Lignin reactions in the initial stage of delignification

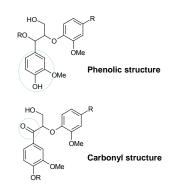
Reactions of phenolic and carbonyl structures

27/01/2005

Disintegrate fibres High yield REACTION KINETICS initial, bulk and residual delignification Pulping conditions Temperature Phenolic structures Carbonyl structures Sulphate pulping, delignification Lignin Non-phenolic structures Bulk delignification LC complexes Peeling Initial delignification Hydrolysis of esther Peeling Bulk delignification Generation of HexA **Polysaccharides** Hydrolysis of glycosidic linkages Hemicelluloses Cellulose LC linkag 27/01/2005 Extractives

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
 - HS ion concentration important
- Reactions:
 - Phenolic and carbonyl structures react
 - 20 % of lignin degrades due to these reactions in the initial stage



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Reactions of phenolic structures

- Main linkages between phenylpropane units of lignin are aryl ether linkages
 - Dominant types are α 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 β -O-4 linkages

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cleavage=lohkeaminen; quinone methide=kinonimetidi; thiol=

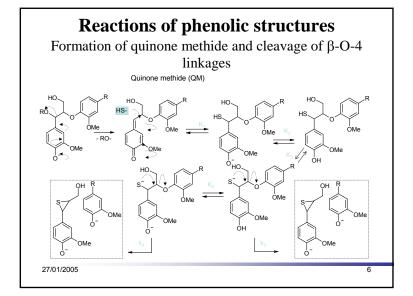
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Reactions of phenolic structures

- 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

Reaction 1: $K_1 = [1] / ([QM][HS^-])$ (1)

Reaction 2: $K_2 = [1] / ([2] [HO^-])$ (2)

Reaction 3: $K_3 = [3] / ([2] [HO^-])$ (3)

Reaction 4: $K_4 = [4] / ([3] [HO^-])$ (4)

[3] = $K_1K_3[QM][HS^-]/K_2$ (5)

 $[4] = K_1K_3K_4[QM][HS-][HO-]/K_2$ (6)

Rate of reaction (cleavage of β – O – 4 bond) = $-k_3K_1K_3[QM]$ [HS-] / K_2 – $k_4K_1K_3K_4[QM]$ [HS-] HO-] / K_2 (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 y- hydroxyl group)

 \Rightarrow formation of enol ethers

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Reactions of phenolic structures Concurrent reactions

Rate of concurrent reaction:

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

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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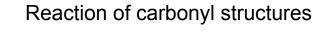
Reactions of carbonyl structures

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

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Effect of [HO-] on cleavage of β-O-4 linkages and formation of enol ethers Log (rate of reaction) Reaction Log (rate of reaction) 8 9 10 11 12 13 14 pH 27/01/2005 Cleavage of β-O-4 (β-aryl ether) linkages (solid line) 10 and the formation of enol ethers (dashed line)



HS- HO
$$_{OMe}$$
 $_{OMe}$ $_{O$

Reaction of carbonyl structures

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

Rate constants:

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

 $K_2 = [3]/[2]$

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 Nucleophilic attack lonisation and addition (HS') (HO') HO HO OME Lonisation (HO') Phenolic lignin structure Quinone methide intermediate

Reactions of carbonyl structures nucleophilic attack and addition (HS' ion) - Addition of nucleophiles - Ionisation of addition group (HS) - Cleavage of β-O-4 linkages