Theory and Practice of Wet Spinning of Cellulose Solutions

Doctoral Course, Part 3

Aalto University
School of Chemical
Engineering

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March 10 – 11, 2022

Schedule

L1	Introduction, Raw material	March 10	9:00 – 9:45
L2	Raw materials. Cellulose solvent	March 10	10:00-10:45
L3	Cellulose solvents	March 10	11:00-11:45
L4	Cellulose solvents	March 10	12:00-12:45
	Break		
L5	Cellulose dissolution	March 10	14:00-14:45
L6	Rheology	March 10	15:00-15:45
L7	Cellulose dissolution/ Coagulation and Regeneration	March 10	16:00-16:45
L8	Coagulation and Regeneration	March 11	9:00 – 9:45
L9	Coagulation and Regeneration	March 11	10:00-10:45
L10	Filament breaches	March 11	11:00-11:45
L11	Types and properties of MMCFs	March 11	12:00-12:45
L12	Q&A	March 11	13:00 -

Outline

1. Introduction, history
2. Pulp as raw material
3. **Cellulose solvents**
4. **Theoretical aspects of cellulose dissolution**
5. **Rheology of cellulose solutions**
6. **Coagulation and regeneration of cellulose**
7. **Filament breaches during spinning**
8. **Types of MMCFs**
9. **Properties of MMCFs**

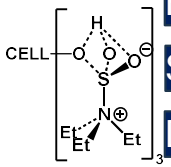
3

Cellulose solvents

- **Overview**
- Direct cellulose solvents
- Alkaline aqueous solutions with&without derivatization
- Assessment of solution state

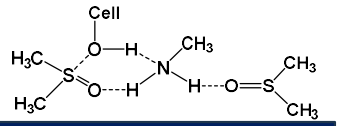
Cellulose solvents

Non-derivatizing



Hydrazine, N_2H_4 (water-free)

SO_2 / $NH(Et)_2$



DMSO / CH_3NH_2

NMMO, N-methyl-morpholin-N-oxide

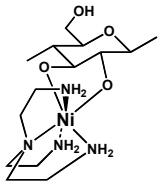
Ionic liquids

DMAc / LiCl

KSCN-DMSO

NaOH / $Zn(OH)_4^{2-}$

Cuam $[Cu(NH_3)_4](OH)_2$*3 H_2O



Cuen $[Cu(H_2N\text{-}(CH_2)_2\text{-}NH_2)_2](OH)_2$

Nitren $[Ni(N(NH_2CH_2CH_3)_3)](OH)_2$

FeTNa, EWWN (Fe(III):Tartaric acid:NaOH (1:3:6))

Derivatizing

$H_3PO_4(> 85\%) + H_2O \rightarrow Cell - O - PO_3H_2$

$HCOOH + ZnCl_2 \rightarrow Cell - O - C(O)H$

$CF_3COOH + CF_3(CO)_2O \rightarrow Cell - O - CCF_3$

$N_2O_4 \xrightarrow{DMF} Cell - O - N = O$

$Me_3SiCl \xrightarrow{Pyridin} Cell - O - SiMe_3$

$HNO_3 \xrightarrow{H_2SO_4} Cell - O - NO_2$

$SO_3 \xrightarrow{ClSO_3} Cell - O - SO_3H$

$\boldsymbol{CS_2 \xrightarrow{NaOH} Cell - O - CSS^-Na^+}$

$\boldsymbol{CO_2(NH_2)_2 \xrightarrow{NaOH} Cell - O - C(O)NH_2}$

$Ac_2O + HOAc \xrightarrow{H^+} Cell - O - C(O)CH_3$

$Me - X \xrightarrow{NaOH} Cell - O - CH_3$

$ClCH_2COO^-Na^+ \xrightarrow{NaOH} Cell - O - CH_2COONa$

$(CH_2)_2O \xrightarrow{NaOH} Cell - O - CH_2CH_2OH$

3

Cellulose solvents

- Overview
- **Direct cellulose solvents**
- Alkaline aqueous solutions with&without derivatization
- Assessment of solution state

Direct Cellulose Solvents

NMMO Monohydrate

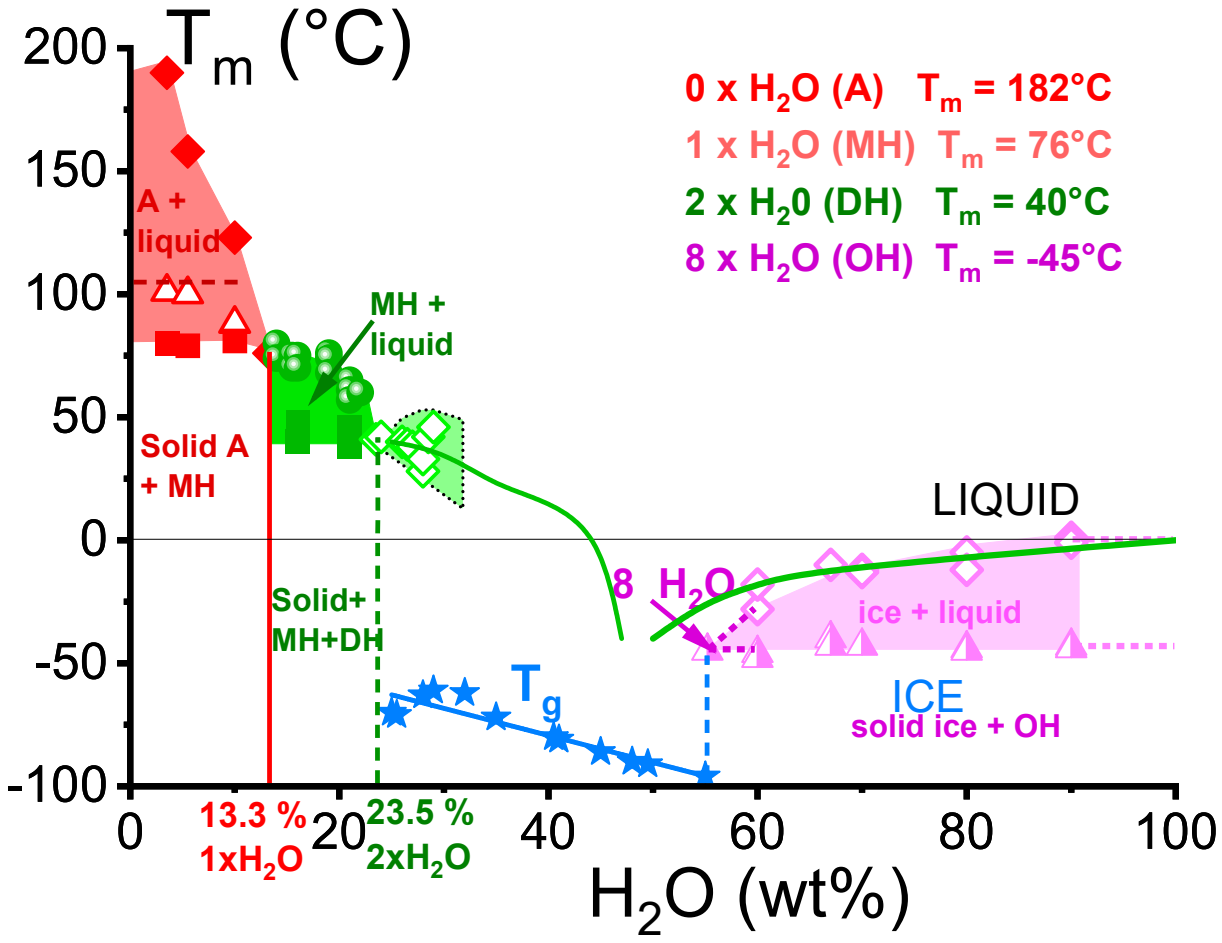
Ionic Liquids

NMMO and NMMO hydrates

Parameter	**NMMO**	**NMMO*$H_2$0**	**NMMO*2.5 H_2O**
Formula	$C_5H_{11}NO_2$	$C_5H_{13}NO_3$	$C_{10}H_{32}N_2O_9$
M (g/mol)	117,1	135,2	324,4
Density (g/cm^3)	1,25	1,28	1,33
Mp (°C)	184	77	39
Crystal form	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$

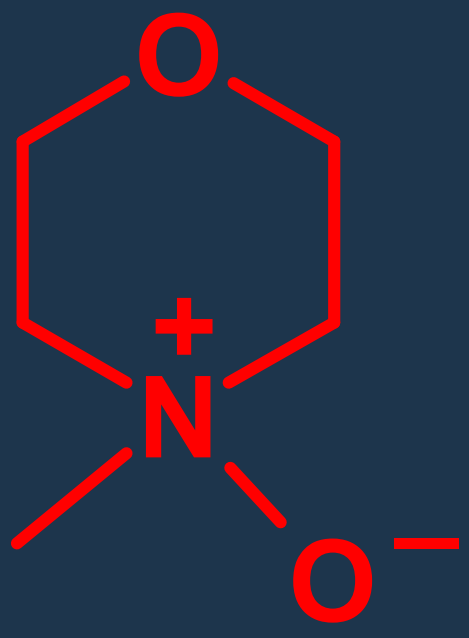
T. Rosenau et al.: *Progr. Polym. Sci.* **2001**, *26 (9),* 1763-1837.

Phase diagram NMMO and water



O. Biganska, P. Navard. *Polymer* 44(**2003**) 1035-1039

Chemistry of NMMO

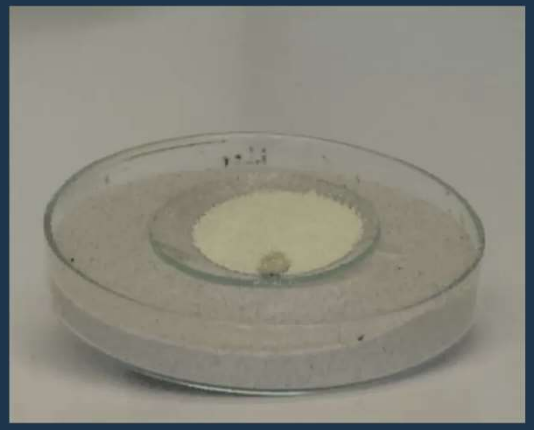


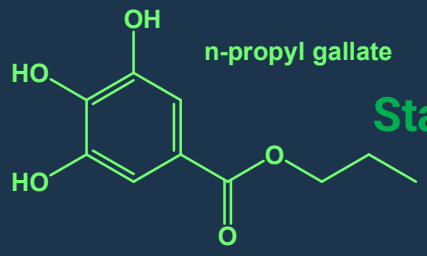
- Highly polar N-O group
- High hydrophilicity, hygroscopicity
- Strong oxidant: primary alkyl, benzyl to the corresponding aldehydes
- N-O bond able to form one or two H-bonds with water or cellulose
- NMMO dissolves cellulose up to a content of 17% water (w/w), corresponding to a 1.2 hydrate.
- The lower limit of water content is 4% as the dissolution temperature comes close to the decomposition point of NMMO

T. Rosenau et al.: *Progr. Polym. Sci.* **2001**, *26 (9)*, 1763-1837.

LYOCELL

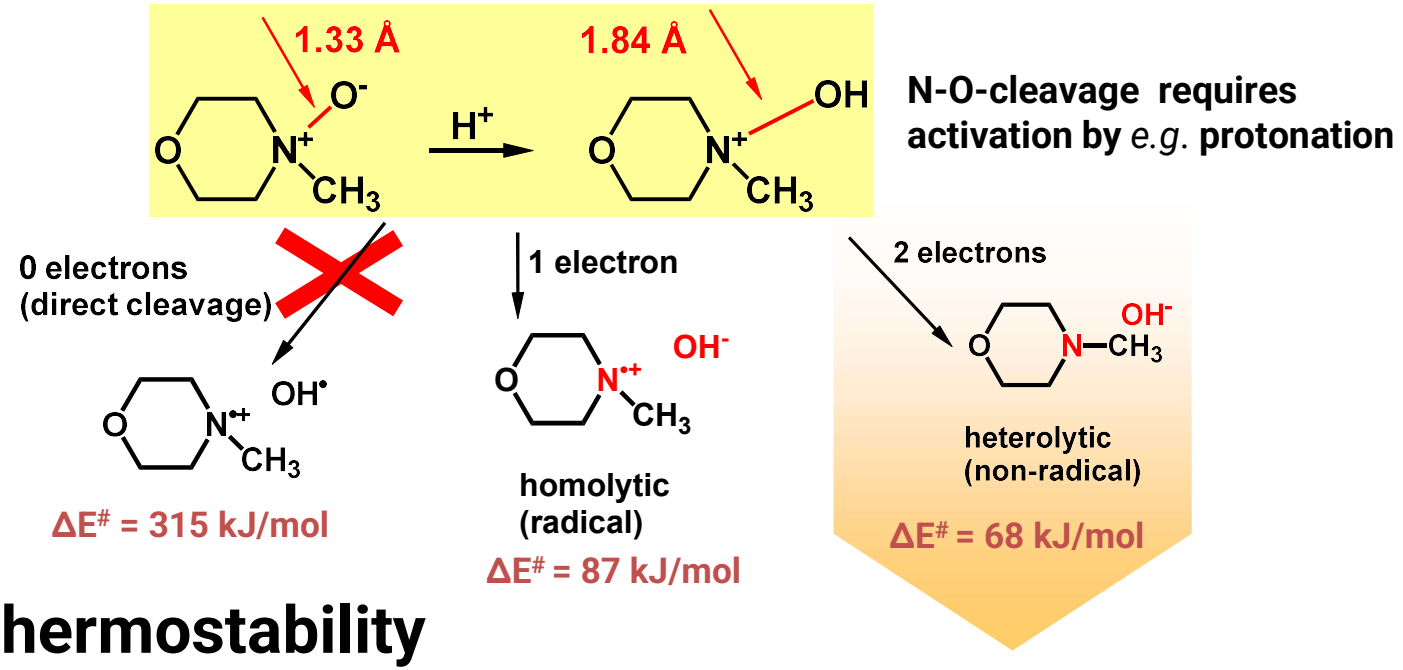
- **NMMO Chemistry**





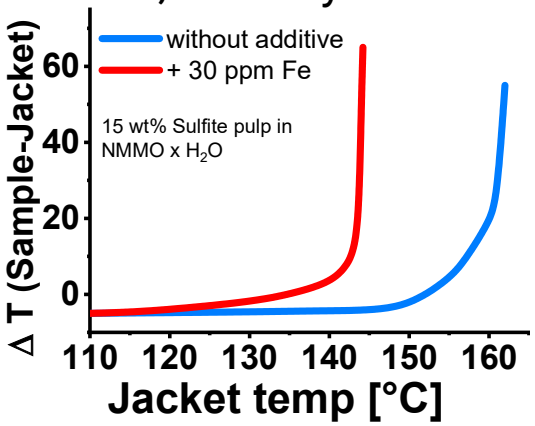
T. Rosenau et al.: *Progr. Polym. Sci.* **2001**, *26 (9)*, 1763-1837.
T. Rosenau et al.: *Cellulose*, **2002**, *9*, 283.

Degradation pathways of NMMO



Thermostability

Sikarex, security calorimeter



Fe and **Cu** ions decreases temperature at which **runaway reactions** start.

Storage of dope at high temperature initiates NMMO decomposition.

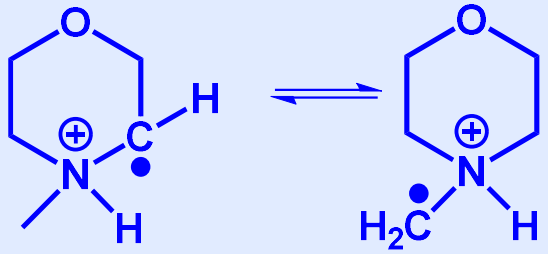
Thermal stabilization of the dope requires:

- Pulp with Low REG content and
- Dope by GPE addition.

H. Firgo, M. Eibl, W. Kalt, G. Meister, Lenz. Ber. 74 (1994) 81-89

Homolytic reactions

- **Activation by protonation or complexation with metal ions**
- **Cleavage via primary Aminyl radical**



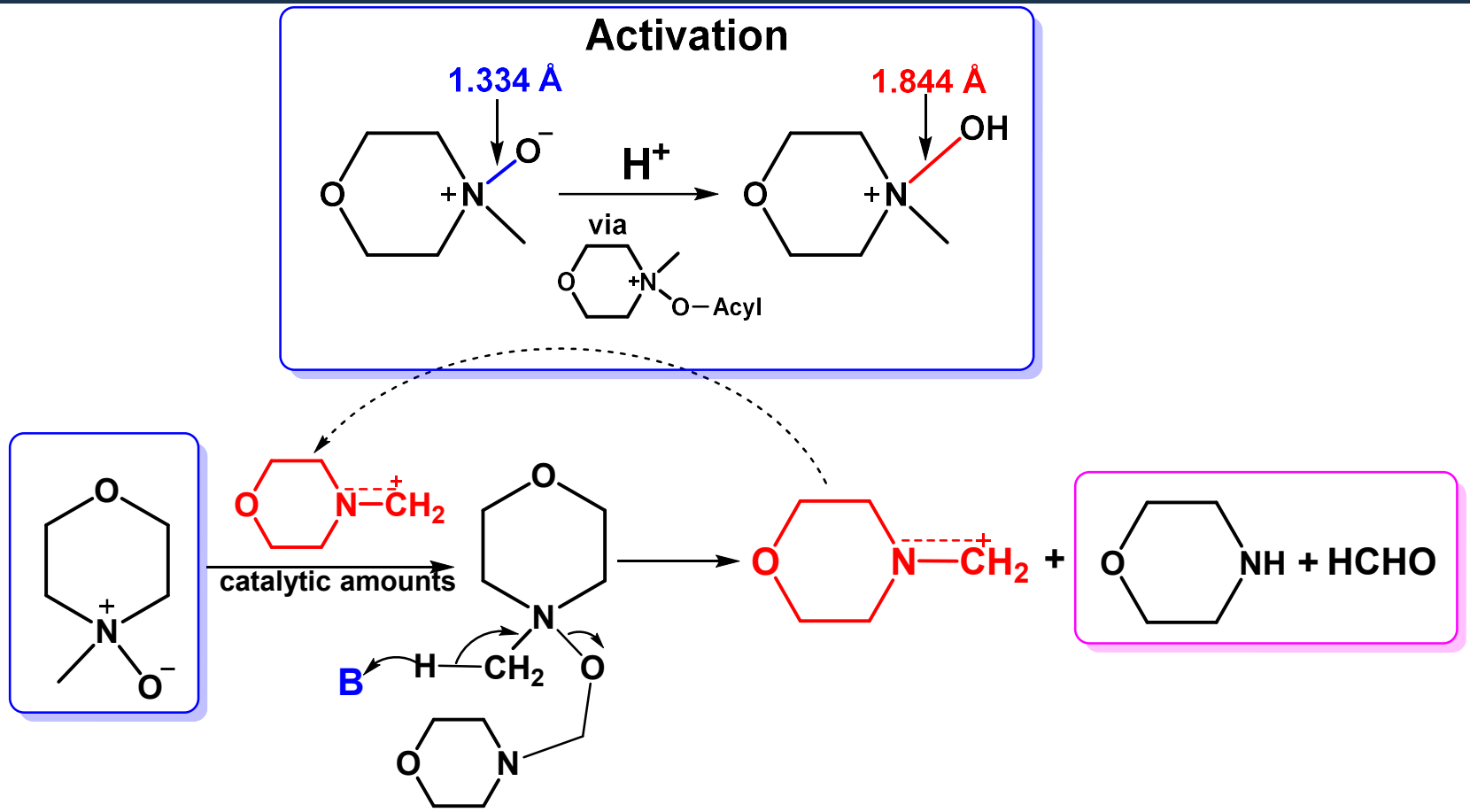
- **Reactions to NMM, M and HCHO**
- **Transition metal ions, Cu, Fe ..., catalyse the decomposition of NMMO**
- **Aminyl radical can oxidize cellulose to 2-keto structures**
- **Presence of O_2 leads to peroxyl radicals which might affect carbohydrates**

T. Rosenau et al.: *Progr. Polym. Sci.* **2001**, *26 (9)*, 1763-1837.

Heterolytic reactions

- **Activation by protonation or O-alkylation**
- **Heterolytic deoxygenation of NMMO to NMM: reducing end groups are oxidized to carboxylic acids.**
- **Polonovski type of reactions: intramolecular redox processes cause degradation of NMMO to M and HCHO.**
- **N-(methylene)morpholinium ions (Mannich intermediates) decompose NMMO into M and HCHO in a heterolytic, autocatalytic process.**
- **Autocatalytic decomposition is highly exothermic, quickly becomes explosion-like –> thermal runaway reactions**

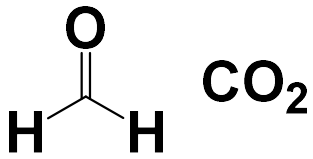
Heterolytic cleavage of N-O



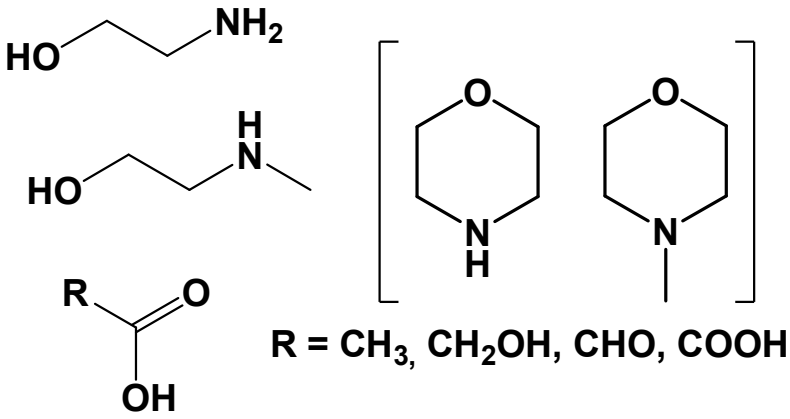
T. Rosenau et al.: *Progr. Polym. Sci.* **2001**, *26 (9)*, 1763-1837.

Thermal decomposition products

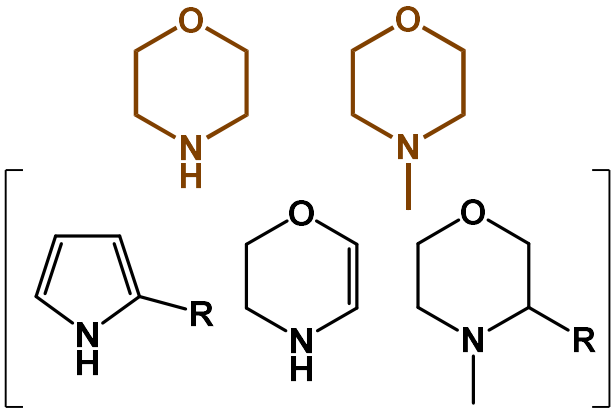
Gas phase



Liquid "aqueous" phase



Viscous, brown "organic phase"



+ highly condensed products

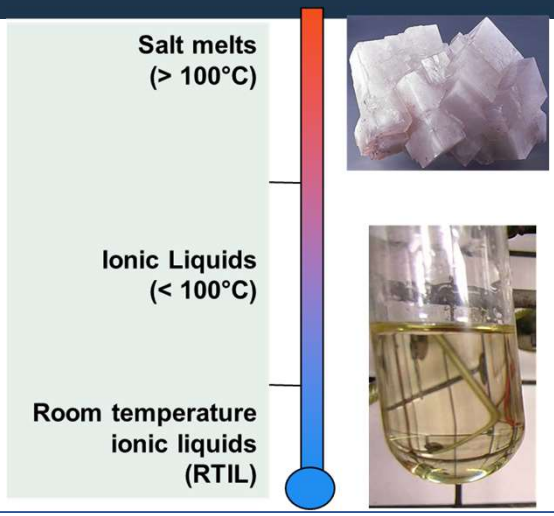
Solid residue:
Carbon,
Highly condensed
(aromatic) structures

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

Direct Cellulose Solvents

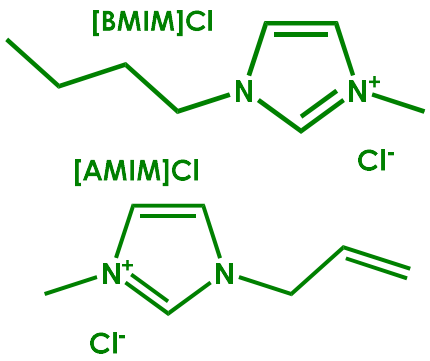
NMMO Monohydrate

Ionic Liquids



First generation IL: Imidazolium-based halides

Ionic liquids tested

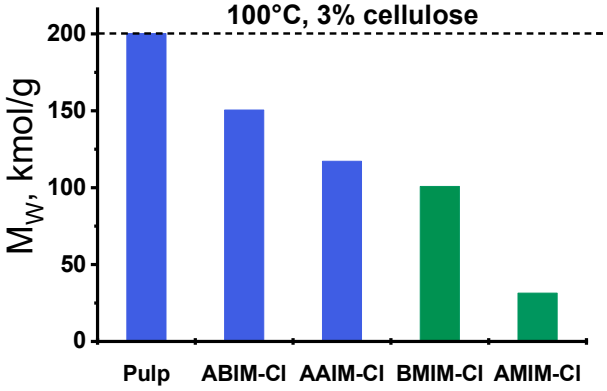


Good solvents, spinning after dope stabilization possible

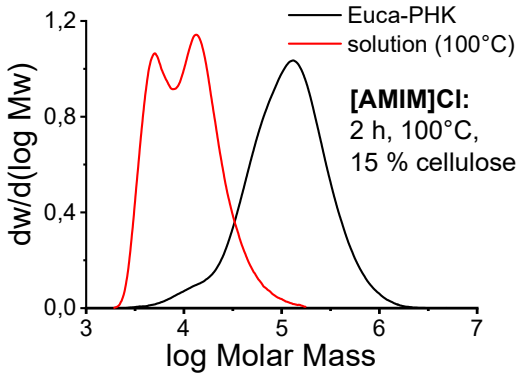
[AAIM]Cl
[ABIM]Cl

Can dissolve cellulose, but problems in spinning

Chlorides can be replaced by dimethylphosphates (DMP). Dissolution successfully tested, no spinning experiments.



Partial DP stabilization by exchange of anion (Cl^- by DMP^-) or trapping the released acid by addition of methyl imidazole or partially by addition of GPE



Lenz. Ber. *(2005), 84, 71-85.*
Lenz. Ber. *(2006), 86, 154-161*

Spinning:

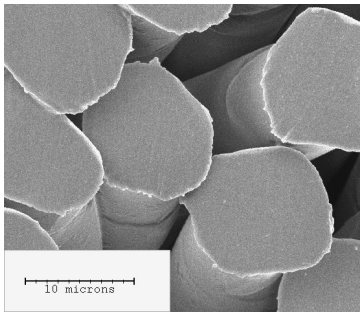
Pulp: *E. urograndis* PHK; 11 wt% cellulose in dope, **GPE+NaOH** as stabilizer; dissolution at 100°C, 30 mbar in vertical kneader; dry-jet wet monofilament spinning at 100°C

Solvent	Titre	Ten-cond	Elong-cond	Ten-wet	Elong wet
	dtex	cN/tex	%	cN/tex	%
[BMIM]Cl	2.1	45.0	7.5	32.8	8.1
[AMIM]Cl	2.2	41.6	12.2	33.4	17.6
NMMO Tencel™	1.3	37.0	15.0	31.0	17.0

Conclusions: No alternative to NMMO

PROS:
- Non-volatile solvent
- No exothermic events

CONS:
- Nearly water-free
- Highly corrosive
- Severe cellulose degradation
- Potentially toxic

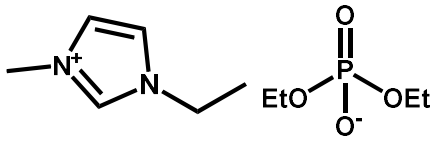


Screening of Halide-free Ionic liquids

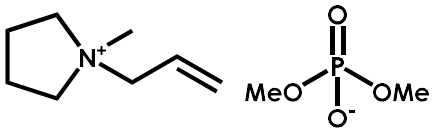
Excellent Cellulose Solvent

[Emim][OAc], [Bmim][OAc]

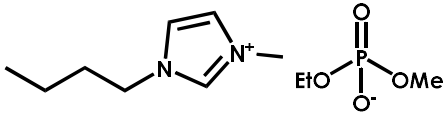
Good Cellulose Solvent



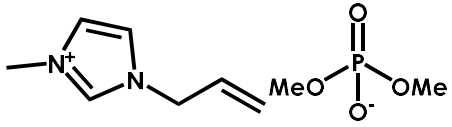
1-ethyl-3-methyl imidazolium diethylphosphate



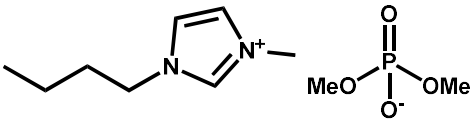
1-allyl-1-methyl-pyrrolidinium di-methyl phosphate



1-butyl-3-methyl-imidazolium ethyl methyl phosphate

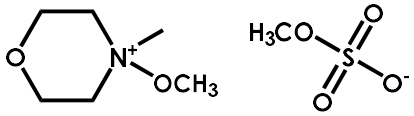


1-allyl-3-methyl-imidazolium dimethyl phosphate

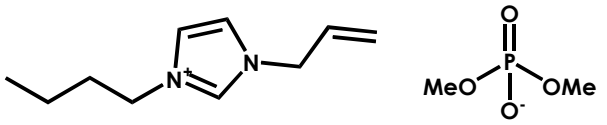


1-butyl-3-methyl-imidazolium dimethylphosphate

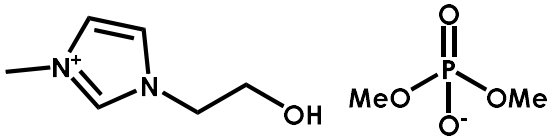
Poor Cellulose Solvent



N-methoxy-N-methylmorpholinium methyl sulfate

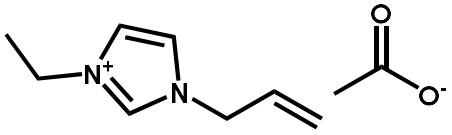


1-allyl-3-butylimidazolium dimethylphosphate

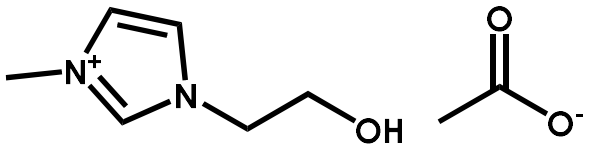


1-(2-hydroxyethyl)-3-methyl-imidazolium dimethyl phosphate

No Cellulose Solvent



1-allyl-3-ethyl imidazolium acetate



1-(2-hydroxyethyl)-3-methylimidazolium acetate

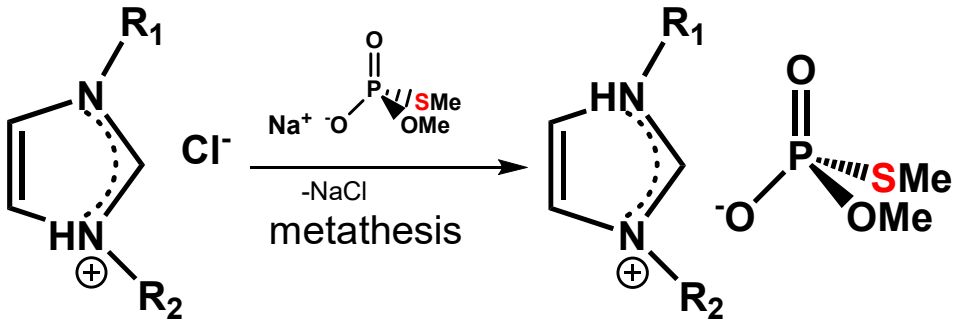
ACS Symposium Series, 2010. **1033**(Cellulose Solvents): p. 229-259.

Screening of ionic liquids with asymmetric phosphate-derived anions

Aim: Stable ILs, with reduced viscosity and melting point:

Proposal: Reduced symmetry of the ions leads to lower melting points and viscosities of the IL

Dimethyl phosphorothioate as asymmetric anion



Acceptable cellulose solubility & stability

R1: Pr, Bn

R2: Me

Certain solubility but severe cellulose degradation

R1: All, Bu, Bn, (HOEt)

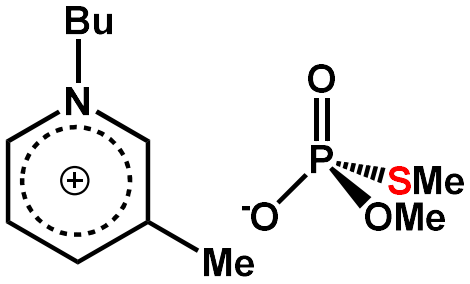
R2: Me

No cellulose dissolution

R1: All

R2: Bu

Acceptable cellulose solubility & stability



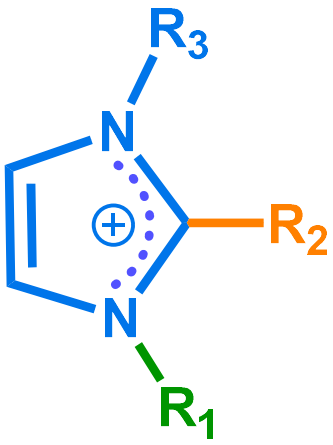
Result:

Objective only partially achieved; no clear trend showing a reduced viscosity related to the asymmetry of the anions; partly strong cellulose degradation.

Green Chem. 13(9), 2507-2517. DOI: 10.1039/C1GC15407A

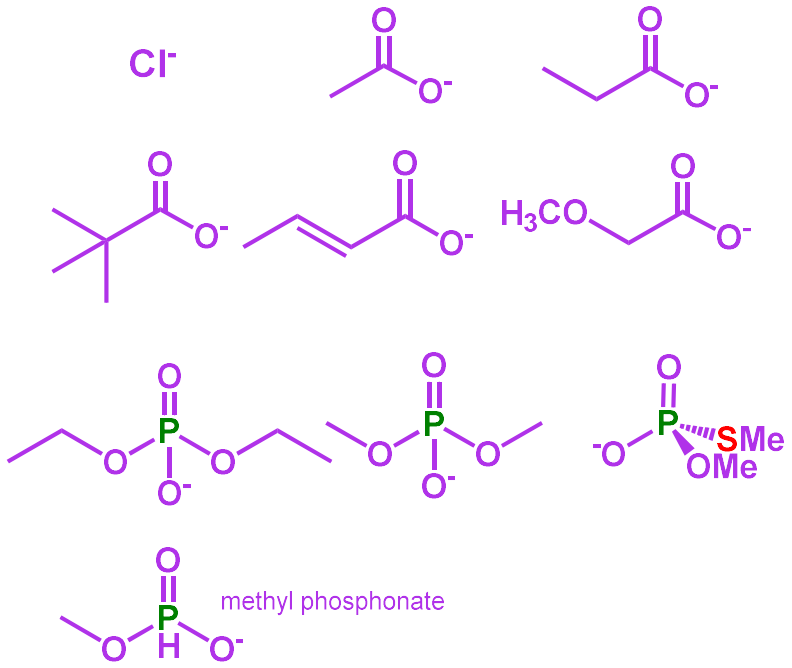
Overview on Imidazolium-based Ionic liquids tested

CATIONS



R_1	R_2	R_3
methyl	H	methyl
Ethyl		ethyl
Propyl		allyl
Allyl		H
Butyl		methyl

ANIONS



[Emim][OAc] shows excellent cellulose solubility, low viscosity and good thermal properties

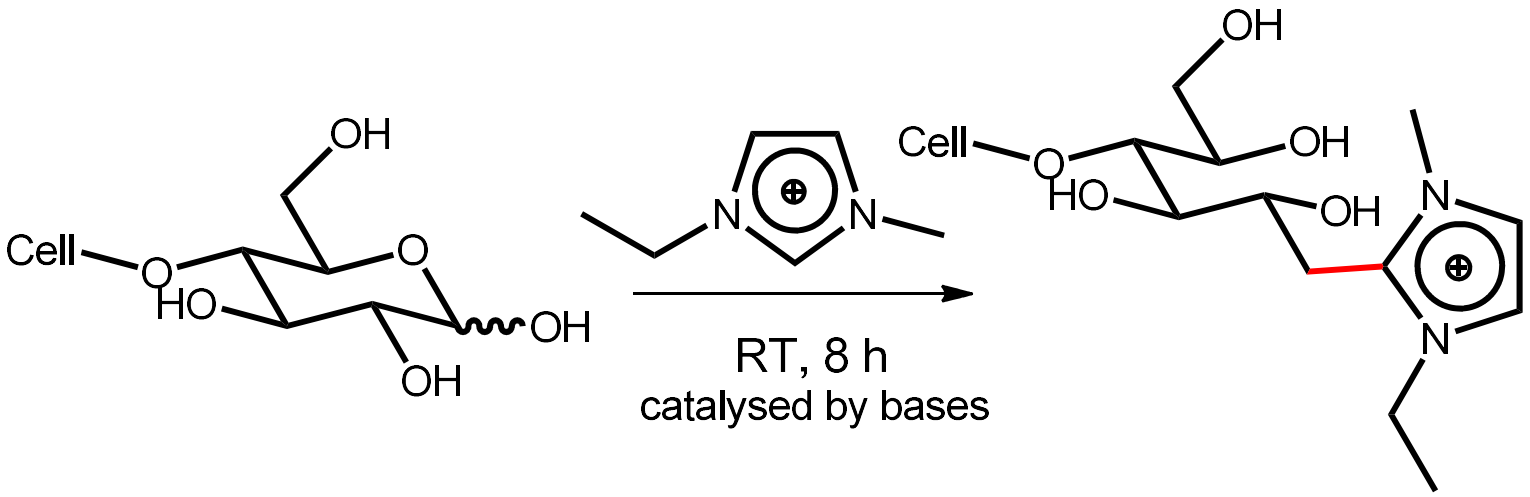
Lenz. Ber (2005), 84:71-85

Lenz. Ber (2006), 86:154-161

Chemistry Letters (2012), 41(9), 945-946.
Green Chem (2011), 13:2507

Polymers **2019**, *11*, 845

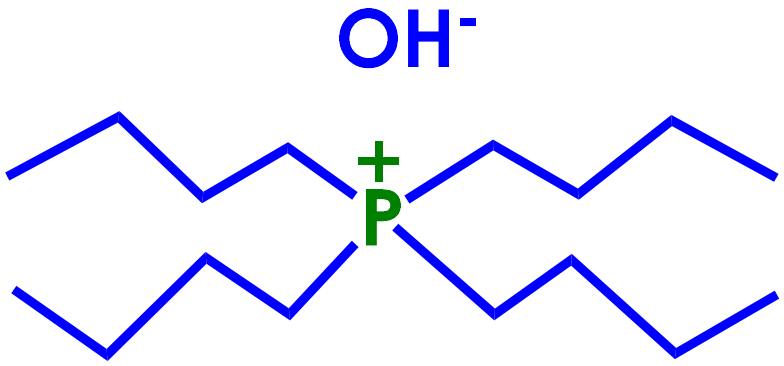
Chemical reactivity of imidazolium-based ILs



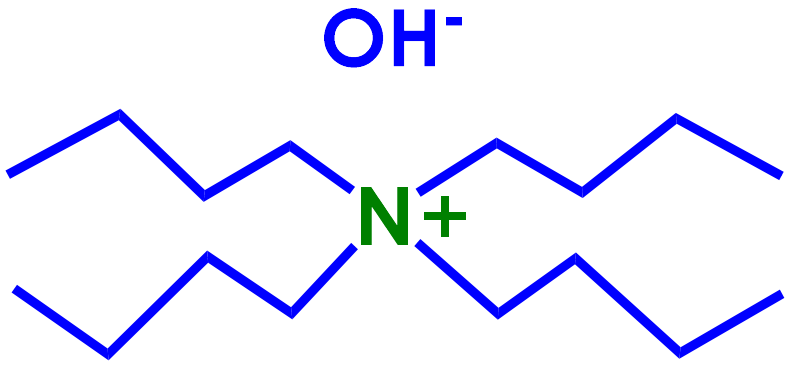
- Formation of carboxylic acids, HCOOH, as a result of pulp degradation
- Accumulation of inorganic salts from the pulp in the IL
- Limited thermal stability (~ 0.01%/h at 100 - 110°C)

Ebner, G. et al. *Tetrahedron Letters* (2008), 49(51), 7322)

Aqueous Onium Electrolytes

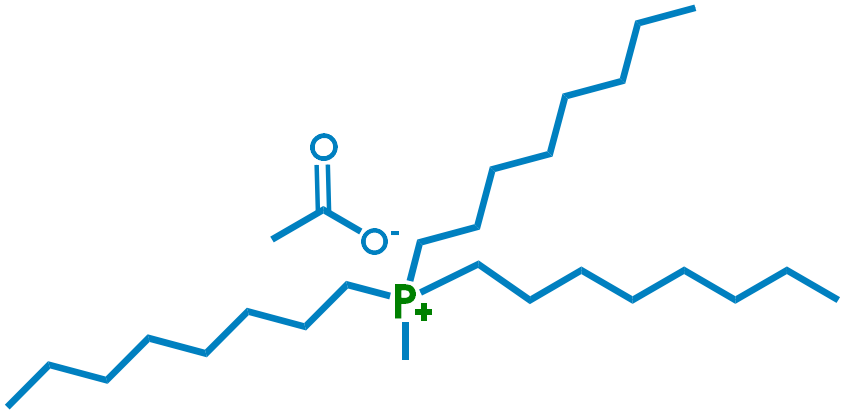


BioResources (2017), 12, 4515
Green Chem (2015), 17, 4432



Cellulose (**2017**), 24, 49-59
ACS Sustainable Chem Eng (**2018**), 6, 2898-2904

Phase-separable ILs



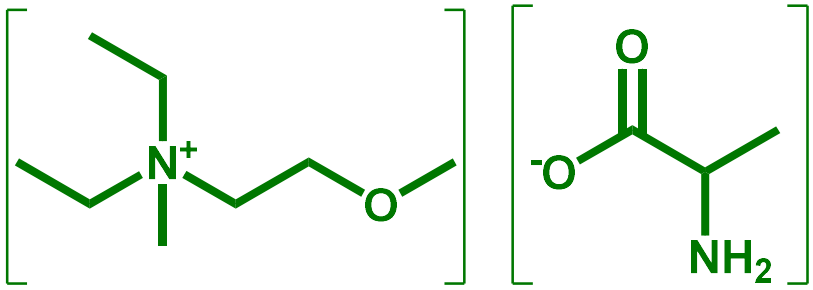
$[P_{8881}][OAc]$ + DMSO

RSC Adv., (**2017**), 7, 17451

60:40 w/w mixture of IL and DMSO dissolved up to 8% cellulose:

60 wt% of the IL recovered via phase separation with a further of 37 wt% after EtOH washing.

Amino Acid Ionic Liquid



$[N_{221ME}][Ala]$

N,*N*,-diethyl-*N*-(2-methoxyethyl)-*N*-methyl-ammonium alanine

Dissolution of cellulose (MCC)

at 100°C, 10 min:

$[N_{221ME}][Ala]$, KT-β = 1.041	12 wt%
$[N_{221ME}][Lys]$,	11 wt%
$[N_{221ME}][OAc]$,	7 wt%

$[N_{221ME}][Ala]$: DMSO = 1:1 (w/w),

χ_{IL} = 0.25 dissolves 22 wt% cellulose at RT

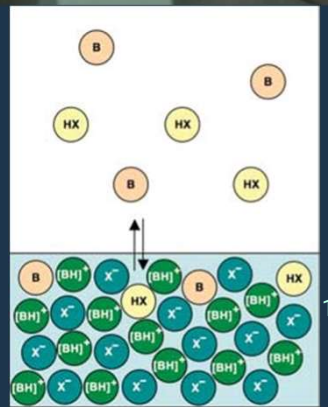
Amino group essential to realize high cellulose dissolution-> amino group may interact with certain parts of cellulose.

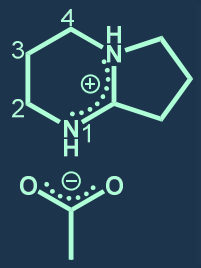
Chem. Lett. 2012, 41, 987-989; *ChemSusChem 2012, 5, 388-391*

PROTIC IONIC LIQUIDS (PILS)

Superbase-based ionic liquids, new generation IL: joint findings of HU and AALTO

$$[DBUH]^+[CO_2Et]^- \leftrightarrows DBU_{(l)} + HCO_2Et_{(l)} \rightleftarrows DBU_{(g)} + HCO_2Et_{(g)}$$





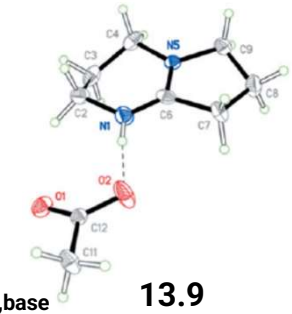
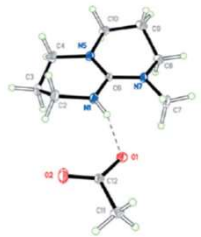
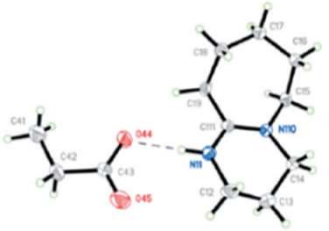
1,5-diazabicyclo[4.3.0]non-5-enium acetate

Nature (2006), 439, 831

Bronsted Acidic Ionic Liquids (BAILs)

- **BAILs with H⁺ on Cation**
- BAILs with H⁺ on anion
- BAILs with H⁺ on cation and anion
- BAILs with acidic functions
- BAILs with acidic functions and H⁺ on anion/cation

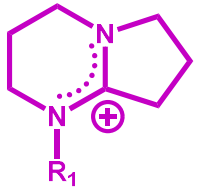
Stoichiometric reactions between Brönsted acids and bases. Stable salts require a complete transfer of the proton from the acid to the base is key! Aqueous pK$_a$ values of precursor acids and bases are regarded as predictive: $\Delta pK_a = pK_{a,base} - pK_{a,acid} > 8 - 10$

	1,5-diazabicyclo[4.3.0] non-5-ene (DBN)	7-methyl-1,5,7-triazabicyclo [4.4.0] dec-5-ene (mTBD)	1,8-diazabicyclo[5.4.0] undec-7-ene (DBU)
			
pk$_{a,base}$	13.9	15.3	14.2
Δpk$_a$	9.1	10.5	9.4

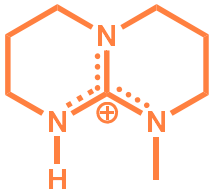
Angew. Chem. Int. Ed. **2011**, *50*, 6301-6305
Ananda S. Amarasekara. *Chem. Rev.* **2016**, 116, 6133−6183

Org.Process.Res.Dev. **2019**, *23*, 1860-1871
Croatica Chemica Acta **2014**, *87* (4), 385-395
Parviainen, A. et al. ChemSusChem **2013**, *6*, 2161-2169

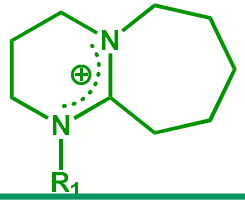
Acid Superbase Conjugates



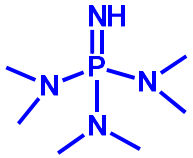
1,5-diazabicyclo[4.3.0] non-5-ene (**DBN**) SOLVENT-1



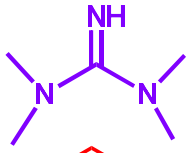
7-methyl-1,5,7-triazabicyclo [4.4.0] dec-5-ene (**mTBD**) SOLVENT-2



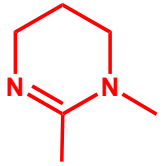
1,8-diazabicyclo[5.4.0] undec-7-ene (**DBU**) SOLVENT-3



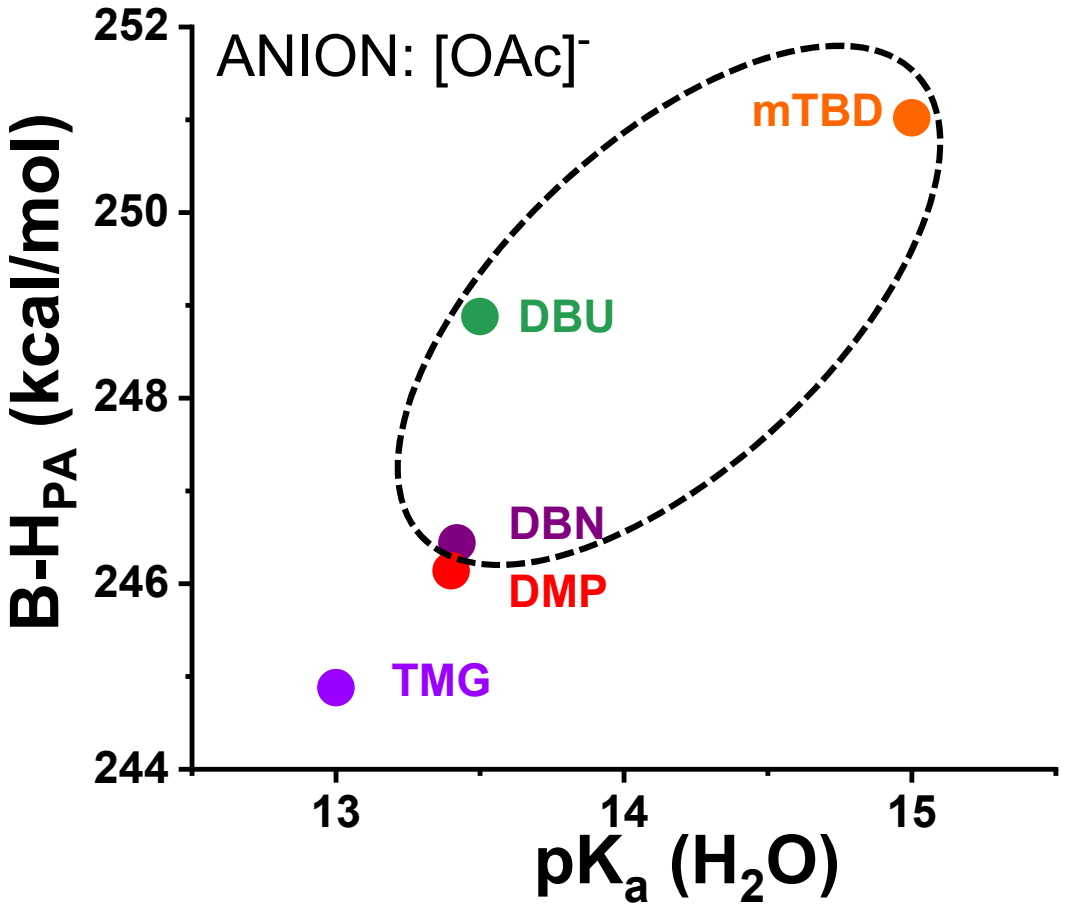
N,N,N,N,NN,-hexamethyl-phosphorimide triamide (**HMPI**)



N,N,N,N,-tetramethyl guanidinium (**TMG**)



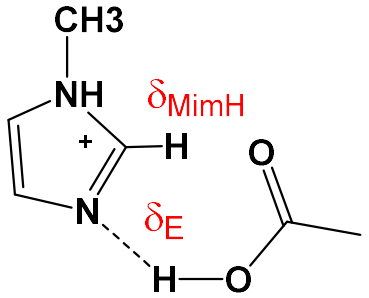
1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (**DMP**)



Croat. Chem. Acta 2014, 87, 385–395

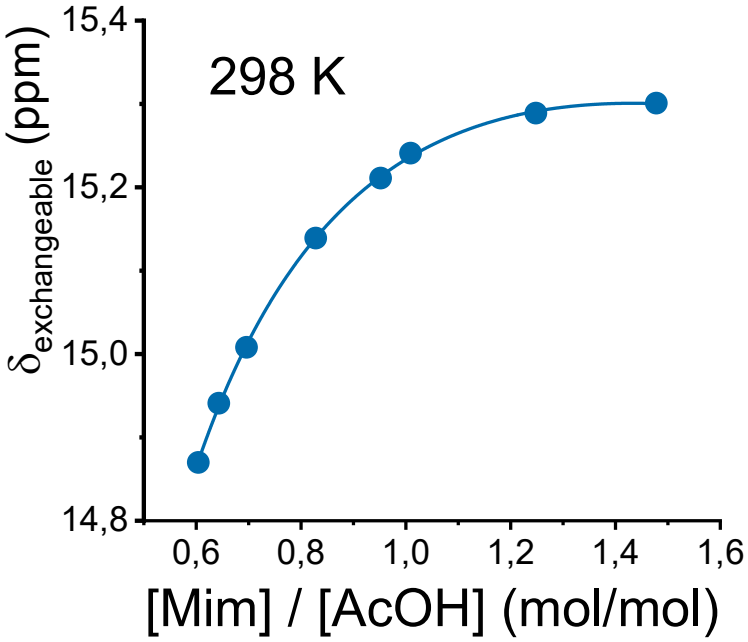
*Parviainen, A. et al. ChemSusChem **2013**, 6, 2161-2169*

Degree of Proton Transfer in BAILs



E = exchangeable proton

[MimH][OAc]



$$\boldsymbol{Mim} + \boldsymbol{AcOH} \rightleftharpoons [\boldsymbol{MimH}][\boldsymbol{OAc}]$$

$\boldsymbol{I}$	$\boldsymbol{x_{Mim}}$	$\boldsymbol{x_{AcOH}}$	$\boldsymbol{0}$
$\boldsymbol{E}$	$\boldsymbol{x_{Mim} - x_{[MimH]}}$	$\boldsymbol{x_{AcOH} - x_{[MimH]}}$	$\boldsymbol{x_{[MimH]}}$

Chemical shift in ^{1}H-NMR: $\boldsymbol{\delta = \delta_{AcOH} \cdot \left(x_{AcOH} - x_{[MimH]}\right) + \delta_{[MimH]} \cdot x_{[MimH]}}$

$$\boldsymbol{K_{eq} = \frac{x_{[MimH]}^2}{\left(x_{Mim} - x_{[MimH]}\right)\left(x_{AcOH} - x_{[MimH]}\right)}}$$

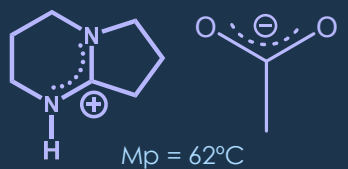
$$\boldsymbol{Proton\ transfer, \% = \frac{\sqrt{K_{eq}}}{\sqrt{K_{eq}} + 1}}$$

$$\boldsymbol{Ionicity = \frac{\sqrt{165}}{\sqrt{165} + 1} = 93\%}$$

J. Phys. Chem. B **2018**, 122, 309−315

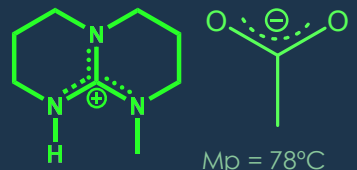
Green solvents

Ionic Liquids, liquid at <100°C



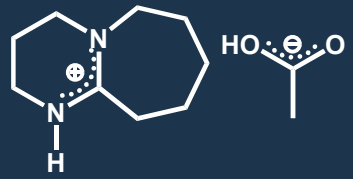
Mp = 62°C

1,5-diaza-bicyclo[4.3.0]non-5-enium acetate

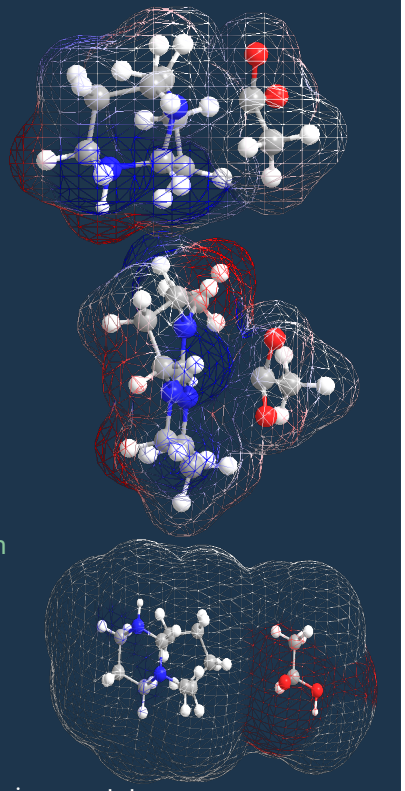


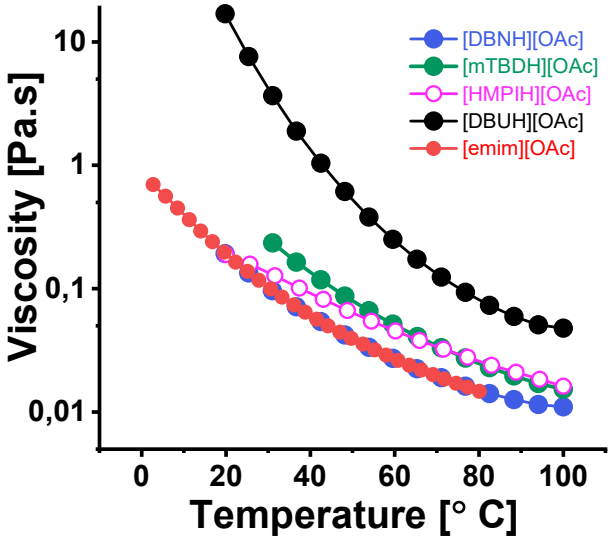
Mp = 78°C

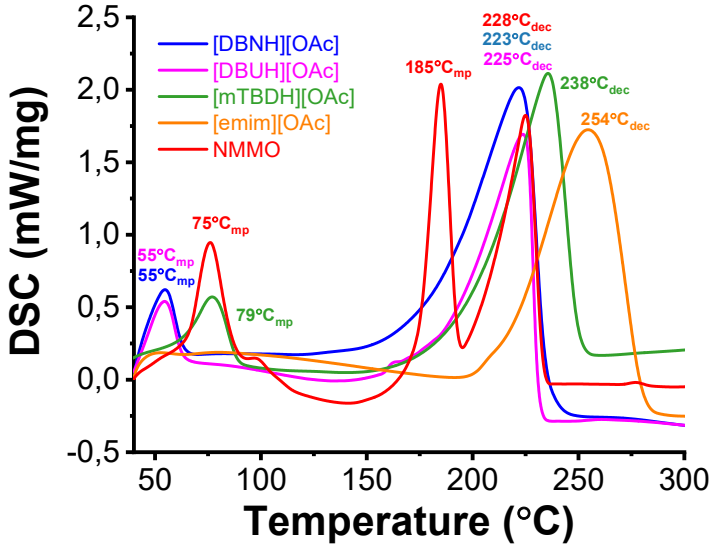
7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-enium acetate



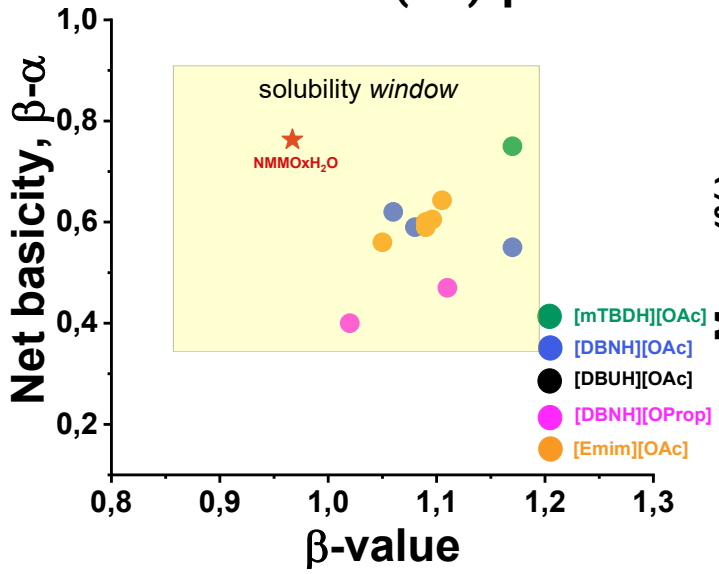
1,8-Diazabicyclo[5.4.0]undec-7-enium acetate

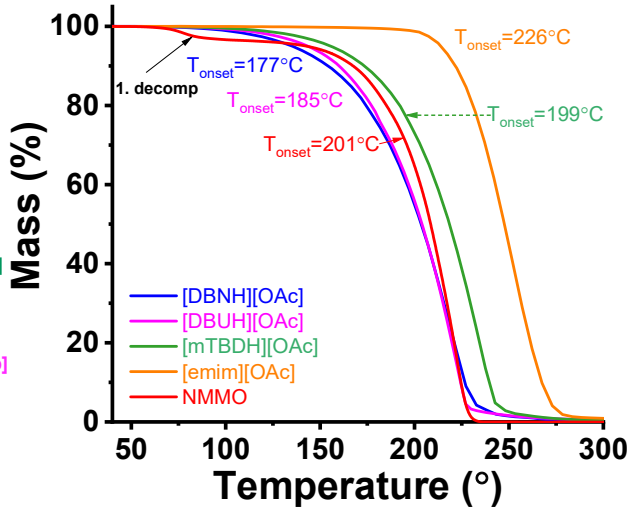






Kamlet-Taft (KT)-parameter



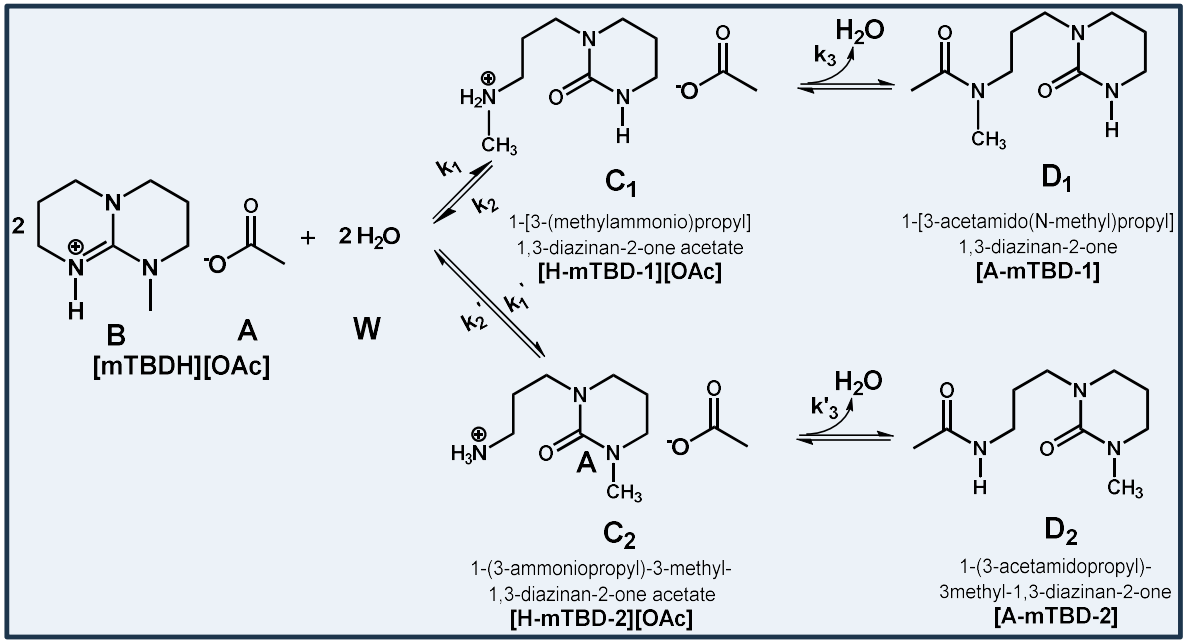


*Parviainen, A. et al. ChemSusChem **2013**, 6, 2161-2169*
Haslinger, S.; Schlapp-Hackl, I. (2020), unpublished

Schlapp-Hackl, I. et al. Ind. Eng. Chem. Res. (2022), 61, 259-268

Hydrolytic instability of Superbases in the Presence of **Water**

Mechanism of hydrolysis of superbases



Model 2: Consecutive reaction with a reversible hydrolysis reaction:

$$BA + W \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + W \xrightarrow{k_3} D + W$$

$$[B]_t = \frac{[mTBD]_0}{\gamma_2 - \gamma_1}\left[(k_2 + k_3 - \gamma_1)e^{-\gamma_1 t} - (k_2 + k_3 - \gamma_2)e^{-\gamma_2 t}\right]$$

$$[C]_t = \frac{k_1[B]_0}{\gamma_2 - \gamma_1}\left[e^{-\gamma_1 t} - e^{-\gamma_2 t}\right]$$

$$[D]_t = [B]_0\left[1 + \frac{k_1 k_3}{\gamma_1(\gamma_1 - \gamma_2)}e^{-\gamma_1 t} + \frac{k_1 k_3}{\gamma_2(\gamma_2 - \gamma_1)}e^{-\gamma_2 t}\right]$$

$[B]_0$	initial concentration of B in mol/L
[B]t, [C]t, [D]t	concentration of B, C, D in (mol*s)/L
k	reaction rate constant ($k_1=\Sigma(k_1+k'_1)$; $k_2=\Sigma(k_2+k'_2)$, $k_3=\Sigma(k_3+k'_3)$)
t	time in h.

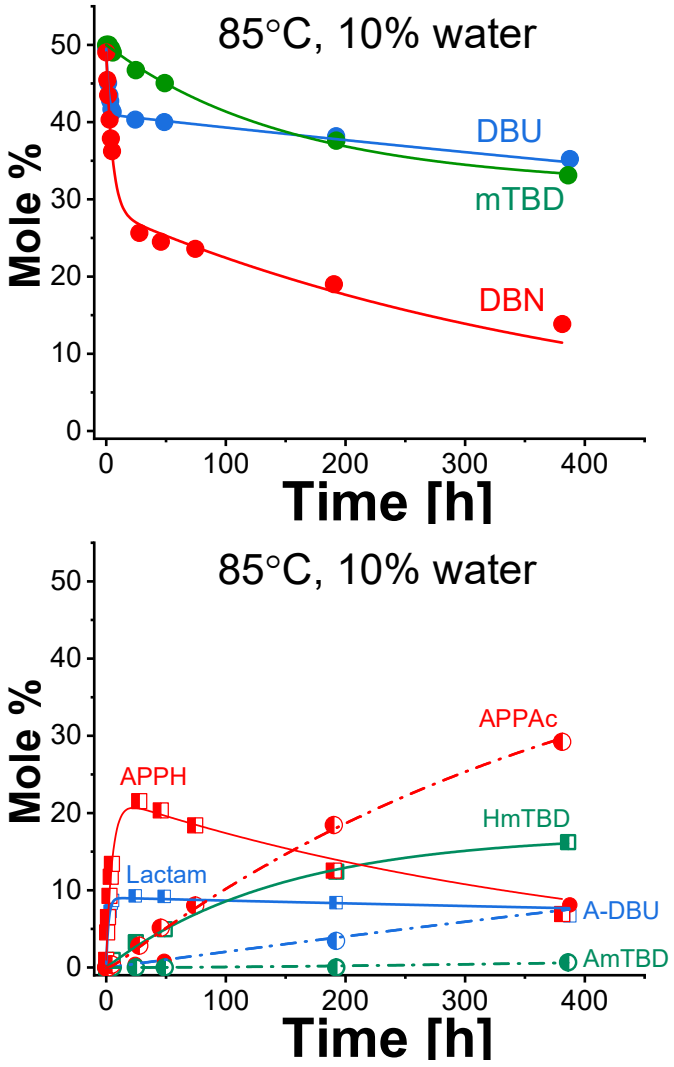
With

$\gamma_1\gamma_2 = k_1k_3$; $\gamma_1+\gamma_2 = k_1 + k_2 + k_3$

$$\gamma_2 = 0.5 \cdot \left(k_1 + k_2 + k_3 \pm \sqrt{{k_1}^2 + 2k_1(k_2 - k_3) + (k_2 + k_3)^2}\right)$$

Schlapp-Hackl, I. et al. Ind. Eng. Chem. Res. (2022), 61, 259-268

Hydrolytic instabilities of superbases

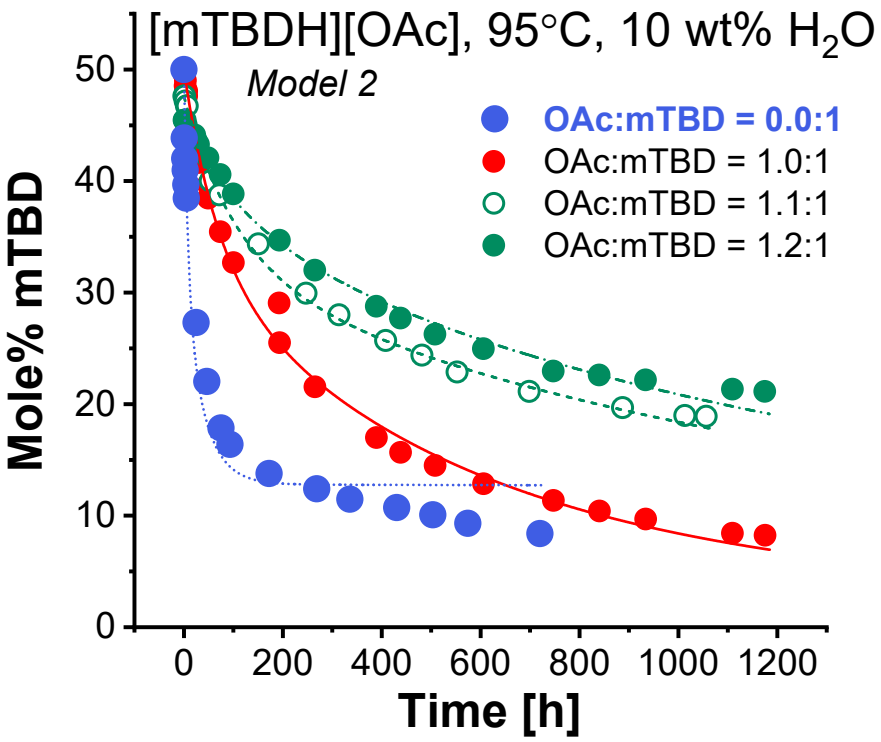


- Bicyclic guanidine-based IL, [mTBDH][OAc], exhibits a central CN3 core.
- Delocalized e^- overlap with the empty π-orbital of the centered sp^2–carbon.
- With HOAc, protonation occurs forming a rigid N-H bond.
- Stabilization ensured by generation of intermolecular H bond.
- In the presence of H_2O, ring opening to cyclic urea occurs
- Stability towards hydrolysis: mTBD > DBU >> DBN

Schlapp-Hackl, I. et al. Ind. Eng. Chem. Res. (2022), 61, 259-268

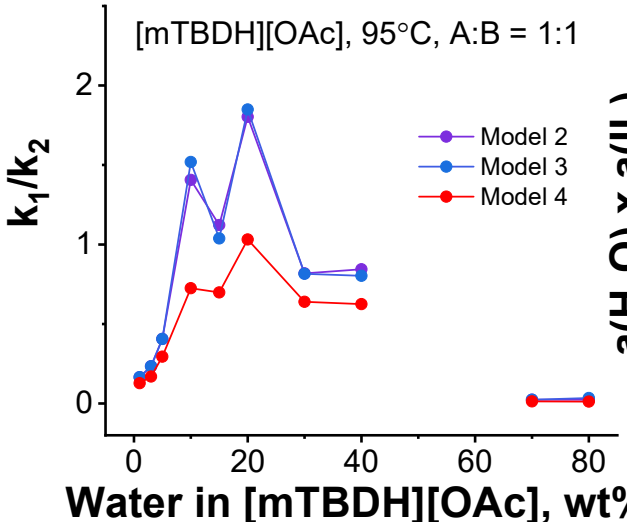
A:B stoichiometry

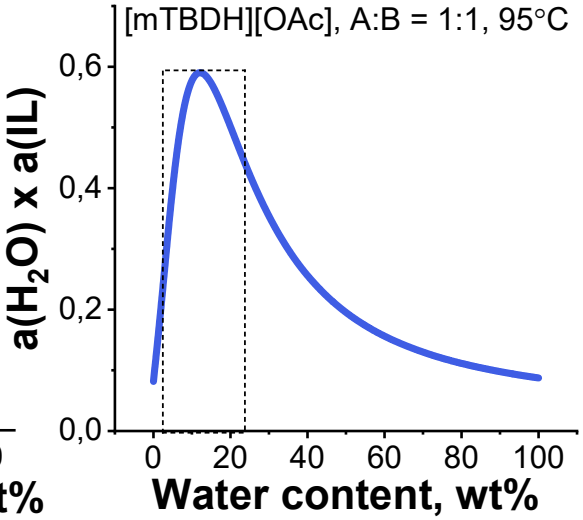
Superstoichiometric amounts of HOAc stabilize mTBD towards hydrolysis



Effect of water content

Stability of mTBD as a function of water content expressed by the equilibrium constant, $K_c = k_1/k_2$





Max. hydrolysis tendency in 10-20 wt% water occurs at **high combined water and mTBD activity**. Available amount of [OH^-] increases up to a water content of 20 wt% before it decreases to almost = at H_2O content > 70 wt%

Schlapp-Hackl, I. et al. Ind. Eng. Chem. Res. (2022), 61, 259-268

3

Cellulose solvents

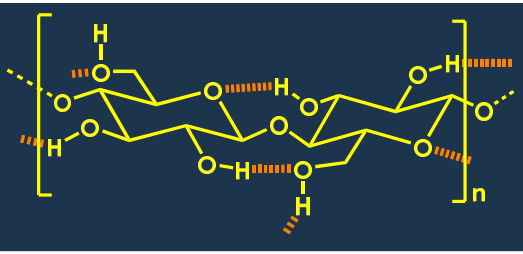
- Overview
- Direct cellulose solvents
- **Alkaline aqueous solutions with&without derivatization**
- Assessment of solution state

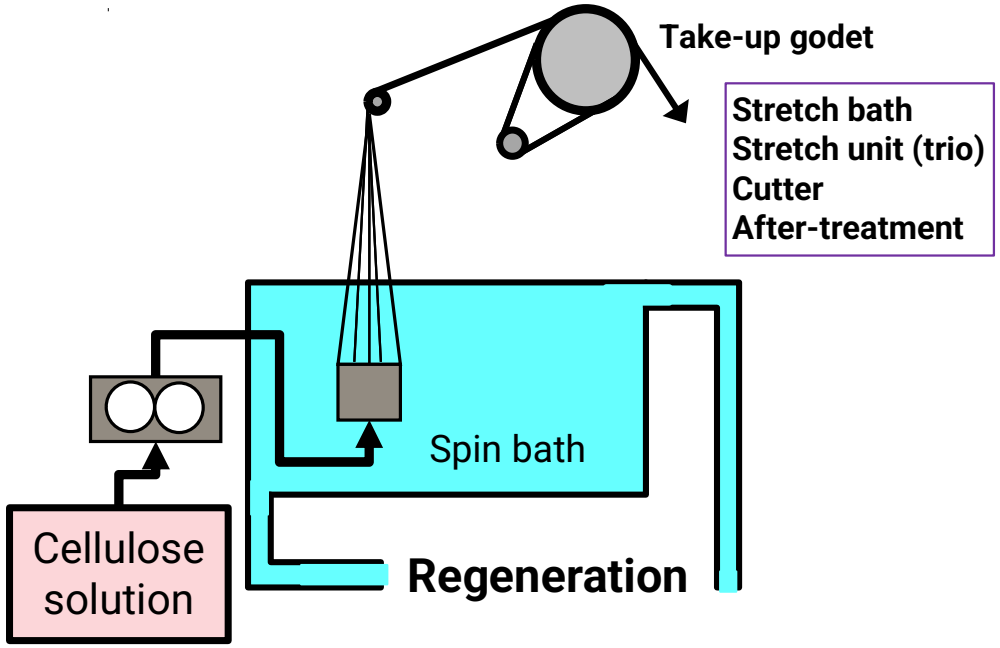
Aqueous solutions

without derivatization

with derivatization

Wet Spinning-1

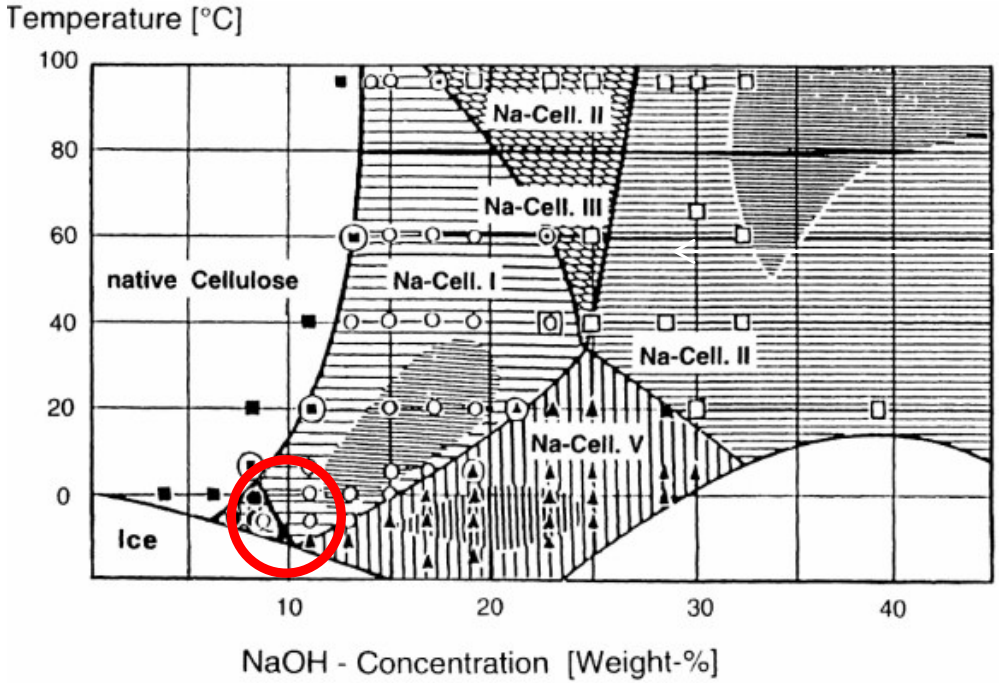




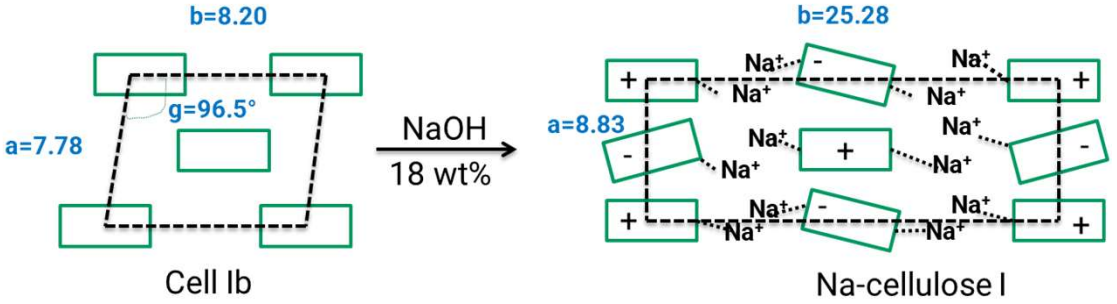
PROCESS	Dissolution	Regeneration	Reference
Lina Zhang	Urea/thiourea, NaOH, (LiOH), ZnO,	H_2SO_4/Na_2SO_4/ NH_4Cl Phytic acid	Journal of Polymer Science: Part B: Polymer Physics, Vol 40, 1521-1529 (2002); Fibers and Polymers (200), 10, 34-39 ACS Sustainable Chem.Eng.(2018), 6, 5314-5321
TreeToTextile	NaOH, ZnO	a) H_2SO_4, Na_2SO_4, $ZnSO_4$ b) Na_2CO_3, NaOH	WO 2020 251463 EP 3231899A1 WO 2020 171767 WO 2020 231315
Biocelsol (NeoCel)	Enzyme, NaOH, ZnO, Additives, Enzymes	a) H_2SO_4, Na_2SO_4, $ZnSO_4$ b) Na_2CO_3, CaO (causticizing)	Cellulose (2020) 27:8681–8693; Chemical Fibers International 2020, 70, 128-130

Cellulose dissolution in $NaOH_{aq}$

Phase diagram of ternary system cellulose / NaOH / water



Sobue, H.; Kiessig, H.; Hess,K. Z. *Phys. Chem.* **1939**, 43, 309



- **Na^+ have polar interactions only with O2 and O3**
- **No intersheet H-bonds as large Na^+ & H_2O molecules separate the chains**

A. *Sarko et al., In ACS Series 340, edited by R.H. Atalla, p169pp*
B. *Zugenmaier, P. Progress in Polymer Science (2001), 26(9), 1341-1417*

Steps of Cellulose Dissolution (1)

1. **Cellulose is amphiphilic: dissolution requires both the elimination of H-bonding and the elimination of hydrophobic interactions.**

2. **Cellulose dissolution governed by the free energy of mixing.**

3. **NaOH forms hydrates with H_2O capable of breaking inter-, intramolecular H-bonds.**

4. **NaOH shows a narrow concentration range where it acts as a solvent due to the concentration-dependent size of the $NaOH x H_2O$ hydrates.**

B. Medronho, B. Lindman / Advances in Colloid and Interface Science 222 (2015) 502–508

Steps of Cellulose Dissolution (2)

5. **Hydroxyl groups (C2, C3) are deprotonated→dissociated counterions strongly contribute to the translational entropy of mixing.**

6. **Dissolution governed by Molar Mass: the higher, the weaker the entropic driving force.**

7. **Polymer dissolution often controlled by kinetics rather than by thermodynamics.**

8. **Dissolution ability of NaOH/water can be improved by addition of ZnO, urea & thiourea: ZnO-> $Zn(OH)_4^{2-}$: forms H-bonds with cellulose**

B. Medronho, B. Lindman / Advances in Colloid and Interface Science 222 (2015) 502–508

Cause of low temperature demand (3)

9. **Breaking of H-bonds in crystalline regions is endothermic.**

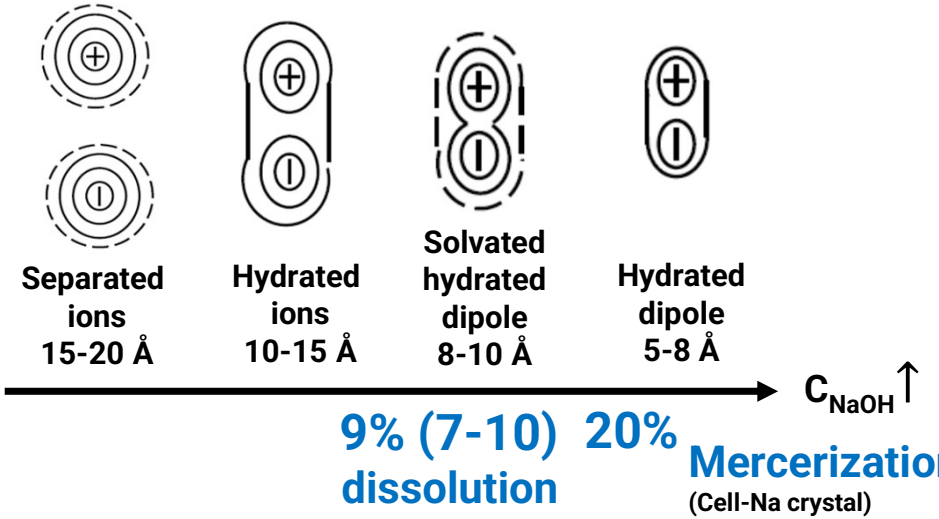
10. **All other interactions between cellulose OH groups and the solvent system are exothermic→Overall exothermic.**

11. **High temperature induces conformational changes of cellulose, making cellulose less polar**

12. **Therefore, attractive interactions with polar solvent are reduced at higher temperatures**

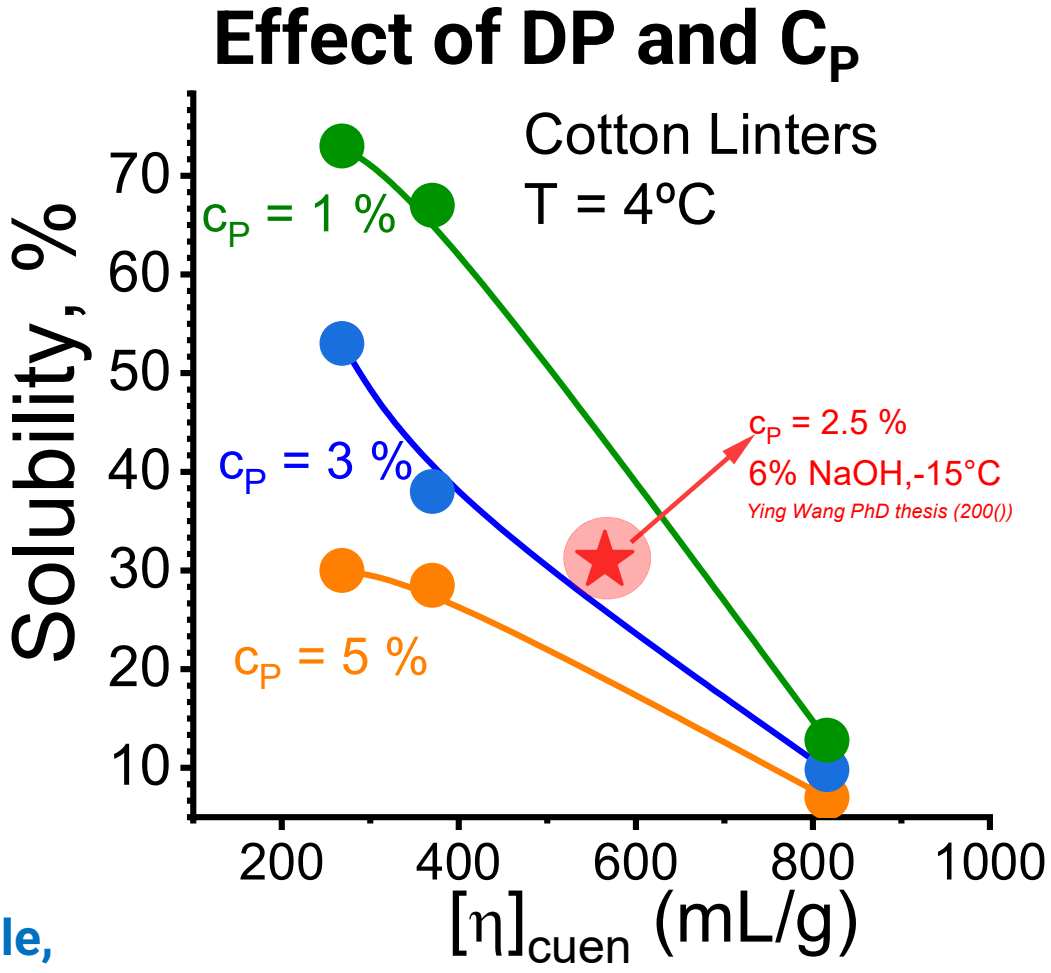
B. Medronho, B. Lindman / Advances in Colloid and Interface Science 222 (2015) 502–508

Solubility of Cellulose in $NaOH_{aq}$



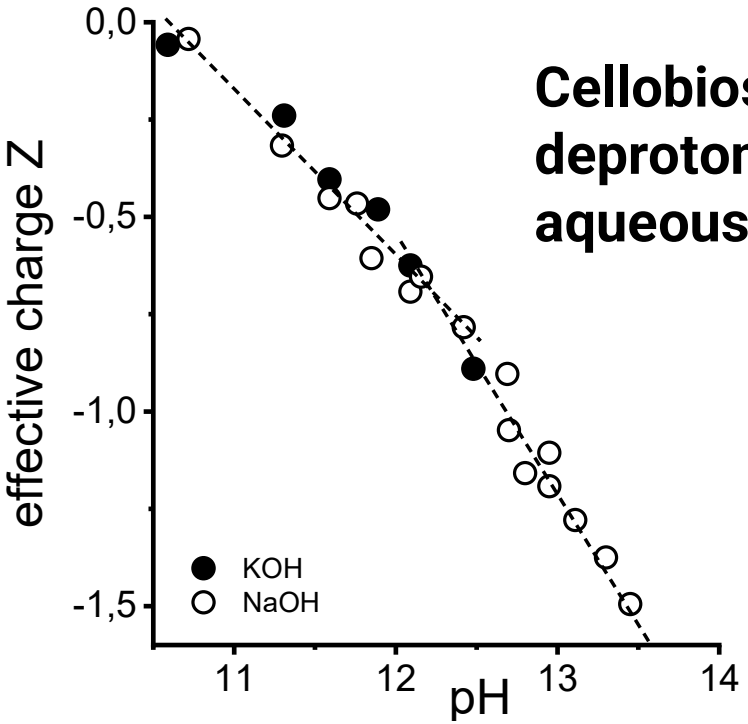
6% NaOH at -15°C followed by adding a 14 wt% NaOH solution→Change in C_{NaOH} leads to cellulose dissolution (**turn point is at 9%):**
NaOH hydrates penetrate into cellulose and detach individual chains into solution.

Low T favors strong network of NaOH hydrates, while, upon heating cellulose chains crosslink and form gels.



Ying Wang, PhD thesis, Georgia Institute of Technology, 2008

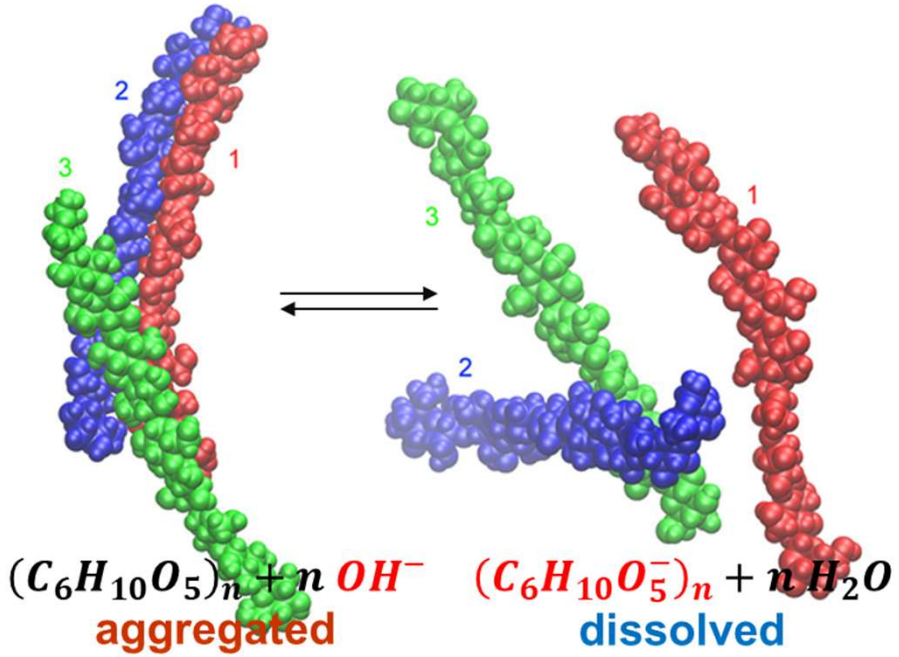
Ionization & Mechanism of Cellulose dissolution



Cellobiose deprotonated in aqueous alkali

2 dissociation steps at pH 12 (hemiacetal OH) **and pH 13.5** (OH on C2 of NREG), **the latter more relevant for cellulose dissolution.**

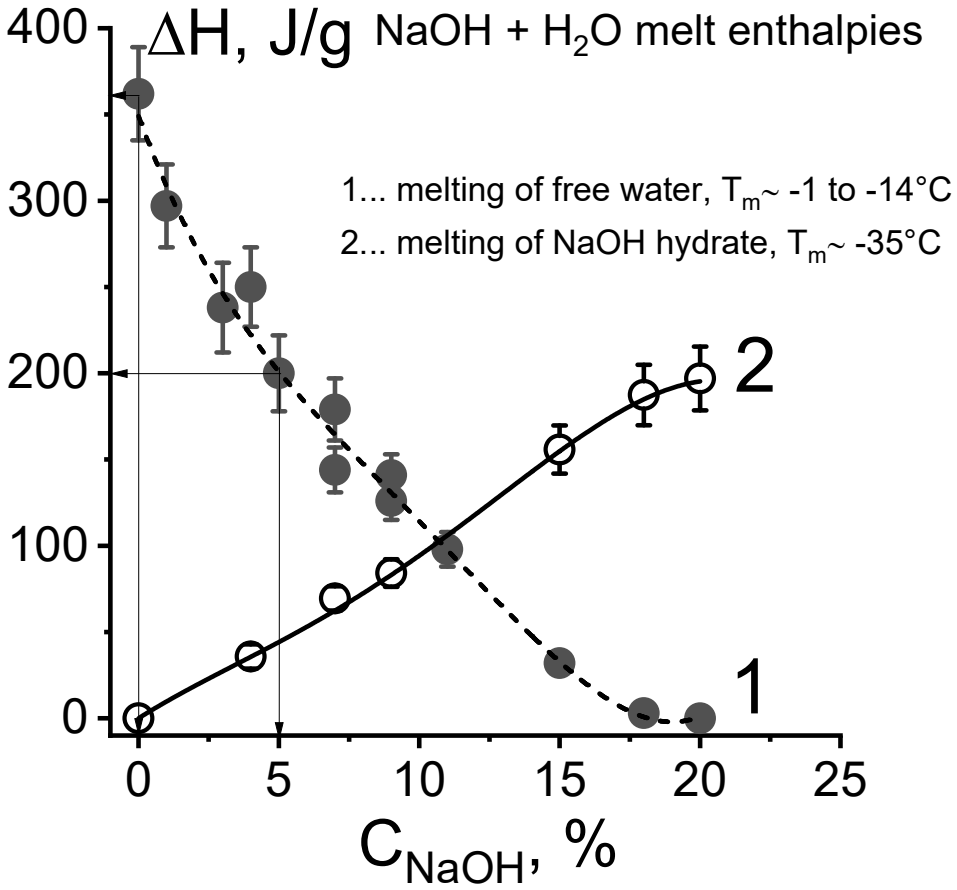
J. Phys. Chem. Lett. 2016, 7, 5044−5048



According to MD simulation, aggregation is suppressed upon charging cellulose in solution→ Crucial for solubilization

Translational entropy very much higher for ionic polymers with dissociating counterions than for non-ionic polymers

Structure of cellulose-NaOH solutions



Roy, C.; et al. Biomacromolecules 2001, 2, 687-693

Number of H_2O bound to NaOH,

$$X = \left(N_{H_2O}/N_{NaOH}\right) = F_{bound}\frac{(100 - C_{NaOH})}{18}\frac{40}{C_{NaOH}}$$

C_{NaOH} = 5%→ $X = 0.45 \cdot \frac{95}{18} \cdot \frac{40}{5} = 19$

C_{NaOH} = 20%→ $X = 1 \cdot \frac{80}{18} \cdot \frac{40}{20} = 9$

NaOH hydrates are composed of a core bound with 9 H_2O/NaOH

Fraction of bound water:

$$F_{bound} = \left(1 - F_{free}\right)$$

$$F_{free,5\%\,NaOH} = \frac{200\,J/g}{365\,J/g} = 0.55;\ F_{bound} = 0.45$$

F_{free} is the same in NaOH+H_2O and Cellulose+NaOH+H_2O

Effect of DP on cellulose dissolution

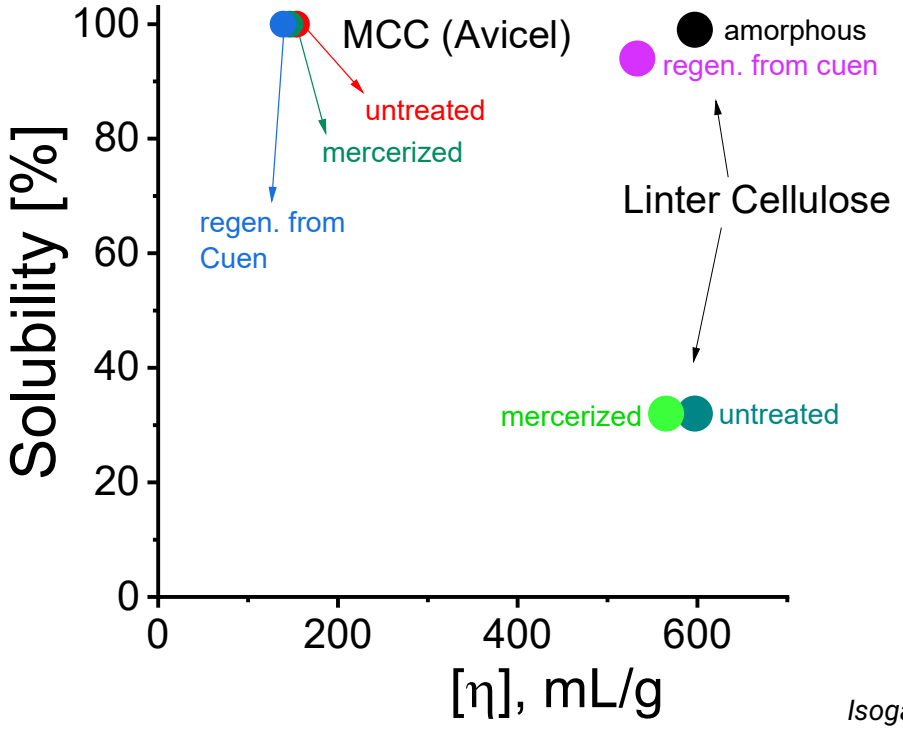
Dissolution procedure:

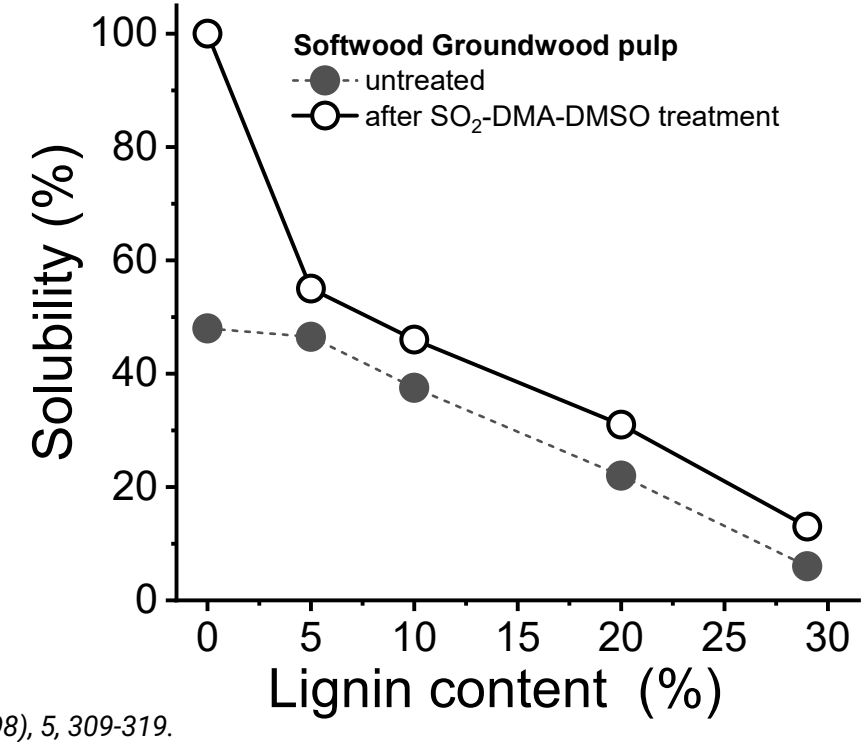
Cellulose/NaOH/H_2O suspension at RT Suspension cooled to -20°C until frozen. Thawing to RT, adding H_2O until clear: **Solution: 2% Cellulose in 5% NaOH**

Effect of DP on solubility clearly visible

Summary

- MCC completely soluble, independent of pre-treatments
- Mercerization does not improve solubility
- Amorphization improves solubility
- Delignification improves accessibility and thus solubility



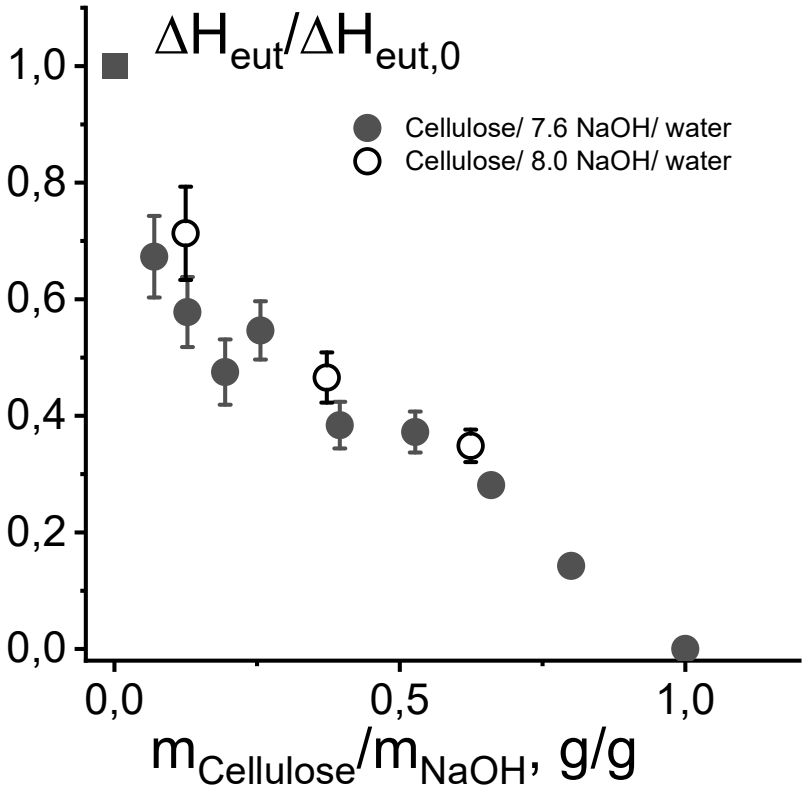


Isogai, A.; Atalla, R.H. Cellulose (1998), 5, 309-319.

Limit of cellulose dissolution

Dissolution procedure:

NaOH dissolved in water in ~ 12%, cooled to -6°C; Avicel PH-101 (DP = 170) mixed with water at +5°C, 2h, separately. Cold NaOH/water added to swollen MCC. Preparation of **0.5-7.6 % MCC** and **7.6-8.0 % NaOH** at -6°C, stirred for 2 h, stored at +5°C.



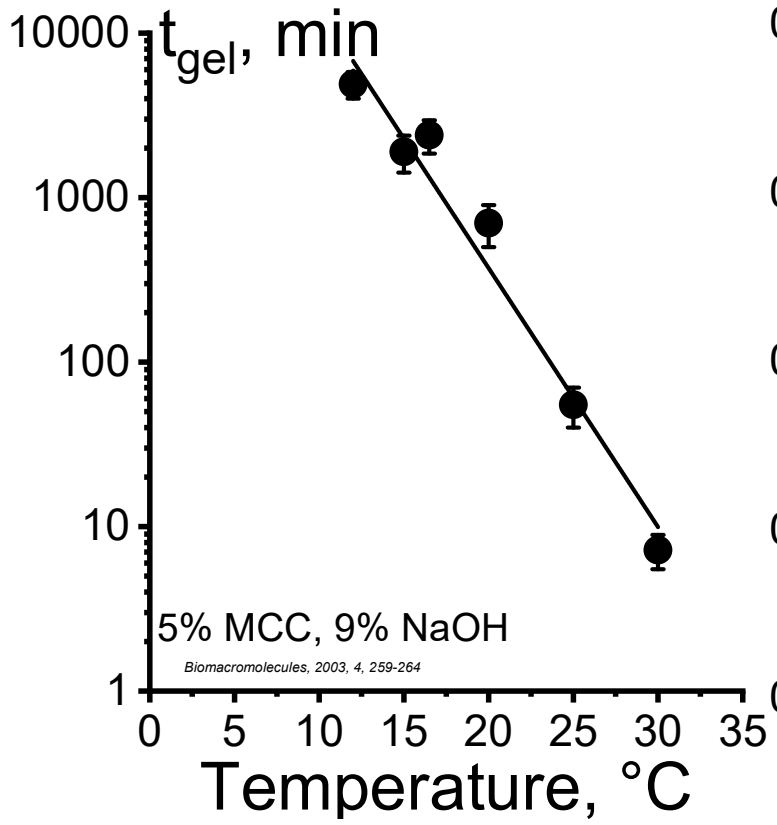
1. **Cellulose/NaOH/Water phase diagram: detailed DSC experiments on MCC/NaOH/water**
2. **DSC: Eutectic mixture, NaOHx5 H_2O & 4 H_2O, melts at ~ -34°C**
3. **When $\Delta H_{eut}/\Delta H_{eut,0} \rightarrow 0$ all NaOH molecules are linked with cellulose**
4. **Eutectic peak disappears at $m_{cellulose}/m_{NaOH}$ = 1, which translates to 4 moles NaOH per mol AGU**
   (6% NaOH*162g/mol/6% cellulose*40 g/mol)
5. **NaOH as cellulose solvent in the range of 6-8%: Thus, 6-8 wt% of cellulose is the maximum that can be dissolved in NaOH/water**

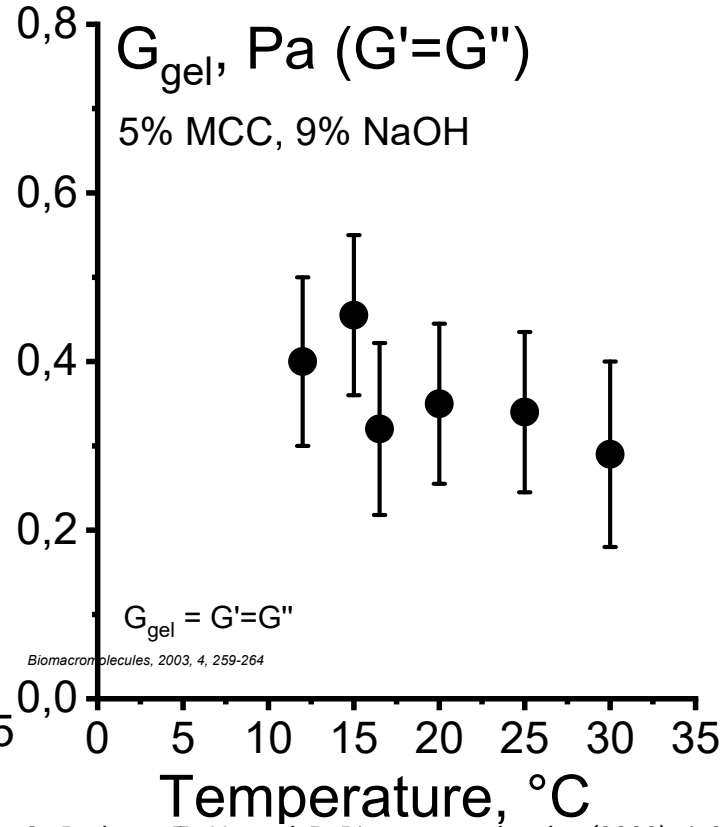
Egal, M.; Budtova, T.; Navard, P. Biomacromolecules (2007), 8, 2282-2287

Gelation of cellulose-$NaOH_{aq}$ solutions

Dissolution procedure:

Avicel PH-101 mixed with 6% NaOH at -6°C, stirred; then an amount of 15% NaOH added to reach a total **NaOH concentration of 9%** at a **5 % cellulose** concentration; final mixture stirred at -6°C

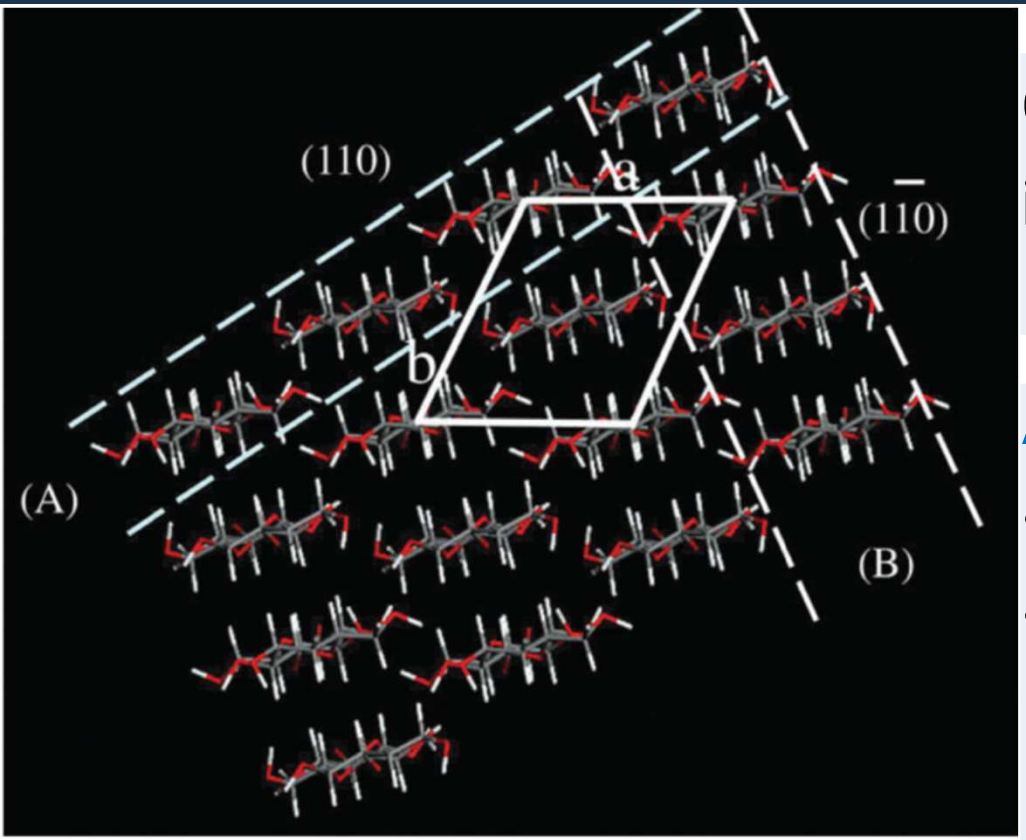




1. **Independence of E_A (~ 20 kJ/mol) of a 9% NaOH solution on [Cellulose] →Cell/NaOH/H_2O mixtures are no real solutions**
2. **At T>20°C, [η] decreases→ compaction of hydrophobic interaction**
3. **Gelation not reversible→local chain segregation**

Roy, C.; Budtova, T.; Navard, P. Biomacromolecules (2003), 4, 259-264

H-bonding vs hydrophobic interactions



(A) H-bonded molecular sheet
(B) Van der Waals-associated sheet

Cellulose chains stack via hydrophobic interactions and form sheet-like structures

Any solvent needs to break both the

- **intermolecular H-bonds in one plane**
- **the hydrophobic interaction forces between the C-H direction in the perpendicular direction**

Phys. Chem. Chem. Phys., 2017, 19, 23704—23718
Carbohydr. Res., 2009, 344(9), 1085-1094
Warwicker, J.O.; Wright, A.C. J. Appl. Polym. Sci., (1967), 11, 659-671

Dissolution kinetics

$$\Delta H_{Dissolution} = \Delta H_{fusion} + \Delta H_{transition} + \Delta H_{interaction} + \Delta H_{mixing}$$

ΔH_{fusion}	disintegration of crystalline domains (endothermic)
$\Delta H_{transition}$	transition of amorphous regions from glas to a elastic state (exothermic)
$\Delta H_{interaction}$	solvation of macromolecules (exothermic)
ΔH_{mixing}	mixing of solvated molecules with solvent to give an infinitely diluted solution (exothermic)

Eyring-Polany equation (1935): activated-complex theory

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

$$k = \left(\frac{k_B T}{h}\right) Exp\left(\frac{\Delta S^{\ddagger}}{R}\right) Exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

$$ln\frac{k}{T} = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

Slope: $-\Delta H^{\ddagger}/R$

Intercept: $\ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^{\ddagger}}{R}$

k	reaction rate constant
T	absolute temperature
$\Delta H^{\ddagger}$	enthalpy of activation
$\Delta S^{\ddagger}$	entropy of activation
k_B	Boltzmann constant ($1.38065*10^{-23}$ J/K
h	Planck's constant ($6.62607*10^{-34}$ J/Hz)
R	gas constant

Ying Wang, PhD thesis, Georgia Institute of Technology, 2008

Dissolution kinetics

EXPERIMENTAL

2.5% Cotton linter, DP_v 800 (SCAN 565 mL/g), in
6 % NaOH in
6% NaOH / 4 % urea
No stirring!

Change in cellulose crystallinity of undissolved cellulose is an indicator the extent of dissolution

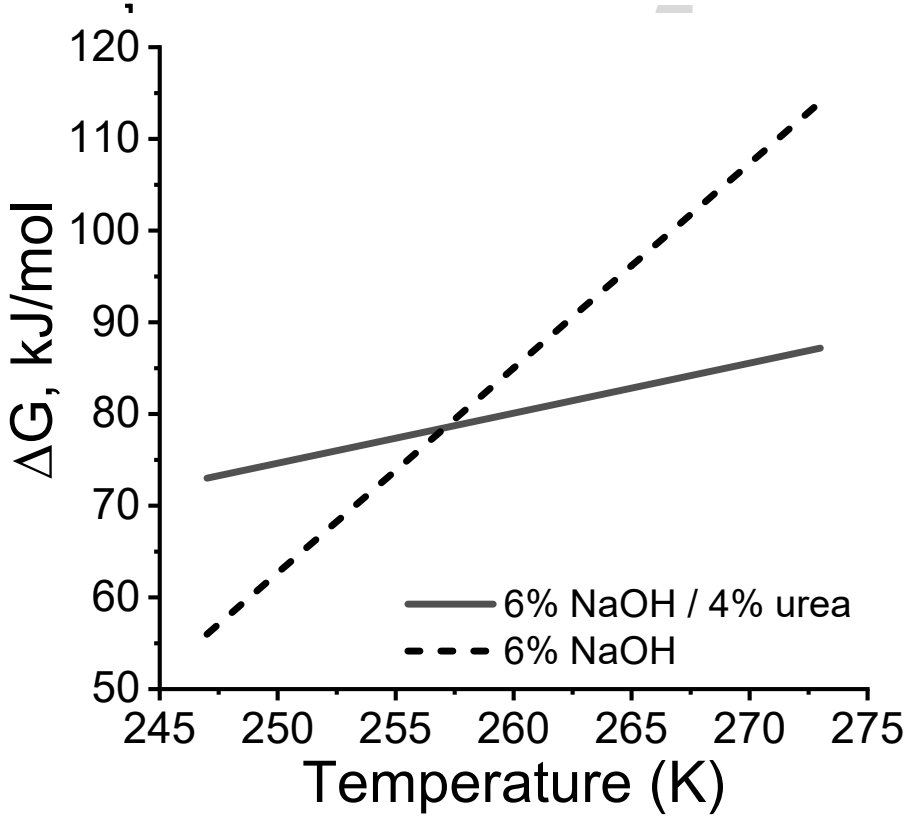
$$I_{cw} = \frac{m_t}{m_0} \cdot \left(1 - \frac{I_{min}}{I_{max}}\right)$$

I_{min} 2θ ~ $17 - 18°$ $(I), 14 - 15°$ (II)
I_{max} 2θ ~ $20 - 22°$ $(I\ (200), II\ (020))$

$$-\frac{dI_{cw}}{dt} = k_{obs} \cdot I_{cw}$$

$$ln\frac{k_{obs}}{T} = \frac{-\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

Ying Wang, PhD thesis, Georgia Institute of Technology, 2008

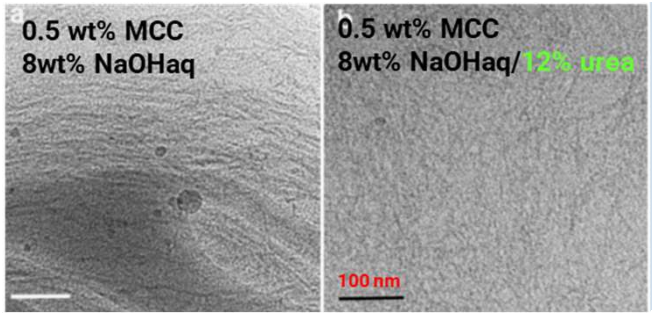


Treatment	Slope	Intersect	ΔH kJ/mol	ΔS kJ/Kmol	ΔG kJ/mol
With urea	7436	-65,65	-61,8	-0,55	**79,0**
Without urea	59595	-268,5	-495,5	-2,23	**80,6**

Role of urea

Solvent System

7 wt% NaOH / 12 wt% Urea, precooled to -12°C.
4-5 wt% Cellulose with $M_\eta \leq 120$ kDa can be fully dissolved within 2-5 min.



Cryo-TEM:

improved cellulose dissolution by reducing hydro-phobic interactions

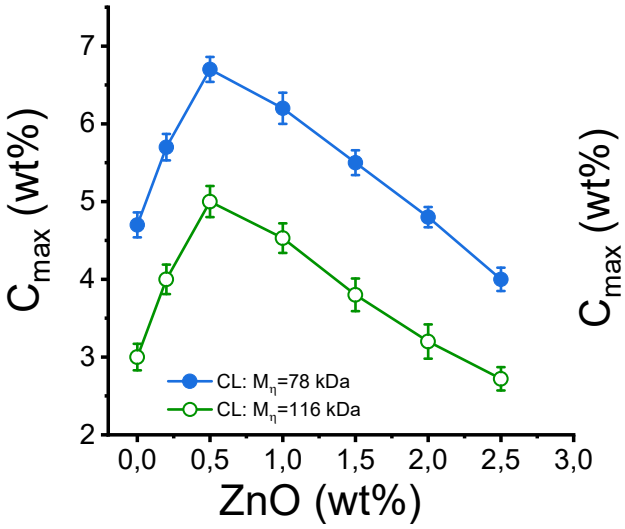
Urea hydrates cannot associate directly with cellulose, but can self-assemble at the surface of NaOH H-bonded Cellulose→ **worm-like inclusion complex**

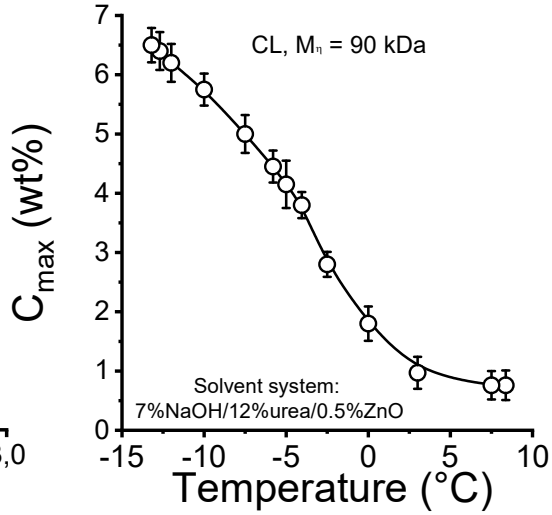
Solid-state NMR: In the presence of urea, C4 peak resonates in amorphous zone

Rheology: presence of urea delays gelation of cellulose, T_g shifted to higher temperature

*Luis Alves, et al. Björn Lindman. Gels **2018**, 4, 87*

Role of $Zn(OH)_4^{2-}$





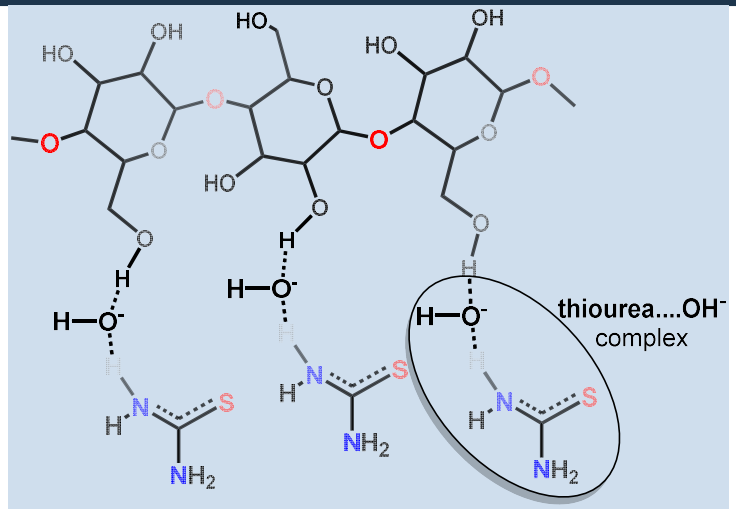
The addition of 0.5% ZnO improved cellulose solubility strongly, while higher ZnO dosage impairs cellulose dissolution

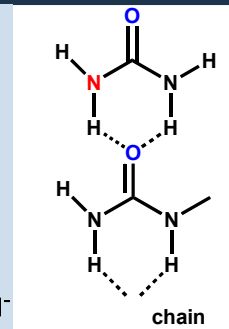
Cellulose solubility dependent on molar mass.

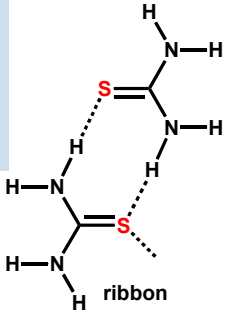
Increased cellulose solubility as a result of stronger interaction between $Zn(OH)_4^{2-}$ and cellulose; it breaks intermolecular H-bonds of cellulose and acts as a spacer between cellulose sheets

Yang, Q.; Zhang, L.; et al. Carbohydrate Polymers 83 (2011) 1185–1191

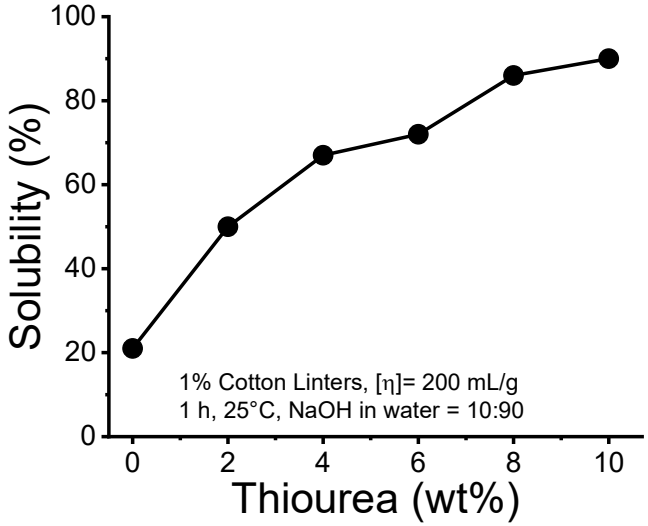
Urea vs thiourea







relative strength of ribbon vs. chain is higher for thiourea leads to stronger interactions in cellulose/NaOH/thiourea



Jiang Z.; Zhang, L. et al. The Journal of Physical Chemistry B, (2017), 121, 1793-1801

Cotton linters pulp: $[\eta]_{cuen}$~ 250 mL/g

Dissolution of 4 wt% cotton linters

i. -10°C: 7.0 wt% NaOH / 12 wt% urea

ii. - 5°C: 9.5 wt% NaOH / 4.5 wt% thiourea

iii. + 8°C: 9.3 wt% NaOH / 7.4 wt% thiourea

Thiourea vs Urea:

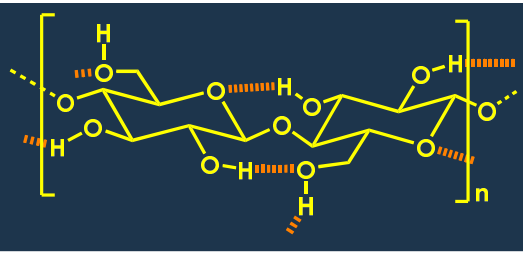
- Rheology: COP (G'=G") shifted from 41°C to 45°C
- Thiourea higher acidity, generates stronger interactions with anions→ stronger dissolving capacity
- Strength of H-bond in thiourea….OH- stronger than in urea….OH-→ reduces the probability of self association of cellulose chains:
- **$NaOH(H_2O)_7$.thiourea** cluster is the most stable cluster and forms a cage

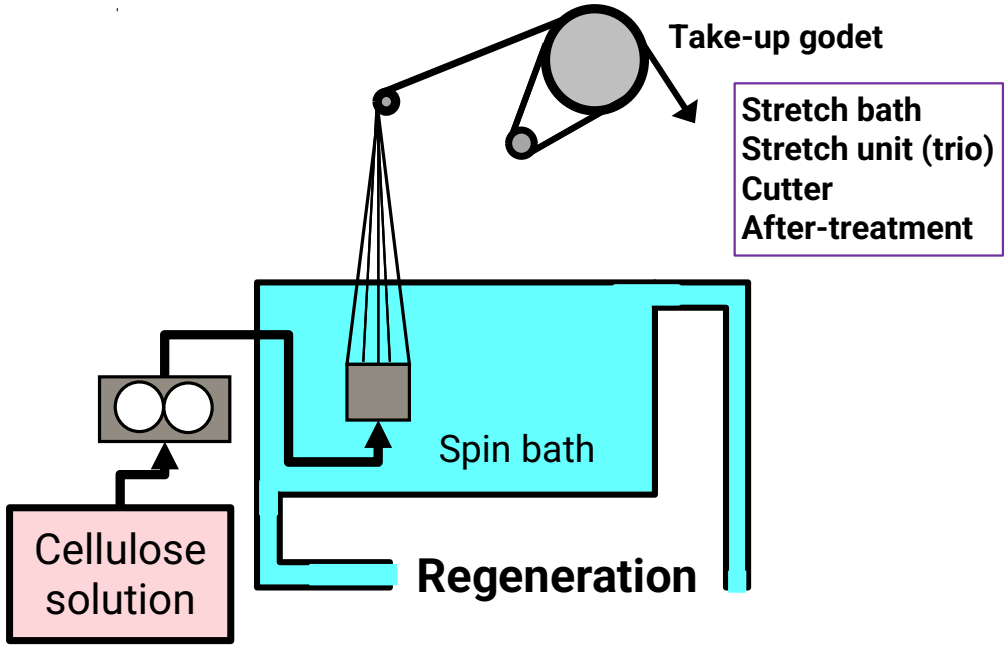
Aqueous solutions

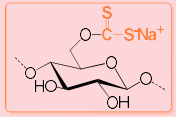
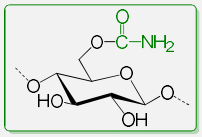
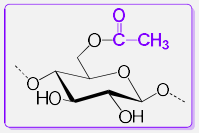
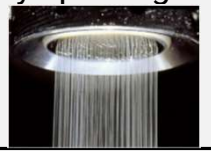
without derivatization

with derivatization

Wet Spinning-2

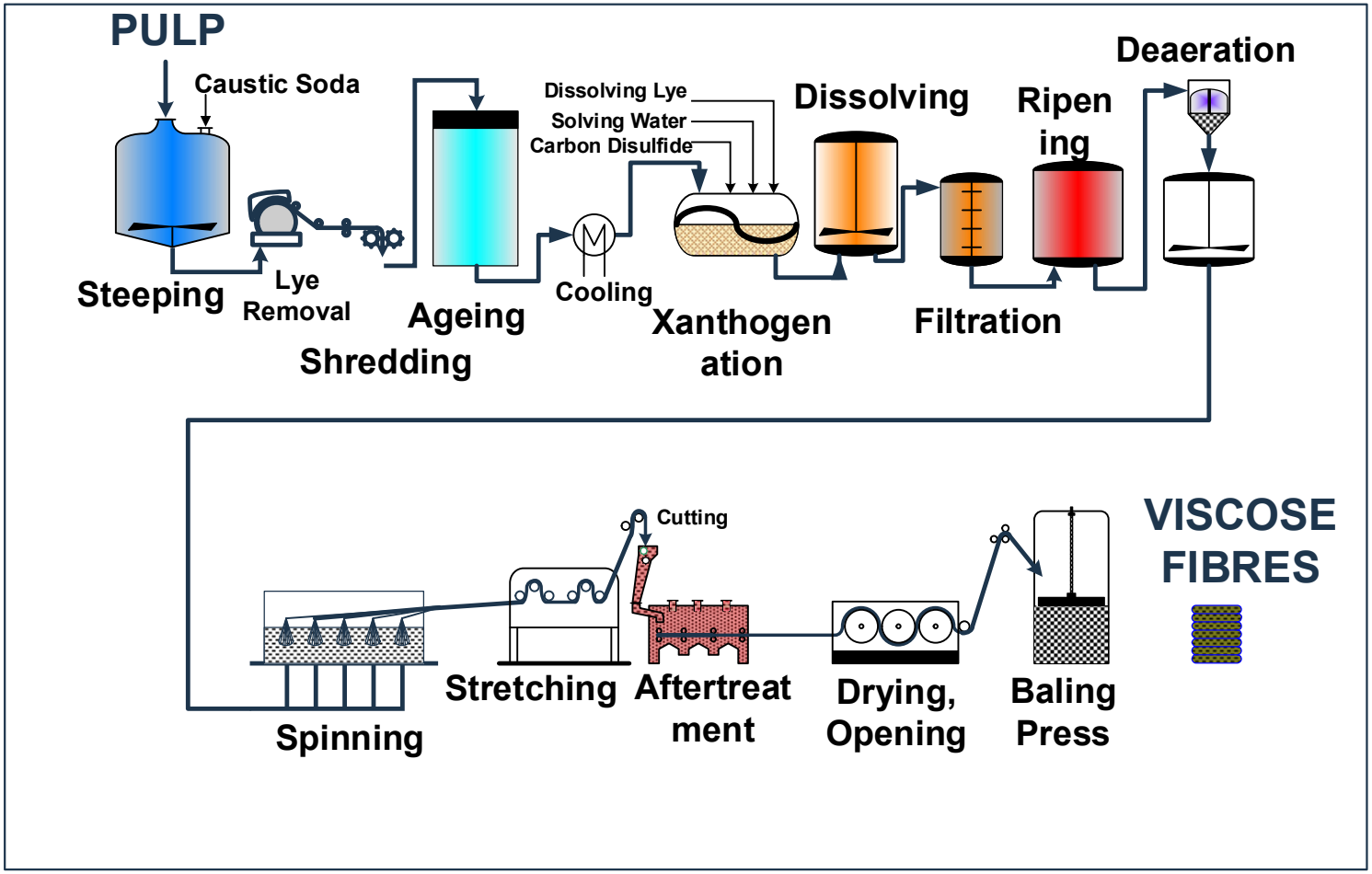




PROCESS	Dissolution	Regeneration	Reference
Viscose 	NaOH, CS_2, (Additives)	H_2SO_4, Na_2SO_4, $ZnSO_4$	Lenzing AG, Kelheim
Carbamate 	Urea, NaOH, ZnO, (H_2O_2)	H_2SO_4, Na_2SO_4	ACS Sustainable Chem. Eng. 2014, 2, 2363−2370 ACS Sustainable Chem. Eng. 2015, 3, 1510−1517 Journal of Cleaner Production 222 (2019) 871
Acetate 	• 2.5 Acetate (CDA) • Dissolution in acetone	CDA in acetone, Dry spinning 	Cellulose Acetates: Properties and Applications (2004) (Ed. P.Rustemeyer) ISBN 3-527-31041-x

VISCOSE

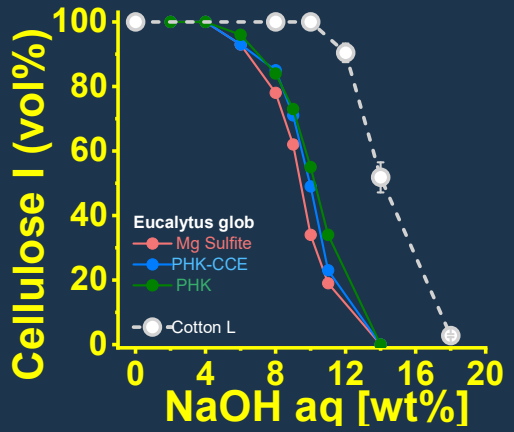
Process Schemes



VISCOSE

- Steeping
- Alkalicellulose
- Ageing

Lattice transition

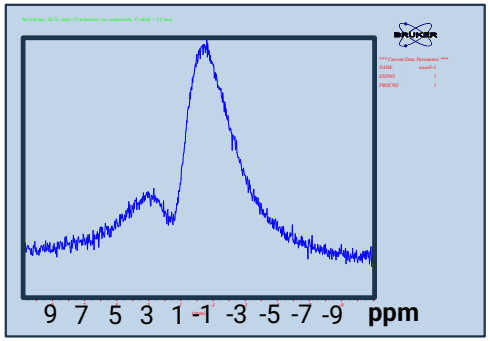


Sixta, H (2000), Lenz Ber
Sawada, D.; Toivari T. (2019) unpublished

Alkalization - Steeping

Pulp slurry in aqueous 18 wt% NaOH in L:S ratio of 18:1. Release of 130 kJ/kg cell heat: wetting, swelling, lattice transformation,etc.

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



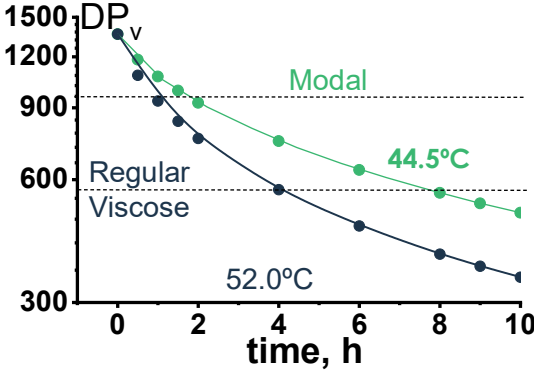
^{23}Na-MAS T1 relaxation shows two Na^{+} components

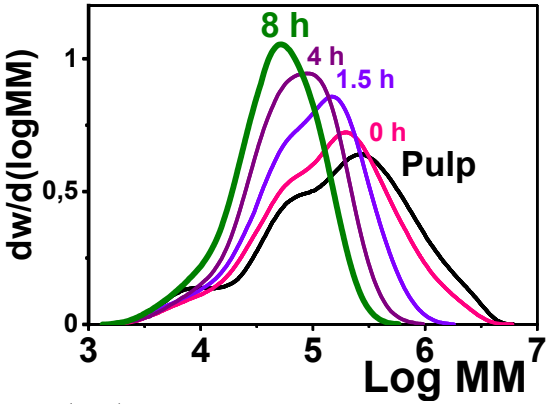
P. Kosma, W. Binder (2002), unpublished
Fink, H-P. et al. Polymer (1986), 27(6), 944-948

Alkali Cellulose

Alkali-Cellulose	wt%	molar ratio
Cellulose	34	1
NaOH	16	2
Water	50	13

DP-adjustment by Ageing

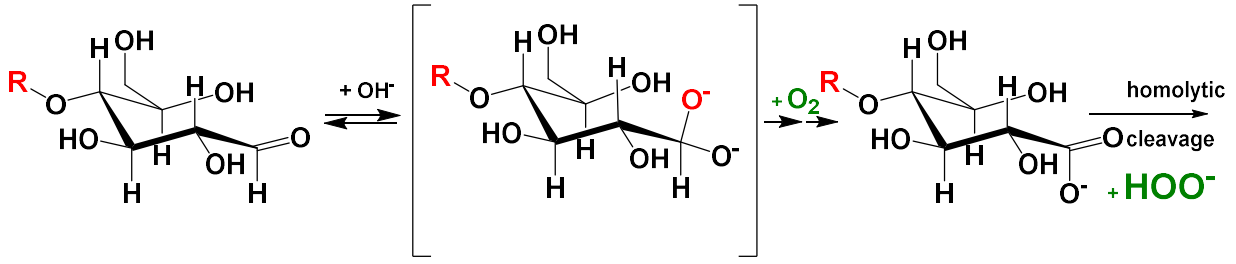




Entwistle, D. et al. Textile Research Journal, 19, 527-546 (1949); Sixta, H. et al. (2006) unpublished

Chemistry of ageing

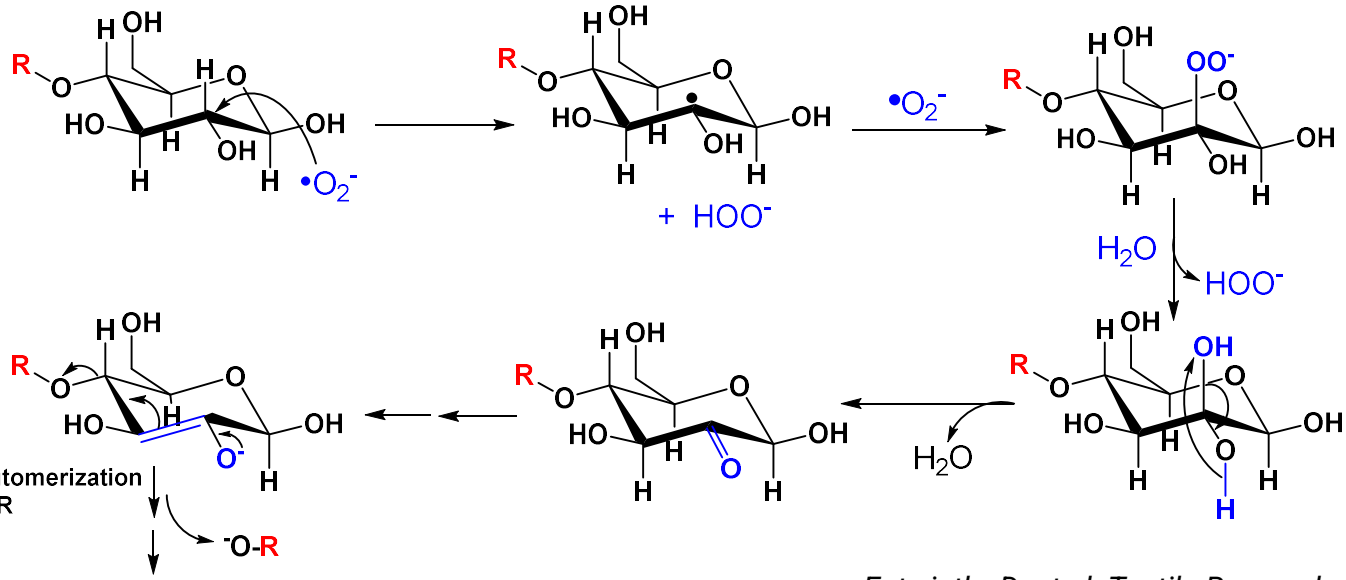
Combined heterolytic and homolytic degradation



Formation of radicals through catalysis

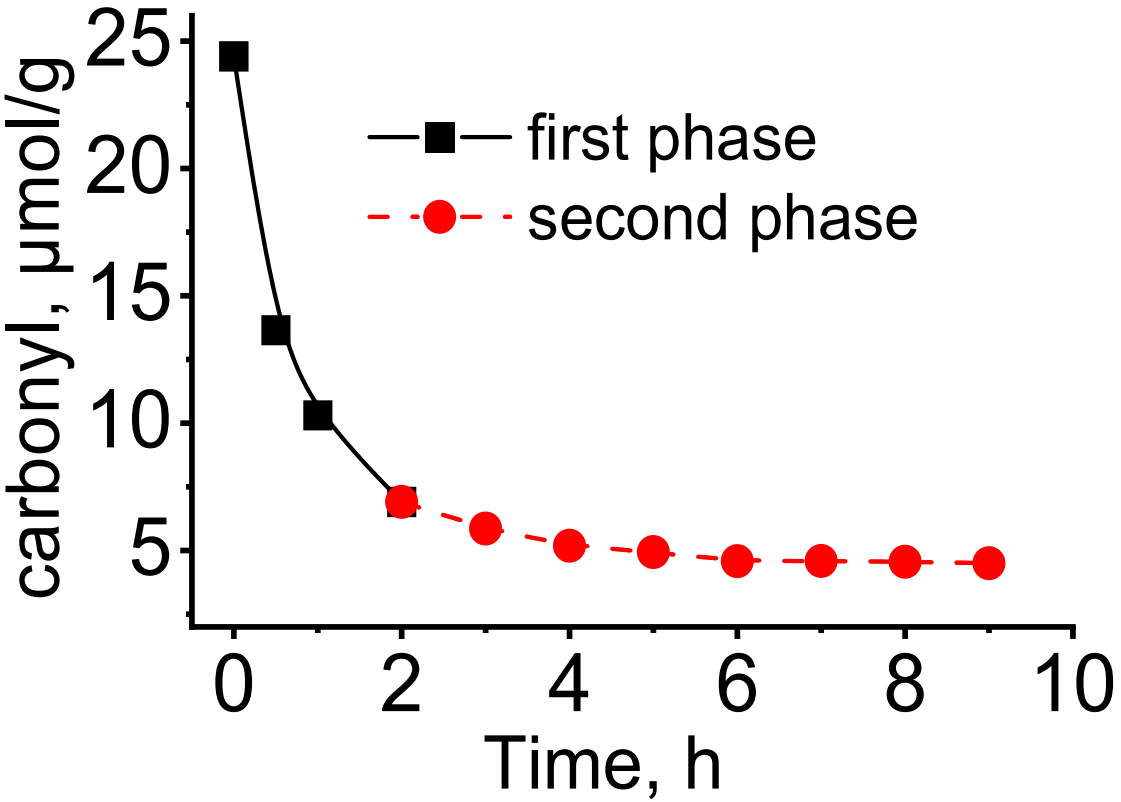
$HOO^- + Me^{n+} \longrightarrow {}^{\bullet}O^- + OH^- + Me^{(n+1)+}$

$Me^{(n+1)+} + HOO^- \longrightarrow Me^{n+} + {}^{\bullet}O_2^- + H^+$



Entwistle, D. et al. Textile Research Journal, 19, 527-546 (1949)

Ageing - Effect on REGs

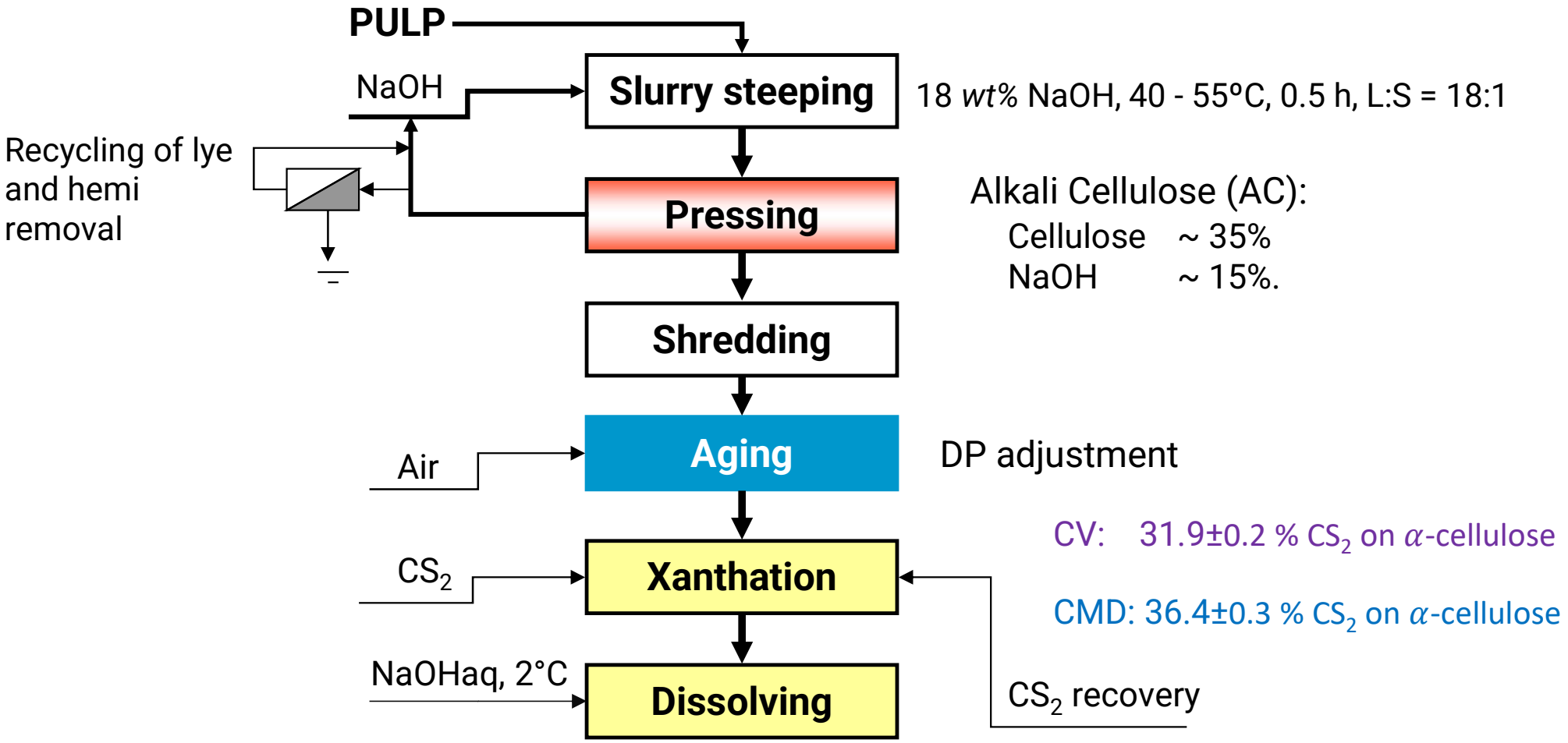


Decrease in carbonyl groups:

Oxidation to aldonic acids

A. Potthast (2003)

Preparation of Viscose



VISCOSE

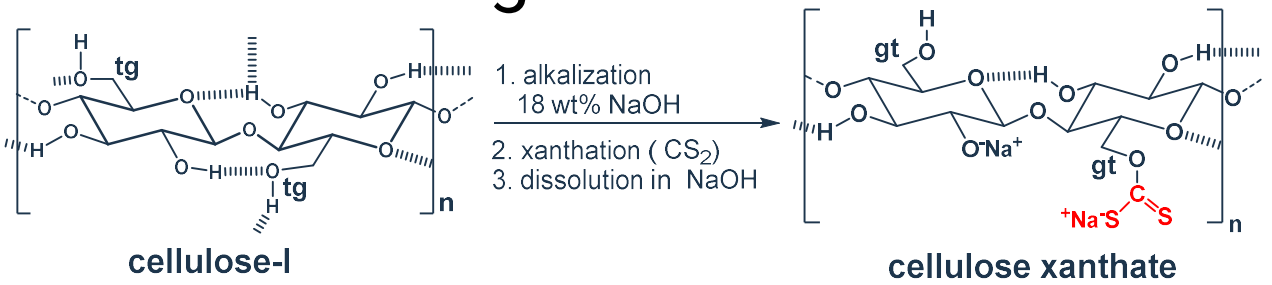
- **Xanthogenation**
- **Viscose**

Xanthate dissolved in 5 – 8 wt% NaOH

CV
8.9% cellulose
5.3% NaOH
2.0% S

CMD
6.0% cellulose
6.0% NaOH
1.6% S

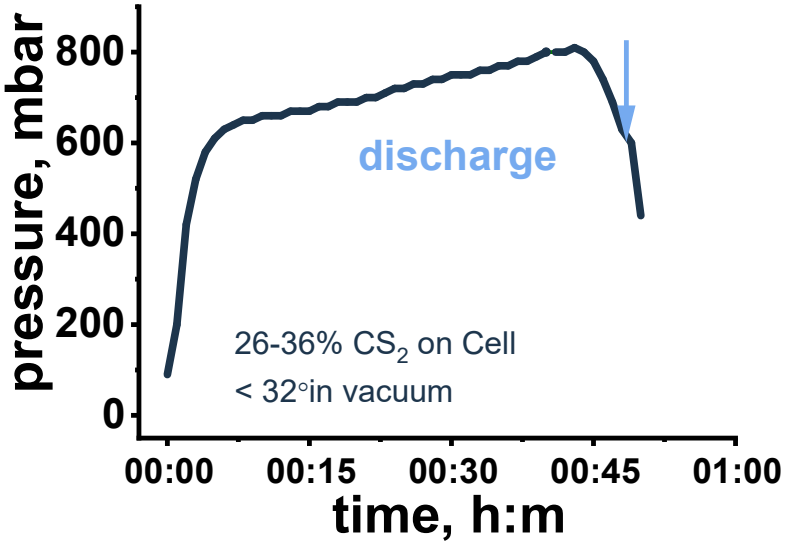
Xanthogenation reaction



cellulose-I

cellulose xanthate

Xanthation



Sixta H. unpublished results

Gas phase reaction starts rapidly at the surface of the AC crumbs and slowly diffuses into the forming lumps.

DS target is 0.5-0.7 (γ = 50-70)

High strength fibers require xanthation to higher γ values!

Prepared viscose is homogenized, dissolved in 5 – 8 % NaOH at ~2°C, filtered and dearated.

Side reactions during viscose preparation

Side product formation:

$$Cell - O - (C = S) - SNa \xrightarrow{H_2O} Cell - O - (C = S) - SH + NaOH$$

$$Cell - O - (C = S) - SH \rightarrow Cell - O - H + \mathbf{CS_2}$$

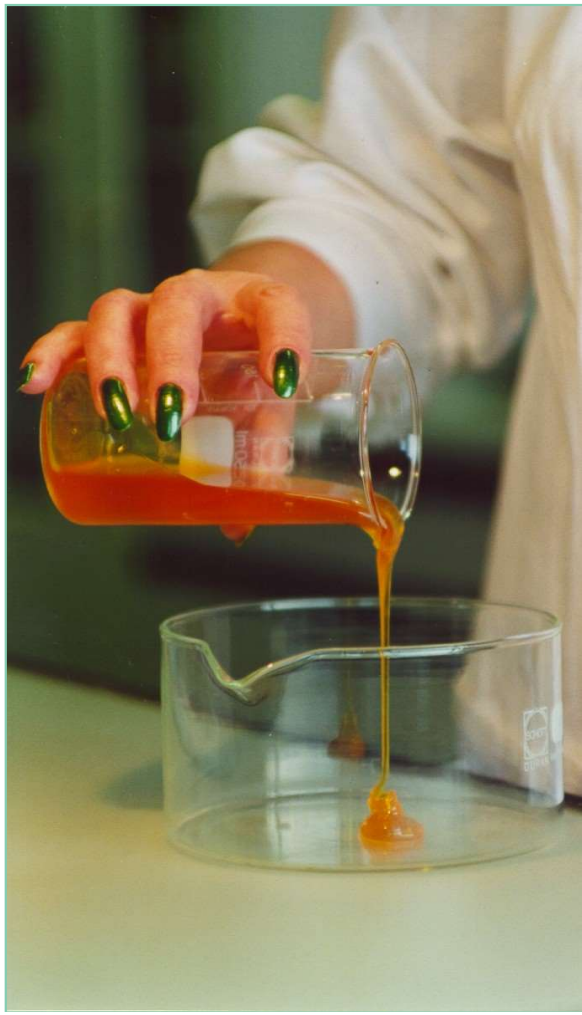
$$\mathbf{2CS_2 + 6NaOH \rightarrow Na_2CS_3 + Na_2CO_3 + Na_2S + 3H_2O}$$

$$\mathbf{Na_2CS_3 + 3\ NaOH \rightarrow Na_2CO_3 + 3NaHS}$$

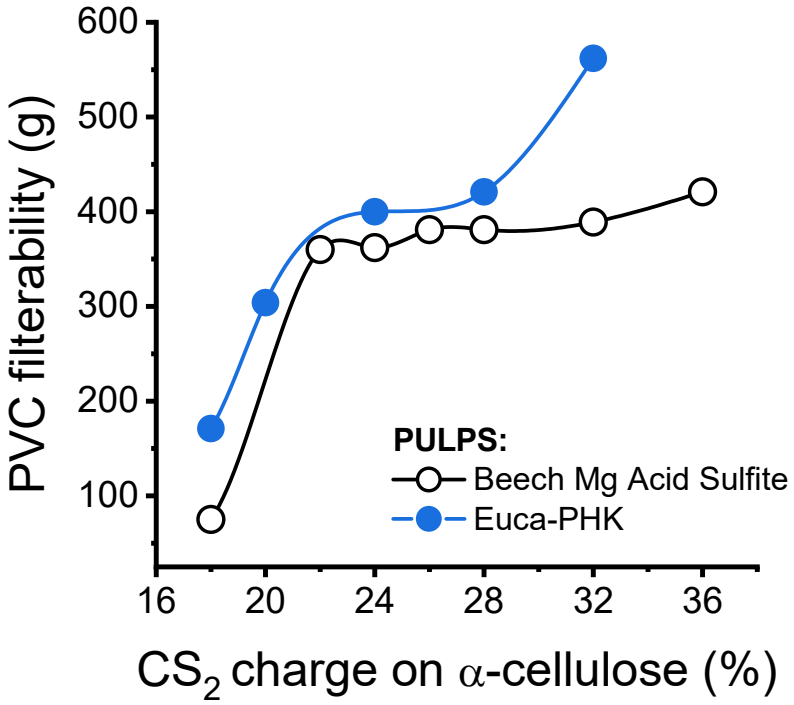
$$\mathbf{CS_2 + 2\ NaHS \rightarrow Na_2CS_3 + H_2S}$$

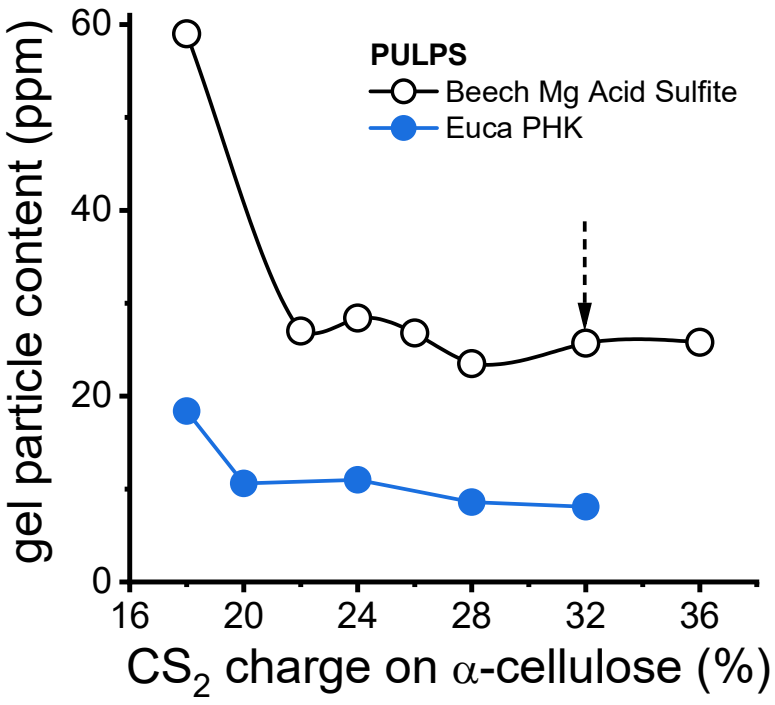
$$\mathbf{H_2S + 2\ NaOH \rightarrow Na_2S + 2H_20}$$

Xanthogenate decomposition and side reactions increase the electrolyte content during ripening; this affects the structural properties of the viscose. Elastic properties of the viscose increase Trithiocarbonate provides the orange color of the viscose



Effect of CS_2 charge on Viscose Quality





Only CS_2-charge modified. Alkali ratio constant (0.6)

High-purity pulps allow a lower CS_2 charge

Viscose Composition & Quality

Modal Viscose (CMD)

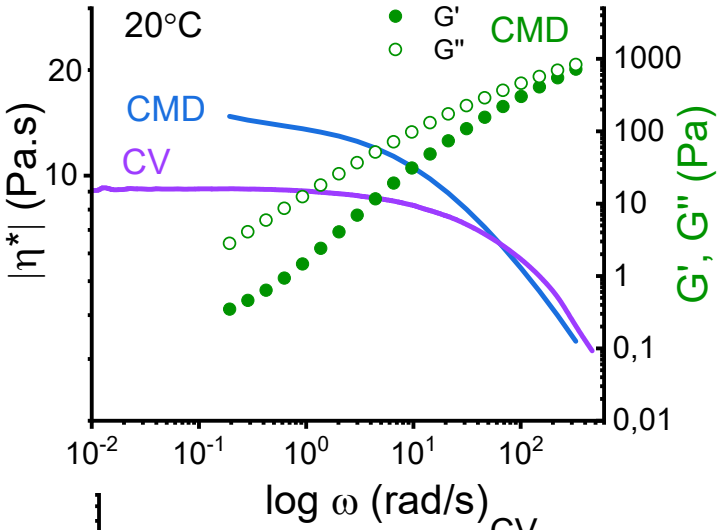
Parameter	Unit	CMD_{fresh}	stdev	CMD_{spin}	stdev
Cellulose	%	5.75	0.19	6.08	0.05
Alkali	%	6.08	0.06	6.10	0.04
Sulfur	%	1.72	0.07	1.85	0.06
$\lvert\eta_0^*\rvert_{20°C}$	Pa.s			14.7	
$tan\delta_{1\,rad/s}$				8.5	
γ-value	%	66.5	1.8	62	1
Ball fall	s	133		121	
Filterability	PVC	305		440	
Particles	ppm	39.2		5	
NaOH	%	4.65	0.08	4.65	0.04
Na_2CO_3	%	0.25	0.04	0.31	0.03
Na_2S	%	0.16	0.02	0.26	0.01
Na_2CS_3	%	0.32	0.05	0.43	0.03

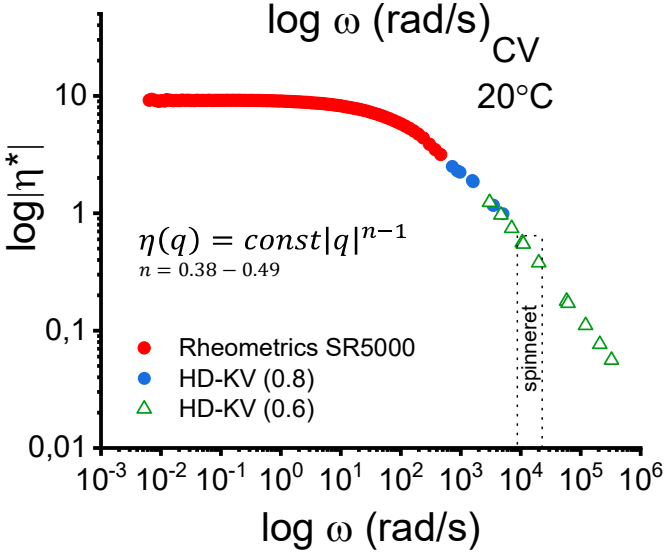
Sixta, H. (2006) unpublished

Regular Viscose (CV)

Parameter		Unit	CV	stdev
Cellulose	spin	%	8.77	0.15
Alkali	spin	%	5.26	0.12
Sulfur	spin	%	2.41	0.04
$\lvert\eta_0^*\rvert_{20°C}$	spin	Pa.s	8.6	1.4
$tan\delta_{1\,rad/s}$	spin		16.3	5.2
γ-value	fresh	%	50	1
Ball fall	spin	s	69	6
Filterability	spin	PVC	156	22
Particles	spin	ppm	12	1
NaOH	fresh	%	2.89	0.03
Na_2CO_3	fresh	%	0.56	0.02
Na_2S	fresh	%	0.45	0.09
Na_2CS_3	fresh	%	0.68	0.03

Rheology: frequency sweep

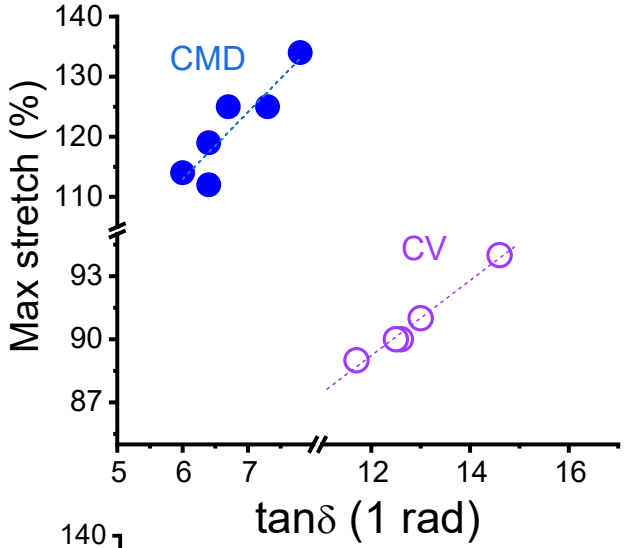


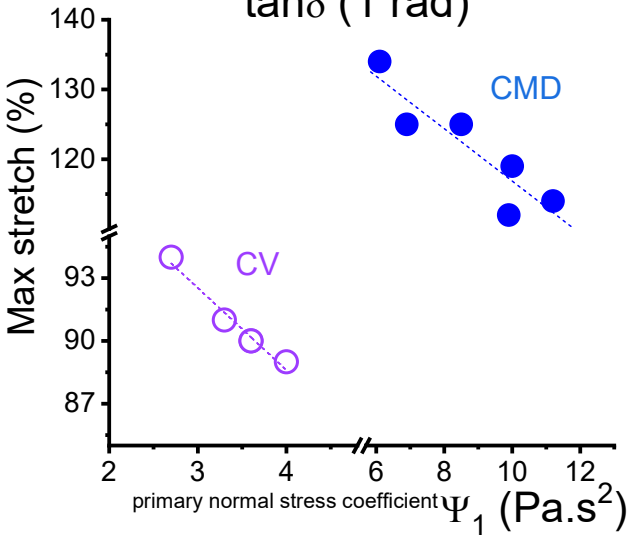


CMD-Viscose has higher $|\eta_0^*|$ than CV

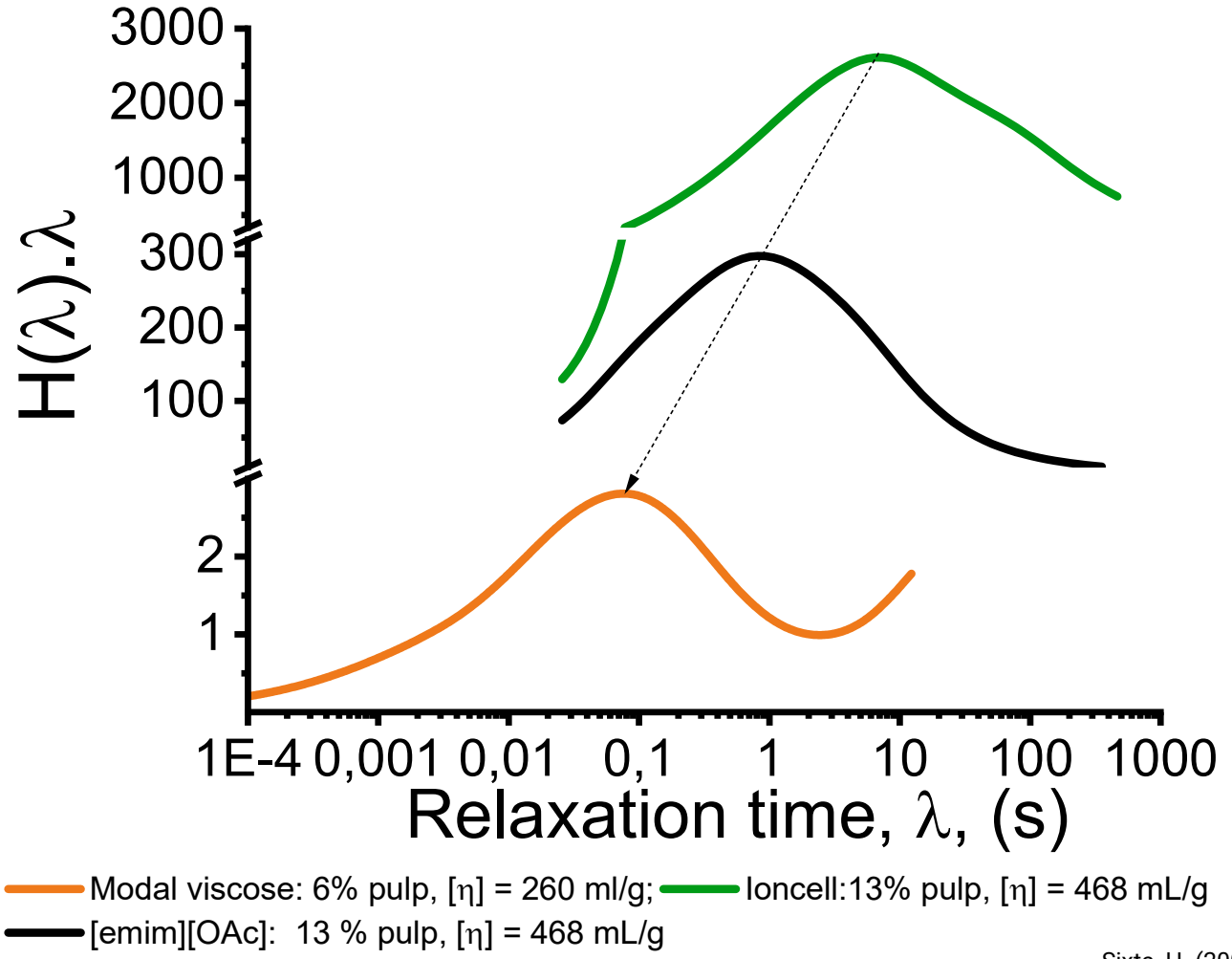
Higher $tan\delta$, lower ψ_1 are favorable for spinning

Sixta, H. (2006) unpublished





Relaxation time spectrum



Sixta, H. (2006)
unpublished

Relaxation time spectrum from frequency sweep measurements

Shift to lower relaxation times reveals reduced elastic & more viscose behavior

Ripening

After first filtration ripening starts; viscose is stored in ripening containers for hours at lower temperature.

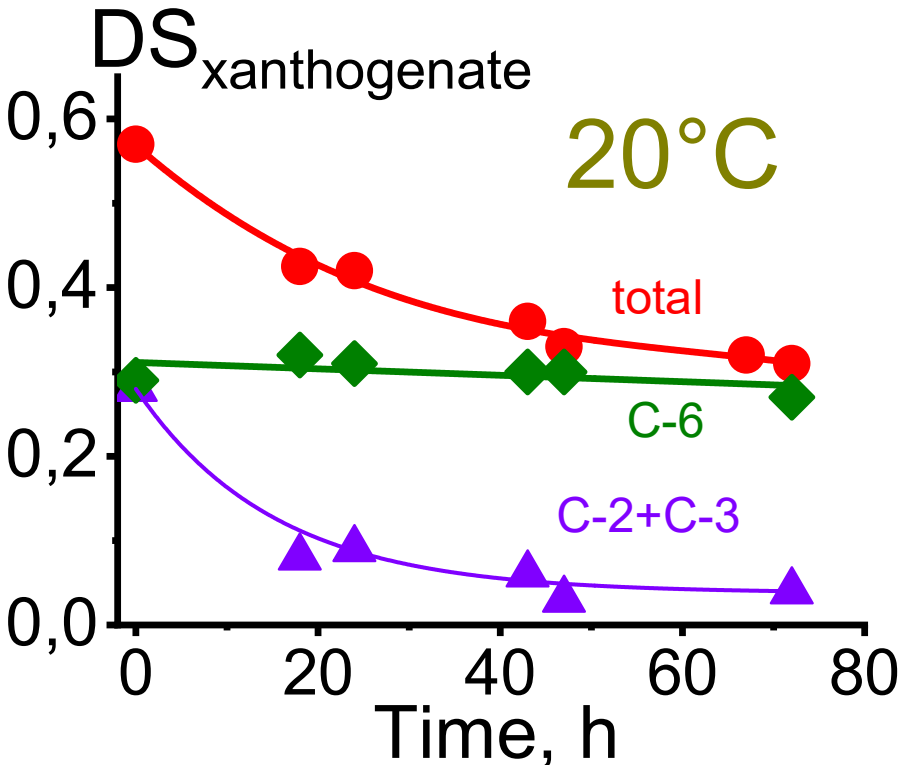
Purpose: Improvement of coagulability and achievement of colloidal chemical maturity

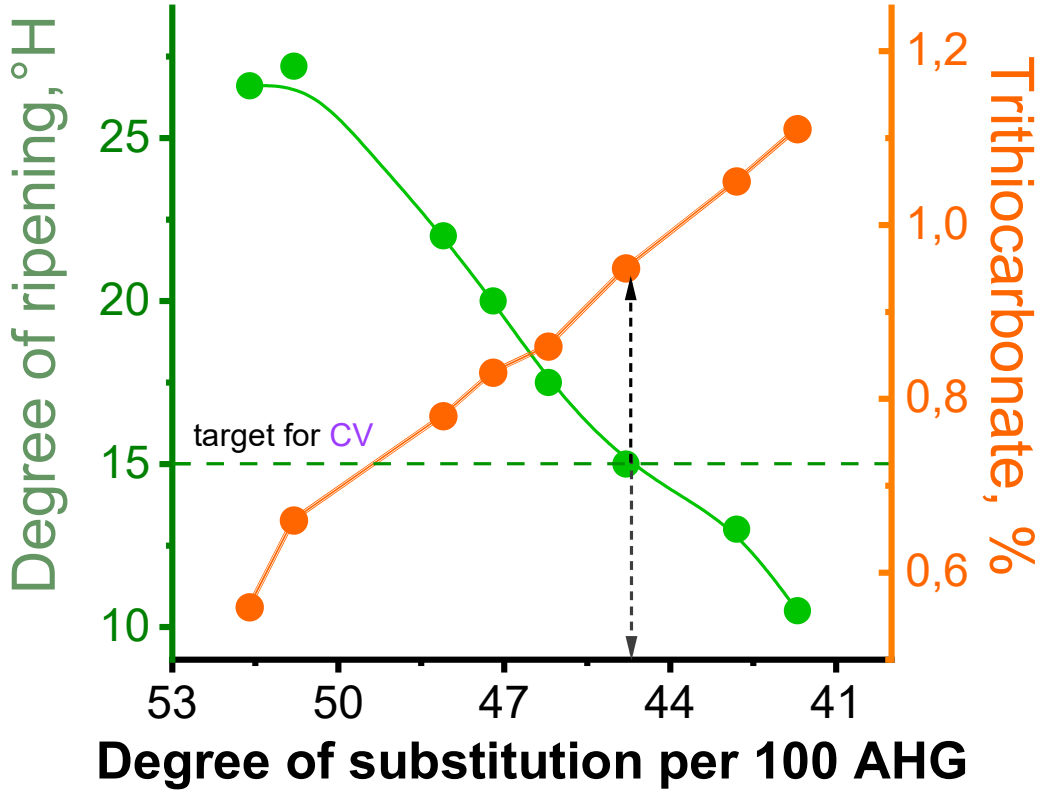
With increasing ripening time, the readiness for coagulation improves→ increase in adhesion points, size of dispersed particles due to association and aggregation

Ability to coagulate the viscose determined by the amount of electrolyte solution (NH_4Cl) necessary to coagulate viscose

Colloid chemical ripening is clearly controlled by the course of chemical ripening, i.e., **the degree of xanthogenate group cleavage.**

Ripening

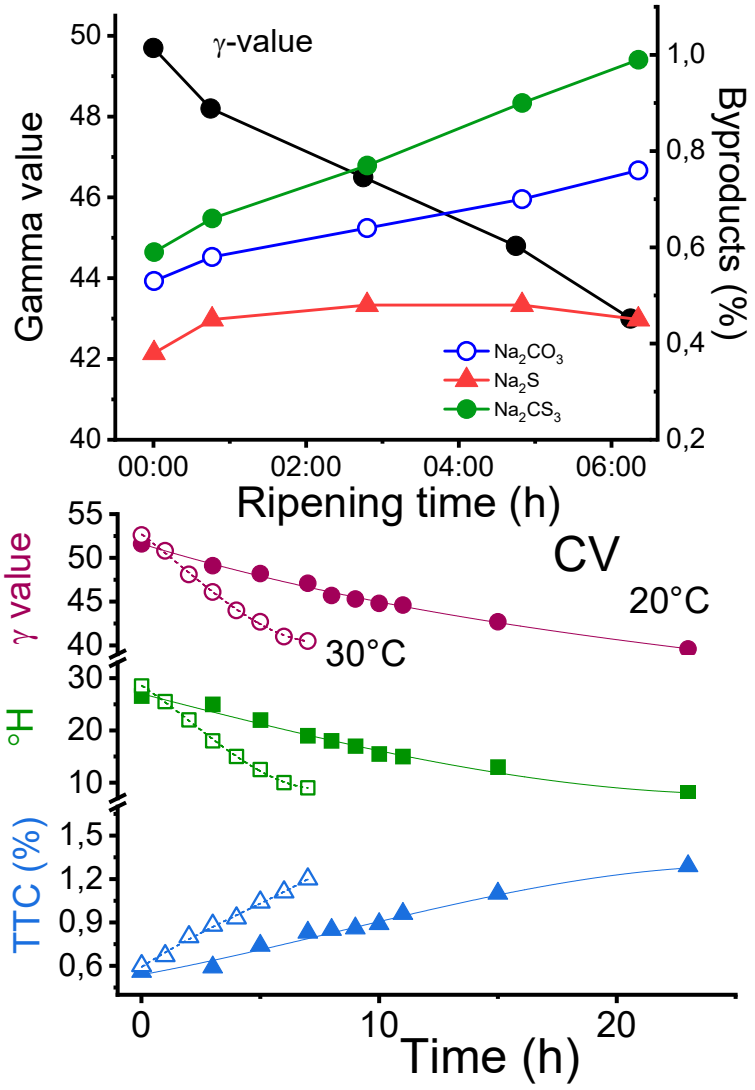


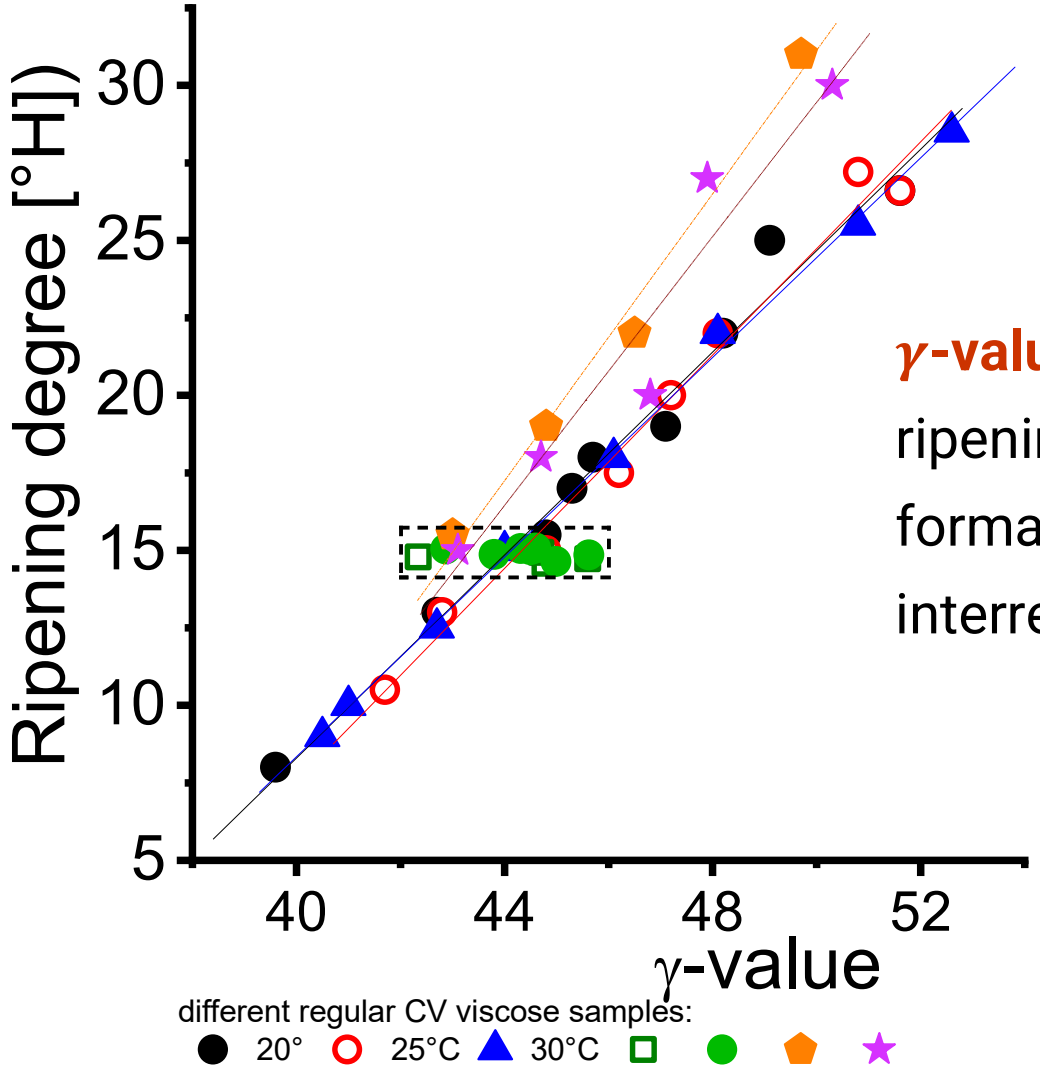


Target γ-value for regular viscose = 50-70 to achieve the colloid chemical ripeness (°H = 11-15)

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

Ripening: colloidchemical changes





γ-value, degree of ripening, **°H**, and **TTC** formation interrelated

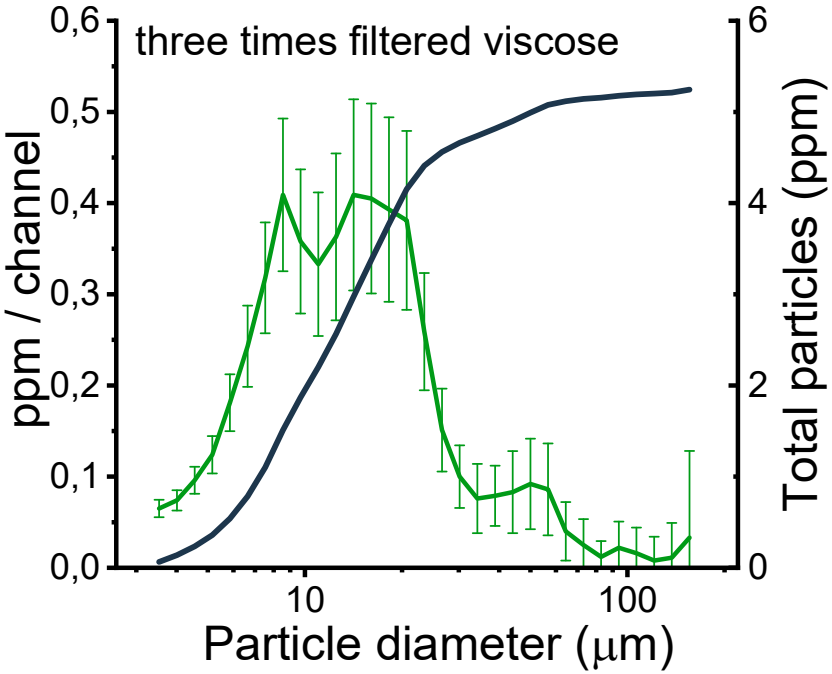
Deaeration, Filtration

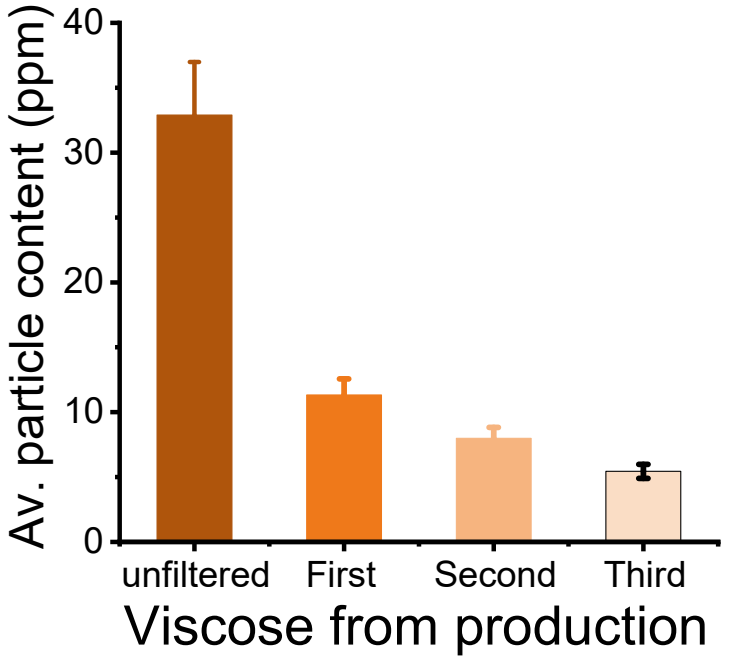
Viscose flash deaerator to remove air removal: boiling under vacuum. $v_{dearation} \propto g \cdot \rho \cdot d^2/12\eta$ (Pakschwer and & Kamyshan). d… air bubble diameter

Viscose filtration: particle removal by means of depth filtration with reject removal in three sequential stages

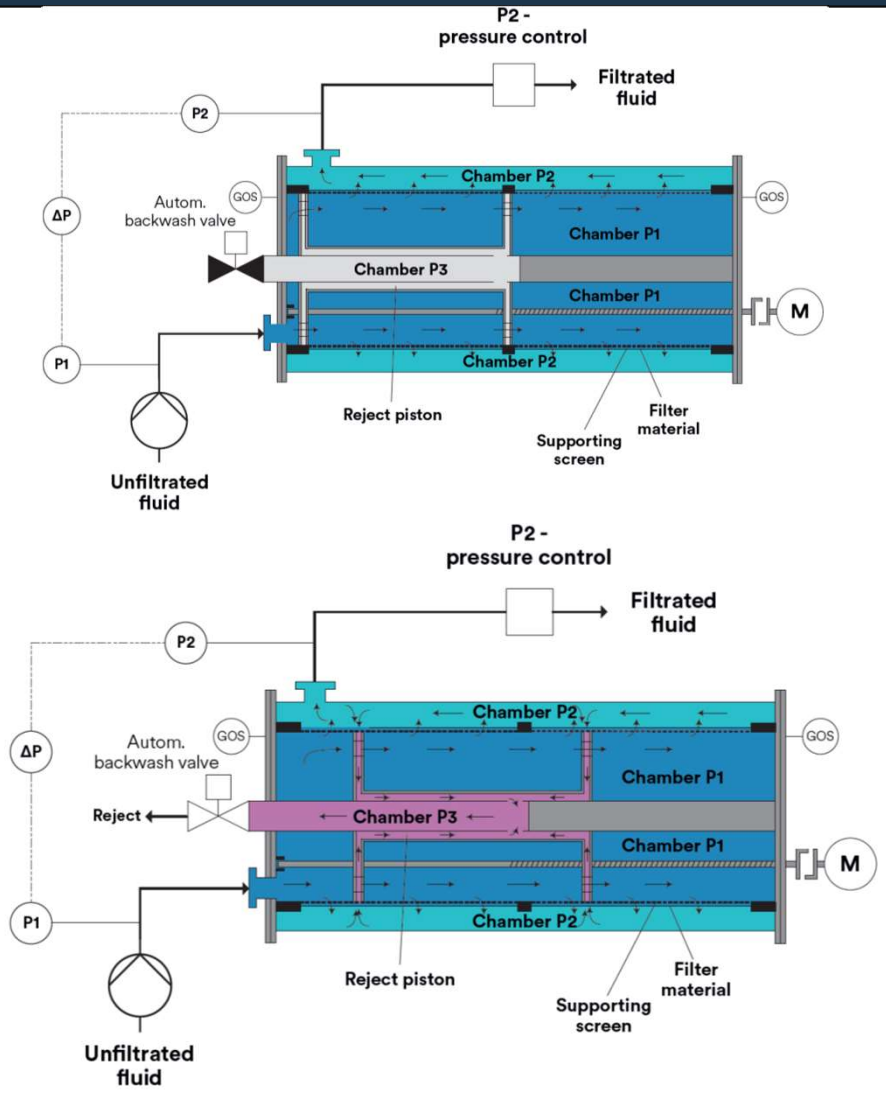
$$\frac{m}{t} = S_0 - S_0 \frac{k}{2} m$$

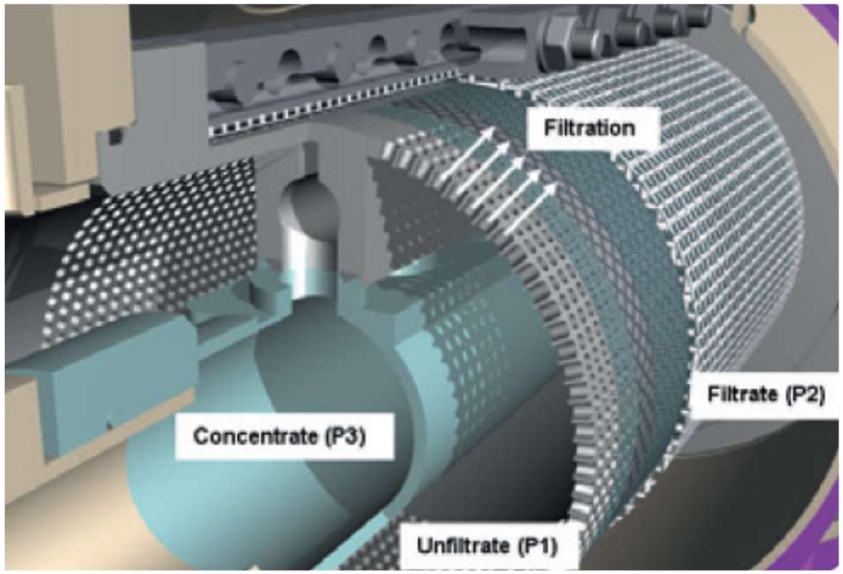
S_0… initial filtration velocity, m/t





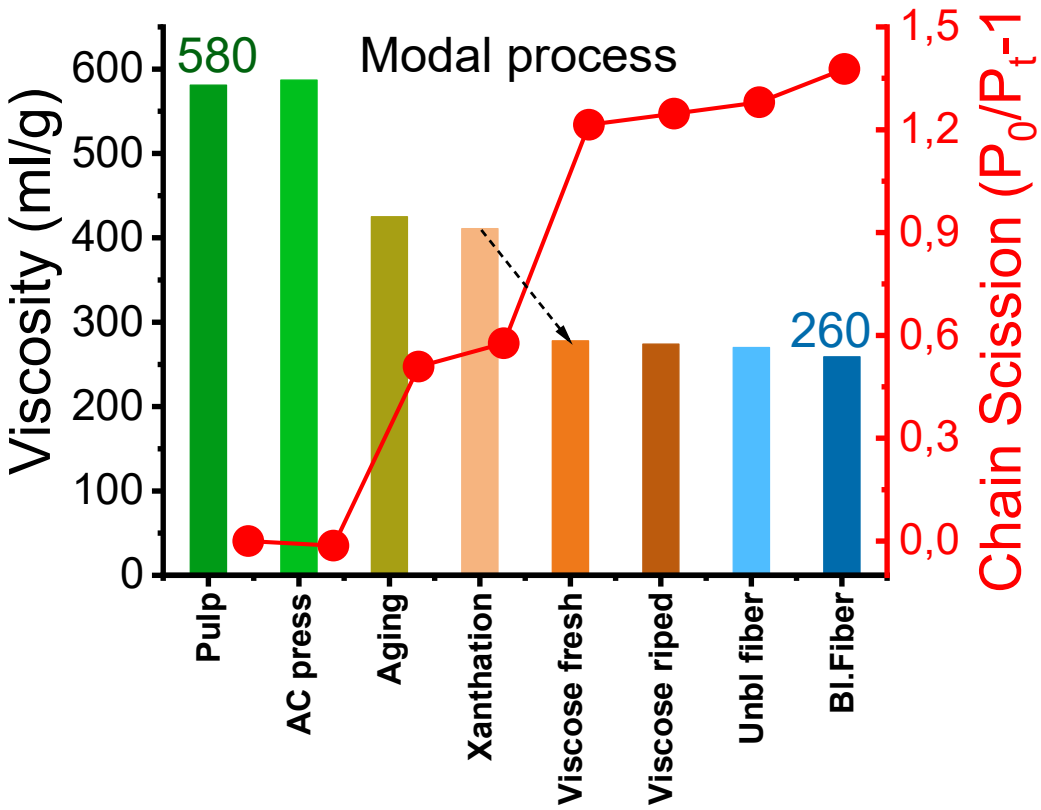
Depth filtration: KKF Filters

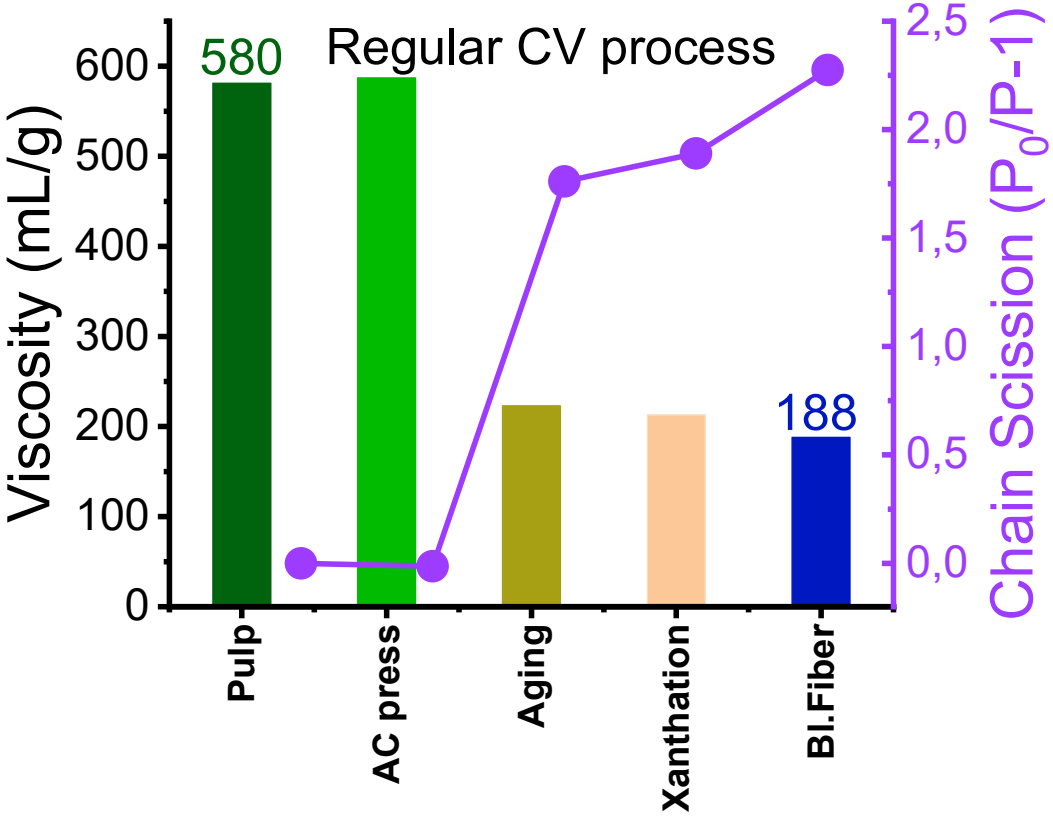




Lenzing Technik, Filtration and Separation Technology

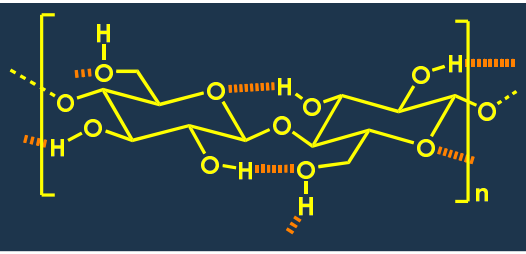
DP profile of cellulose

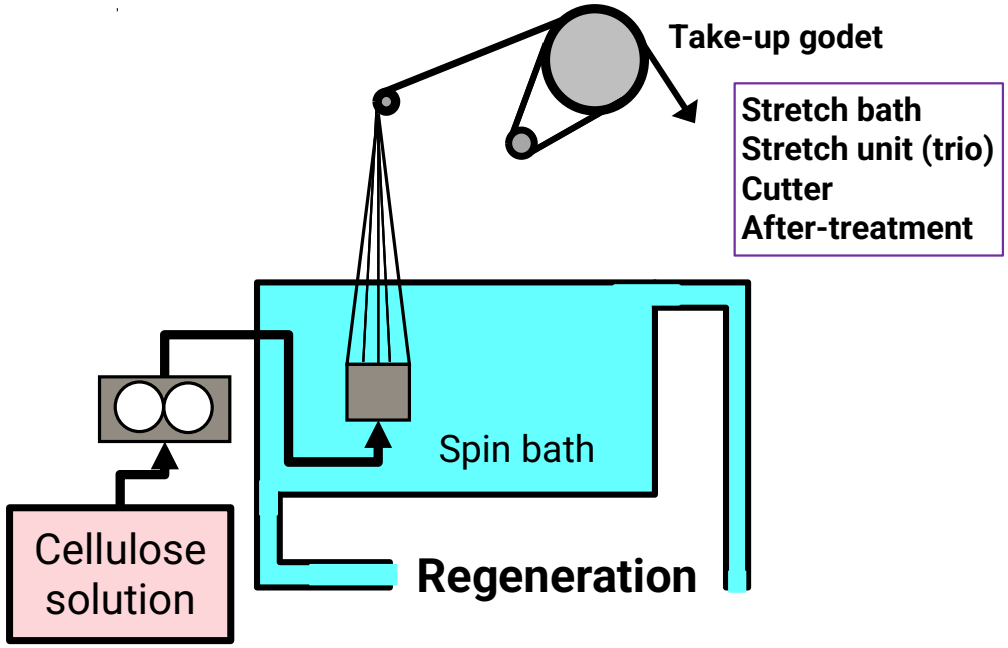


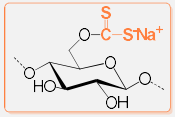
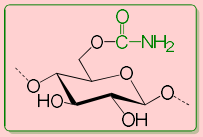
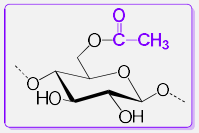
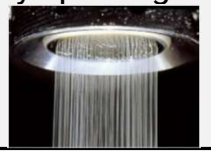


Significant DP degradation (wanted) during aging and xanthate dissolution in case of Modal (unwanted)

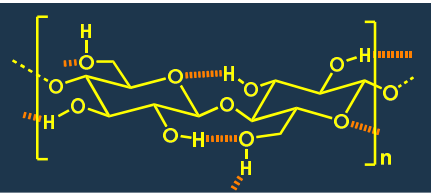
Wet Spinning-2





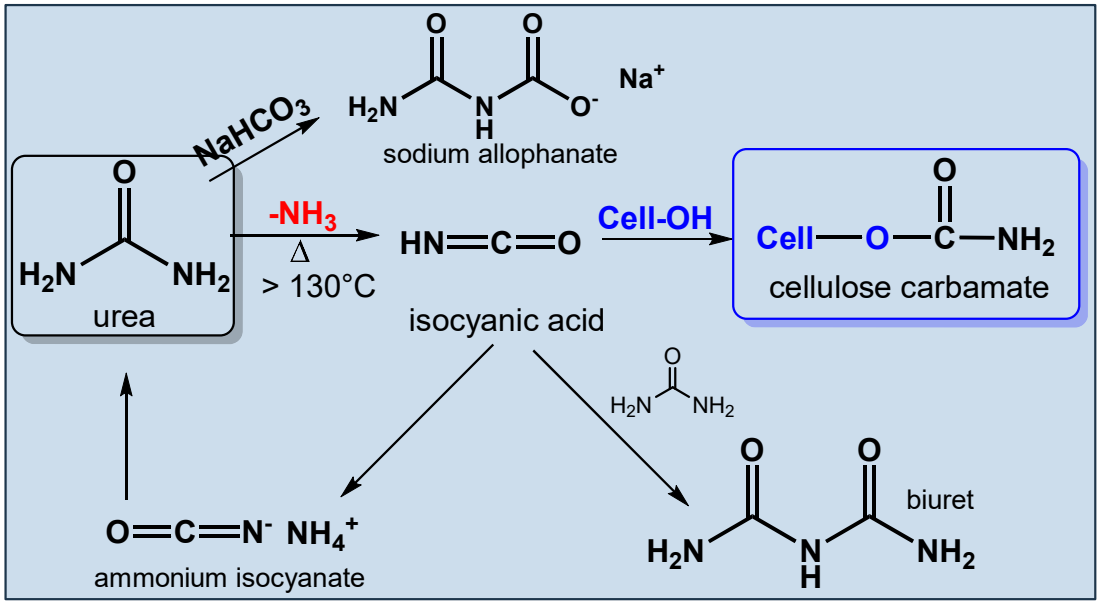
PROCESS	Dissolution	Regeneration	Reference
Viscose 	NaOH, CS_2, (Additives)	H_2SO_4, Na_2SO_4, $ZnSO_4$	Lenzing AG, Kelheim
Carbamate 	Urea, NaOH, ZnO, (H_2O_2)	H_2SO_4, Na_2SO_4	ACS Sustainable Chem. Eng. 2014, 2, 2363−2370 ACS Sustainable Chem. Eng. 2015, 3, 1510−1517 Journal of Cleaner Production 222 (2019) 871
Acetate 	• 2.5 Acetate (CDA) • Dissolution in acetone	CDA in acetone, Dry spinning 	Cellulose Acetates: Properties and Applications (2004) (Ed. P.Rustemeyer) ISBN 3-527-31041-x

Cellulose Carbamate



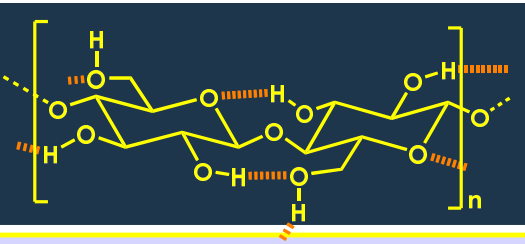
1. **Environmentally friendly alternative to Viscose technology (end of 1970s)**
2. **Pioneers: Hill, J.W. and A. Jacobson, DuPont (1937)**[1]: Cellulose dissolved with a N-content of 1-3.5%
3. **Segal, L; Eggerton, F.V**[2]: first describes the reaction product with urea cellulose carbamate
4. **Neste Oy (Kemira Sateri Oy): Successful laboratory trials 1982**[3]
5. **Challenge: Impregnation, activation**
   $NH_{3,\ liquid}$ (Cellca); super-criticalCO_2, alkali-cellulose; mechanical activation (ball mill, hammer mill); enzymatic activation; reactions in organic media, *e.g.*, xylene at 80°C-140°C (CarbaCell); microwave heating, **Conventional heating ~170°C, 2h**.

Chemistry of urea and carbamate

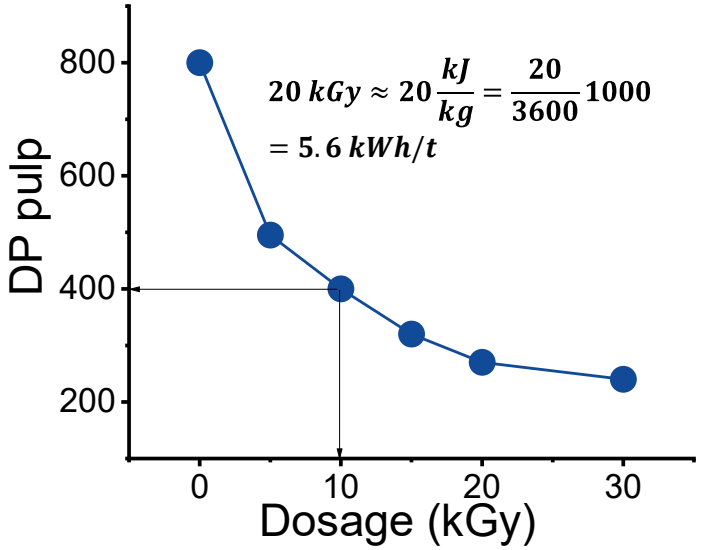


[1]*US2,134,825; US2,134,825* [2]*Segal, L.; Eggerton, F.V. Text. Res. J. (1961), 31, 460*
[3]*Finnish Patent 61,033 (1982), Lenz. Ber. (1984), 57, 38-40; Lenz. Ber. (1985), 59, 111-117*

Cellca Process from Neste Oy



DP adjustment bei EBeam



- DP adjustment is important because the DP strongly influence the rheology.
- E-beam treatment is simple and cost-effective and is suitable for recycling white cotton waste (hospital linen).

Impregnation of DP adj. pulp:

Liquid ammonia at -35°C, immersion with a 10% (w/w) urea solution→ drained→ dried first RT, then at 100°C

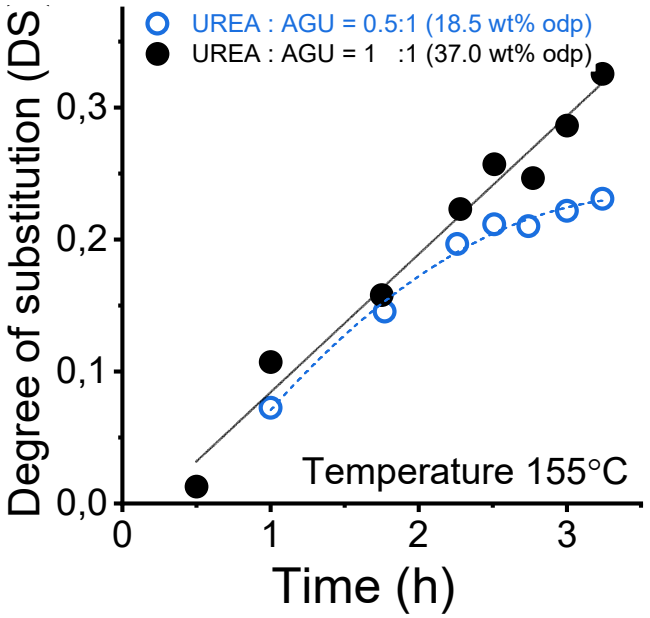
Reaction rate

155°C, 1 to 3 hours, with varying molar ratios of **urea: cellulose: 0.5-1.0**.

Reactions are first order & endothermic: **80 kJ** per substituted carbamate group

Biuret formation with increasing T

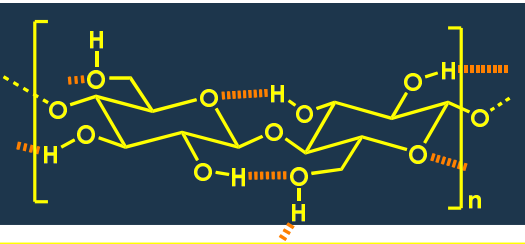
$$DS = \frac{162 \cdot N\%}{(14 - 43 \cdot N\%)}$$



DS of 0.15 to 0.25 is sufficient to obtain a good spinning solution

Ekman, K.; et al, Modification and Hydrolysis, John Wiley & Sons: New York, 1986; pp 131_148.

Cellca Process from Neste Oy



Effect of ZnO

Addition of zincate (ZnO) enhances dissolution and filterability of the CC solution and retards gelation

Spinning dope

Typical composition:
5-7 wt% CC; 7-9 wt% NaOH,
ZnO 1-1.6 wt%, DP = 400 – 600,
DS 0.15-0.25

Spinning

Diameter of spinneret orifices 50-80 µm; spin bath: H_2SO_4 / Na_2SO_4 preferred; DS of the fibres halved due to hydrolysis in the dope.

Carbamate analysis

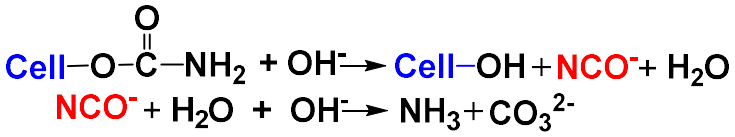
IR: λ at 1715 cm^{-1}→ $\nu_{stretch} C=O$; $\frac{\nu_{1715}}{\nu_{1315}} \propto with\ N\%$

^{13}C-NMR: 168.5 ppm, C6 is shifted downfield

FIBER Property		Stretch		
		50%	75%	100%
Titer	dtex	1.8	1.8	1.9
Tenacity-cond	cN/tex	20	25	**30**
Tenacity-wet	cN/tex	11	15	17
Wet modulus	cN/tex	60	80	120
Elongation-cond	%	20	17	**15**
Elongation-wet	%	19	16	12

Carbamate stability

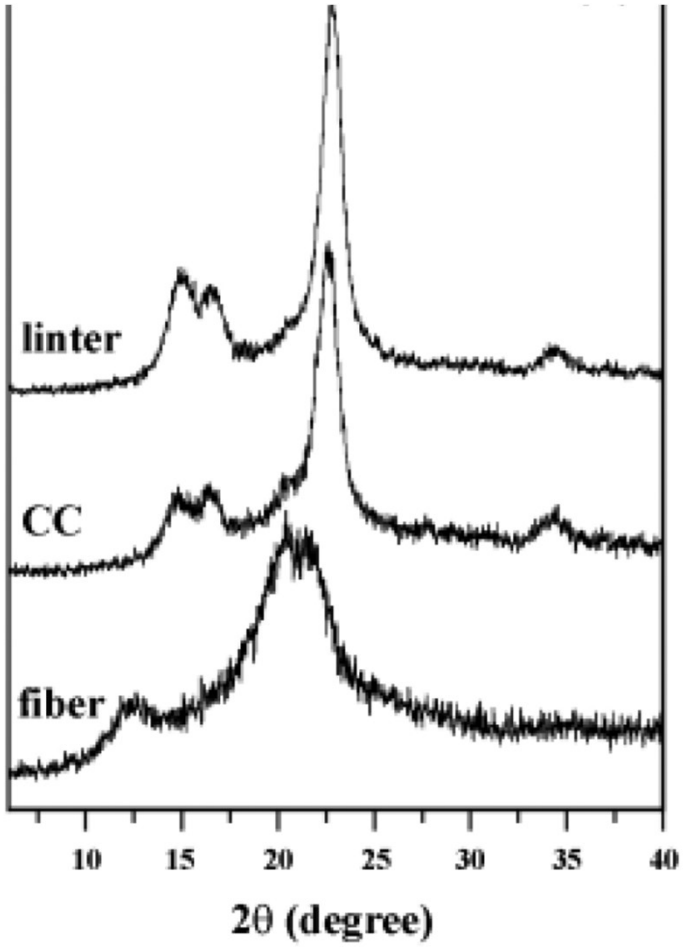
Quite stable under acidic conditions
Alkaline hydrolysis efficient:



FIBER Property		3min NaOH treatment			
		NO	0.75%	3%	4%
Tenacity cond	cN/tex	24.0	24.0	23.0	22.0
Tenacity-wet	cN/tex	9.0	12.0	12.0	11.0
Elong-cond	%	10	11	15	15
Elong-wet	%	15	15	14	14
Nitrogen	%	1.2	0.4	0.18	0.14
DS	%	**0.14**	**0.05**	**0.02**	**0.02**
DP Fiber		310		305	

Ekman, K.; et al, Modification and Hydrolysis, John Wiley & Sons: New York, 1986; pp 131_148.

Crystalline structure of Cellulose

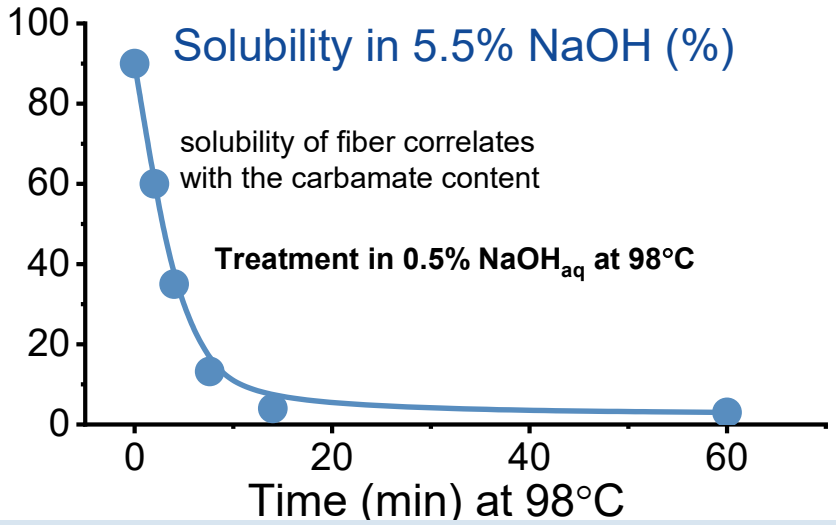


ACS Sustainable Chem. Eng. 2014, 2, 2363−2370

- CC showed unchanged Cellulose Iβ crystalline form.
- Chemical derivatization did not change the lattice of cellulose Iβ
- A slight decrease in crystallinity, χ_c, from 72% (CL) to 65% in CC was observed → partial decrystallization
- During subsequent dope preparation and cellulose regeneration into fibers, the crystal structure changes to cellulose II

Fiber Post-Treatment

About half of the original carbamate groups are retained in the fibers after treatment in sulfuric acid spinbath



Carbamate groups hydrolyse more easily in alkaline media, e.g., **$NaOH_{aq}$ in a subsequent step:**

- Wet tenacity and conditioned elongation increase
- Wet elongation decreases
- With the removal of the carbamate groups to a N content of 0.2%

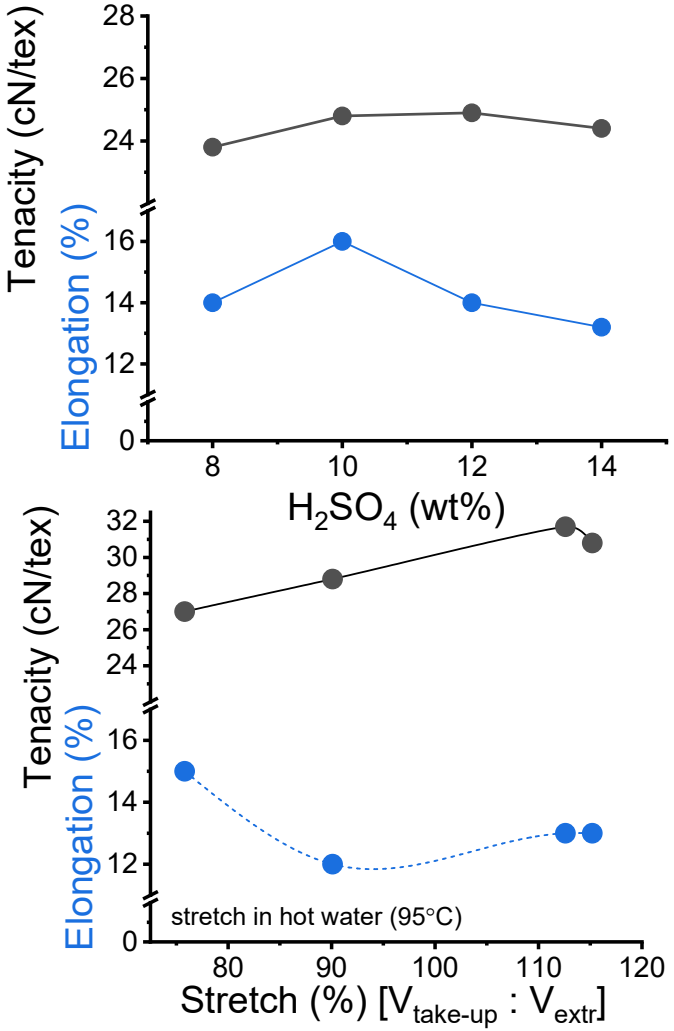
Spinning in salt solutions

Additives to the spin bath seem to affect the fiber properties significantly:

Substrate	Titer	σ	ε	Wet modulus
In spinbath	dtex	cN/tex	%	cN/tex
$NaHSO_3$	2.8	21	4	140
$Al_2(SO_4)_2$	2.7	20	14	40
Na_2CO_3	2.7	21	7	80
70 MeOH 30 Water	2.6	23	4	170

Lenz. Ber. (1985), 59, 111-118

Influence on Cellca Fiber Properties



Composition of spin bath similar as for viscose spinning: H_2SO_4 / Na_2SO_4

High H_2SO_4: stable spinning, but stiff fibers

Addition of $Al_2(SO_4)_2$

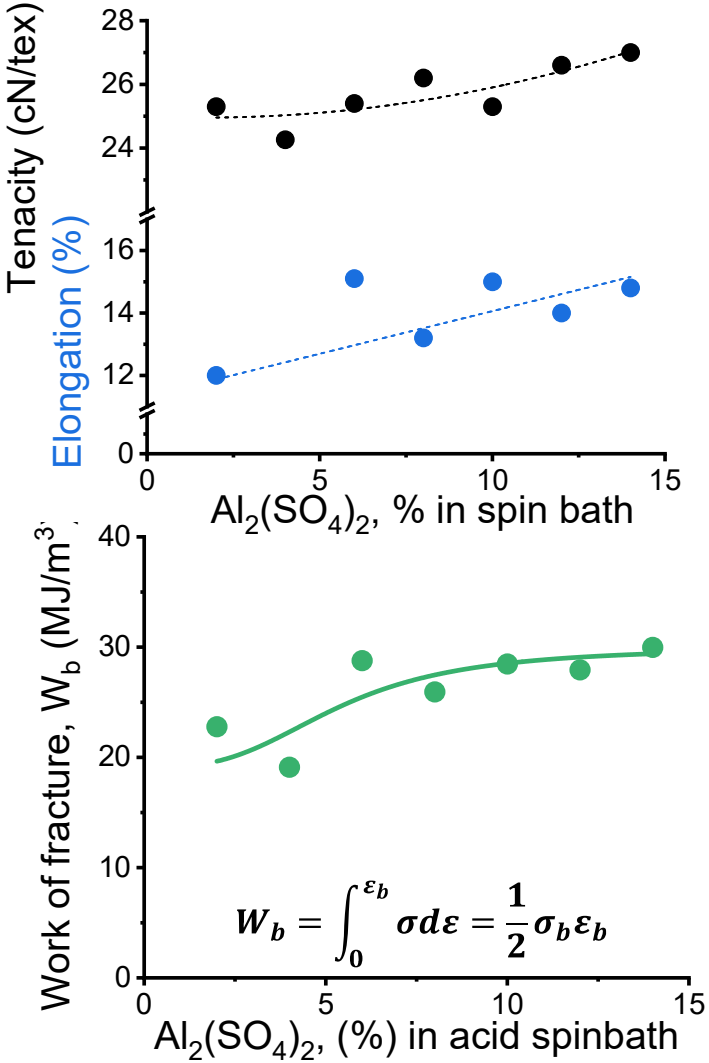
Both stress & strain increase as the Al salt conc is raised.

The cross-section changes from circular to starshaped.

Stretchability

Stretch of CC solution in hot water, 85 - 95°C, to > 110%; tenacity increased up to 30-32 cN/tex.

Use of modifiers as used in viscose spinning had **no effect** on fiber properties

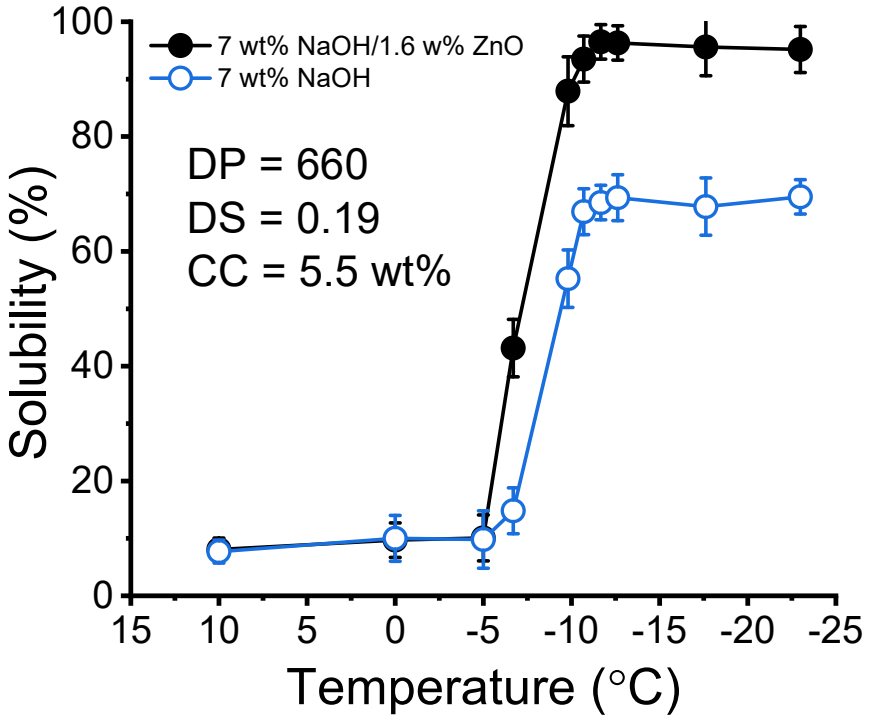


Ekman, K.; et al, Modification and Hydrolysis, John Wiley & Sons: New York, 1986; pp 131_148.

Lenz. Ber. (1985), 59, 111-118

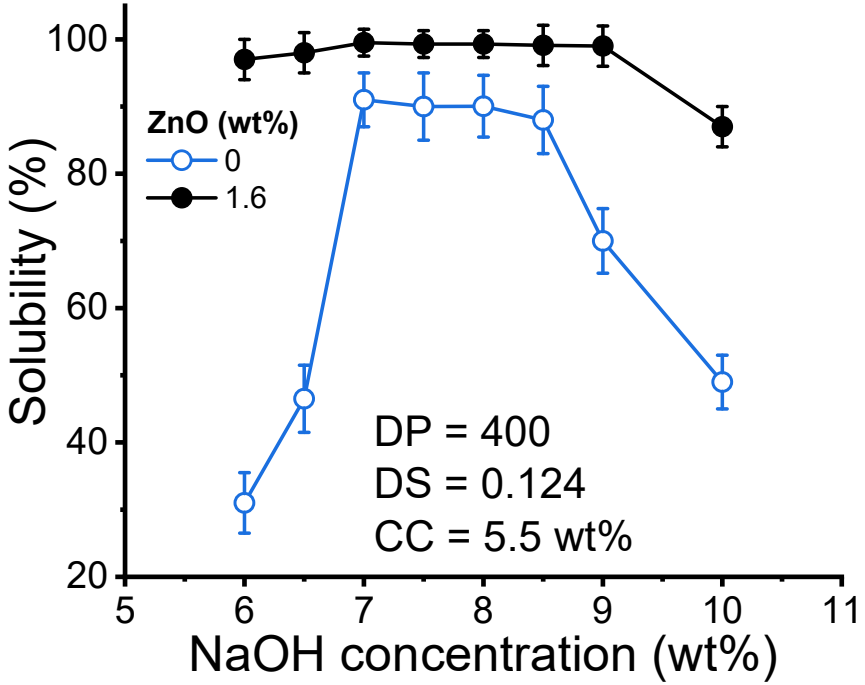
Cellulose Carbamate Solubility

Effect of Temperature



The addition of ZnO to the aqueous NaOH solution decisively increases the solubility of CC

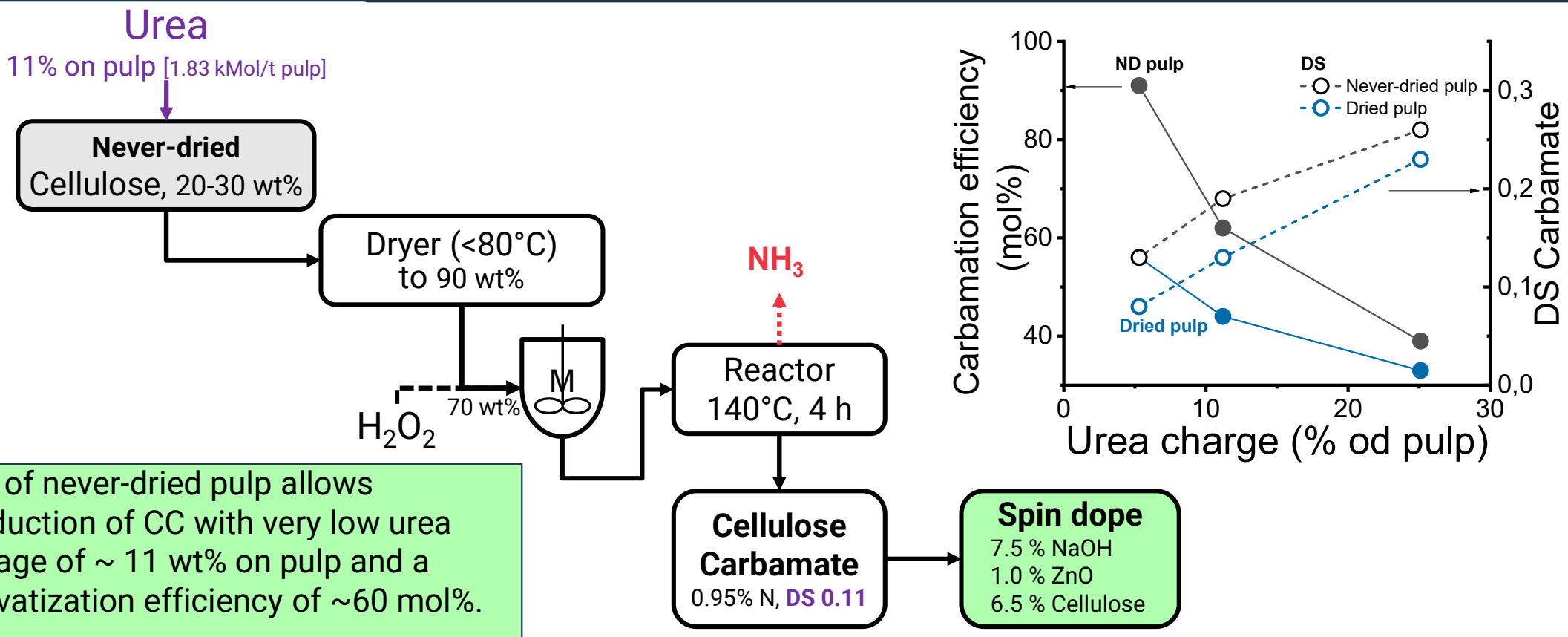
Effect of [NaOH]



With lower DP of CC, e.g., 400, the solubility increases up to 90% even without ZnO

ACS Sustainable Chem. Eng. 2014, 2, 2363−2370

Use of Never-dried pulp (Stora)

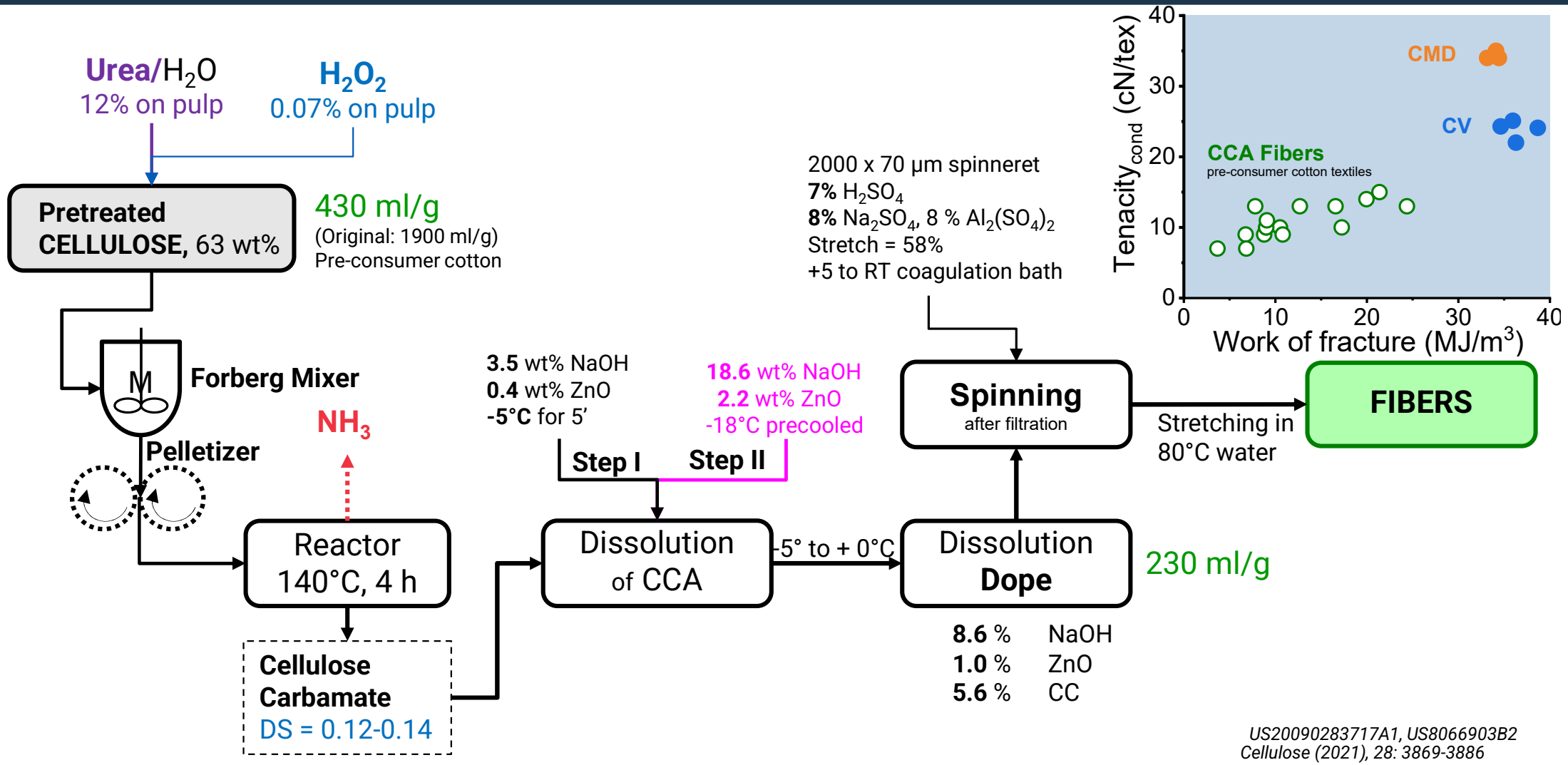


Use of never-dried pulp allows production of CC with very low urea dosage of ~ 11 wt% on pulp and a derivatization efficiency of ~60 mol%.

However, neither spinning results nor the composition and amount of wastewater are available.

WO2015198218, priority 27-06-2014

Infinited CC Fiber Process



US20090283717A1, US8066903B2
Cellulose (2021), 28: 3869-3886

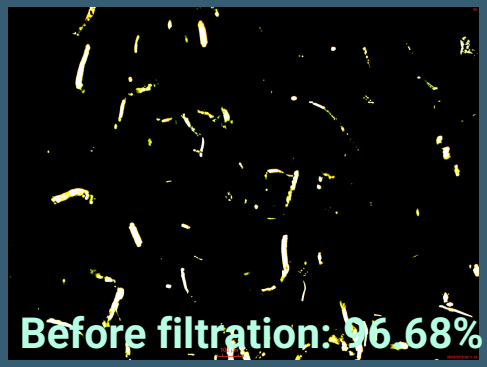
3

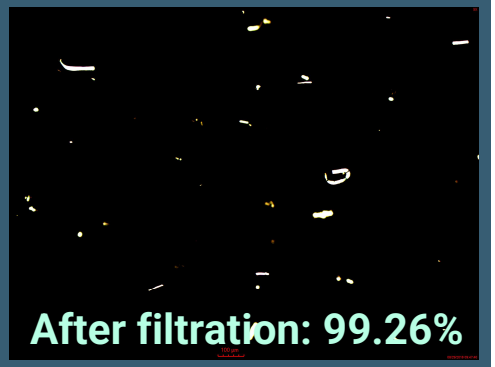
Cellulose solvents

- Overview
- Direct cellulose solvents
- Alkaline aqueous solutions with&without derivatization
- **Assessment of solution state**

Assessment of dissolution by Image analysis

Example cellulose/IL solution

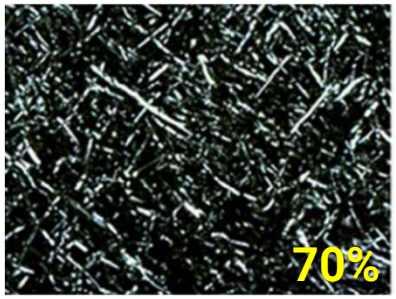


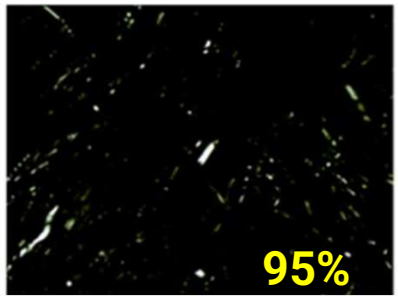


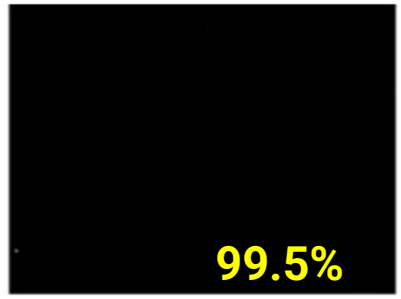
Evaluation by Python script

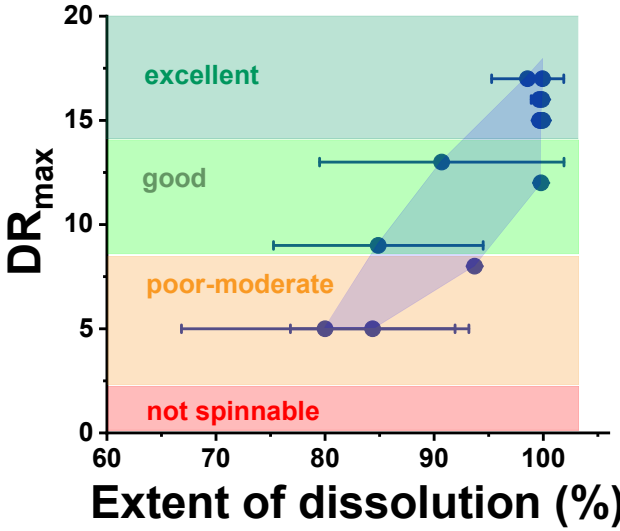
$$dissolution(\%) = 100\left(1 - \frac{\sum_i \sum_j M}{255\ N}\right)$$

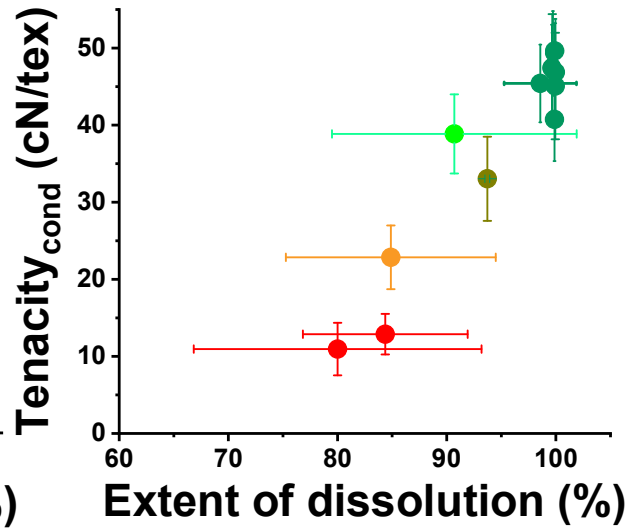
M: matrix of pixels
N: number of pixels











Microscope set to cross-polarized light mode ; glass plates heated to 80°C with 20°C/min; images analyses (5/sample) by **ImageJ software** of by detecting the ratio of the bright (undissolved) to the black (dissolved) areas.

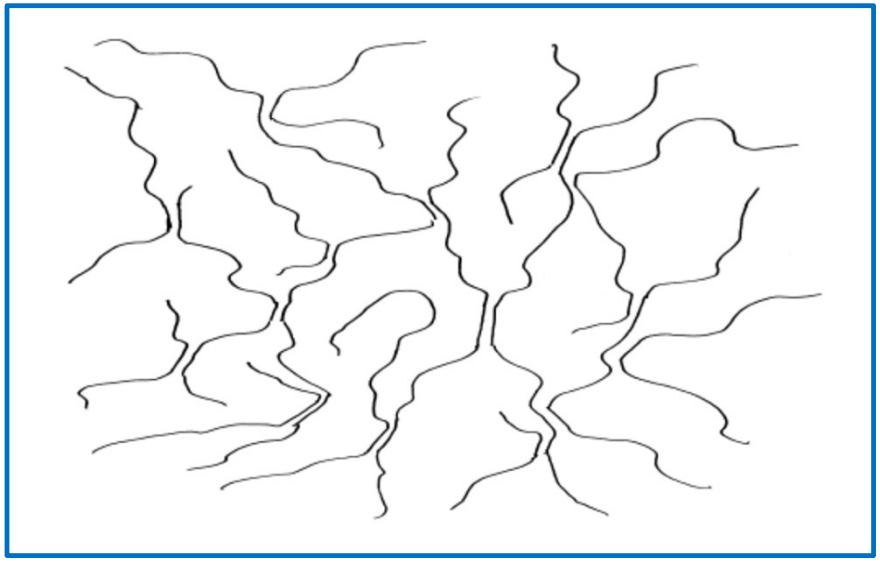
Ind. Eng. Chem. Res. 2020, 59, 20211-20220

Viard, B.; Master's Thesis, PAGORA, AALTO, June 2019

Static light scattering (SLS) of viscose

Viscose solution, diluted 1:9 with water subjected to SLS:
Mw = 4.3×10^6 g/mol, R_G=227 nm

At an average DP of 470 and a DS of 1, it can be estimated that 35 cellulose molecules form one aggregate

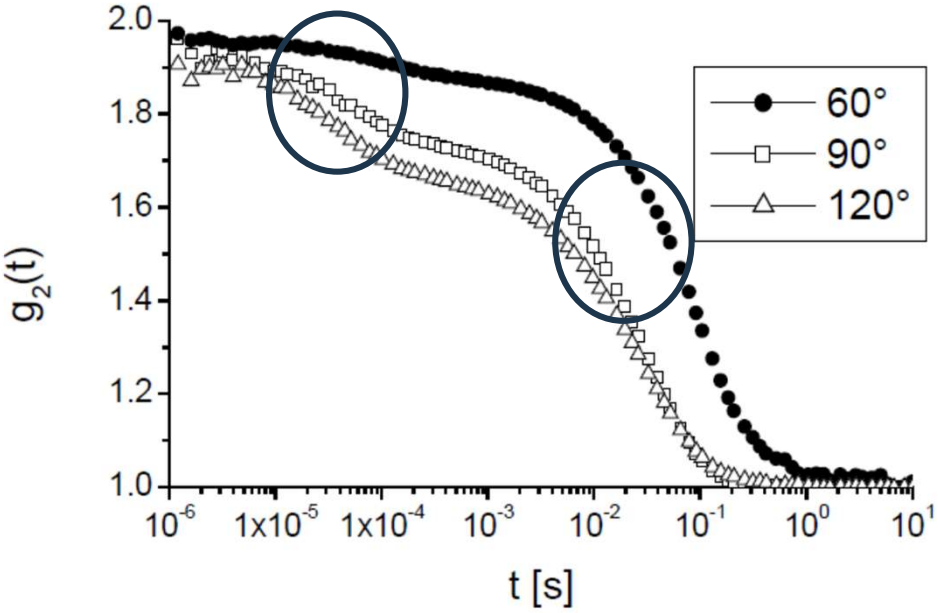


Suggested structure for viscose:

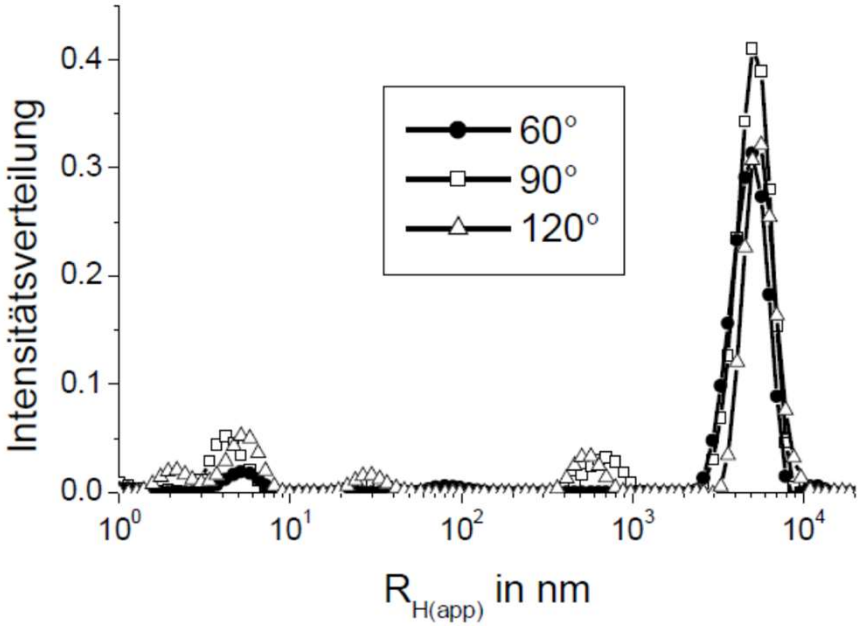
Loose network with gel particles

Lenz Ber, 82 (**2003**), 118-127

Solution structure in technical viscose Dynamic light scattering



Intensity autocorrelation functions of a Modal viscose diluted in water 1:9, DLS at different angles



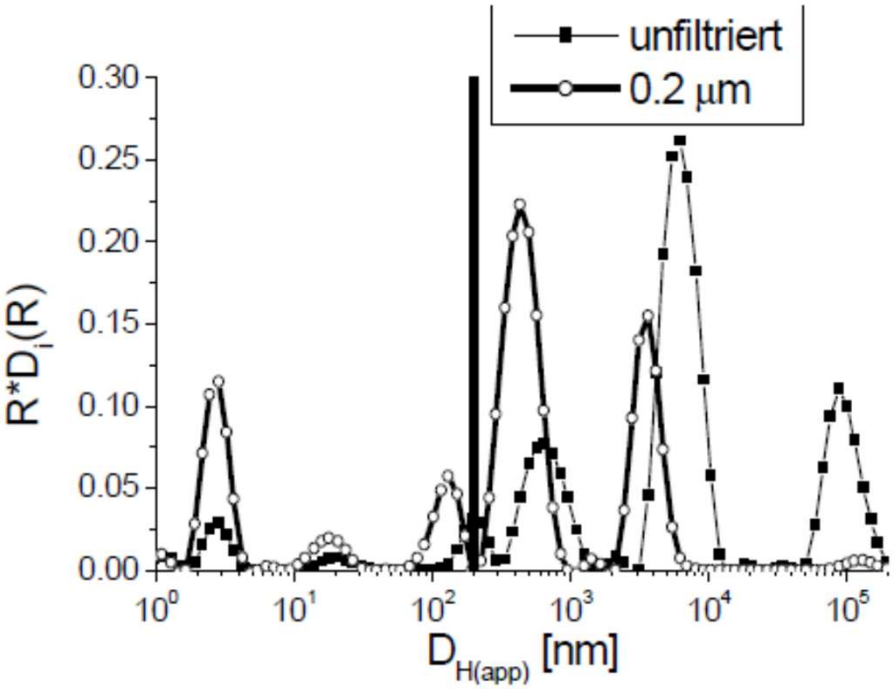
Intensity distributions of the hydrodynamic radii for a Modal viscose

Correlation times between 10^{-5} and 10^{-4} s can be assigned to single molecules, those from 10^{-2} to 10^{-1} s to aggregates with particle sizes up to 80 µm.

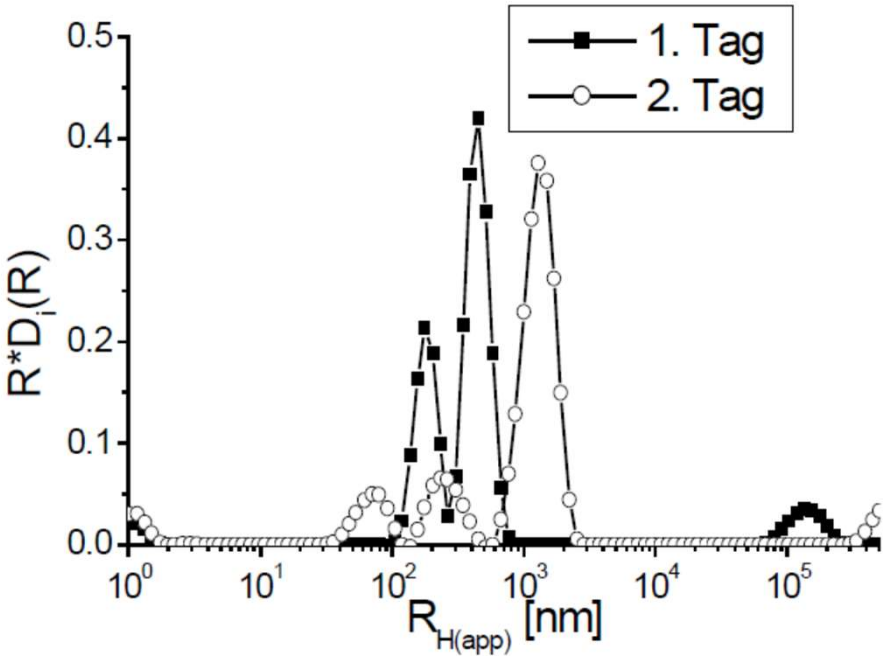
Lenz Ber, 82 (**2003**), 118-127

Particle size in viscose solution

Standard viscose : water = 1:9, 90°



unfiltered and filtered through 0.2 µm diameter: **Aggregates not completely separated by filtration.**



With increasing lifetime, the apparent hydrodynamic radius of the aggregates increases; formation of (visible) gels.

Lenz Ber, 82 (**2003**), 118-127

Pulp Reactivity Determination

Practical Approach

1. **Dissolution behavior**
2. Fibril aggregate dimensions
3. **Viscose Filterability**
4. Cellulose triacetate solution quality
5. Acetylation kinetics.

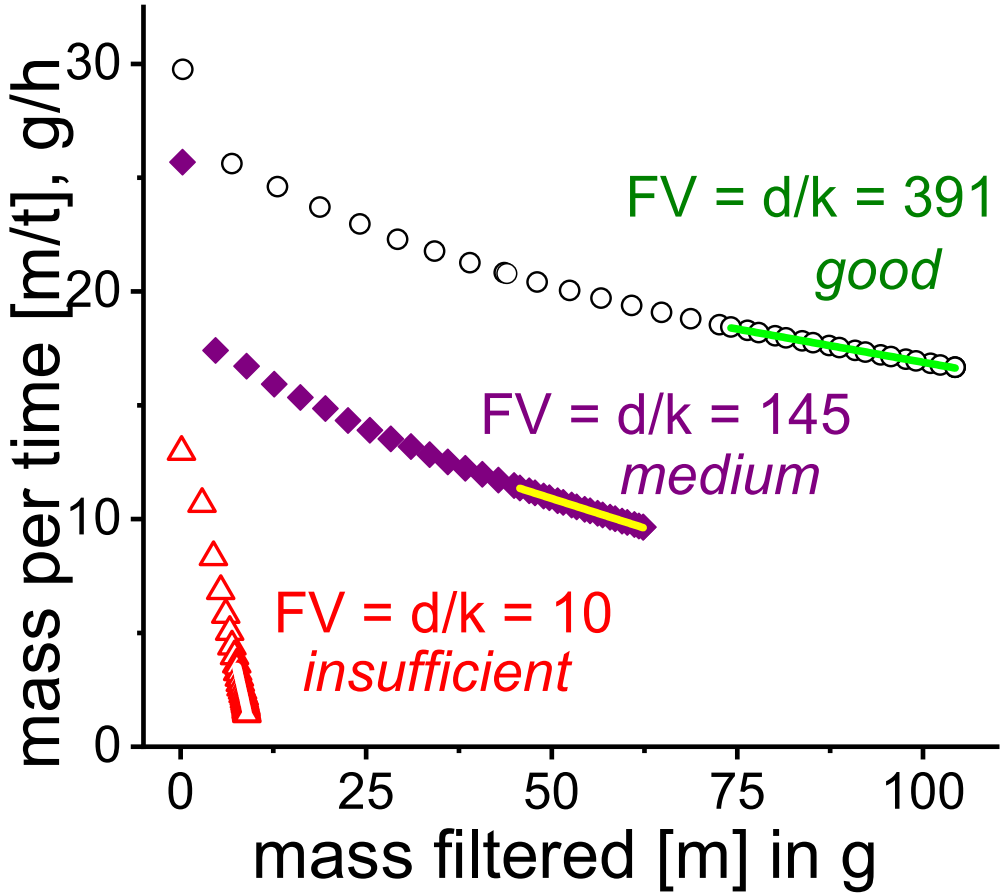
Krässig, H.A. Cellulose . Vol 11. Gordon and Breach Science Publishers, 165-215

Viscose filterability

Viscose Filterability determined by „deep filtration“ where **Standard filtration** law can be applied:

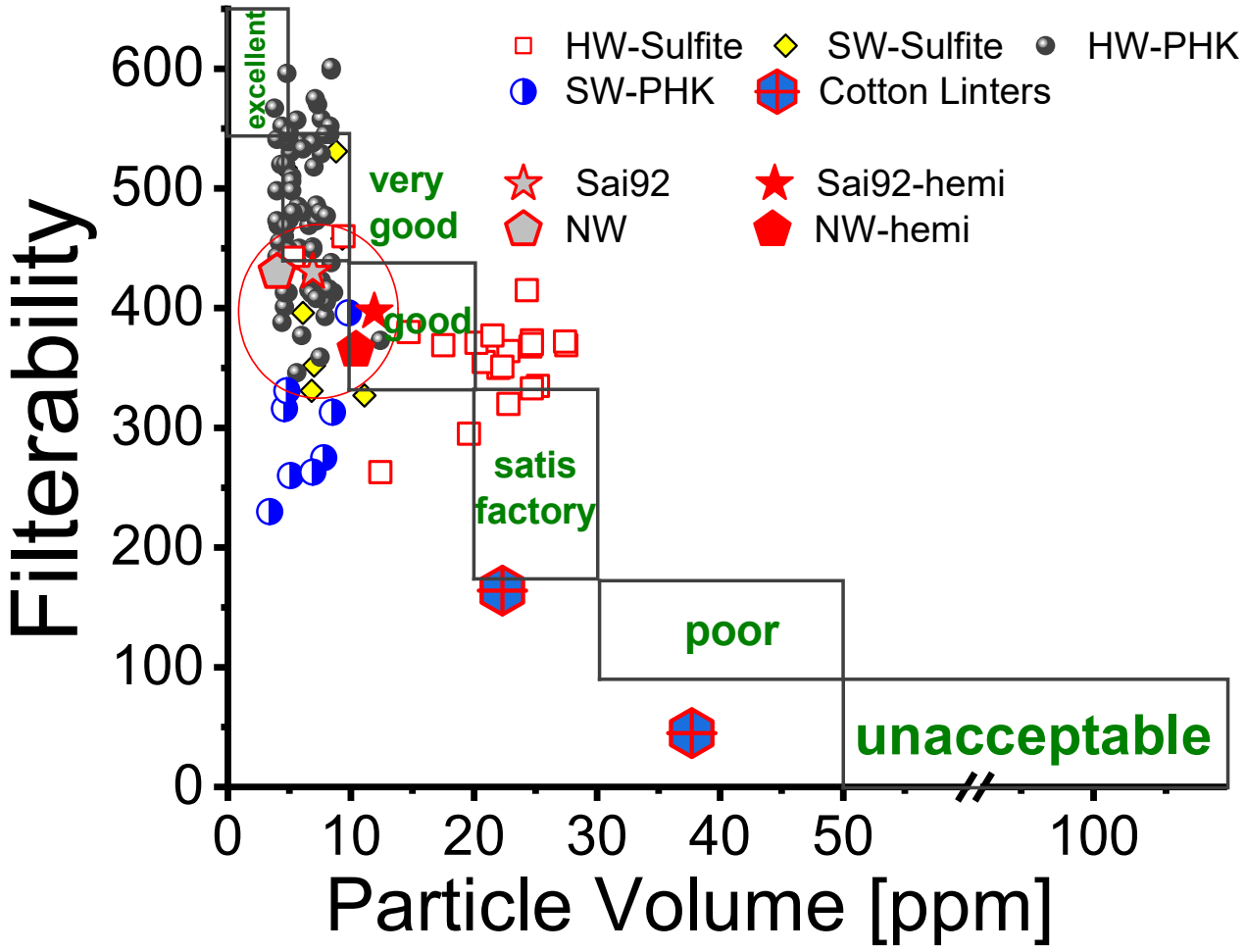
S_0... initial filtration velocity, m/t

$$\frac{m}{t} = S_0 - S_0 \frac{k}{2} m$$



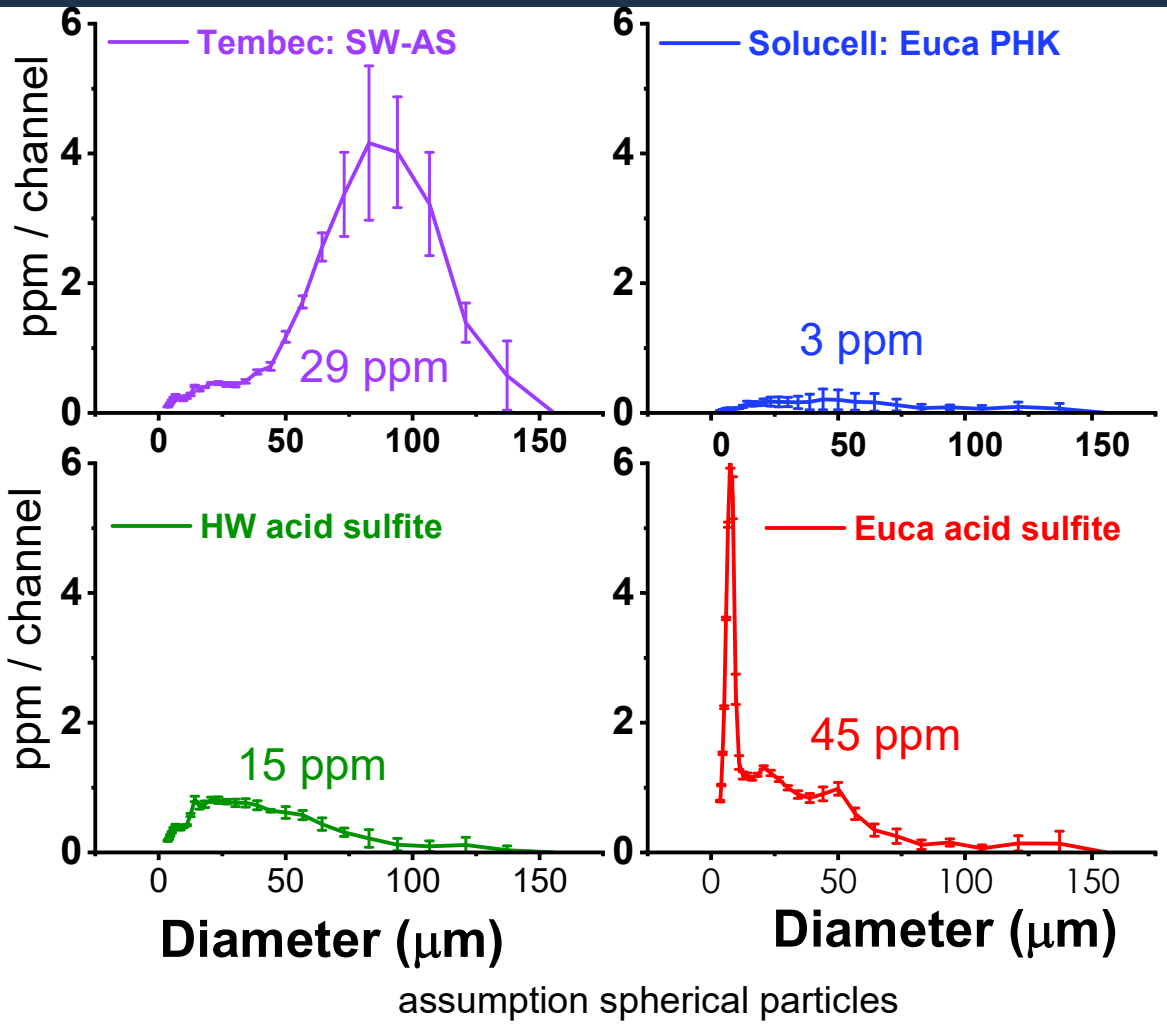
Hermans, P., H.L. Bredee. *J. Soc. Chem. Ind.*, London, 15, T1 (1936)
Treiber, E. *Monatshefte f. Chemie*, 93, 455 (1962).

Benchmark of viscose filterability



Viscose Preparation and characterization according to a modified method of Treiber [Treiber E., 1962; Hüpfl, J.; Zauner, J., 1966]

Particle size distribution in viscose

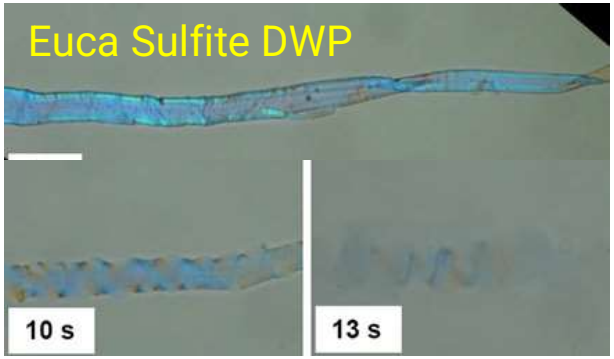


assumption spherical particles

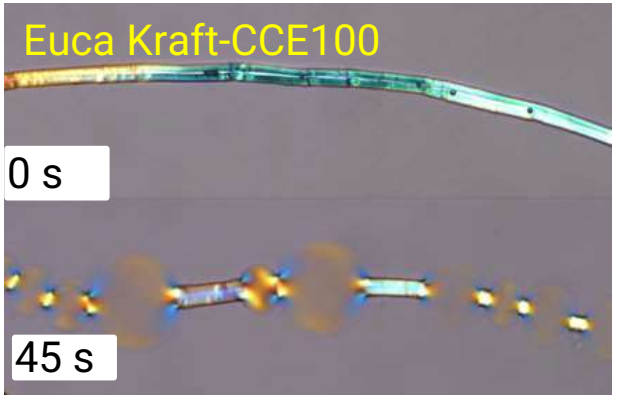
Lenz Ber, 82 (2003), 118-127

The particle content in technical viscose solutions (Pamas device - light blockade principle), particles are calculated as spheres

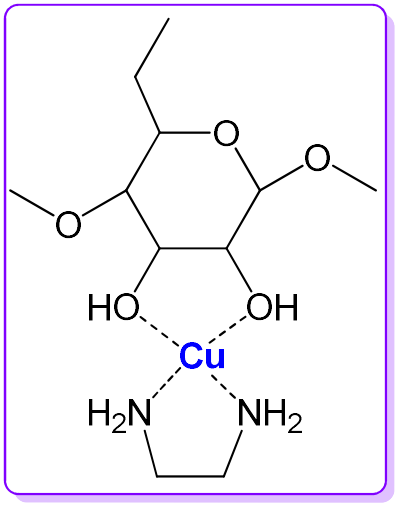
Pulp dissolution behavior



Complete dissolution by left-handed untwisting of cellulose fibrils



Increased swelling, no dissolution
Ballooning, formation of collars



Cupri ethylendiamine

- [0.5 M] (instead of 1.0 M), **cuen** dissolves only highly accessible & reactive cellulose.
- Dissolution kinetics as a measure for pulp reactivity

Gehmayr, V., Potthast, A., H. Sixta, *Cellulose* (2012)

Dissolution-based torque reactivity (DTR)

CED Solvent

Max 1.5 h

HOMOGENIZATION
(12.5 mL pulp at 1.5% solids)

DISSOLUTION
(12.5 mL CED 1 M)

TORQUE ANALYSIS

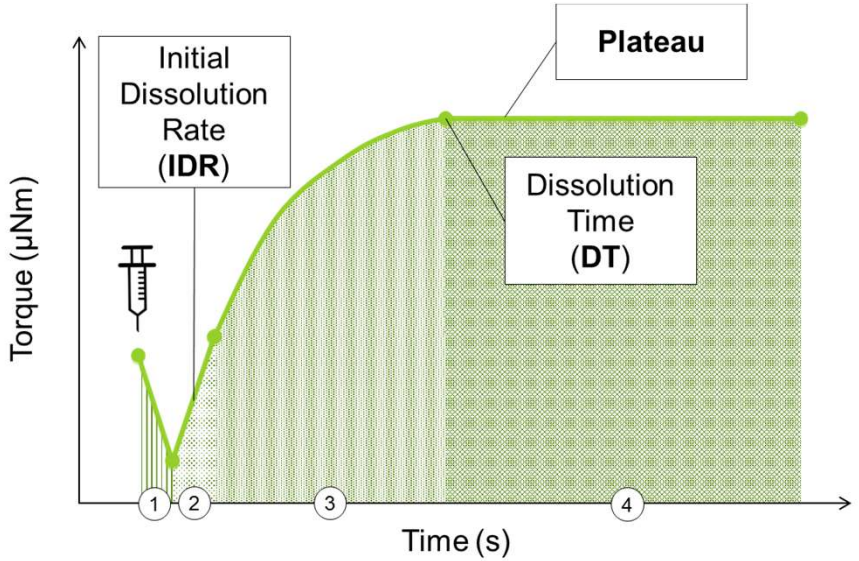
PULP REACTIVITY

- DISSOLUTION RATE
- DISSOLUTION TIME
- PLATEAU

Fast rheology-based method.

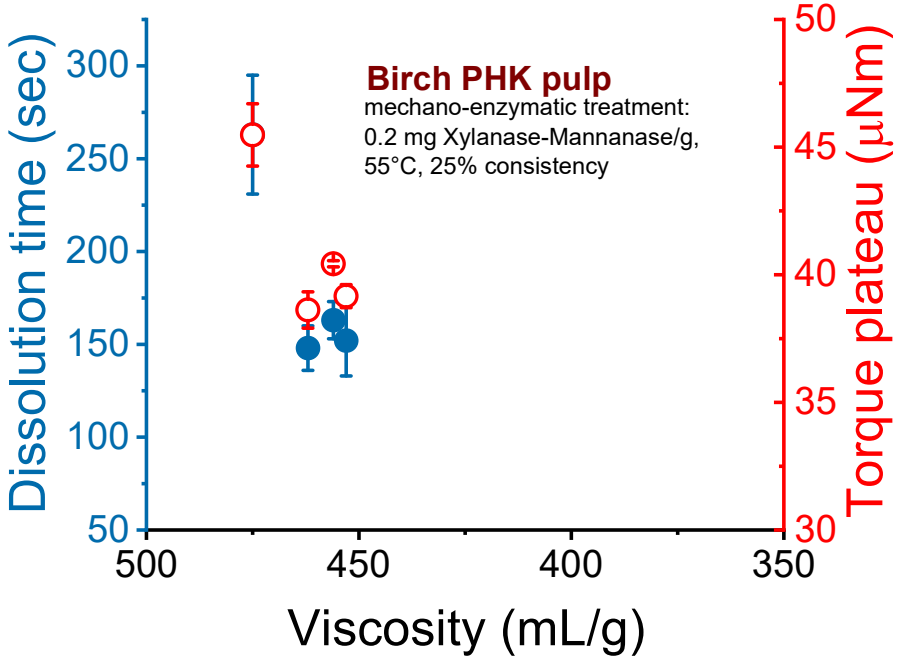
Pulps that are slower to dissolve are less reactive.

The plateau may give information about the completeness of dissolution.

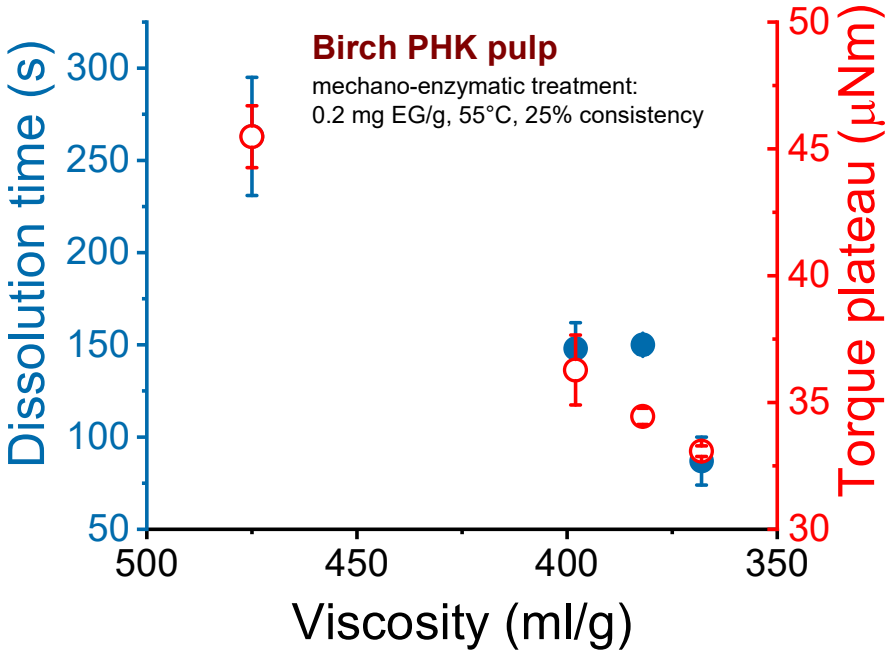


*Ceccherini Sara, Maloney Thad. Cellulose (**2019**) 26 (18), 9877-9888*

Effect of enzyme treatment



Combined **Xylanase and Mannanase (XM)** treatment of a Birch-PHK pulp leads to a **moderate decrease** in viscosity, dissolution time & torque plateau



Endoglucanase (EG) treatment of a Birch-PHK pulp leads to a **proportional decrease** in viscosity, dissolution time & torque plateau

Sara Ceccherini et al., Biomacromolecules 2021, 22, 4805−4813