Formation of hexenuronic acid groups of xylan

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

Outline

Carboxyl groups of conventionally cooked kraft pulp

<table>
<thead>
<tr>
<th>METHOD</th>
<th>INFORMATION</th>
<th>COOH (mmol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potentiometric titration</td>
<td>Carboxylic acids</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Uronic acids of xylan</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>Carboxyl acids of lignin</td>
<td>17</td>
</tr>
<tr>
<td>Polyelectrolyte titration</td>
<td>Net charge (M_w=8000)</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Surface charge (M_w=2000)</td>
<td>30</td>
</tr>
<tr>
<td>Entsymatic hydrolysis</td>
<td>Uronic acids of xylan</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>HexA</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>MeldoA</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>MeGlcA</td>
<td>11</td>
</tr>
</tbody>
</table>

(Vuorinen et al., Hililhydraatit 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

Rate of reaction

• Formation and degradation of HexA:
  \[ \frac{d[\text{HexA}]}{dt} = k_1[\text{HO}^-][\text{MeGlcA}]-k_2[\text{HO}^-][\text{HexA}] \]  
  \[ \text{where} \quad [\text{MeGlcA}] \text{ is concentration of 4-O-methylglucuronic acid} \] (1)
  \[ \Rightarrow [\text{HexA}]=[\text{MeGlcA}]/(e^{-k_1[t]}-e^{-k_2[t]})/(k_2-k_1) \] (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:
\[ \log\left(\frac{k}{k_0}\right) = 2AzAzB\mu^{1/2} \]  
(3)

where \( k_0 \) 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
\( \mu \) electrolyte concentration

* in practice the equation (3) can be presented as:
\[ \log\left(\frac{k}{k_0}\right) \sim \mu^{1/2} \]  
(4)

Effect of \([\text{HO}^-]\) and electrolyte concentration on formation of HexA

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., HiHydraatt prosessiteolleisuudessa, Teknologiaohjelmaraportti 9/96)

<table>
<thead>
<tr>
<th>Cooking method</th>
<th>Kappa number</th>
<th>Amount of xylan (%)</th>
<th>Uronic acid (mol/100 mol of xylose)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional kraft</td>
<td>24.2</td>
<td>9.0</td>
<td>8.7</td>
</tr>
<tr>
<td>SuperBatch</td>
<td>11.8</td>
<td>6.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>
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

Removal of HexA:

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

Influence of hexenuronic acid groups on pulping and bleaching

- Hexenuronic acid groups:
  - consume certain bleaching chemicals
    - ClO₂, O₂, Cl₂, HCl and peroxycids
    - increased bleaching costs
  - environmental aspect
  - bind heavy metal ions
    - Cu, Fe and Mn
    ⇒ degradation of peroxides in bleaching
  - cause colour reversion of pulps

Hexenuronic acid groups - summary