7th ICEP

Chemical Reactions Causing Carbohydrate Yield Losses During Alkaline Pulping of Wood.

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Why is it interesting?

- Degradation of polysaccharides generates yield losses during pulping. Much money lost.
- In some cases non-cellulose carbohydrates are wanted in the product (papers), but sometimes not (dissolving pulps).
- In such cases can hemicellulose be extracted and used as polymers of converted to products as furfural and alditols, or used in fermentations – biorefinery.
- In the black liquor carbohydrate degradation products are normally non-fermentable sugar acids.

How are the carbohydrates lost?

- **1 Dissolution.**
  - Polysaccharides are dissolved in the process liquors.
- Degradation.
  - Polysaccharides are degraded into los molecular weight components and solubilized. Several mechanisms. Most important:
    - **2 Alkaline hydrolysis.**
    - **3 Peeling reaction.**
- *What can we do about it?*

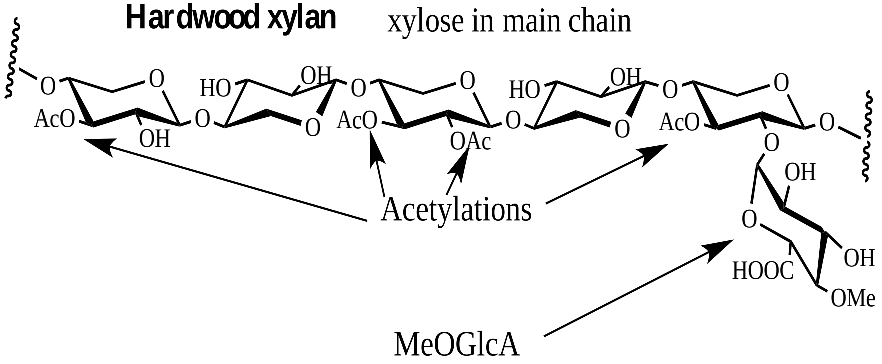
There are differences between hardwoods and softwoods.

Wood component	**Pine kraft pulp** Mass % wood	**Birch kraft pulp** (Wood values)
Cellulose	35 (39)	34 (40)
Glucomannan	4 (17)	1 (3)
Xylan	5 (8)	16 (30)
Pectin and Other carb.	~0 (5)	~0 (4)
Lignin	3 (27)	2 (20)
Extractives	<0.2 (4)	0.5 (3)

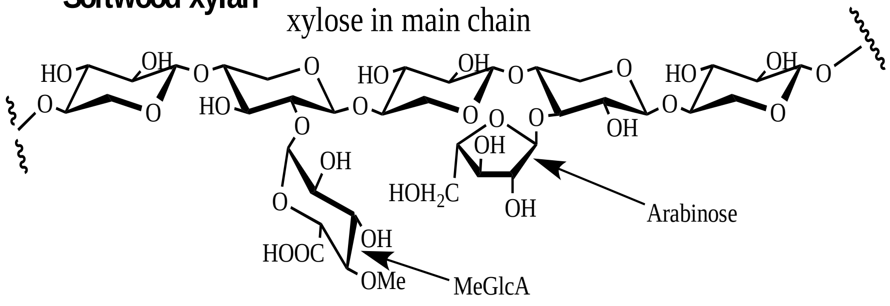
- Yield losses in carbohydrates is normally higher in softwoods than in hardwoods.
- The hemicellulose composition is different between hardwoods and softwoods.
  - Yield losses are higher for glucomannan than for xylans

Hemicellulose structures

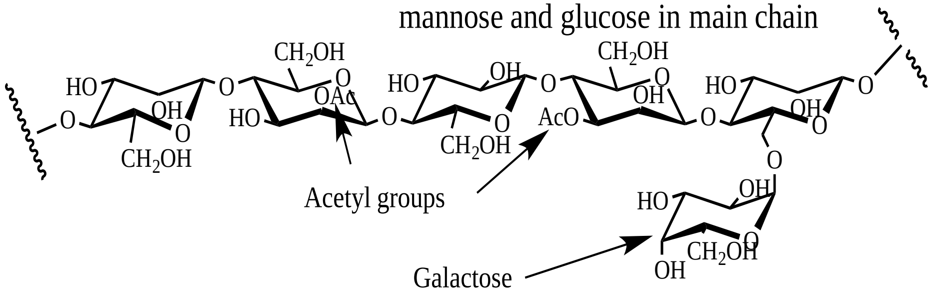
Hardwood xylan



Softwood xylan

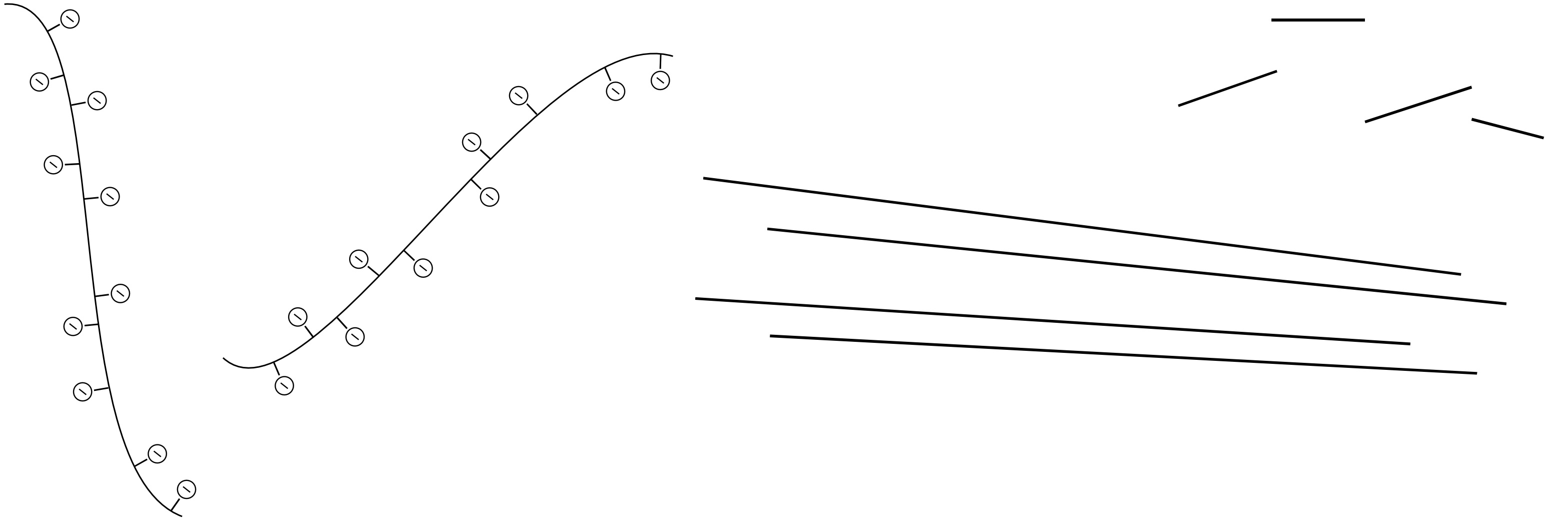


Softwood glucomannan



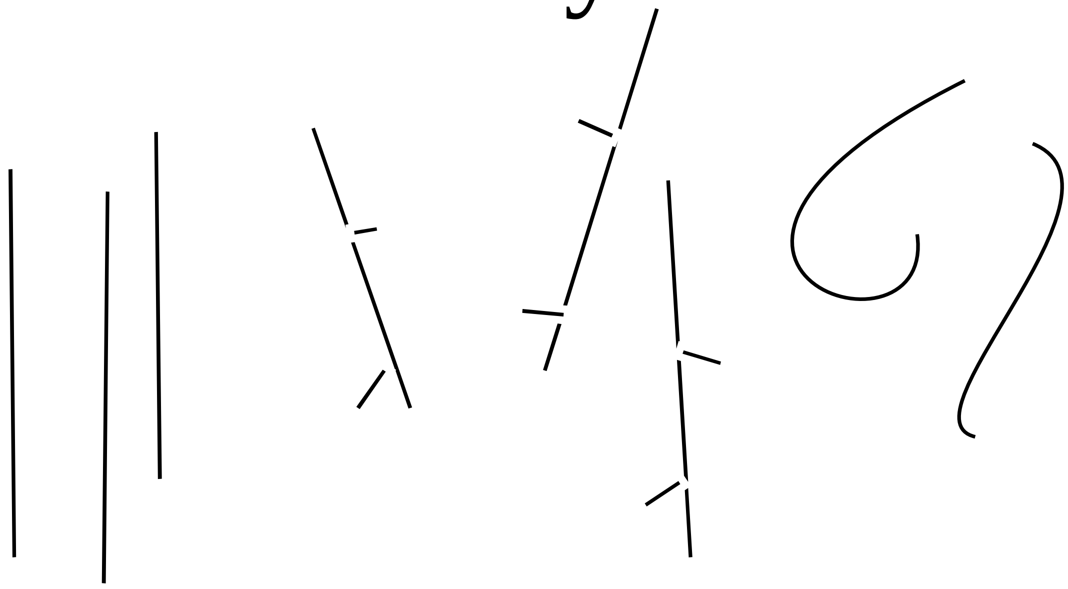
- Softwood is dominated by glucomannans
- Hardwood dominated by xylans.
- There are important differences between the xylans of hardwoods and softwoods is that the content of arabinose side chains is much higher in softwood xylan.

1. Solubility of hemicellulose



- *Charged groups*. Electrical charges on the polymer increase the solubility in water. In hemicelluloses, it is carboxylic acid on xylan that is interesting.
- *Degree of polymerization*. A lower degree of polymerization generally increases i the solubility

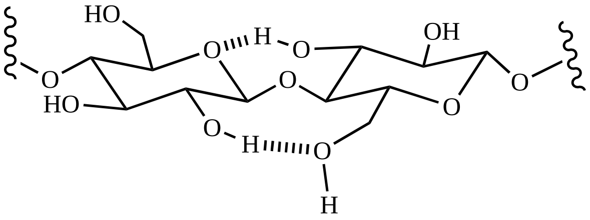
Solubility cont.



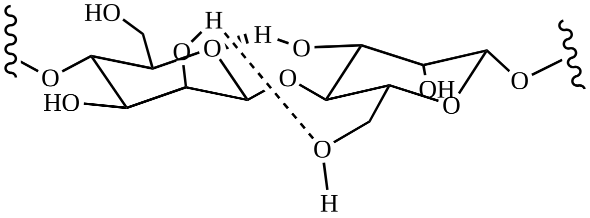
- *Number of side groups*. Side groups generally increase solubility, since they prevent aggregation.
- *Acetylations*. High degree of acetylation make the polysaccharide hydrophobic and decrease solubility. Low degree of acetylation might also increase the solubility in water. However, acetyl groups are quickly removed during alkaline pulping and their technical significance for losses during pulping is therefore small.
- *Stiffness of the main chain*. Stiffer main chains are often related to lower solubility

Stiffness of glycosidic bond

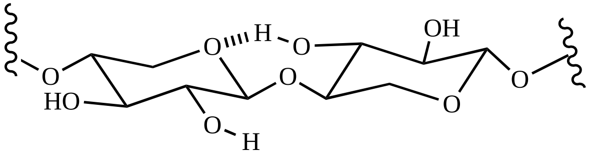
C-type *Xyloglucan,"glucan part" of glucomannan and cellulose*
The glucosidc bond is stabilized by two hydrogen bonds.



M-type *"Mannan part" of glucomannan* The glucosidc bond is stabilized by two hydrogen bonds, but can they act on the same time?



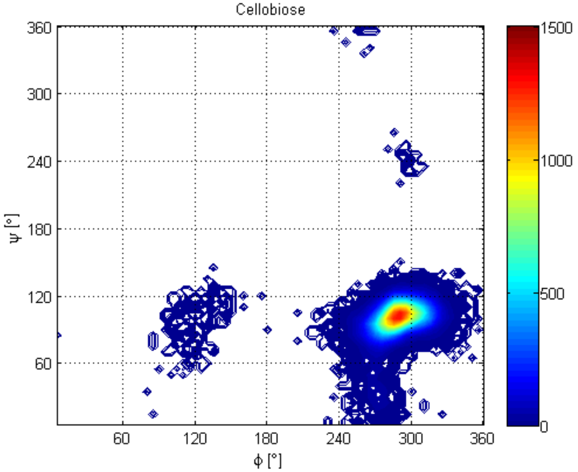
X-type *Arabinoxylan*
The glucosidc bond is stabilized by one hydrogen bond.



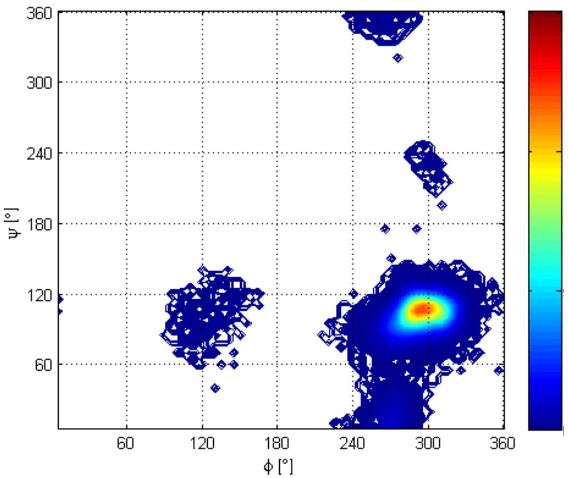
- The gluciosidic bond in the main chain is important for stiffness.
- Nearly always β1,4 glycosidic bond
- Three main types in hemicellulose main chain, *C*-, *M*- and *X-type*
- When we looked at the different glycosidic bonds it appeared as X-type should be more flexible than M-type and C-type the stiffest.
- ”We” performed computer simulations or relevant disaccharides in water solution.

Results from computer simulations

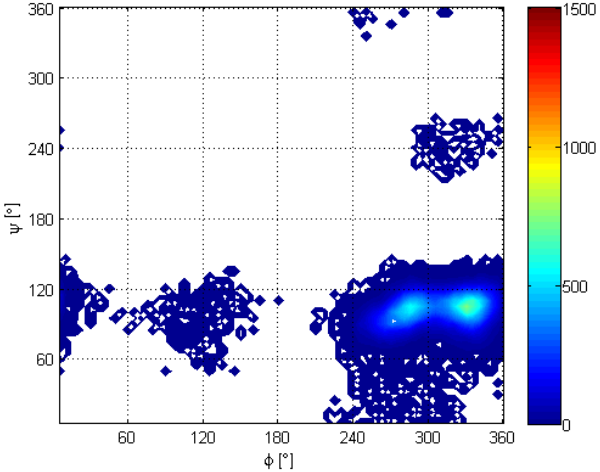
C-type

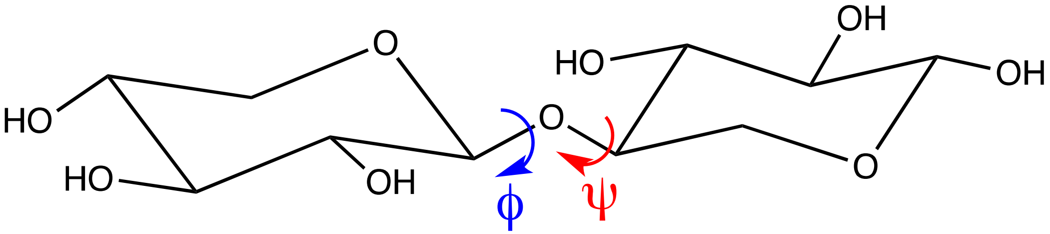


M-type



X-type



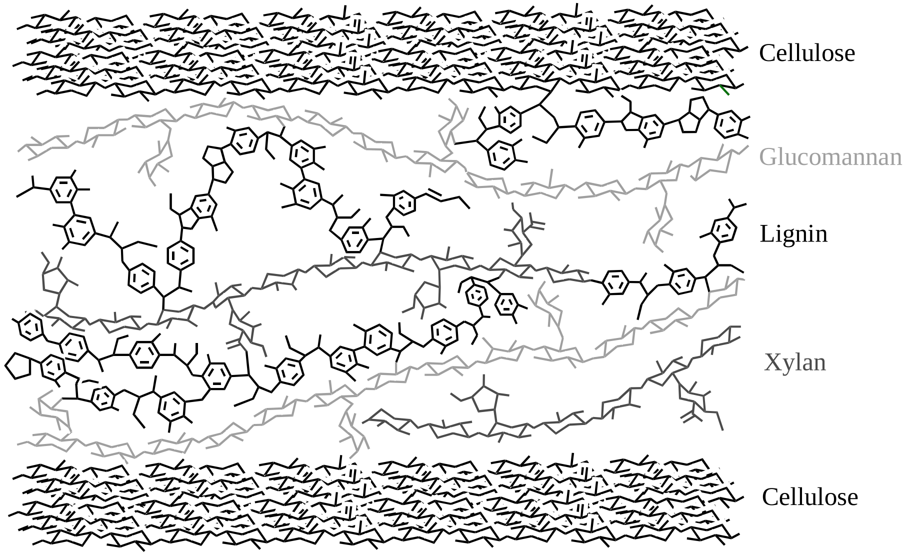


- So far simulations in water by dimers. Results seems to confirm that X-type is the most flexible and C-type the least flexible.
- May play important role for the properties of the polysaccharides

Xylan is the most soluble hemicellulose

- Taken together everything it gives that xylan have the highest solubility.
- However, loss of side chains and lower alkalinity towards the end of a cook leads to that is can precipitate on the fiber surfaces.
- *What can we do about it?*
  - Control over pH and temperature profiles can minimize the losses of hemicelluloses by dissolution.

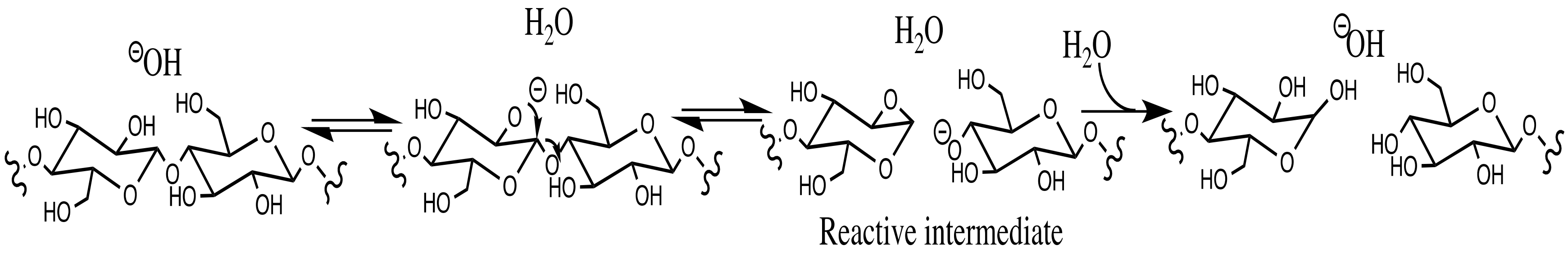
Covalent bonds to lignin – an obstacle for extractions



- Lignin polysaccharide networks form obstacle for direct extrction during pulping.

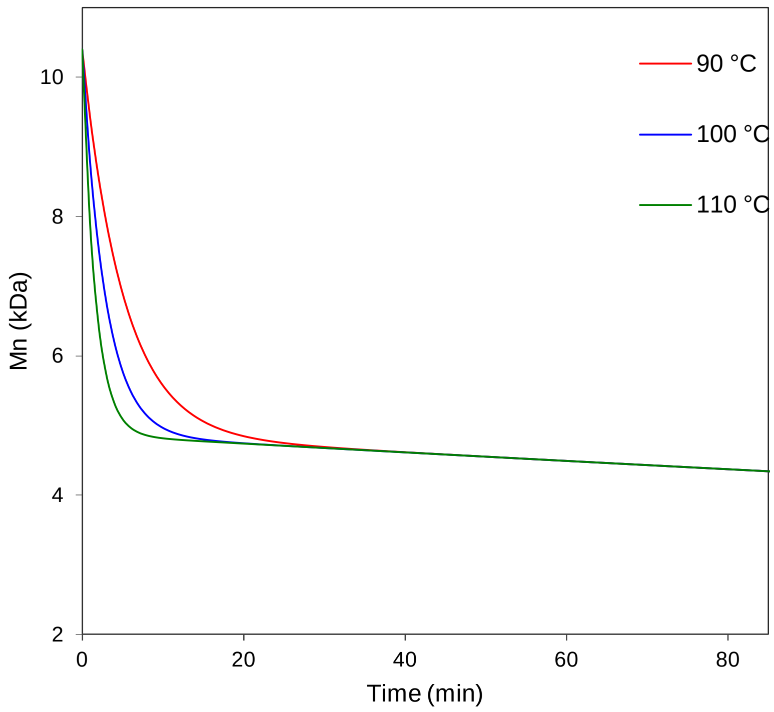
- Extraction with very hot over-pressurized water (180°C or higher) can extract large amounts of hemicellulose, but both hemicellulose and cellulose lose some degree of polymerization.

2. Alkaline hydrolysis



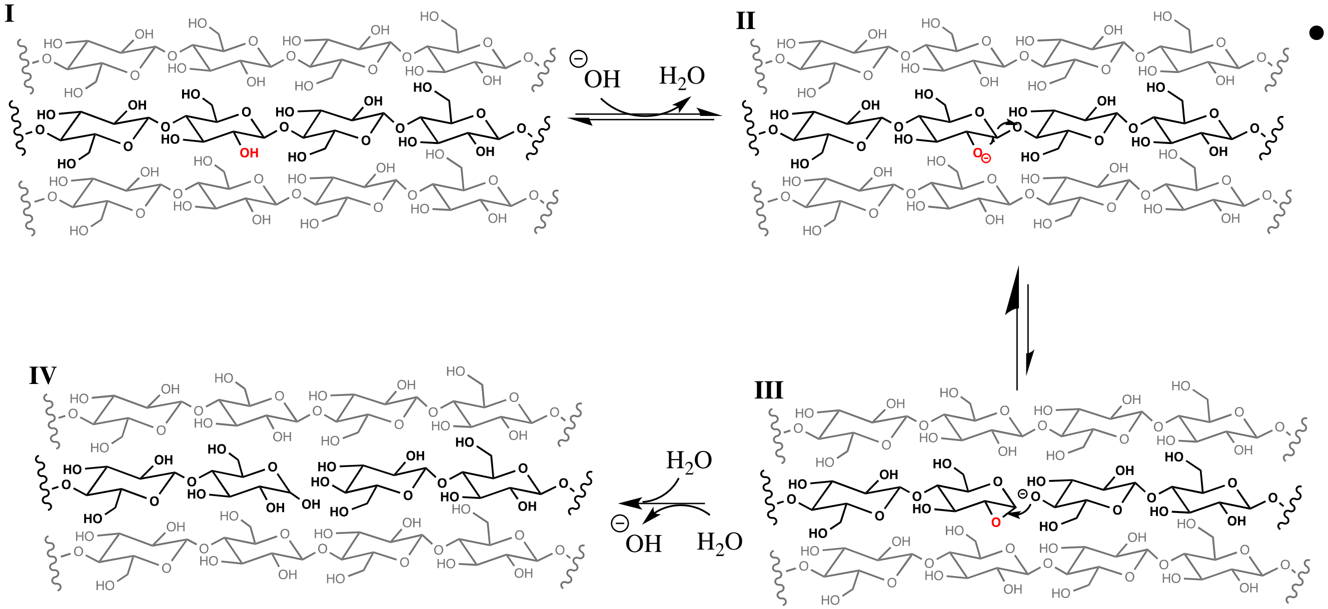
- Our suggestion of the main mechanism of alkaline hydrolysis of polysaccharides:
  - Deprotonized C2 alcohol is the nucleophile and there is an reactive intermediate consisting of deprotonozed alcohol and epoxide, where the reaction principally can ”go back” again.
  - Why not hydroxy ion as nucleophile?
    - Weaker and not “fixed” in the right position

Are different bonds hydrolyzet at different rates?



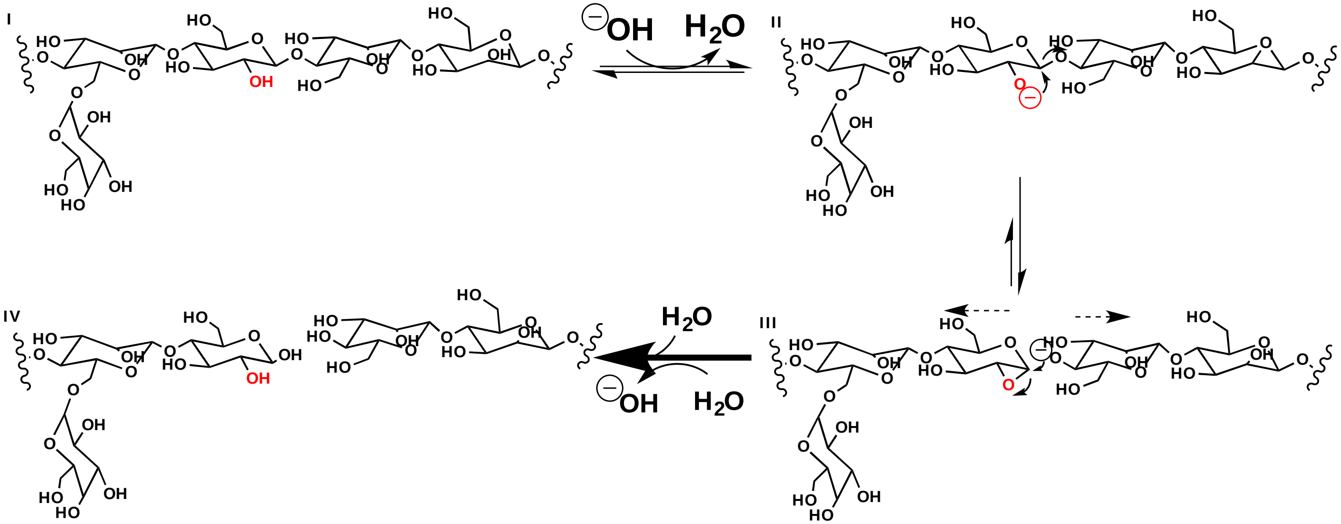
- Galactoglucomannans were treated by 0.5 M NaOH at different temperatures and the decrease in DP were followed by Size exclusion chromatography.
- Two faces, one fast and one slow.
- Activation energy was calculated For glucomannan 65.8 kJ/mole for the fast phase and it was close to zero for the slow phase (2.02E-9 kJ/mole).
- Cellulose have considerable higher activation energies than the glucomannan.

Explanation – the alkaline hydrolysis is reversible until the activated intermediate.

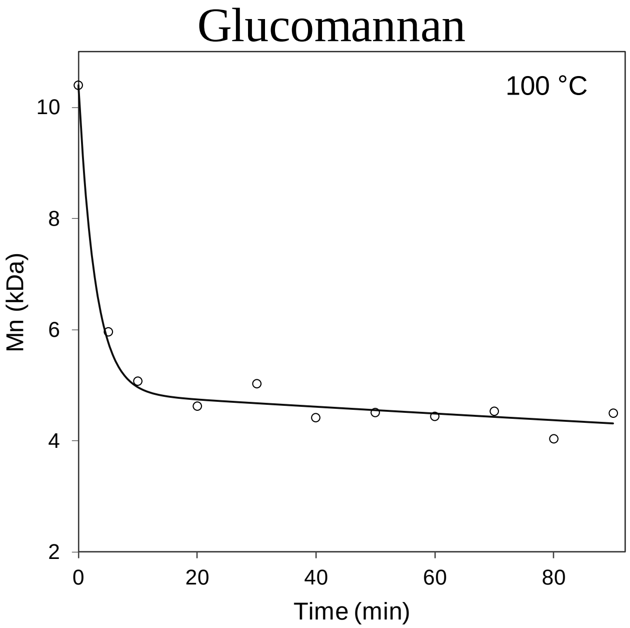


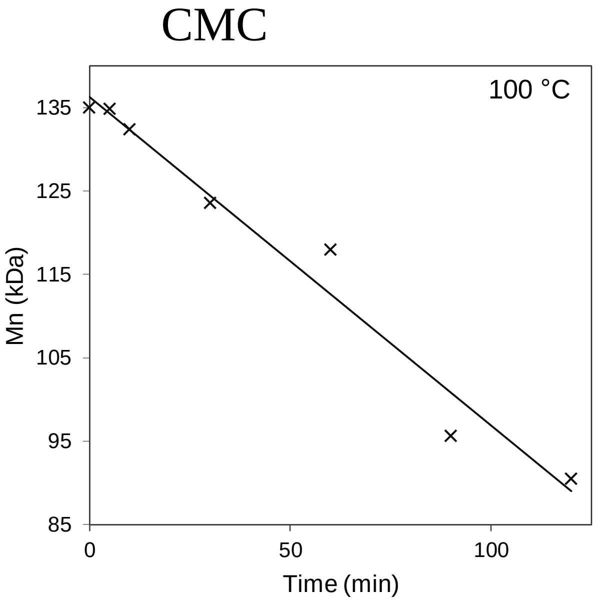
- Cellulose
  - The crystal structure hold reactive intermediate close together and than can re-ligate

- Hemicellulose
  - The reactive intermediate can move from each other and react with water - hydrolysis



Why two phases?

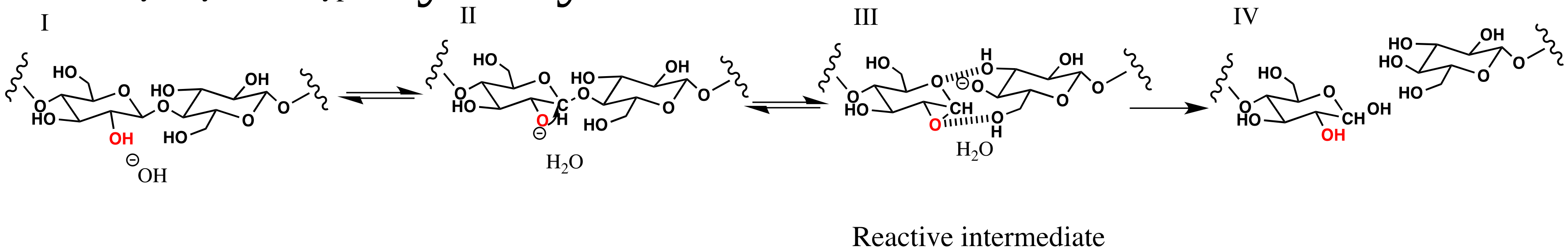

Glucomannan


CMC

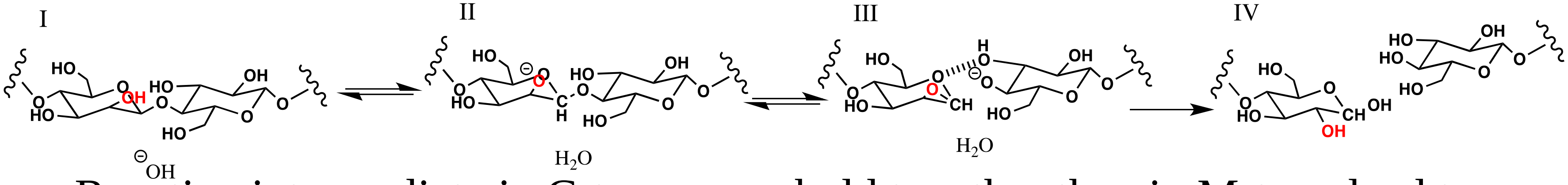
- We compared with carboxymethyl cellulose (CMC) and here we saw only one phase.
- *Ergo*: The complex structure of the hemicellulose affects the degradation kinetics.
  - How?

Also in soluble hemicellulose the glycosidic bonds are hydrolyzed at different rates.

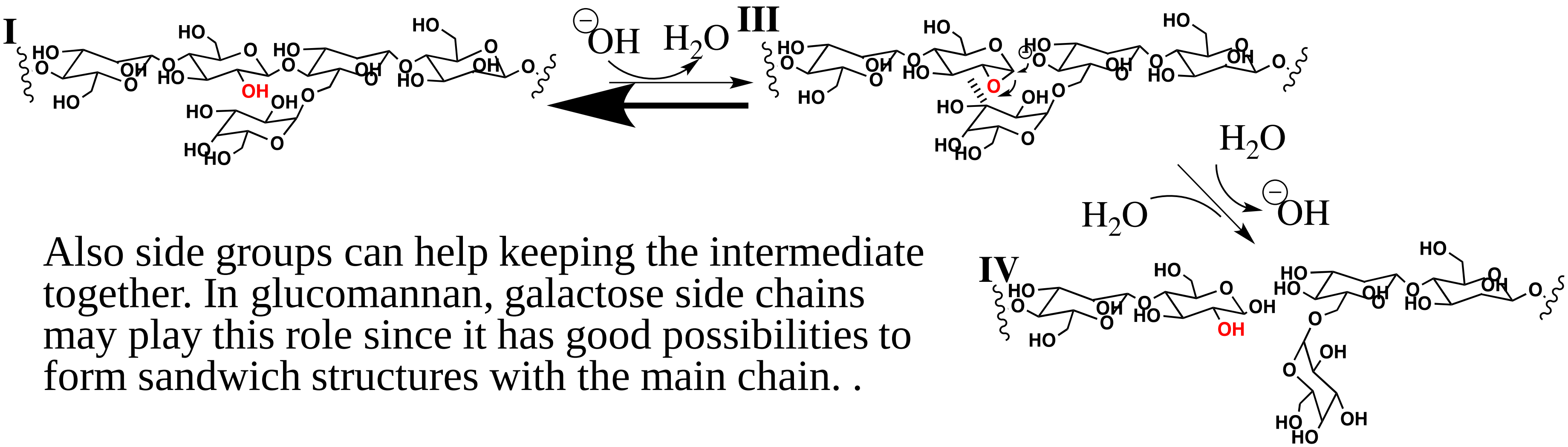
Alkaline hydrolysis of C-type



Alkaline hydrolysis of M-type



- Reactive intermediate in C-type more hold together than in M-type lead to slower degradation? Cannot explain all.

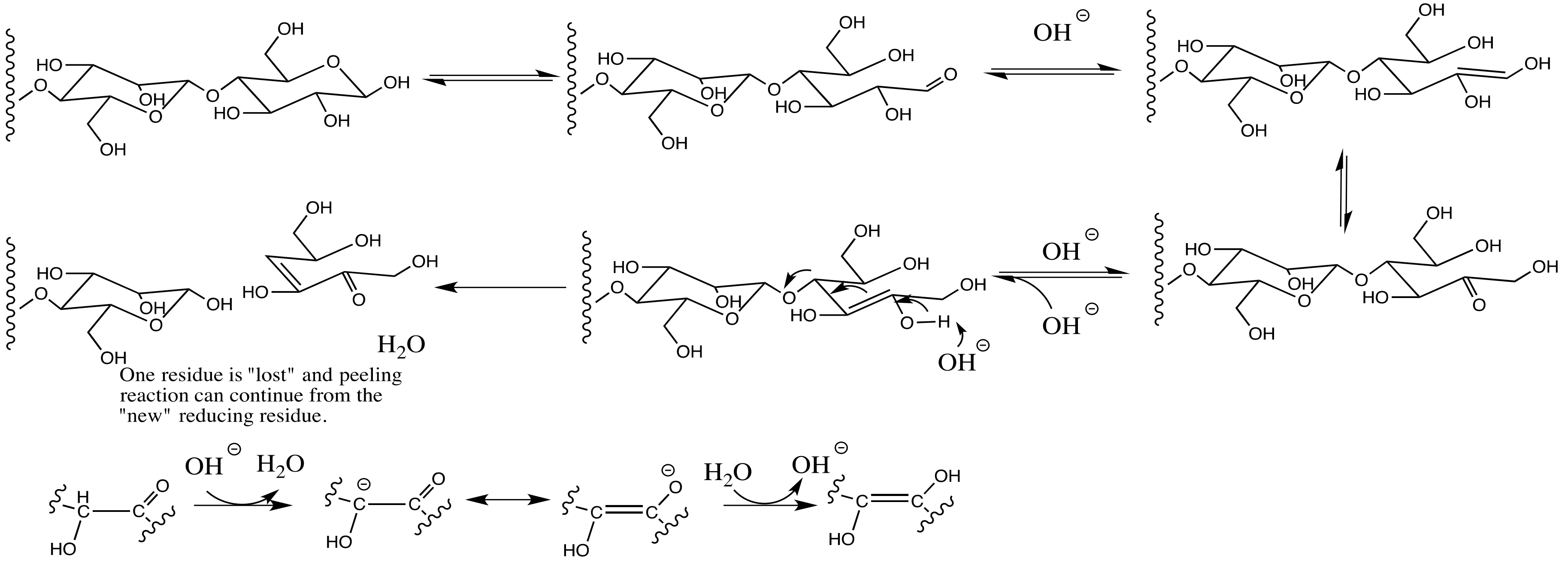


- Also side groups can help keeping the intermediate together. In glucomannan, galactose side chains may play this role since it has good possibilities to form sandwich structures with the main chain. .

What can we do about alkaline hydrolysis?

- By choosing conditions - not very much more than what we do already, since also lignin is degraded by an alkaline hydrolysis, but at least we (I?) understand better why cellulose is so relative undamaged by alkaline pulping.
- Maybe knowledge of the properties if the degradability of glycosidic bonds of hemicelluloses can be an inspiration of design of transgenic trees.
  - More glucose in main chain and more 6-bound galactose side groups in hemicelluloses?

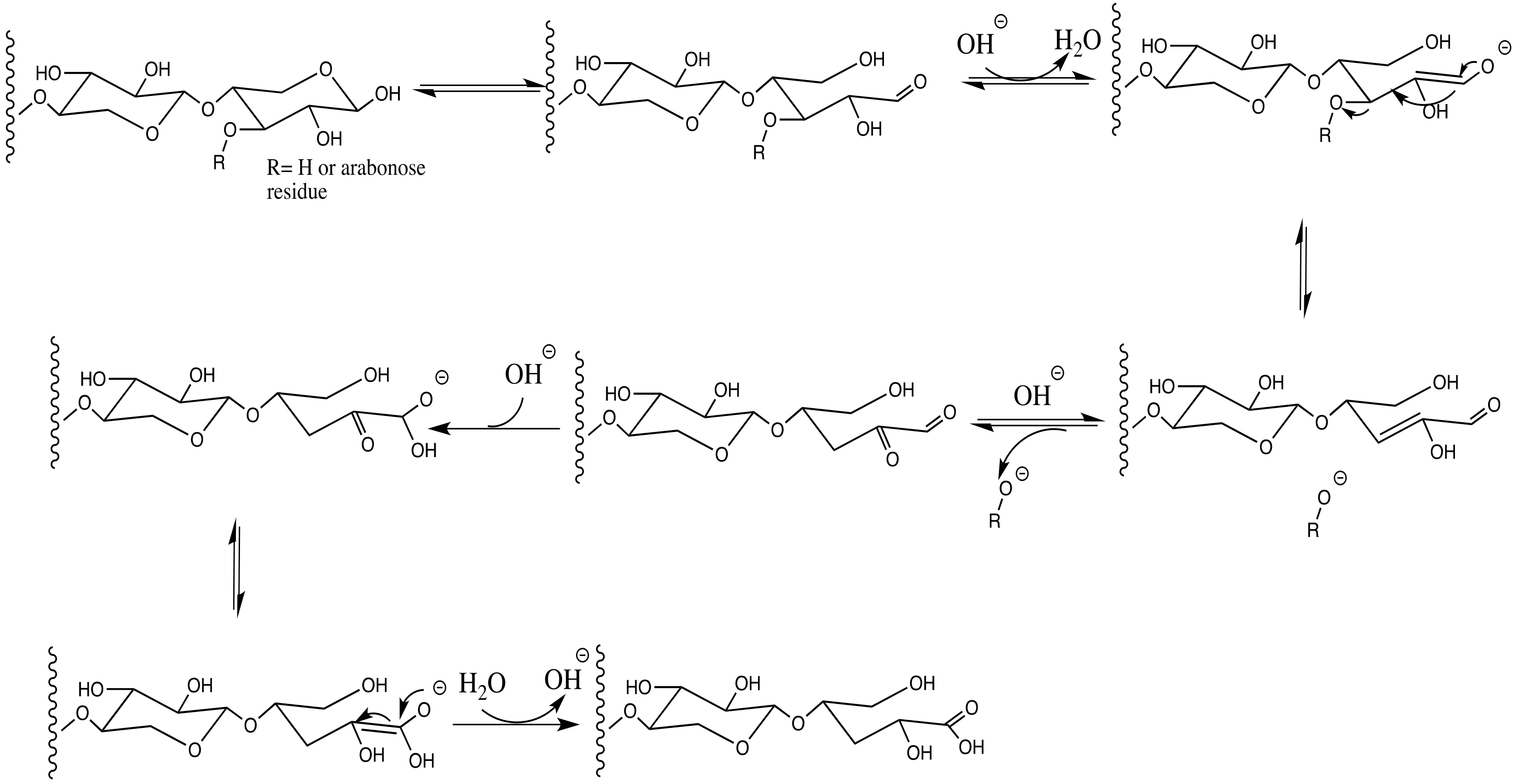
3. The Peeling Reaction



One residue is "lost" and peeling reaction can continue from the "new" reducing residue.

- The peeling reaction consist of a number of enol-equlibria, that is alkaline catalyzed, and an alkaline catalyzed elimination reaction.

Stopping reaction

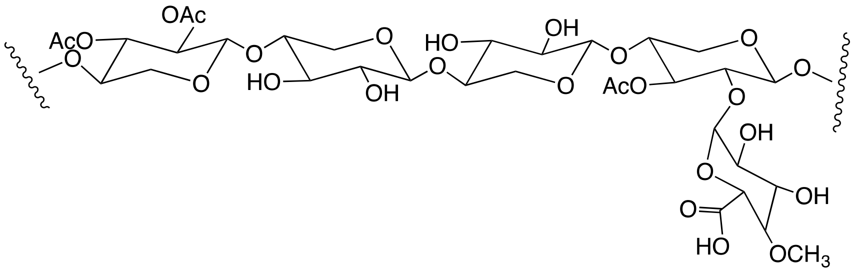


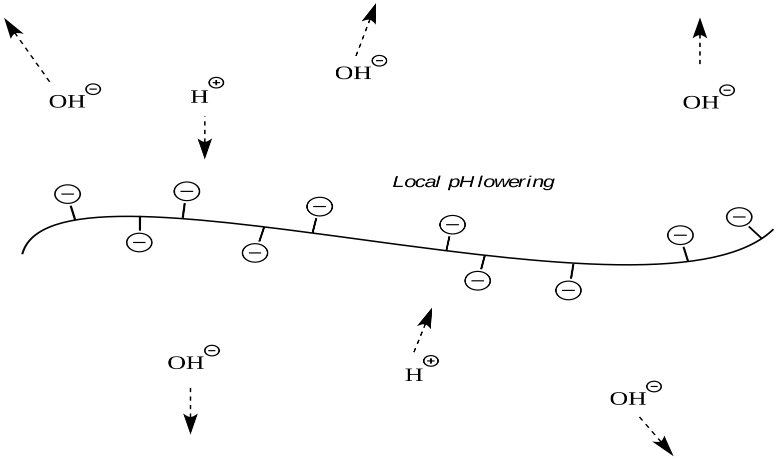
R= H or arabonose residue

This structure is stable against the peeling reaction.

- This is the ”traditional” way to explain the stability of xylan. A group is ”sacrificed” instead of the reducing end and this works better if it is a good reducing group as arabinose than a less good leaving group as hydroxyl ion.

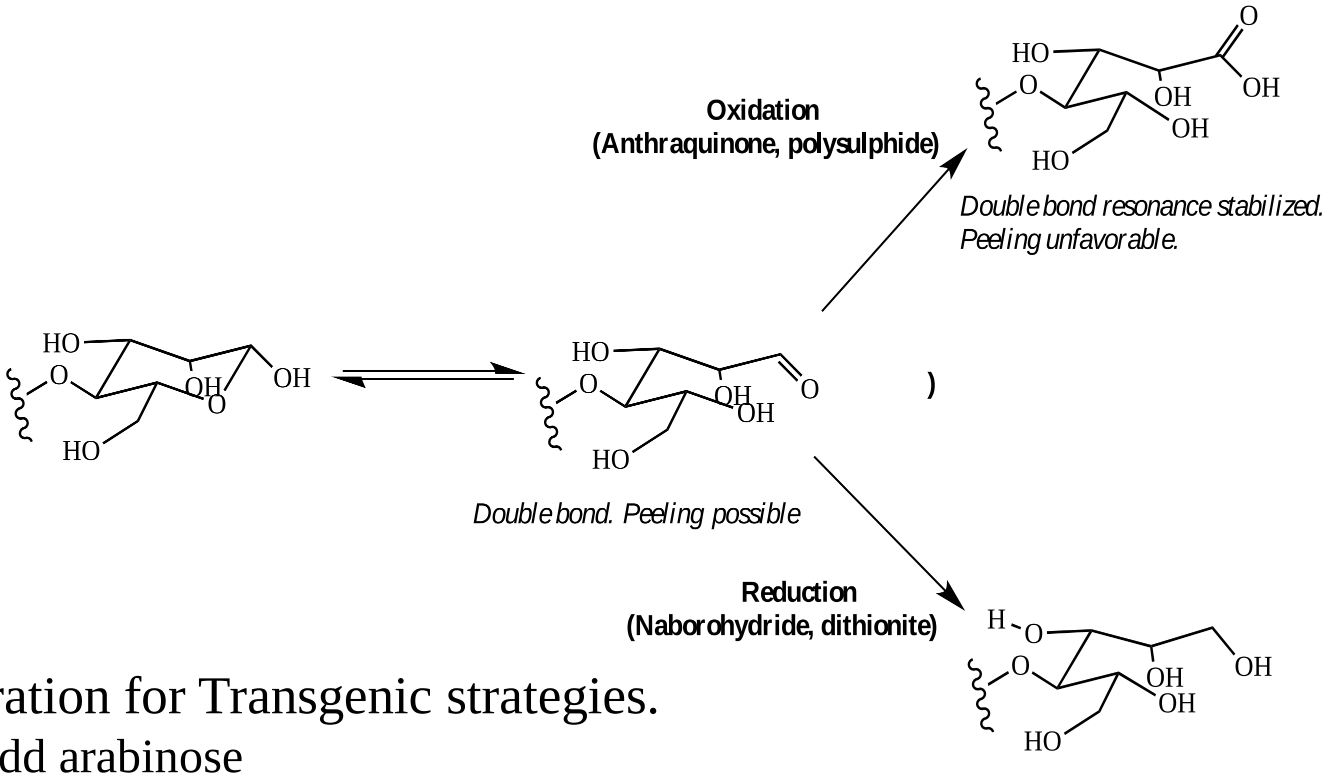
Why is hardwood xylan relatively stable?





- There is little or no arabinose in the hardwoods xylan, but anyway it is not degraded to the same extent as glucomannans.
- Can glucuronic acid play the same role as arabinose in stopping reaction? (”Sacrificing ” leaving group)
  - Probably not. It is not possible
- A better suggestion might be that xylan is ”shielding” the polymer from alklaine catalyzed reactions by creating a lower ”micro pH” around the polymer?

What can we do about it?



Oxidation
(Anthraquinone, polysulphide)

Double bond resonance stabilized.
Peeling unfavorable.

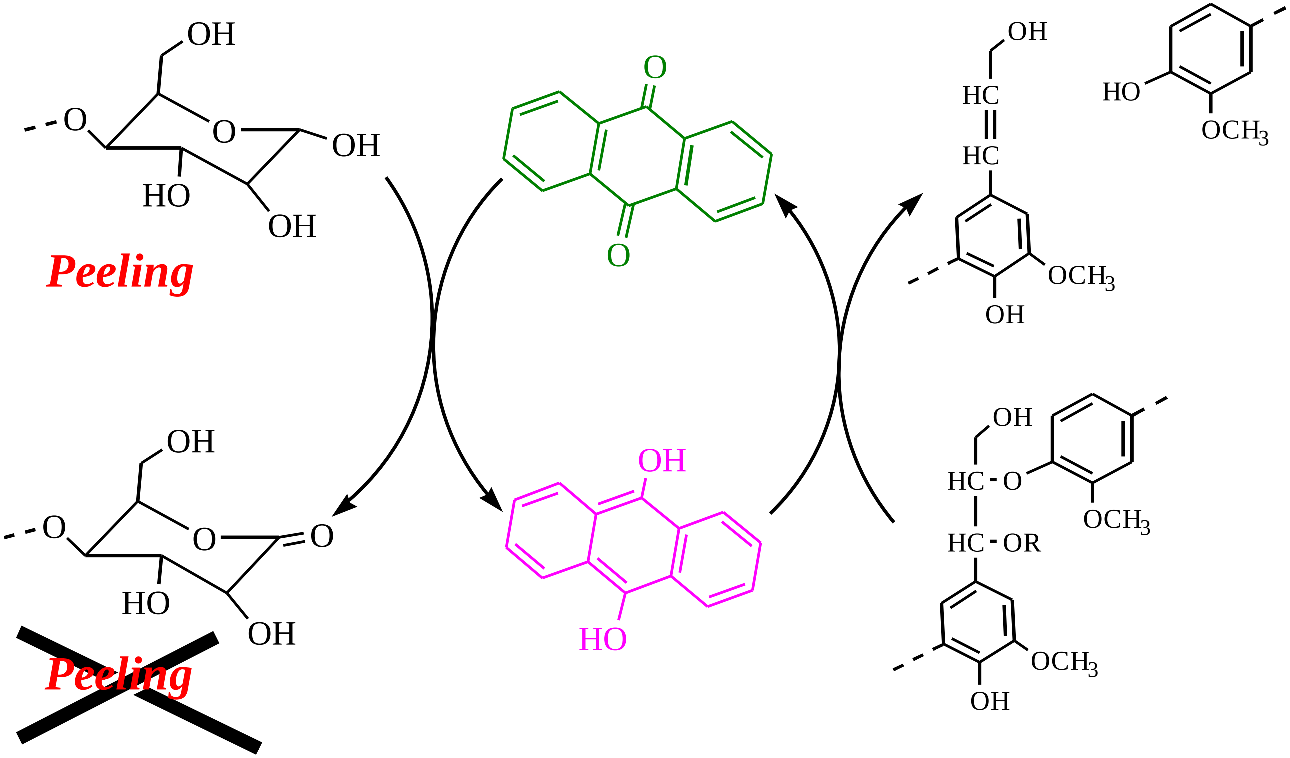
Double bond. Peeling possible

Reduction
(Naborohydride, dithionite)

No double bond Peeling impossible..

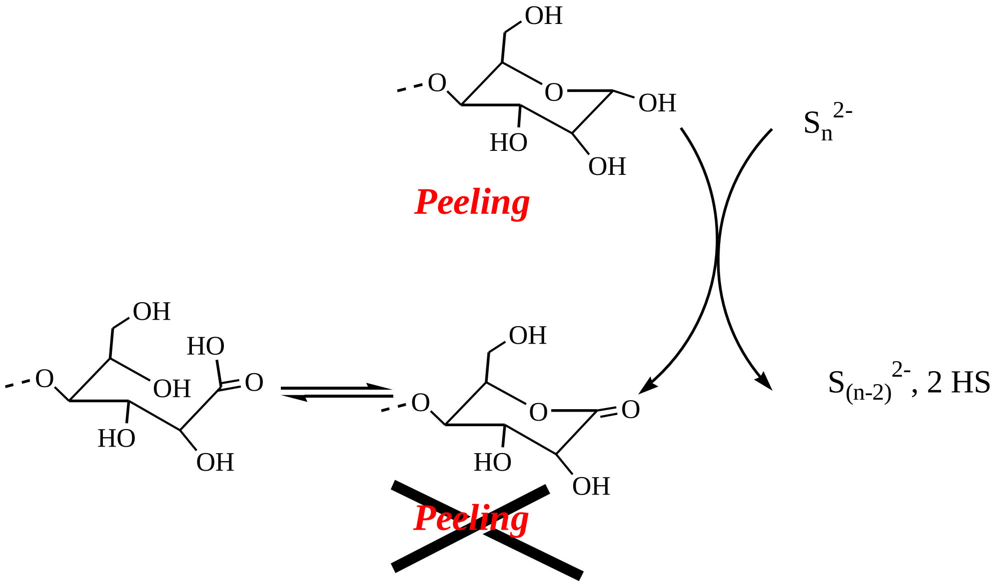
- Inspiration for Transgenic strategies.
  - Add arabinose
  - Add more charged groups?
- Additives to the white liquor can prevent peeling.
- Two main strategies. Oxidation and Reduction.
- Methods can not add any non-process elements, since it will disturb the closing system.

Oxidation I Antraquinone-soda/kraft



- The reducing ends in the polysaccharides provide the ”reducing power” for the delignification by oxidation.
- This oxidations stops (or rather slows down) peeling reaction, and anthraquinon pulping thus gives higher yield than normal kraft pulping.
- Anthraquinone have been very popular way to increase yield. There are indications that anthraquinone can be carcinogenic.
- In many countries it is on the way out!

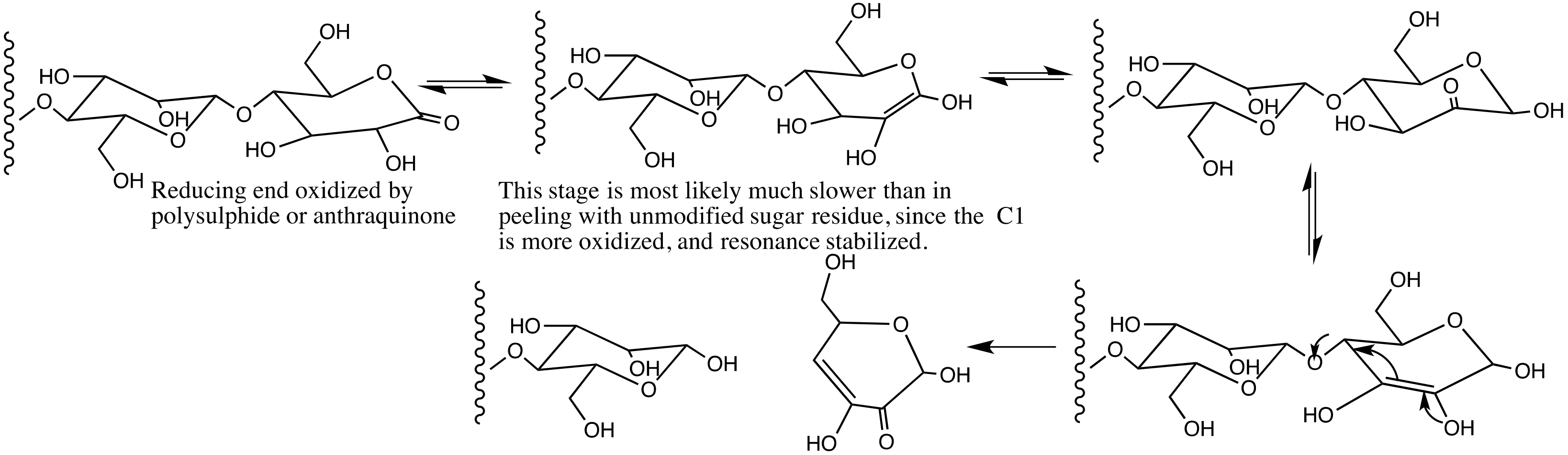
Polysulphide – stabilization towards peeling



- The stabilization reaction of polysaccharides increase the yield especially of glucomannan.
- Polysulphide is made by oxidation of white liquor.
- Often a problematic step, since active sulphur can be lost, but improved oxidation techniques have been developed

Reduction more efficient?

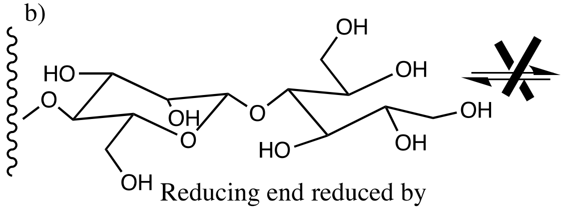
a)



Reducing end oxidized by polysulphide or anthraquinone

This stage is most likely much slower than in peeling with unmodified sugar residue, since the C1 is more oxidized, and resonance stabilized.

b)

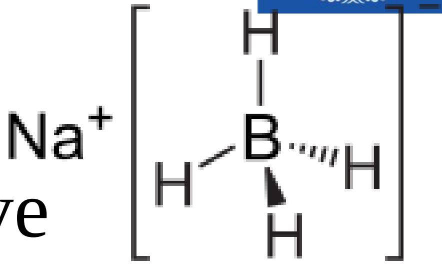


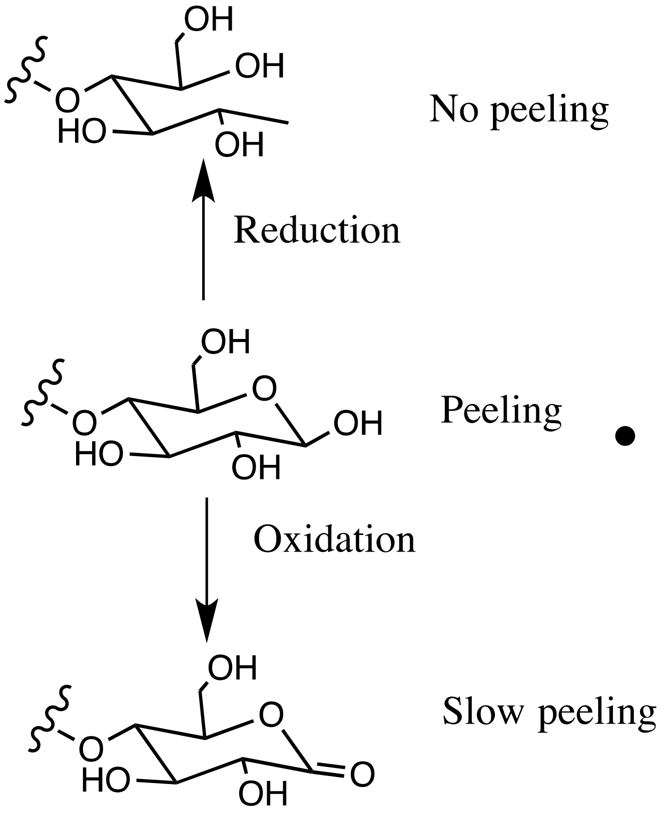
Reducing end reduced by sodium borohydride

No peeling reaction possible, since no double bond.

- When we have compared oxidative pretreatment and the reduction with sodium borohydride, the lattes seems more efficient.
- One possible explanation is that peeling actually may occur, but slower also on the oxidized end group.
- Reduction may be more efficient than oxidation. Can we use this industrially?

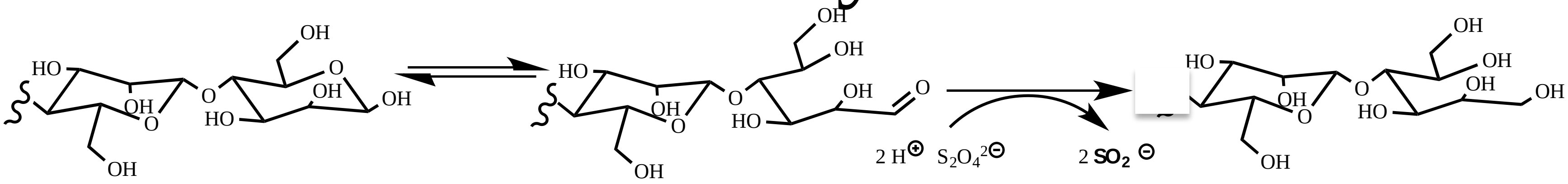
Reduction with what?





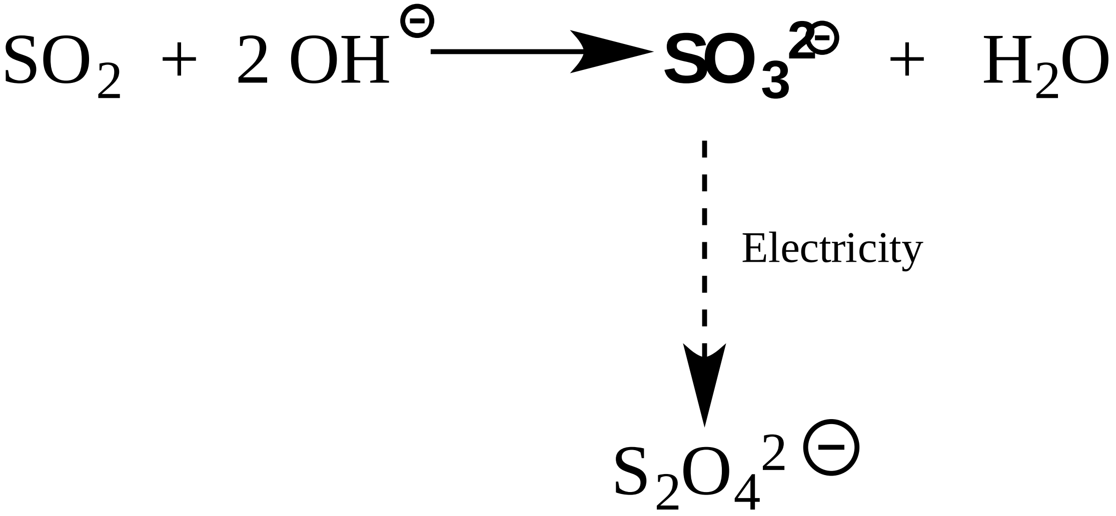
- Sodium borohydride have been tested with good result, but it is expensive and might disturb the chemical recovery system.
- H_2S is suggested, and have got some good results, but difficult to work with (poisonous gas) and some uncertainties about the mechanisms.

Dithionite have the potential to increase yield!



- We have tested the system and it seems to works good on model compounds. (Mono sugars and polysaccharides)
- Preliminary pulping experiments gave higher yield, brightness and viscosity, and lower lignin content, but weaker effects than we hoped on.
- In pulping it is complicated since it is instable at high temperatures, but we have some promising results and a similar system were tested already in the 50thies.

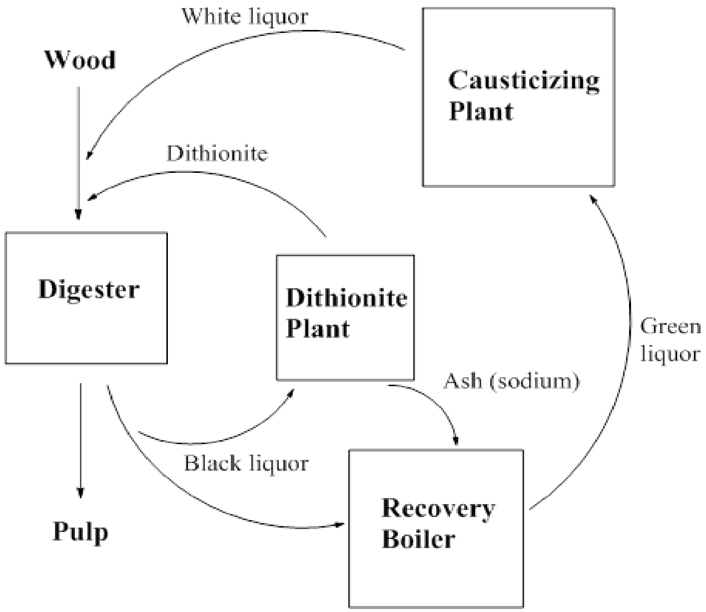
Can is work with closing?



$$\mathrm{SO_2} + 2\,\mathrm{OH}^{\ominus} \longrightarrow \mathrm{SO_3}^{2\ominus} + \mathrm{H_2O}$$

Electricity

$$\mathrm{S_2O_4}^{2\ominus}$$



- Dithionite can be generated from SO_2 with the help of electricity.
- It should be possible to include dithionite in kraft pulping.
- More studies are needed!

Conclusions

- The main part of the carbohydrate losses is due to degradation of hemicelluloses.
- Yield losses are due to dissolution and chemical degradation by alkaline hydrolysis and peeling.
- The structures of the polysaccharides are of large importance for their hydrolysis rate.
- Glucomannan is most sensitive to degradation followed by hardwood xylan and thereafter softwood xylan. Cellulose is relatively stable.
- The relatively high stability of xylan may be due to stopping reactions, but could also to shielding effects of the carboxylic acids of the polysaccharide.
- Controlled alkaline profiles and temperature profiles can, to some extent, lower carbohydrate losses, but for higher yield savings, oxidations and reductions of the reducing end are to be preferred.
- Dithionite treatment may represent an industrial interesting alternative for increasing the yield of kraft pulping.

THANK YOU FOR LISSENING!