

NATURAL POLYMERS

Polysaccharide II

CELLULOSE 2

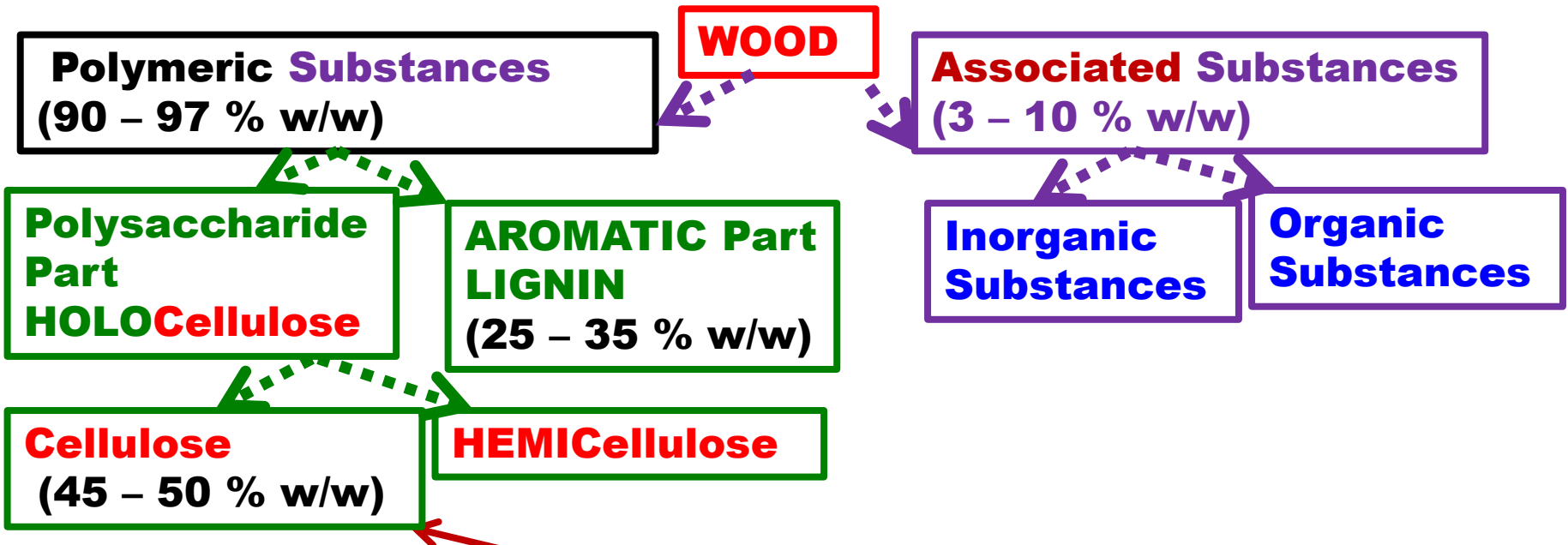
**Cellulose is the most
widespread BIOPOLYMER
on Earth, up to $1,5 \times 10^9$ tons
per annum is arising**

Dr. Ladislav Pospíšil

Time schedule

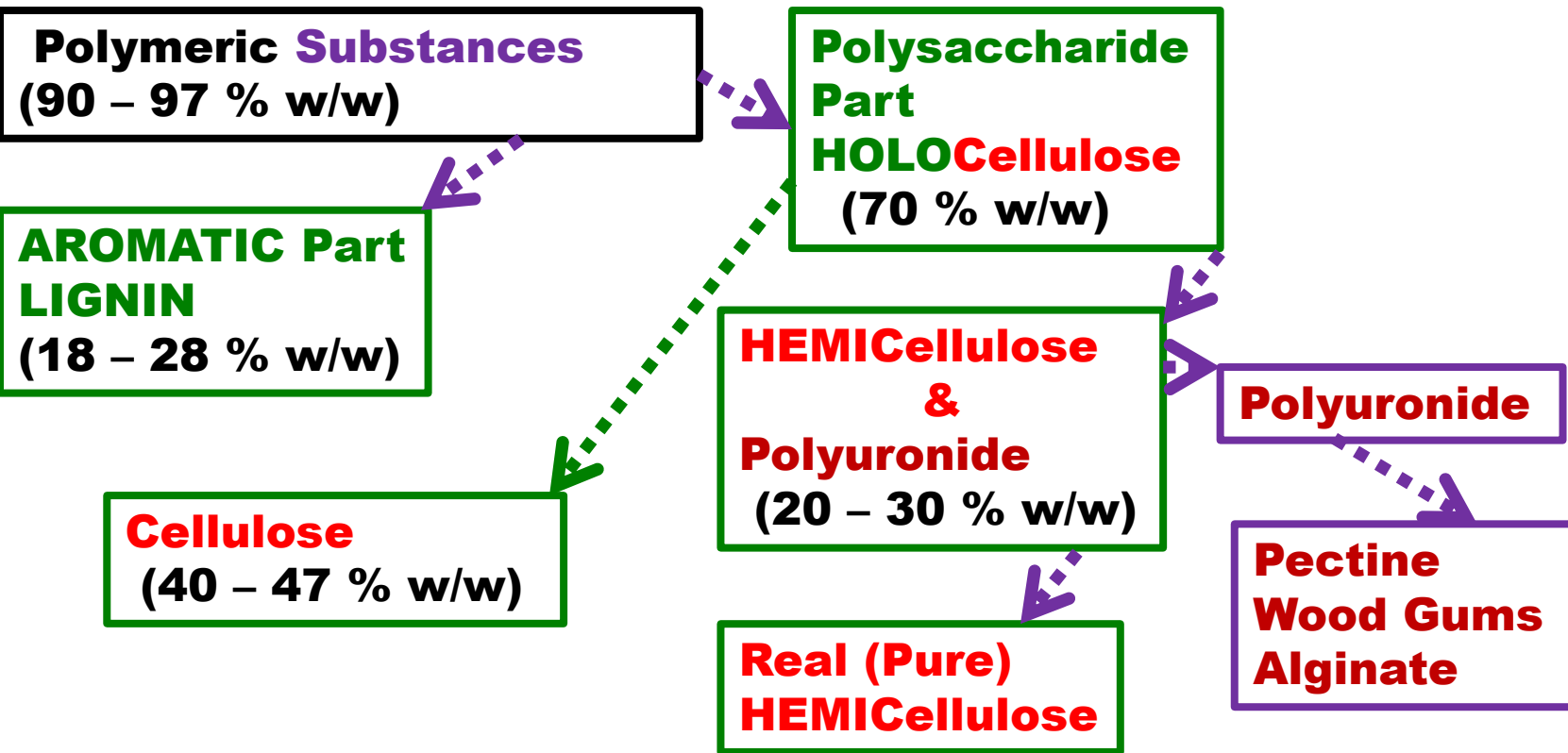
LECTURE	SUBJECT
1	Introduction to the subject – Structure & Terminology of nature polymers, literature
2	Derivatives of acids – natural resins, drying oils, shellac
3	Waxes
4	Plant (vegetable) gums, Polyterpene – natural rubber (extracting, processing and modification), Taraxacum_kok-saghyz
5	Polyphenol – lignin, humic acids
6	Polysaccharides I – starch
7	Polysaccharides II – cellulosis
8	Protein fibres I
9	Protein fibres II
10	Casein, whey, protein of eggs
11	Identification of natural polymers
	Laboratory methods of natural polymers' evaluation

Cellulose natural Abundance in WOOD



The only approx. 1/3 of the whole Tree is Cellulose, including a Root and a Tree stump!

Cellulose natural Abundance in WOOD— another Scheme



Occurrence of the Associated Substances in WOOD

Substance

Saccharide

Essential/ethereal oil (**terpeny**)

Tannine

Sterols (it belongs to **TERPENOIDES**)

Inorganic Substances (Ash)

Fats, Oils, Waxes

Resinous Acids (e.g. Abietic Acid, which is a Part
Resins)

Proteins

Aliphatic Acids

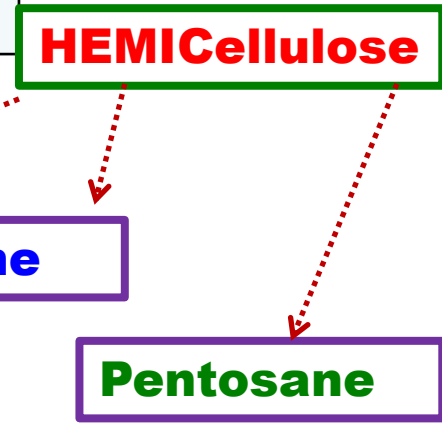
Cellulose natural Abundance

Chemical Composition of COTTON versus WOOD

Component % w/w	COTTON Linters	Coniferous Tree	Broad Leaf Tree
HOLOCellulose	90 – 94	50 – 58	52 – 54
Pentosanes	1,5 – 2,0	11	25
Lignin	2,0 – 3,0	26 – 28	17
Pektines	2,0	1,0	1,5 – 2,0
Proteins	1,5 – 2,0	0,5 – 0,8	0,5 – 0,8
Fats & Waxes	0,5 – 1,0	1,0 – 2,0	1,0 2,0
Ash	1,0	0,25 – 0,5	0,25

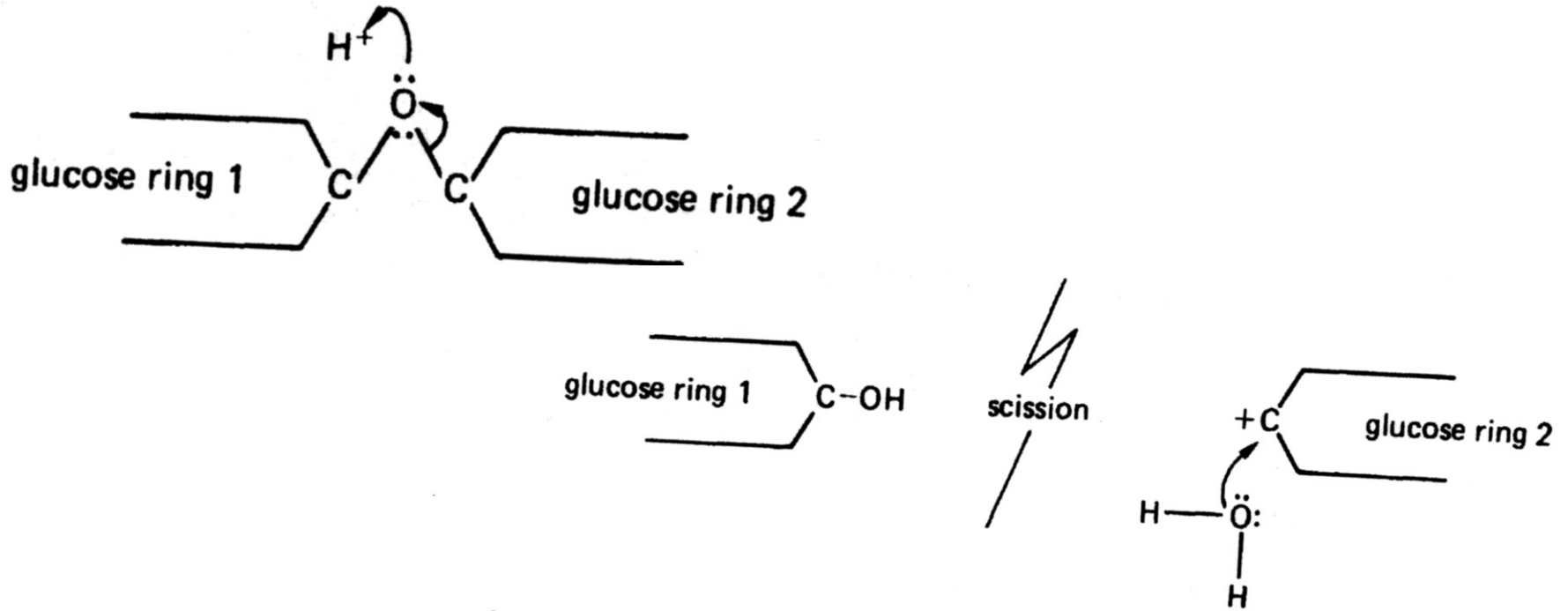
Linters = short Cotton Fibers, which are not able to be spun to Thread

PDM = MEAN DEGREE OF POLYMERIZATION

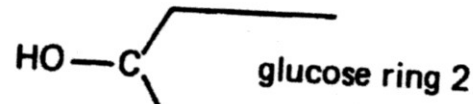


Cellulose Sort (Source)	PDM
Cotton	1750 – 3356
Wood	650 – 1256
REGENERATED Cellulose	200 - 500

DEGRADATION of PAPER based on Cellulose 1

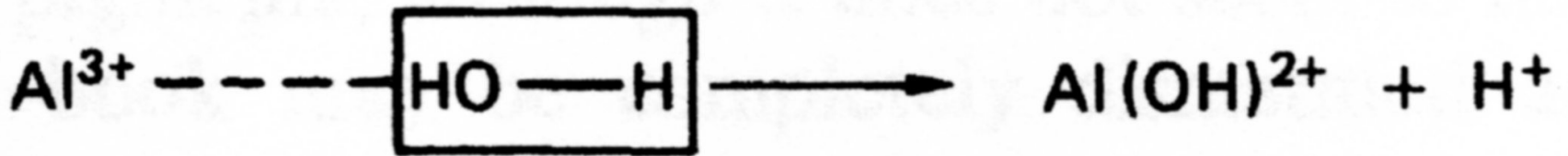


and an H^+ ion is regenerated:

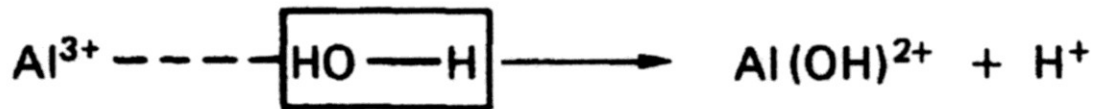


The regenerated hydrogen ion can repeat the process elsewhere. It appears that if as few as 1–2% of the ether-type bridges are cut, the paper becomes brittle and easily fragments.

DEGRADATION of PAPER based on Cellulose 2

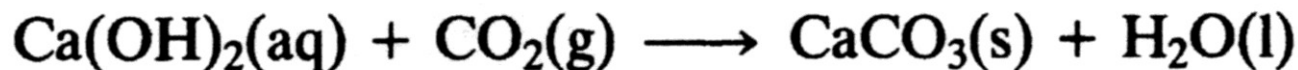


The very small, triply charged aluminium ion strongly attracts nearby water molecules, causing one or more to split up, releasing hydrogen ions:

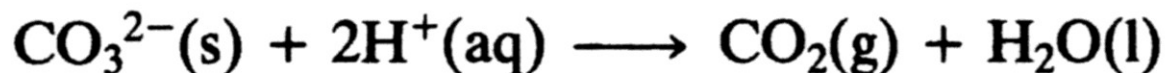


DEACIDIFICATION of PAPER based on Cellulose 1

Lime-water remaining in the paper, as it dries, reacts with carbon dioxide in the air, to form calcium carbonate, which is precipitated on and among the fibres of the paper:



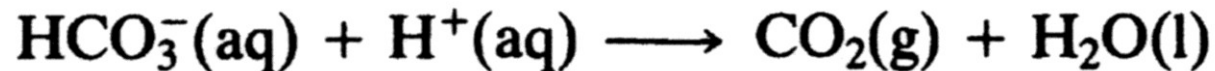
The carbonate acts as a reserve to destroy any subsequent acidity, as follows:



DEACIDIFICATION of PAPER based on Cellulose 2

Sometimes barium hydroxide is used (with due care, as it is poisonous) instead of calcium hydroxide. It is considerably more soluble in water and can also be dissolved in methanol, when there is reason to avoid the use of water on 'mobile' pigments. Residual barium hydroxide in the paper is similarly converted to barium carbonate by atmospheric carbon dioxide.

Magnesium hydrogencarbonate (bicarbonate) is also used routinely. Existing acid is readily neutralised:



DEACIDIFICATION of PAPER based on Cellulose 3

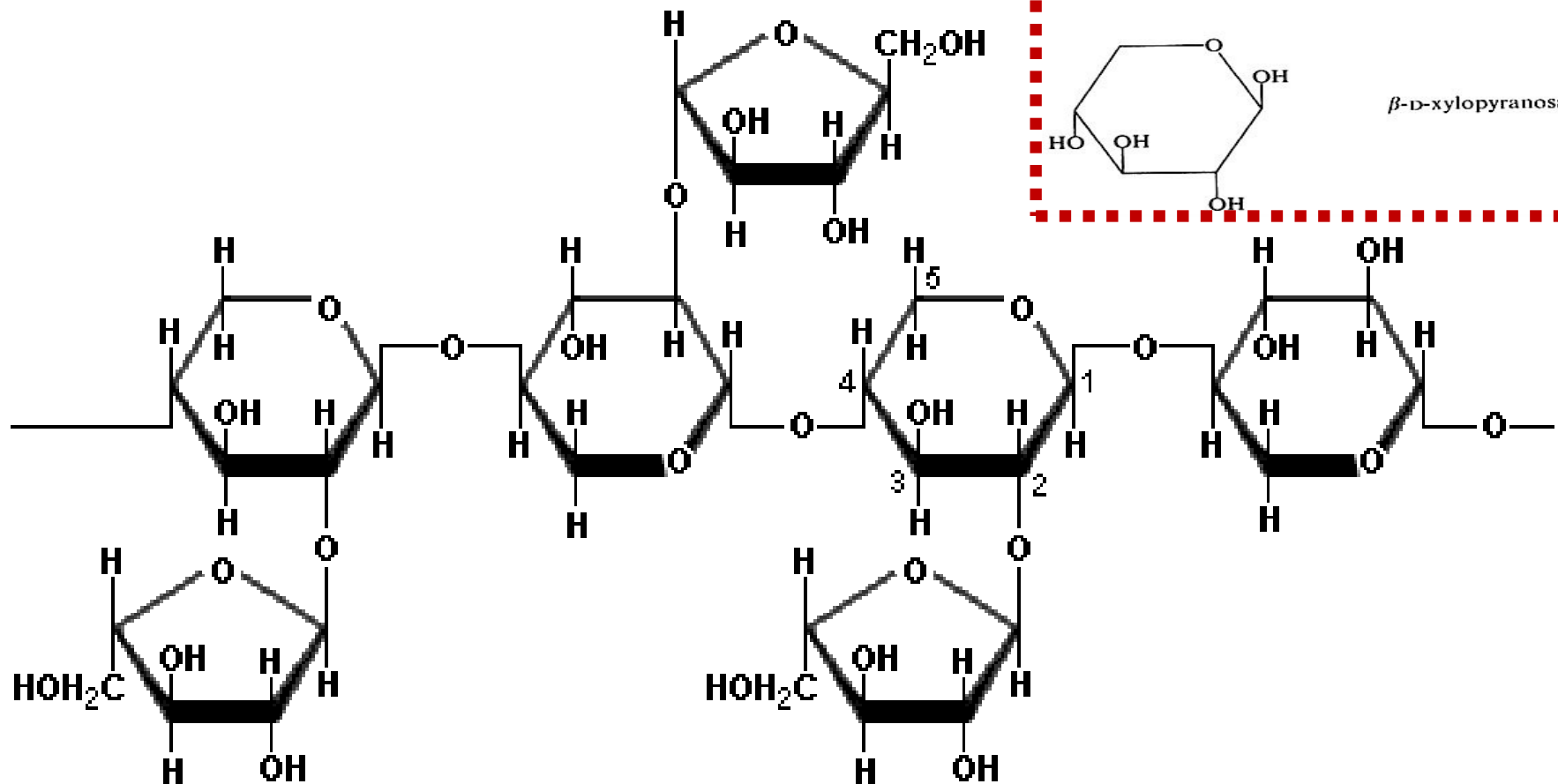
De-acidifying solution remaining in the paper is again precipitated as (magnesium) carbonate, to act as a reserve for the future:



Figure 1.5 shows how an acidic ink has produced holes in a sixteenth century manuscript.

PENTOSANE - an Example

XYLANE - belongs to HEMICELULOSES



PENTOSANE – an Example

MANAN - belongs to HEMICELULOSES

Manose

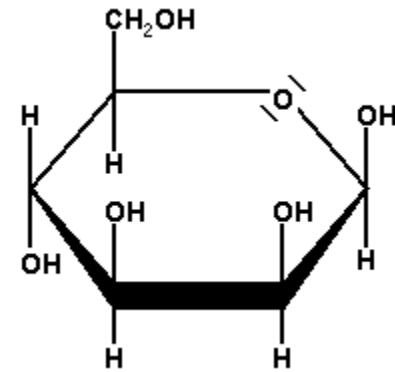
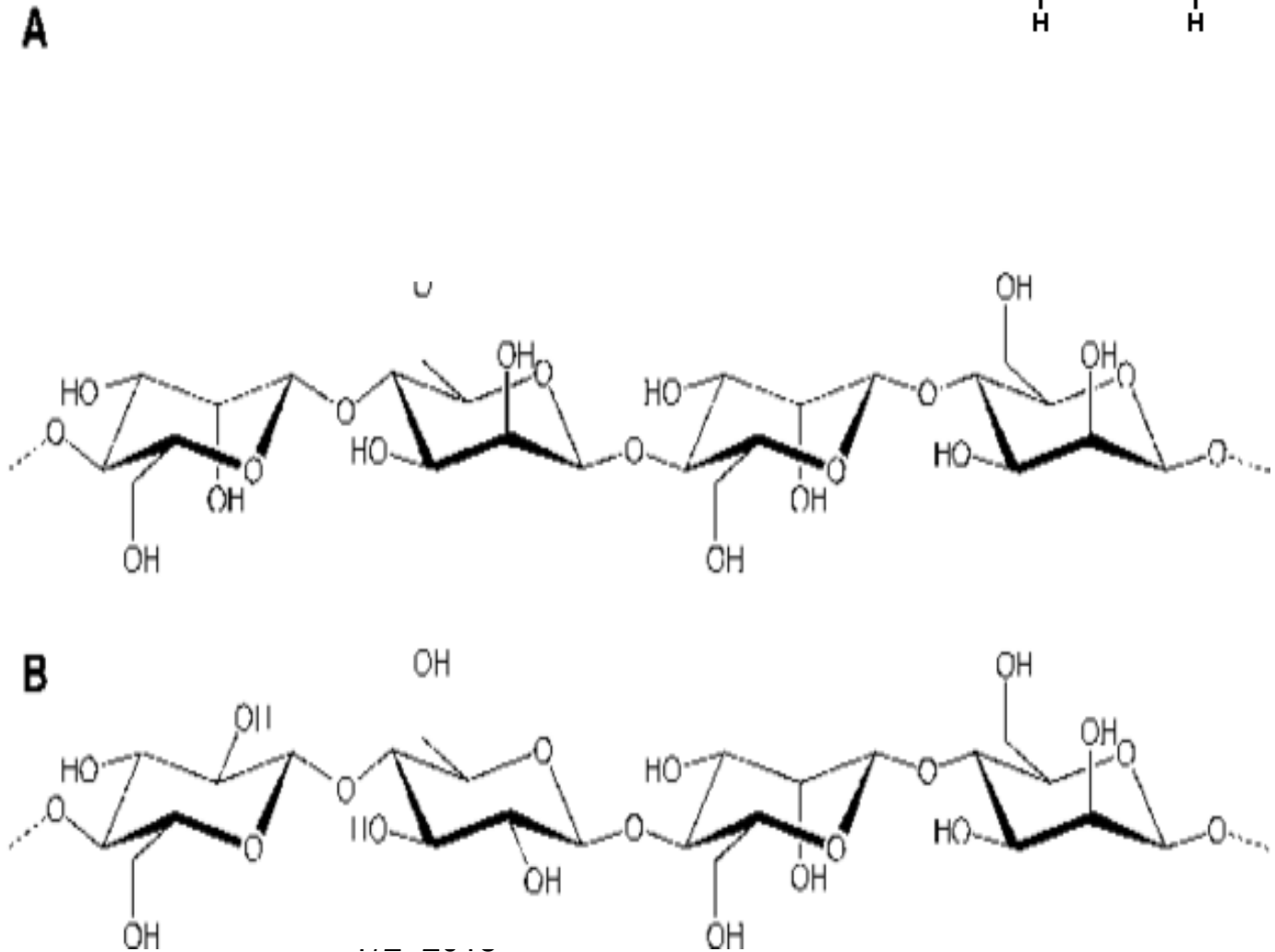


Fig. 2 Primary structure of two mannan-type hemicelluloses,
A galactomannans and
B glucomannans



MAIN of the Associated Substances in Cellulose 1

- Hemicelulose
- *Lignin*
- Essential/ethereal oil (**terpeny**) (in Wood)
-

! COTTON Fibres have almost no Hemicelluloses or LIGNIN !

LIGNIN - DETERMINATION

INTERNATIONAL NORM	ISO/AWI Standard
English Denomination	Pulps -- Determination of lignin content -- Acid hydrolysis method
Date of Issue	Under development (18. 1. 2018)

MAIN of the Associated Substances in COTTON Cellulose 1

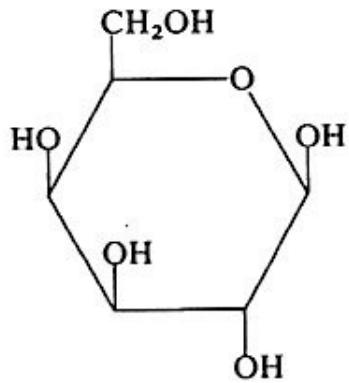
Chemical Composition of COTTON	
Component	Content (% w/w)
Cellulose	95,3
Saccharides	0,18
Reduced Saccharides	0,04
Nitrogen Compounds	0,17
Waxes	0,73
Pectines	1,20
Water extractable Compounds	3,07
Organic Acids	0,20
Ash	0,86

The Figures from different Sources could be a bit different, what is **PROBABLY** due to COTTON sort

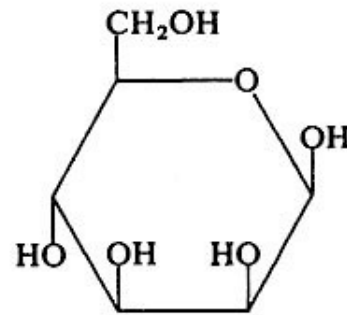
The Rest to 100 % is probable **HUMIDITY**

Cellulose & Associated Substances Concentration in COTTON					
Component	Cellulose	Pectines	Proteins	Waxes	Ash
Primary Wall	54	9	14	8	3
Secondary Wall	96	1	1,1	0,4	1,0
COTTON Fiber	94	1,2	1,3	0,6	1,2

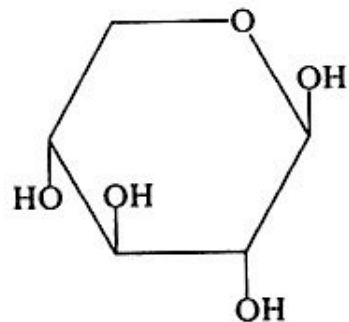
Hemicelulose – what are composed of? 1



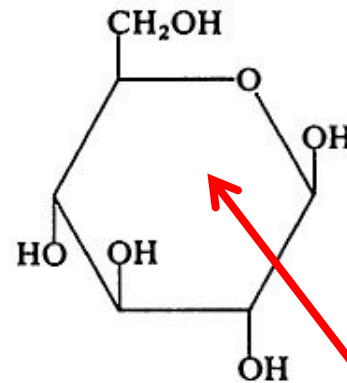
β -D-galaktopyranosa



β -D-mannopyranosa



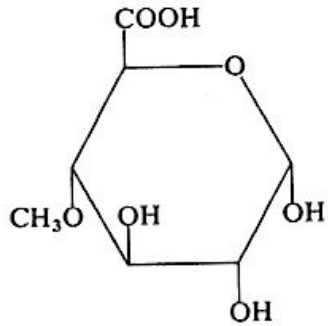
β -D-xylopyranosa



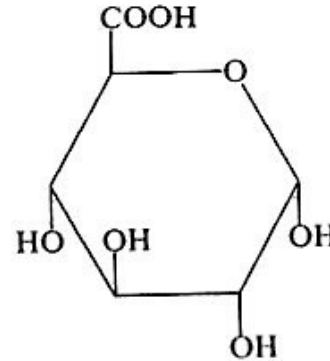
β -D-glukopyranosa

**The same Unit as the
CELULOSE is**

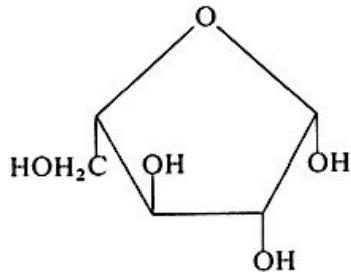
Hemicelulose – what are composed of? 2



4-O-methyl-β-D-glukuronová kyselina



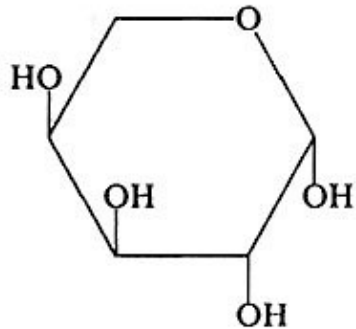
α-D-glukuronová kyselina



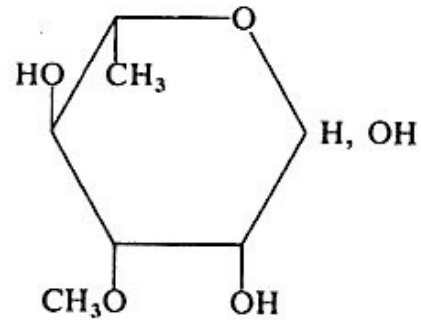
α-L-arabinofuranosa

ATTENTION: this is FURANOSE!
The five atoms Curcle only!

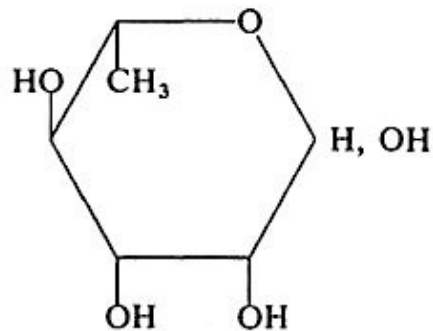
Hemicelulose – what are composed of? 3



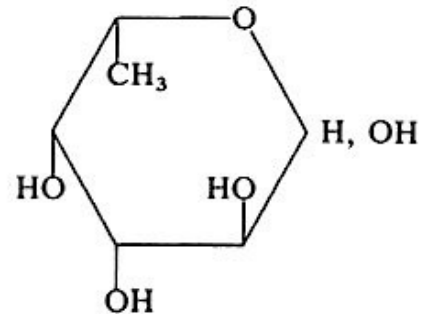
α -L-arabinopyranosa



3-O-methyl-L-rhamnopyranosa



L-rhamnopyranosa

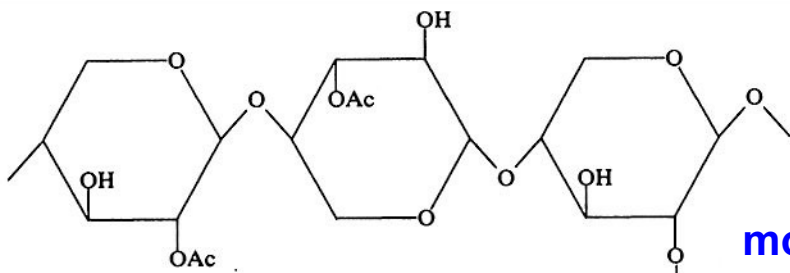


L-fukopyranosa

Hemicellulose

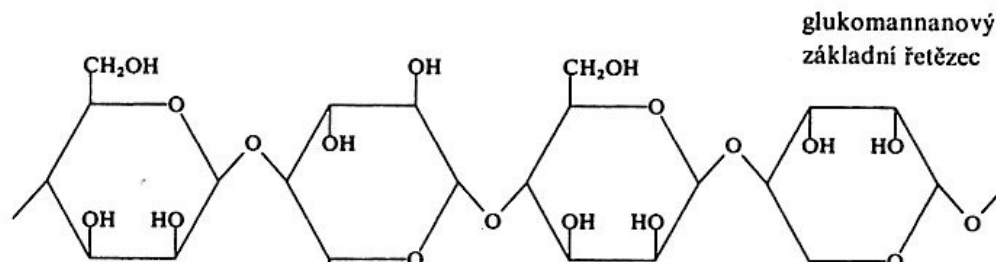
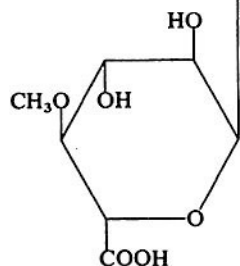
- **There is approx. 17 – 41 % w/w of Hemicellulose in the Wood, more in the broad-leaved Trees**
- Polysaccharides with lower **MEAN DEGREE OF POLYMERIZATION** (approx. 100 – 200)
- They are more easy to hydrolyse by both Acids and Bases
- The short side Chains are frequently present
- **Hemicelluloses are sorted accordingly to their main building Components as follows:**
 - **Xylan (mostly broad-leaved Trees)**
 - *Mannan (mostly coniferous tree)*
 - *Galactan (mostly coniferous tree)*

Hemicellulose



4-O-methylglukuronoxylan

mostly broad-leaved Trees



mostly coniferous tree



galaktoglukomannan

(6.29)

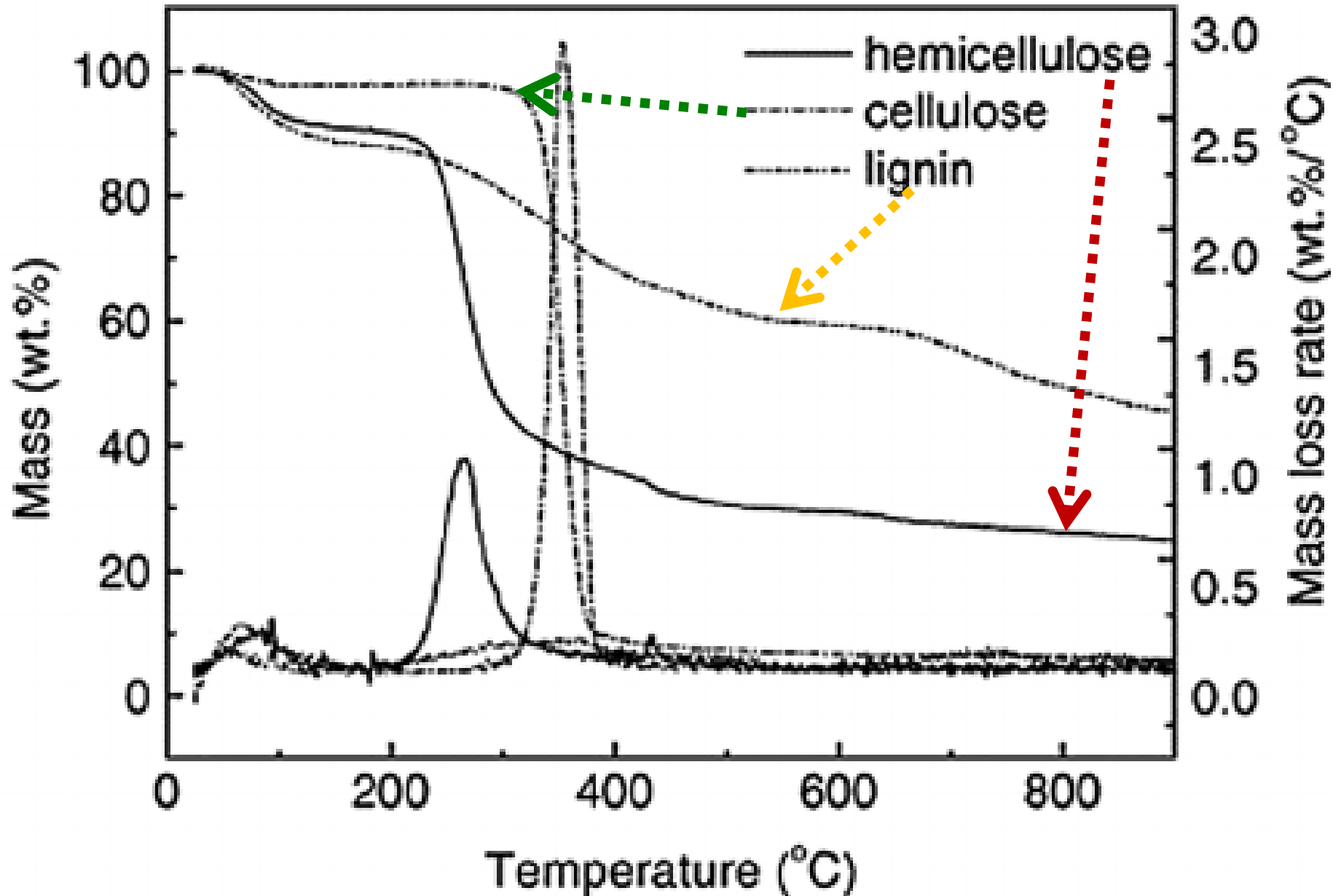
CELLULOSE - Thermic Degradation 1

At temperatures above 350 °C, cellulose undergoes thermolysis (also called 'pyrolysis'), decomposing into solid char, vapors, aerosols, and gases such as carbon dioxide.^[32] Maximum yield of vapors which condense to a liquid called bio-oil is obtained at 500 °C.^[33]

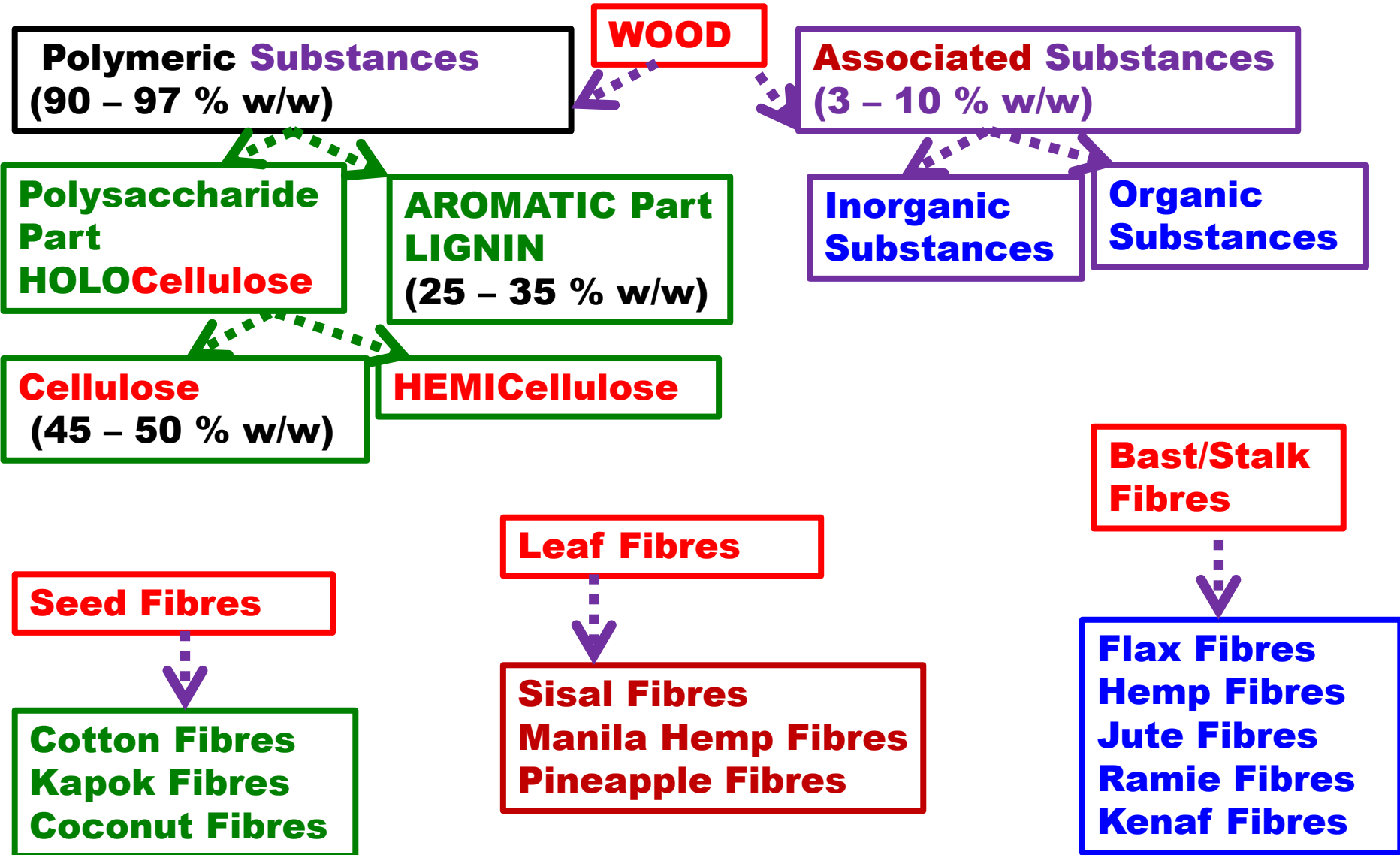
Semi-crystalline cellulose polymers react at pyrolysis temperatures (350–600 °C) in a few seconds; this transformation has been shown to occur via a solid-to-liquid-to-vapor transition, with the liquid (called *intermediate liquid cellulose* or *molten cellulose*) existing for only a fraction of a second.^[34] Glycosidic bond cleavage produces short cellulose chains of two-to-seven monomers comprising the melt. Vapor bubbling of intermediate liquid cellulose produces aerosols, which consist of short chain anhydro-oligomers derived from the melt.^[35]

Continuing decomposition of molten cellulose produces volatile compounds including levoglucosan, furans, pyrans, light oxygenates and gases via primary reactions.^[36] Within thick cellulose samples, volatile compounds such as levoglucosan undergo 'secondary reactions' to volatile products including pyrans and light oxygenates such as glycolaldehyde.^[37]

CELLULOSE - Thermic Degradation 2



Production of Cellulose I



Production of Cellulose II

- **Seed Fibres – Cotton > the Harvesting and Cleaning are only necessary**

**The Fibre has already
Sufficient Fineness
(tex, denier),
it is Fibre diameter**

**Fibre length and Fineness
Are different according
to Place of growing
(Egypt, Asia)**



Cotton Field

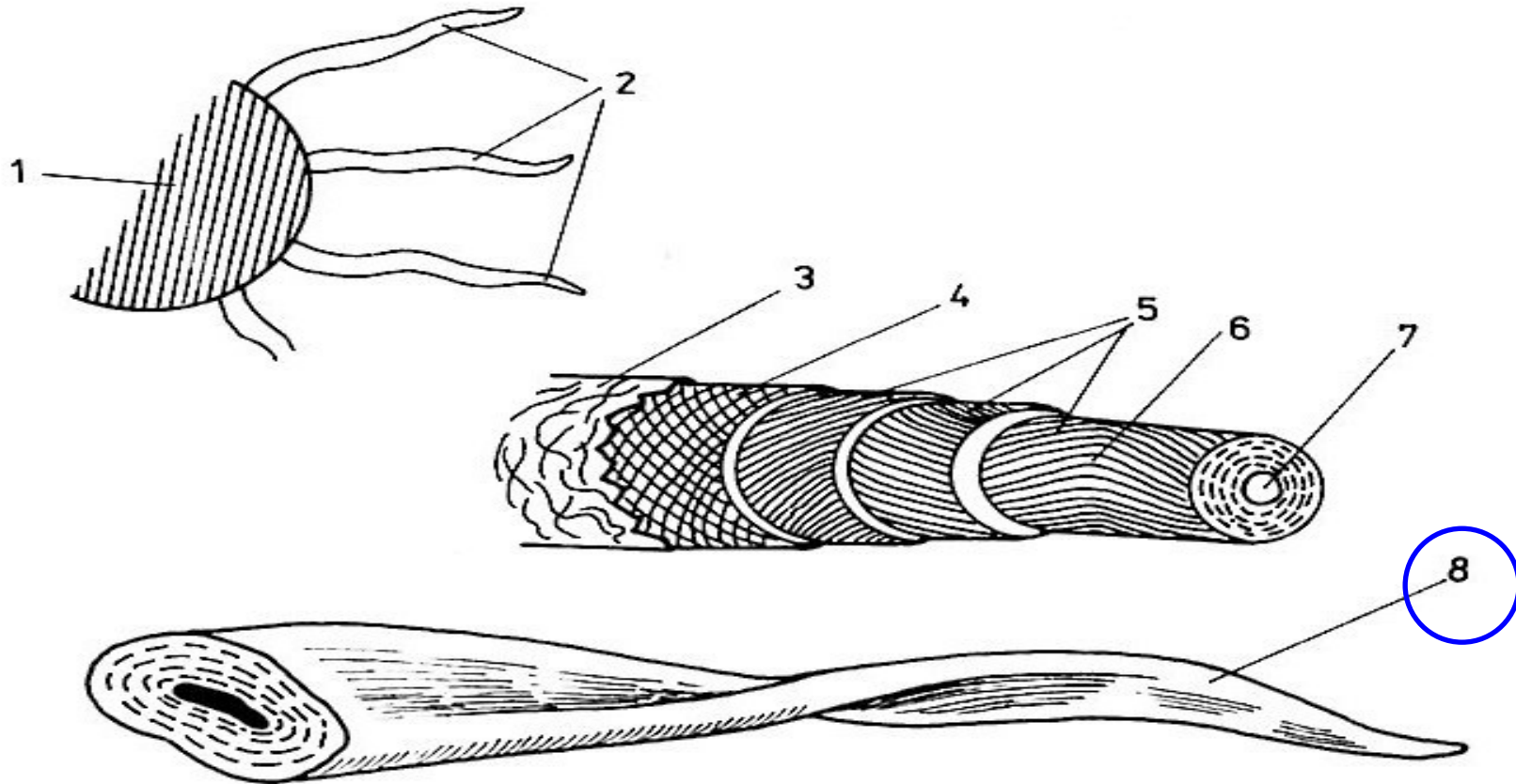
Cotton entered
Europe during 18. and
19. Centuries



**Harvesting
by Hand or
by Machine**

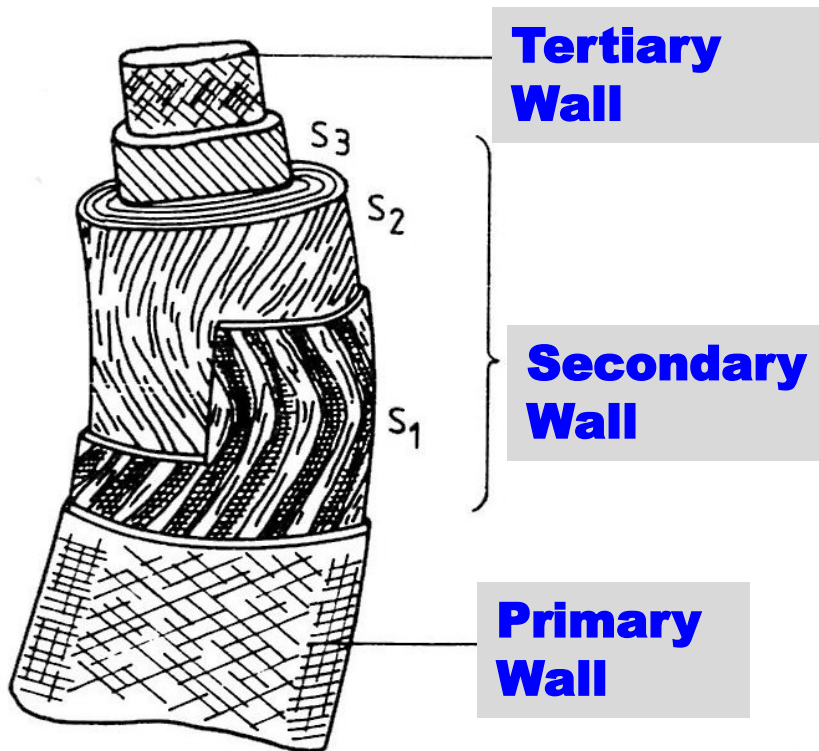


Morphology of the Cellulose Fibre 1



1) Cotton Seed, 2) Fibre, 3) Skin, 4) Primary Wall (approx. 0,1 mm), 5) Secondary Wall (approx. 4 mm), 6) Change of Fibrils' Turning, 7) Lumen, 8) Fibre after lost of Water

Morphology of the Cellulose Fibre 2



cellulose **91.00%**

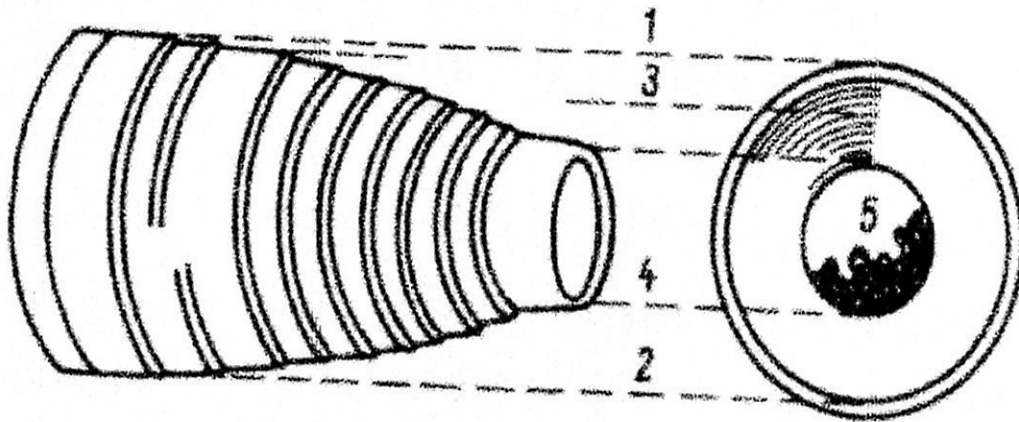
water **7.85%**

protoplasm, pectins
0.55%

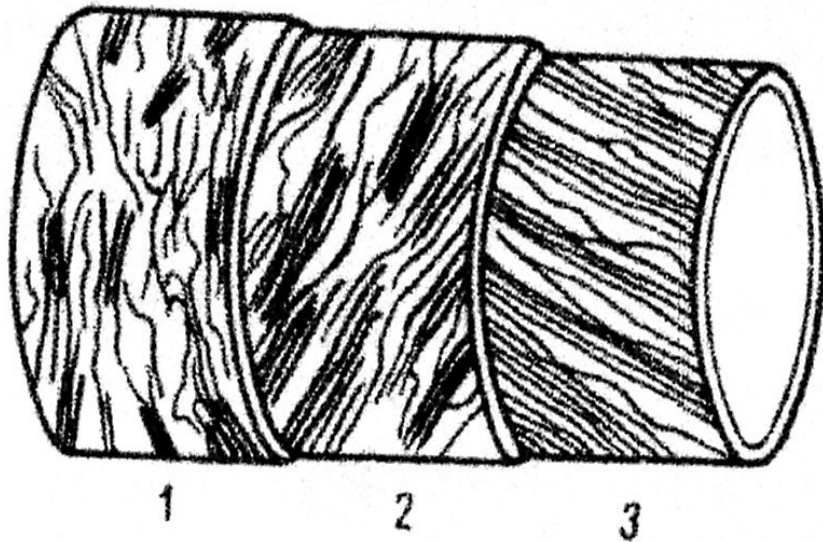
waxes, fatty
substances **0.40%**

mineral
salts **0.20%**

Morphology of the Cellulose Fibre 3



1) Primary Wall (approx. 0,1 μm), 2) Outer Part of Secondary Wall (approx. 4 μm), 3) Middle Part of Secondary Wall 4) Inner Part of Secondary Wall Lumen, 5) Chanel with Rest of the Protoplasm

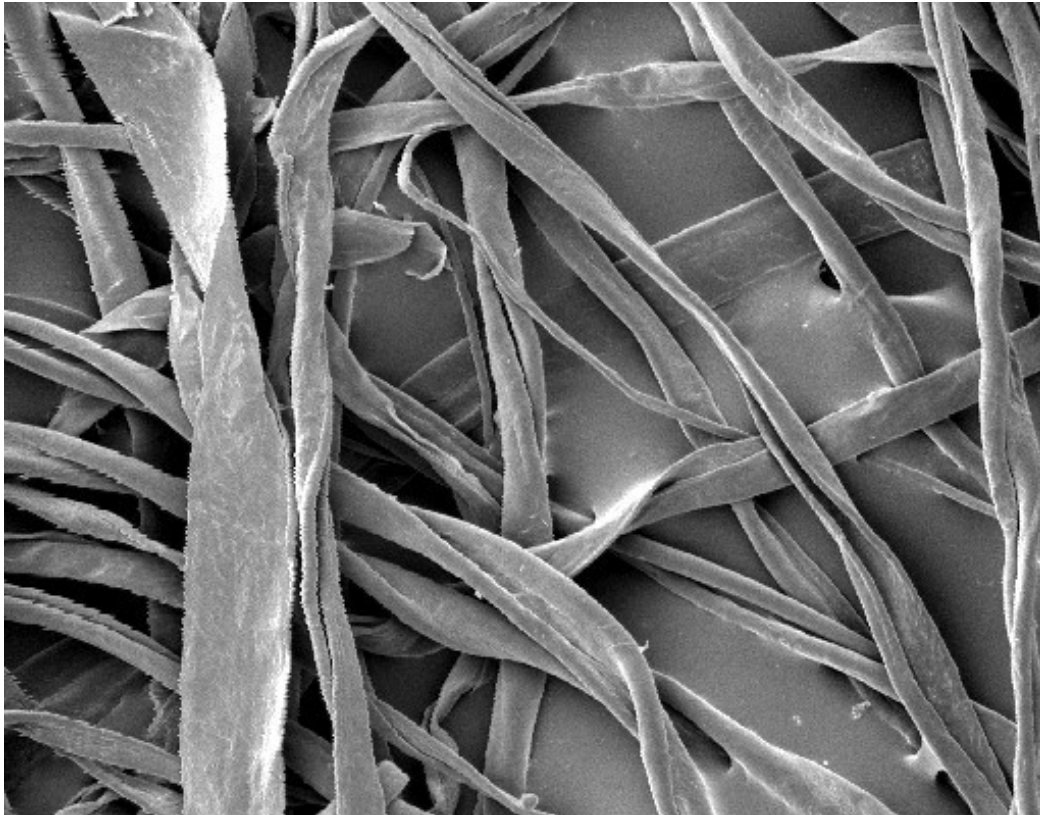


SCHEMA OF THE ARRAGAMENT OF THE COTTON WALLS

1) Primary Wall, 2) Outer Part of Secondary Wall, 3) Middle Part of Secondary Wall

PROPERTIES OF THE COTTON SINGLE FIBER

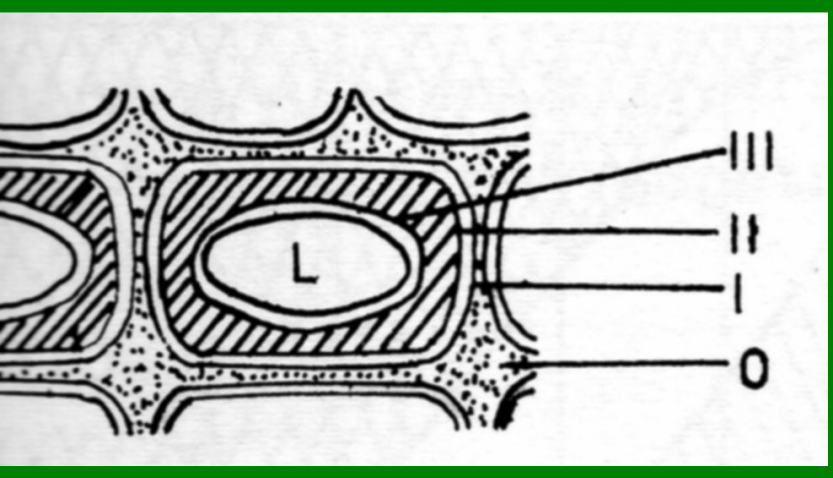
Fairly uniform in **width**, 12–20 micrometers;
length varies from 1 cm to 6 cm ($\frac{1}{2}$ to $2\frac{1}{2}$ inches);
typical length is 2.2 cm to 3.3 cm ($\frac{7}{8}$ to $1\frac{1}{4}$ inches).



cellulose 91.00%
water 7.85%
protoplasm, pectins 0.55%
waxes, fatty substances
0.40%
mineral **salts** 0.20%

SEM,
Magnification
approx. 1000x

Morphology of WOOD 1



L – Cell lumen (Air)

SL – middle Lamella (LIGNIN)

P – Primary Wall

S1, S2 – Secondary Wall

T (S3) – Tertiary Wall

B – warted Layer

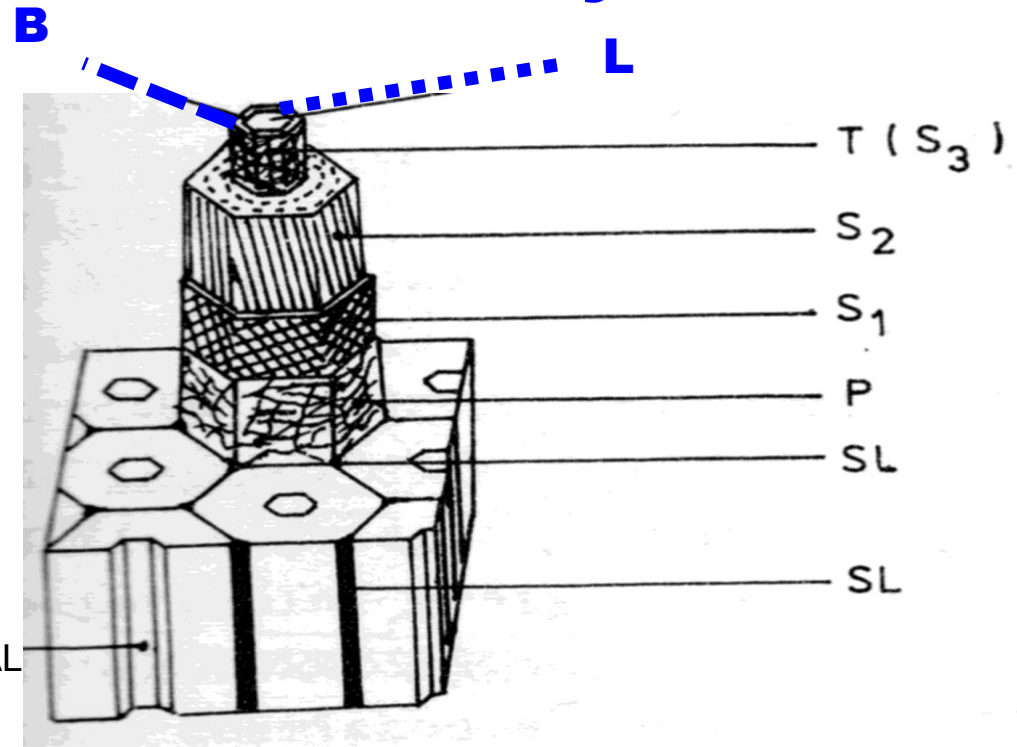
O – middle Lamella (LIGNIN)

I – Primary Wall (P)

II – Secondary Wall (S)

III – Tertiary Wall (T)

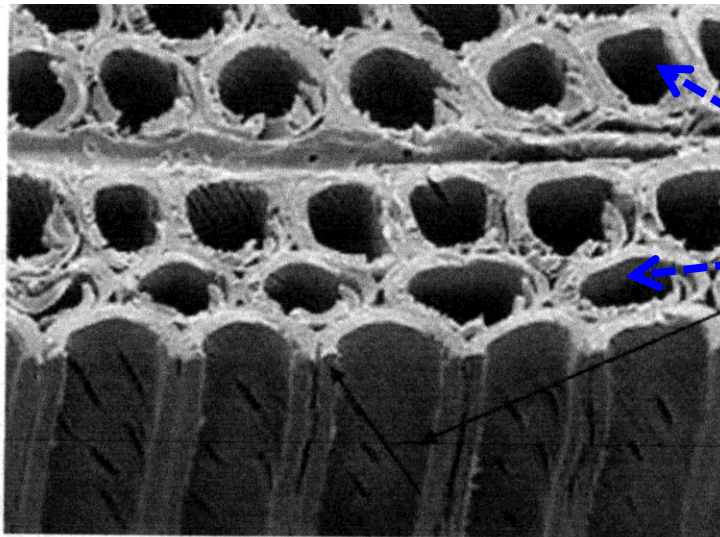
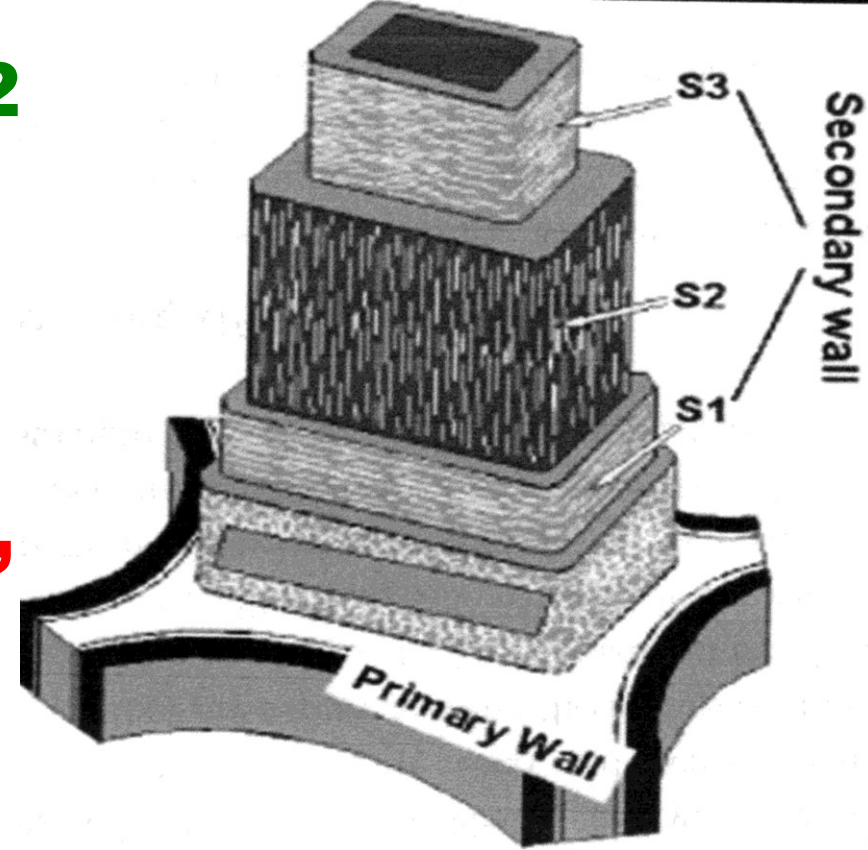
L – Cell lumen (Air)



Morphology of WOOD 2

Pay Attention to:

- **DIFFERENT Fibrils Orientations in DIFFERENT Walls S1, S2 a S3**



Tracheids

MFA

Figure 5. SEM micrograph showing the microfibrils in the S₂ layer of Norway spruce wood sample. Seppo Andersson, 2007.

Morphology of Cellulose Fibre 4

Fibre Length
Fibre thickness
Tensile Strength at Dry
Tensile Strength at Wet
Ductility
Density
Moisture Content

13 – 33 mm
10 – 40 μm
 $3,5 \cdot 10^5 - 5,5 \cdot 10^5 \text{ J kg}^{-1}$ ($\approx 3,5 - 5,5 \text{ p dtex}^{-1}$)
 $3,8 \cdot 10^5 - 7 \cdot 10^5 \text{ J kg}^{-1}$ ($\approx 3,8 - 7 \text{ p dtex}^{-1}$)
4 – 13 %
 $1,54 - 1,56 \text{ g cm}^{-3}$
7 – 8 %

Textile Units!

SI Units

• $\text{cN dtex}^{-1} =$
cca. p dtex^{-1}

OLD Units

• $\text{p} = \text{pond} = \text{g} * 9,81 =$
 $0,0098 \text{ N} = 0,98 \text{ cN}$

dtex = Mass of the 10 km of Fibre expressed in grams (g)

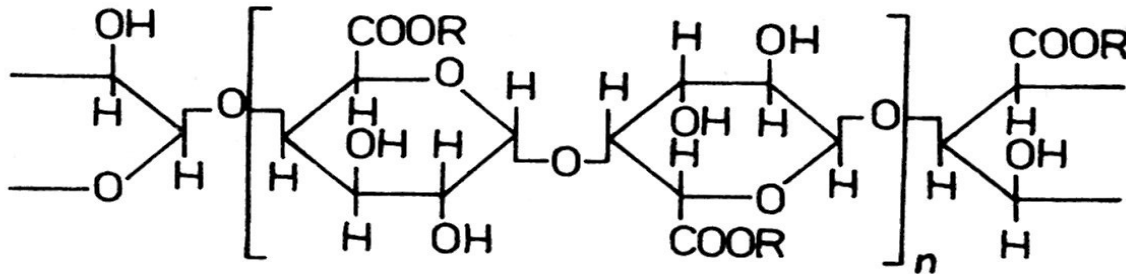
Cellulose Production III

- **Herb (Plant) Bast/Stalk – Flax, Hemp, Jute**
- **It is necessary to remove BIOLOGICALLY Pectins and then to remove Wooden Part of the Stalk**
- **Fibre is long, but rough**
- **Tensile Strength is higher than Cotton**
- **It is necessary to fine the Fibres for Textile utilisation**
- **Yield rate of Fibre is low, approx. 10 % w/w of the Whole Plant**

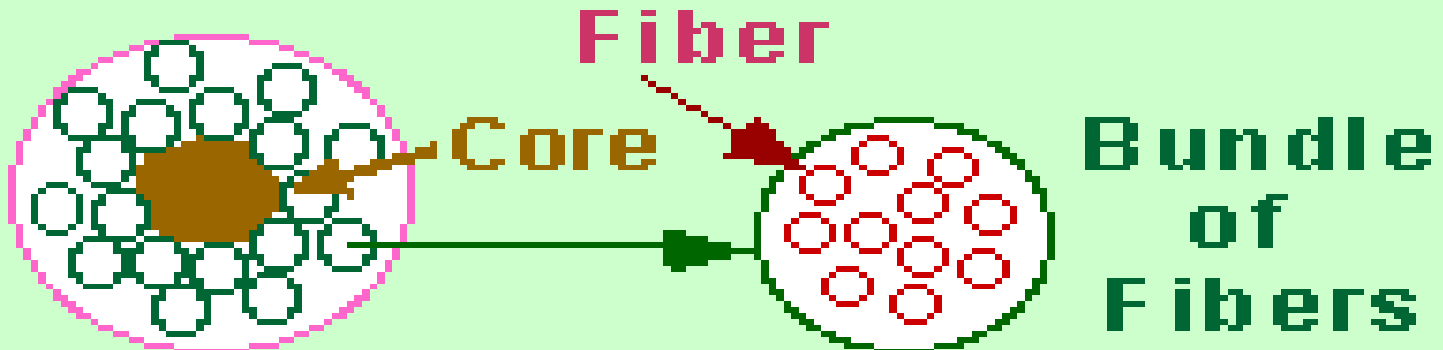
Flax = Plant
Linen = Fibre

Flax Stalk – CROSSCUT

The stem varies from 60 to 120 cm in length and consists of fiber bundles lying between the outer **BARK** and a **WOODY CORE**. The **INDIVIDUAL FIBERS**, 10 to 40, are held together in the bundles by **PECTINS**. The bundles lie around the core and are attached to it and one another by pectins.



Structure Formula
of PECTIN
R = H or -CH₃



Flax stem



FLAX is in Bloom

Flax is harvested in Europe from the Turn of Millennium since

Dew-retting of Flax on the Field

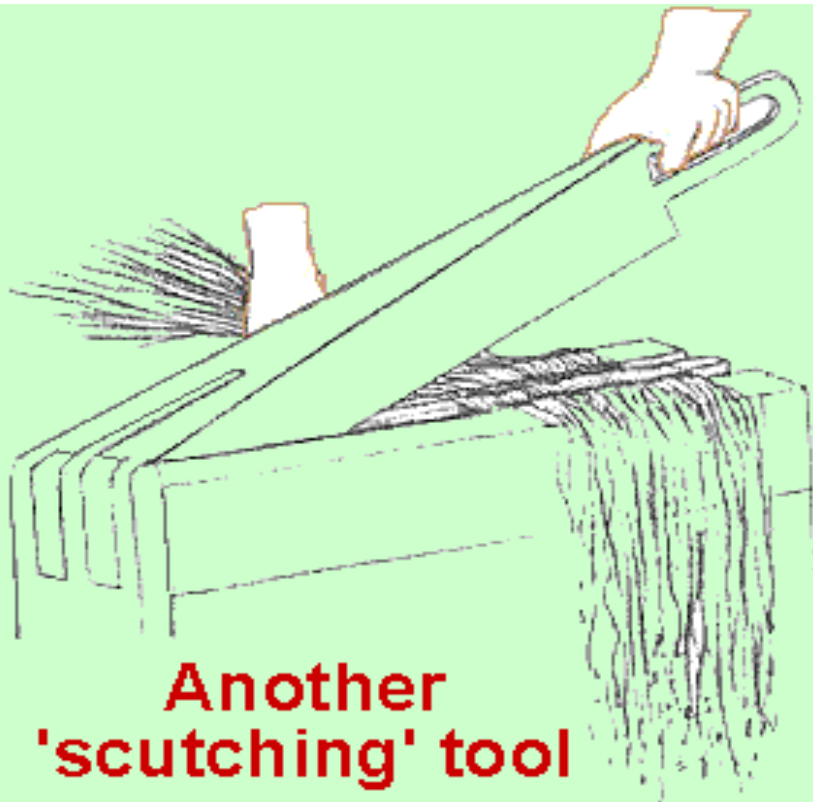


January 18 2018

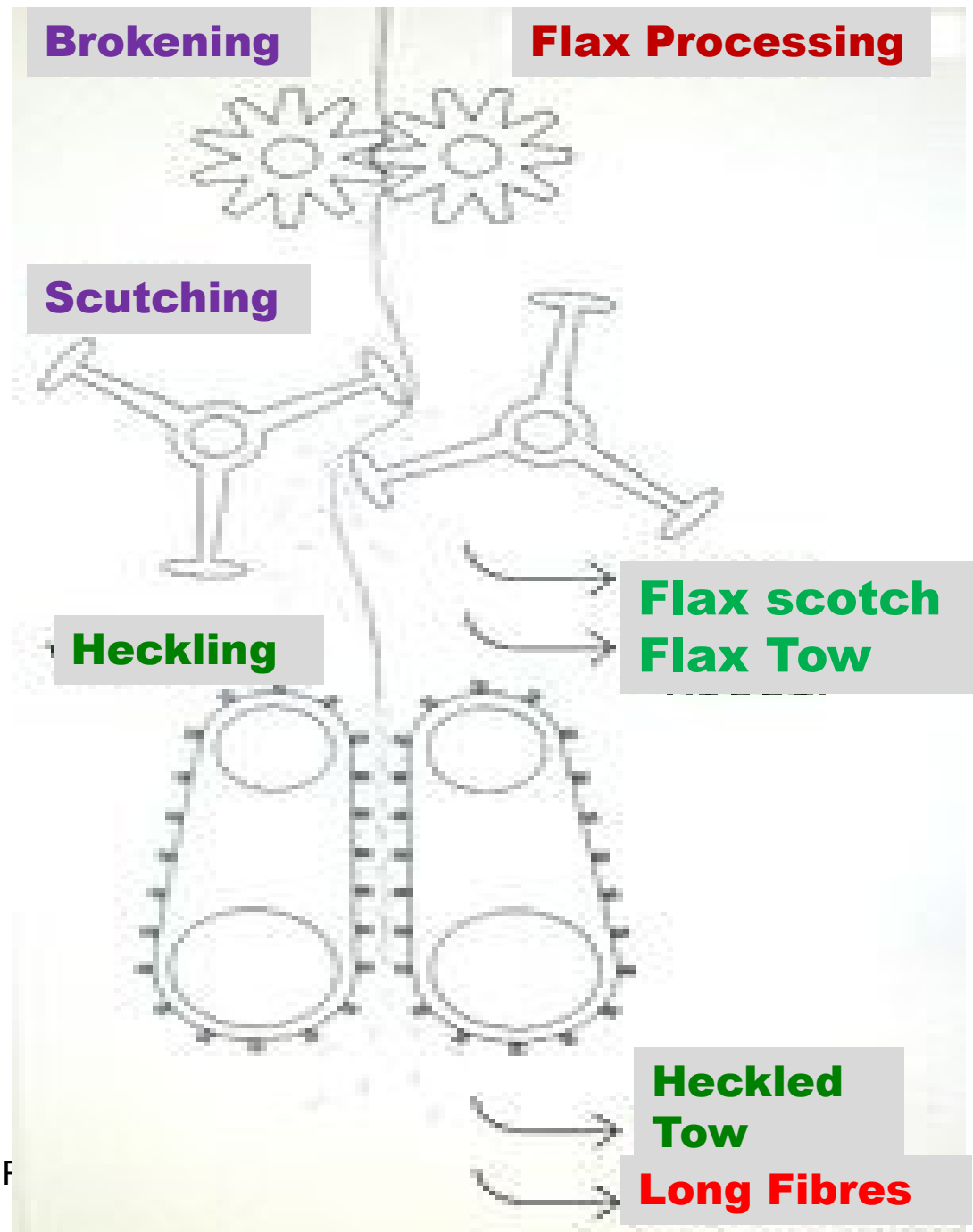
NATURAL PO
7/1

Cellulose Production III B

HISTORICAL Method of Linen gaining



CURRENT **Industrial Method** **of Linen gaining**



Flax & Linen:

- Stalk,
- Fiber,
- Weaving yarn,
- Fabric



**Hemp
scotch**



Hemp scotch Board
It has the better Mechanical
Properties then Wood Fibres one





Flax scotch

**The similar Fibres, but
Hemp has different
Colour**



Ja **Hemp scotch**

Cellulose Production IV – WOOD

- Natronový postup s NaOH (listnaté dřevo, sláma, odpad)
- Sulfitový postup (smrk, listnaté dřevo)
- Sulfátový postup (buk, bříza, borovice, sláma, odpad)
- **Výtěžky jsou jen cca. 25 % hmot. (údaje se liší podle zdroje i podle typu dřeva) z celkové ve dřevě obsažené celulóze**

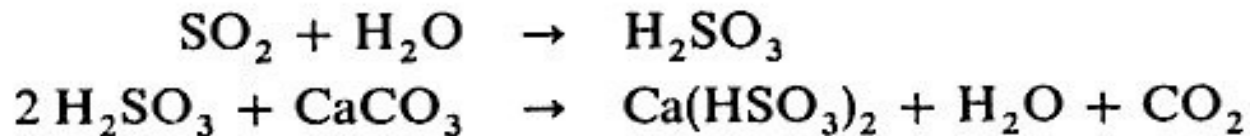
Soda pulping

is a chemical process for making wood pulp with sodium hydroxide as the cooking chemical. In the Soda-AQ process, anthraquinone (AQ) may be used as a pulping additive to decrease the carbohydrate degradation. The soda process gives pulp with lower tear strength than other chemical pulping processes (sulfite process and kraft process), but has still limited use for easy pulped materials like straw and some hardwoods.^[1]

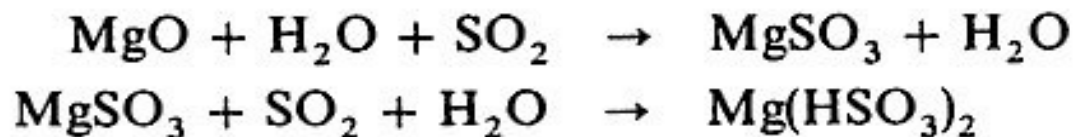
- 5 – 12 % NaOH
- 150 – 180 °C
- 700 – 1000 kPa
- 3 – 6 hodin

The **sulfite process** produces wood pulp which is almost pure cellulose fibers by using various salts of sulfurous acid to extract the lignin from wood chips in large pressure vessels called digesters. The salts used in the pulping process are either sulfites (SO_3^{2-}), or bisulfites (HSO_3^-), depending on the pH. The counter ion can be sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) or ammonium (NH_4^+).

- **$\text{Ca}(\text{HSO}_3)_2$, SO_2**
- **130 °C**
- **300 – 400 kPa**
- **3 – 6 hodin**



It is possible to substitute Ca^{+2} by Mg^{+2} or by NH_4^+

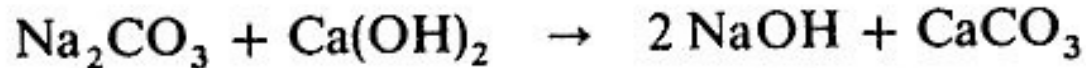


Sulphate Process

- Na_2SO_4 , Na_2CO_3 , Na_2S , Na OH
- 150 – 180 °C
- 700 – 1000 kPa
- 3 – 6 hodin



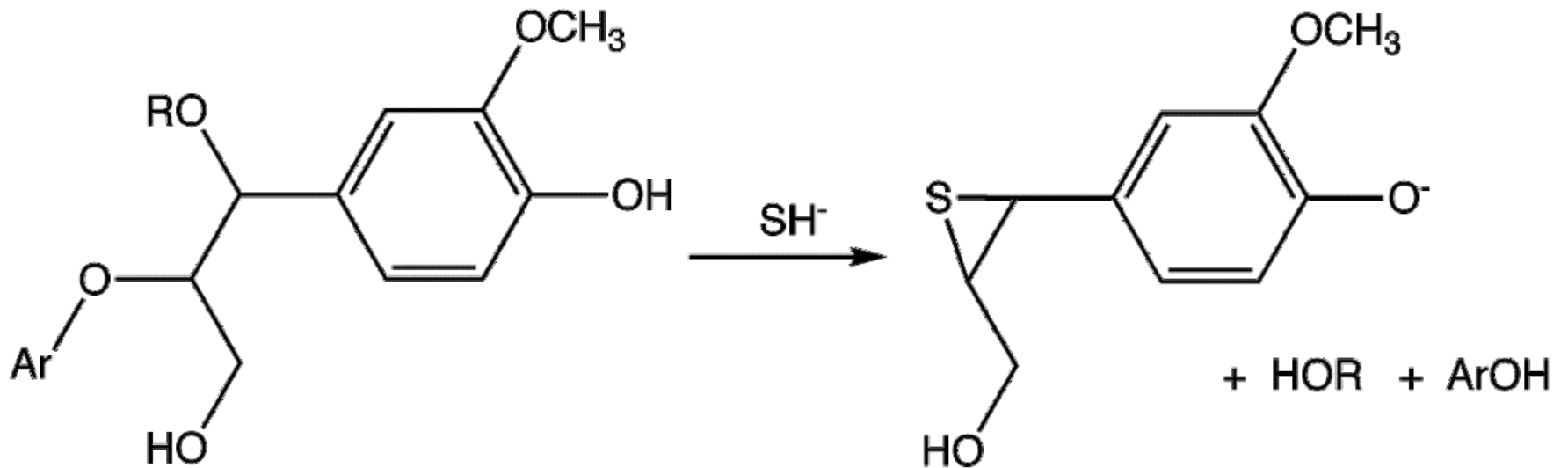
It is possible to get back from the Melt of the NaS, but most importantly Na_2CO_3 , which is Caustified as follows:



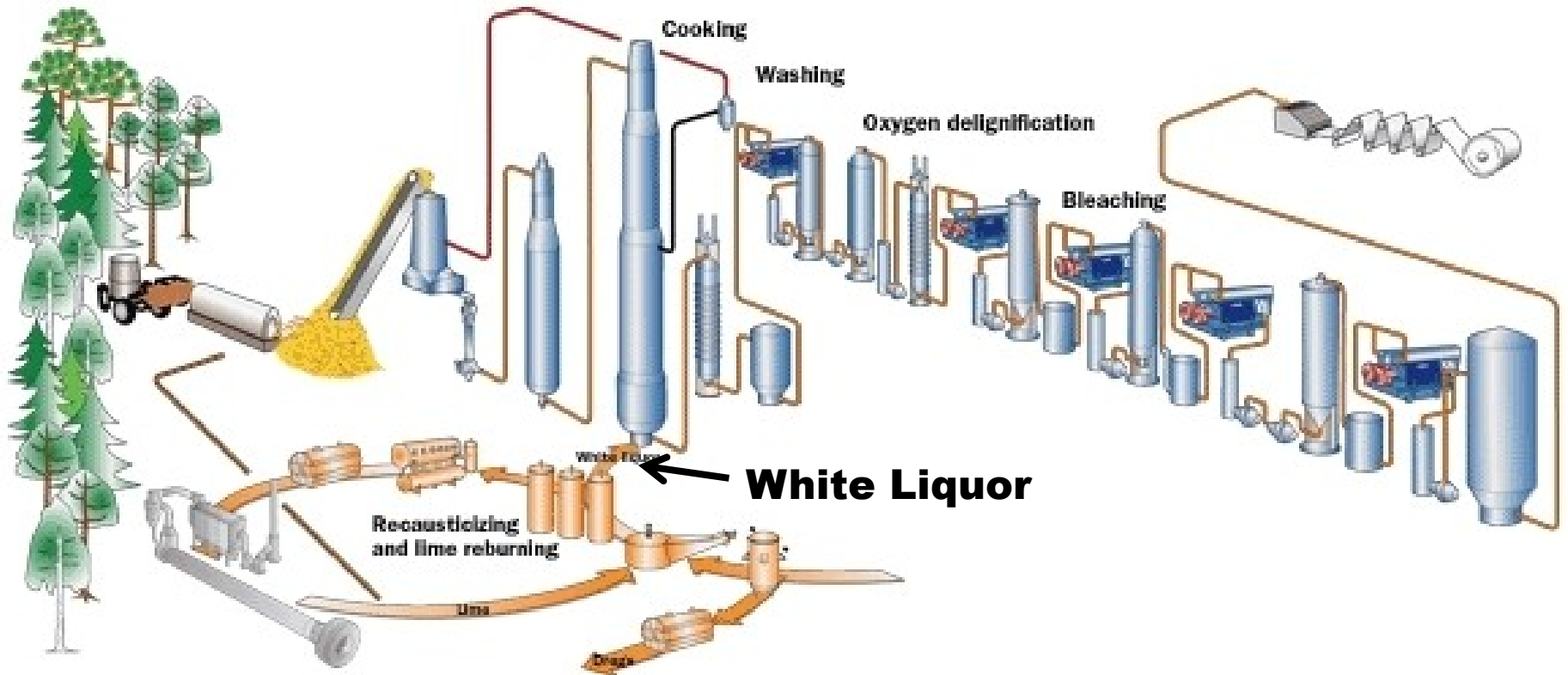
The new Cooking Liquor is possible to get via this Procedure

The Sulphate Process is suitable to be employed for all Kinds of Wood and has the Best Economy of Cellulose Production

DELIGNIFICATION of Wood by DEPOLYMERISATION Sulfate Process



Sulphate Process



Utilisation of Cellulose (Pulp)

- **The pulp papermaking process**
- **Textile Production**
- **Pharmacy**
- **Regenerated Cellulose**

DERIVATIVES of CELLULOSE

- **Esters**
- **Nitrates**
- **Alkyl (aryl)cellulose**
- **Carboxymethylcellulose**
- **Hydroxyethylcellulose**

The pulp papermaking process

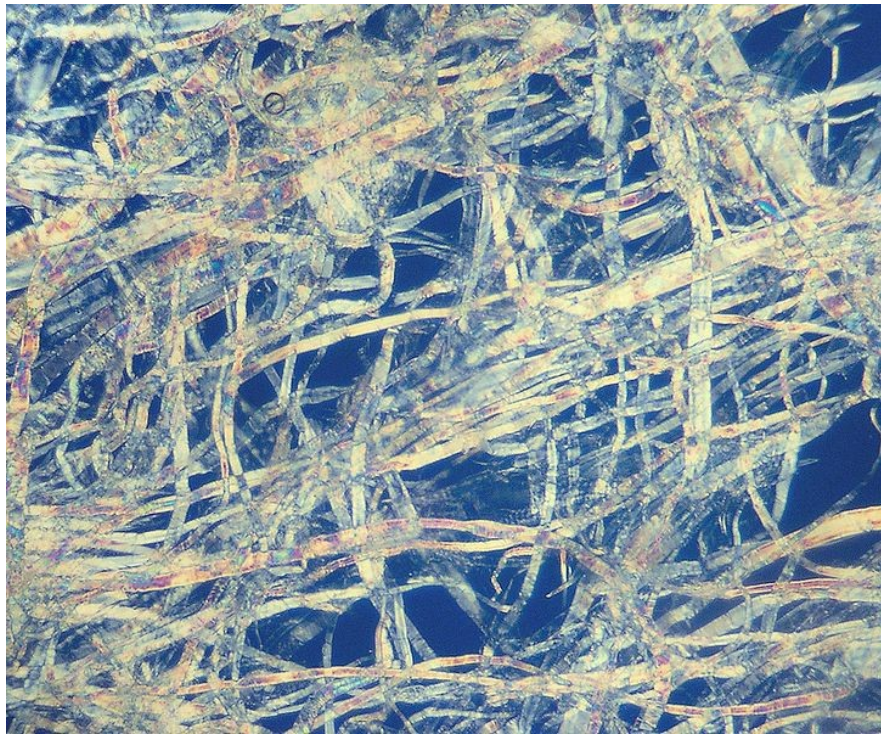
Paper is a thin material produced by pressing together moist fibres of cellulose pulp derived from wood, rags or grasses, and drying them into flexible sheets.

Paper is the Sheet Material with having the Weight up to 250 g/m², made of Fibres and the Additives, which determine its Specification.

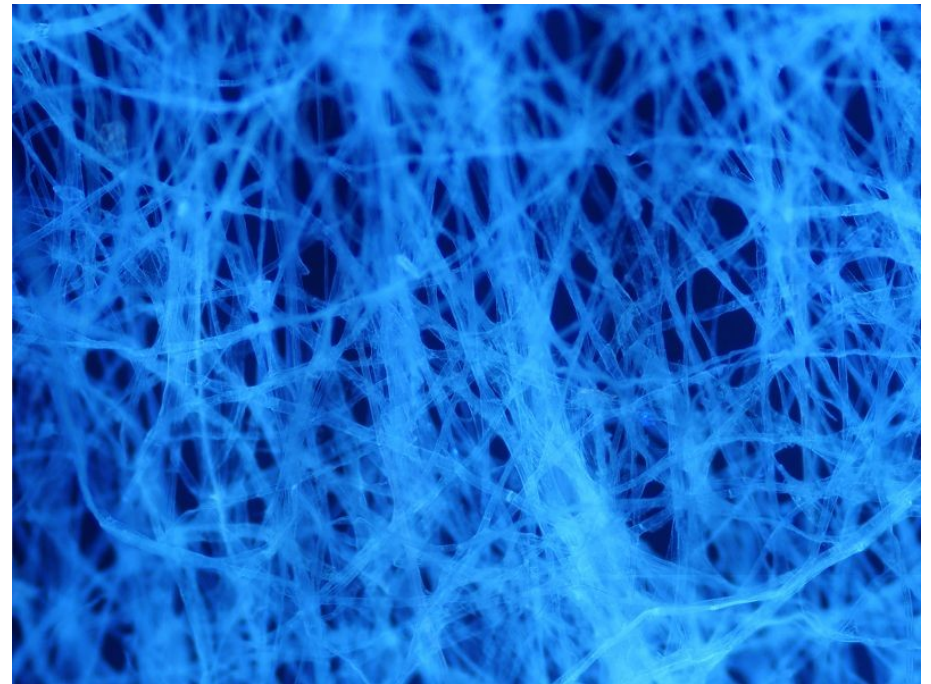
- **Cardboard and Paperboard > 250 g/m²**

The pulp papermaking process

PAPÍR



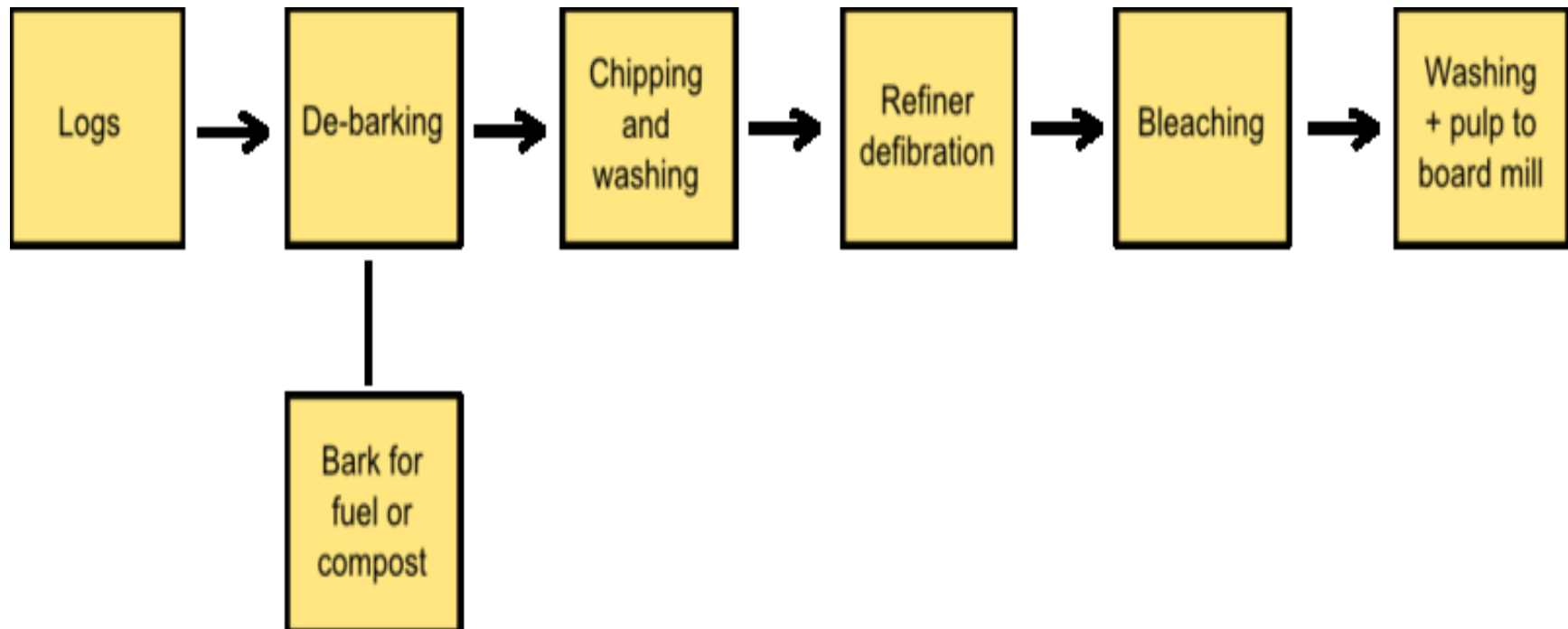
Pulp 200x



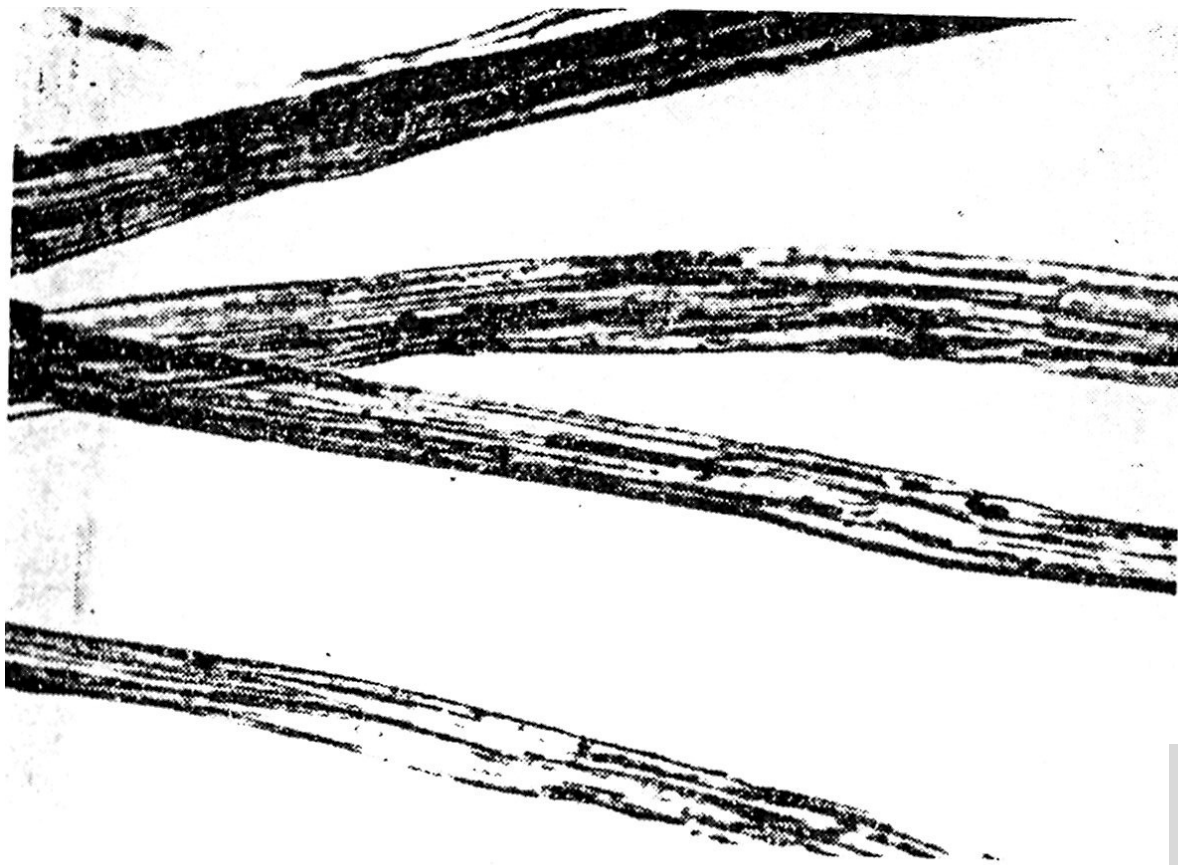
Paper 800x

The wood pulp papermaking process

- **Mechanical wood pulp** – mechanical Wood Pulping & Fibre Sorting & Bleaching >>> Lowcost Papers, e.g. Newspapers and Lavatory Paper



Stalk Fiber 1



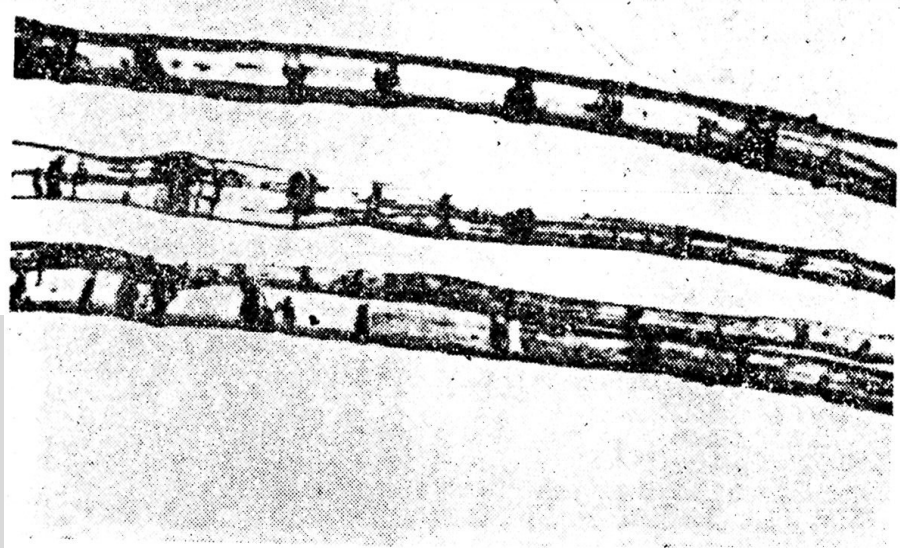
January 18 2018

NATURAL POLYMERS MU SCI
7/2 2018

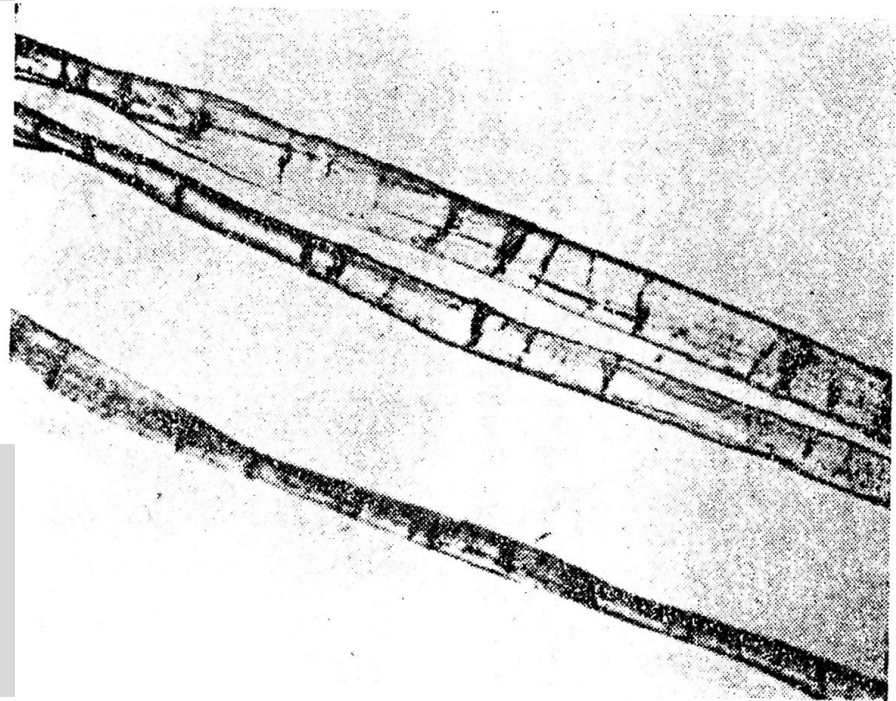
**Jute,
Magnification
180x**

Stalk Fibers 2 & 3

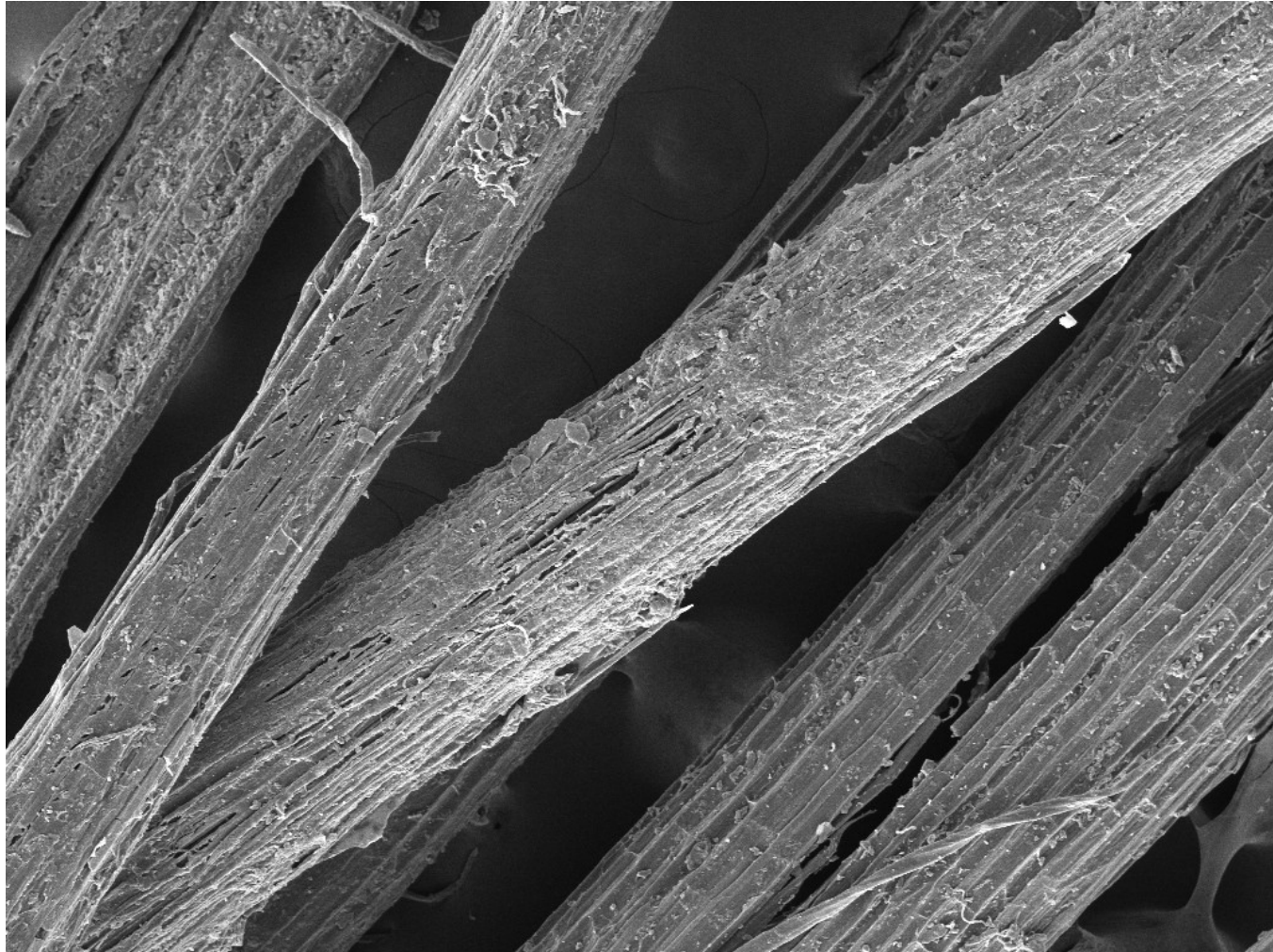
**Flax,
Magnification
180x**



**Hemp,
Magnification
180x**

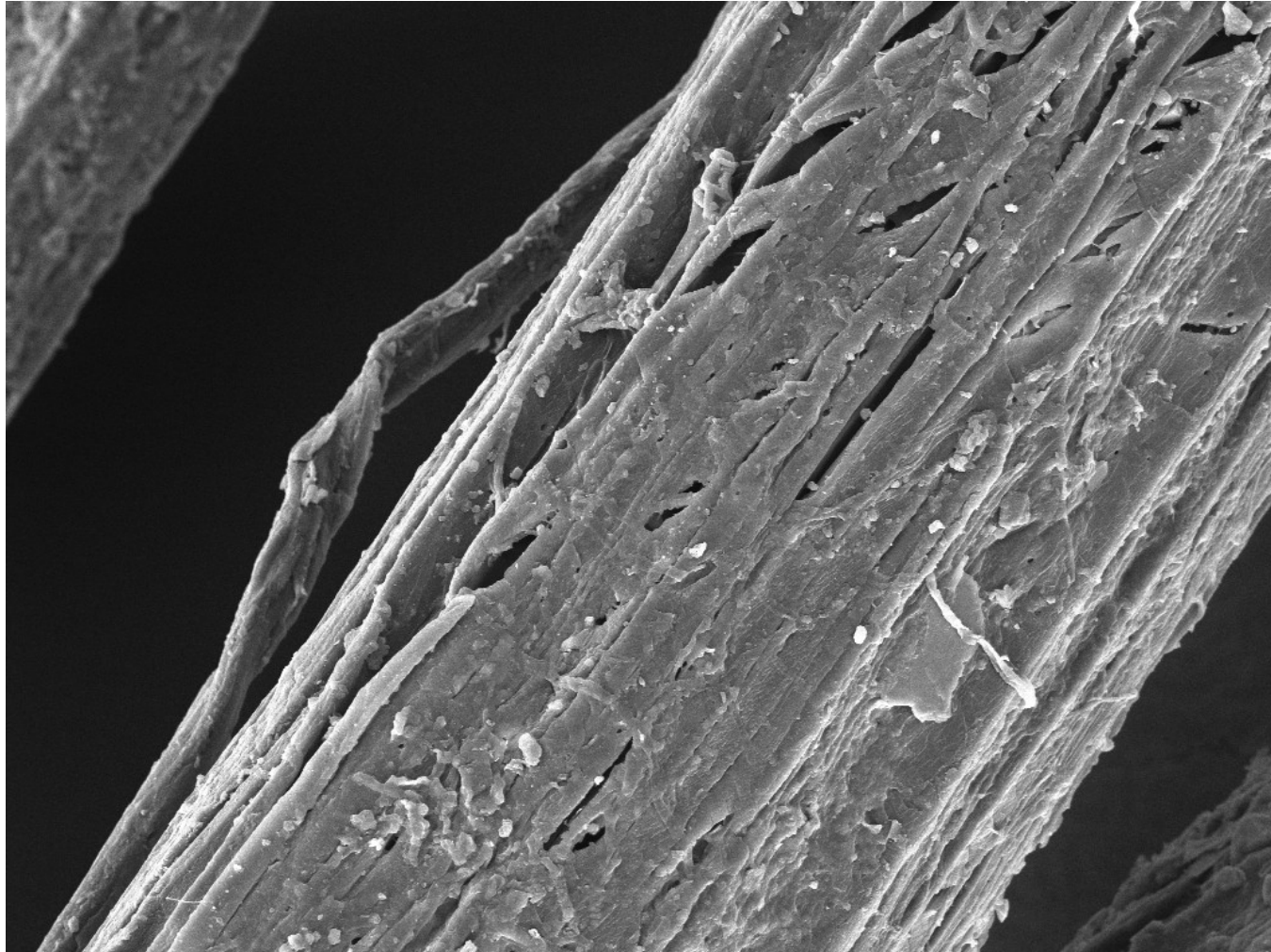


LEAF FIBER 1 – SISAL NATIVE



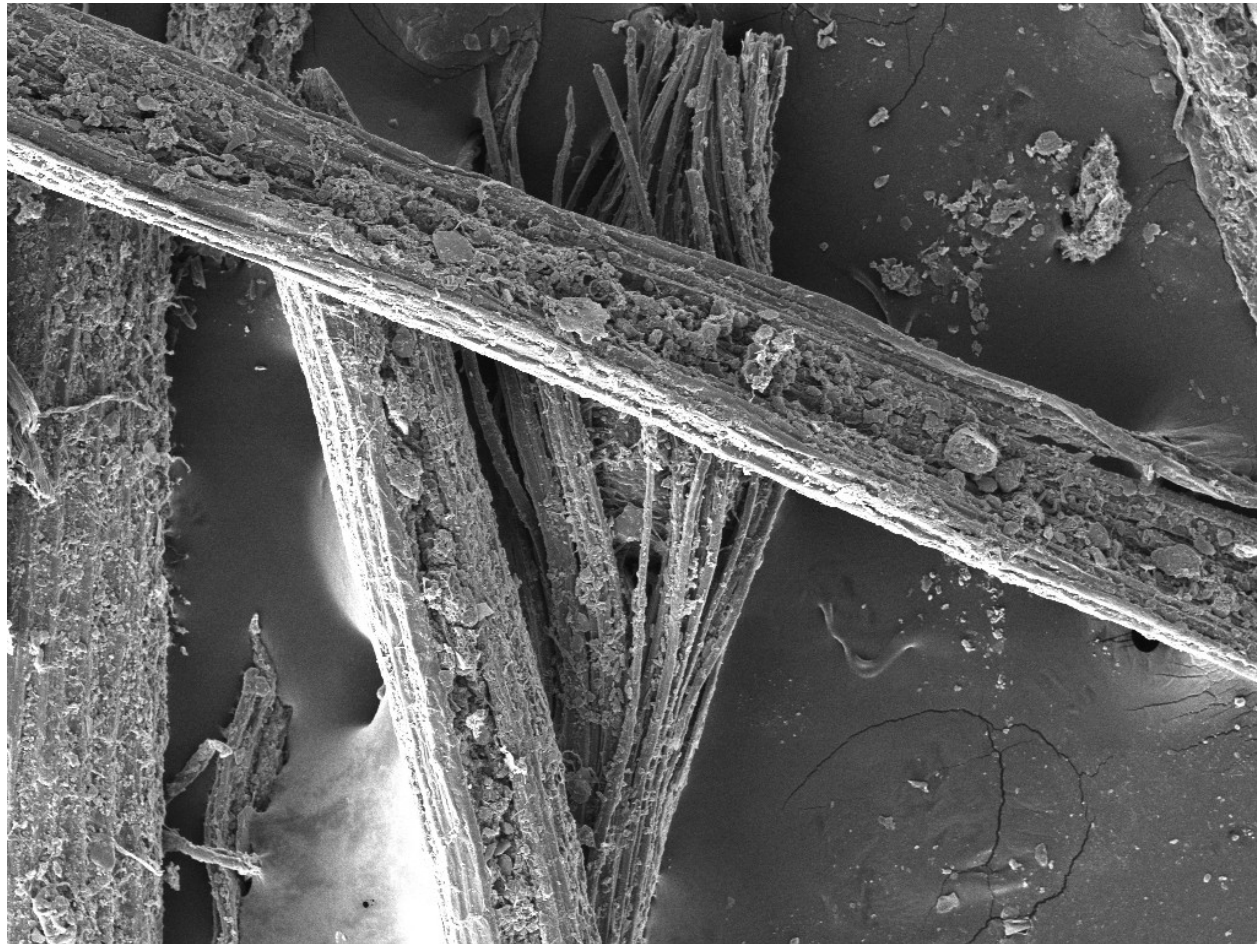
SEM HV: 15.0 kV	WD: 14.41 mm		MIRA3 TESCAN
View field: 1.38 mm	Det: SE	200 μ m	
SEM MAG: 200 x	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT	

LEAF FIBER 1 – SISAL NATIVE



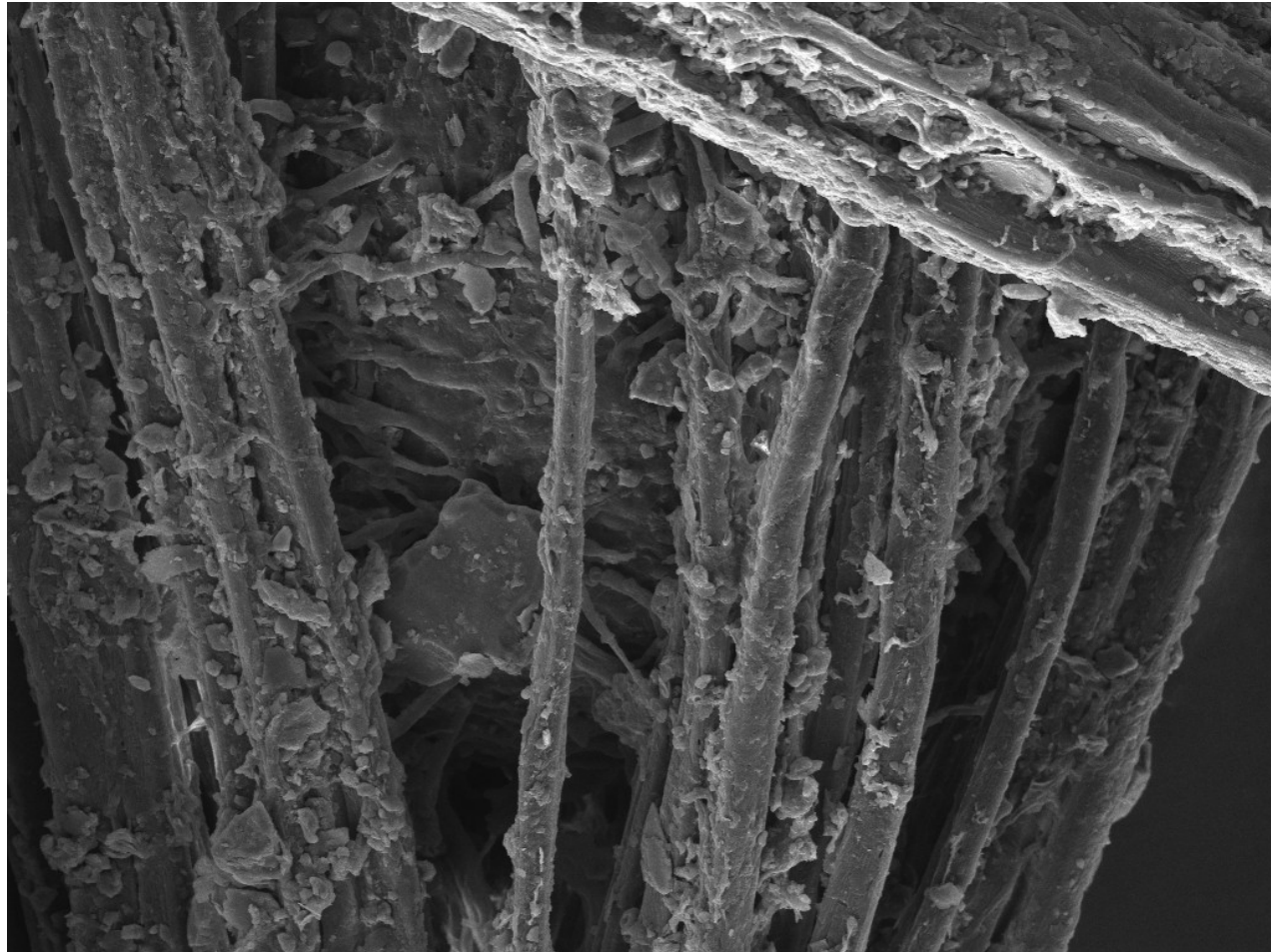
SEM HV: 15.0 kV	WD: 14.33 mm		MIRA3 TESCAN
View field: 270 μ m	Det: SE	50 μ m	
SEM MAG: 1.02 kx	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT	

LEAF FIBER 3 – SISAL AFTER EXPOSURE IN OUDOOR approx. 3years



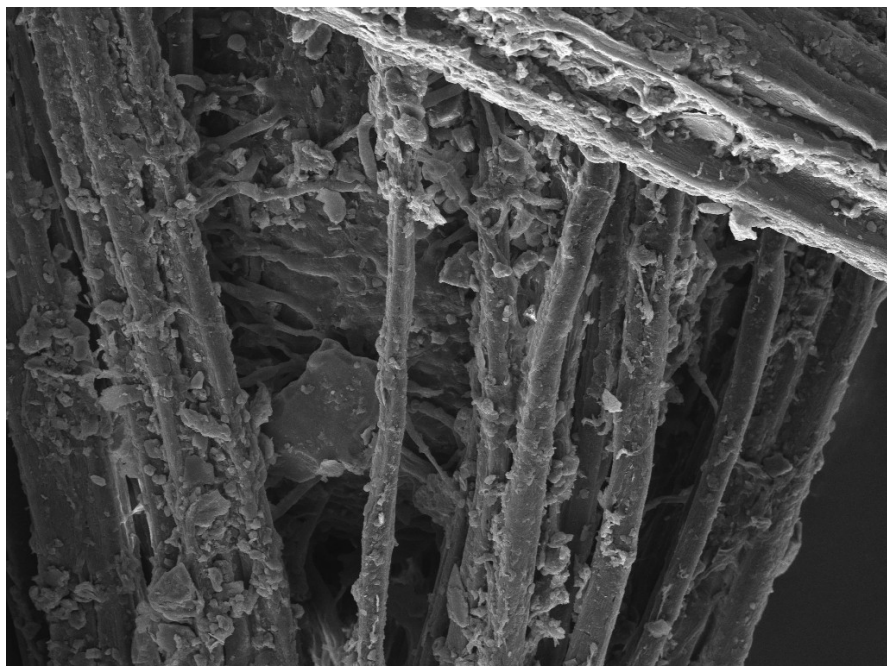
SEM HV: 15.0 kV	WD: 14.43 mm		MIRA3 TESCAN
View field: 1.38 mm	Det: SE	200 μ m	
SEM MAG: 200 x	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT	

LEAF FIBER 3 – SISAL AFTER EXPOSURE IN OUDOOR approx. 3 years

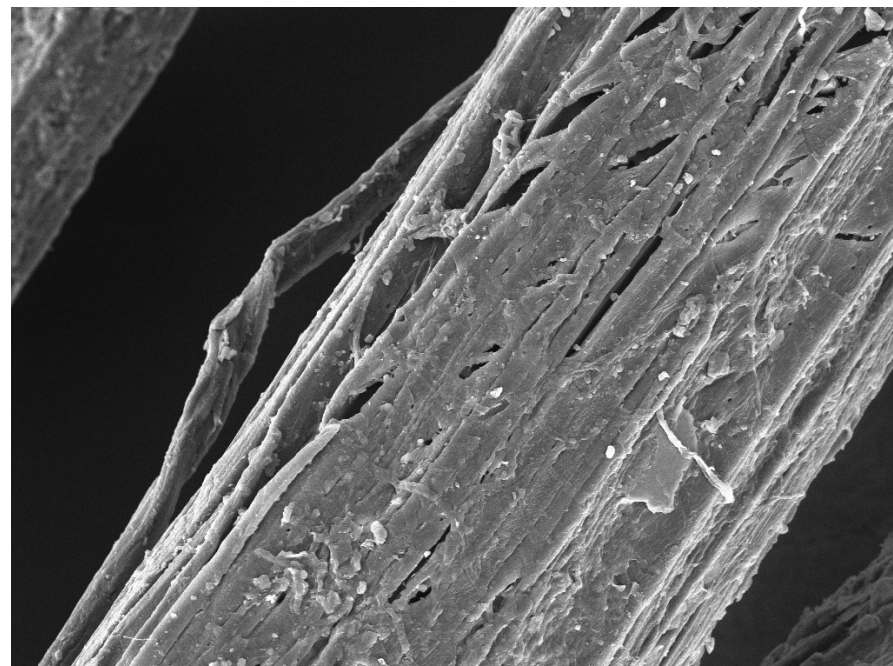


SEM HV: 15.0 kV	WD: 14.56 mm		MIRA3 TESCAN
View field: 278 μm	Det: SE	50 μm	
SEM MAG: 994 x	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT	

LEAF FIBER 4 – SISAL Influence of the Outdoor Exposure EXPOZICE



SEM HV: 15.0 kV	WD: 14.56 mm	MIRA3 TESCAN
View field: 278 μ m	Det: SE	50 μ m
SEM MAG: 994 x	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT



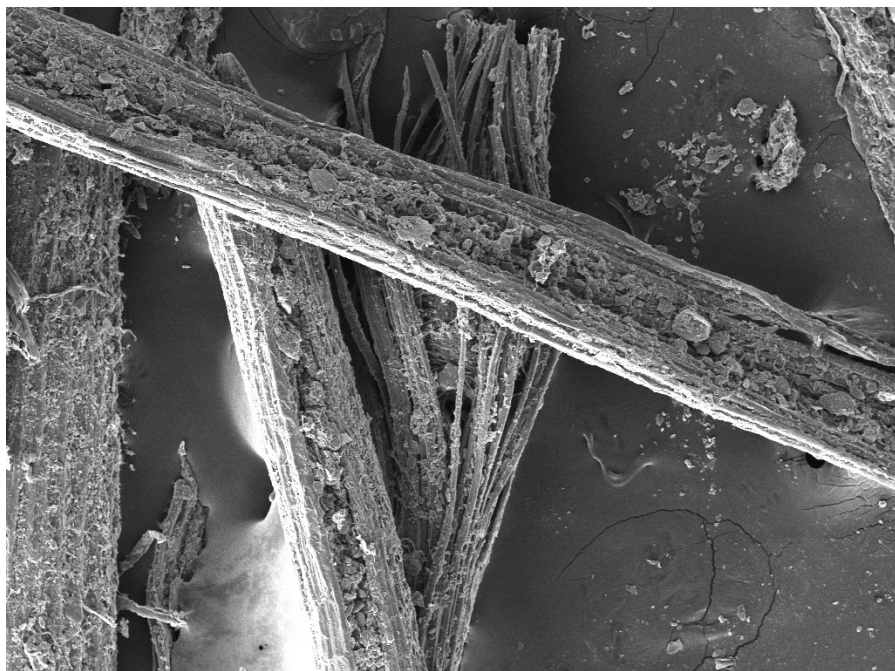
SEM HV: 15.0 kV	WD: 14.33 mm	MIRA3 TESCAN
View field: 270 μ m	Det: SE	50 μ m
SEM MAG: 1.02 kx	Date(m/d/y): 10/25/16	Department of Physical Electronics, CEPLANT

In the Outdoor
approx. 3 years

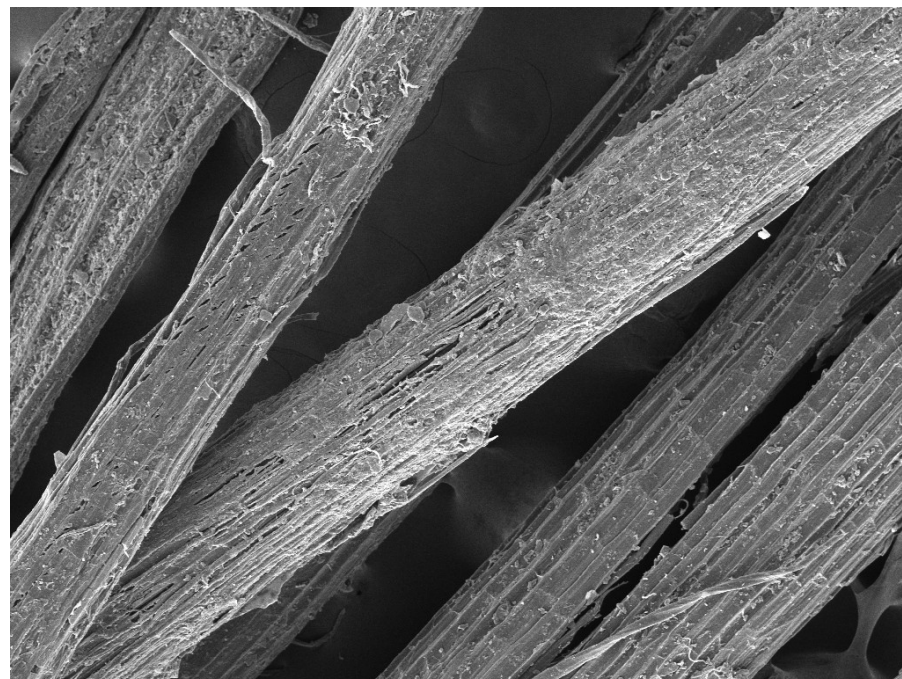
NATIVE

Magnification 1000x, SEM

LEAF FIBER 4 – SISAL Influence of the Outdoor Exposure EXPOZICE



SEM HV: 15.0 kV WD: 14.43 mm MIRA3 TESCAN
View field: 1.38 mm Det: SE 200 µm
SEM MAG: 200 x Date(m/d/y): 10/25/16 Department of Physical Electronics, CEPLANT



SEM HV: 15.0 kV WD: 14.41 mm MIRA3 TESCAN
View field: 1.38 mm Det: SE 200 µm
SEM MAG: 200 x Date(m/d/y): 10/25/16 Department of Physical Electronics, CEPLANT

In the Outdoor
approx. 3 years

NATIVE

Magnification 200x, SEM