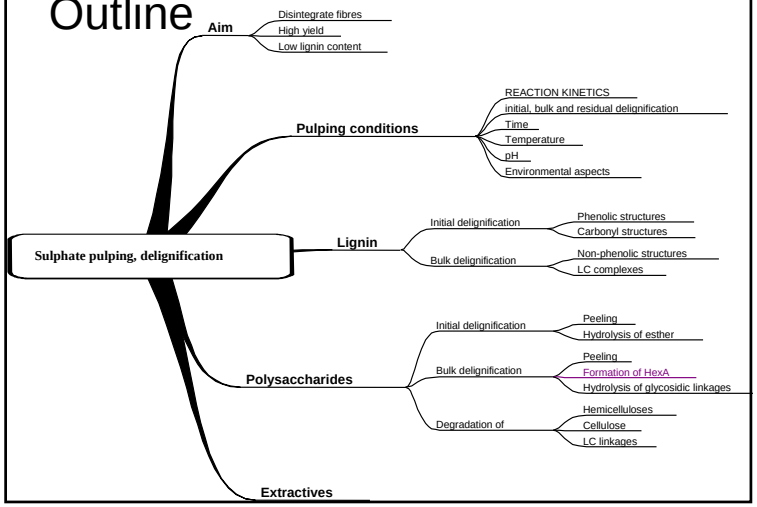
Formation of hexenuronic acid groups of xylan

Outline



Hexenuronic acid groups

- Alkaline cooking liquor is able to ionize carboxylic acid groups
- the main part of the anionic groups of kraft pulp consist of hexenuronic acid groups of xylan

Carboxyl groups of conventionally cooked kraft pulp

κ =25,9

METHOD	INFORMATION	COOH (mmol/kg)
Potentiometric titration	**Carboxylic acids**	**85**
	uronic acids of xylan	**68**
	carboxyl acids of lignin	**17**
Polyelectrolyte titration	**Net charge (M_w=8000)**	**100**
	Surface charge(M_w=2000)	**30**
Entsymatic hydrolysis	**Uronic acids of xylan**	**60**
	HexA	**47**
	MeIdoA	**2**
	MeGlcA	**11**

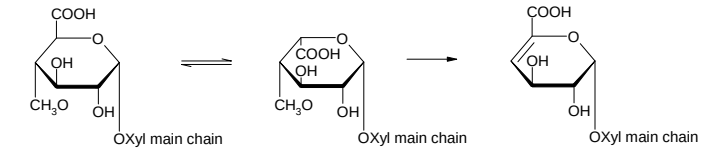
(Vuorinen *et al.,* Hiilihydraatit prosessiteollisuudessa, Teknologiaohjelmaraportti 9/96)

Formation of hexenuronic acid groups

- Step 1:
  - alkali-catalyzed demethoxylation of 4-O-methylglucuronic acid groups of xylan in the initial delignification phase
  - cleavage of methanol units continues in the bulk delignification stage

  ⇒formation of hexenuronic acid groups (HexA)
- Step 2:
  - cleavage of hexenuronic acid groups of the polysaccharide chain in the bulk delignification

Formation of hexenuronic acid groups



Methylglucuronic acid MeGlcA | Methyliduronic acid MeIdoA | Hexenuronic acid HexA

Rate of reaction

- Formation and degradation of HexA:

$$d[HexA]/dt = k_1[HO^-][MeGlcA] - k_2[HO^-][HexA] \quad (1)$$

where [MeGlcA] is concentration of 4-O-methylglucuronic acid

$$\Rightarrow [HexA] = [MeGlcA]_0 k_1 (e^{-k1[HO^-]t} - e^{-k2[HO^-]t})/(k_2 - k_1) \quad (2)$$

- rate constants k_1 and k_2 are dependent on the ion concentration

Mechanism for the reaction

- Formation of a HexA group is based on collision of two anions
- Electrical repulsion lowers the rate of reaction

  Rate of reaction is dependent on the electrolyte concentration
- Debye-Hückel equation describes the effect of electrolyte concentration

Debye-Hückel equation:

$$\log(k/k_0) = 2Az_Az_B\mu^{1/2} \qquad (3)$$

where k_o is rate constant in zero electrolyte concentration

A Debye-Hückel constant (0,51 $M^{-1/2}$ at 25ºC)

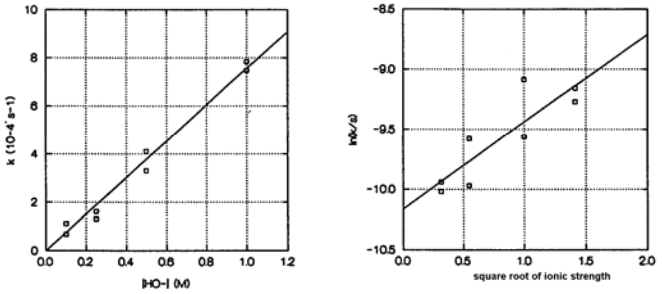
z_A, z_B charge numbers of ions

μ electrolyte concentration

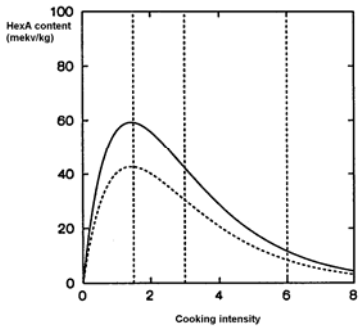
- in practice the equation (3) can be presented as:

$$\log(k/k_0) \sim \mu^{1/2} \qquad (4)$$

Effect of $[HO^-]$ and electrolyte concentration on formation of HexA



Formation of HexA during pulping



Effect of cooking method on the amount of uronic acid groups in xylan

- Cooking method has a effect on the structure of xylan (Table 2)
  - especially the amount of uronic acid group
- Cooking method also affects the total amount of xylan in pulp

Table 2. (Vuorinen *et al.*, Hiilihydraatit prosessiteollisuudessa, Teknologiaohjelmaraportti 9/96)

Cooking method	Kappa number	Amount of xylan (%)	Uronic acid (mol/ 100 mol of xylose)
Conventional kraft	24,2	9,0	8,7
SuperBatch	11,8	6,7	1,7

Importance of hexenuronic acid groups

- HexA consists of doubly bonded carbons
- As observed earlier also lignin contains these -C=C- structures
- Kappa number is often used for indication of the lignin content in pulp
- The method is based on the consumption potassium permanganate by lignin
- However permanganate reacts with all unsaturated hydrocarbons (-C=C- structures)
- Therefore the kappa number expresses the amount of lignin *and hexenuronic acid* in pulp

Influence of hexenuronic acid groups on pulping and bleaching

- Hexenuronic acid groups:
  - consume certain bleaching chemicals
    - ClO_2, O_2, Cl_2, HOCl and peroxyacids
    - increased bleaching costs
    - environmental aspect
  - bind heavy metal ions
    - Cu, Fe and Mn

    $\Rightarrow$degradation of peroxides in bleaching
  - cause colour reversion of pulps

Removal of HexA:

- Hexenuronic acid groups can be removed by selective hydrolysis
- Subject will be discussed more in the Lecture 10

Hexenuronic acid groups - summary