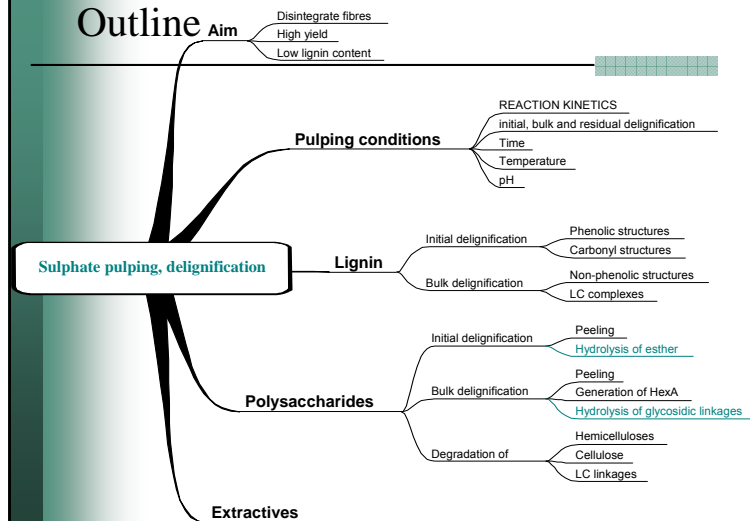


## Alkali-catalyzed degradation of the cell wall polysaccharides

*Part II : Acid- and base-catalyzed hydrolysis of esters and glycosidic linkages*



## Outline



## 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 dissolve
  - ⇒ 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 acids (HexA)
- readsorption of xylan

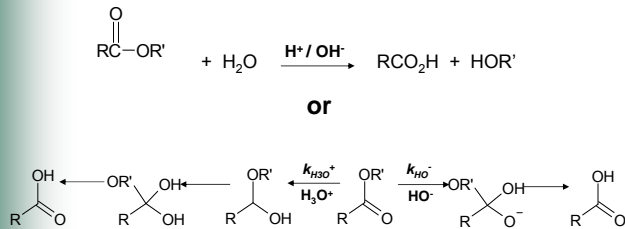
peeling = päätepilkkoutuminen; degradation product = pilkkoutumistuote; deacetylation = deasetylointi, asetyyliyhymien poisto; xylan = ksylaani

## Esters in wood

- Soft wood galactoglucomannans and hard wood xylans consist of acetyl groups
- Galacturonic acid groups of pectin in the primary cell wall are partly methylesters
- Part of the linkages between lignin and hemicelluloses are esters
- Hydrolysis of these esters is relatively easy both in acid and alkaline conditions

## Acid- or base- catalyzed hydrolysis of esters

- Hydrolysis can be defined as cleavage by water
- the mechanism of acid- or base-catalyzed hydrolysis of esters can be presented accordingly:



## Rate of reaction

- Alkali- or base-catalyzed hydrolysis of ester:

$$d[\text{E}]/dt = -k_{\text{HO}^-}[\text{E}][\text{HO}^-]$$

where  $[\text{E}]$  is concentration of ester

- Acid-catalysed hydrolysis of ester:

$$d[\text{E}]/dt = -k_{\text{H}_3\text{O}^+}[\text{E}][\text{H}_3\text{O}^+]$$

- Total rate of reaction

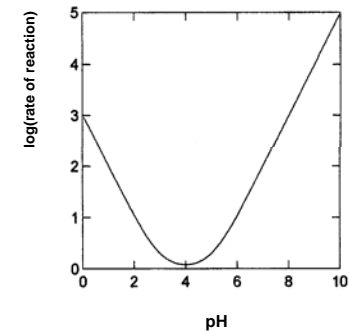
$$d[\text{E}]/dt = -k_{\text{H}_3\text{O}^+}[\text{E}][\text{H}_3\text{O}^+] - k_{\text{H}_2\text{O}}[\text{E}] - k_{\text{HO}^-}[\text{E}][\text{HO}^-]$$

## Effects of hydrolysis of esters

- Hydrolysis of esters is rapid also in room temperature when  $\text{pH} > 8$ 
  - ⇒ hemicelluloses are deacetylated from the moment they are put in contact with alkaline cooking liquor or bleaching agent
  - ⇒ cleavage of ester linkages between hemicelluloses and lignin

## Hydrolysis of esters

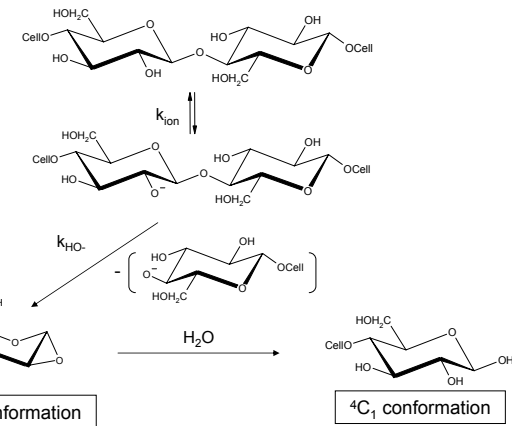
### Influence of pH on the rate of reaction



## Alkali-catalyzed hydrolysis of glycosidic linkages

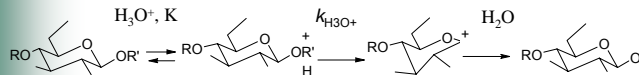
- The mechanism for the reaction is  $S_N2$  (bimolecular nucleophilic substitution)
- However in this case the nucleophile is an internal nucleophile => intramolecular reaction
  - an ionized hydroxy group
- intramolecular reactions have higher entropy than intermolecular reactions as it was observed in lignin depolymerization reactions

## Alkali-catalyzed hydrolysis of glycosidic linkages



## Acid-catalyzed hydrolysis of glycosidic linkages

- Acid hydrolysis is an important reaction in **sulphite pulping**
- Compared with bases acids can easily cleave glycosidic linkages of polysaccharides
- Reaction mechanism ( $S_N1$ ):



## Hydrolysis of glycosidic linkages

### Rate of reaction

- Alkali-catalyzed reaction:

$$d[G]/dt = -k_{HO^-}[G] = -k_{HO^-}K_{ion}[HO^-][G]/(1+K_{ion}[HO^-])$$

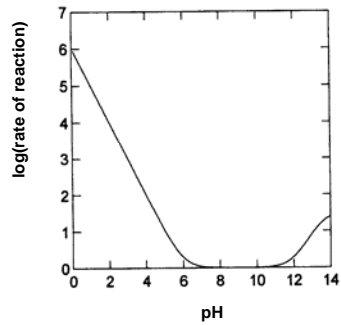
- Acid-catalyzed reaction:

$$d[G]/dt = -k_{H_3O^+}[GH^+] = -k_{H_3O^+}K[H_3O^+][G]$$

- Total hydrolysis (acid, alkali and water-catalyzed):

$$d[G]/dt = -k_{H_3O^+}K[H_3O^+][G] - k_{H_2O}[G] - k_{HO^-}K_{ion}[HO^-][G]/(1+K_{ion}[HO^-])$$

## Hydrolysis of glycosidic linkages Influence of pH on the rate of reaction



## Effect of hydrolysis of glycosidic linkages on polysaccharides

- The hydrolysis leads to cleavage of glycosidic linkages
  - ▷ formation of new reducing end groups
  - ▷ secondary peeling of polysaccharids
    - depolymerization of celluloses => lost of yield
- During the bulk delignification the alkali-catalyzed hydrolysis of celluloses is a very slow reaction and has a high enthalpy ( $150 \text{ kJmol}^{-1}$ ) in comparison with depolymeration of lignin  $\Delta H = 120 \text{ kJmol}^{-1}$