NEW PERSPECTIVES FOR BIOMASS-BASED FUNCTIONAL MATERIALS

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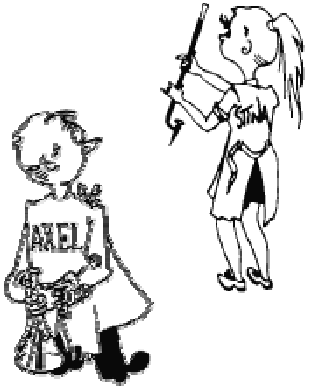
ÅBO AKADEMI UNIVERSITY

- Founded 1918
- Swedish-language university
- Multi-faculty university, seven faculties
- Today 7.000 students, over 600 international students
- Two campuses: Åbo and Vasa
- Small and personal university

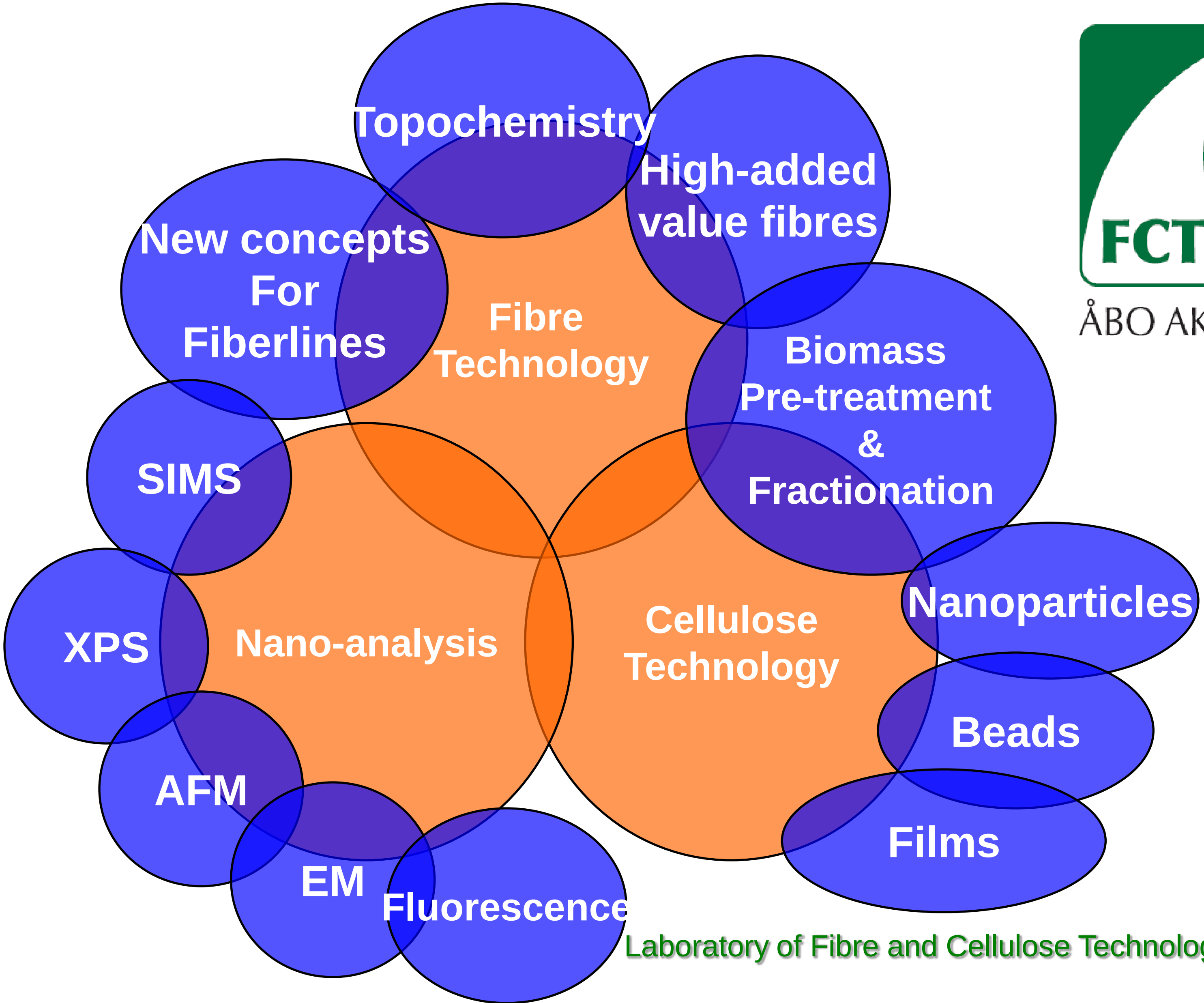
- www.abo.fi
- www.abo.fi/fa/ie/indexeng.htm

Faculty of Technology

- Two departments:
  - chemical engineering
  - information technologies
- Founded in 1920 as Faculty of Chemical Engineering, named changed in 2006
- Main specialisation areas: computer science, information systems, process chemistry, process system engineering and pulp and paper technology
- The faculty has two centres of excellence in scientific research appointed by the Academy of Finland: Process Chemistry Centre (PCC) and Center for Functional Materials (FUNMAT).
- The faculty offers master's of science degrees in Technology, Science and Economics and Business Administration.



Our Research and Education Areas



FCT
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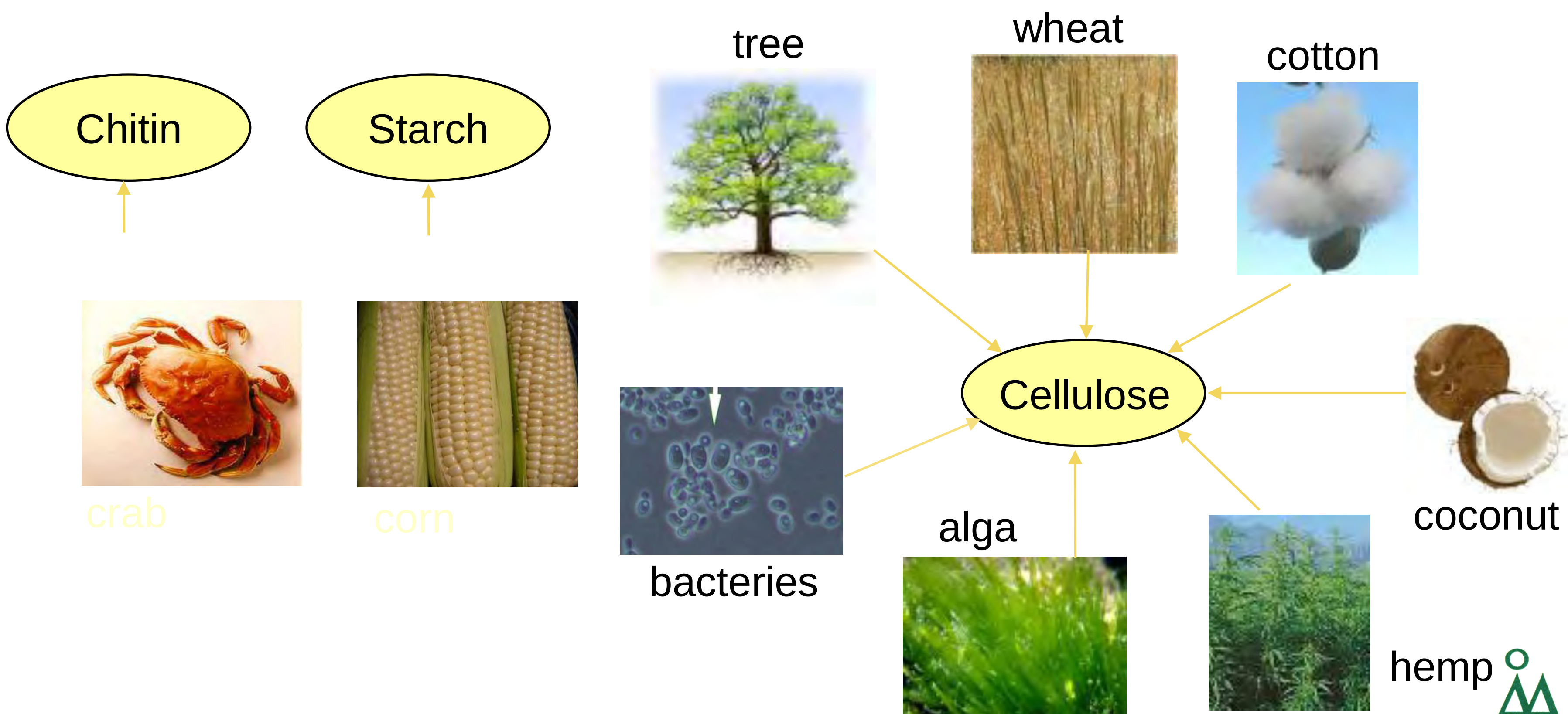
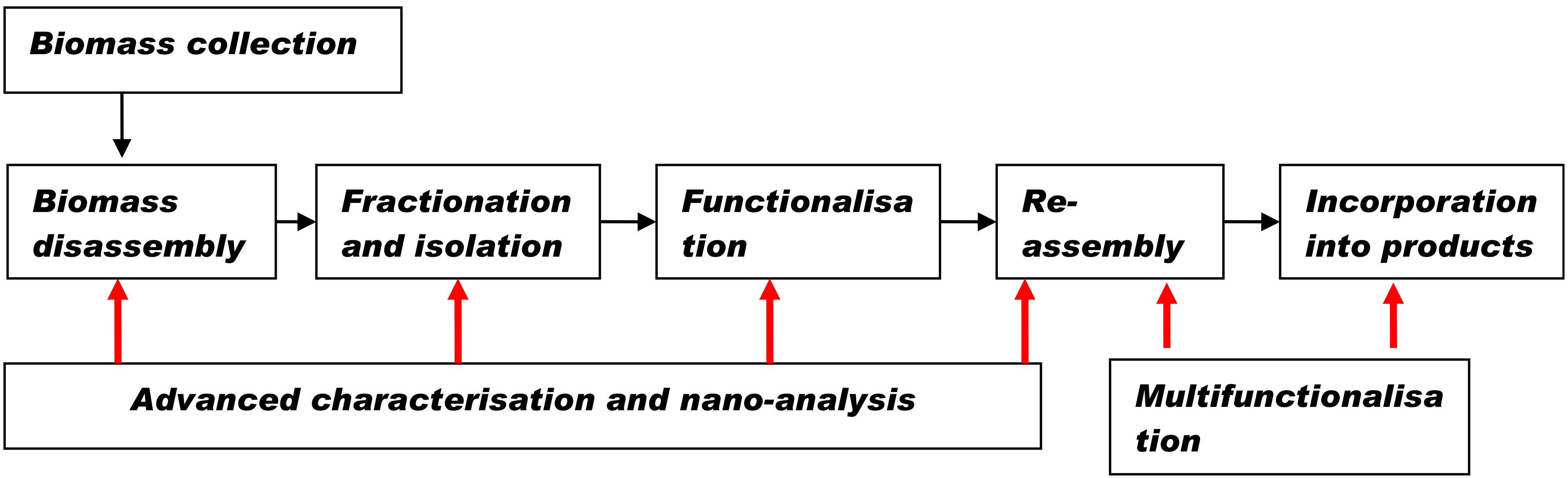
NEW PERSPECTIVES FOR BIOMASS-BASED FUNCTIONAL MATERIALS

Polysaccharides

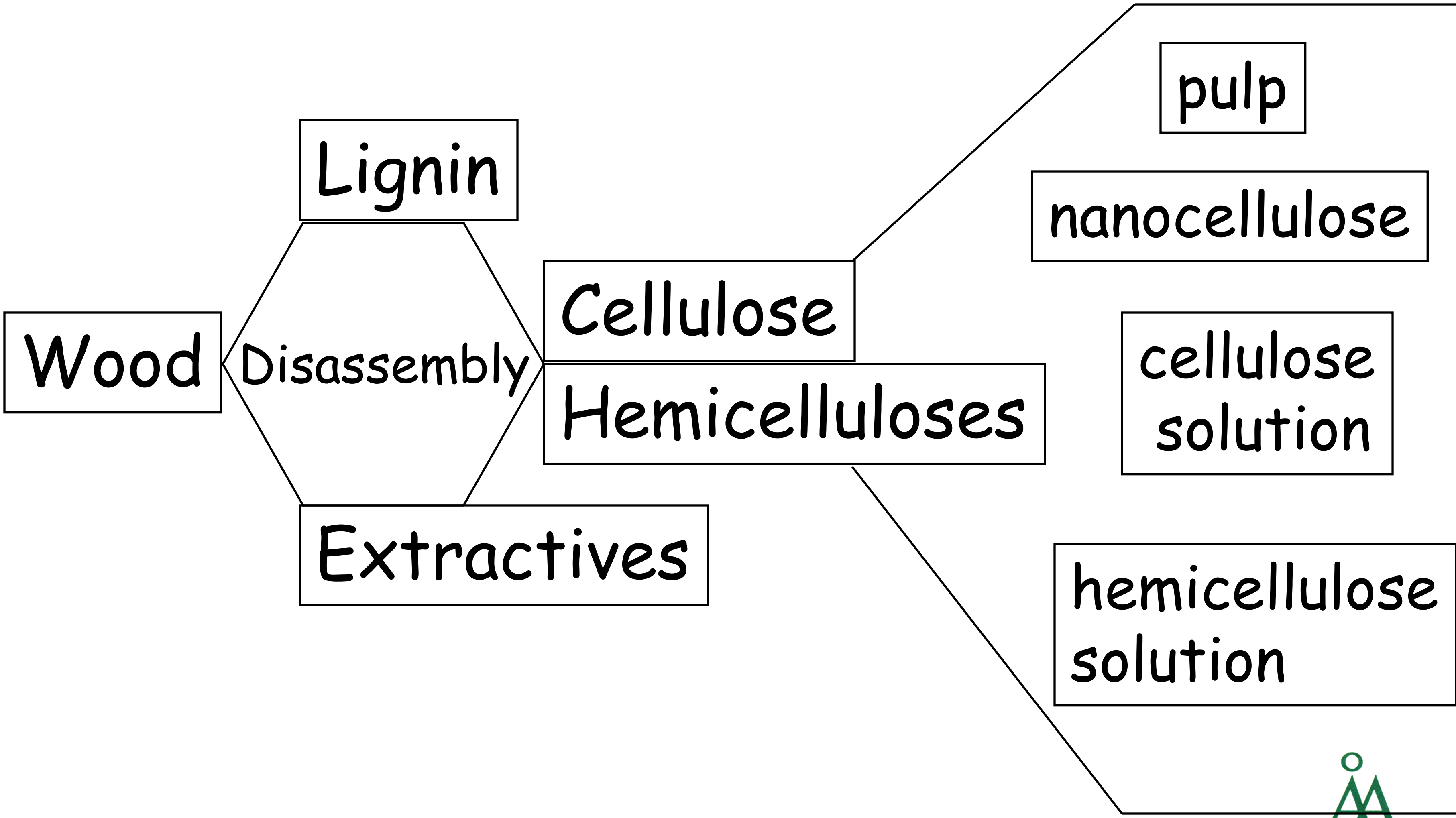
- Natural polymers such as starch, cellulose, chitin, carrageenan
- Produced by plants and animals



From biomass to functional materials

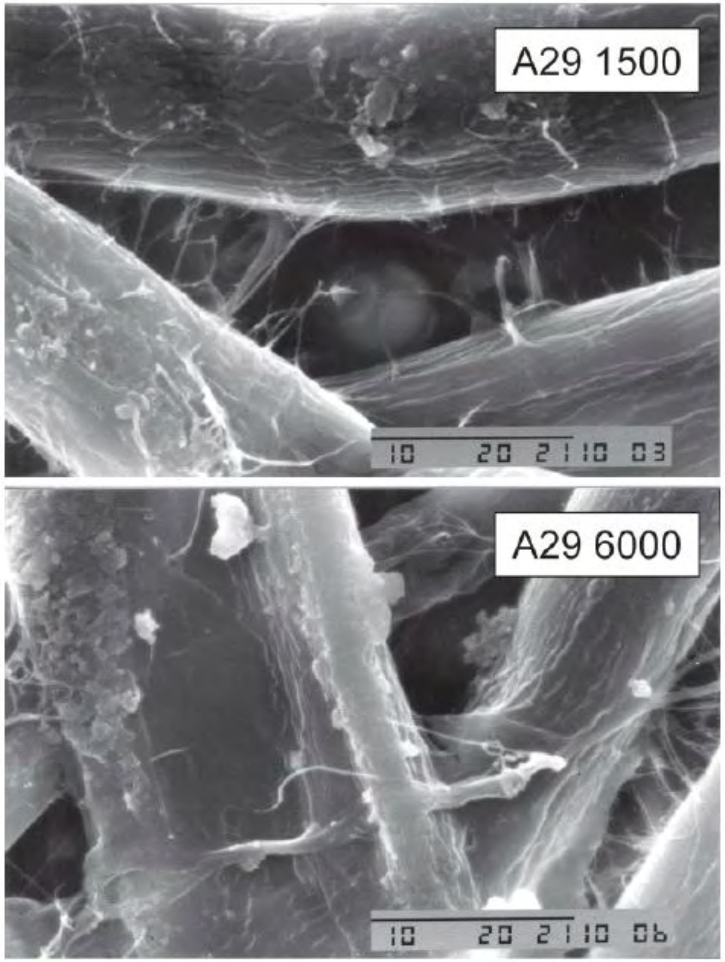


From wood to polysaccharides



Pulp fibres: Functional Material?

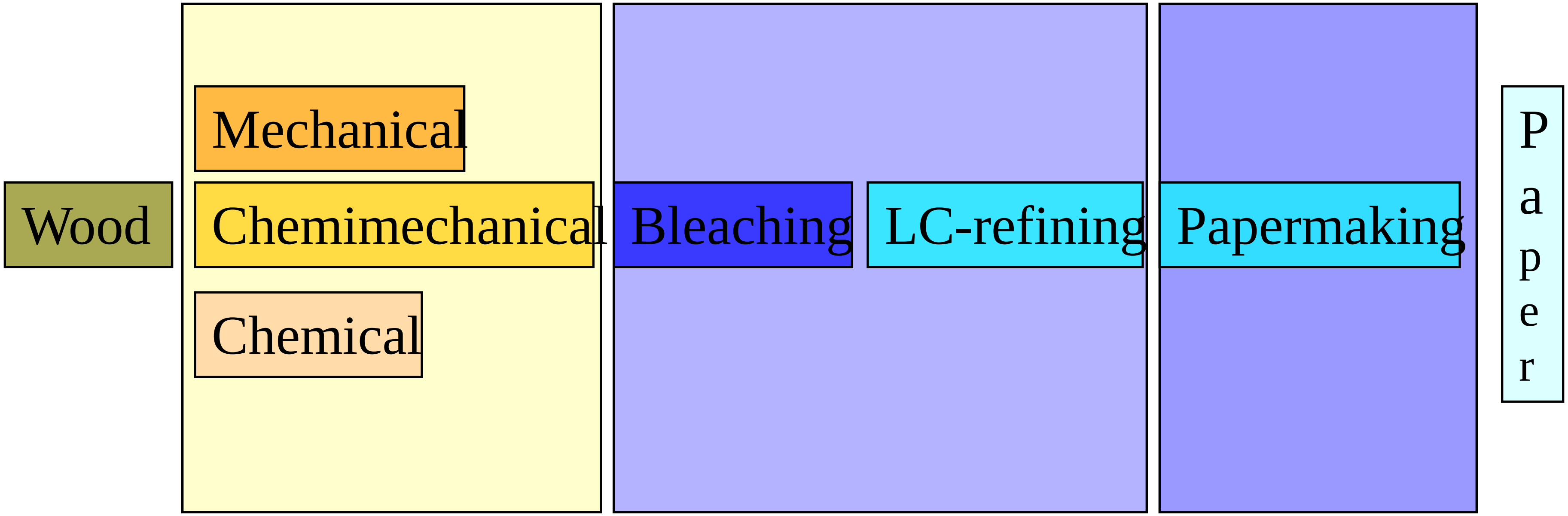
- Pulp: 350 million ton worldwide
- Used in paper, packaging, tissue, composites
- Available value chain (collection - recycling)
- Tailored optical and mechanical properties
- Other functionalities unexplored



Fibre Technology at FCT

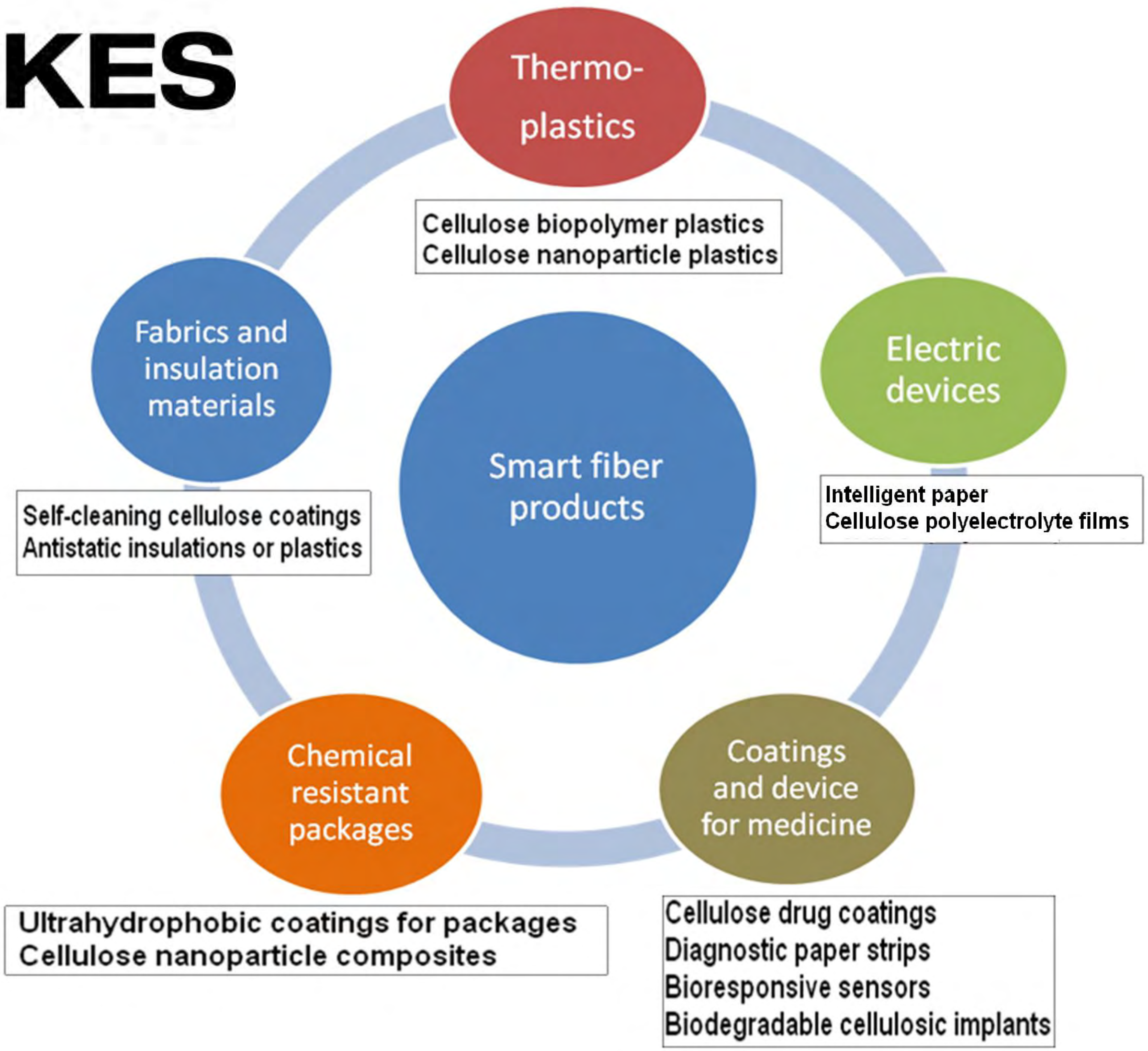
Fibre separation

Fibre functionalisation



SMART FIBRE CONCEPT

TEKES

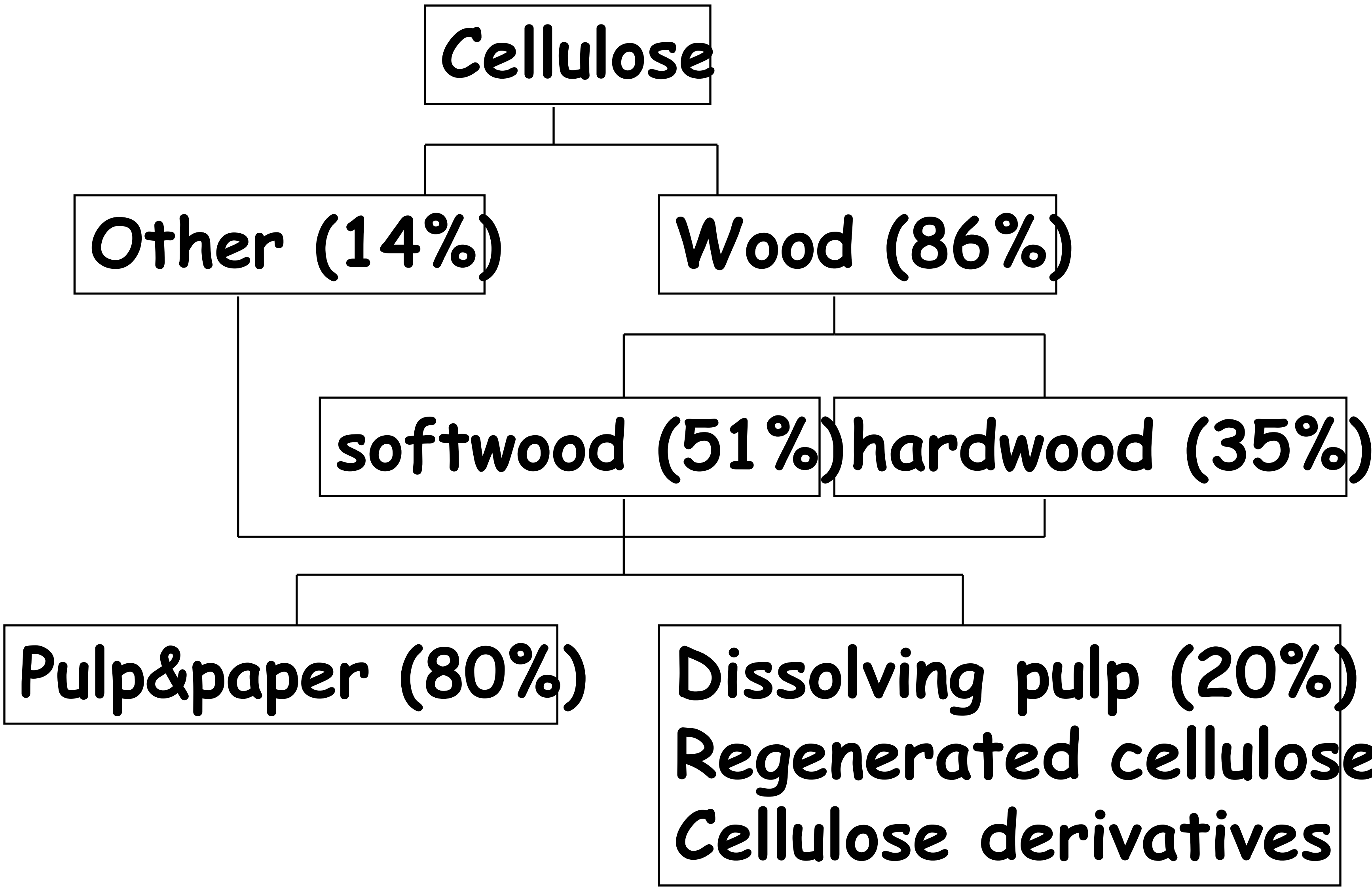


Challenges and opportunities for functional pulps

- Conditions of functionalisation compatible with current processes/technology
- Functionality is transferred to final product
- Sustainable, low energy intensive, recyclable
- Availability of value chains
- Opportunity to replace oil-based materials

Cellulose

- 50 % of biomass on earth
- 100-150 billion-ton per year
- One tree: ~14 g of cellulose per day
- Vegetal (plants)
- Seaweed (valonia, microdycon)
- Biosynthesised by bacteria (acetobacter xylonium)


Cellulose
Other (14%)
Wood (86%)
softwood (51%)
hardwood (35%)
Pulp&paper (80%)
Dissolving pulp (20%)
Regenerated cellulose
Cellulose derivatives

Chemical modification of cellulose

- Homogeneous reaction medium (HM)
  - one phase, requires dissolution
- Heterogeneous reaction medium (HT)
  - two phase

Cellulose dissolution

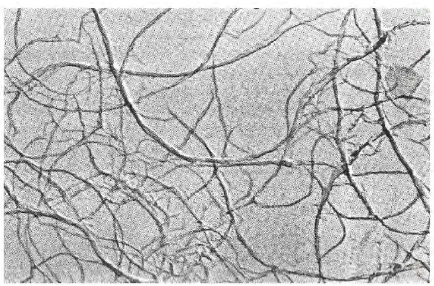
- Raw material (availability, costs, pretreatment)
- Choice of solvent system
  - Viscose (xanthate)
  - NMMO (N-methylmorpholine N-oxide)
  - NaOH-water (urea, ZnO)
  - Ionic Liquids (ILs)
  - Others (several derivative and non-derivative)
- Environmental aspects
- Is the solvent inert?

Cellulose based materials

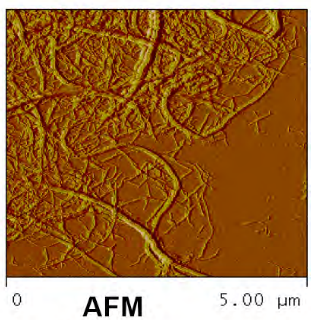
- Microfibrillar or nanocellulose (HT)
- Cellulose nanorods or crystals (HT)
- Regenerated cellulose from solution (HM) (fibres, particles, films, aerocellulose)
- Cellulose derivatives (HT or HM)

Nanocellulose and nanocrystals

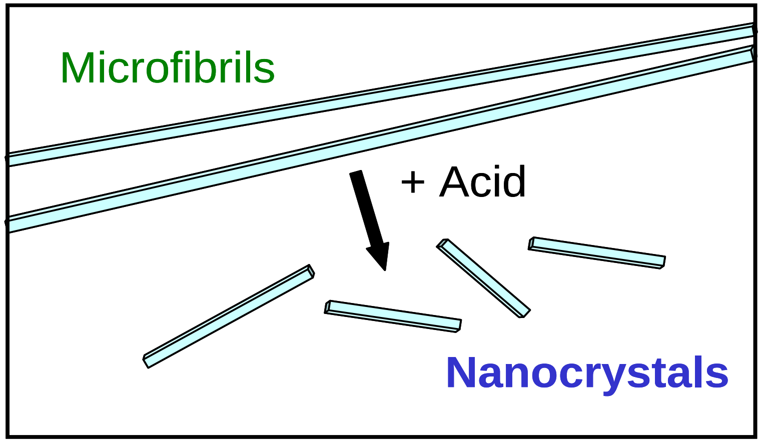
SEM and AFM of MFC



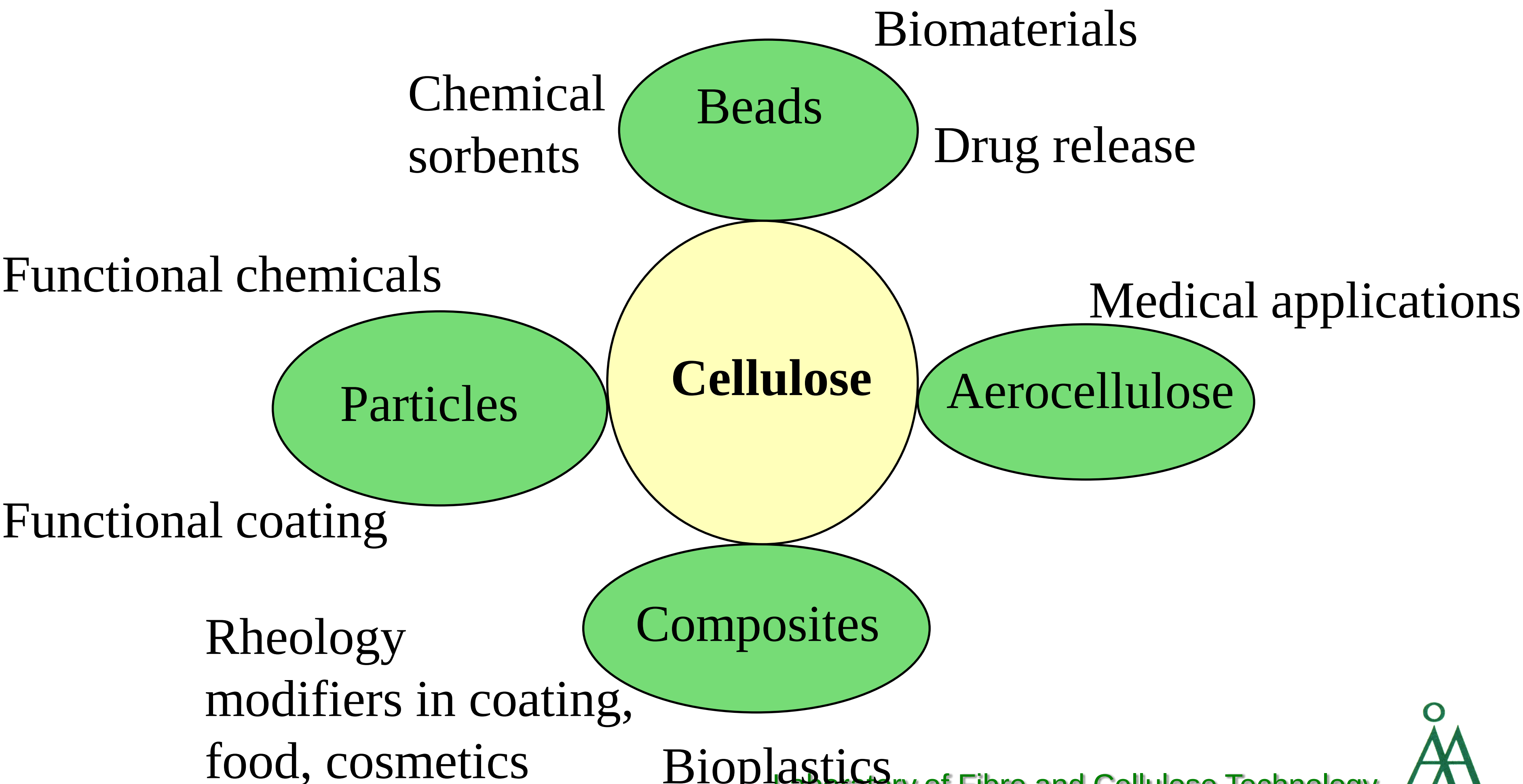
SEM (40000x)
Lindström and Winter, 1988



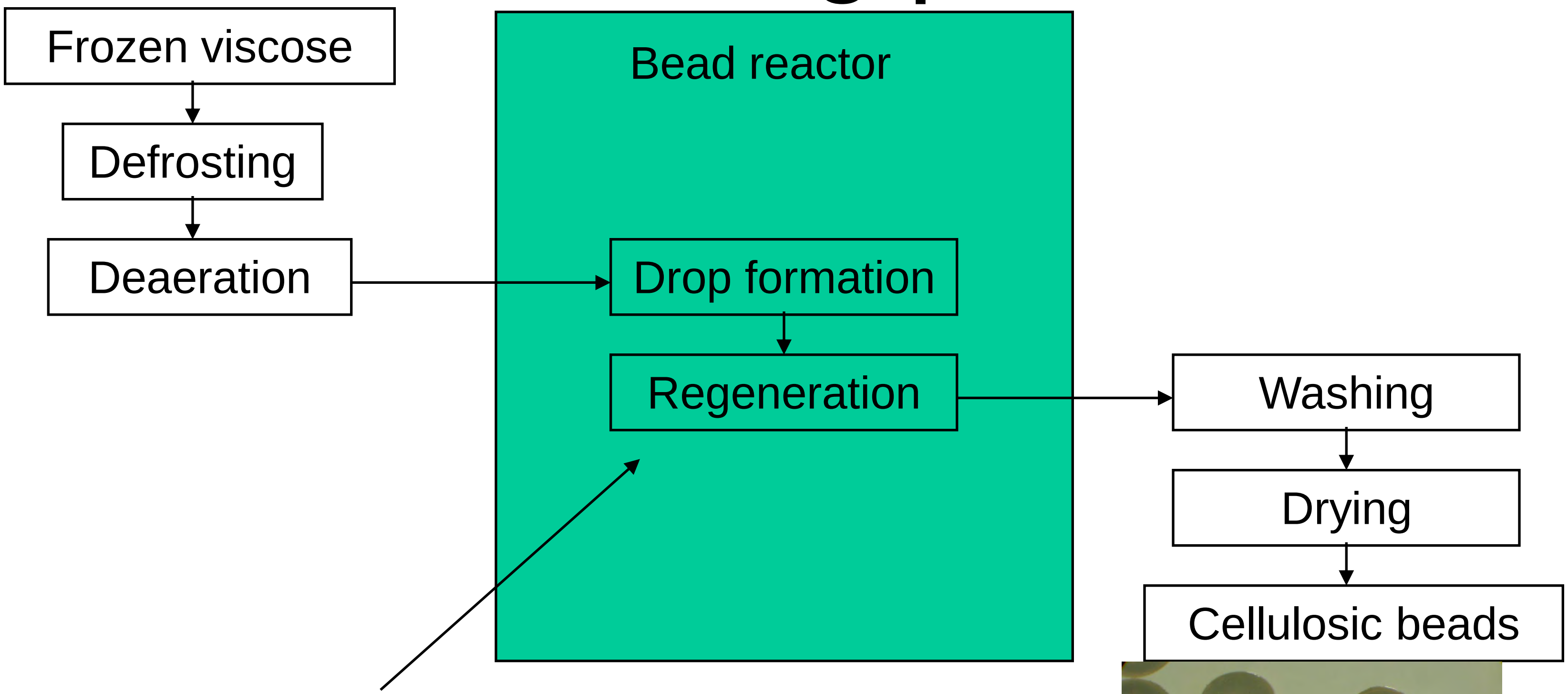
AFM
Notley, 2003

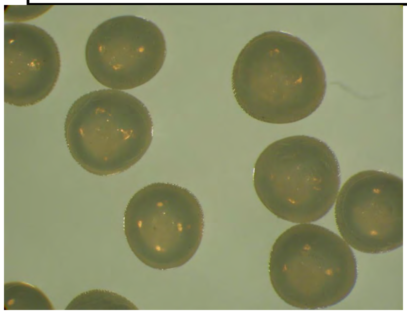


Cellulose Technology at FCT



Bead-making process



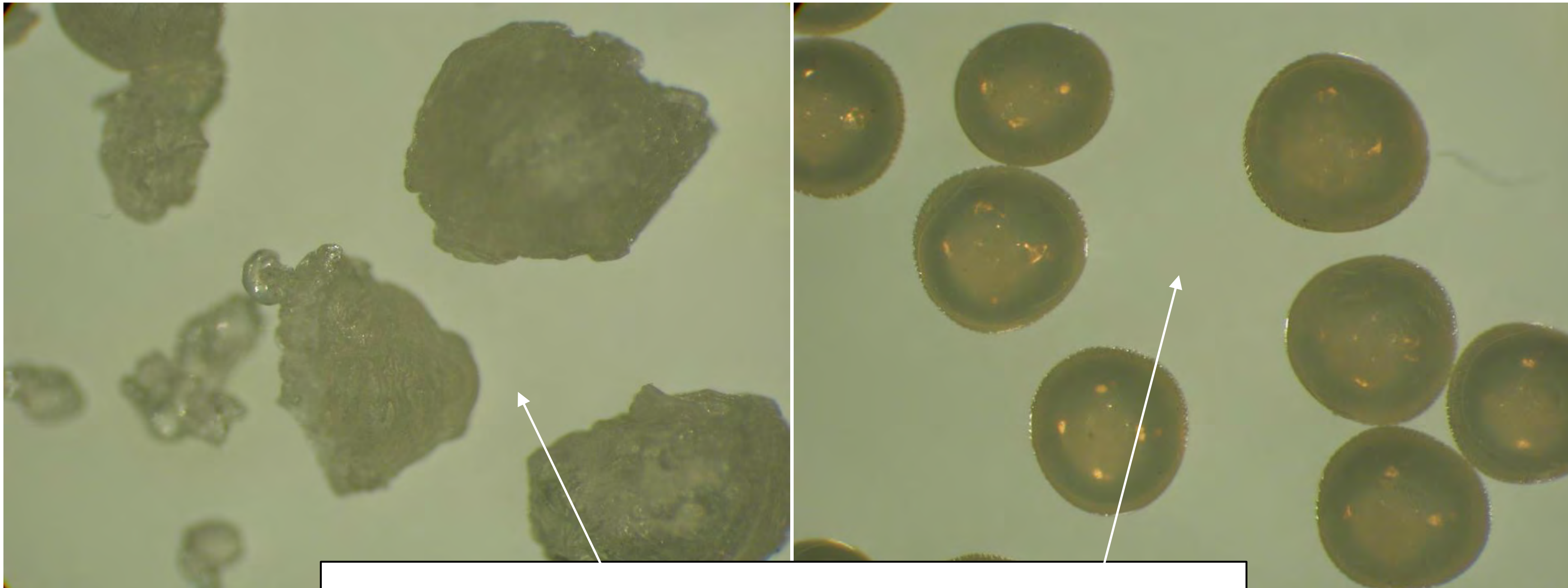


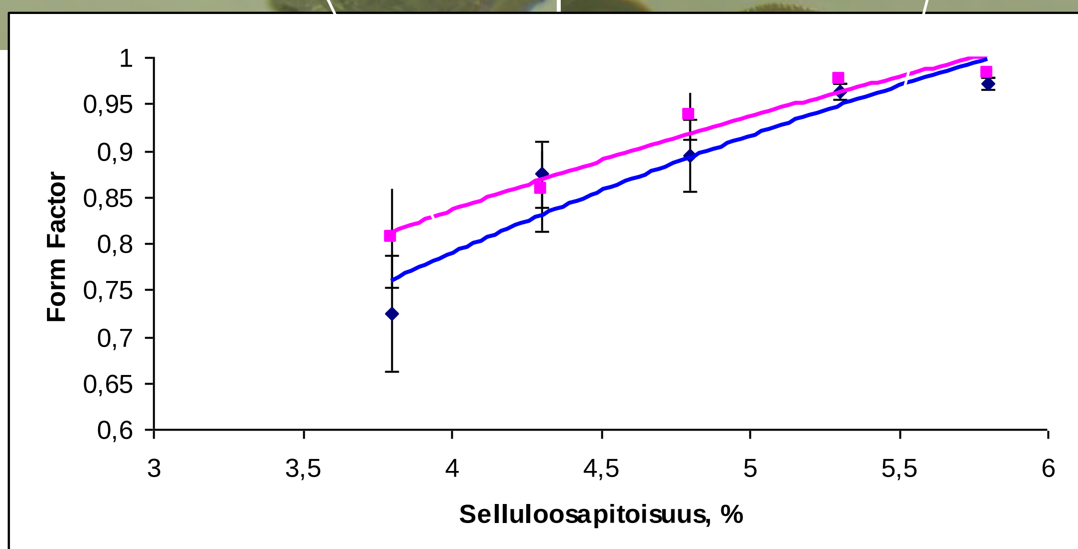
2 Cellulose-$OCS_2Na + H_2SO_4$

→ 2 Cellulose-$OH + Na_2SO_4 + 2\ CS_2$

Cell I → Cell II (irreversible)

Form factor

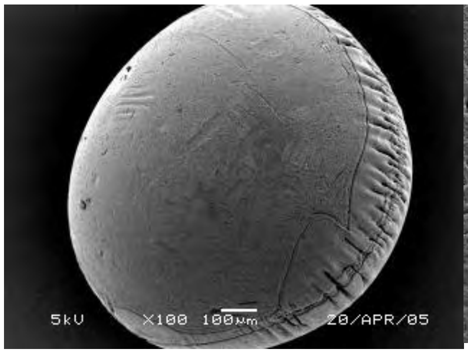




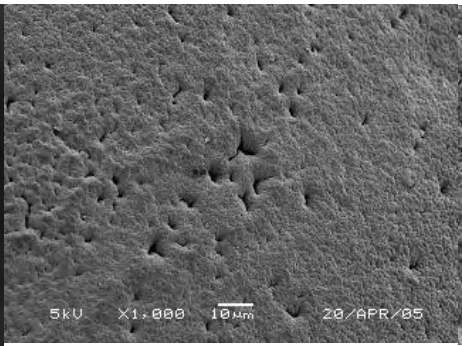
Form Factor
1
0,95
0,9
0,85
0,8
0,75
0,7
0,65
0,6
3
3,5
4
4,5
5
5,5
6
Selluloosapitoisuus, %

Beads of regenerated cellulose

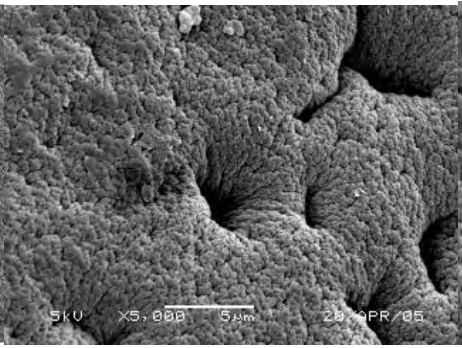
x100



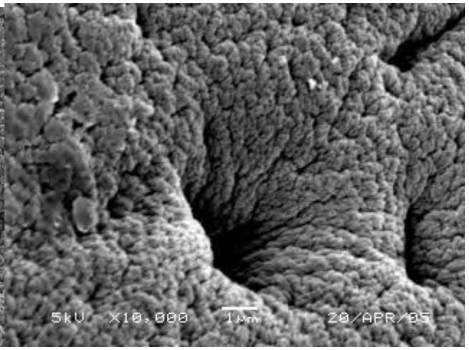
x1000



x5000



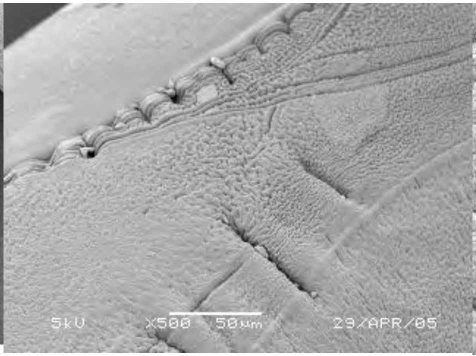
x10000



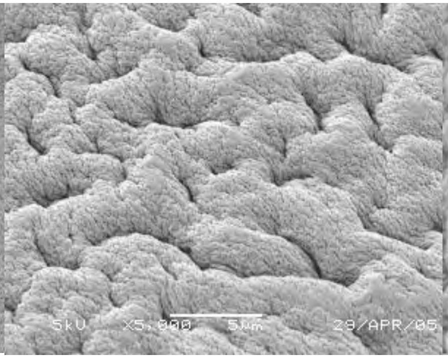
100 µm — 10 µm — 5 µm — 1 µm

x100

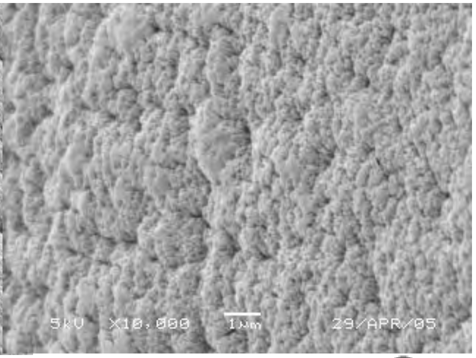
x500



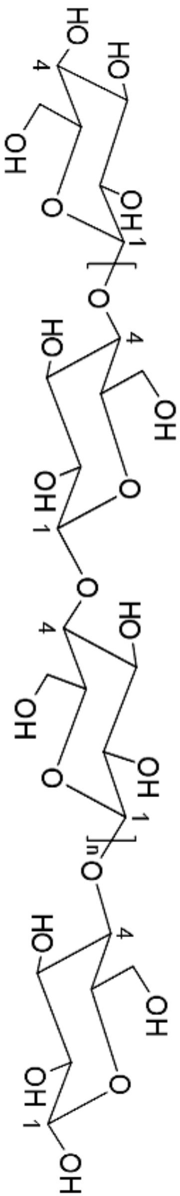
x5000

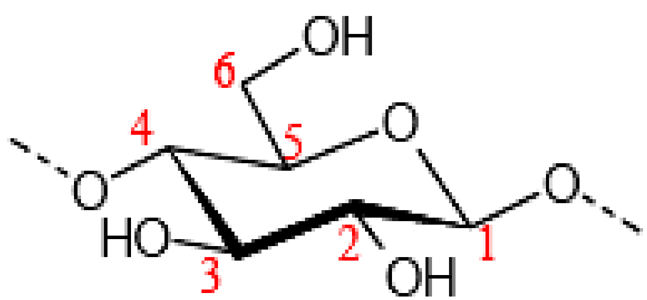


x10000



Cellulose chemistry: opportunity to tailor functionality of materials





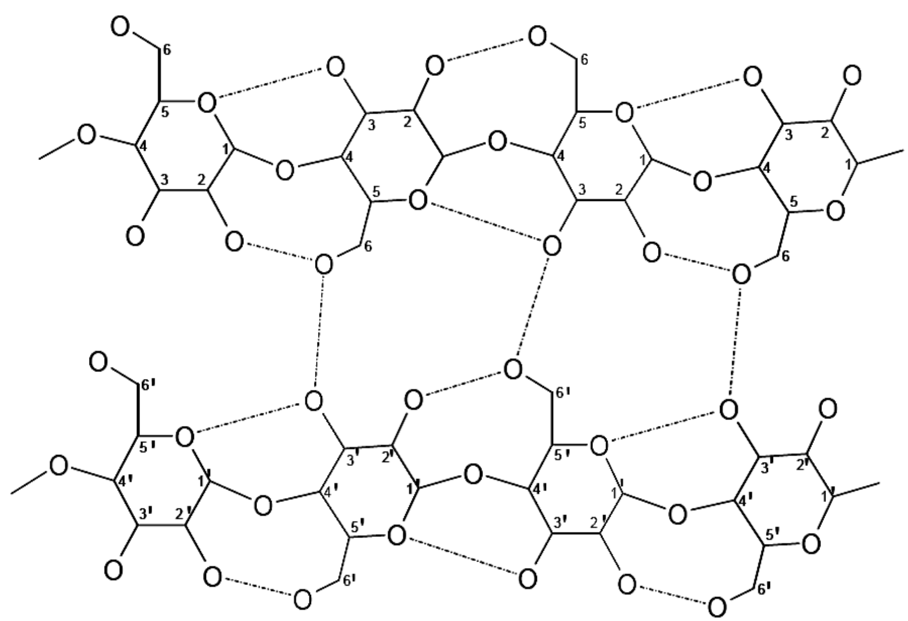


Table 5. Conditions and results of the acetylation of cellulose (2.9%, w/v) dissolved in dimethylsulfoxide/tetrabutylammonium fluoride trihydrate (16.6%, w/w) with vinyl acetate at 40 °C for 70 h.

Molar ratio[a)]	Catalyst[(b)] [mg]	Partial DS		DS[(c)]	Solubility
		at *O*-6[(c)]	*O*-2/3		
1:2.3	—	0.49	0.55	1.04	Dimethylsulfoxide
1:2.3	20	0.52	0.55	1.07	Insoluble
1:1.5	20	0.39	0.24	0.63	Insoluble
1:10.0	20	0.98	1.74	2.72	Dimethylsulfoxide

a) Molar ratio of vinyl acetate to anhydroglucose unit (mole/mole).

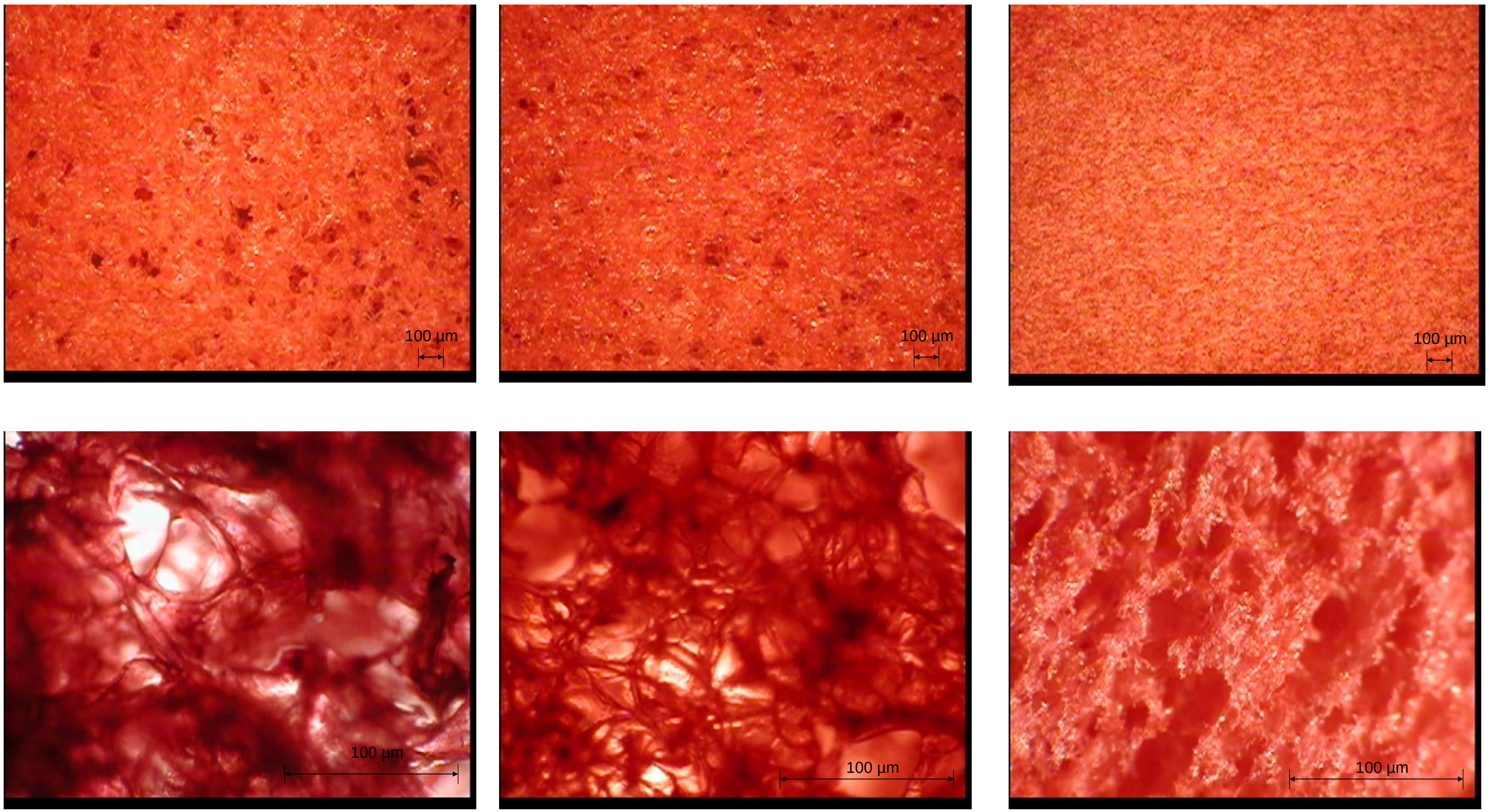
b) Mixture of KH_2PO_4 and Na_2HPO_4.

c) Degree of substitution calculated from ^1H-NMR spectra.

Aerocellulose (with tailored porosity)

1x

4x



1250 µm | 600 µm | 250 µm

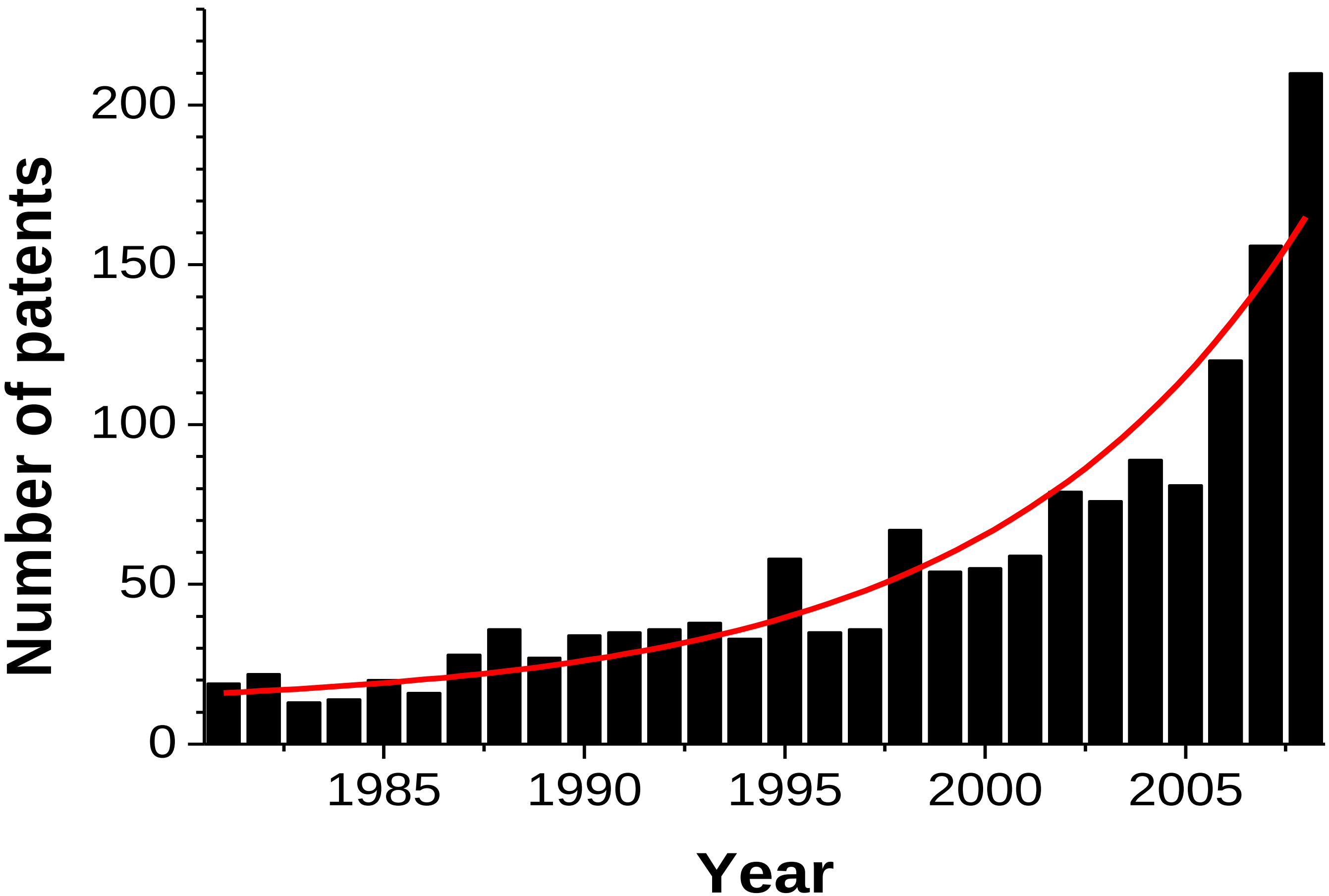
Challenges and opportunities for functional cellulose

- Challenges:
  - Dissolution in inert solvents and purity of raw materials
  - Evenness of functionalisation, stabilization of suspension in heterogeneous conditions
- Opportunities
  - Renewable resource with high availability
  - Excellent possibilities for chemical and physical functionalisation. New functional materials

What are hemicelluloses?

- Biopolymers present in different biomass materials (wood, plants, cereals)
- A moderate low DP in comparison with cellulose (50-300 vs 3000-10000)
- A multitude of combinations of sugar units as backbone and side groups
- Interesting properties: bioactive, biodegradable, water soluble

Number of patents containing term hemicellulose during 1980-2008 searched (19.1.2009) by SciFinder Scholar.



POLYSMART consortium

SUOMEN AKATEMIA
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2008-2011
SUSTAINABLE
ENERGY

CB UdeC
Centro de Biotecnología
Universidad de Concepción
Región del Bio-Bio

LRR

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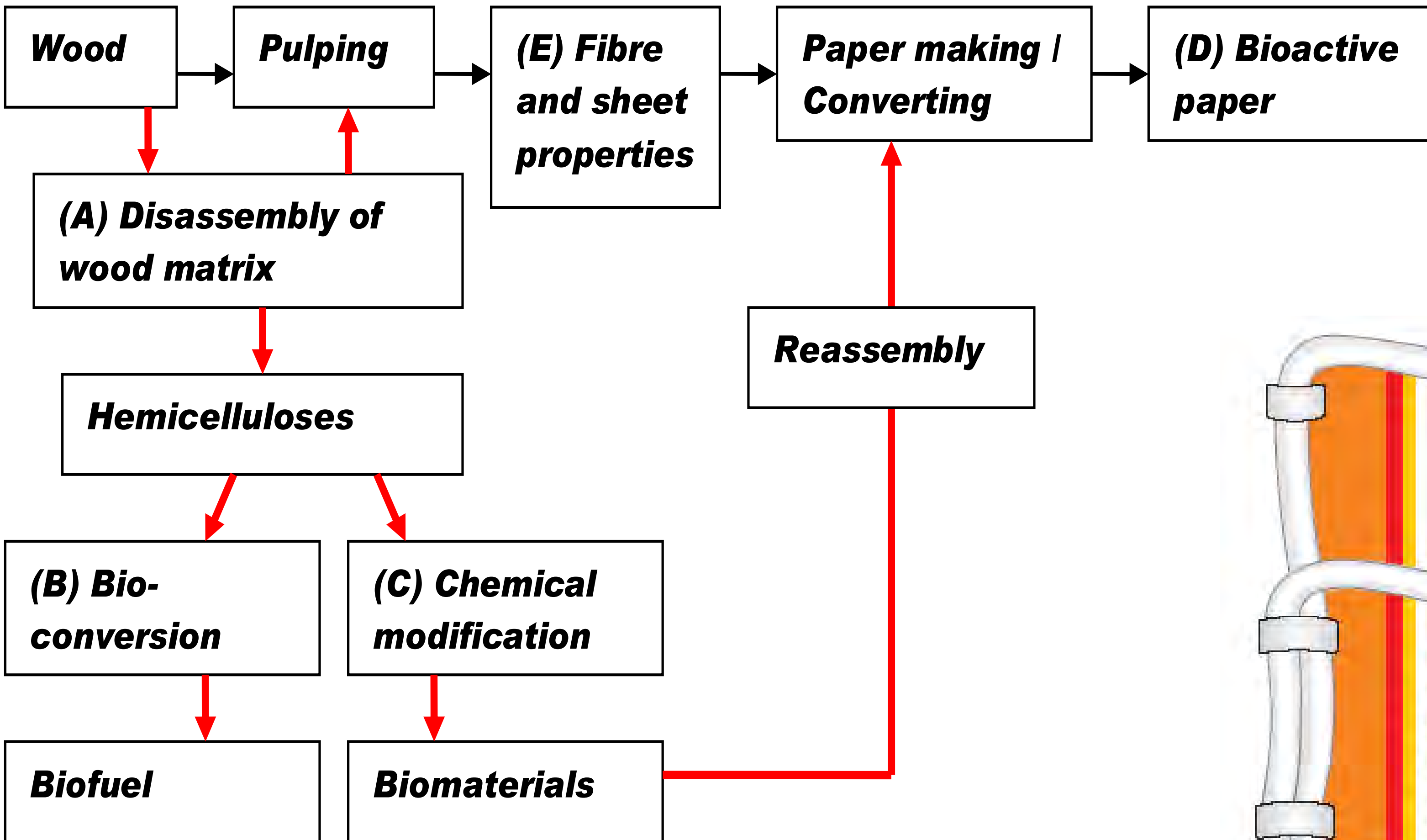
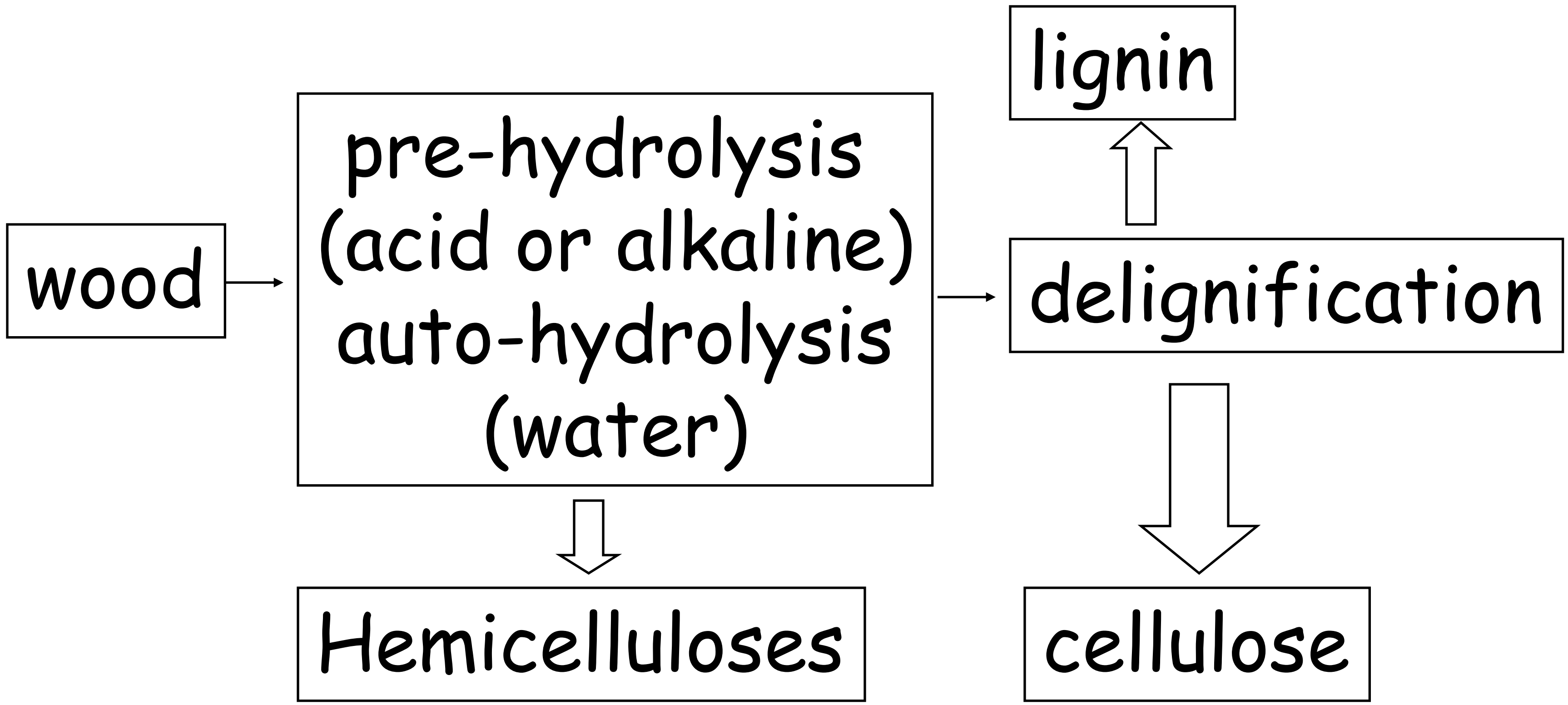
Polysmart overview



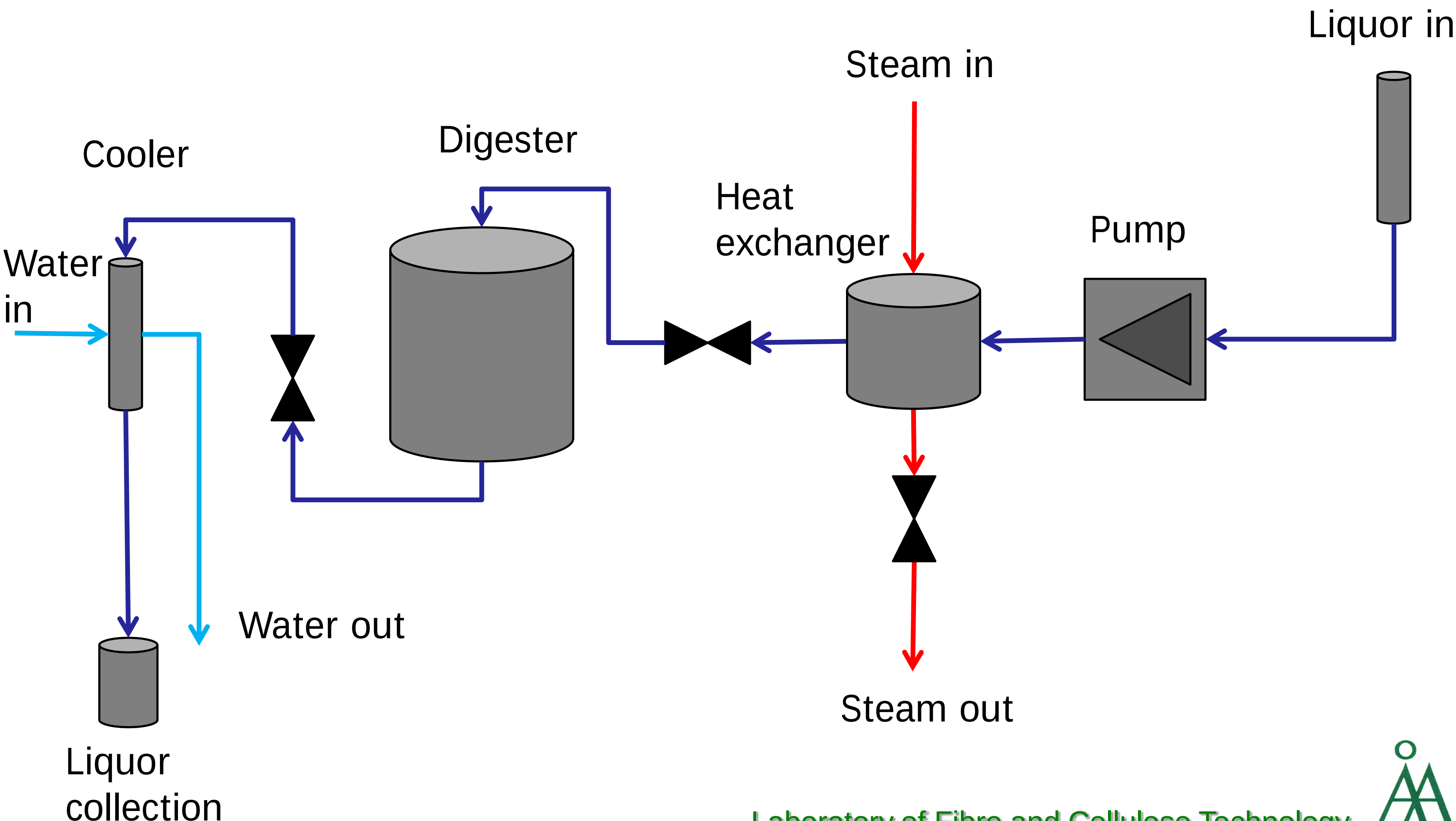
SusEn 2008-2011 SUSTAINABLE ENERGY

Disassembly of hemicelluloses by hydrothermal treatment

Extraction of hemicelluloses



Extraction equipment (PHWE)



Extraction equipment (LiqCir)

200 g of wood/biomass

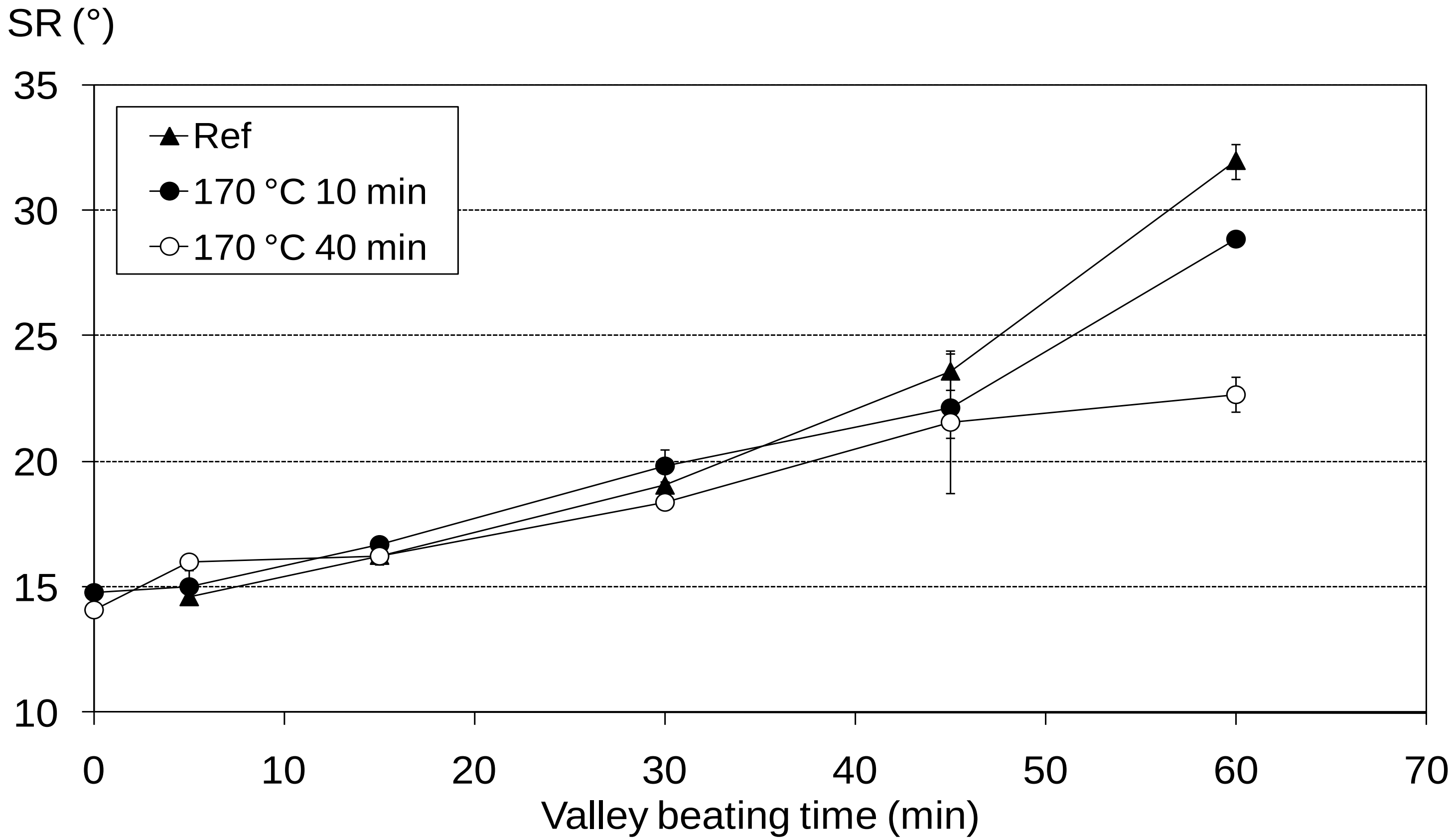
4000 g of wood/biomass

Summary of exploratory experiments

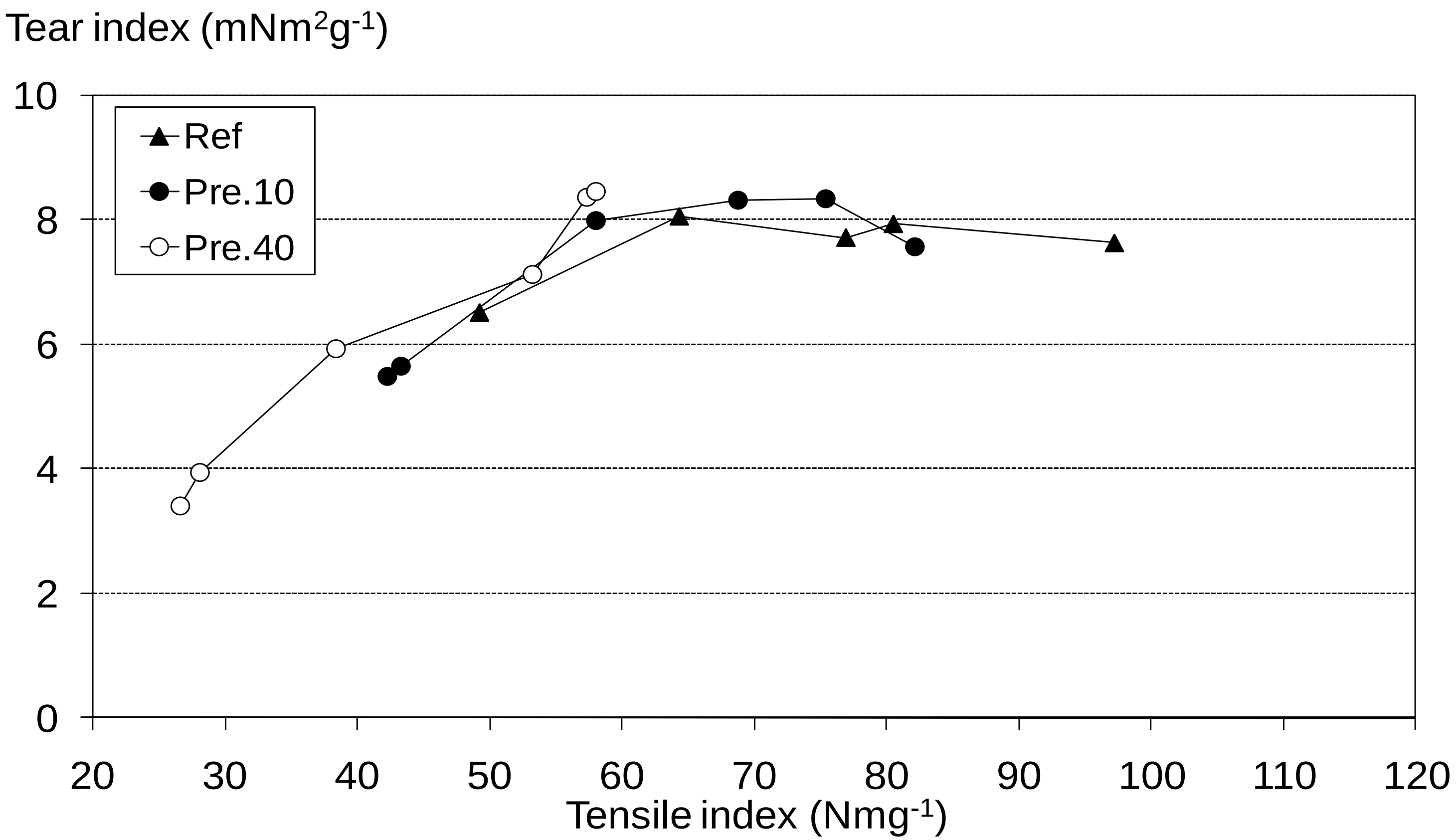
- Time and temperature are main variables in extraction of xylan
- Xylan can be disassembled from wood at different levels up to 95% w/w
- Higher xylan disassembly leads to disassembly of lignin up to 30% w/w
- About 29% of xylan in wood (11% on wood basis) can be disassembled without removal of lignin

Effects of hemicellulose extraction on fibre properties

Refining - SR


SR (°)
35
30
25
20
15
10
0
10
20
30
40
50
60
70
Valley beating time (min)
Ref
170 °C 10 min
170 °C 40 min

Tensile vs Tear



Effect of Hemicellulose extraction on Kraft Pulping and Fibre Chemistry

- Extraction of xylan reduces the yield in kraft cooking (about 10% lower)
- Lower dosages of alkali are needed in cooking (33 % reduction in active alkali)
- Only 3% of residual hemicelluloses in birch after water extraction and pulping
- Dissolving pulp grade possilbe after 40 min pre-treatment + kraft pulping + bleaching

Effects of hemicellulose extraction on fibre properties

- Refining (higher energy consumption)
- Decrease the fibre length
- Slightly increase in bulk of handsheets
- Reduction in tensile index
- Benefitial for tear index after refining
- Positive for light scattering of handsheets

Utilization of hemicelluloses

- Fibre modification
- Paper coatings/converting
- Bioactive packaging
- Bioactive films in tissue healing
- Food and cosmetic additives
- Biofuels
- Pharmaceuticals

Challenges and opportunities for functional hemicelluloses

- Challenges:
  - Disassembly from wood
  - Negative impact on fibre properties using current technology
  - Purity/evenness of biopolymer
- Opportunities
  - Large availability
  - Incorporation into products
  - Few commercial exploitation

Complementary research activities between Finland and Japan

- Fractionation technology
- Cellulose chemistry and technology
- Lignin chemistry and utilization
- Fibre based functional materials
- Nanoscale characterisation

Acknowledgements

TEKES

SUOMEN AKATEMIA

epnoe

FCT
ÅBO AKADEMI

CONFERENCE 2009

"Polysaccharides as a Source of Advanced Materials"

Turku, Finland
September 21-24, 2009

Important dates
Last minute abstract submission: March 30, 2009
Early bird registration: June 30, 2009

epnoe
European Polysaccharide Network Of Excellence

http://congress.utu.fi/epnoe2009