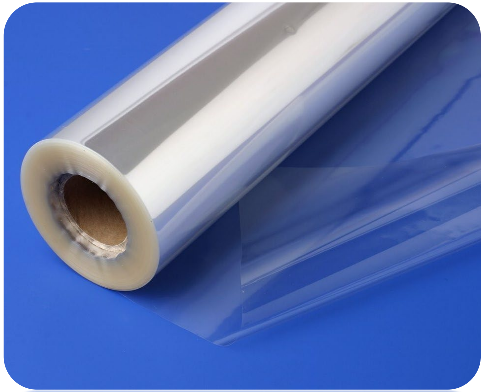
Aalto University
School of Chemical
Engineering

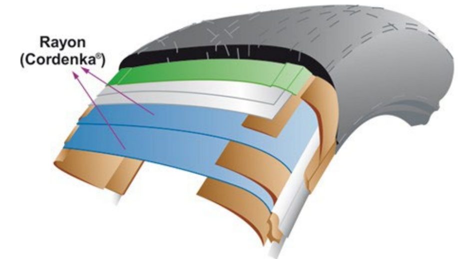
Shaping of cellulose through dissolution and regeneration

CHEM-L2010 - Cellulose Chemistry

Michael Hummel

Cellulose products





Learning outcomes

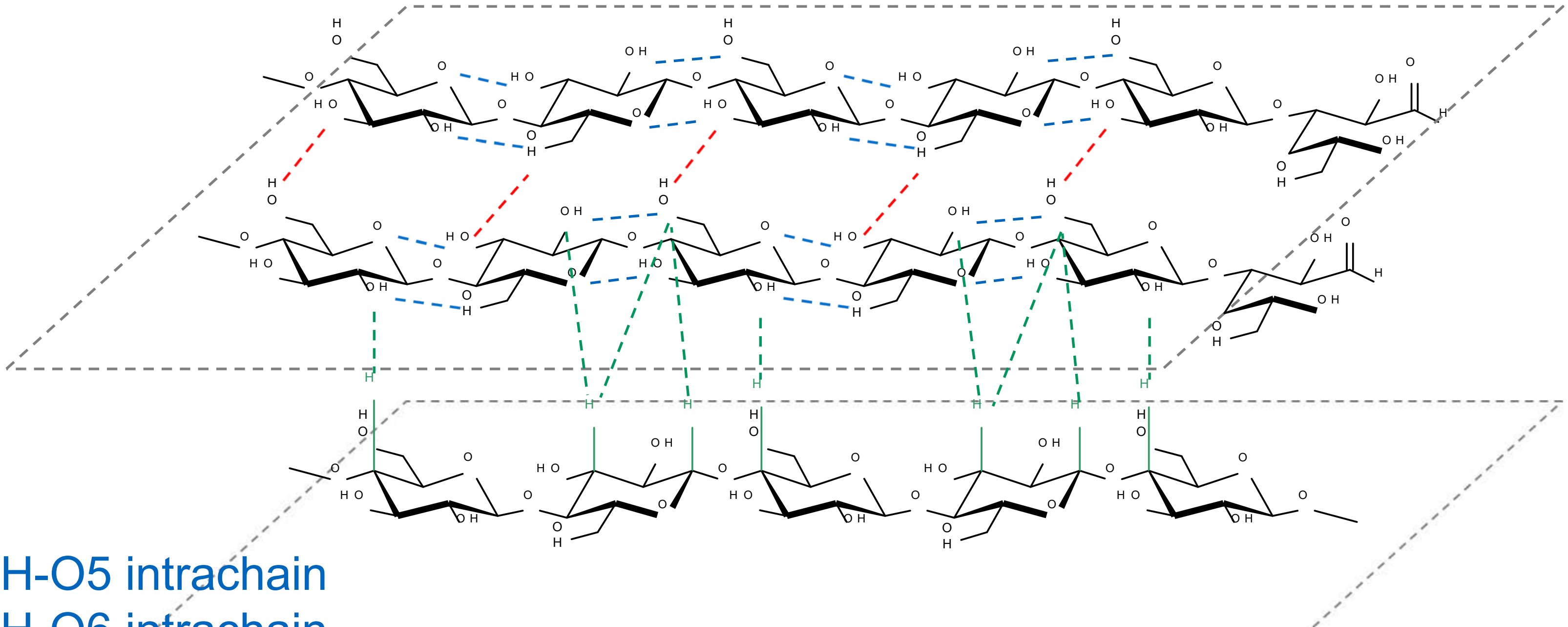
After this lecture you

- **are familiar with a short history of manufactured cellulosic fibers**
- **know different cellulose solvents**
- **understand the difference between regeneration and coagulation**
- **are familiar with the viscose, Tencel, and Ioncell processes**

Content of today's lecture

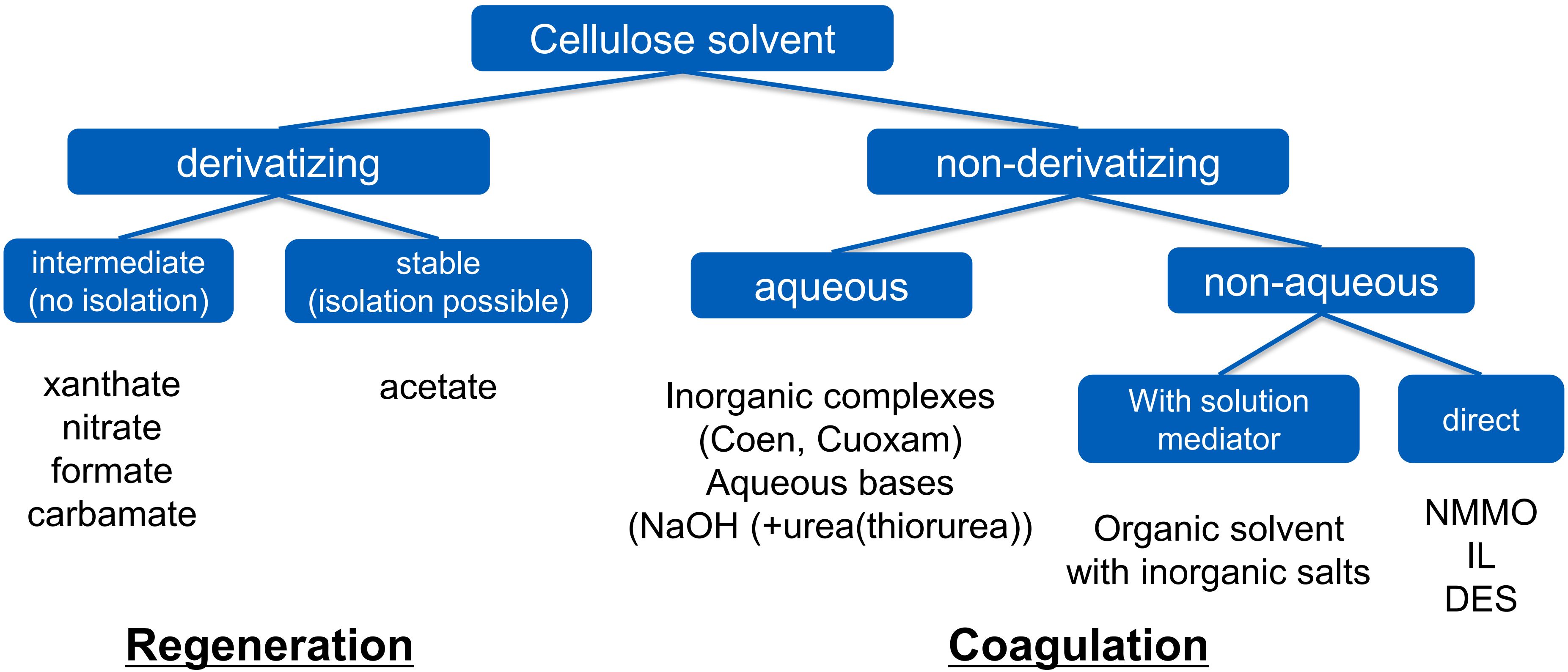
- **History of cellulose solvents**
- **Cellulose dissolution and regeneration**
- **Regeneration**
  - Viscose process
- **Coagulation**
  - Tencel
  - Ioncell

Non-covalent bonds in cellulose



O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond

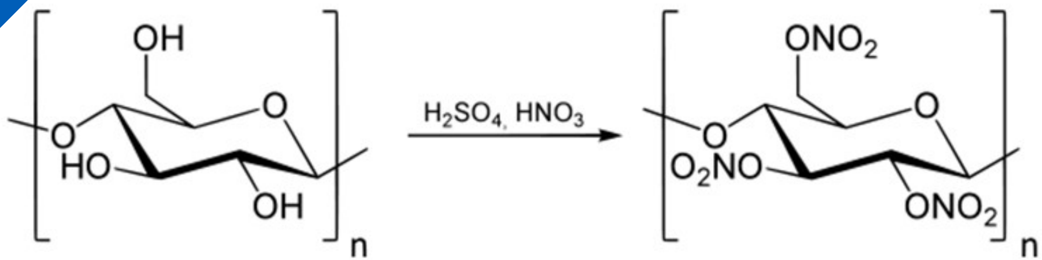
Cellulose dissolution - overview



History of cellulose solvents

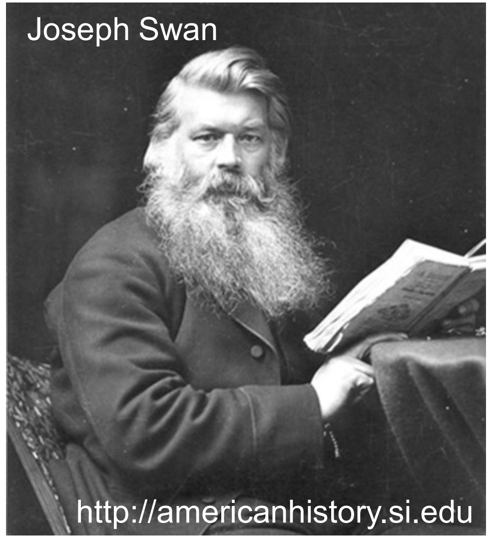
1846: Cellulose nitrate

derivatizing



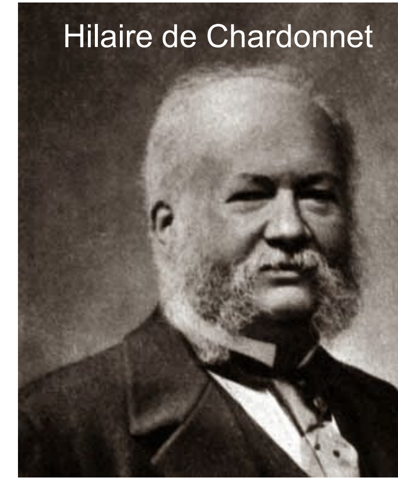
= guncotton, highly flammable

Swan developed the process to spin cellulose nitrate and de-nitrate the cellulose using ammonium bisulfate; yet he did not pursue this process further



1889: Chardonnet silk

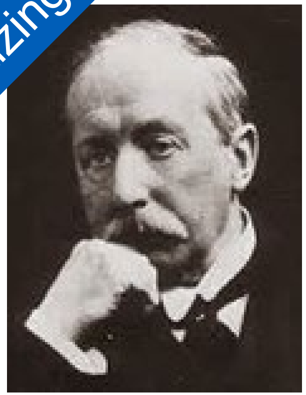
Cover illustration by Albert Edelfelt



Developed spinning of cellulose nitrate to a commercial level.
Nowadays called the Father of “Father of Rayon” and the founder of the MMCF industry

1892: The viscose process

derivatizing

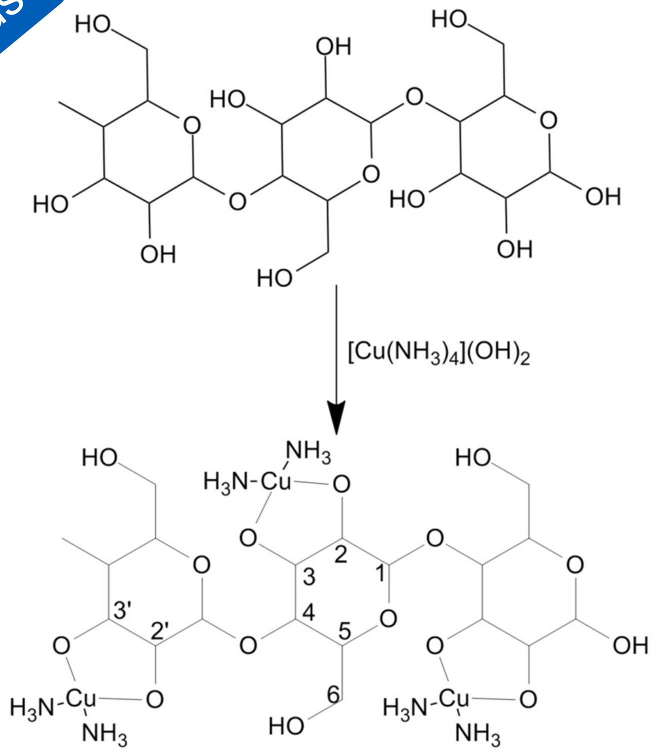


1892: Charles Frederick Cross, Edward John Bevan, Clayton Beadle file a patent describing today's viscose process

1905: Courtauld Fibres installs first commercial viscose plant in Coventry, UK

1857: Schweizer’s reagent

aqueous



wikipedia.com

Schweizer's reagent is an alkaline solution of copper sulfate in ammonia, $[Cu(NH_3)_4]\ (OH)_2.3H_2O$, named after Matthias Eduard Schweizer (1818-1860)

1934: direct dissolution

direct

Patented Jan. 9, 1934 1,943,176

UNITED STATES PATENT OFFICE

1,943,176

CELLULOSE SOLUTION

Charles Graenacher, Basel, Switzerland, assignor to Society of Chemical Industry in Basle, Basel, Switzerland

No Drawing. Application September 16, 1931, Serial No. 563,218, and in Switzerland September 27, 1930

21 Claims. (Cl. 260—100)

This invention relates to new cellulose solutions and the application thereof for making various products chemically or mechanically, and necessary, with suitable anhydrous diluents or other suitable additions. As such additions may be named, for example, substances having a re-

Charles Graenacher: father of direct solvents:

organic solvents that are capable of dissolving cellulose without derivatization or additional solubilization-mediator

Cellulose dissolution and regeneration

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Cellulose swelling: gross structure of cellulose as a moiety of particles, fibers, or a film (i.e., solid cellulosic phase) maintained, despite significant changes of physical properties and an increase in sample volume due to uptake of the swelling agent

Cellulose dissolution: transition from a two-phase system to a one-phase system (clear solution), in which the original supramolecular structure of cellulose is destroyed

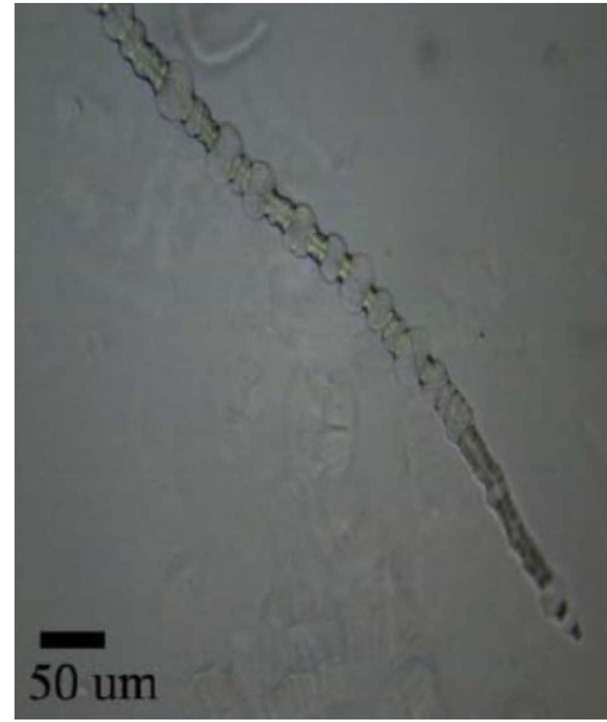
<u>However, there is often no clear-cut borderline between a swelling process and a dissolution process</u>

Balloning

Swelling and dissolution

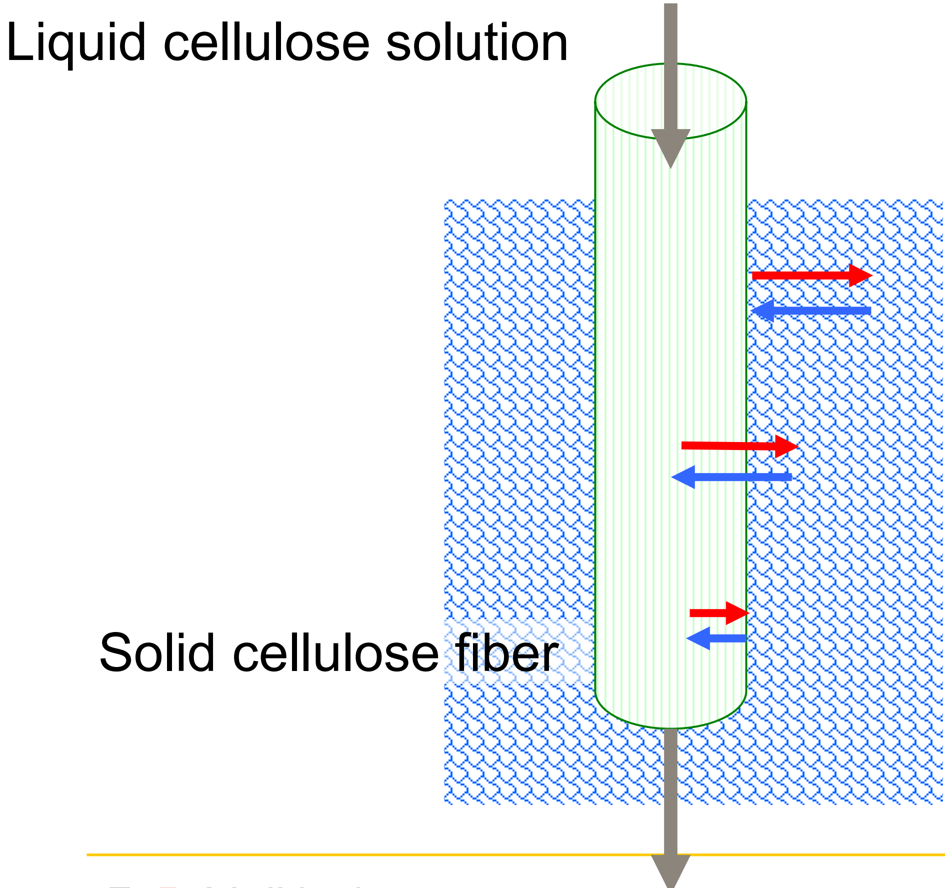
Solvent quality

- **Mode 1:** Fast dissolution by disintegration into rod-like fragments
- **Mode 2:** Large swelling by ballooning and then dissolution of the whole fiber
- **Mode 3:** Large swelling by ballooning and partial dissolution of the fiber, still keeping its fiber shape
- **Mode 4:** Homogeneous swelling and no dissolution of any part of the fiber
- **Mode 5:** No swelling and no dissolution (non-solvent)



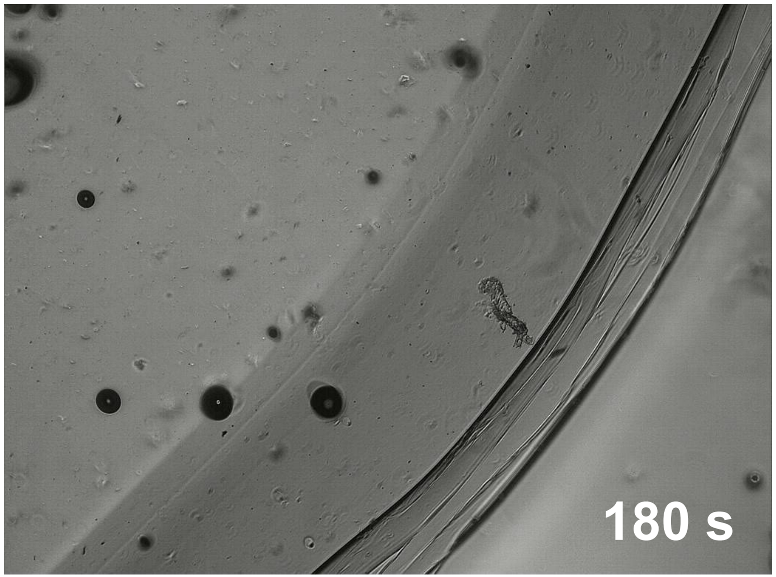
Coagulation/regeneration
≠
inverse of dissolution

Regeneration / coagulation



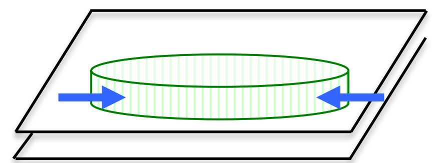
- Cellulose solution immerges into coagulation bath
- Solvent and anti-solvent diffusion
  - filament-water interface
  - in coagulation bath
  - in fiber body
- Structure formation; fiber morphology

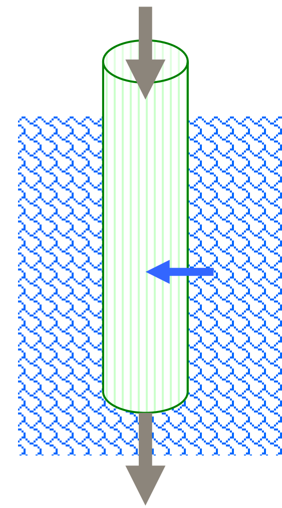
Regeneration / coagulation



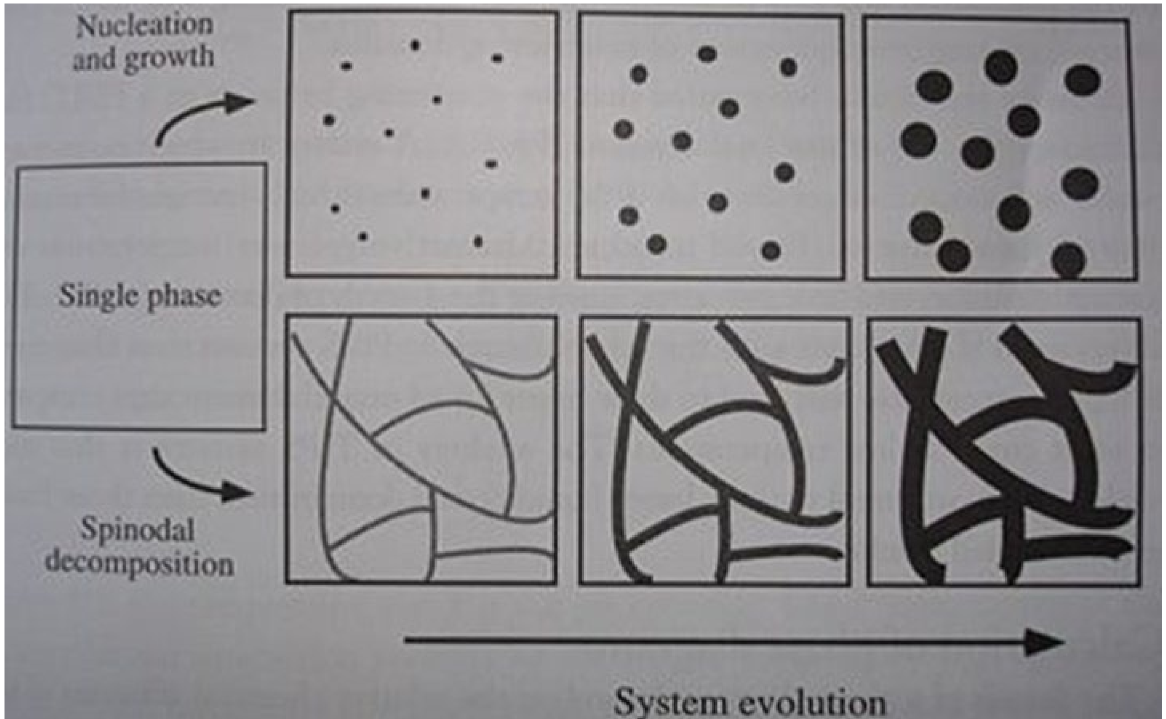
Regeneration / coagulation proceeds from the surfaces towards the center of the solution

Shell-core formation

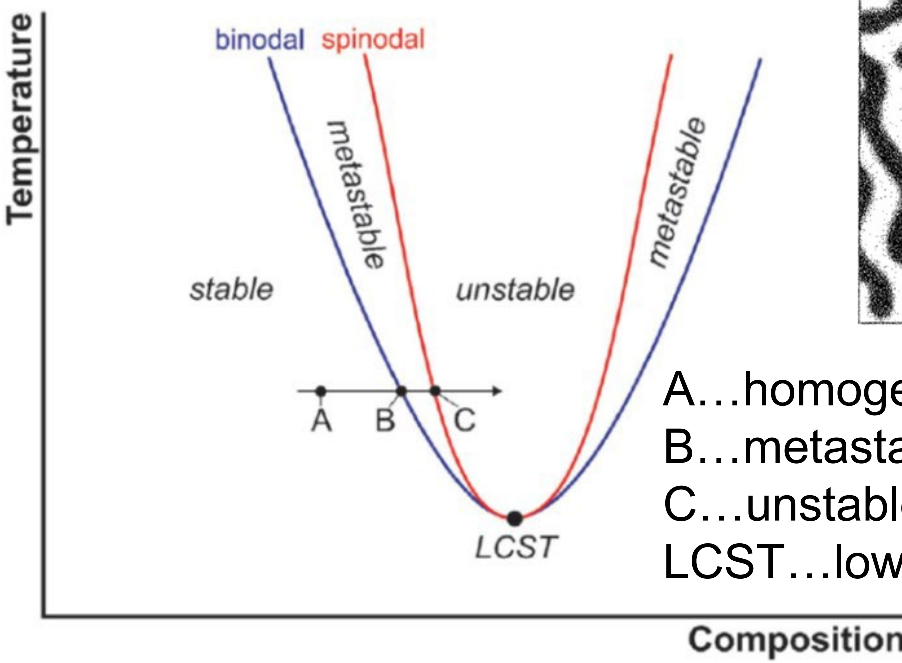


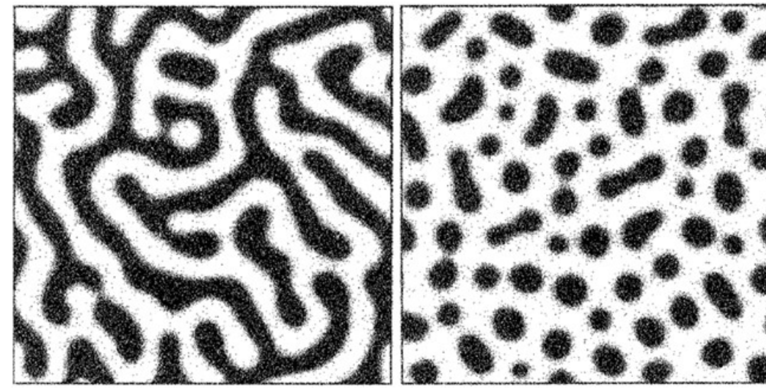


Spinodal decomposition vs. Nuleation & growth



Spinodal decomposition vs. Nuleation & growth





A…homogeneous region, stable solution
B…metastable solution; binodal demixing = nucleation
C…unstable solution, phase separation inevitable
LCST…lower critical solution temperature

Gebauer *et al.* Chem. Soc. Rev. 2014, 43, 2348.
García-Ojalvo, *et al.* Europhys. Lett., 1998, 42, 125.

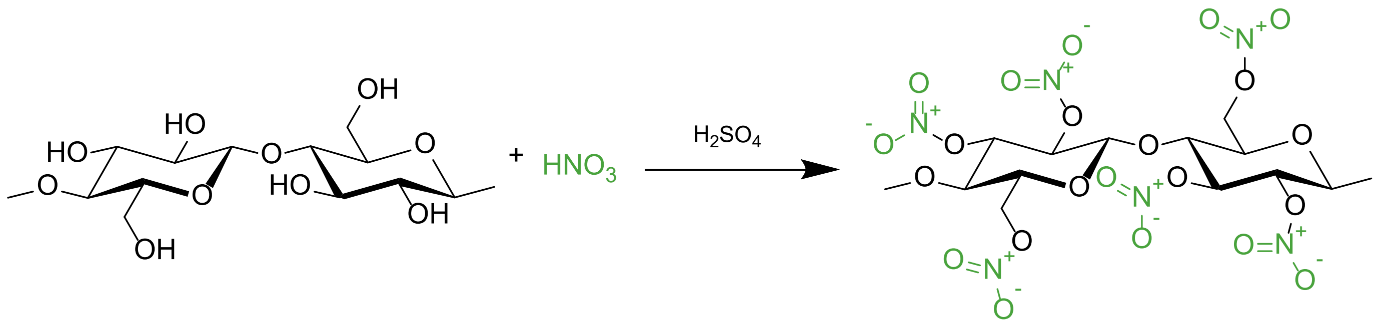
Summary questions

- **What is the difference between regeneration and coagulation?**
- **What is the difference between spinodal decomposition and nucleation & growth?**

Regeneration

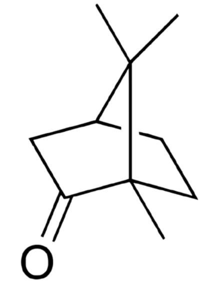
Intermediate Derivatization

Cellulose nitrate



- Alternatively in DMF/N_2O_4
- Cellulose nitrate soluble in ether/ethanol/acetone
- Solution spun through nozzles into regeneration bath containing $(NH_4)(HSO_4)$
- Flammable ("mother-in-law silk")

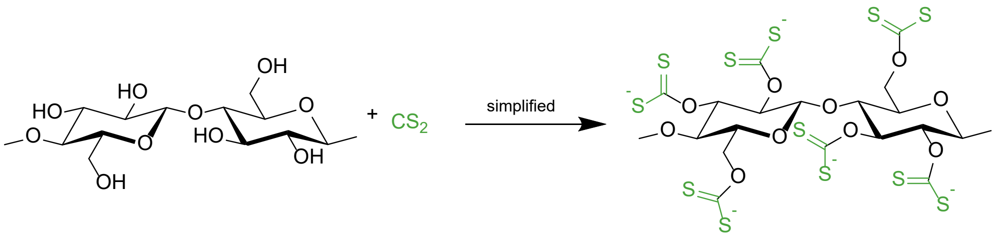
Cellulose nitrate - Celluloid

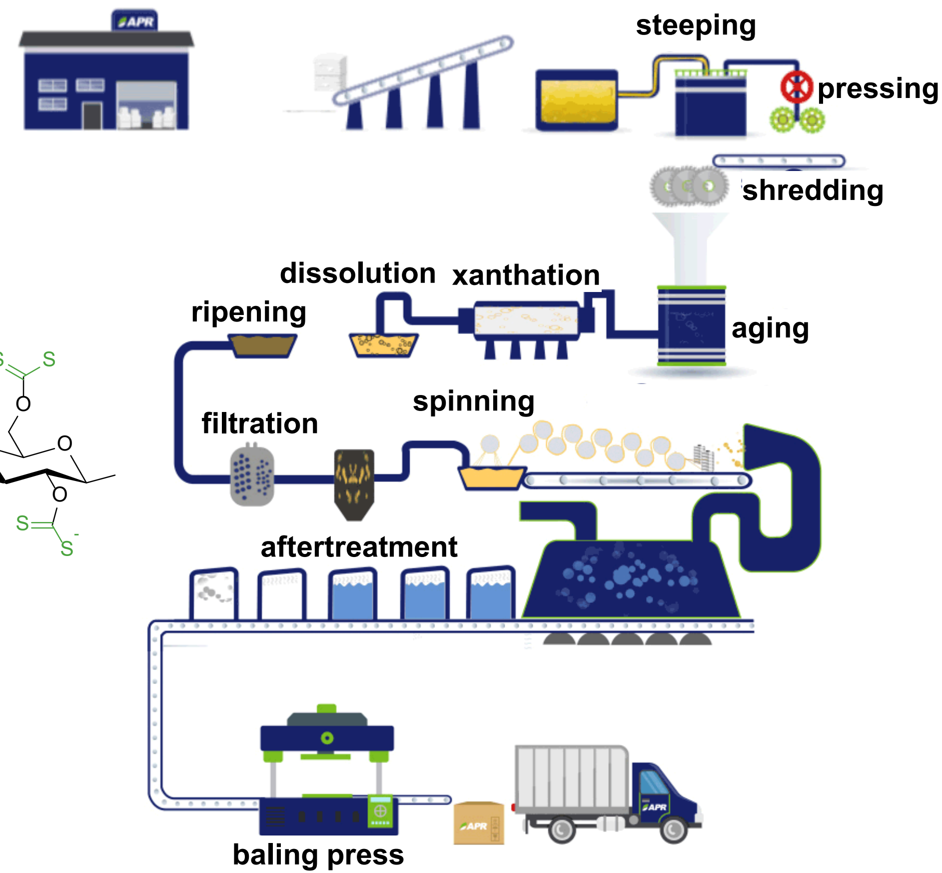


Celluloid = thermoplast containing cellulose nitrate and camphor

1856 first created by Alexander Parkes; called it Parkesine
1870 John Wesley Hyatt patents it as „Celluloïd“ to be sold through the Celluloid Manufacturing Company

Viscose process





https://www.aprayon.com/en/articles/how-is-viscose-made/

YouTube: The production of viscose fibres at Kelheim Fibres GmbH

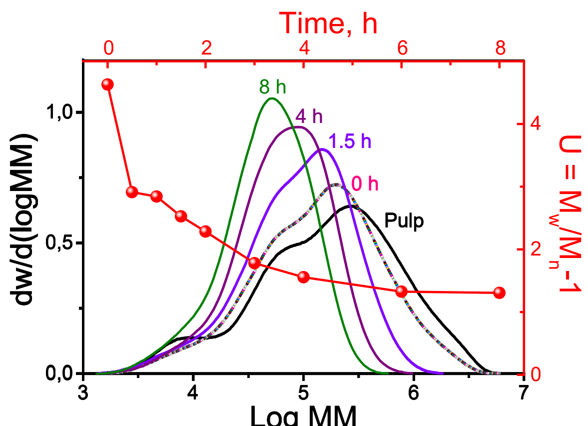
Viscose process

Steeping (alkalization):

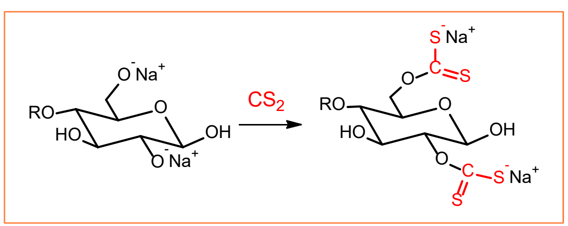
conversion to cellulose-II lattice

$$Cell - OH + NaOH \longrightarrow Cell - O^{-}Na^{+} + H_2O$$

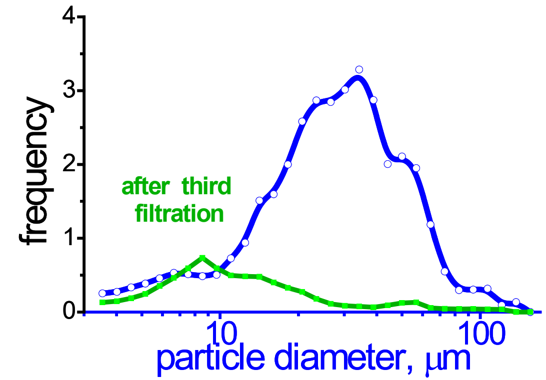
Ageing (DP adjustment)



Xanthation



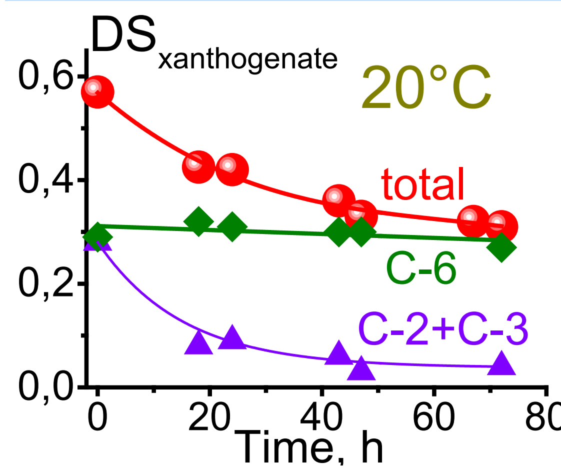
Viscose Filtration



Ripening

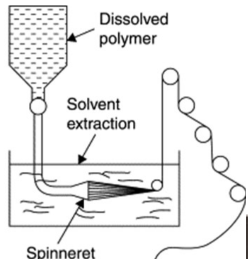
$$2CS_2 + 6\,NaOH \rightarrow$$

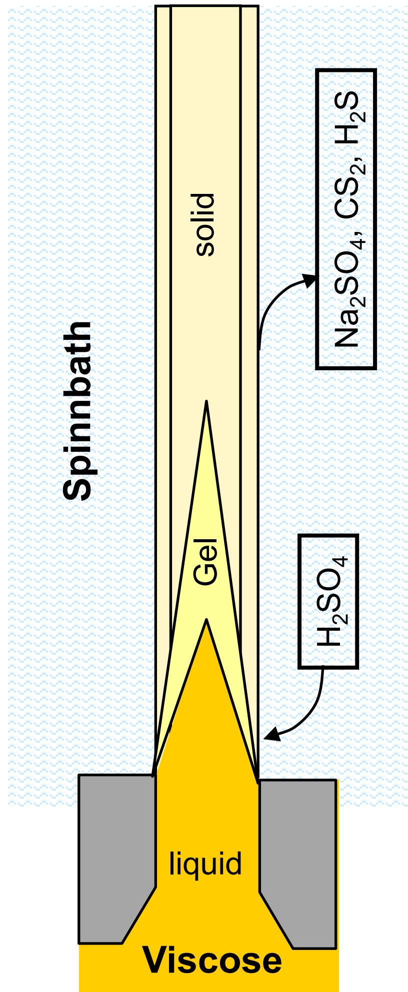
$$Na_2CS_3 + Na_2CO_3 + Na_2S + 3H_2O$$



Schwaighofer, A. et al. *Anal Bioanal Chem* (2011) 400:2449-2456

Viscose process



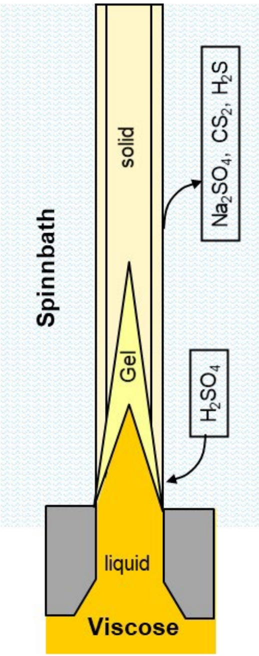


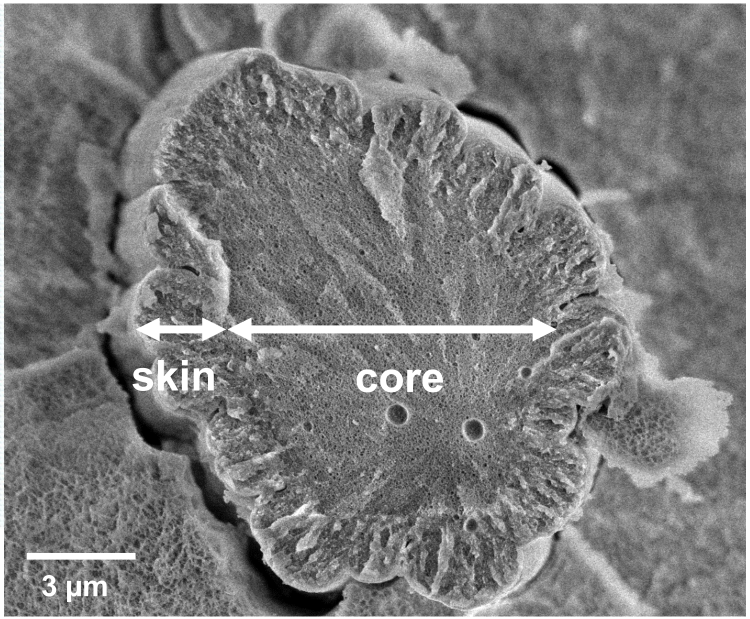
wet spinning process

- H_2SO_4: precipitation and decomposition of the xanthate
- Na_2SO_4: deswelling the gel-filament by water extraction
    - Primary structure formation by coagulation
    - Secondary structure formation by dehydration/densification; regeneration; orientiation, crystallisation
- high tenacity viscose fibres: require an extension of the time until complete regeneration
    - length of spin bath immersion
    - <u>$ZnSO_4$</u>: retarding coagulation and regeneration:
        - Intermediate complex formation
        - Reduces deswelling of the fibre

Source: H. Harms "Chemistry and technology of the viscose fiber process"; Bio2Future course "Man-made cellulose fibers" Department of Bioproducts and Biosystems, Aalto University, August 19-23, 2019

Viscose process





a quickly solidifying „skin“ retards diffusion and the supply of coagulating agent

- Skin: acid induced fast formation
- Core: diffusion controlled coagulation of the gel in the core

Modal process:

- retarded coagulation and regeneration (more skin)
- high NaOH concentration in the solution
- Zn^{2+} and modifier in the spin bath

Viscose process

Filaments in fibre spinning processes start as fiber tow

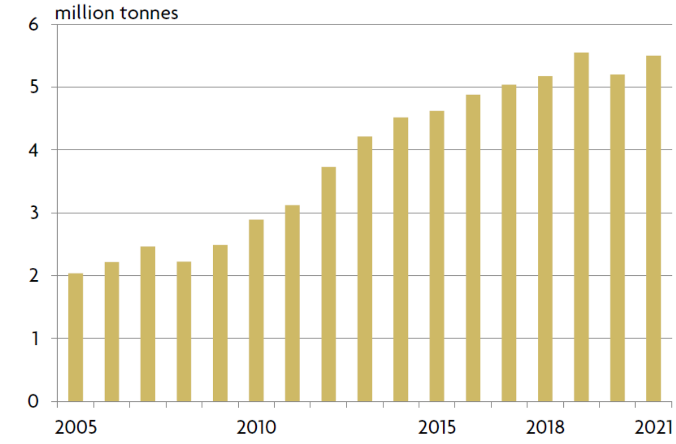
- ~ 100 cluster spinneret positions,
- each with ~30 spinnerets,
- having ~ 2000 holes each

- produce a continuous tow of 6 million filaments
  (10 million dtex @ 1.7 dtex)
- spinning speed of ~ 60 m/min

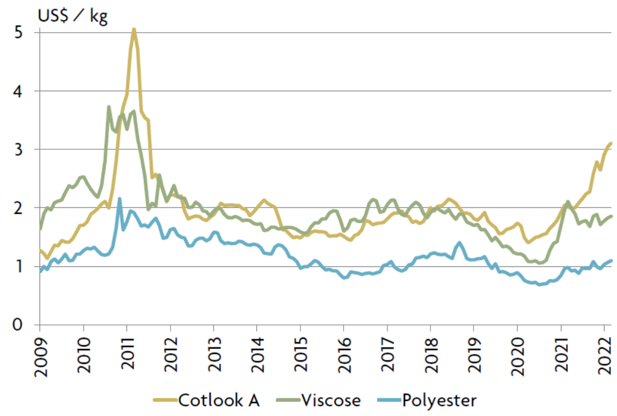
Viscose market

- 94% of the viscose fiber capacity located in Asia
- American manufacture phased out mid-2013
- European activities limited to Germany, Austria, UK
- further capacity expansions in China, Indonesia, India

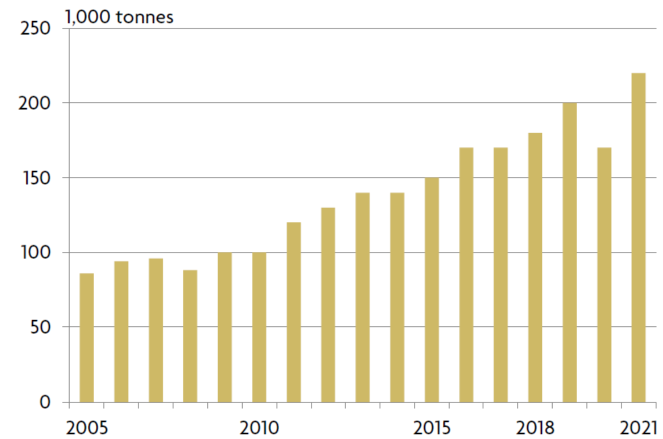
Viscose Staple Fiber Production



Cotlook A vs. Chinese Viscose & Polyester Staple Fiber Net Prices



Modal Fiber Production



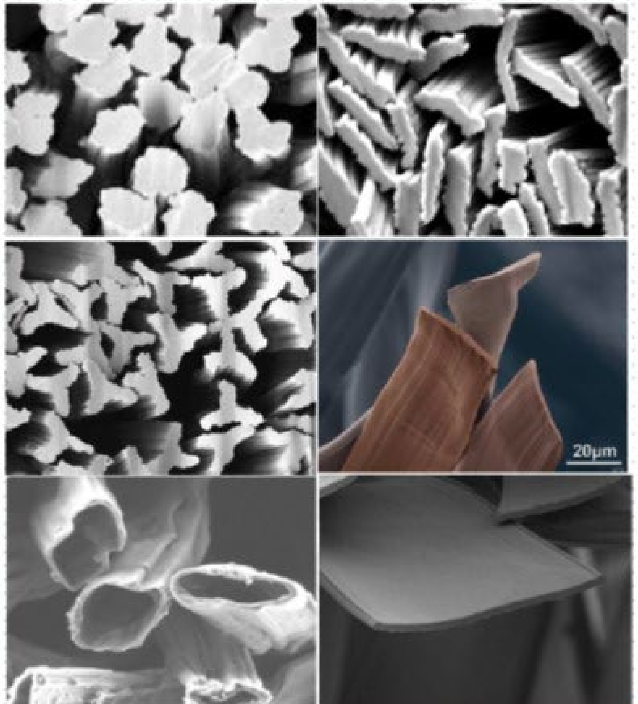
Viscose applications

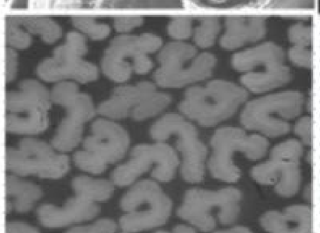
- each “target application” requires different and often very specific fiber properties

	Viscose	Viscose-Blends	Lyocell LF/A100	Lyocell-Blends	Modal	Modal-Blends
Apparel						
Underwear				✓✓ ✓	✓ ✓✓	
Knits	✓✓	✓✓	✓✓	✓✓		✓✓
Bottom weights		✓✓	✓✓	✓✓✓		✓✓
Active wear				✓✓✓		
Socks				✓✓✓	✓ ✓✓	
Shirts / Blouses		✓✓	✓✓	✓ ✓✓		
Home textiles						
Bed linen			✓✓	✓✓✓		
Towels				✓✓	✓✓✓	
Filling				✓✓		
Nonwovens						
Cleaning rags	✓✓	✓✓		✓✓		
Sanitary articles	✓✓✓	✓✓		✓✓		
Baby wipes		✓✓		✓✓✓		

H. Harms "Chemistry and technology of the viscose fiber process“; Bio2Future course "Man-made cellulose fibers“
Department of Bioproducts and Biosystems, Aalto University, August 19-23, 2019

Viscose variations



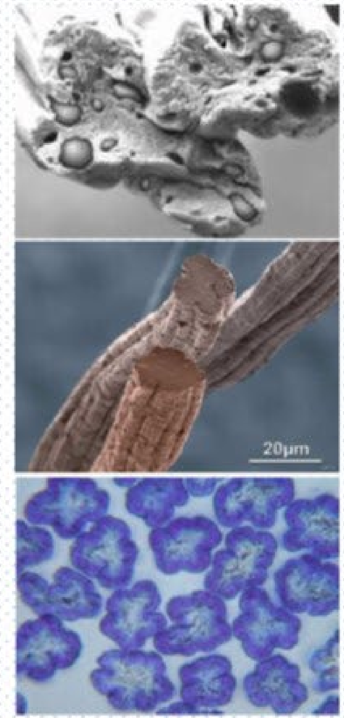


a) 7 types of cross-sections

Standard Flat (1:5)
Trilobal Superflat (1:20)
Hollow Smooth (1:40)
Letter shaped

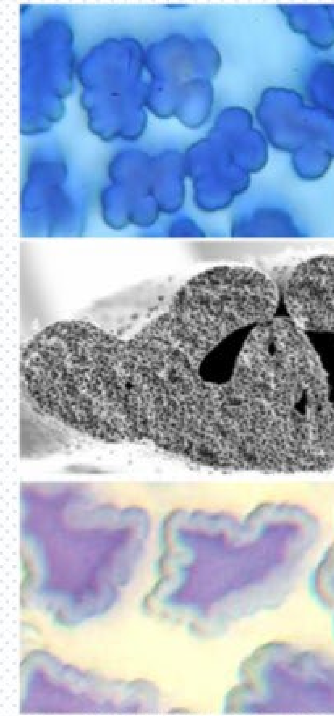
b) Titer (diameter):
0,5dtex–28dtex,
(7–48µm)

c) Fibre length:
3–120mm;
endless tow



d) Incorporation of particles/ chemicals

Pigments,
Microcapsules,
Ion exchange additives,
…



e) Polymer blends

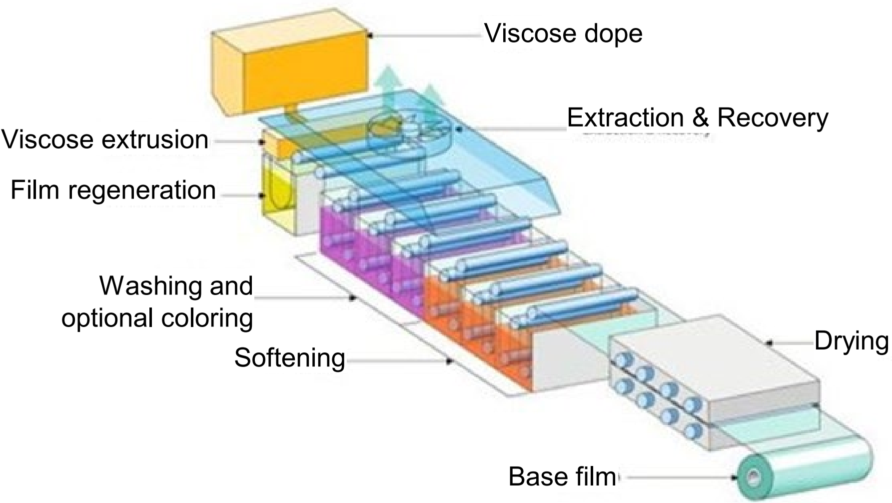
f) Coating, impregnation

Inorganic polymers
Biopolymers
Modified biopolymers
Synthetic polymers

Viscose variations

H. Harms "Acel Symposium", Helsinki, May 19, 2017

Viscose – Cellophane



Good barrier properties regarding air and grease

Coating needed to decrease water permeability

Viscose – Cellophane

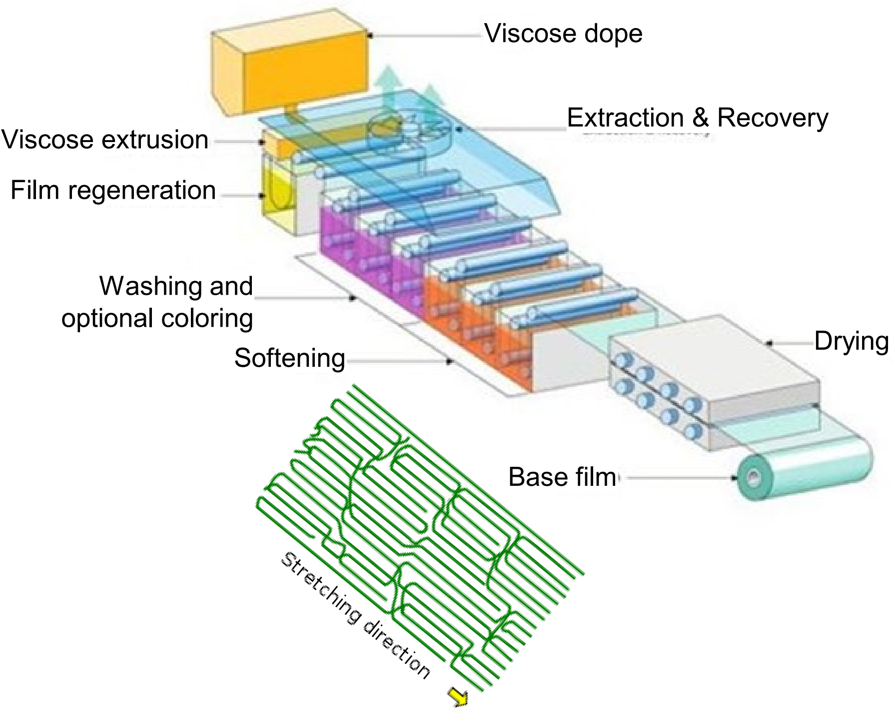


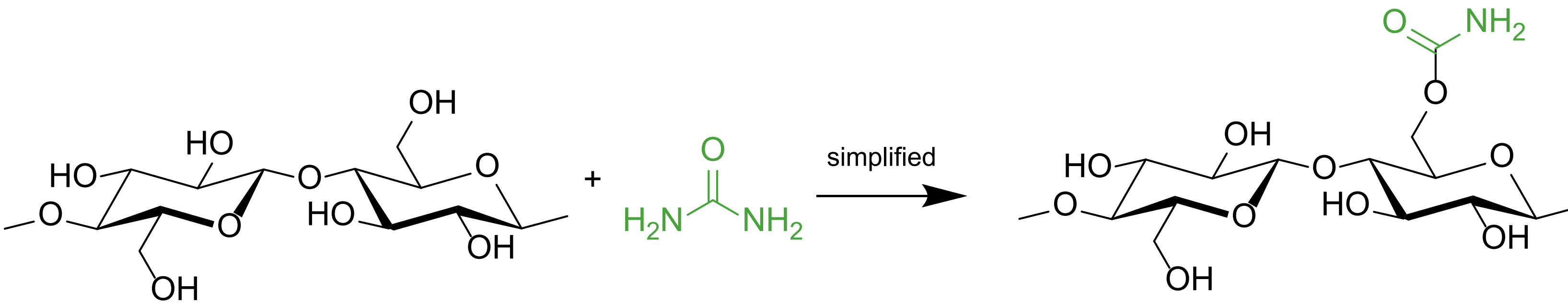
TABLE II
Mechanical Anisotropy of Test Specimens

Specimen	Tensile dynamic modulus $E_\delta \times 10^3$, kg/mm²[a]						
	$\delta = 0°$[b]	$\delta = 10°$	$\delta = 20°$	$\delta = 30°$	$\delta = 45°$	$\delta = 60°$	$\delta = 90°$[b]
C-1-D_{ex}	7.7	7.6	7.3	6.8	6.0	5.6	5.4
C-1-D_{el}	6.2	6.2	6.1	5.6	5.3	4.7	4.7
C-1-D_{st}	5.4	5.3	5.2	4.5	4.4	4.0	3.7
C-1-W	0.21	0.20	0.18	0.14	0.11	0.09	0.08
C-2-D_{ex}	7.7	7.2	7.0	6.8	6.3	5.9	5.5
C-2-D_{el}	6.8	6.4	6.4	5.6	5.2	4.7	4.5
C-2-D_{st}	5.6	5.4	5.0	4.6	4.3	3.9	3.9
C-2-W	0.20	0.20	0.17	0.15	0.11	0.09	0.08
C-3-D_{ex}	6.7	6.6	6.5	6.1	5.5	5.5	5.4
C-3-D_{el}	6.0	5.7	5.6	5.4	4.7	4.5	4.6
C-3-D_{st}	5.0	4.9	4.7	4.5	4.1	4.0	3.8
C-3-W	0.16	0.16	0.14	0.12	0.10	0.09	0.08

[a] Measured by the Viscoelastic spectrometer at 20°C. The modulus is the real part of the tensile complex dynamic modulus at 11.0 cps.
[b] The angle 0° corresponds to the x_3 axis (the machine direction); and 90° corresponds to the x_2 axis (the transverse direction) within the film plane; δ is the angle between the direction of tensile deformation and the machine direction.

Nomura *et al. J. Polym. Sci. A-2,* **1969,** 7, 325-355

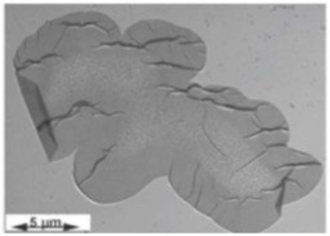
Carbamate

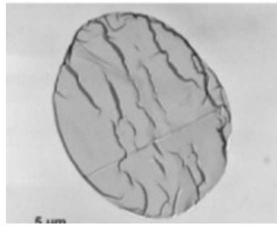


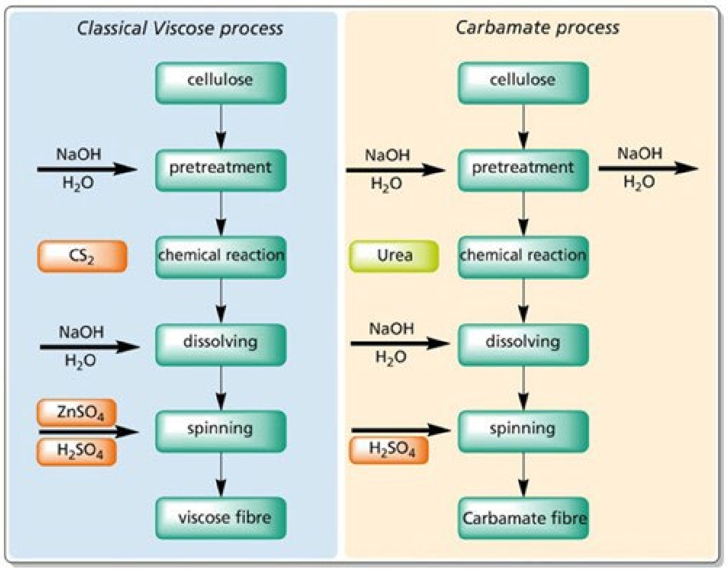
- pioneers: Hill, J.W. and A. Jacobson, DuPont (1937): Cellulose dissolved with a N-content of 1-3.5% (US patents 2,134,825; US 2,134,825)
- initial development by Neste Oy (Kemira Sateri Oy): Successful laboratory trials 1982 (Finnish Patent 61,033 (1982), Ekman et al. Lenz. Ber. 1984 57, 38-40)
- N-content between 2.5 and 4.5 %, corresponds to a DS between 0.3 and 0.6

- soluble in caustic solution with 5-10 wt% NaOH

Carbamate

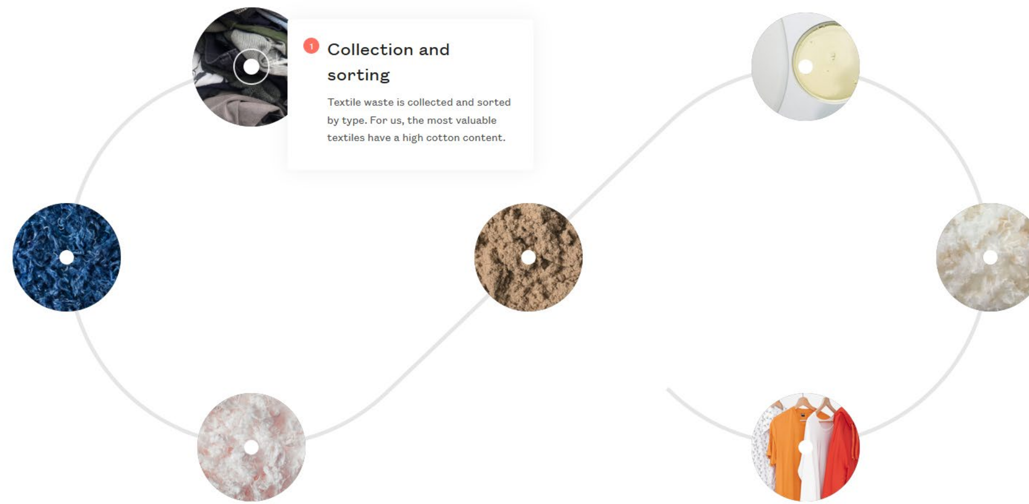






Fink *et al.* *Cellulose*, **2014,** 21, 31-51

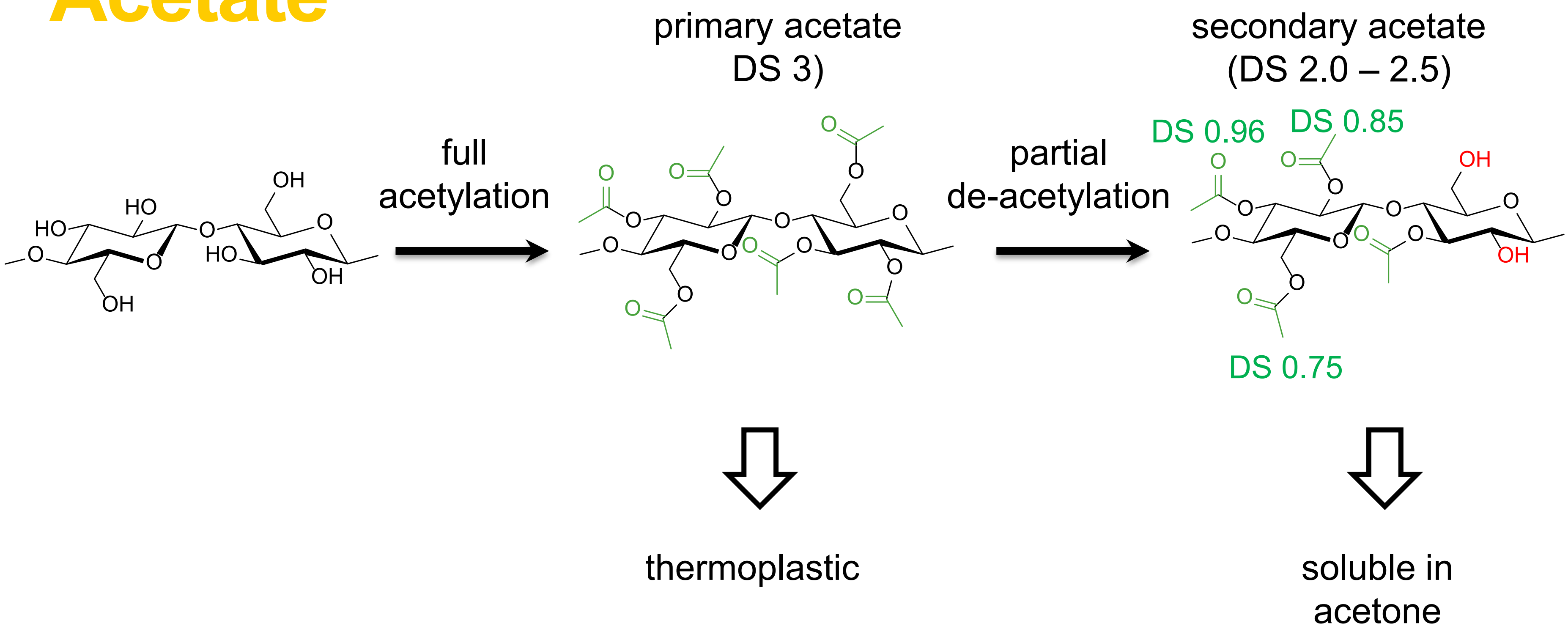
INFINITED FIBER



https://infinitedfiber.com/our-technology/

Stable derivatives

Acetate



Fischer *et al. Macromol. Symp.* 2008, 262, 89–96

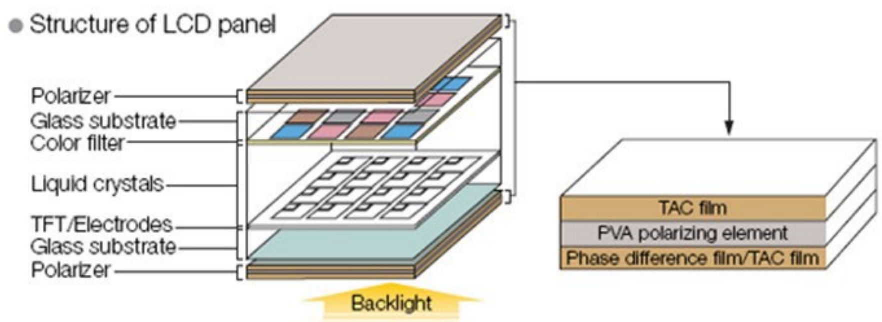
Acetate

Melt processed:

- Frames for glasses
- First Lego bricks (today acrylonitrile butadiene styrene)
- TAC films for LCD

Solution spun:

- Fiber tows for cigarette filters



Fortisan: regenerated CA

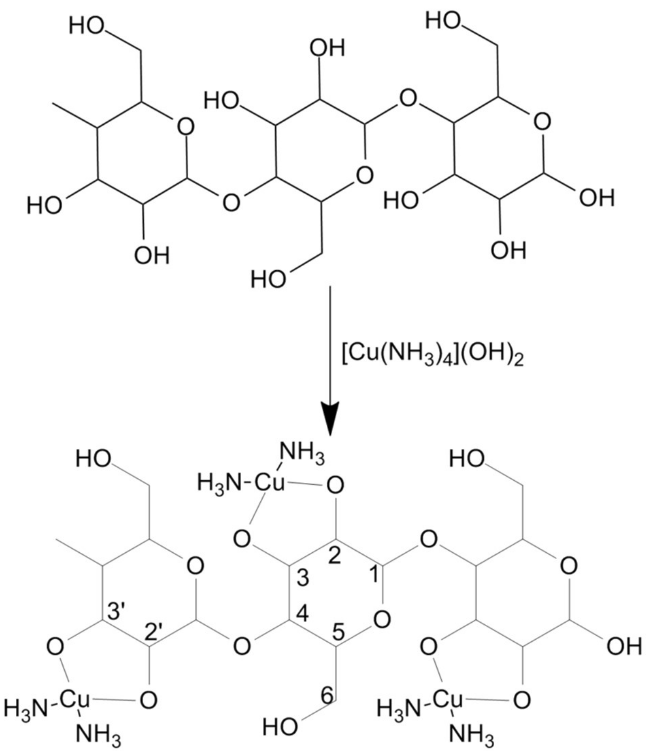
CA fiber is spun and then stretched under steam, resulting in high molecular orientation

The fiber is then saponified (de-acetylated = regenerated) to yield pure cellulose with high strength (cf. next lecture)

Coagulation

Non-derivatizing – aqueous

Metal complexes

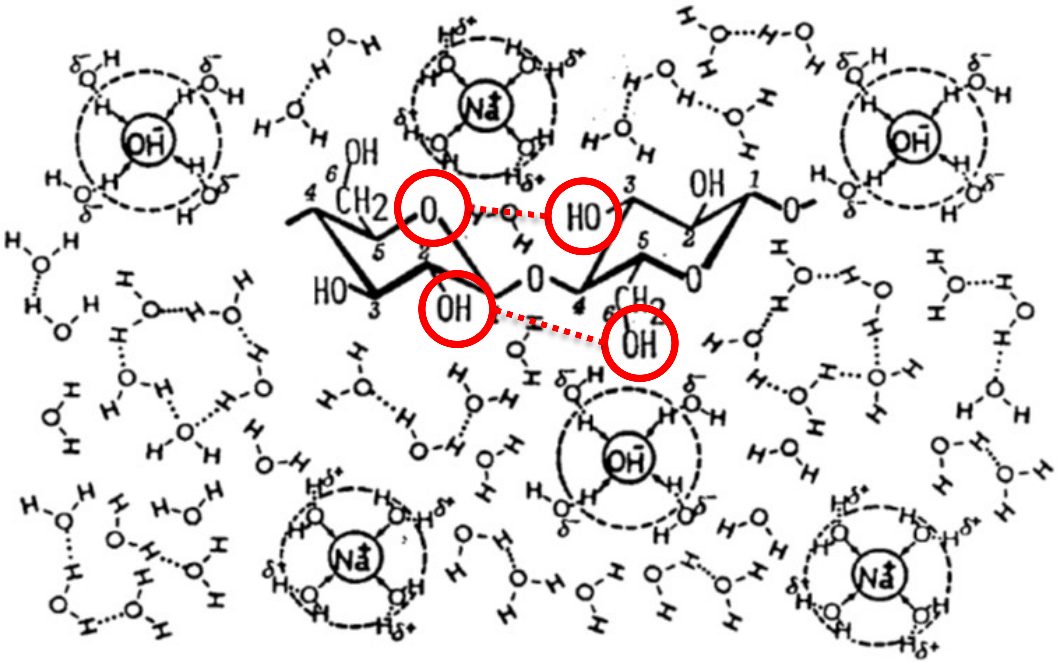


- Cuoxam: tetraammine diaqua copper hydroxide, $[Cu(NH_3)_4(H_2O)_2](OH)_2$
- Cuen: Copper(II) ethylenediamine hydroxide
- Nioxam ($[Ni(NH_3)_6][OH]_2$)
- Zincoxen ($[Zn(NH_2(CH_2)_2NH_2)_3][OH]_2$)
- Cadoxen ($[Cd(NH_2(CH_2)_2NH_2)_3][OH]_2$)
- Nitren ($[Ni(NH_2CH_2CH_2)_3N][OH]_2$)
- Pden ($[Pd(NH_2(CH_2)_2NH_2)][OH]_2$)
- Ferric sodium tartrate complex $Na_6[Fe(III)(C_4H_3O_6)3]$

Dissolution through complex formation; spun into acidic spin bath which causes de-complexation and regeneration of cellulose

Commercial cupro fiber (Cuoxam, tradename Bemberg™ fiber) produced on a scale of ca. 25 000 t/a as specialty fiber

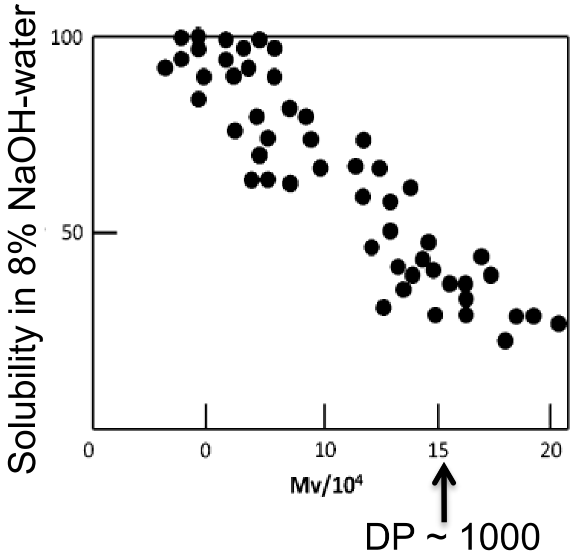
NaOH solutions



Deconstruction of intramolecular O_3-H…O_5' and O_2-H…O_6' H-bonds

Yamashiki *et al. Polym. J.* 1988, 20, 447-457
Kamide *et al. Cell. Chem. Technol.* 1990, 24, 23-31

NaOH solutions

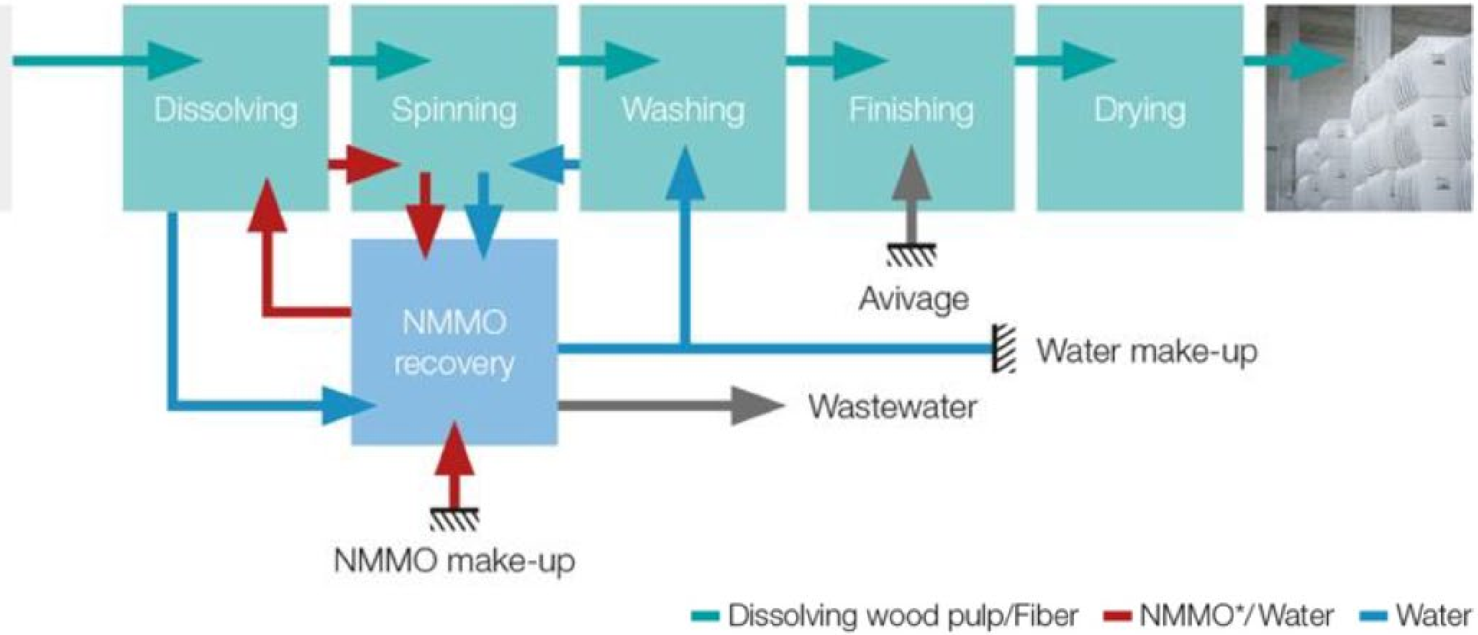


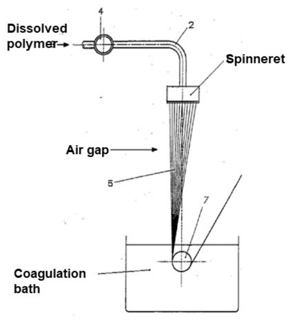
- Major limitation of NaOH as solvent: solubility of cellulose strongly dependent on DP
- Upper limit for relevant cellulose concentration;
- Limited mechanical properties of regenerated products

Budtova, Navard *Cellulose* 2016, 23, 5-55
Kamide *et al. Polym. J.* 1992, 24, 71-96

Non-derivatizing – non-aqueous

Lyocell Process



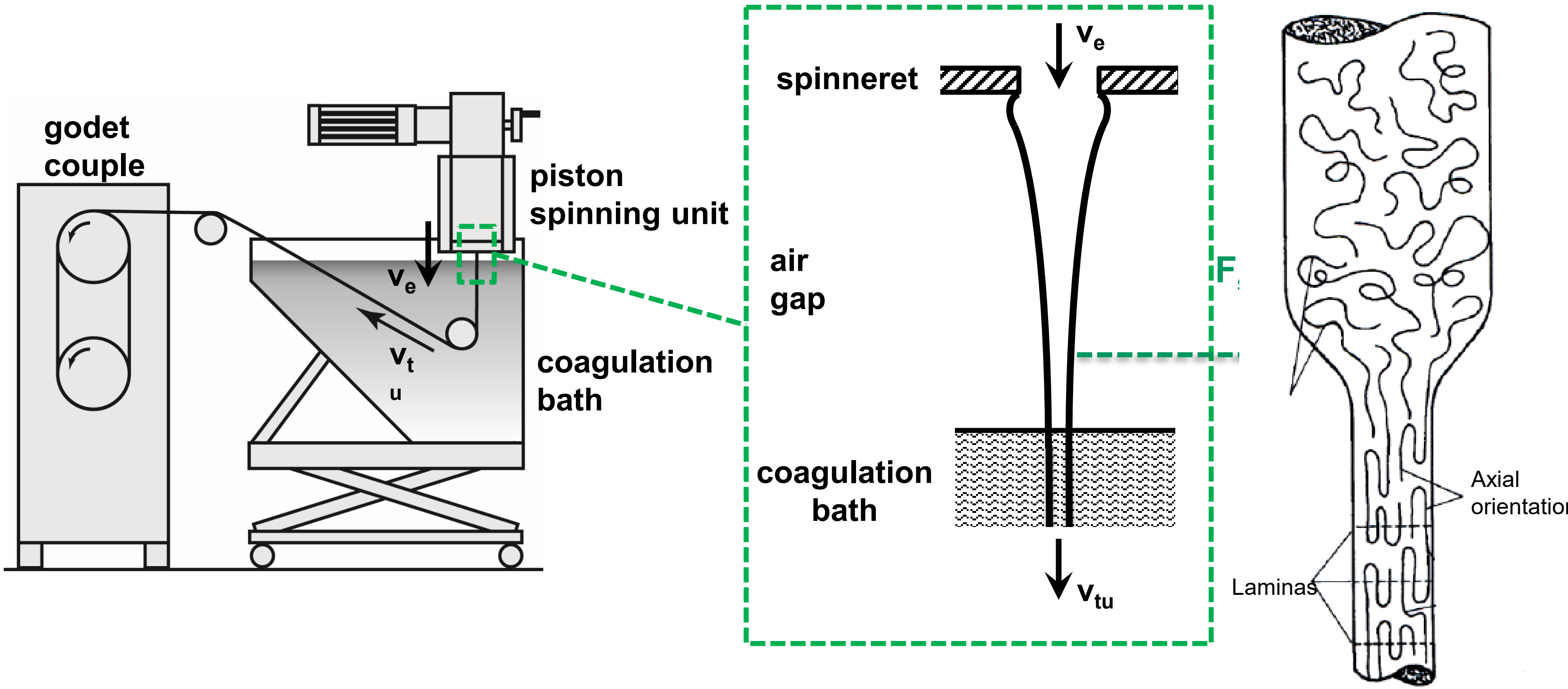


Dry-jet wet spinning

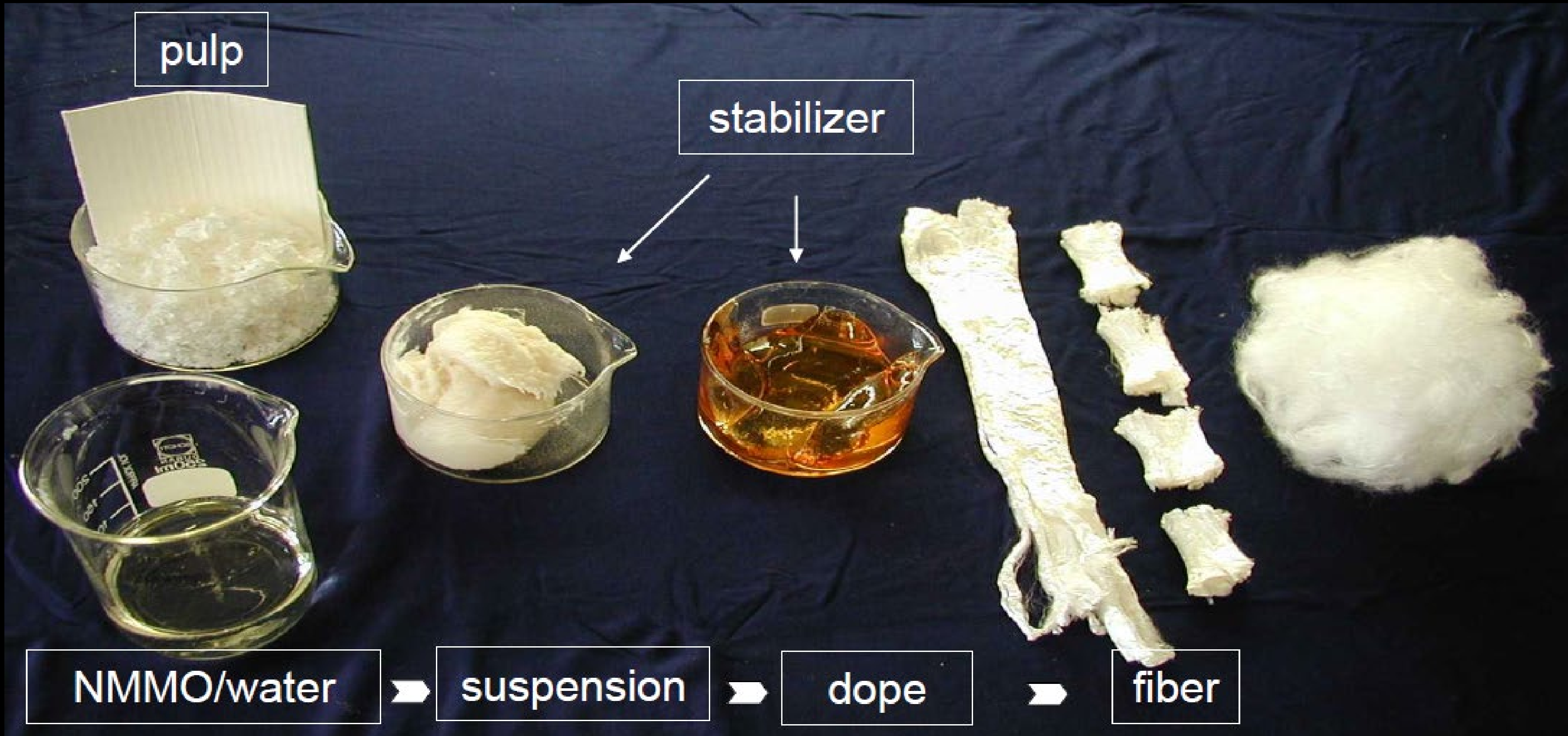
Aalto University
School of Chemical Engineering

Source: G. Kroner "Innovative by Nature – Lyocell Process"; Bio2Future course "Man-made cellulose fibers"
Department of Bioproducts and Biosystems, Aalto University, August 19-23, 2019

Lyocell Process

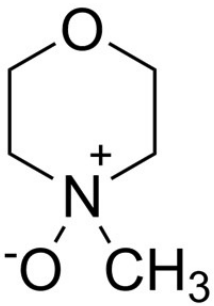


Draw ratio: $D_R = \frac{v_{take-up}}{v_{extrusion}}$



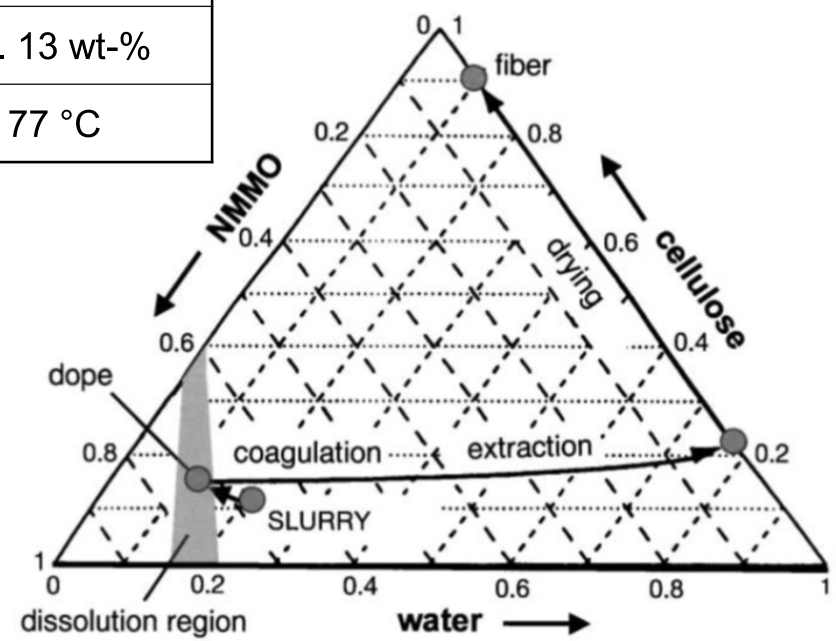
Source: G. Kroner “Innovative by Nature – Lyocell Process“; Bio2Future course "Man-made cellulose fibers“
Department of Bioproducts and Biosystems, Aalto University, August 19-23, 2019

N-methylmorpholine *N*-oxide monohydrate

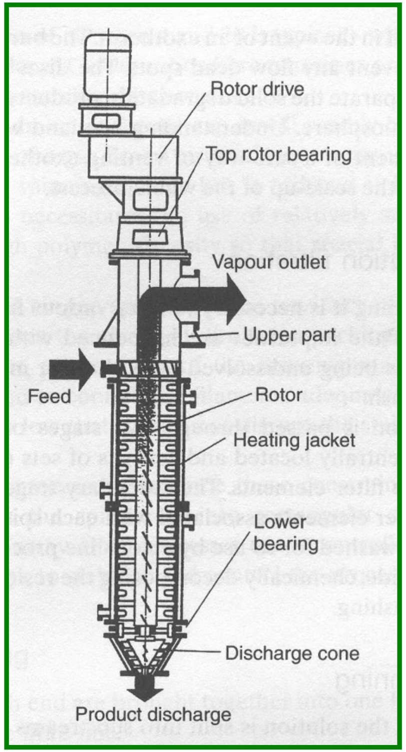


	NMMO	NMMO*H_2O
Formula	$C_5H_{11}NO_2$	$C_5H_{13}NO_3$
weight-% H_2O	0	ca. 13 wt-%
Melting point	184 °C	77 °C

- Initial development started at the very end of the 1960s by American Enka/Akzona Inc.
- It took until 1992 when Courtauld started its first full-scale production plant in Mobile (USA), followed by Lenzing AG in Heiligenkreuz (Austria) in 1997.
- Today, Lenzing owner of all spinning sites (Grimsby, UK)



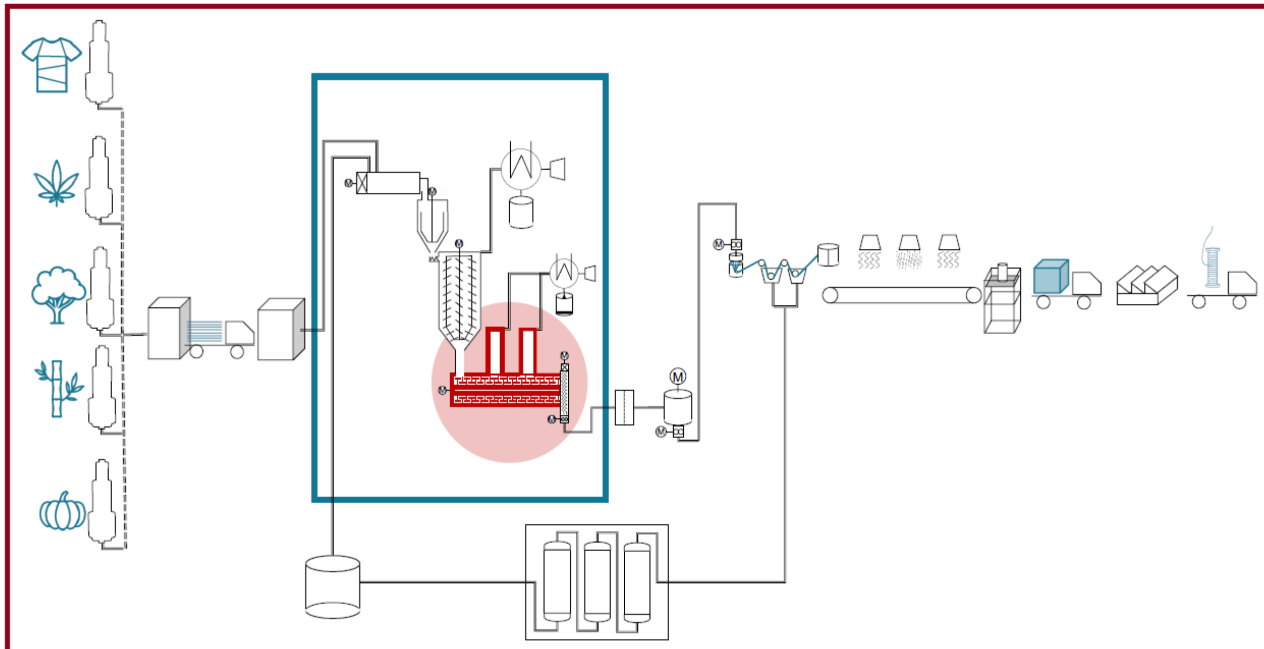
Lyocell Dope Preparation



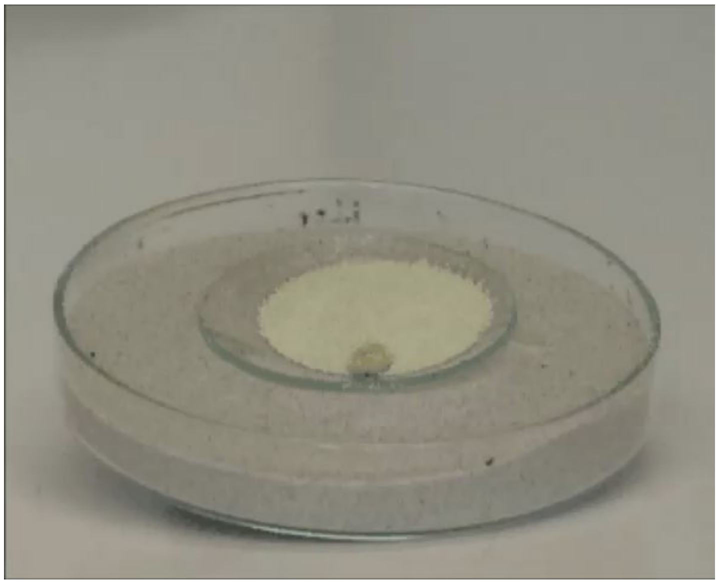
Buss Filmtruder

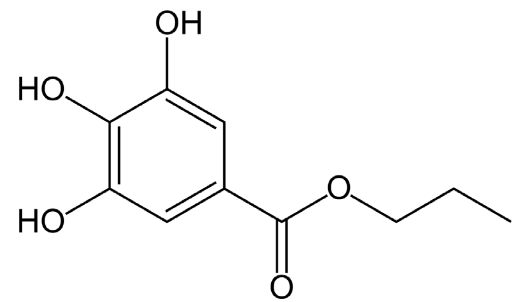
Long vertical vessel with steam heating in jackets around the vessel.

A shaft down the center of the vessel with blades attached to its circumference is rotated to smear the material around the heated surface to promote the evaporation process.



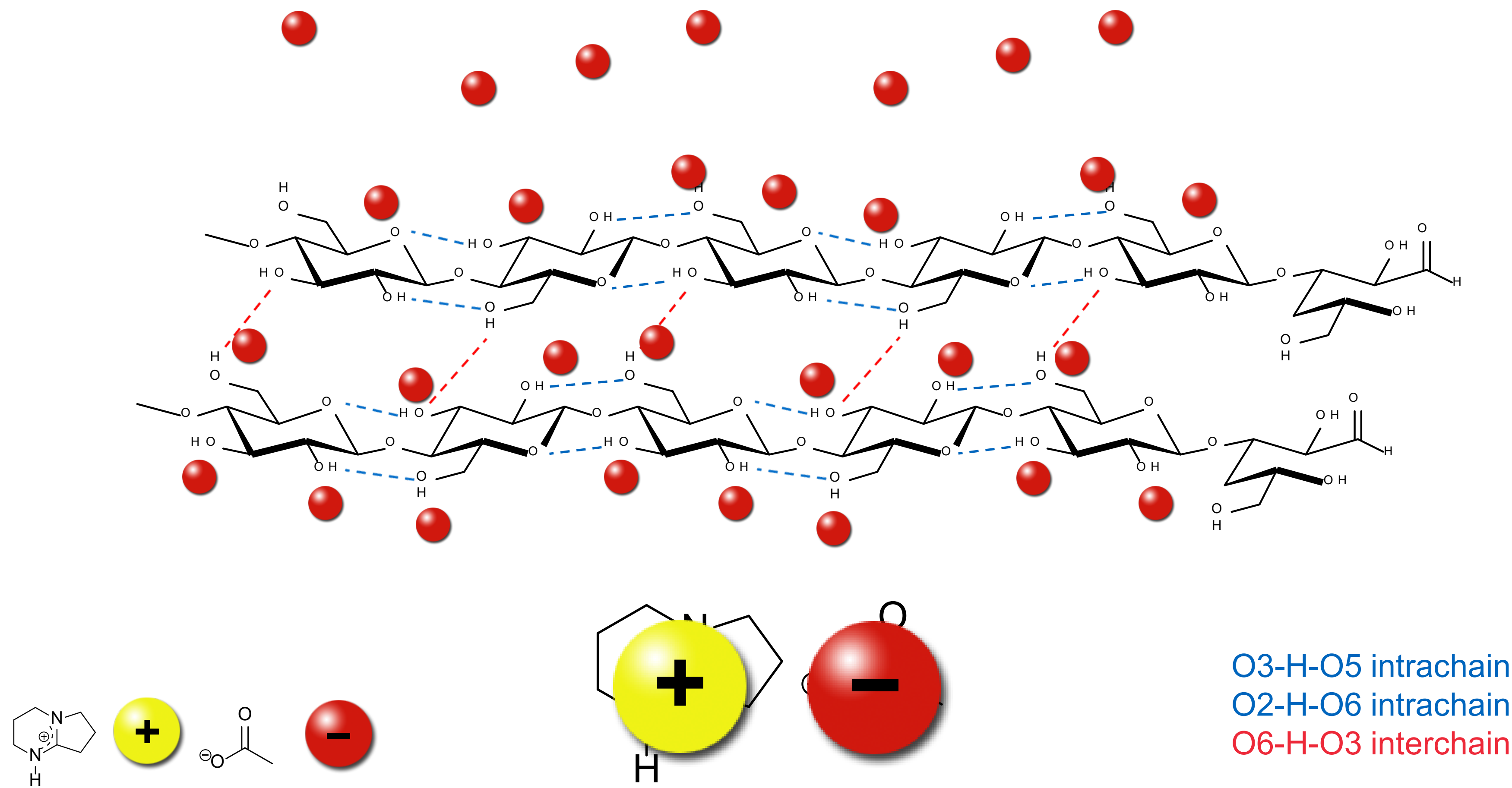
Instability of NMMO



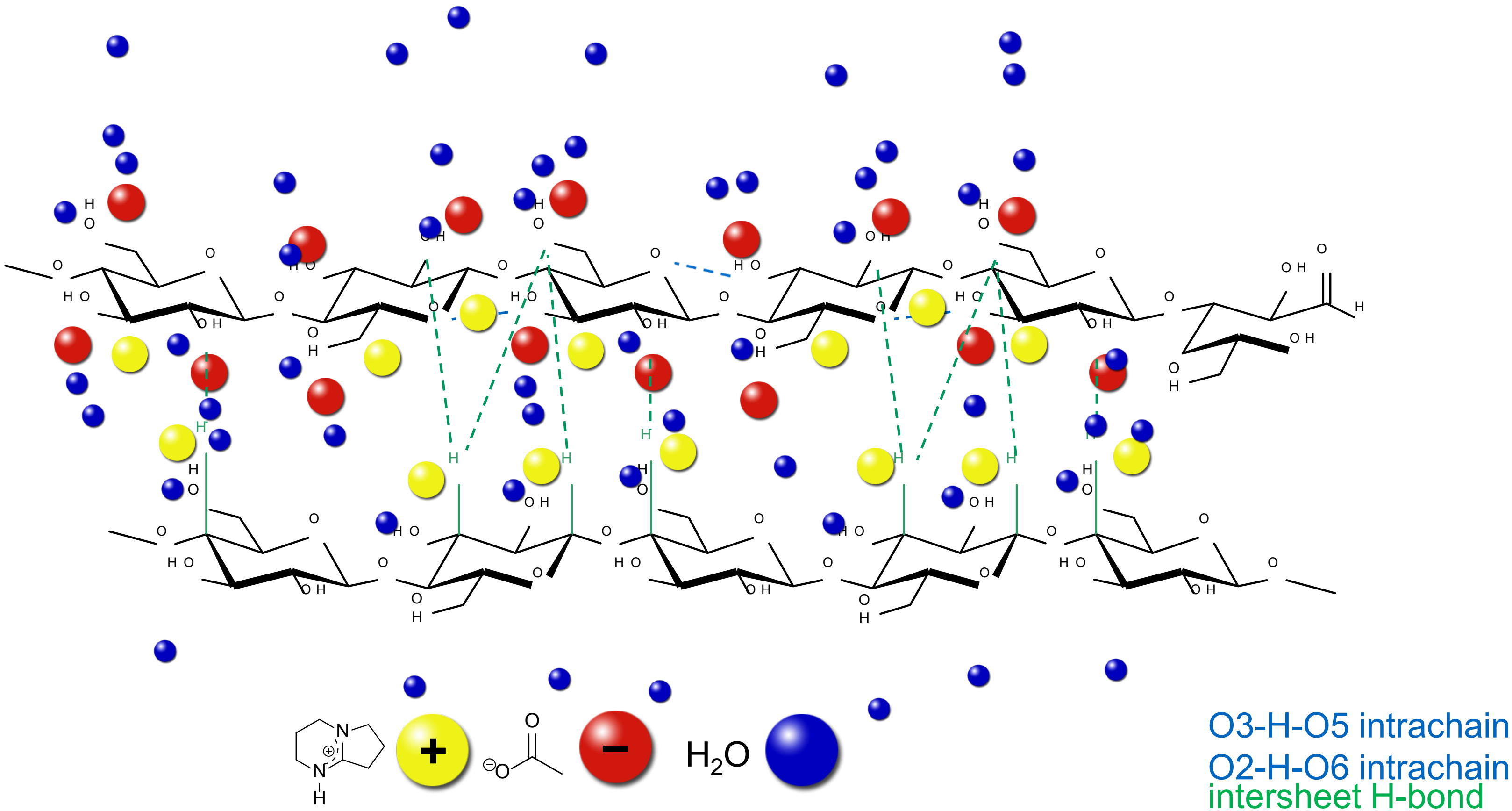


- propyl gallate as stabilizer to prevent thermal run-away reactions
- acts as radical scavenger

Rosenau, T. et al. Progress in Polymer Science, 2001, 26(9), 1763-1837

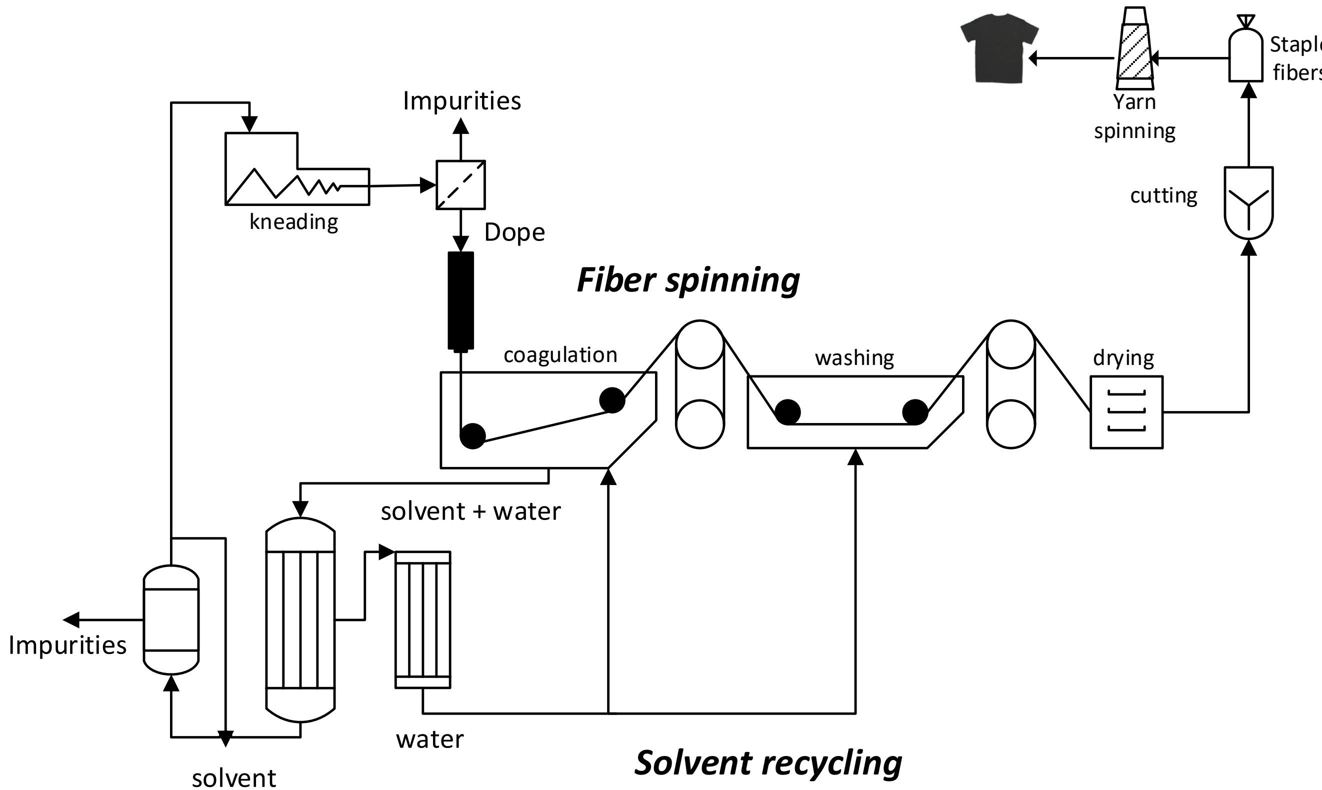


O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain



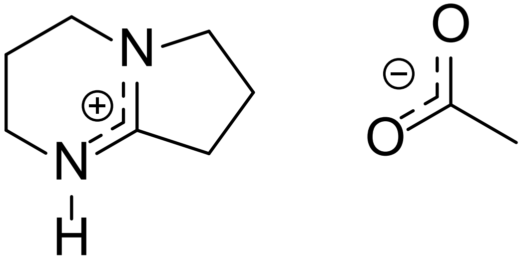
Liu, H.; Sale, K.L.; Simmons, B.A.; Singh, S. *Phys. Chem. B* **2011,** 115, 10251–10258.

Ioncell®

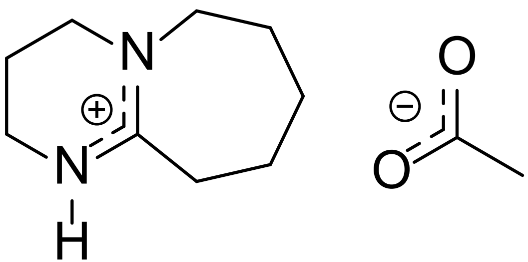


Staple fibers
Yarn spinning
Impurities
kneading
Dope
cutting
Fiber spinning
coagulation
washing
drying
solvent + water
Impurities
water
solvent
Solvent recycling

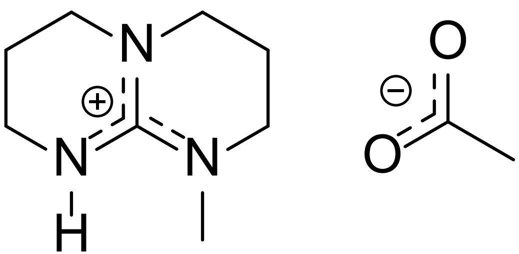
Ioncell®



[DBNH]OAc
1,5-diazabicyclo[4.3.0]non-5-enium acetate



[DBUH]OAc
1,5-diazabicyclo[4.3.0]undec-5-enium acetate



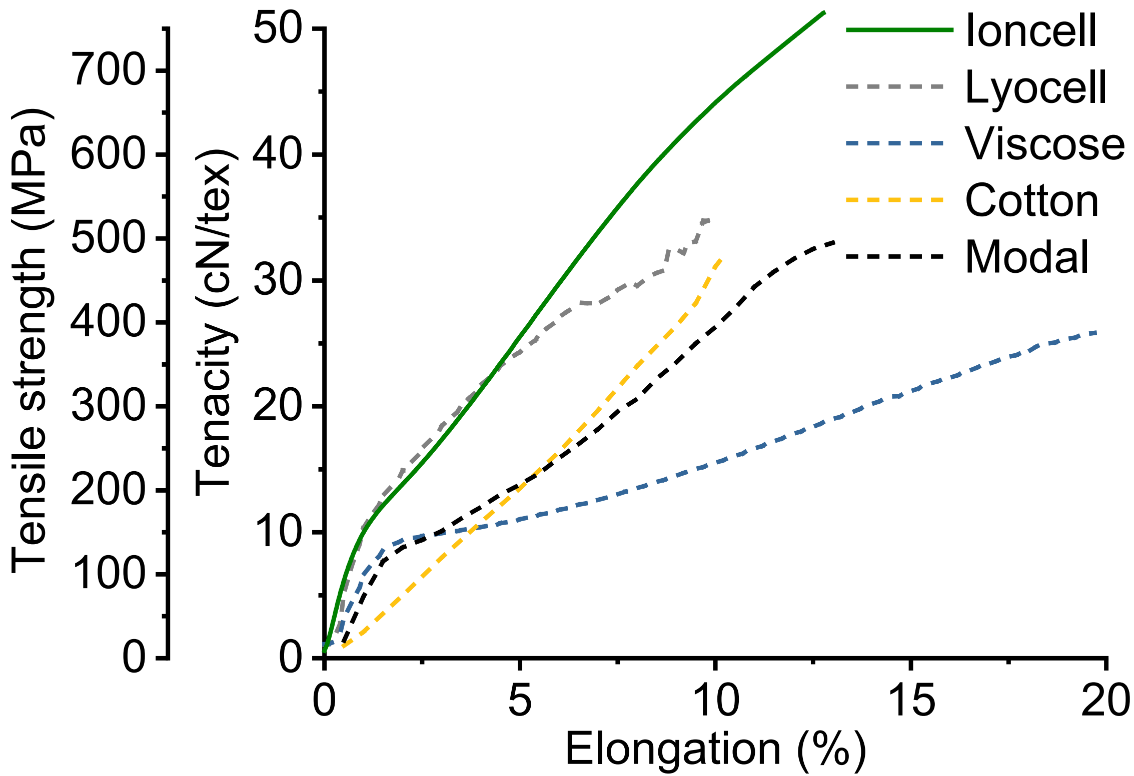
[MTBH]OAc
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate

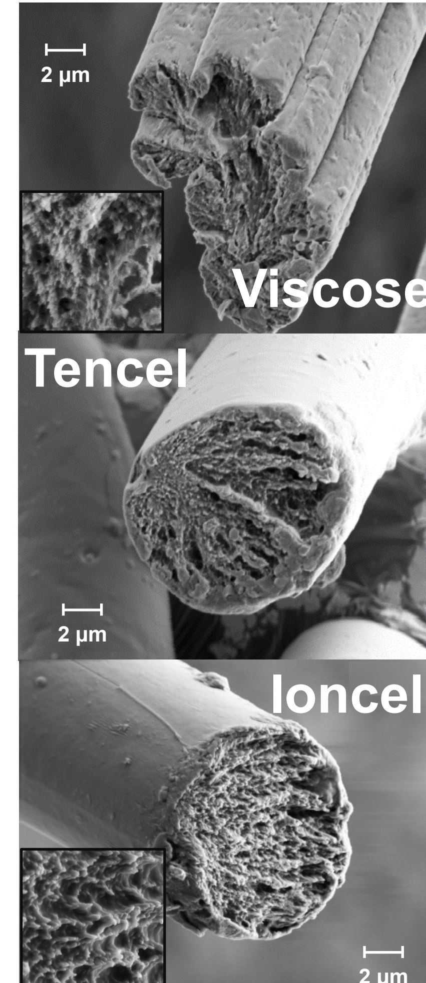
UNIVERSITY OF HELSINKI

Ilkka Kilpeläinen

Alistair King

Ioncell®





Michud *et al. Textile Res. J.* **2016,** 86, 543-552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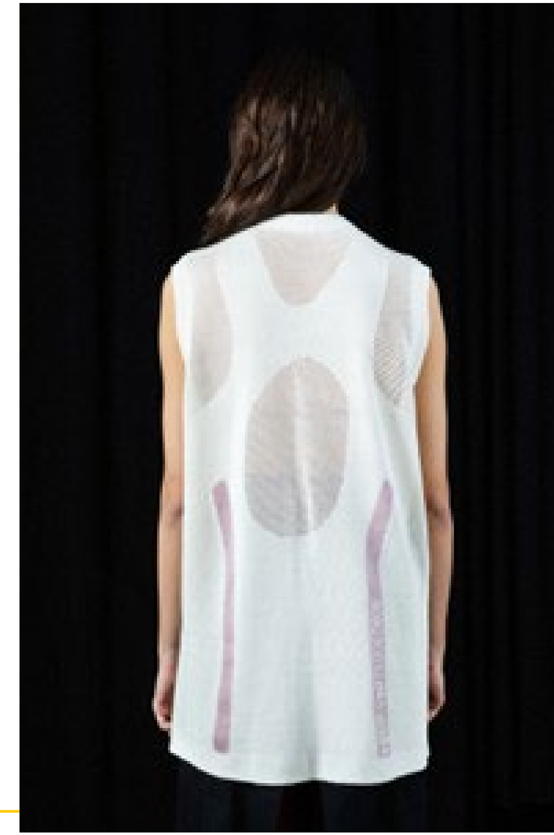
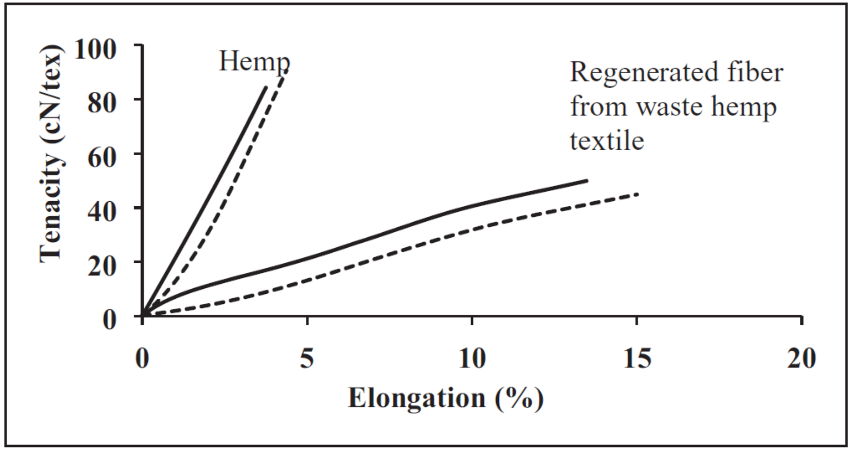
School of Chemical
Technology

Ioncell® - Recycling of cotton

	waste cotton		stand. Ioncell	
Linear density [dtex]	**1.3 ± 0.1**		1.3 ± 0.1	
	cond.	**wet**	**cond.**	**wet**
tenacity [cN/tex]	**60 ± 3**	**54 ± 4**	**54 ± 2**	**49 ± 3**
elongation [%]	**11 ± 1**	**13 ± 1**	**12 ± 1**	**13 ± 1**



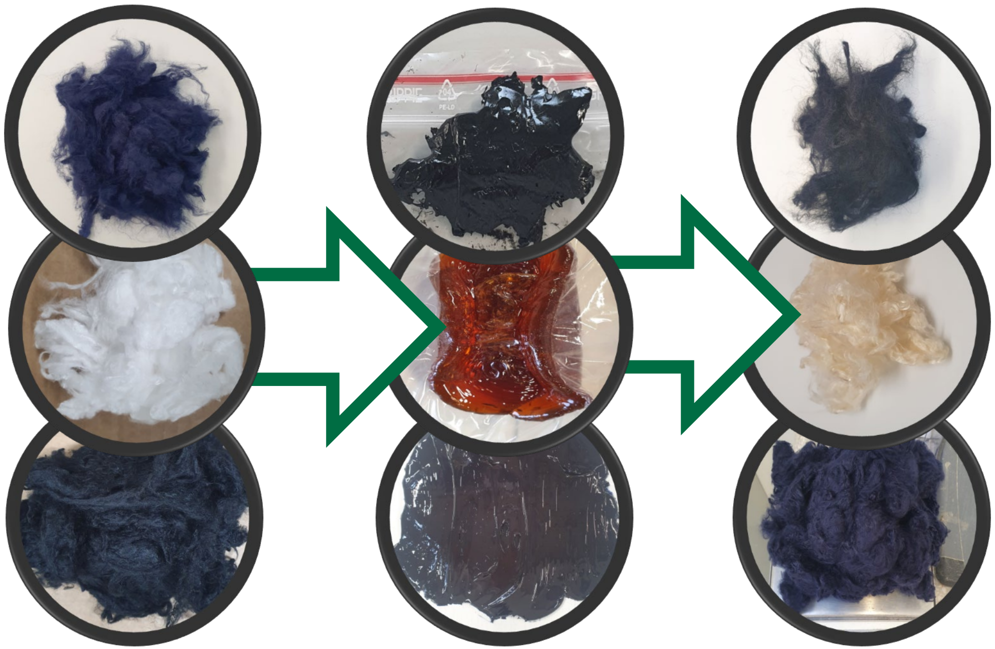
Ioncell® - Recycling of hemp

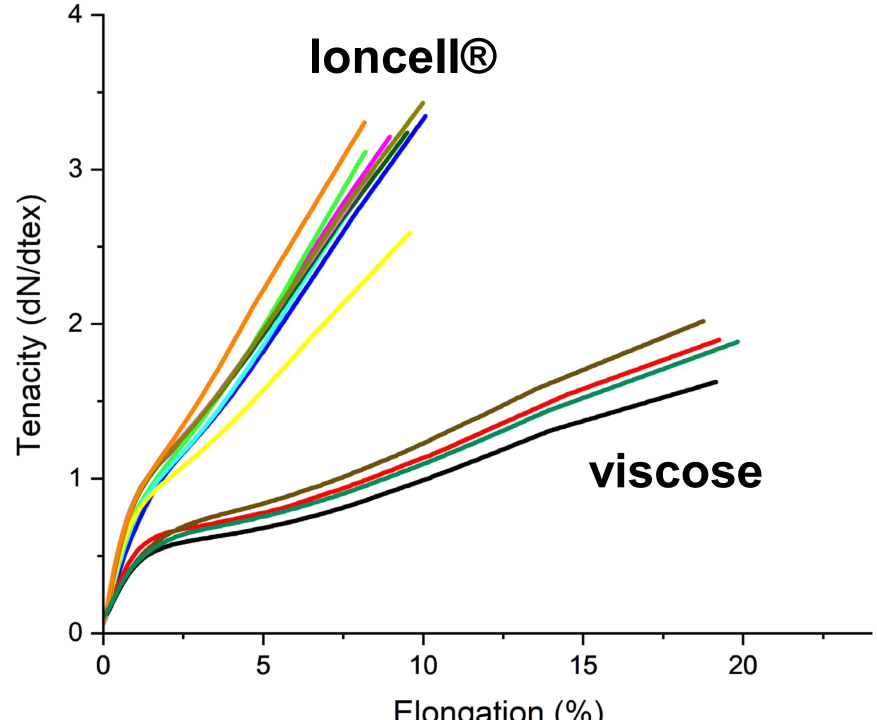


	hemp fiber		recycled via Ioncell	
Linear density [dtex]	3.5 ± 0.9		1.3 ± 0.2	
	cond.	wet	cond.	wet
tenacity [cN/tex]	84.3 ± 18.8	90.6 ± 21.3	49.9 ± 3.9	45.0 ± 4.1
elongation [%]	3.7 ± 0.8	4.4 ± 0.8	13.5 ± 1.9	15.1 ± 1.5

Rissanen, Sixta, *et al.* Chemical recycling of hemp waste textiles via the ionic liquid based dry-jet-wet spinning technology. Textile Research Journal 2022. DOI: 10.1177/00405175221143744

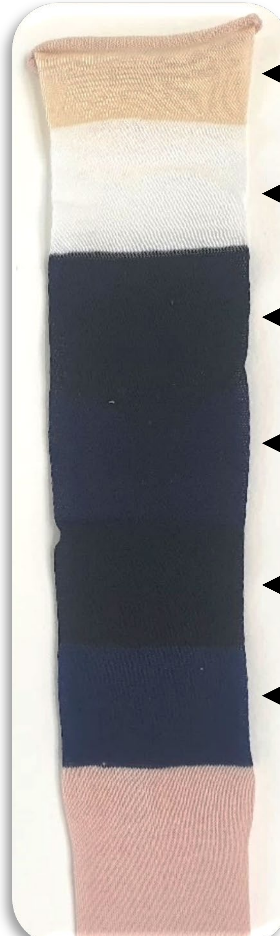
Ioncell® - Recycling of viscose





Ioncell® - Recycling of viscose

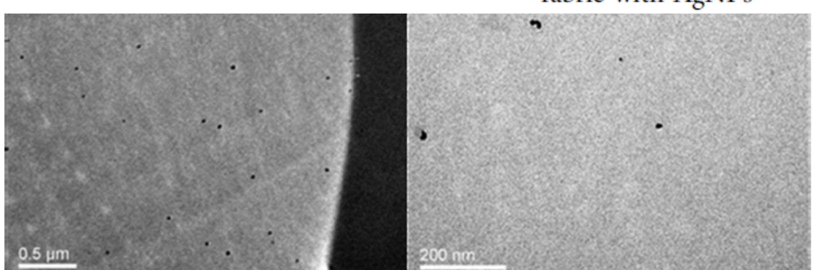
	Viscose fibres	Ioncell®
Linear density (dtex)	1.38 1.47 1.83	2.11 2.28 2.08
Tenacity (cN/dtex)	20.19 16.26 18.85	32.79 32.38 34.31
Elongation (%)	18.76 19.22 20.17	9.57 9.59 10.04



Ioncell® - Nanoparticles

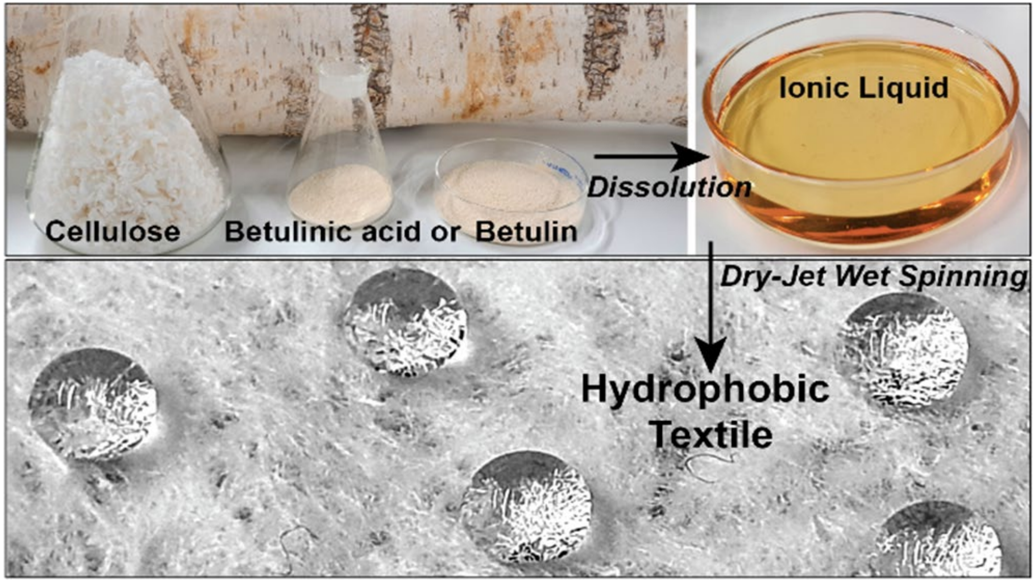
in situ reduction of $AgNO_3$ and $HAuCl_4$

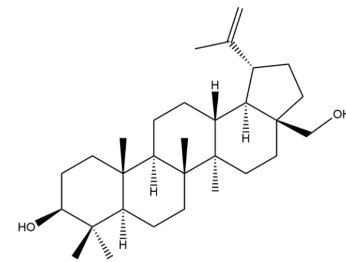
	sample	cover factor[b,c]	T(UVA)/%	T(UVB)/%	UPF
knitted fabric	uncoated fabric	3.4	25.8 ± 2.7	19.6 ± 2.6	4.9 ± 0.7
	fabric with AuNPs	3.2	22.9 ± 1.9	19.8 ± 1.9	4.9 ± 0.5
	fabric with AgAuNPs	3.3	23.2 ± 2.2	19.9 ± 2.2	4.9 ± 0.5
	fabric with AgNPs	3.3	23.3 ± 2.3	21.3 ± 1.7	4.6 ± 0.4
woven fabric[d] (24 threads/cm)	uncoated fabric	19.9	8.8 ± 0.6	3.7 ± 0.4	22.5 ± 2.1
	fabric with AuNPs	18.8	4.2 ± 1.0	2.1 ± 0.7	43.2 ± 14.6
	fabric with AgAuNPs	19.4	3.6 ± 1.1	1.8 ± 0.6	49.6 ± 12.4
	fabric with AgNPs	19.6	5.7 ± 2.7	3.5 ± 1.1	26.8 ± 8.2



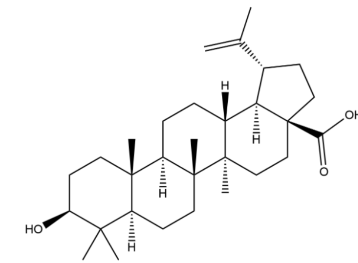
ACS Sustainable Chem. Eng. 2020, 8, 649−658

Ioncell® - hydrophobization

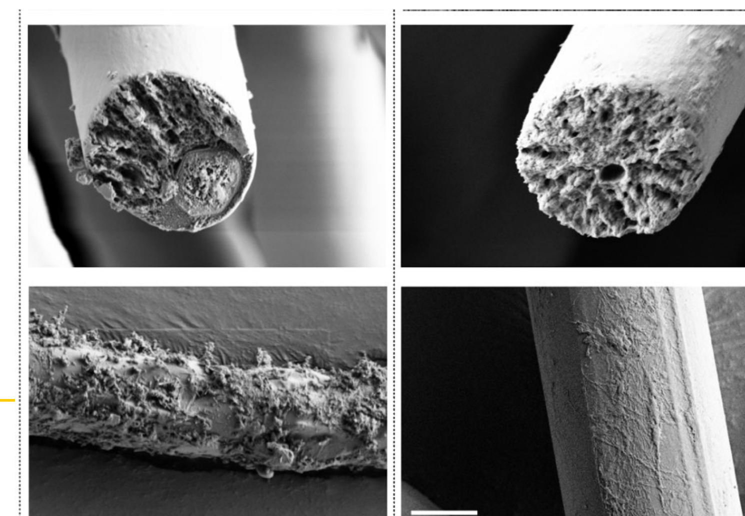




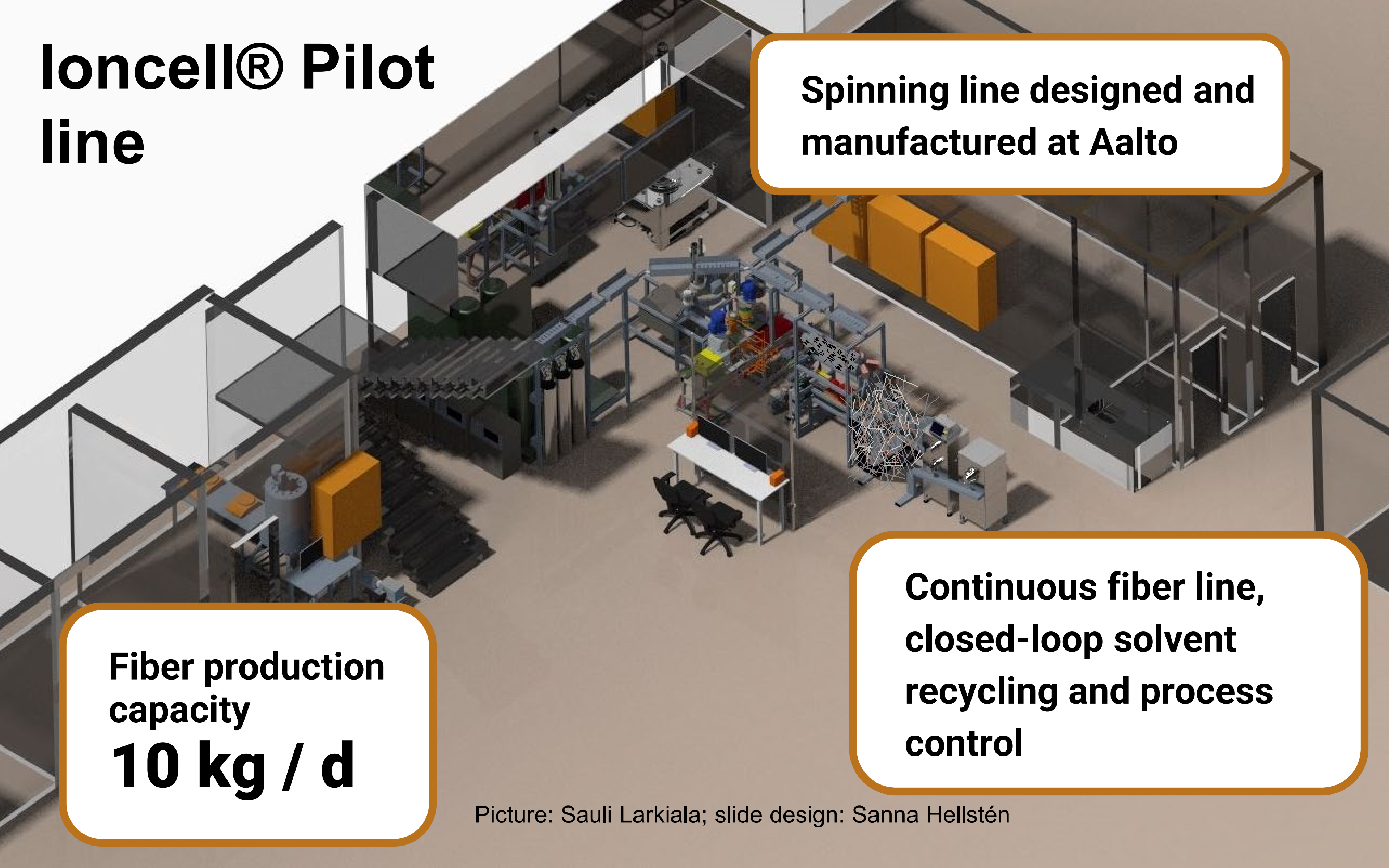
betulin



betulinic acid



Ioncell® Pilot line



Spinning line designed and manufactured at Aalto

Fiber production capacity

10 kg / d

Continuous fiber line, closed-loop solvent recycling and process control

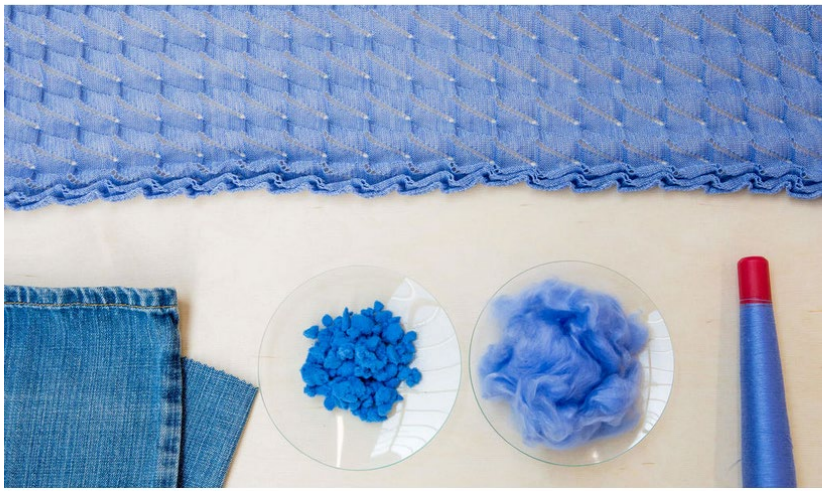
Picture: Sauli Larkiala; slide design: Sanna Hellstén

Ioncell Oy – commercilization

Aalto University becomes a founding partner in Ioncell Oy

Published: 17.5.2022

The new company will commercialise and develop ecological textile fibre technologies.



Ioncell® technology enables the production of high-quality textile fibres from wood and cellulosic textile waste in an ecologically sustainable way.
Photo: Aalto University / Mikko Raskinen.

Aalto University is one of the founding shareholders of the newly established Ioncell Oy, a company which will commercialise the Ioncell® technology developed at Aalto. The technology enables the production of high-quality textile fibres from wood and cellulosic textile waste in an ecologically sustainable way. These textiles can be used to

Antti Rönkkö

Herbert Sixta