Fibers and Fiber Products CHEM - E2120

Thad Maloney/Eero Hiltunen

Fall 2021

Course activities

Lectures

Reading

Exam (75% of final grade) – Oct. 28.

Laboratory Exercises (25%) – E. Hiltunen; Antti Koistinen

Lecture	Date	Subject	Lecturer
1	14.9.21	Introduction/Fiber Ultrastructure	Maloney
2	16.9.21	Fiber Properties	Maloney
3	21.9.21	Fiber Swelling	Maloney
4	23.9.21	Hornification and Recycled Pulp	Maloney
5	28.9.21	Fiber and Paper strength	E. Hiltunen
6	30.9.21	Mechanical Pulping	E. Hiltunen
7	5.10.21	Pulp refining	Maloney
8	7.10.21	Fiber and Paper physics	Maloney
9	12.10.21	Pulp Reactivity	S. Ceccherini
10	14.10.21	Case Study: Super Capacitor Papers	Josphat Phiri

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Introduction to fiber structure

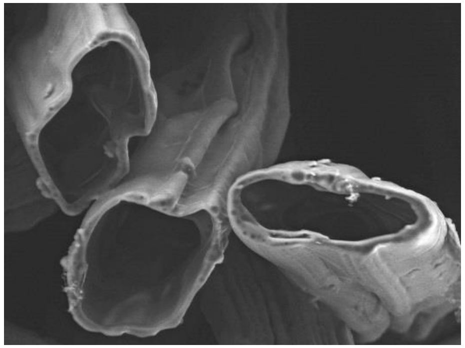
Thad Maloney

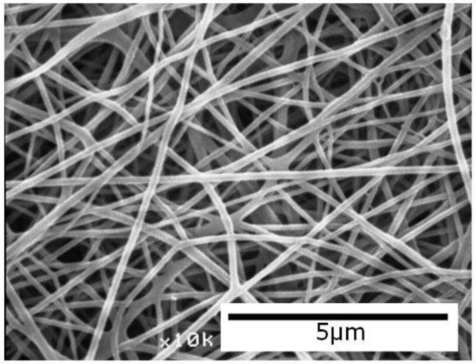
140921

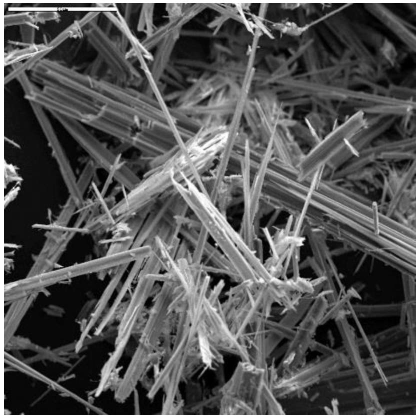
Fiber – A slender and greatly elongated solid substance.

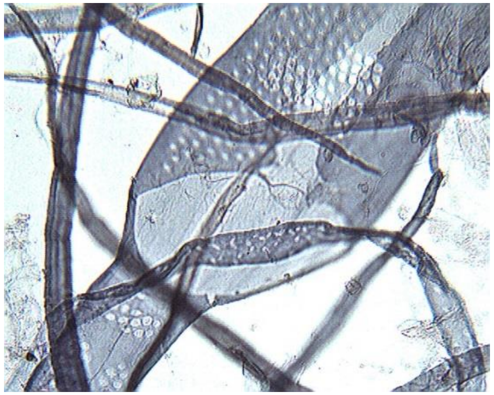
Types of fibers

- Natural
  - Organic
    - Cellulosic
      - Wood-based
        - Hardwood
        - Softwood
      - Annual plant
    - Protein
  - Inorganic
- Synthetic
- Semi-synthetic









Uses of Fibers

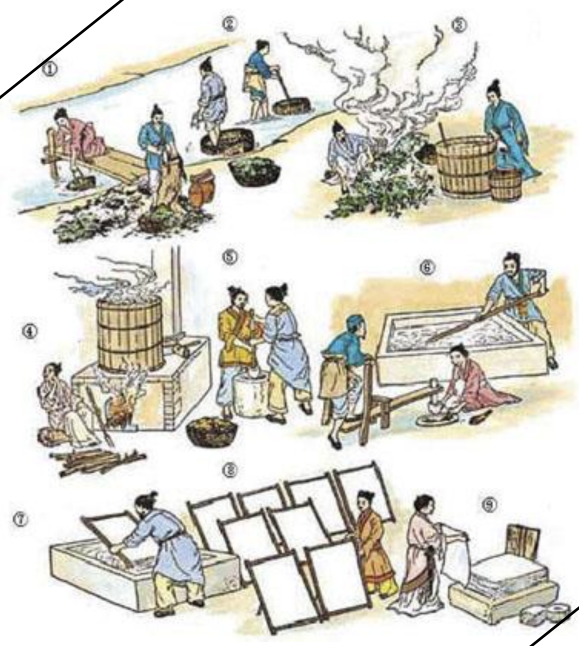
- As the load-bearing element in structural composites
- The main structural component in self-bonded web products (paper and board) and externally bonded products (non-wovens).
- As a functional component in a range of material applications e.g. excipients in medicine., filtration and sorption media, sensor applications.
- Woven into textile materials

Use of Pulp Fibers

- The most important source of cellulosic fibers is trees.
- Global paper and board production about 400 M tons/a, cotton production, 25 M tons/a.
- Graphical papers (40% of total) are in secular decline, other paper sectors enjoy GDP growth.
- There is intense interest in most companies to increase the share of renewable materials in products; increased use of cellulosics is an important theme.

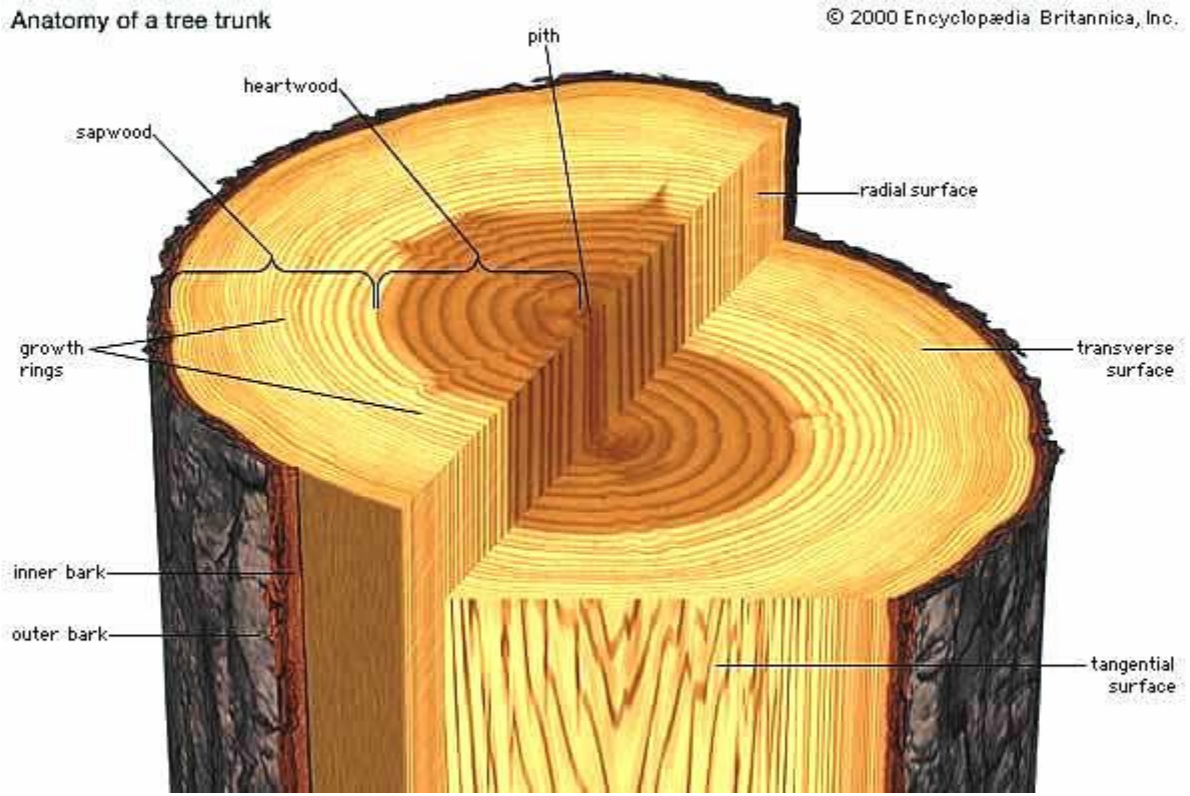
Evolution of fiber-based industry and technology

Size of the building blocks decreases meter→µm→nm

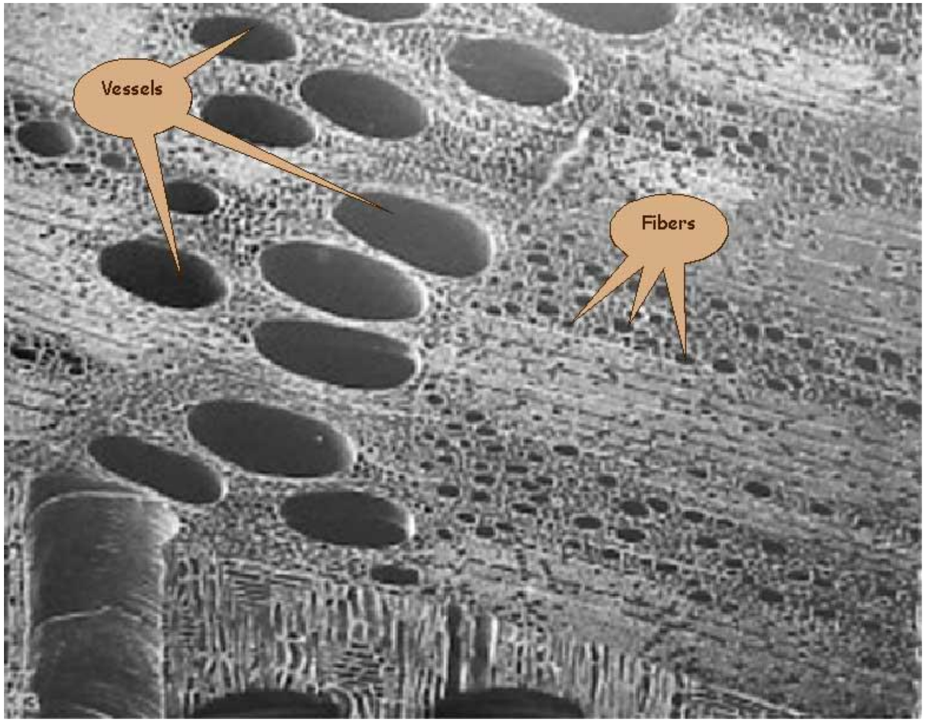


- *Functionality increases*
- *Performance increases*
- *Manufacturing complexity increases*
- *Costs??*

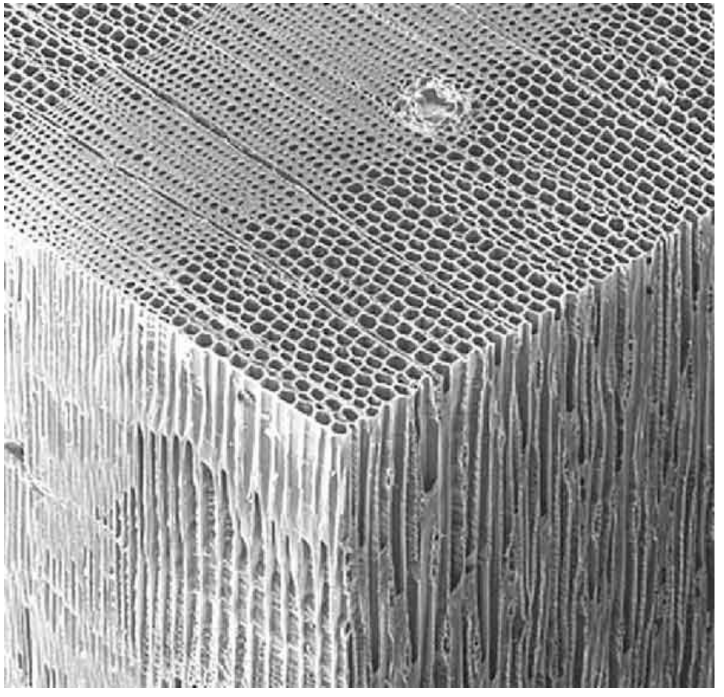
Wood- the most important source for natural cellulosic fibers

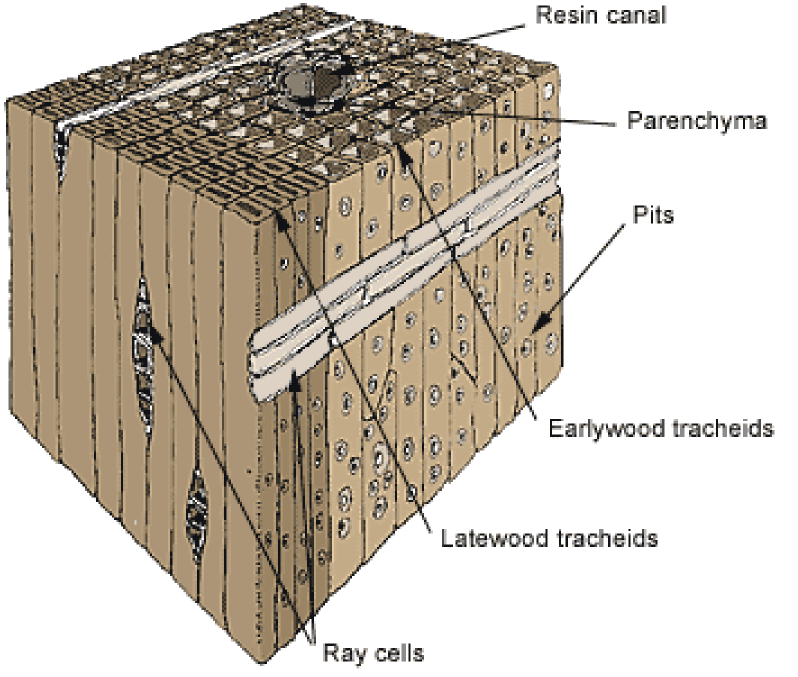


Hardwood Anatomy



Softwood anatomy



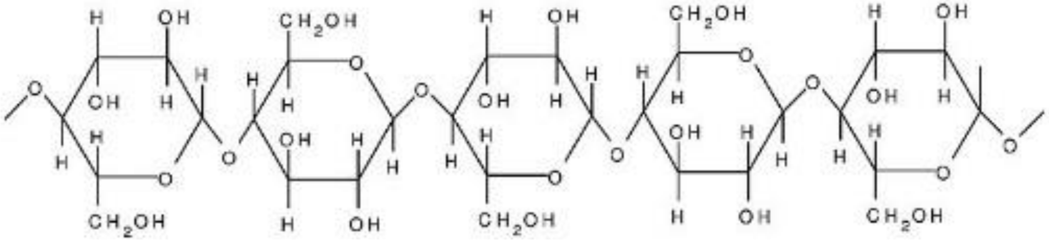


Wood chemical make-up

Cellulose - around 40%
Hemicelluloses – 20-30%
Lignin – 23-27%
Extractives – few percent

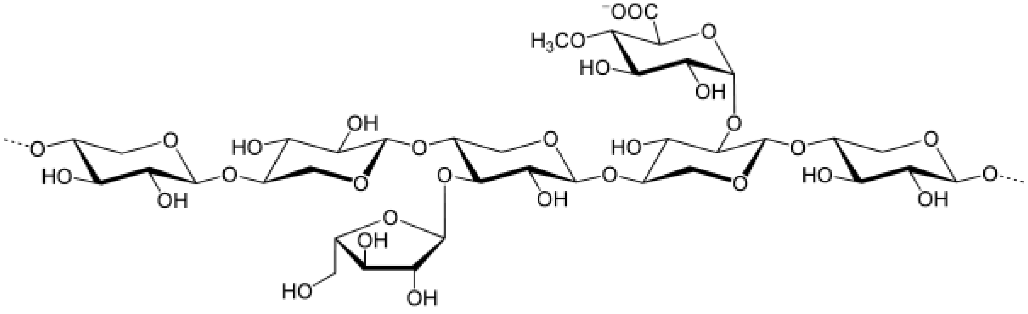
Cellulose

- Linear polymer based on glucose repeating units
- DP-300-2000
- Crystallinity 50-70%
- Organized into fibril structure
- No glass transition, decomposes below melting temperature
- Safe. Odorless, tasteless
- Strong: 100-300 Gpa, similar to iron
- Can be (easily) chemically modified
- Hydrophilic, slightly swelling, insoluble in water



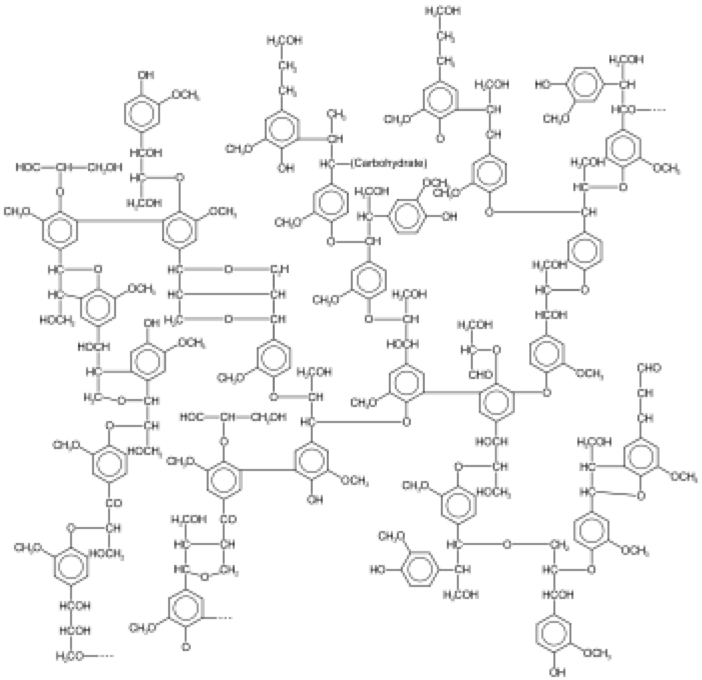
Hemicellulose

- A family of mostly 5 carbon sugars
- DP 20-200
- Branched
- Amorphous and very water swollen
- Glass transition below room temperature
- Anionic
- In wood links cellulose to lignin
- In fibers acts as bonding agent



Lignin

- A complex 3-dimensional polymer of different phenolic alcohol repeating units
- Hydrophobic
- Thermoplastic
- In wood, lignin glues the fibers together
- In fibers, lignin interferes with hydrogen bonding.
- Lignin is brown and subject to alkali and uv darkening reactions
- Carries anionic charge
- Lignin can be used as a fuel or converted to adhesives or carbon fibers.



Extractives

- Volatile organic compounds in wood have a range of protective and other functions
- Are generally negative for fiber properties and down stream processes
- Can be extracted in the fiber production process and converted into value added chemicals or fuel.

		Heartwood	Sapwood
Total extractives		0.39	0.37
Volatile extractives			
Terpenes and phenols		3.6	2.1
Free fatty acids		22.9	22.7
Sterols		47.8	47.3
	β-sitosterol	39.0	45.9
Monoglycerides		3.0	2.9
Diglycerides		0.0	0.0
Triglycerides		15.9	15.1
Unidentified		6.8	9.9

Eucalyptus Grandis

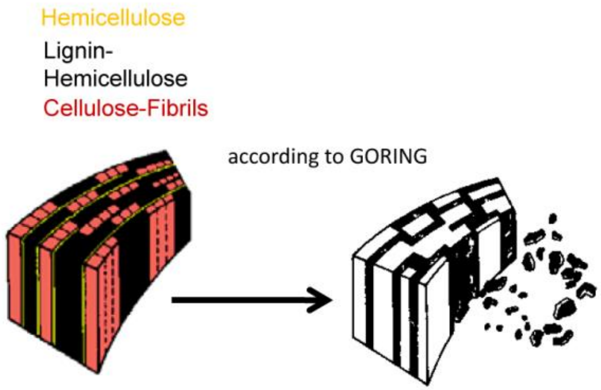
Fiber classification

- Natural vs synthetic
- Wood vs wood pulp
- Chemical vs. mechanical pulps
- Bleached vs unbleached
- Hardwood vs softwood
- Virgin vs recycled (previously dried)
- Refined vs unrefined

Major routes for producing virgin fibers

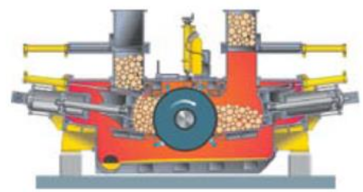
Primary pulps (virgin fibers)

Chemical pulping

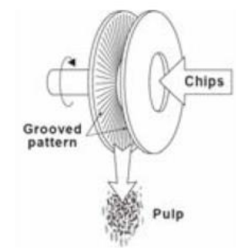


- Lignin and hemicelluloses dissolve from the fiber wall
- Fiber wall becomes thinner and more flexible
- Chipping shortens the fiber length

Mechanical pulping



Grinding

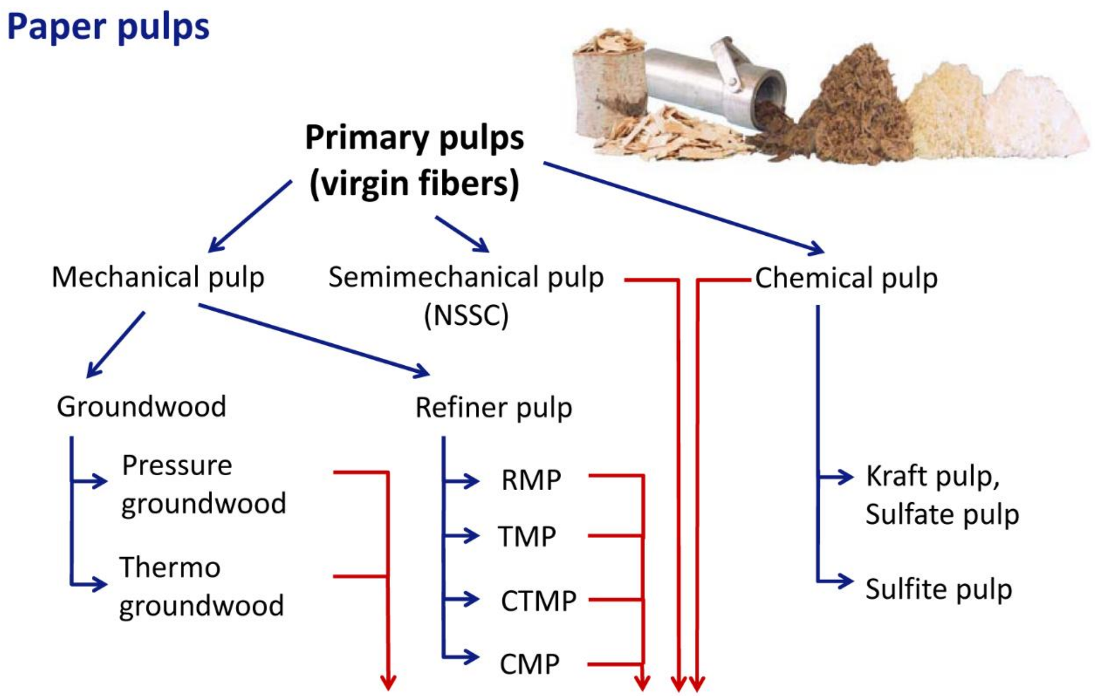


Refining

About

- ⅓ of wood becomes fines
- ⅓ of wood becomes broken fiber particles
- ⅓ of wood is defibrated into fiber-like material

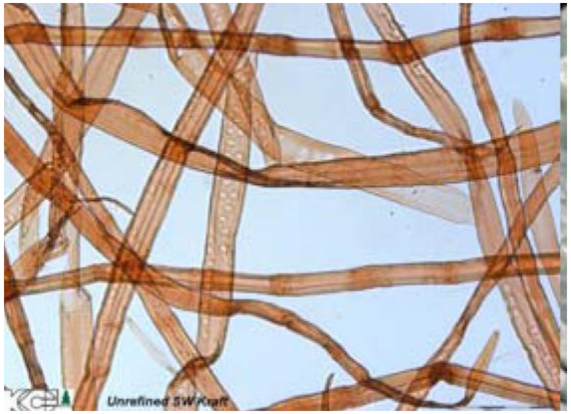
Types of Chemical and Mechanical Pulp



Bleaching

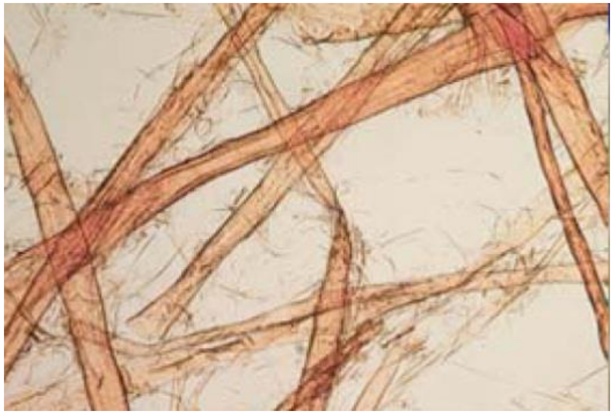
- Lignin containing fibers are often bleached to increase whiteness
- Mechanical pulps are "brightened" chemical pulps "bleached".
- A range of bleaching chemistries are used; chlorine, dithionite, peroxide, oxygen – based.
- Bleaching usually degrades cellulose, weakens fiber
- Bleaching changes fiber chemistry e.g. adds acid groups, exposes cellulose surfaces

Chemical vs Mechanical Pulps



Chemical Pulp

- Yield 45-50%
- Strong fibers
- Flexible
- Homogenous
- Bleached fibers give stable brightness



Mechanical pulp

- Yield 95-100%
- Heterogeneous
- High charge but low swelling
- Lignin chemistry
- High amount of fines gives good optics and surface properties
- High charge but low swelling

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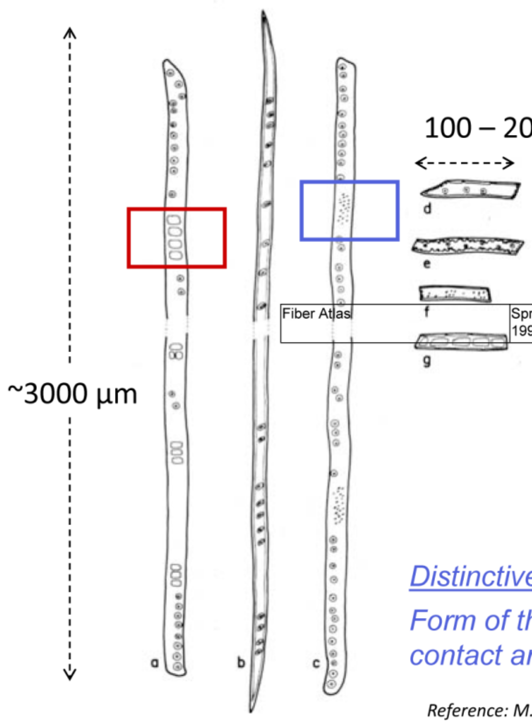
Softwood fiber types



Softwood fiber types

a. Earlywood tracheid of **pine**

b. Latewood tracheid of **pine**

c. Earlywood tracheid of **spruce**

d. Ray cell tracheid of **spruce**

e. Ray cell tracheid of **pine**

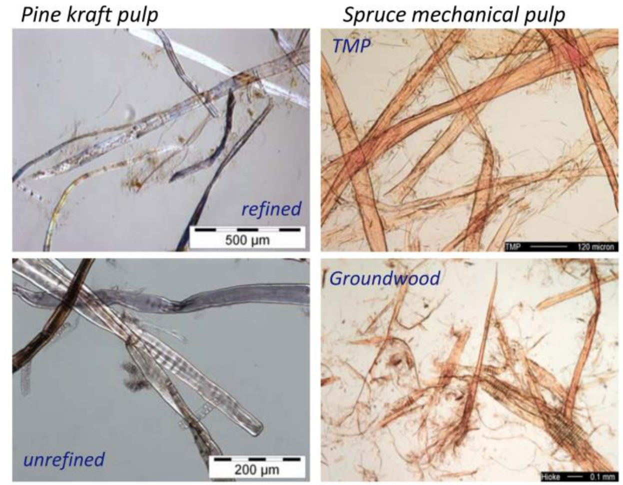
f. Ray cell of **spruce**

g. Ray cell of **pine**

Distinctive feature:

Form of the pits (pores in the fiber wall) at the contact area between tracheid and ray cell

Reference: M.-S. Ilvessalo-Pfäffli, Fiber Atlas, Springer Berlin Heidelberg, 1995



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Hardwood fibers

Hardwood fiber types

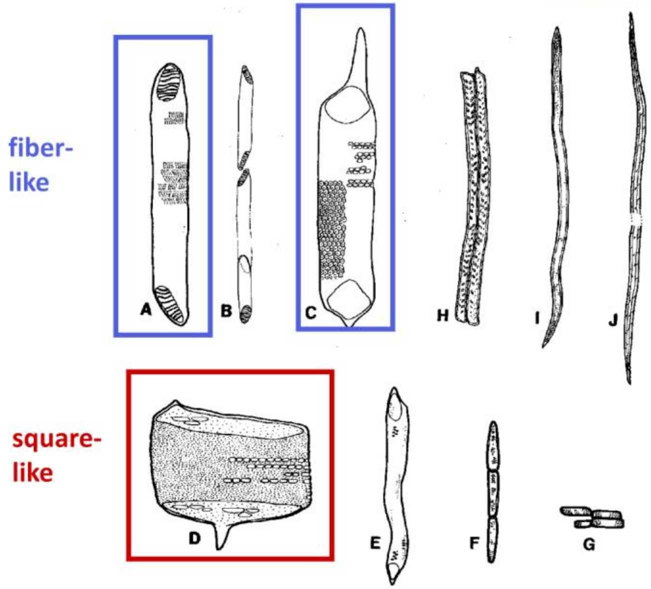
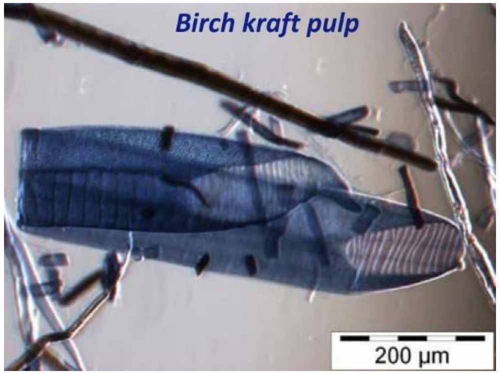
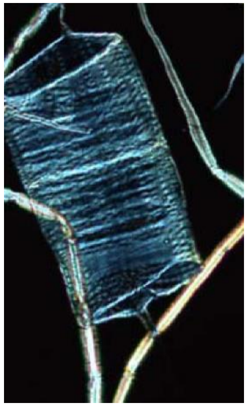


Fig. 2.26. Hardwood cells.
A Vessel element of birch
B Vessel of birch
C Vessel element of aspen
D Earlywood vessel element of oak
E Latewood vessel element of oak
F Longitudinal parenchyma cells
G Ray parenchyma cells
H Tracheid of oak
I Tracheid of birch
J Libriform fiber of oak

Distinctive feature:
Shape and pit structure of vessel cells

Reference: M.-S. Ilvessalo-Pfäffli, Fiber Atlas, Springer Berlin Heidelberg, 1995

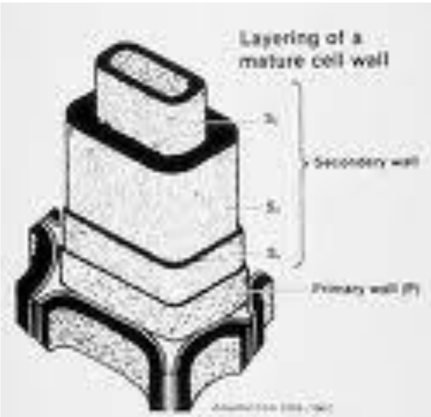


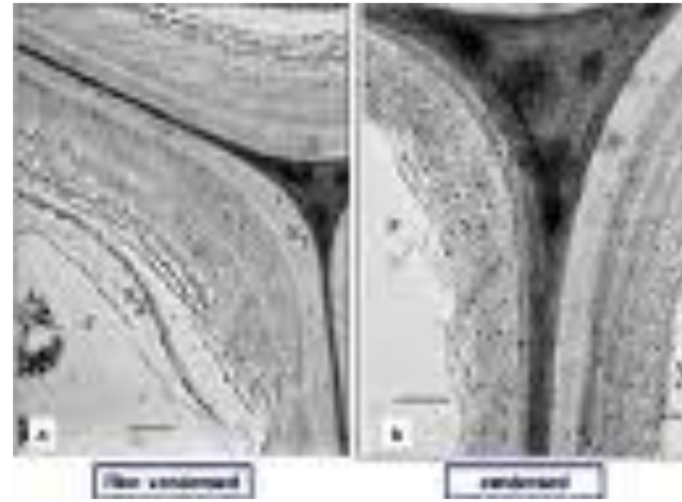


Eucalyptus Vessel

Ultrastructure-

Cell wall as a composite structure





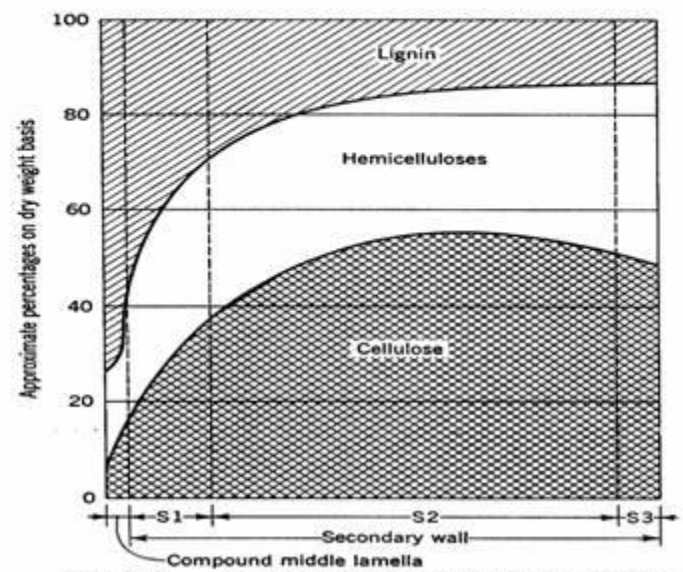


FIG. 3-10 Distribution of the principal chemical constituents within the various layers of the cell wall in conifers.

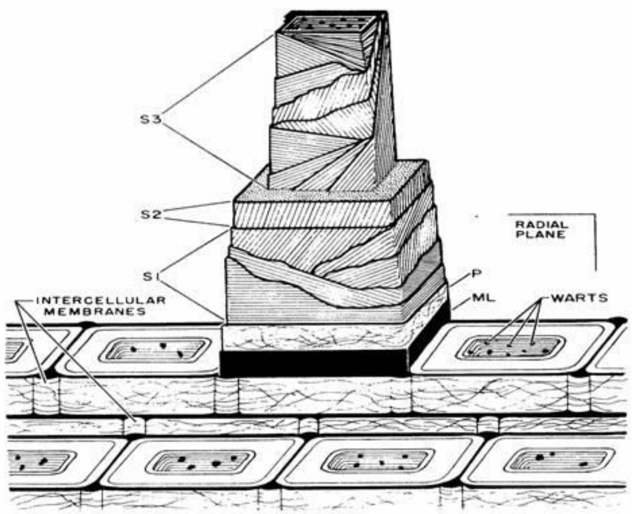
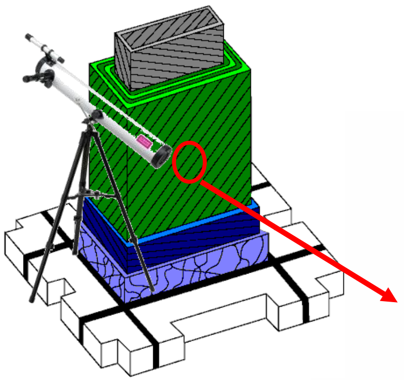
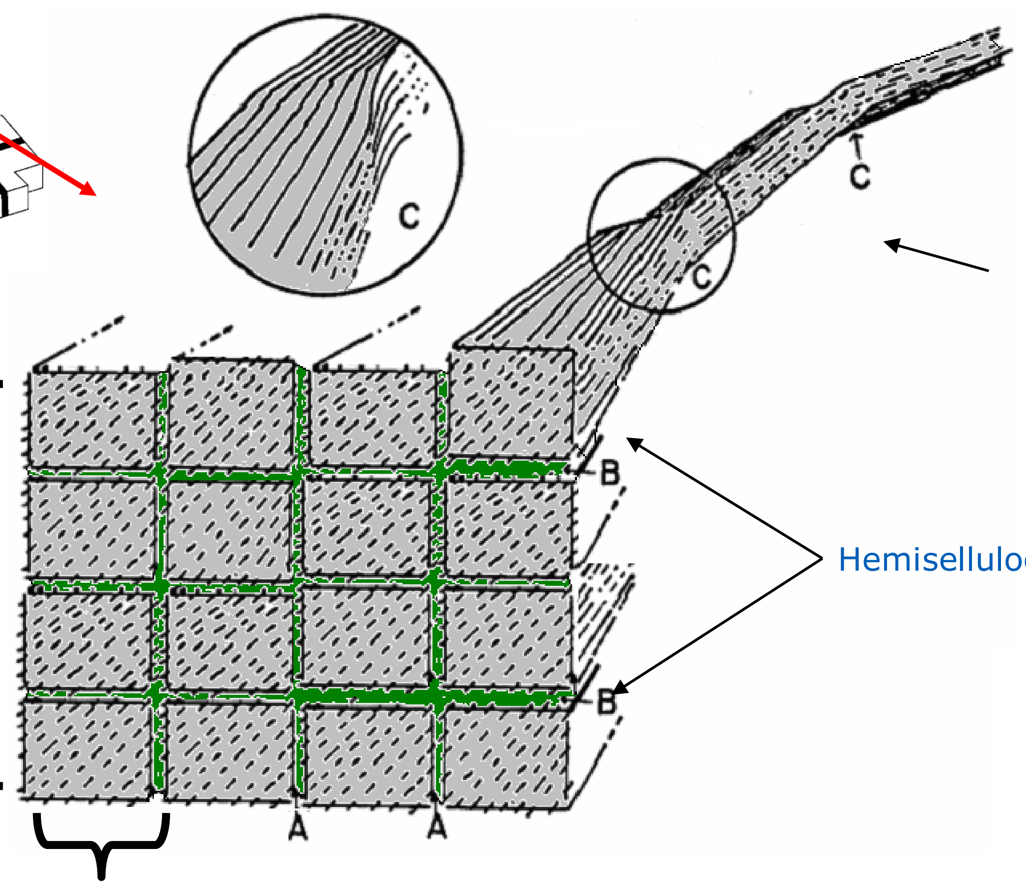


Figure 5-8.—Cell-wall structure of longleaf pine. A latewood longitudinal tracheid is exposed to show lamellae of the three layers of the secondary cell wall. Lines indicate alignment of microfibrils. ML is middle lamella. P is primary wall. S_1, S_2, and S_3 are layers of the secondary wall. (Drawing after Dunning 1969b.)

Structure of a microfibril



(macro)Fibrill aggregate
Ø~20±10nm
$\sim 3^2$-7^2
(elementry) microfibrils



Hemiselluloosaa

Av. macrofibril thickness

= 15.3 nm

→ SA = **170 m^2/g**

Microfibril Ø~4nm
~30-40 cellulose chains

Fiber pore structure

- Macropores are gaps visible between fibril aggregates.
- Even some larger cracks in the cell wall are visible.

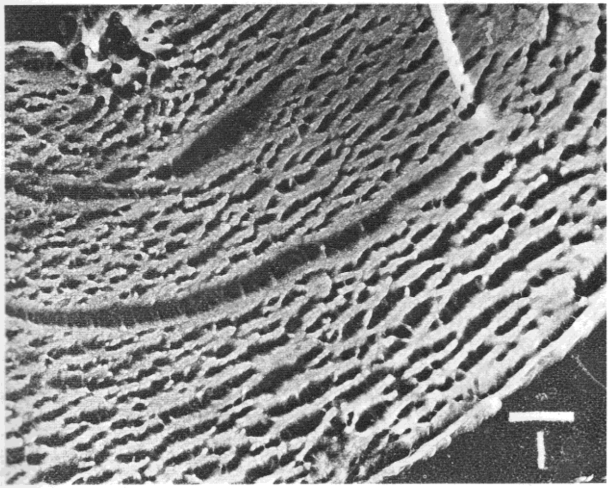


Fig. 11—An electron micrograph of a cross-section of a spruce sulphite fibre prepared after solvent-exchange of the fibre from water to a mixture of butyl and methyl methacrylates, followed by polymerisation. After sectioning, the polymer was washed out and the section metal shadowed. Inset 1 μm. Micrograph by G. M. A. Aberson[5]

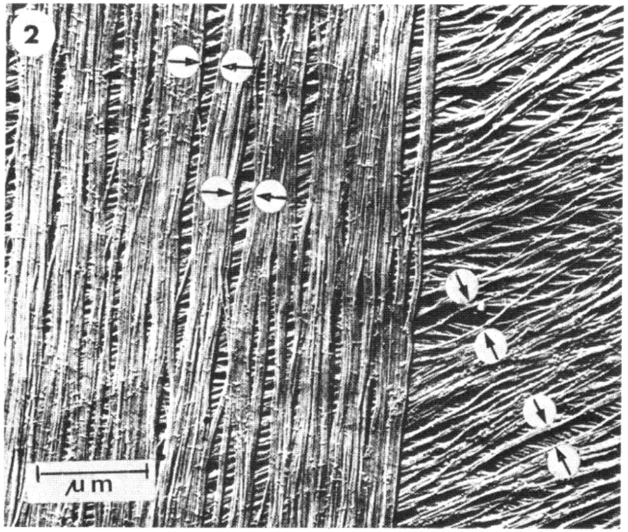
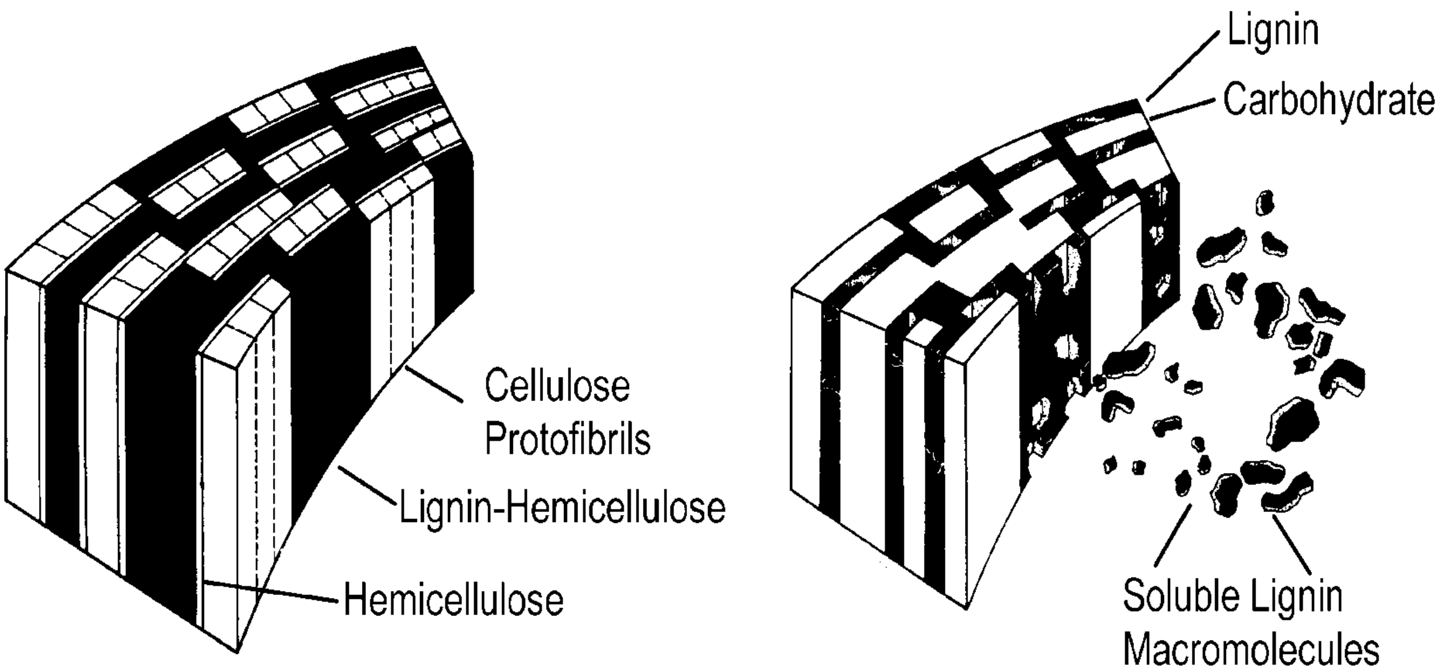


Fig. 10—One of a number of micrographs published by Boyd and Foster[41] and variously attributed to A. Frey-Wyssling and R. D. Preston. This one of an inner wall of *Cladophora prolifera* shows clearly the type of 'lenticular opening' within lamellae which are suggested as common amongst plant cell walls

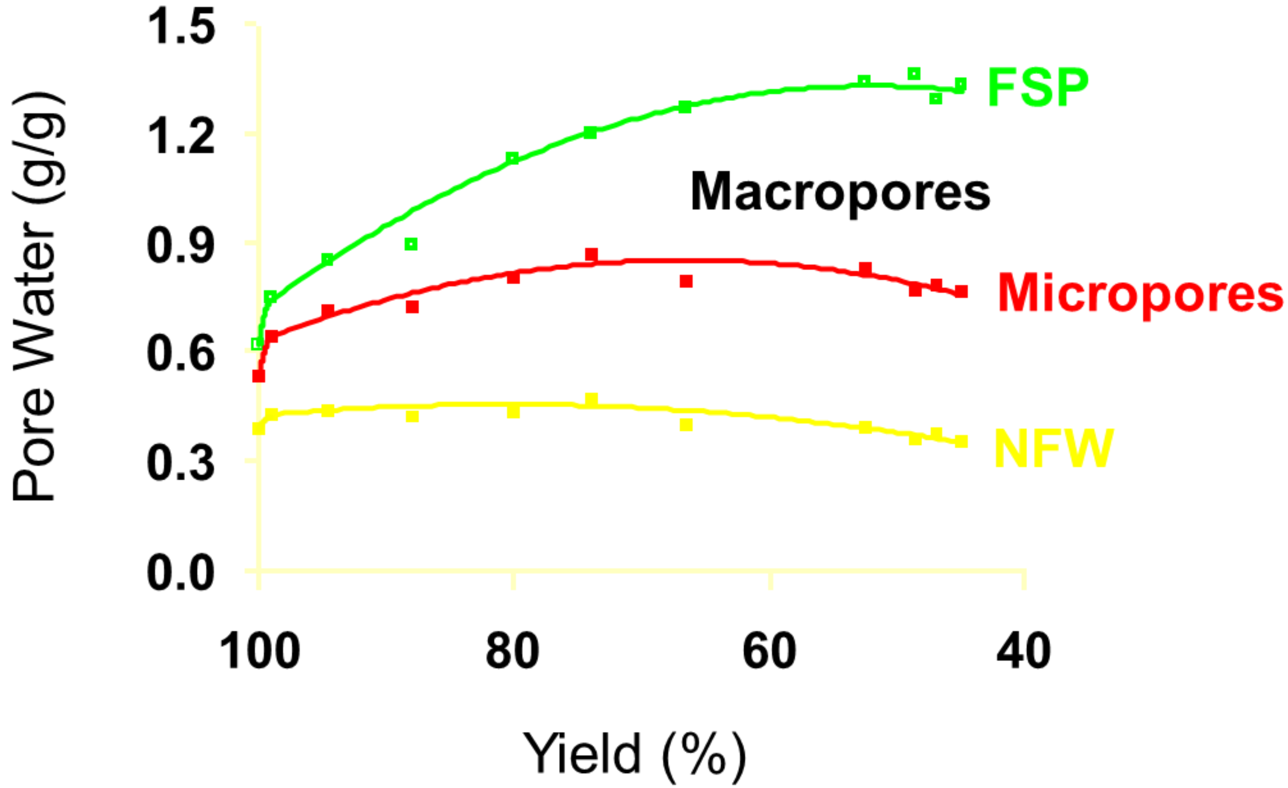
A. M Scallan

Formation of pores in the cell wall



(Goring et al., 1984)

Pore Formation in Kraft Pulping



FSP = Fiber saturation point, a measure of fiber swelling.

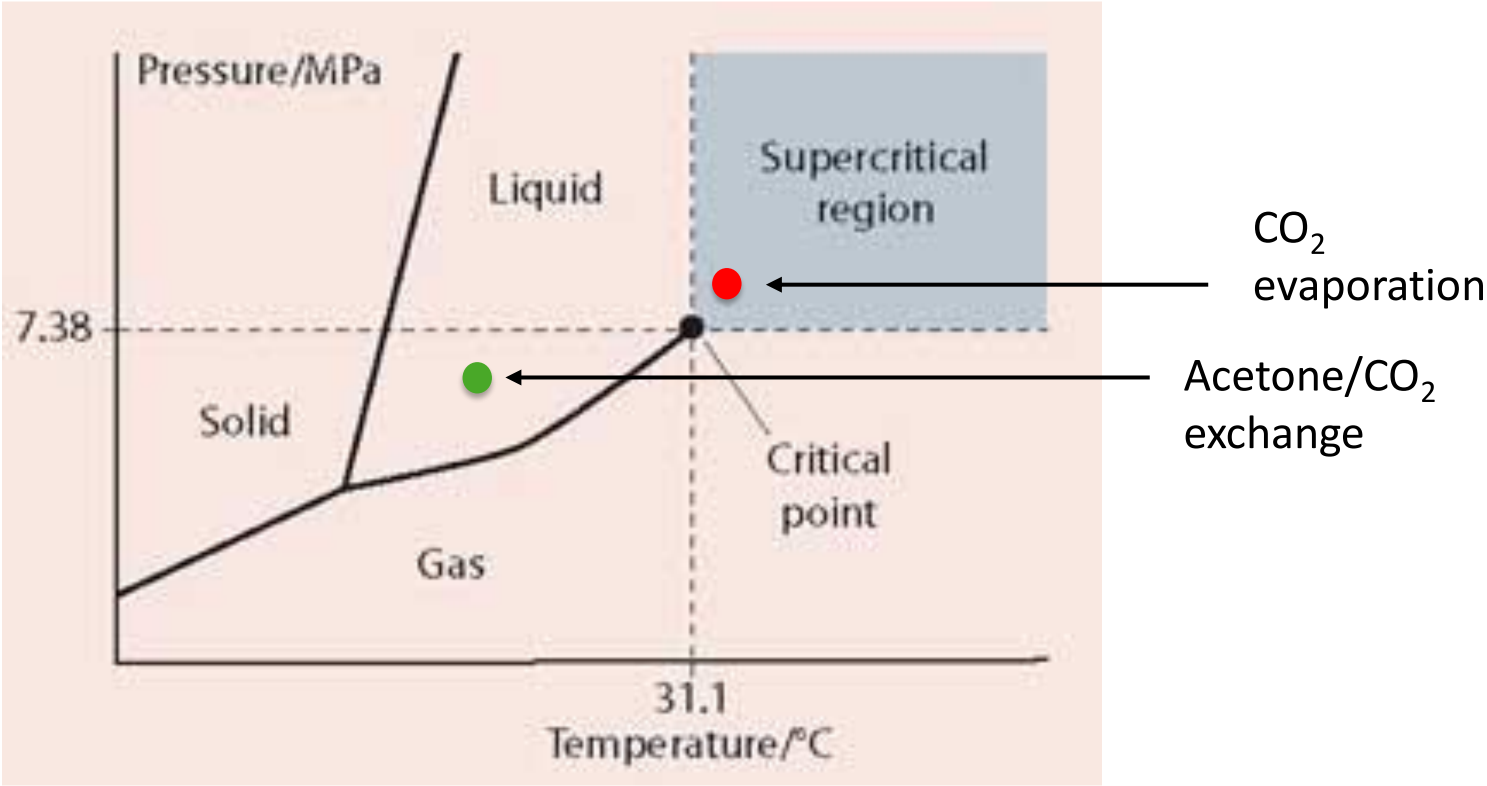
Fiber analysis by critical point drying

Fibers have there full structural details only in the wet state, but the scanning electron microscope (and many other methods), demands dry samples.

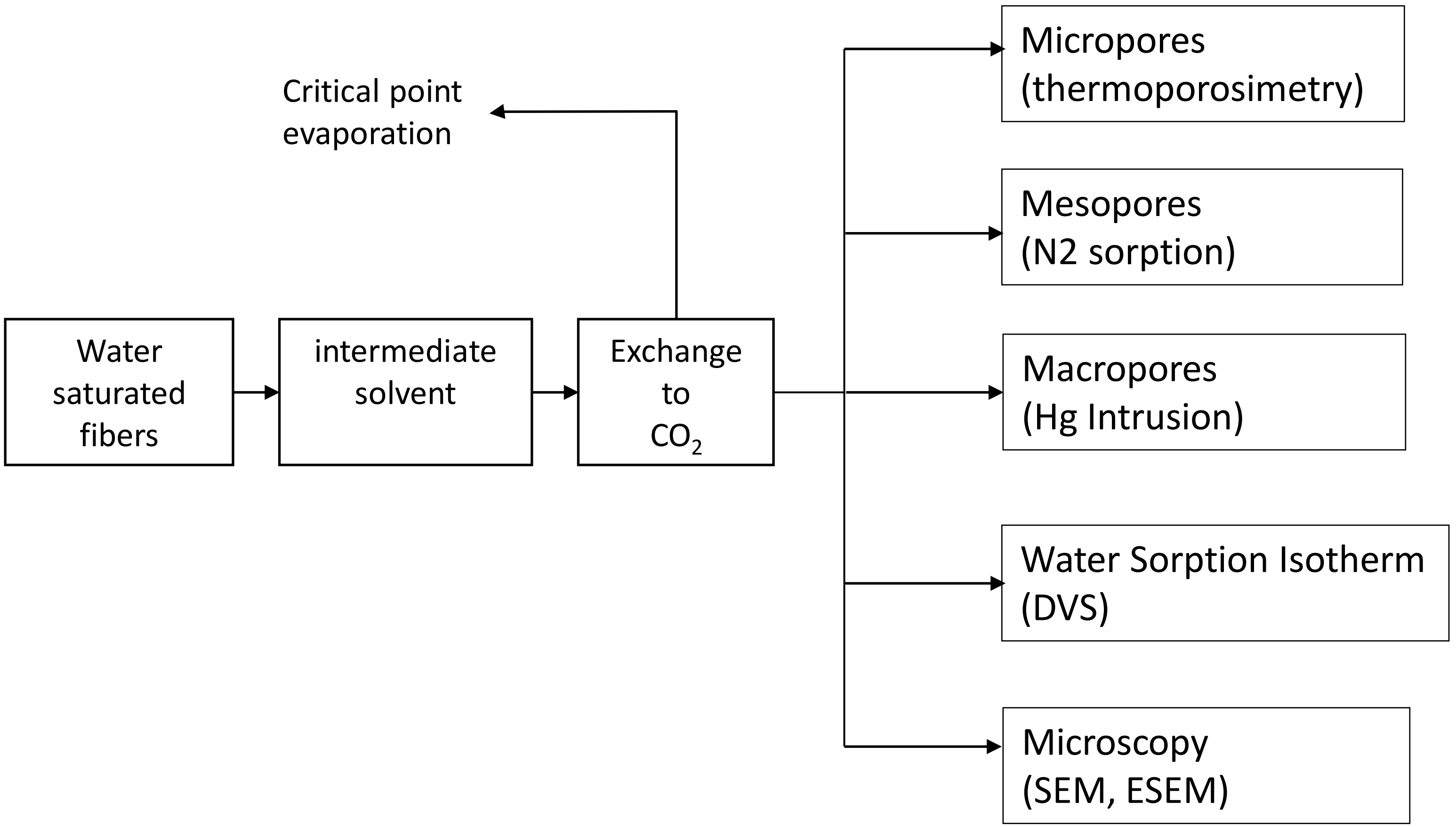
How can we solve this problem?

Removing the Solvent and Preventing the Pore Collapse

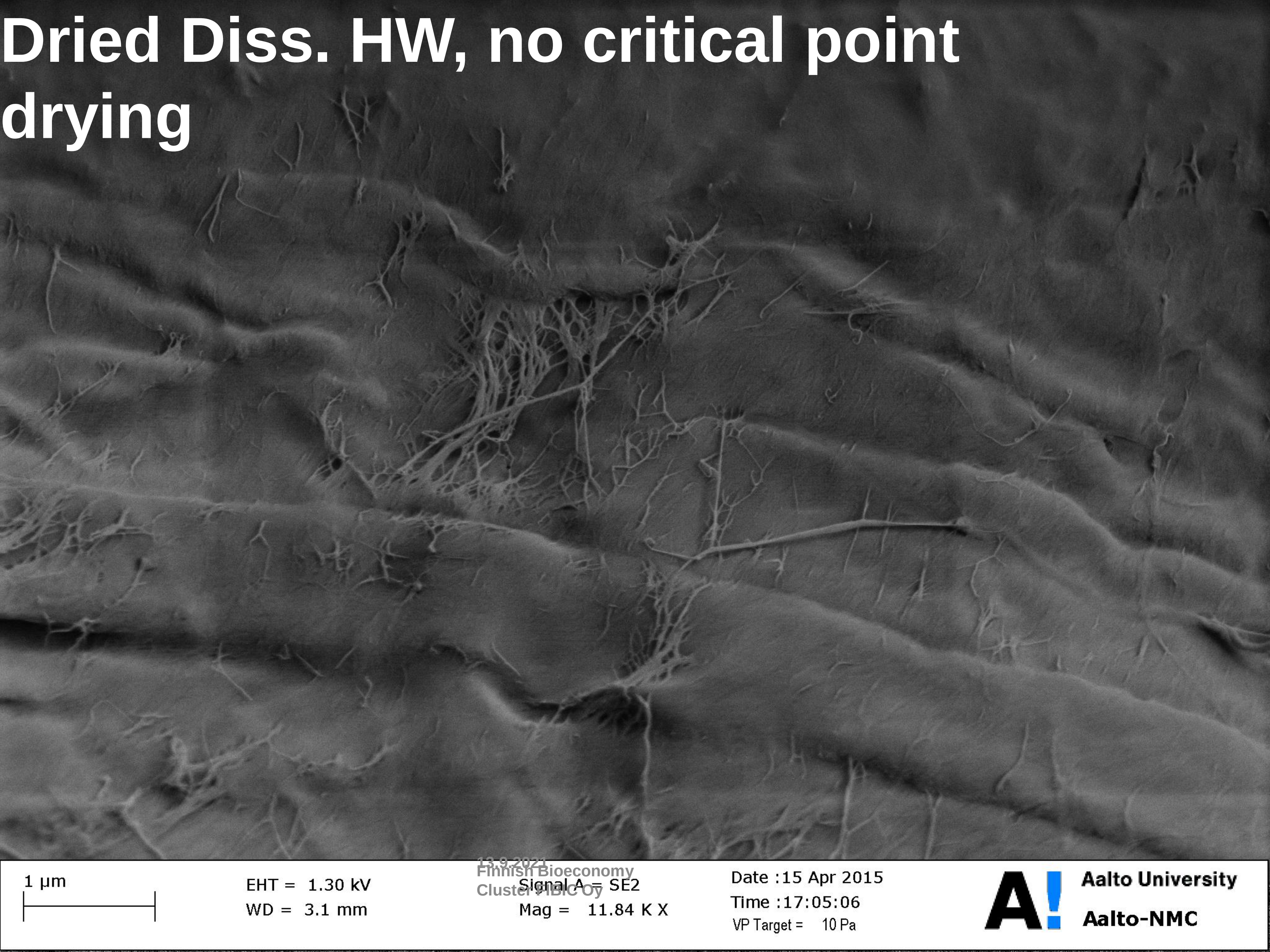
CO_2 phase diagram



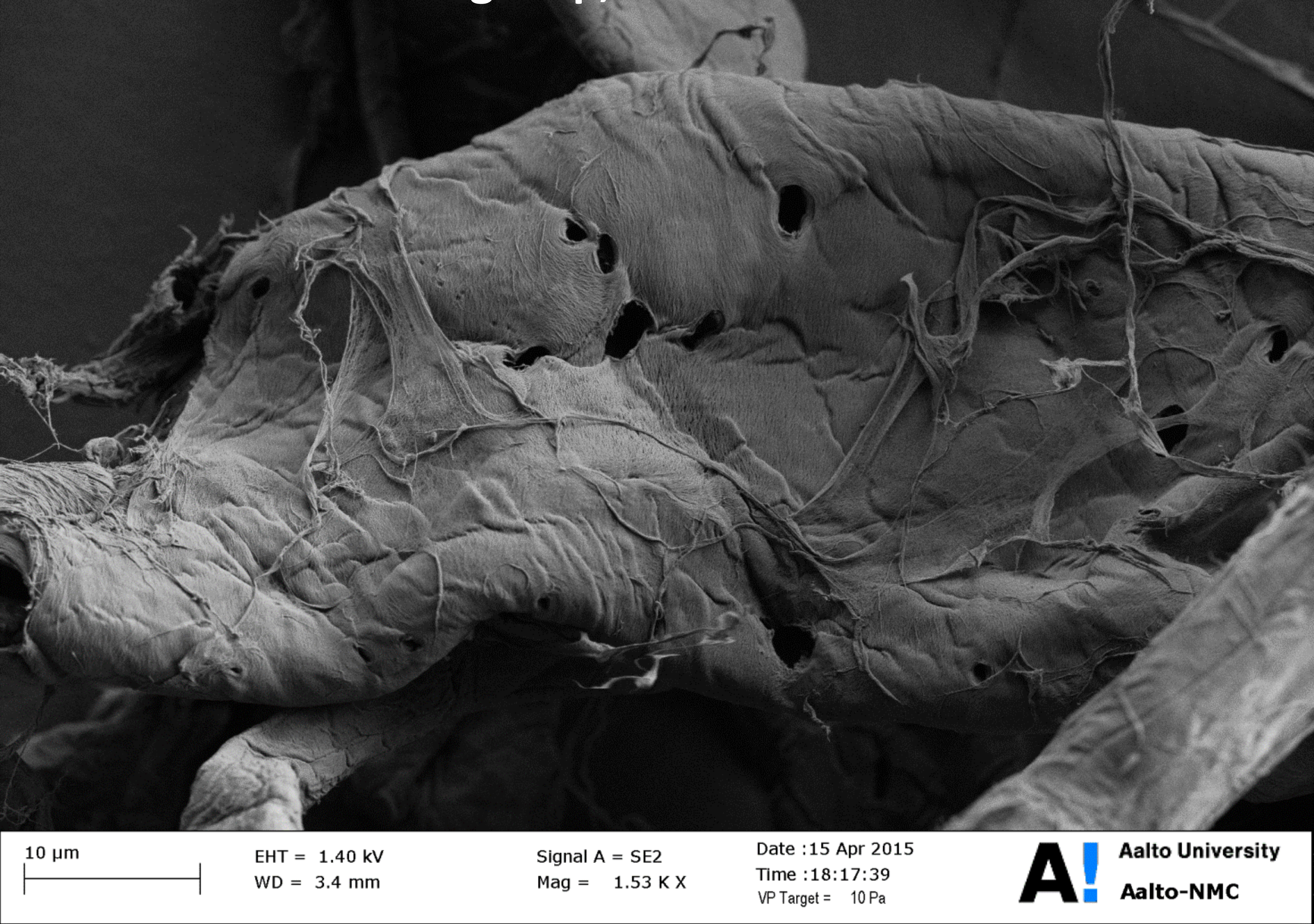
Analysis of Dry, Porous Fibers



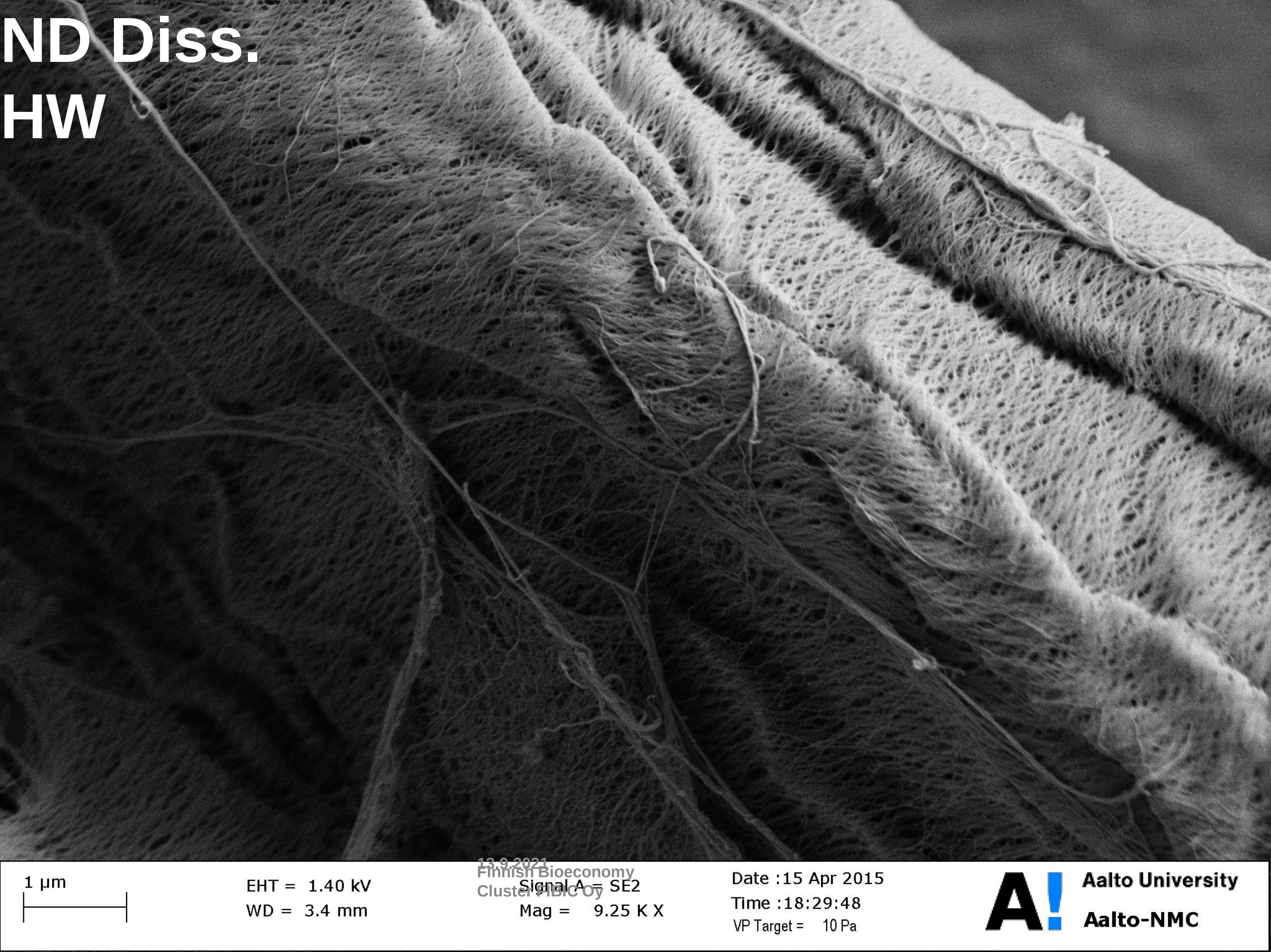
Dried Diss. HW, no critical point drying



Never-dried Dissolving Pulp, Hardwood



ND Diss. HW



1 µm
EHT = 1.40 kV
WD = 3.4 mm
Signal A = SE2
Mag = 9.25 K X
Date :15 Apr 2015
Time :18:29:48
VP Target = 10 Pa
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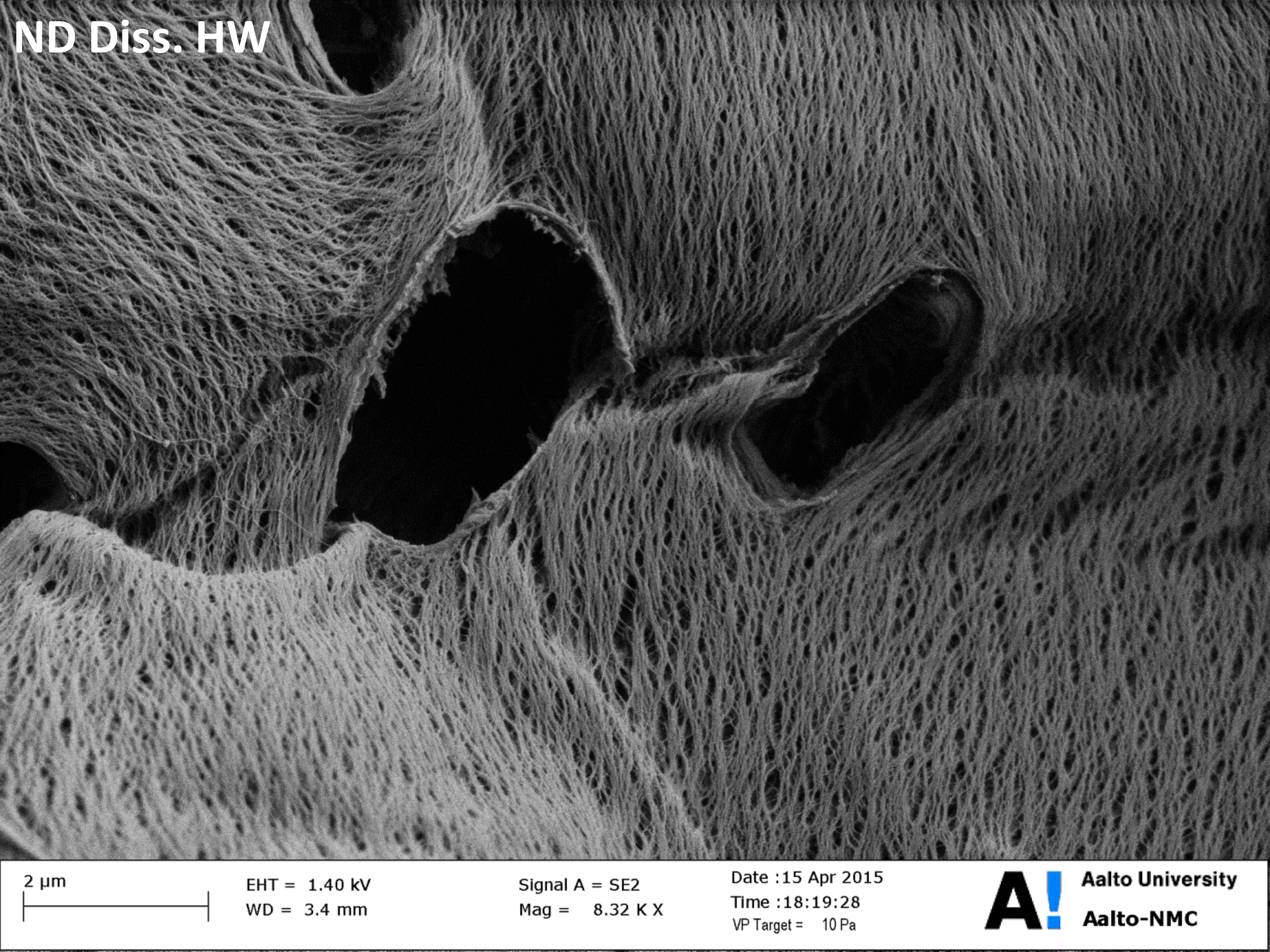
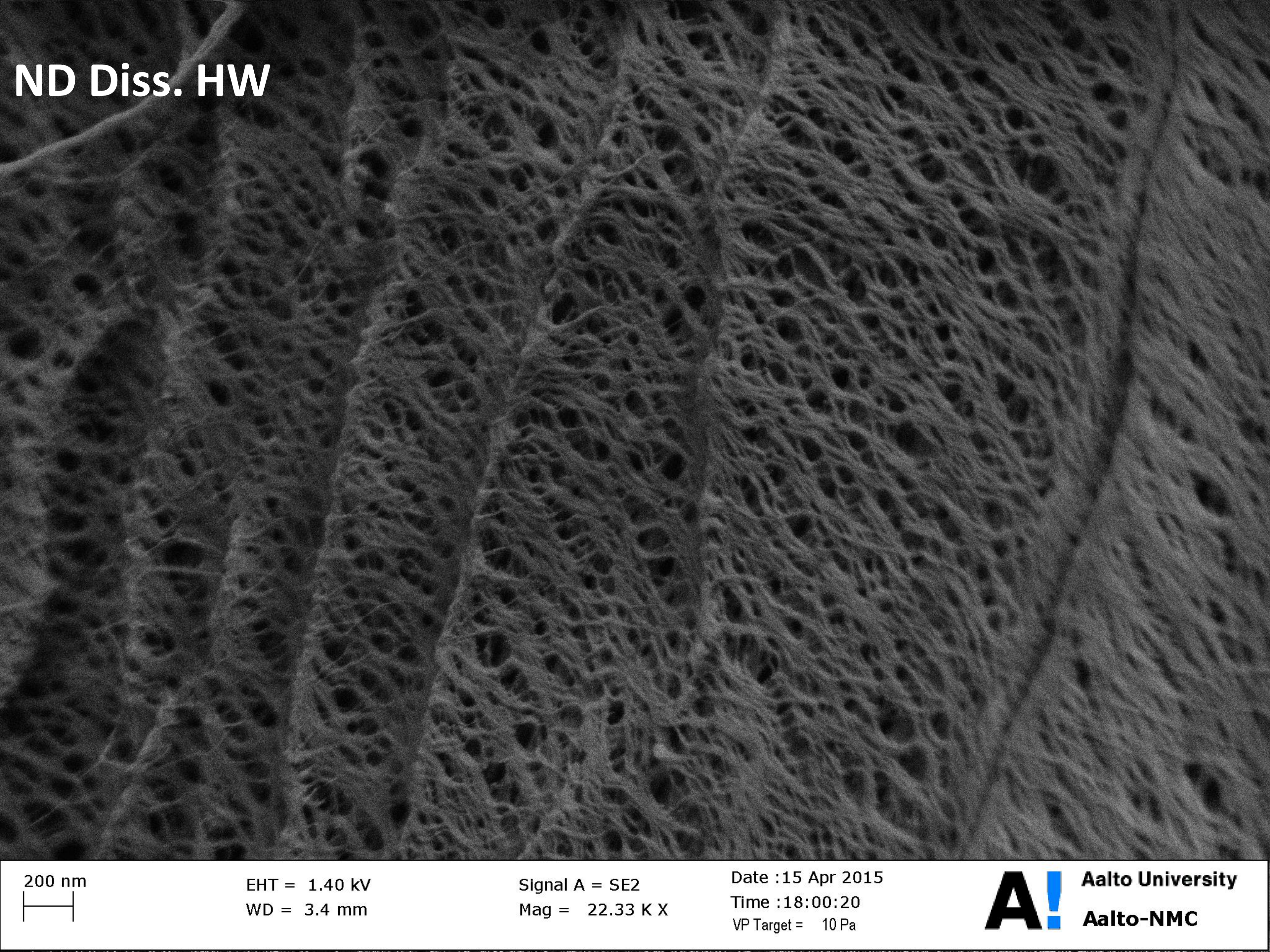

ND Diss. HW
2 µm
EHT = 1.40 kV
WD = 3.4 mm
Signal A = SE2
Mag = 8.32 K X
Date :15 Apr 2015
Time :18:19:28
VP Target = 10 Pa
Aalto University
Aalto-NMC


ND Diss. HW
200 nm
EHT = 1.40 kV
WD = 3.4 mm
Signal A = SE2
Mag = 22.33 K X
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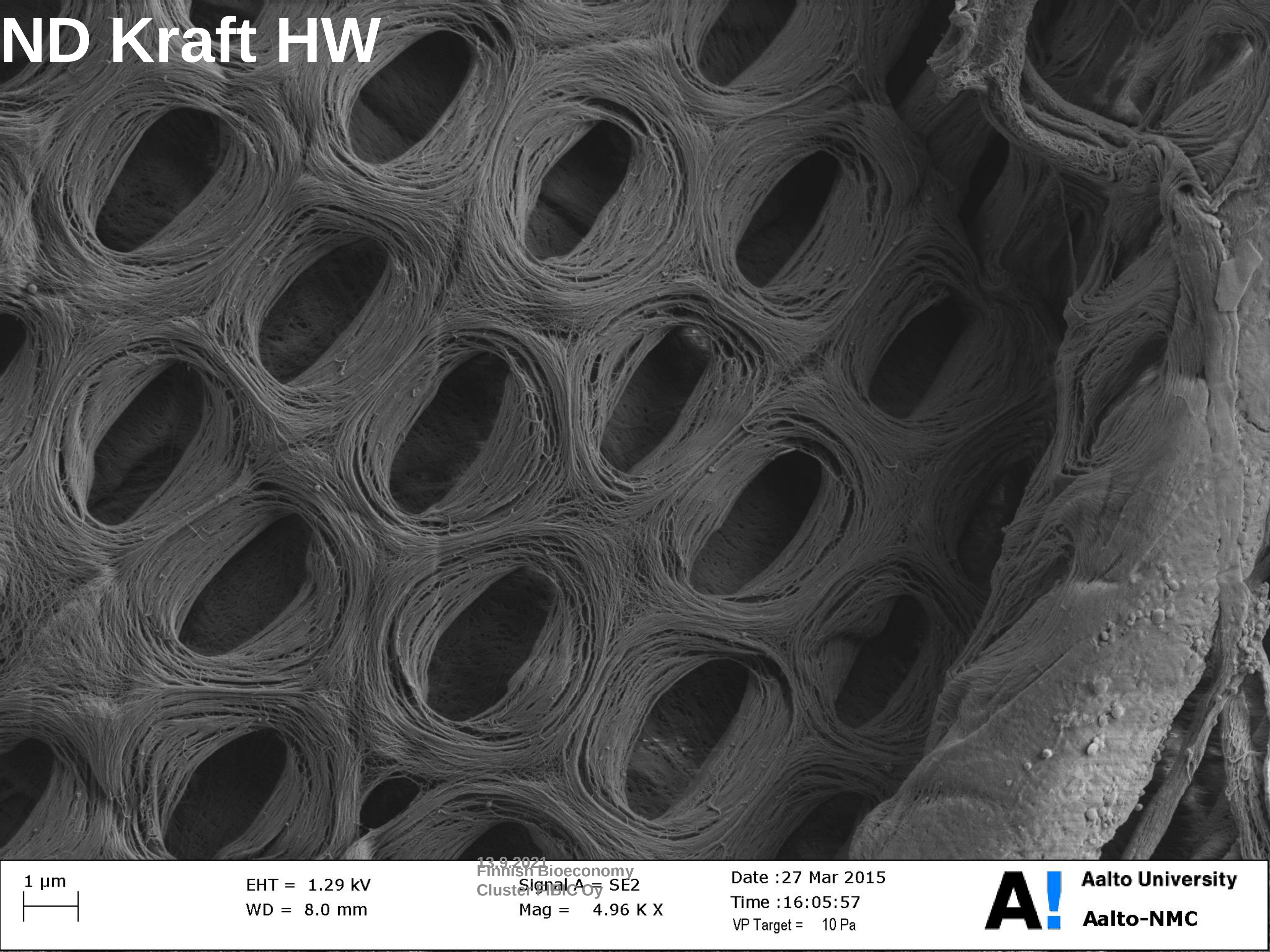
VP Target = 10 Pa
Aalto University
Aalto-NMC

ND Kraft HW



1 µm
EHT = 1.29 kV
WD = 8.0 mm
Signal A = SE2
Mag = 4.96 K X
Date :27 Mar 2015
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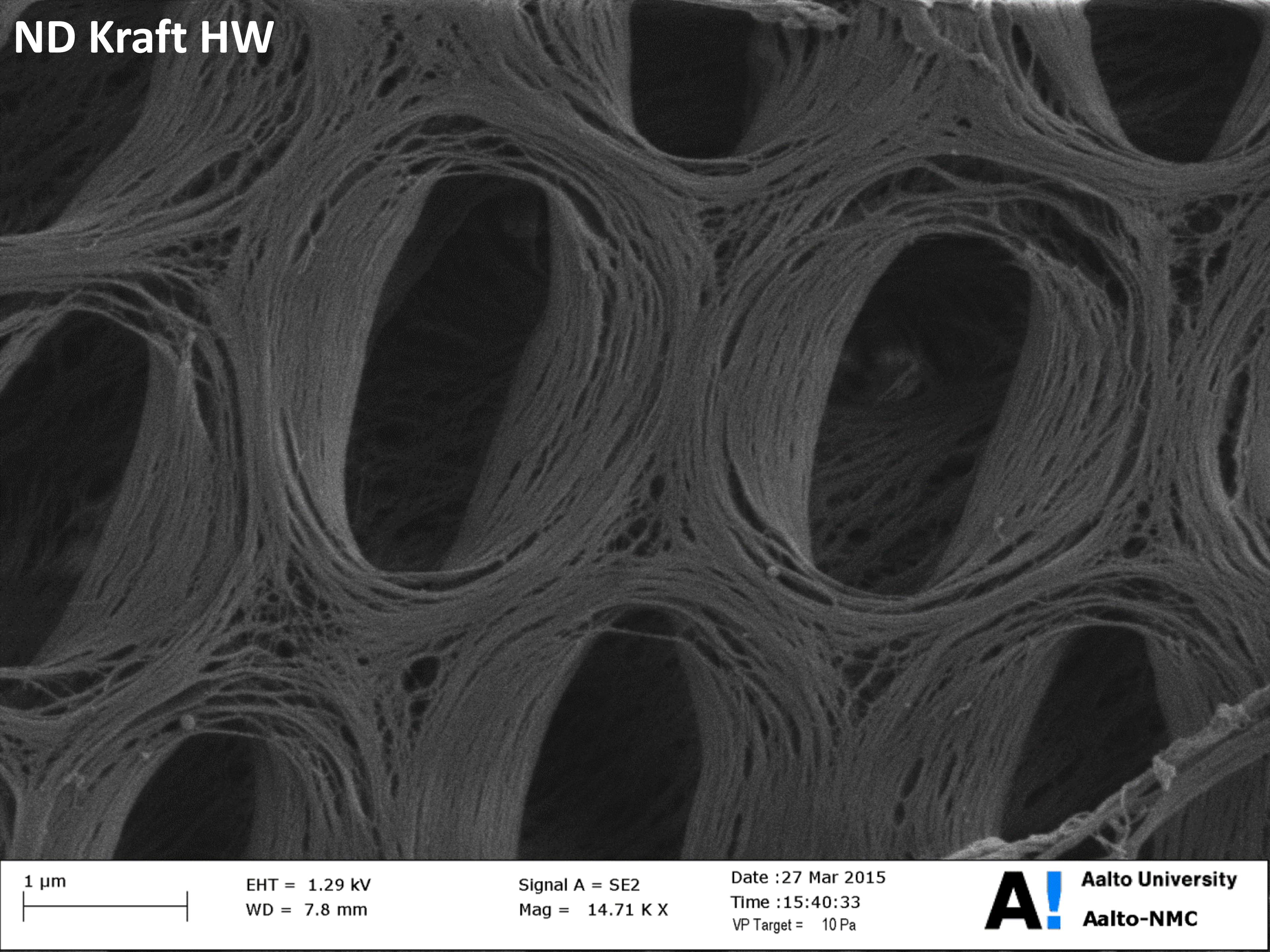
Aalto University
Aalto-NMC



ND Kraft HW
1 µm
EHT = 1.29 kV
WD = 7.8 mm
Signal A = SE2
Mag = 14.71 K X
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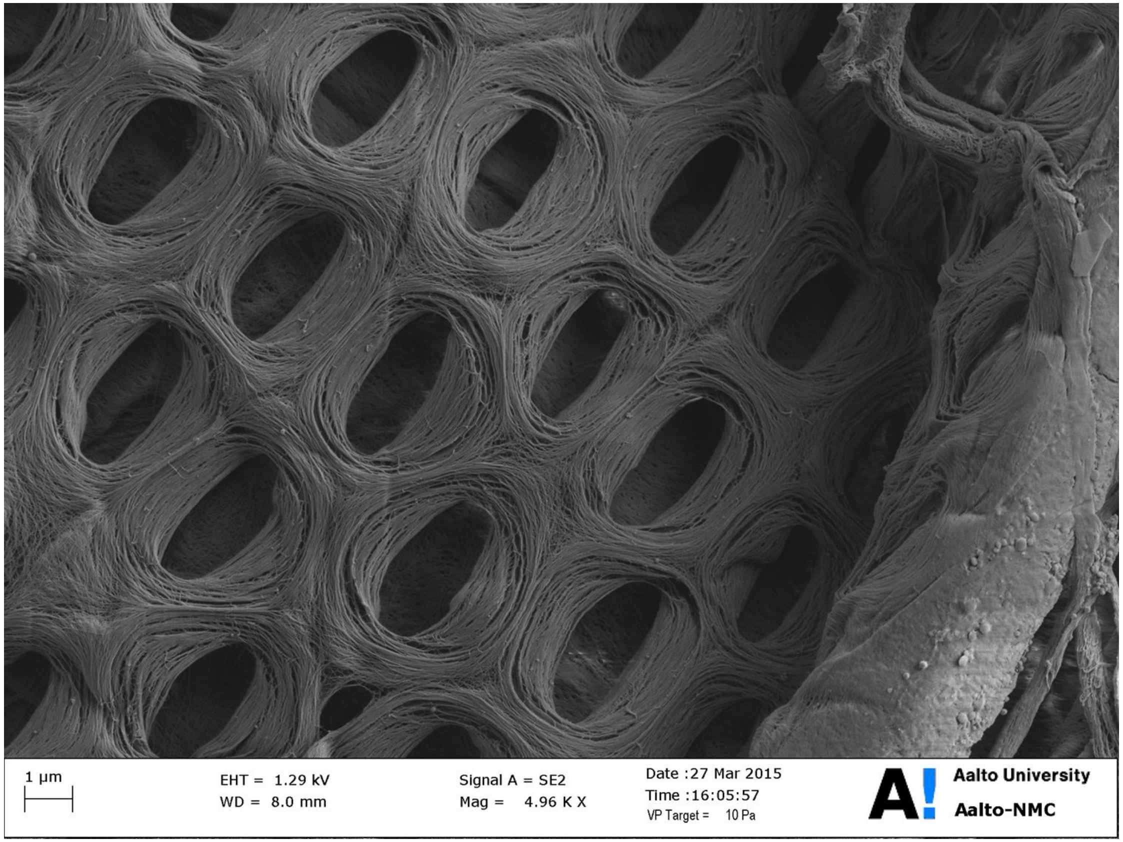
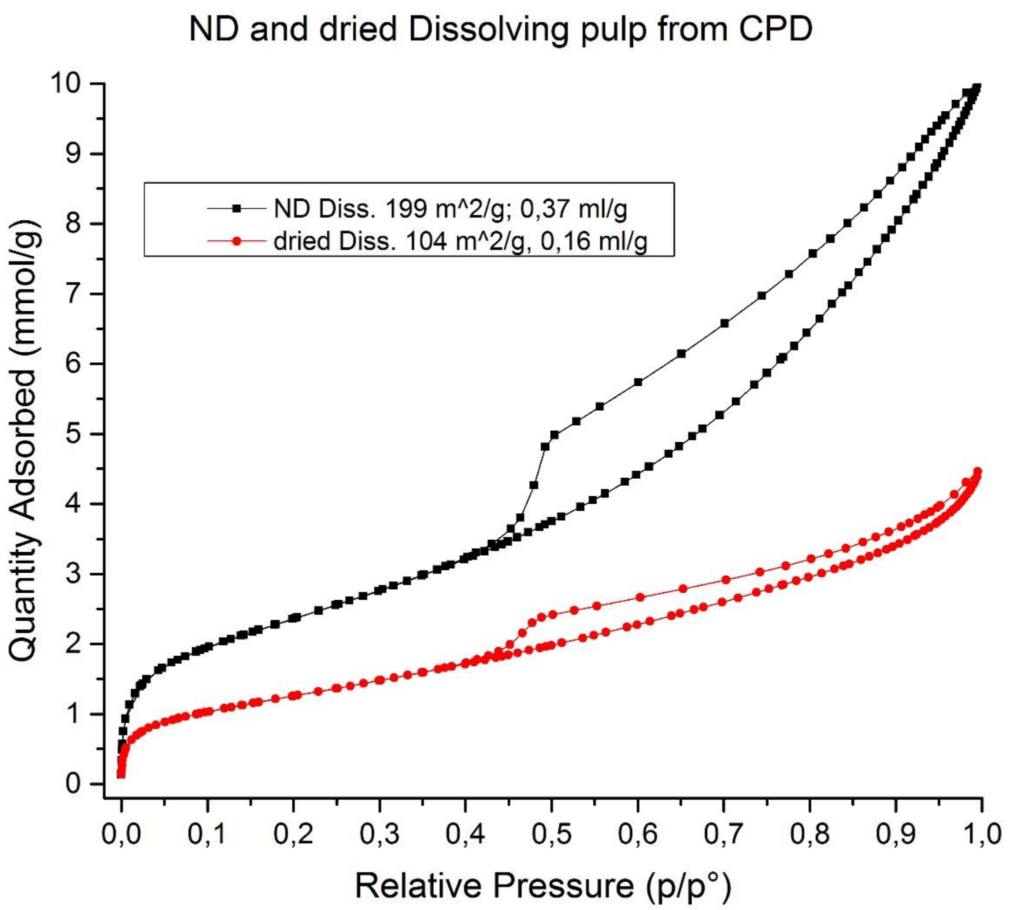
Time :15:40:33
VP Target = 10 Pa
Aalto University
Aalto-NMC

Micropores and compact cell wall regions



N_2 Isotherms for Never-dried and Previously-dried Dissolving Pulp



Pore Size Distribution for Dissolving Pulps, N_2 Sorption