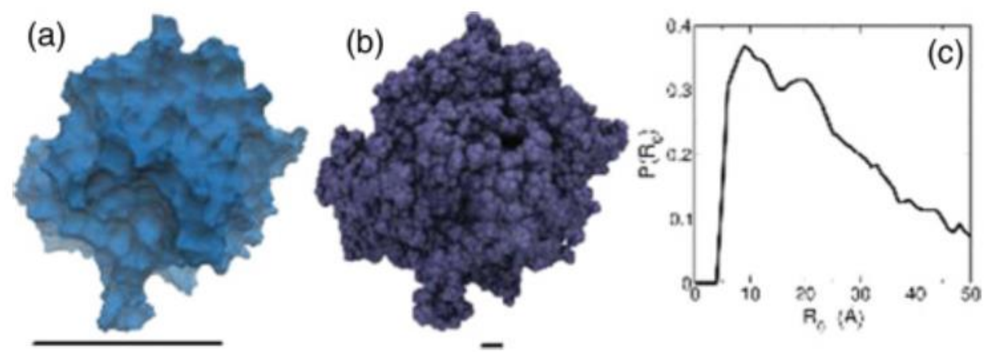
Driemeier, Oliveira, Curvelo 2016

Hydrothermal and delignification increase nano porosity.

Hydrothermal has thermoporometric signature (@ FBW <4 nm).

lignin ↔ pores <4 nm

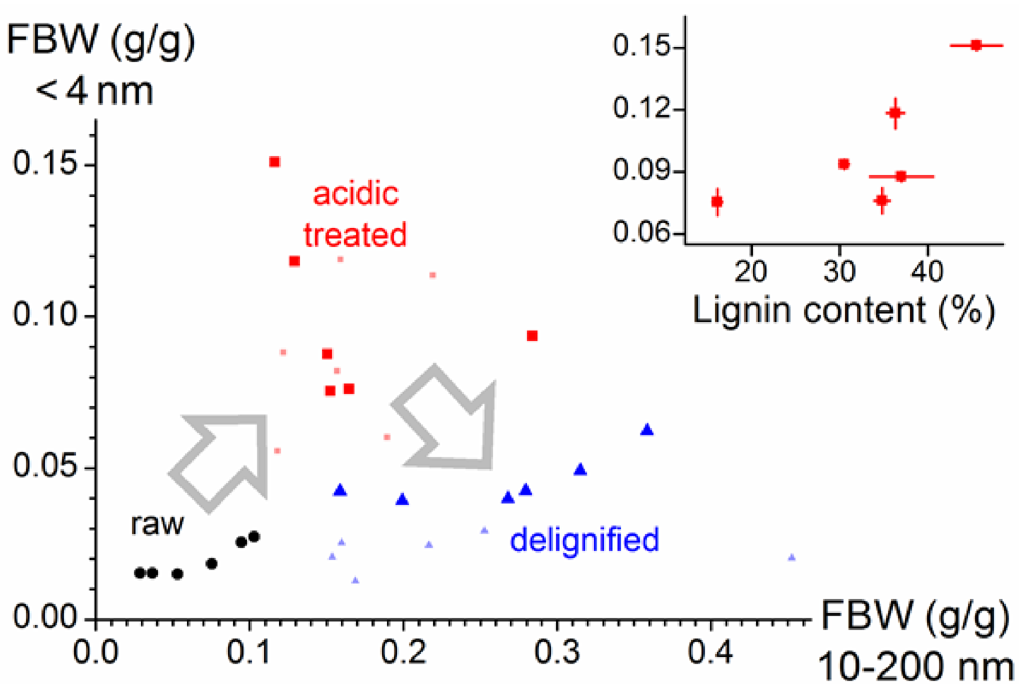
Nano-irregularities at the surface of lignin aggregates



Petridis et al. 2011

Porosity <4 nm:

- correlated with lignin content
- removed by delignification



Driemeier, Oliveira, Curvelo 2016

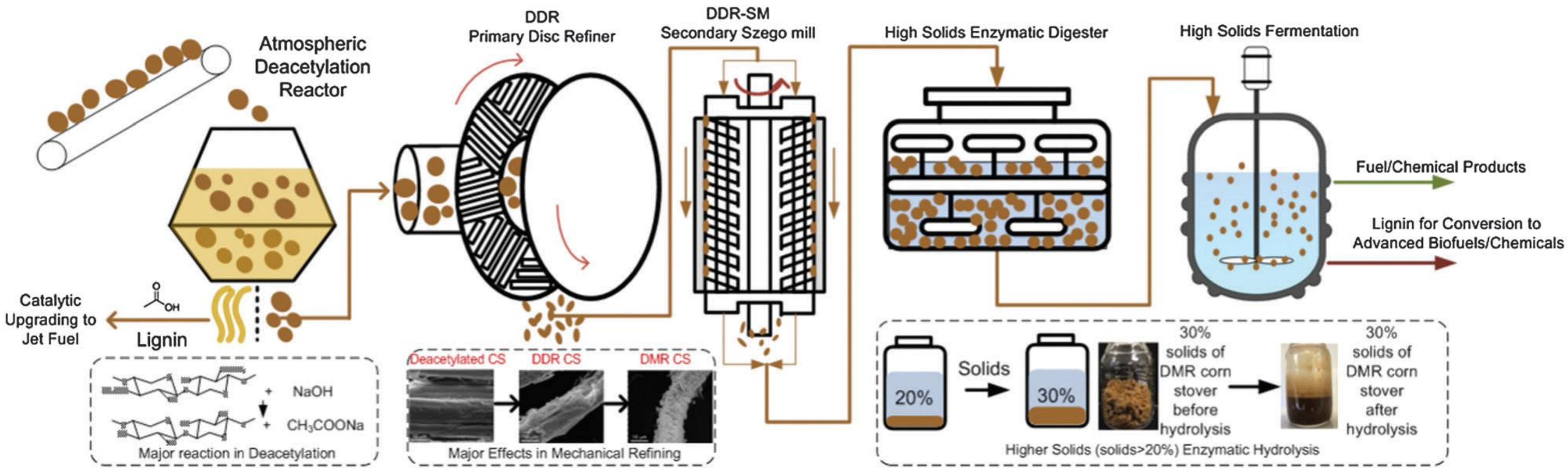
Outline

- Nano changes in hydrothermal pretreatments
- Nano changes in mild alkaline pretreatments
- Mineral particles observed by microtomography

Limits of hydrothermal pretreatments
(similar for dilute acid!)

- Water only – no catalyst recovery
- Reactor high CAPEX
- Reactor complex operation
- Liquor toxicity
- Lignin condensation
- Nanoscale cohesion

DDR/DMR route for cellulosic ethanol



Mild chemistry

0.4% m/m NaOH, 2h, 80C

Atmospheric pressure

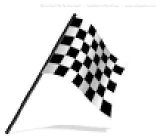
Specialized mechanics

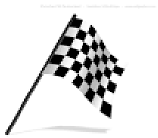
1) Disk refining (cut and shear)
2) Moinho Szego (crush)

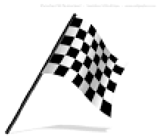
Chen X, Kuhn E, Jennings EW, et al (2016) Energy Environ Sci. doi: 10.1039/C5EE03718B

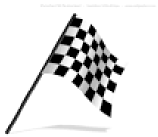
Alkaline deacetylation in comparison

 NaOH recovery

 Reactor high CAPEX

 Reactor complex operation

 Liquor toxicity

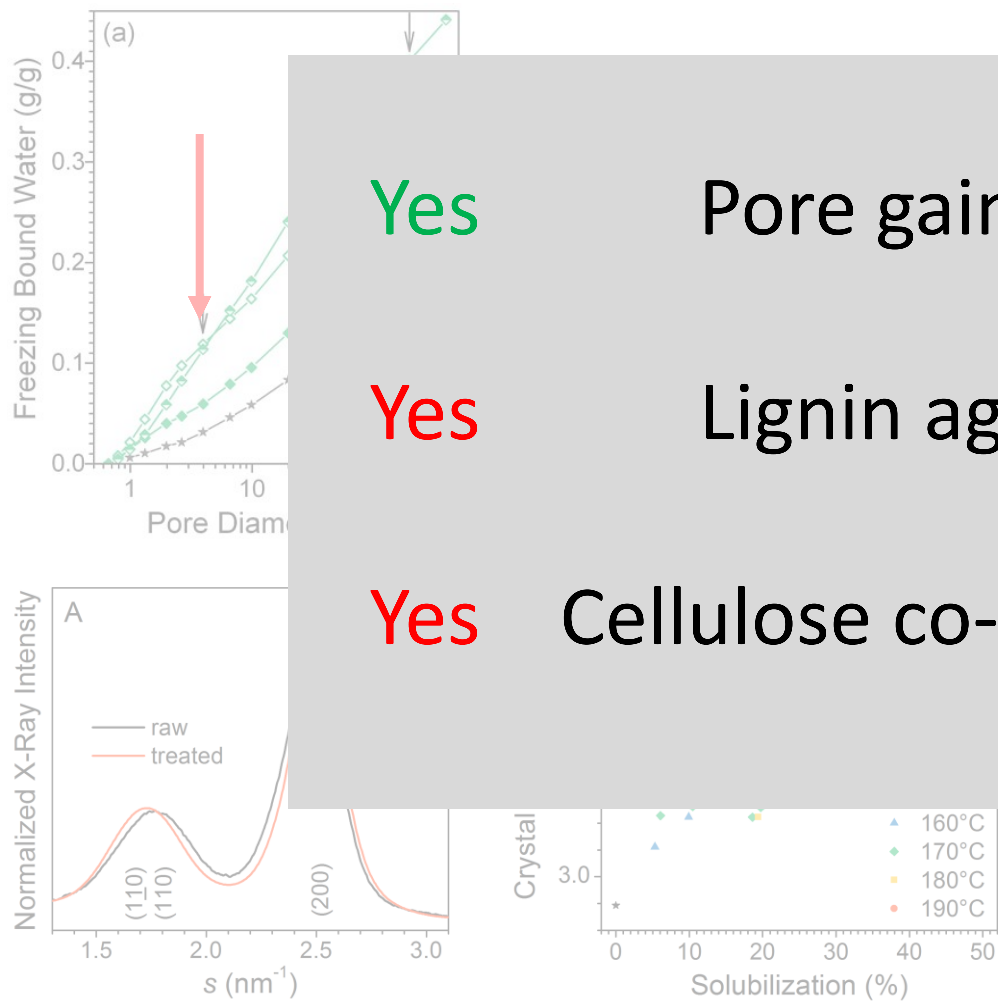
 Lignin condensation

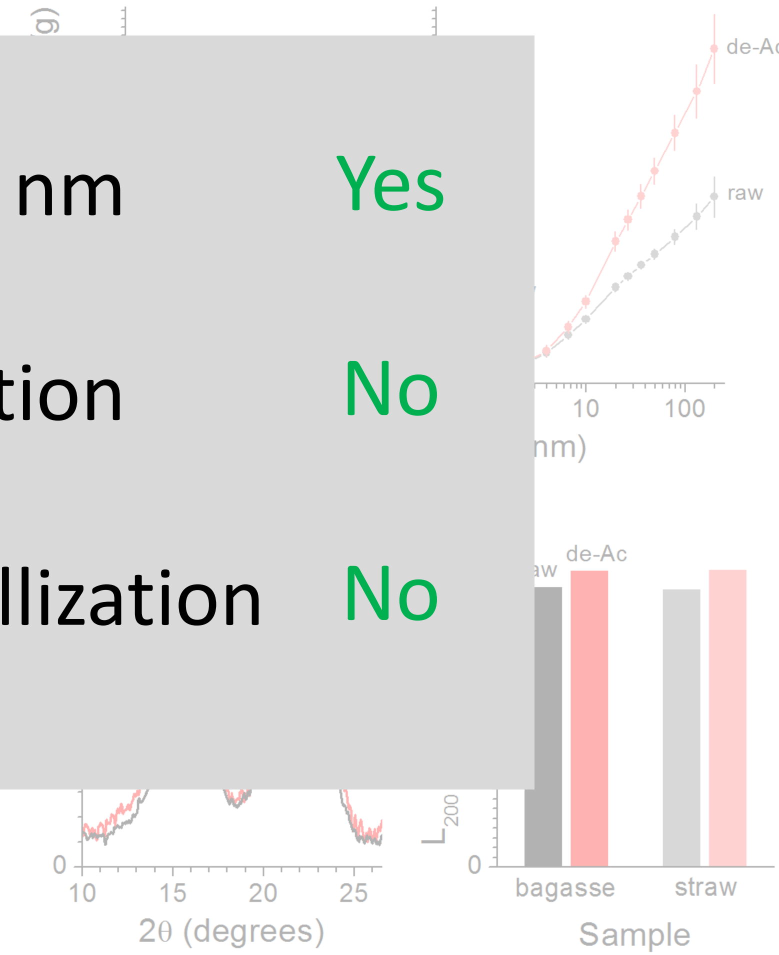
 Nanoscale cohesion

Comparing nano changes

Hydrothermal

Alkaline deacetylation





Hydrothermal		Alkaline deacetylation
Yes	Pore gains >10 nm	Yes
Yes	Lignin aggregation	No
Yes	Cellulose co-crystallization	No

Driemeier, Mendes, Santucci, Pimenta 2015

Lima, Rabelo, Ciesielski, Roberto, Rocha, Driemeier (submitted)

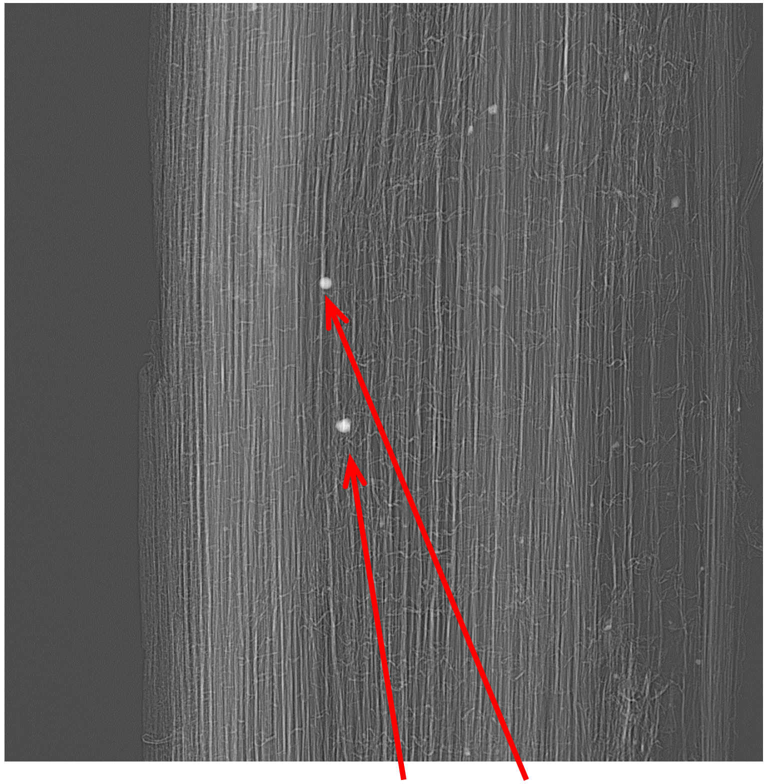
Outline

- Nano changes in hydrothermal pretreatments
- Nano changes in mild alkaline pretreatments
- Mineral particles observed by microtomography

Mineral particles in bagasse

Exposure: 200-350 ms,
1001 projections
Voxel 0.82 µm
F. View: 1.6 mm

X-ray projection

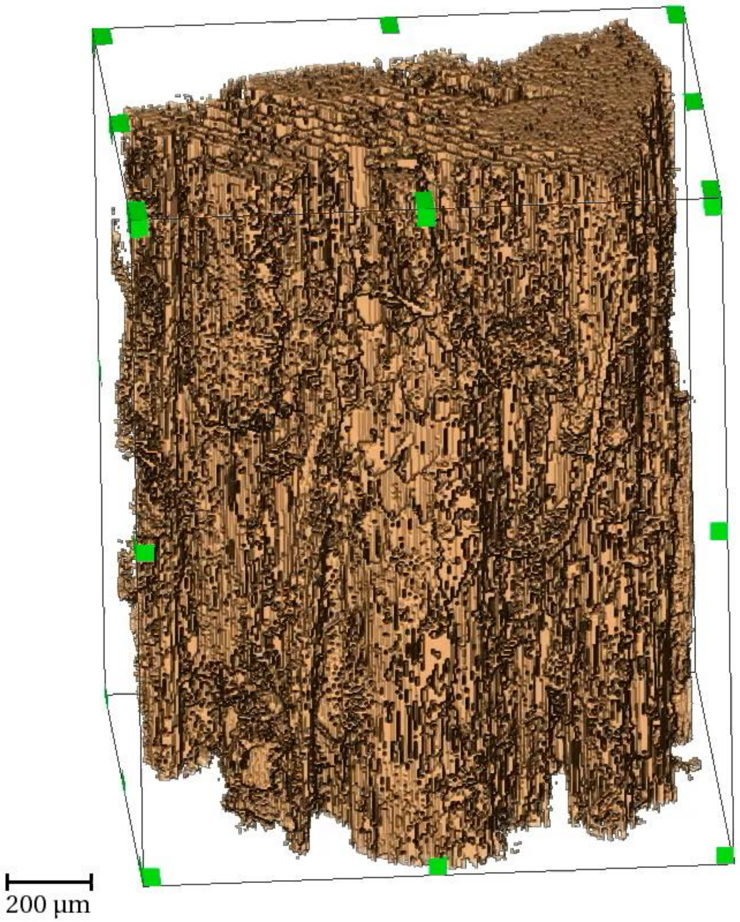


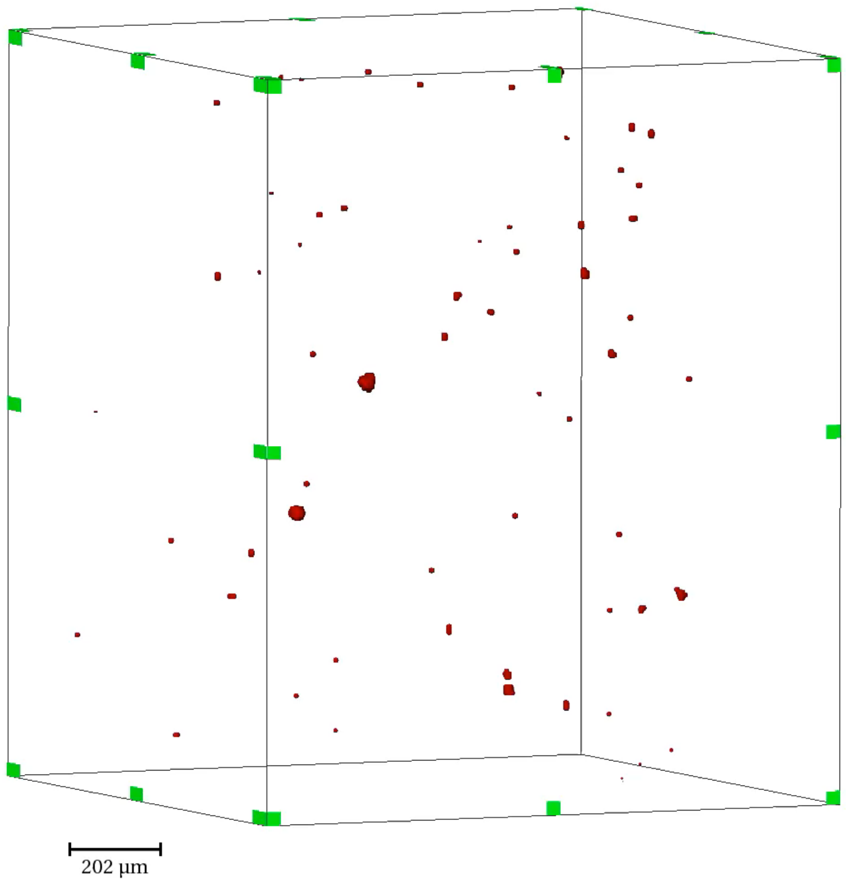
Mineral particles

Screw feeder

Reactor @ CTBE pilot plant

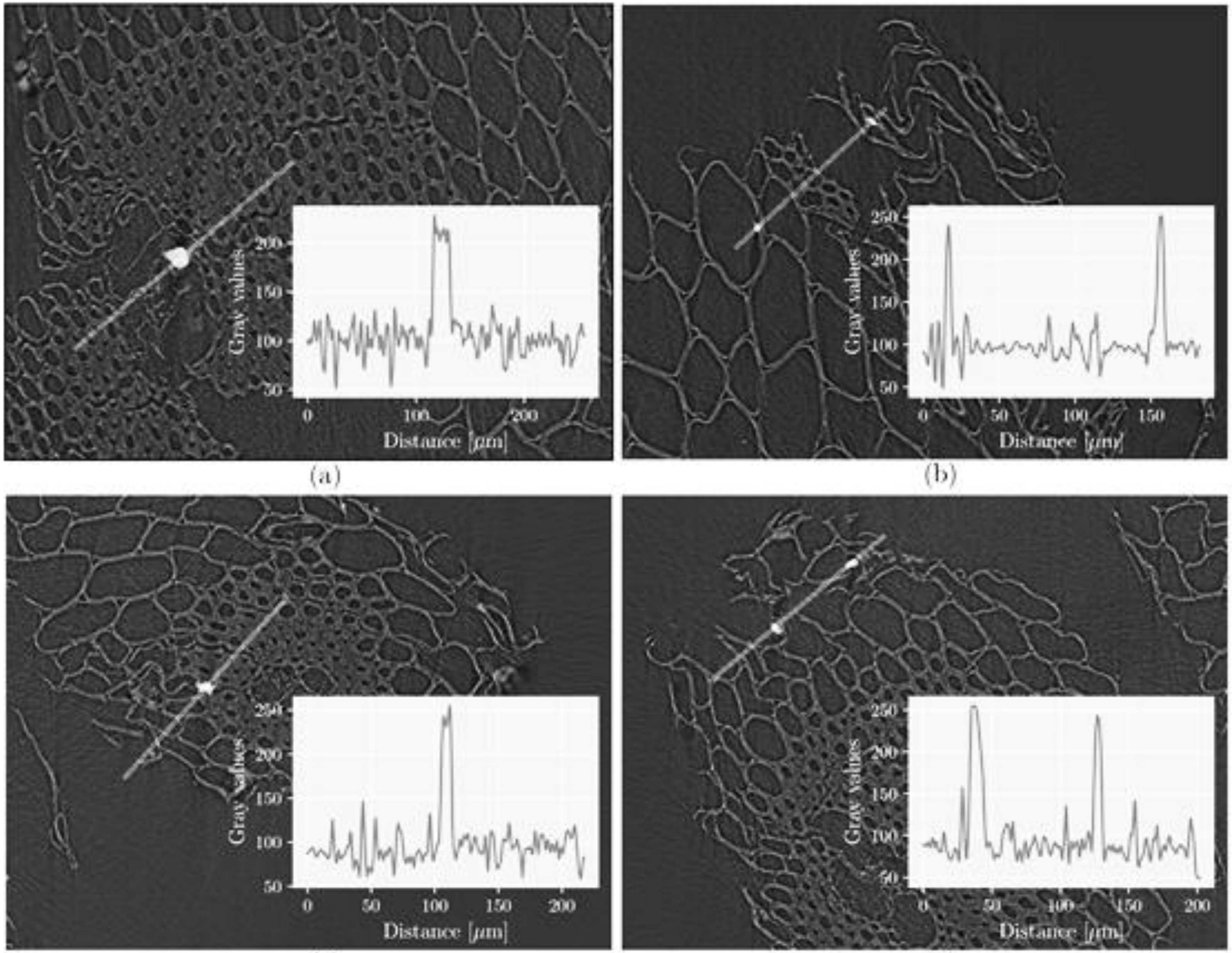
3D visualization: minerals in bagasse





Caballero, Ling, Archilha, Ferreira, Driemeier (2017)

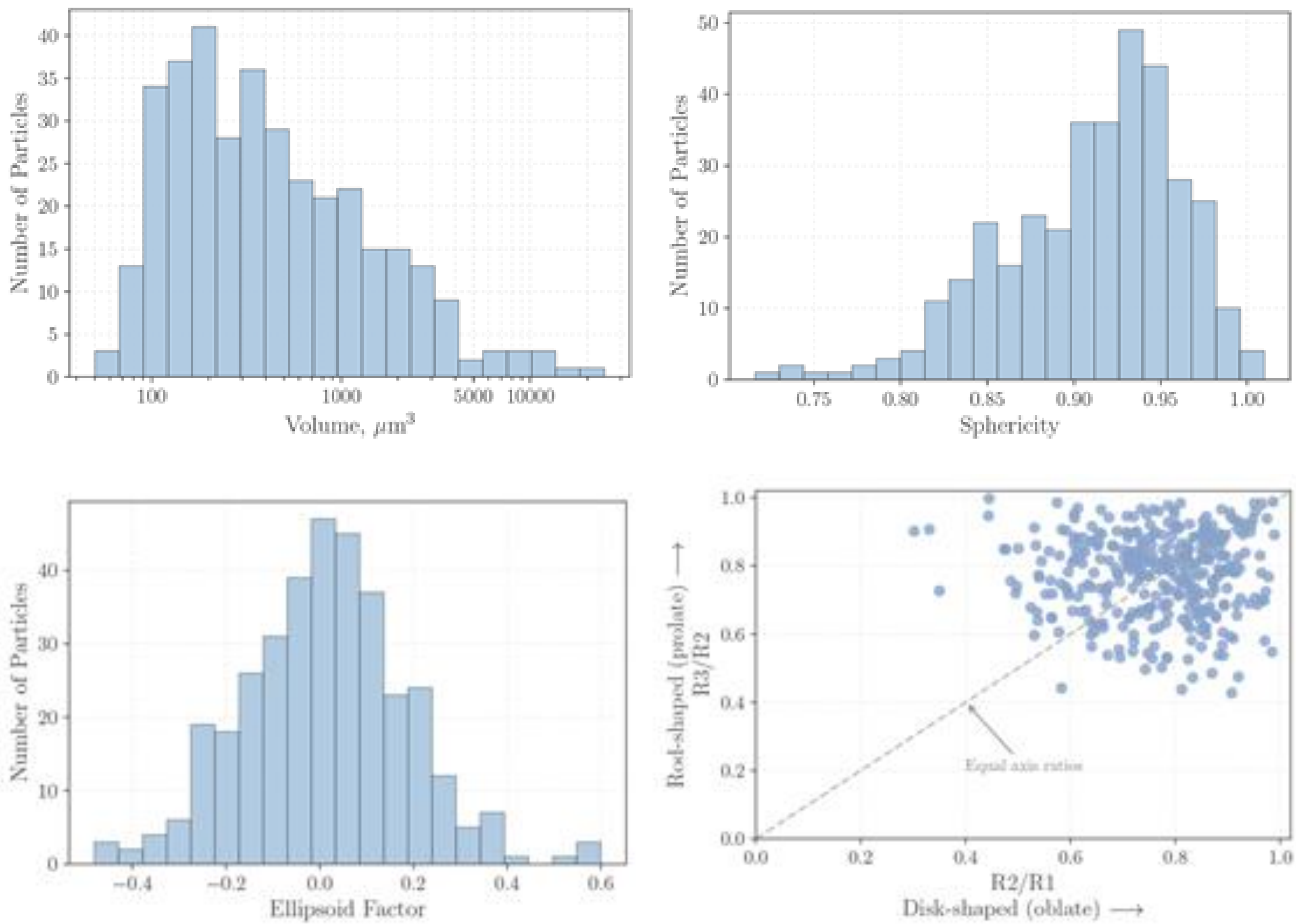
Particle cross-section



(a) (b) (c) (d)

Caballero, Ling, Archilha, Ferreira, Driemeier (2017)

Mineral particle morphometry



Caballero, Ling, Archilha, Ferreira, Driemeier (2017)

Mineral particle localization

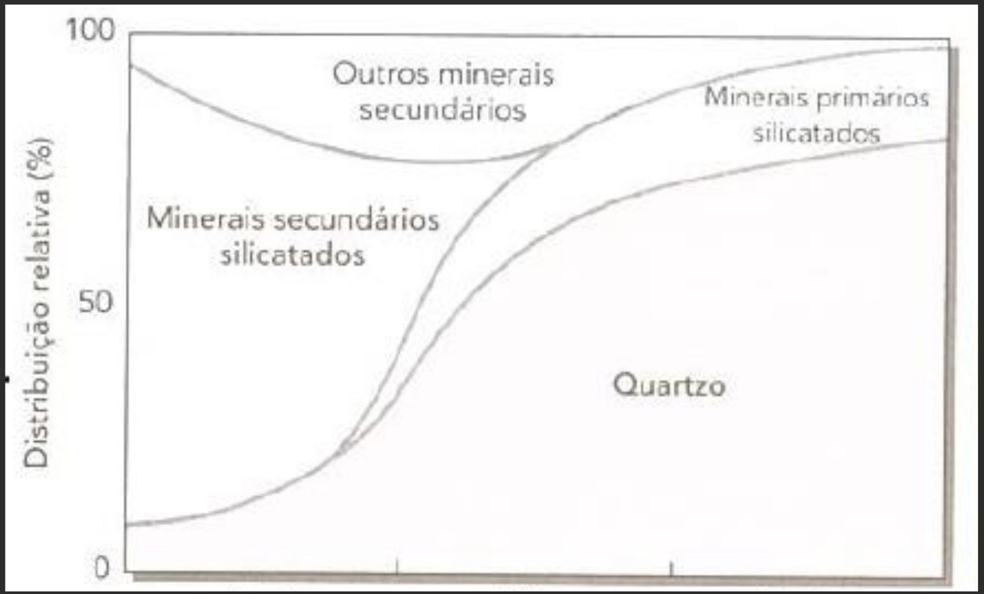
Cell type	Macro location			Total (all macro locations)
	External Surface	Crack surface	Tissue interior	
Parenchyma (round)	4	14	33	51
Parenchyma (smashed)	8	26	37	71
VB fibers	0	0	8	8
Xylem vessel	0	2	2	4
Epidermis region	5	0	2	7
Undetermined	117	90	5	212
Total (all cell types)	134	132	87	353

Caballero, Ling, Archilha, Ferreira, Driemeier (2017)

Soil for Thought

Textbook Information

Mineralogy



Clay Silt Sand

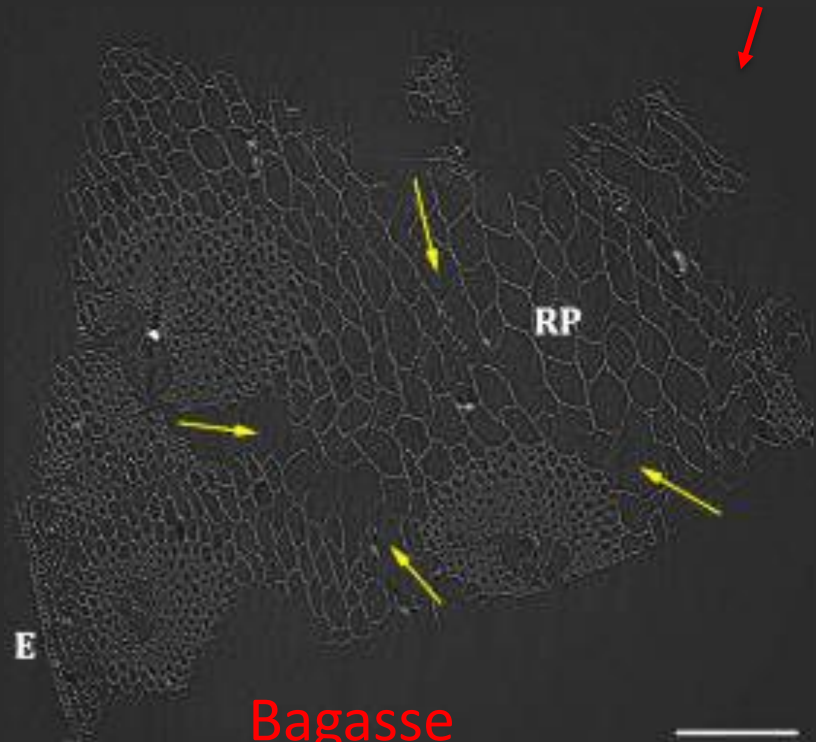
Size

2 µm 60 µm 2 mm

Observed Particles

Clay

Silt



Bagasse

Summary

- Nano changes in hydrothermal pretreatments
  - Opening of nanoscale pores
  - Cellulose aggregation/co-crystallization
  - Lignin aggregation
- Nano changes in mild alkaline pretreatments
  - Opening of nanoscale pores
  - No cellulose co-crystallization. No lignin aggregation
- Mineral particles in sugarcane bagasse
  - Major problem in biomass valorization
  - Non-invasive visualization (353 mineral particles)
  - Locations: external surfaces, crack surfaces, inside parenchyma
  - Biomass size, mineral size, soil mineralogy

Acknowledgements

Mineral particles

Daison Yancy-Caballero

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LNLS/IMX beamline staff

Alkaline deacetylation

Cleilton Lima

Sarita Rabelo

Peter Ciesielski (NREL)

Prof. Inês Roberto (EEL-USP)

Prof. George Rocha (EEL-USP)

Hydrothermal

Marcelo Oliveira

Fernanda Mendes

Beatriz Santucci

Maria Teresa Pimenta

Prof. Aprigio Curvelo (IQSC-USP)

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