Alkalicellulose – a prerequisite for cellulose etherification

Ola Sundman, Department of Chemistry, Umeå University

Bio4Energy Biopolymers and Biochemical Conversion Technologies

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Cellulose ethers. Why? What is it?

- Cellulose is a very strong and versatile biopolymer.

- But - hard to dissolve.

- Does not melt.

- Makes it diffcult to use.

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If the chemical stucture is changed!

- Cellulose derivatives are easier to dissolve.

- Might not melt.

- Could be highly water soluble (*e.g.* Carboxy Methyl Cellulose)

- Could be hydrophobic (*e.g.* Benzyl Cellulose[1], Veratryl Cellulose[2])

- Could be water soluble BUT hydrophobic (e.g. Methyl Cellulose)
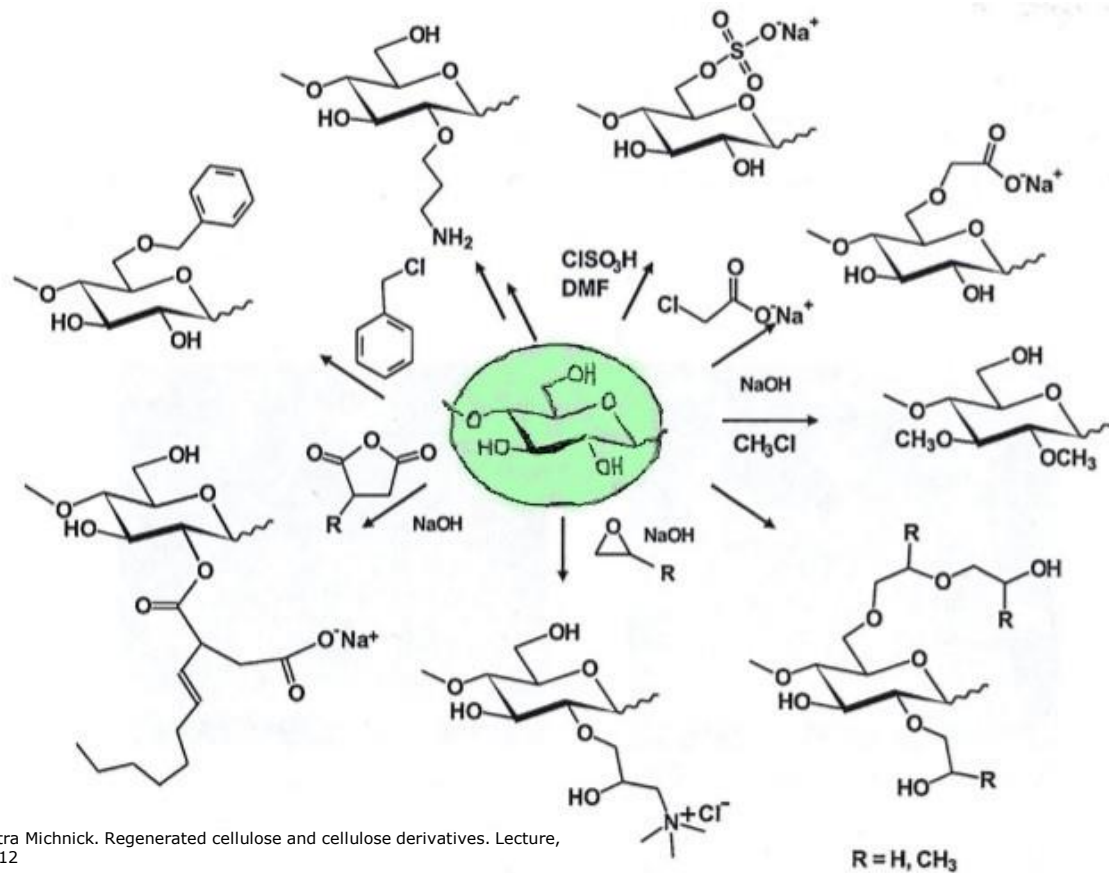
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[1] Sundman et al (2015) *Cellulose Chemistry and Technology*, [2]Yahia and Sundman (2022) *Bioresources*

Derivatization of cellulose
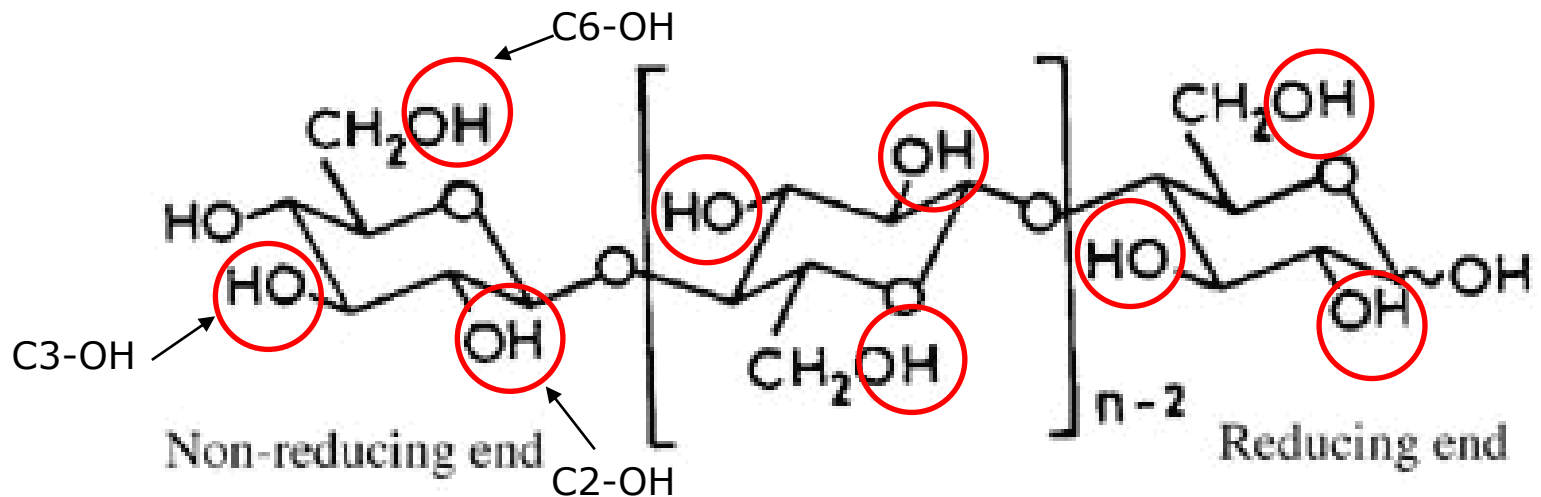
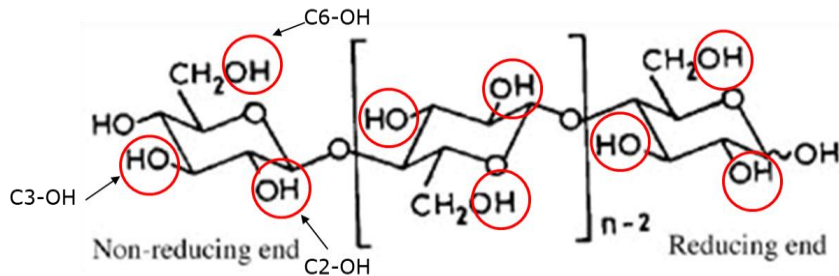These hydroxy-groups are either esterified or etherified.

Derivatization of cellulose

As you see. Cellulose ethers are much more common(!)

Petra Michnick. Regenerated cellulose and cellulose derivatives. Lecture, 2012

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Derivatization of cellulose

- These hydroxy groups will NOT react with e.g. benzyl chloride or ethyl chloride.
- They have to be activated first.
- Cellulose is an unusual polyalcohol since NaOH is strong enough to deprotonate it.
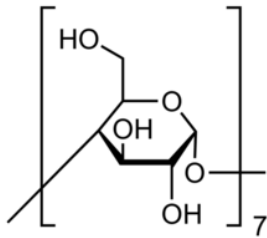
Derivatization of cellulose Deprotonation with NaOH

- pK_a of *glucose* = 12.3
- pK_a (C2, C3)-OH for *β-cyklodextrine* = 13.5 lower for C6-OH
- pK_a (C2, C3)-OH 10 – 12
- pK_a (C6-OH) ≈ 14

Gaidamauskas et al (2009) Carbohydrate research

Seymour/Carraher's Polymer Chemistry, 6th Ed. Charles E. Carraher, Jr. (2003)

www.sigmaaldrich.com

- pK_a för H_2O ≈ 14

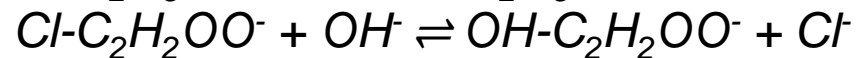BIO4ENERGY

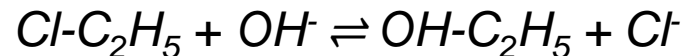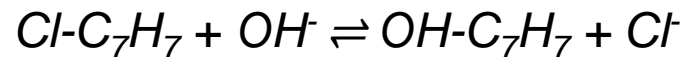# Derivatization of cellulose
Deprotonation with NaOH

BUT!

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Derivatization of cellulose Deprotonation with NaOH

Unwanted side reactions in an aqueous environement:
e.g.
$Cl\text{-}C_7H_7 + OH^- \rightleftharpoons OH\text{-}C_7H_7 + Cl^-$
$Cl\text{-}C_2H_5 + OH^- \rightleftharpoons OH\text{-}C_2H_5 + Cl^-$
$Cl\text{-}C_2H_2OO^- + OH^- \rightleftharpoons OH\text{-}C_2H_2OO^- + Cl^-$

The solution chosen by the industry is to remove the excess NaOH and water!

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Alkalicellulose – a prerequisite for cellulose etherification

Traditionally this done by addiding ≈ 18 % NaOH(aq) and then pressing out the excess NaOH solution.

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ORIGINAL PAPER

The influence of different parameters on the mercerisation of cellulose for viscose production

Diana Carolina Albán Reyes · Nils Skoglund ·
Anna Svedberg · Bertil Eliasson · Ola Sundman

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The influence of different parameters on the mercerisation of cellulose for viscose production

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other variables. The optimum point for both DoT and yield in this study was found to be 29 °C, 45 s and 21 % [NaOH].
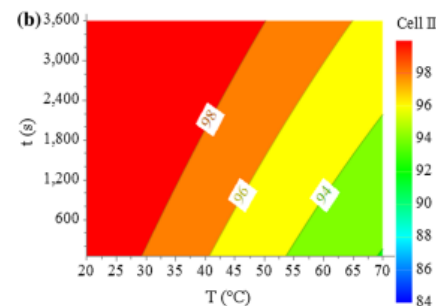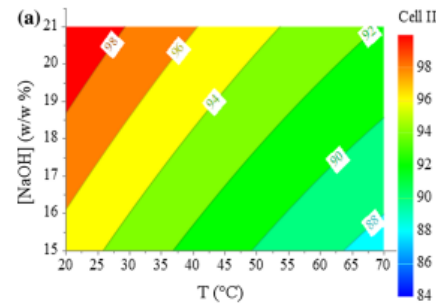

Fig. 9 Contour plot for the DoT of the mercerised samples as **a** a function of temperature and [NaOH] at 45 s, and **b** as a function of temperature and time at 21 % [NaOH]. Terms on the X-axis: T = temperature in °C, and on the Y-axis t = time in seconds and $[NaOH]$ = NaOH concentration in (w/w)%. (Color figure online)

Fig. 10 Contour plot for yield of the mercerised samples as **a** a function of temperature and [NaOH] at 45 s, and **b** as a function of temperature and time at 21 % [NaOH]. Terms on the X-axis: T = temperature in °C, and on the Y-axis t = time in seconds and $[NaOH]$ = NaOH concentration in (w/w)%. (Color figure online)
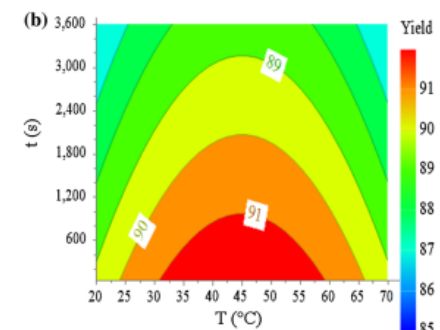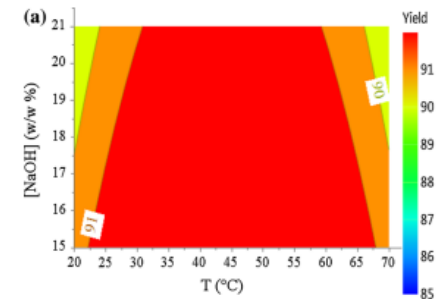
11

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Traditionally this done by addiding ≈ 20 % NaOH(aq) and then pressing out the excess NaOH solution.
But even if you press out as much as possible (say that the moisture content is 40%). Then you still have 4 g of 20% NaOH(aq) /6 g cellulose.
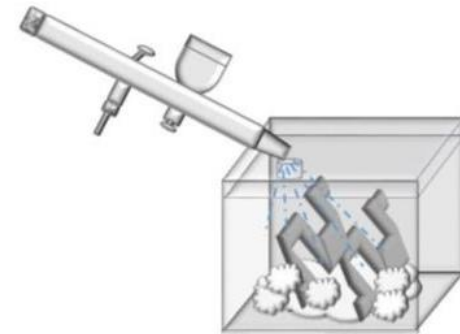
I.e. 2.3 g H_2O / 5 g cellulose -> >4 H_2O molecules/cellulose AGU

Therefore, cellulose is "sprayed" with a small amount of highly concentrated NaOH(aq) solution.

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Alkalicellulose – a prerequisite for cellulose etherification

Therefore, cellulose is "sprayed" with a small amount of highly concentrated NaOH(aq) solution.

We did this in Örnsköldsvik, at MoRe research.

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Alkalicellulose – a prerequisite for cellulose etherification

Therefore, cellulose is "sprayed" with a small amount of highly concentrated NaOH(aq) solution.
We did this in Örnsköldsvik, at MoRe research.

Alkalization of dissolving cellulose pulp with highly concentrated caustic at low NaOH stoichiometric excess

Diana Carolina Albán Reyes[a], András Gorzsás[a], Kjell Stridh[b], Paul de Wit[c], Ola Sundman[a,*]

ORIGINAL PAPER

Is there a diffusion of alkali in the activation of dissolving cellulose pulp at low NAOH stoichiometric excess?

Diana Carolina Reyes Forsberg · Kjell Stridh · Paul P. de Wit · Ola Sundman

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Alkalicellulose – a prerequisite for cellulose etherification

Contents lists available at ScienceDirect
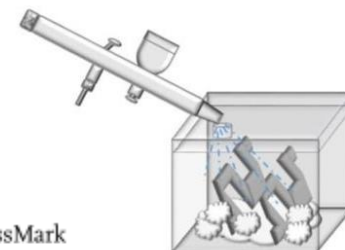
Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Alkalization of dissolving cellulose pulp with highly concentrated caustic at low NaOH stoichiometric excess

Diana Carolina Albán Reyes[a], András Gorzsás[a], Kjell Stridh[b], Paul de Wit[c], Ola Sundman[a,*]

[a] Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden
[b] AkzoNobel, SE-444 85 Stenungssund, Sweden
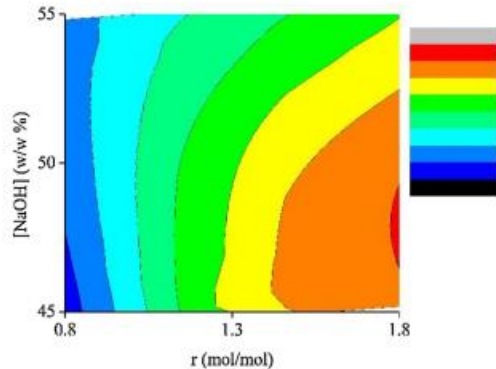[c] AkzoNobel, 6827AV 73 Arnhem, The Netherlands

Fig. 6. Contour plot depicting the measured DoA in LWC mercerisation, as a simultaneous function of (r) (stoichiometric ratio of NaOH/AGU, X axis) and [NaOH] (in% w/w), Y axis).
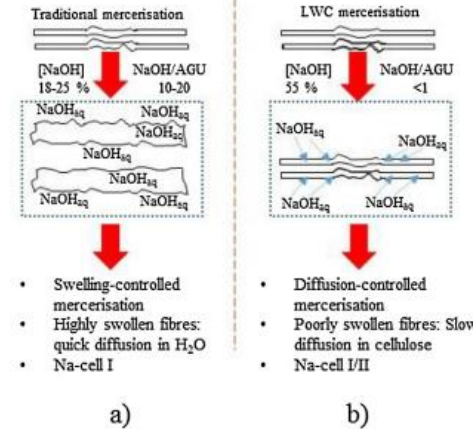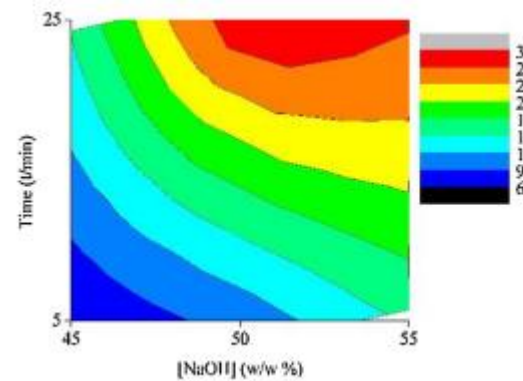

Fig. 8. Schematic comparison of hypothetic mechanisms for (a) traditional (swelling-controlled) and (b) LWC (diffusion-controlled) mercerisation.

15

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Fig. 3 DoA of mapping areas versus reaction time for samples where a) (r) = 0.8 and b) (r) = 1.3 after subsequent addition of dry dissolving cellulose pulp, Set 1. (r) = NaOH/AGU (anhydroglucose unit) stoichiometric ratio, [NaOH] is 50% w/w. "Pre" refers to the pre-mercerised cellulose, while t5 represents 5 min after addition of non-mercerised cellulose, i.e. the starting point for the diffusion study. t10 and t25 refers to 10 min and 25 min after addition of non-mercerised cellulose, respectively

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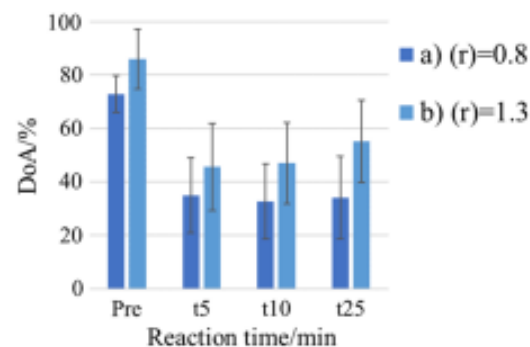Diana Carolina Reyes Forsberg · Kjell Stridh · Paul P. de Wit · Ola Sundman

Fig. 4 DoA versus reaction time for samples mercerised at $(r) = 0.8$ (orange) and at $(r) = 1.3$ (blue) and at different [NaOH], Set 2. **a** 10%, and **b** 20%, **c** 30%, **d** 40% and **e** 50% [NaOH]. $(r) = $ NaOH/AGU (anhydroglucose unit) stoichiometric ratio. (Color figure online)
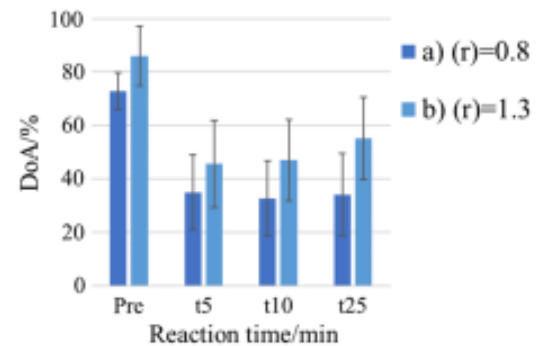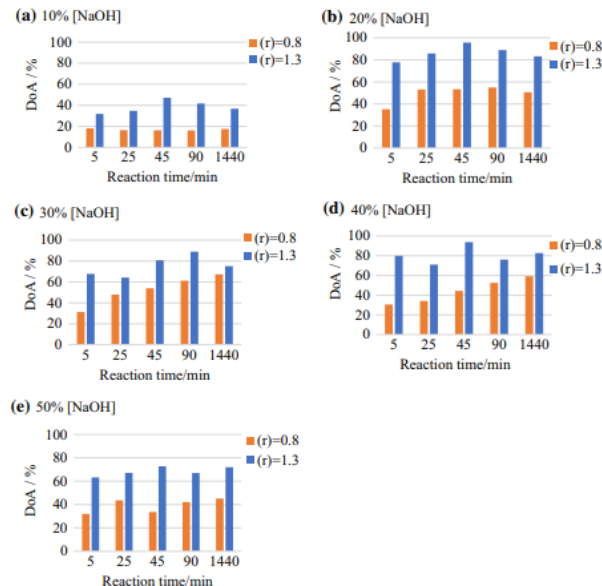
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17

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We could not definitly reject the hypothesis (that "diffusion" exist also a LWC).
Neither could we statistically confirm it.

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ON THE IMPORTANCE OF VARIATION OF ALKALISATION CONDITIONS

ON CELLULOSE ETHER SYNTHESIS

DIANA CAROLINA REYES FORSBERG[*] and OLA SUNDMAN[**]

[*]MoRe Research AB, SE-891 22 Örnsköldsvik, Sweden
[**]Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden
✉ Corresponding author: Ola Sundman, ola.sundman@umu.se

- Diana defended her thesis in 2018
- I felt that "it's about time!"

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ON CELLULOSE ETHER SYNTHESIS

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[*]*MoRe Research AB, SE-891 22 Örnsköldsvik, Sweden*
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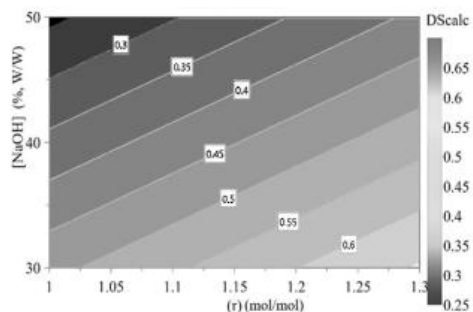✉ *Corresponding author: Ola Sundman, ola.sundman@umu.se*

Figure 1: Contour plot showing the DS_{calc} for S samples, as a simultaneous function of NaOH/AGU stoichiometric ratio ((r), X-axis) and added [NaOH] (in % w/w, Y-axis) at 35 min
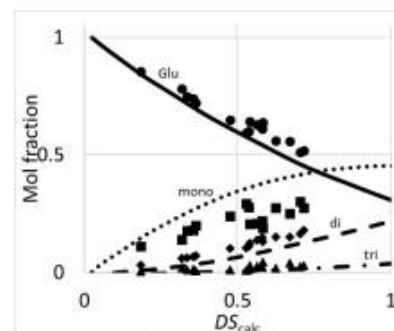

Figure 2: Molar fraction of glucose (Glu, solid line and circles), 2-; 3-; 6-mono-*O*-carboxymethyl glucose (mono, dotted line and squares), 2,3-; 2,6-; 3,6-di-*O*-carboxymethyl glucose (di, dashed line and diamons), and 2,3,6-tri-*O*-carboxymethyl glucose (tri, dashed-dotted line and triangles) in hydrolysed CMC samples versus DS_{calc} (symbols represent the samples, lines – statistical distribution proposed by Spurlin.[41] DS_{calc} – DS derivate through the HPLC method)

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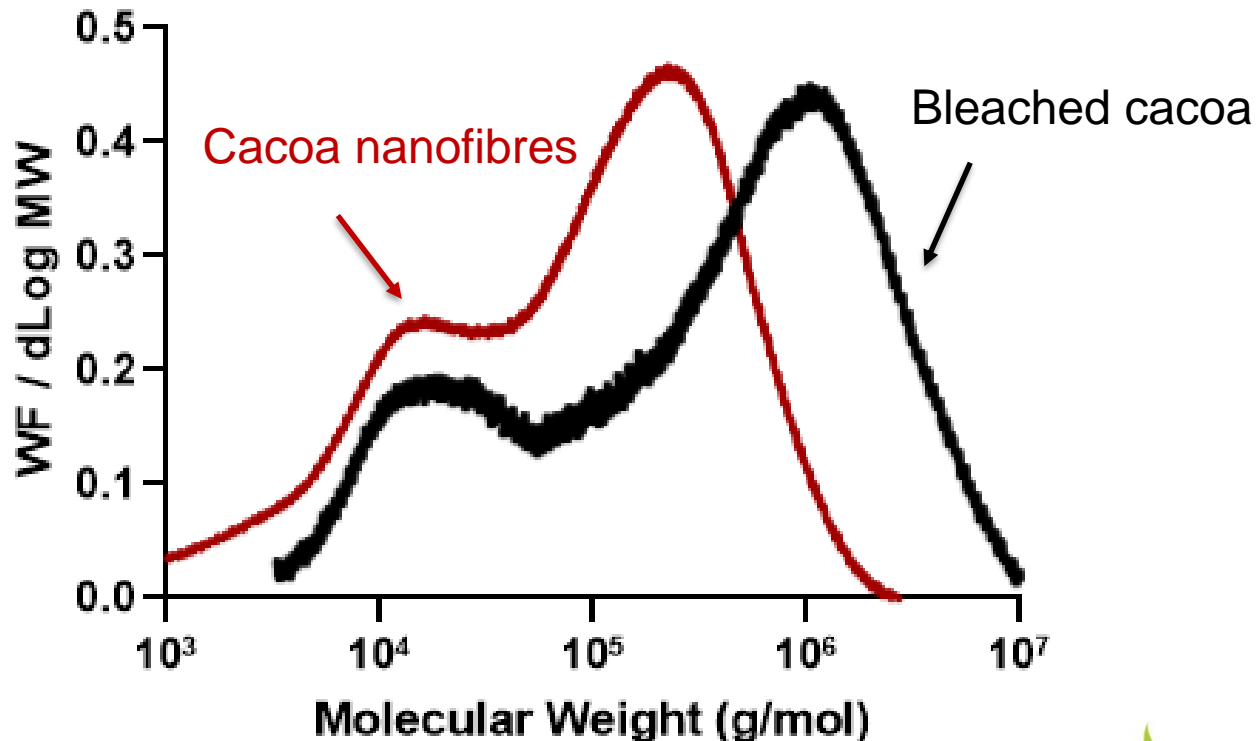[**]*Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden*
✉ *Corresponding author: Ola Sundman, ola.sundman@umu.se*

- Mercerisaton affect DS but not to the expected degree.
- Mixing of the components are even more important for cellulose ethers than just mercerisation – questionable if we have any "diffusion" at the time scale studied.
- $\bar{X}_3 < \bar{X}_2 \approx \bar{X}_6$
- $\bar{X}_3$ is LESS (compared to $\bar{X}_2$ and $\bar{X}_6$) affected by the decrease in DS when [NaOH] is decreased.

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Size Exclusion Chromatography on the Biopolymer Analytical Platform (SLU/UmU)

- Size exclusion chromatography of (bio-)macromolecules.
  - *E.g. lignin, cellulose, hemicellulose or polyhydroxybutararate*

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Size Exclusion Chromatography on the Biopolymer Analytical Platform (SLU/UmU)

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