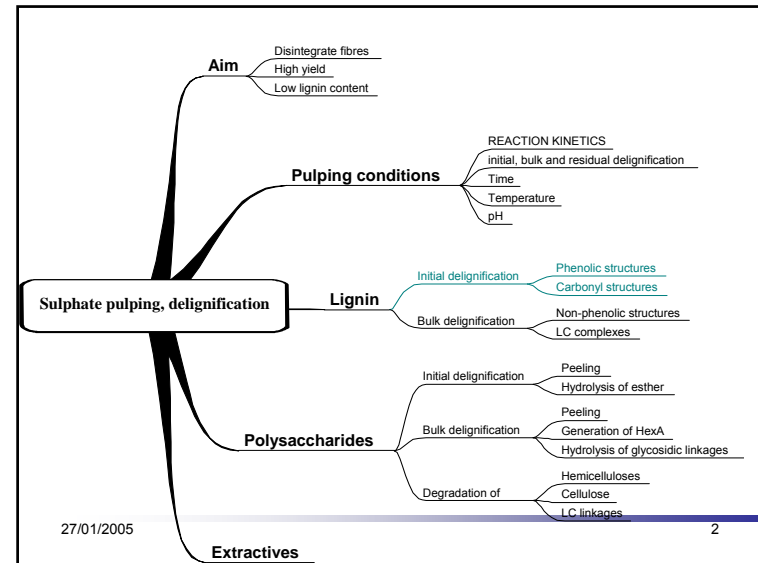


Lignin reactions in the initial stage of delignification

Reactions of phenolic and carbonyl structures

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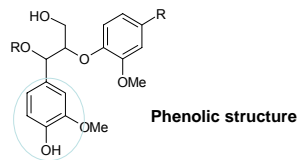


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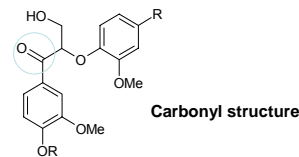
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Initial stage of kraft pulping

- Pulping chemicals: NaOH and Na₂S
 - Nucleophilic reactions
 - OH and HS ions
- Initial delignification
 - impregnation phase
 - temperature < 140 C
 - HS ion concentration important
- Reactions:
 - Phenolic and carbonyl structures react
 - 20 % of lignin degrades due to these reactions in the initial stage



Phenolic structure



Carbonyl structure

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Reactions of phenolic structures

- Main linkages between phenylpropane units of lignin are aryl ether linkages
 - Dominant types are $\alpha - O - 4$ and $\beta - O - 4$ (50 -70%)
- The main reaction of phenolic lignin structures in the alkaline media involves formation of quinone methide and cleavage of $\beta - O - 4$ linkages

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cleavage=lohkeaminen; quinone methide=kinonimetidi; thiol=merkaptani; sulfidoketone

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Reactions of phenolic structures

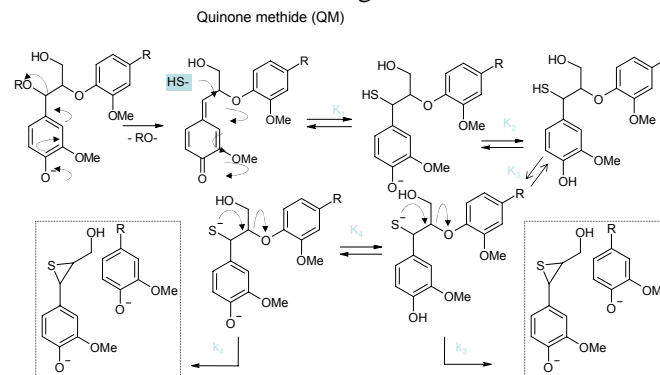
- Reaction of phenolic structures start by elimination of α -substituent (hydroxide or phenoxide ion [also known as cleavage of α -aryl ether, α -O-4, linkage])
=> Formation of quinone methide (QM)
- HS ions react with the quinone methide to form a thiol structure (mercaptide)
- Cleavage of beta aryl ether (β -O-4) linkages

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Reactions of phenolic structures

Formation of quinone methide and cleavage of β -O-4 linkages



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Reactions of phenolic structures

$$\text{Reaction 1: } K_1 = [1] / ([\text{QM}] [\text{HS}^-]) \quad (1)$$

$$\text{Reaction 2: } K_2 = [1] / ([2] [\text{HO}^-]) \quad (2)$$

$$\text{Reaction 3: } K_3 = [3] / ([2] [\text{HO}^-]) \quad (3)$$

$$\text{Reaction 4: } K_4 = [4] / ([3] [\text{HO}^-]) \quad (4)$$

$$\Rightarrow [3] = K_1 K_3 [\text{QM}] [\text{HS}^-] / K_2 \quad (5)$$

$$[4] = K_1 K_3 K_4 [\text{QM}] [\text{HS}^-] [\text{HO}^-] / K_2 \quad (6)$$

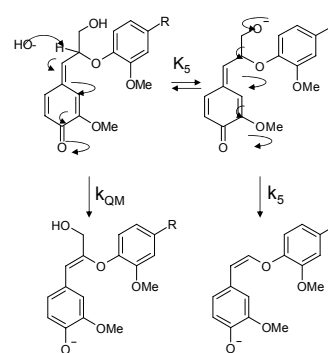
$$\text{Rate of reaction (cleavage of } \beta - \text{O} - 4 \text{ bond)} = -k_3 K_1 K_3 [\text{QM}] [\text{HS}^-] / K_2 - k_4 K_1 K_3 K_4 [\text{QM}] [\text{HS}^-] [\text{HO}^-] / K_2 \quad (7)$$

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Reactions of phenolic structures

Concurrent reactions



- Quinone methide structure can also undergo other reactions:

- Elimination of a proton (bimolecular reaction) or a formaldehyde (intramolecular reaction); ionization of γ - hydroxyl group)

=> formation of enol ethers

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Reactions of phenolic structures

Concurrent reactions

Rate of concurrent reaction:

$$K_5 = [5]/([QM][HO^-])$$

$$\text{Rate} = -k_{QM}[QM][HO^-] - k_5 K_5 [HO^-][QM]/(1 + K_5[HO^-])$$

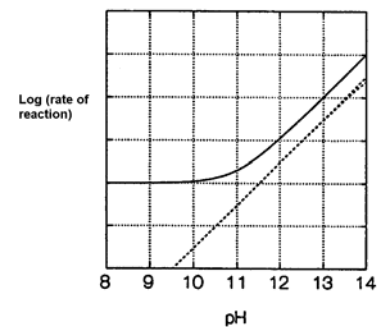
⇒ Rate of reaction depends on

- HO⁻ concentration
- degree of ionization of γ- hydroxyl group

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Effect of [HO⁻] on cleavage of β-O-4 linkages and formation of enol ethers



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Cleavage of β-O-4 (β-aryl ether) linkages (solid line) and the formation of enol ethers (dashed line)

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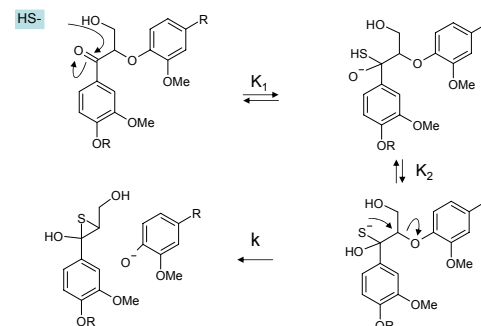
Reactions of carbonyl structures

- Native lignin consists of α-carbonyl and coniferyl aldehyde structures
- Nucleophiles can form addition products with carbonyl structures

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Reaction of carbonyl structures



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Reaction of carbonyl structures

- An addition reaction of HS⁻ to α-carbonyl structure:

Rate constants:

$$K_1 = [2]/([1][HS^-])$$

$$K_2 = [3]/[2]$$

$$\text{Rate} = -k[3] = -kK_1K_2[1][HS^-]$$

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SUMMARY: Reaction of lignin in pulping (Initial stage)

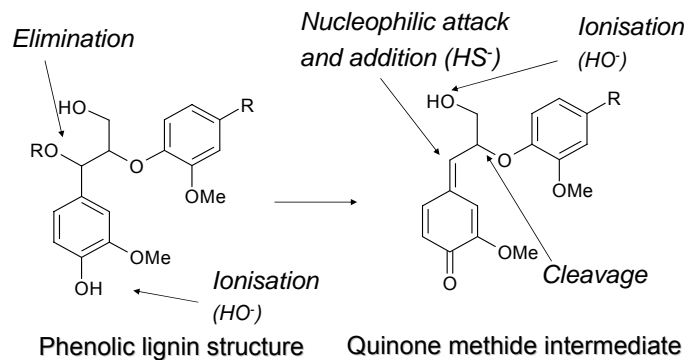
I Reactions of phenolic structures

- Formation of quinone methide
- Addition of nucleophiles
- Ionisation of α - substituent (HS)
- Cleavage of β-O-4 linkages

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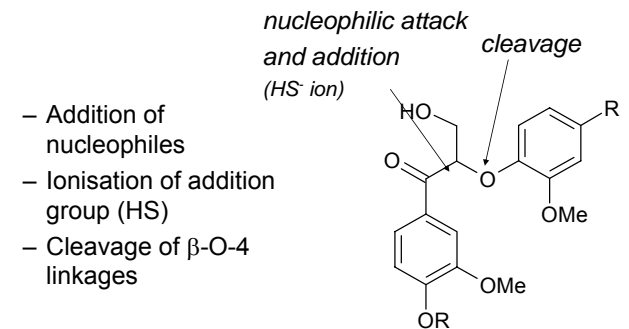
Possible reactions of phenolic structures



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Reactions of carbonyl structures



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