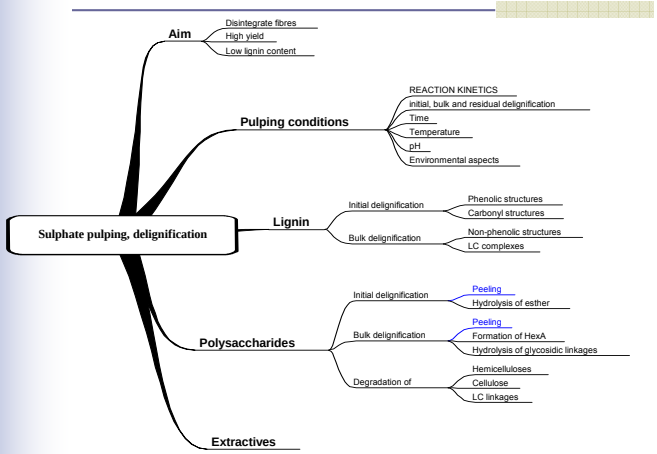
Alkali-catalyzed degradation of the cell wall polysaccharides

Part I: Primary peeling reactions of reducing end groups

Outline



Reactions in pulping

- Aim of kraft pulping is to remove lignin and disintegrate fibres
- However selectivity of kraft pulping is low
  - alkaline pulping solution attacks polysaccharides
  - degradation of polysaccharide chains
  - lost of yield

Reactions of the polysaccharides during pulping

- 20-30 % of the polysaccharides degrade during pulping
- The reactivity of polysaccharides depends on the supramolecular and chemical structure
  - cellulose is more stable than hemicelluloses
  - cellulose has crystalline nature and high degree of polymerization
  - the reactivity of hemicelluloses also differ notably
    - the amount of side chains and substituents

crystalline = kiteinen; heating-up period = nostovaihe; yield = saanto

Main reactions of polysaccharides during alkaline pulping

INITIAL DELIGNIFICATION
t < 140°C

- Alkali-catalyzed primary peeling of end groups
- Stopping reaction of peeling
- ⇒ Large amounts of hemicelluloses degrade and disssolve
  - ⇒ mainly glucomannans
- Alkali-catalyzed hydrolysis of esters

BULK DELIGNIFICATION
t >140 °C

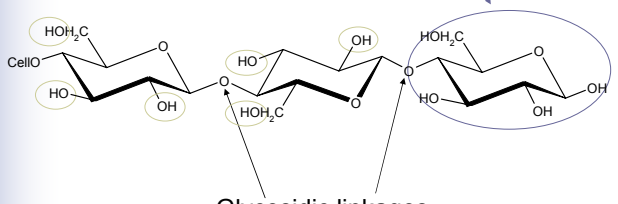
- **Alkali-catalyzed primary peeling of end groups**
- **Stopping reaction of peeling**
- ⇒ **Dissolution of hemicelluloses**
  - ⇒ **mainly xylan**
- **Alkali-catalyzed hydrolysis of glycosidic linkages (160 °C - 170 °C)**
- **Secondary peeling reaction**
- ⇒ **Cleavage of cellulose and hexenuronic acid groups (HexA)**
- **readsorption of xylan**

peeling = päätepilkkoutuminen; degradation product = pilkkoutumistuote; deacetylation = deasetylointi, asetyyyliryhmien poisto; xylan = ksylaani

The main reactive sites of carbohydrates

Hydroxyl groups

Reducing end groups, (e.g. hemiacetal structures)

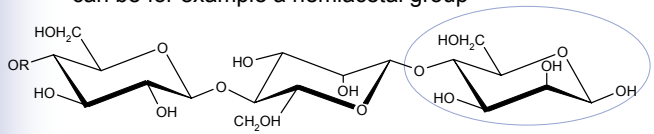


Glycosidic linkages

N.B. Also ester linkages are reactive in alkaline media.

Reducing sugars and end groups

- Reducing sugar is a carbohydrate that can be oxidized by a mild oxidizing agent
  - Sugar (a reducing agent) is oxidized and an oxidizing agent is reduced
  - E.g. oxidation of an aldehyde group to carbonyl group
  - Reducing sugars contain a reducing end group that can be for example a hemiacetal group



β-D-Glcp-1→ 4- β-D-Manp-1→ 4- β-D-Manp
Glucomannan

reducing sugar = pelkistävä sokeri; oxidizing agent = hapetin, reducing agent = pelkistin

- hemicelluloses
  - branched structure and more substituents
  - the amount of substituent effect solubility
  - glucomannan has less substituents in C-2 and C-3 positions than xylan and is therefore is more reactive

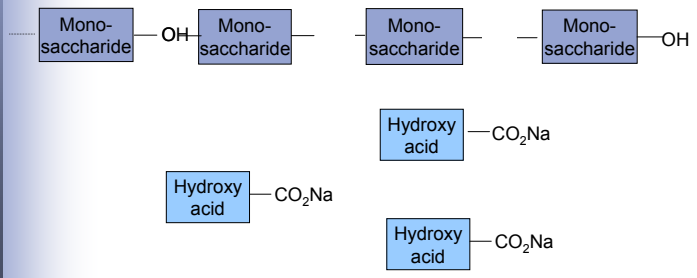
Degradation of polysaccharides
Alkaline peeling of reducing end units

- Alkaline peeling or endwise depolymeration can be defined as elimination of monosaccharide end units from the polysaccharide chain

1. In case of 1→4 bonded polysaccharides, like glucomannans, the reaction starts with isomerization of a reducing end groups
2. After that β-alkoxy elimination takes place
   - cleavage of a monosaccharide unit

isomerization = isomeroituminen, toisiintuminen; reducing end group = pelkistävä pääteryhmä; aldose = aldoosi; ketose = ketoosi; alkoxy = alkoksi-; hydroxycarboxy acid = hydroksi(karboksyylihappo);

Primary peeling of reducing end groups



Degradation of polysaccharides
Alkaline peeling of reducing end units

The results of peeling reaction:

- polysaccharide chain becomes shorter
- formation of a new reducing end group
- soluble degradation products; hydroxy carboxylic acids

- Due to neutralization reactions degradation products consume main part of the alkaline cooking liquor
- Main part of the cooking liquor is consumed in the initial phase of pulping

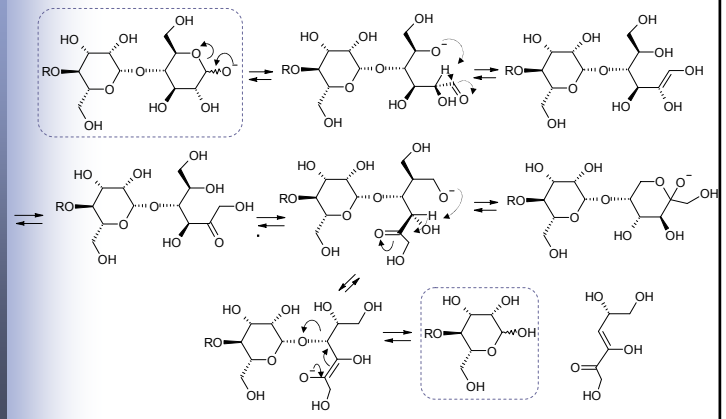
Stopping reaction

- Stopping reaction terminates the degradation of a polysaccharide chain
- Reaction mechanism:

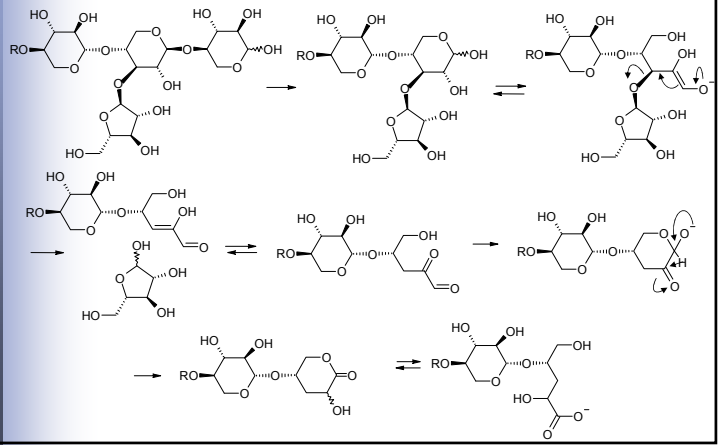
1. β-hydroxy elimination
   - cleavage of a hydroxyl group from the monosaccharide end unit
2. Formation of alkali-stable end units which prevent peeling reactions
   - carboxylic acid groups

Degradation of hemicelluloses

Primary peeling of reducing end groups of glucomannan



Stopping reaction



Rate of reaction

- Rates of reactions (peeling and stopping) are determined by enolization
- Enolization is an intramolecular reaction and is dependent on the degree of ionization

⇒ Rate of peeling reaction:

$$dc/dt = kx_{ion}c = kK_{ion}[HO^-]c/(1+K_{ion}[HO^-])$$

enolization = enolisoituminen; enol = enoli , HO-CH=CH2

Rate of reaction

- Amount of reducing end groups remains constant during the main peeling reaction (Reaction 1)
- Competing stopping reaction can reduce the amount of reducing end groups (Reaction 2):

$$[Re] = [Re]_0 e^{-k't}$$

where

[Re]	is concentration of reducing end groups
k'	is rate constant of stopping reaction

Rate of reaction

- Competing stopping reaction has a lower rate than the peeling reaction
  - the stopping reaction has a higher entalpy of activation
- As the temperature increases the rate of stopping reaction increases

  ⇒ In theory the degree of polysaccharide degradation is lower in higher temperature (primary peeling reaction)

  70-80% of glucomannans are peeled off during the initial delignification

Rate of reaction
Degradation products

- Formation of degradation products:

$$d[A]/dt = k[Re]_0 e^{-k't}$$

where

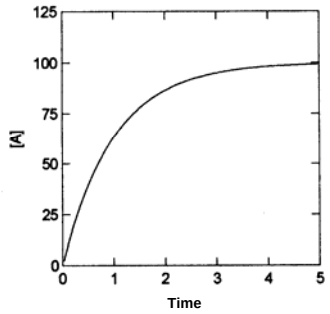
[A]	is concentration of degradation products
k	is the rate constant of peeling reaction

⇒ $[A] = [Re]_0(1- e^{-k't}) \; k/k'$

k/k' expresses the amount of monosaccharide end units peeled off before the polysaccharide chain stabilizes (order of magnitude 10^2)

degradation product = pilkkoutumistuote

Formation of degradation products

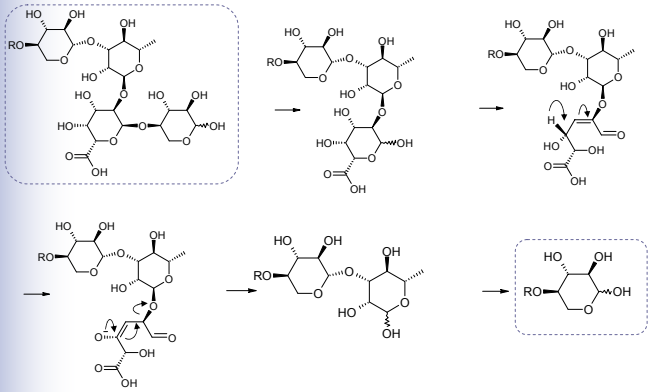


Formation of degradation products as a function of time (k/k'=100, k=1)

Degradation of hemicelluloses
Dissolution of xylan – reaction A

- Degradation of xylan differs from degradation of glucomannans (reaction 1)
- The reaction happens in higher temperature than reactions of glucomannans
- Reducing end units of hardwood xylan are peeled off without isomerization
- The main reaction is β-hydroxy elimination followed by enolization (3,4 – enolate)

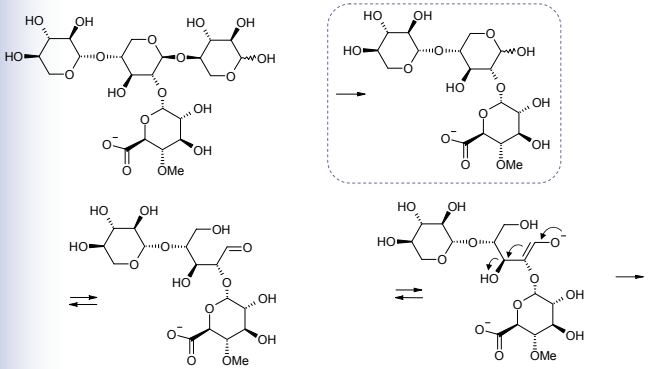
Degradation of hemicelluloses
Dissolution of xylan – reaction A



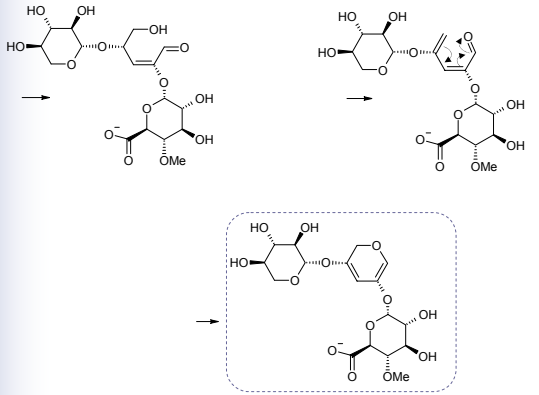
Degradation of hemicelluloses
Dissolution of xylan – reaction B

- If the reducing end unit contains a 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid) substituent the main reaction is different from reaction A
- The main mechanism is a direct β-hydroxy elimination

Degradation of hemicelluloses
Dissolution of xylan – reaction B (1/2)



Degradation of hemicelluloses
Dissolution of xylan – reaction B (2/2)



Degradation of hemicelluloses Dissolution of xylan

- Xylans are more stable against peeling than glucomannans:
  - arabinose side groups in softwood xylan
  - presence of 4-O-methylglucuronic acids in soft wood and hard wood xylans
  - glucomannans don't have substituents at C2 or C3 positions that could retard the peeling reactions
- Reactions of xylan are slower and 40-50 % of xylan is peeled off during pulping

Degradation of hemicelluloses Dissolution of xylan

- Degradation products of xylan are polymers
- Dissolution of xylan polymers is dependent on the porosity of cell wall
  - Large polymers cannot penetrate the cell wall
  - After the degradation of lignin and other hemicelluloses, like glucomannans, porosity of cell wall increases and improves the dissolution of xylan

Degradation products in kraft black liquor (% of total dry matter)

Component	Pine	Birch
Lignin	31	25
Aliphatic carboxylic acid	29	29
Formic acid	6	4
Acetic acid	4	8
Glycolic acid	2	2
Lactic acid	3	3
2-Hydroxybatanoic acid	1	5
3,4-Dideoxypentonic acid	2	1
3-Deoxypentonic acid	1	1
Xyloisosaccharinic acid	1	3
Glucoisosaccharinic acid	6	3
Others	3	3
Other organics	7	9
Extractives	4	3
Carbohydrates (hemicellulose-derived fragments)	2	5
Miscellaneous	1	1
Inorganics	33	33
Sodium bound to organics	11	11
Inorganic compounds	22	22

Summary

- Hydroxyl ion catalyzes the peeling reaction of carbohydrates
- Degree of degradation of hemicelluloses is significant in comparison with celluloses
  - 70-80 % of glucomannans is peeled off during pulping (initial stage)
  - reactions of xylan are slower and 40-50 % of xylan is peeled off during pulping
    - dissolution of xylan is dependent on the porosity of the cell wall