Oxygen delignification

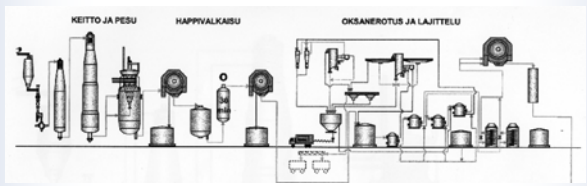
Lecture 12

General

- Oxygen delignification was introduced in the 1970s' in industrial applications.
- Oxygen is a cheap chemical.
  - A cost efficient way to reduce the consumption of other chemicals.
- Environmentally friendly.
  - Less chlorinated compounds are formed in the following ECF bleaching.

General

- Oxygen stage is situated before bleaching processes.
- The stage is called oxygen delignification or oxygen bleaching.



Conditions in oxygen delignification

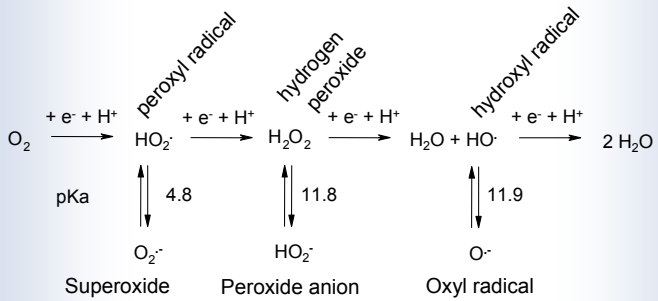
- Temperature 80°C – 100°C
- Elevated pressure (~5-6 bar) to achieve adequate oxygen dissolution.
- Alkaline, pH >10
- Approximately 50 % of the residual lignin can be removed
  - Pulp quality problems occur if the limit is exceeded

Reactions of oxygen

- Oxygen is reduced to water in *one-electron steps* and the substrate is oxidized.
- $O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O$
- During the reaction several intermediates are formed (i.e. hydrogen peroxide, hydroxyl radicals etc.)

Reactions of oxygen

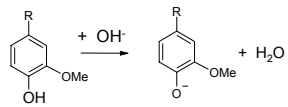
Stepwise reduction of oxygen during bleaching :



(Carlton W. Dence and Douglas W. Reeve (editors) "Pulp Bleaching, Principles and Practice" TAPPI PRESS, Atlanta 1996.)

Chemistry of Oxygen Delignification

- In normal state oxygen is a weak oxidant
- Reactivity can be improved by
  - Raising the temperature
  - Providing a reactive substrate
    - Alkaline process conditions ionize free phenolic hydroxyl groups in the residual lignin



⇒Radical chain reaction

Radical chain reaction

The mechanism of oxygen delignification

Initiation	$RO^- + O_2 \rightarrow RO\cdot + O^-_2\cdot$	(1)
	$RH + O_2 \rightarrow R\cdot + HO_2\cdot$	(2)
Propagation	$R\cdot + O_2 \rightarrow RO_2\cdot$	(3)
	$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$	(4)
Termination	$RO\cdot + R\cdot \rightarrow ROR$	(5)

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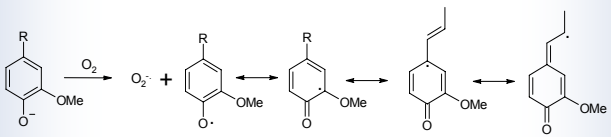
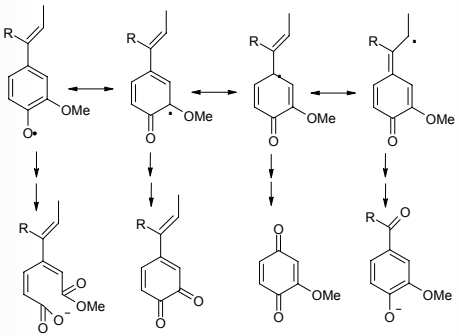
Lignin reactions

- Oxygen is
  - a weak oxidant
  - a radical
- Reacts with dissociated phenolic lignin structures



Lignin reactions

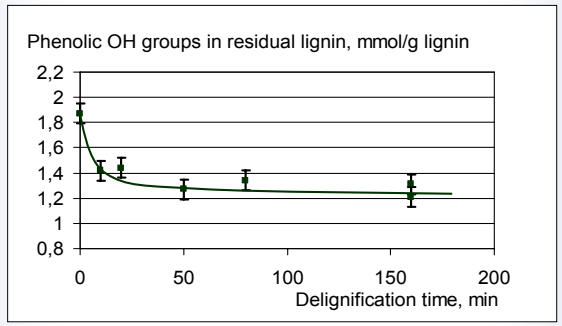
R is H, OAr, or an alkyl group



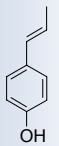
Lignin reactions

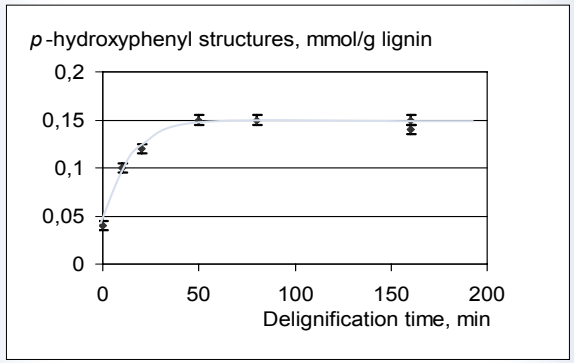
- As a result of these reactions lignin becomes oxidized and more hydrophilic
  - It is easier to remove from the pulp
- Up to some extent oxygen reacts with phenolic structures, but all of these structures are not reactive
  - p-phenols vs. m-phenols

Phenolic hydroxyl groups



p-hydroxyphenyl structures





Oxygen does not remove p-hydroxyphenyl structures. Why?

Selectivity

- Approximately 50 % of the residual lignin can be removed
  - Pulp quality problems occur if the limit is exceeded
- Peroxide is formed in the stepwise reduction of oxygen.
- Peroxide can decompose forming among others hydroxyl radicals (HO·).
- Hydroxyl radicals are highly reactive and react with lignin and polysaccharides.

transition metal = siirtymämetalli; decomposition = hajoaminen

Selectivity

- Pulps contain transition metals, such as Mn, Cu and Fe.
- Transition metals act as catalysts for peroxide decomposition.
  - ⇒More hydroxyl radicals (HO·) formed.
- Harmful effects of transition metals can be reduced by addition of magnesium salts (e.g. $MgSO_4$).
  - ⇒ Formation of inactive metal complexes .

transition metal = siirtymämetalli; decomposition = hajoaminen

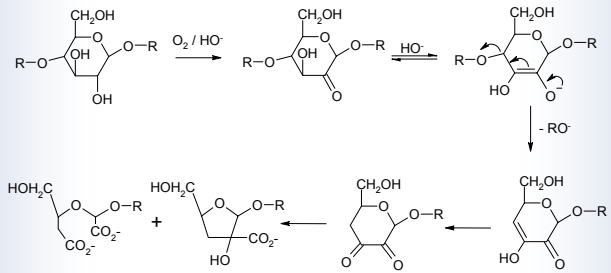
Carbohydrate reactions

- Degradation of polysaccharides:
  1) cleavage of glycosidic linkages
  2) peeling reaction
- Cleavage of glycosidic linkages is more significant during oxygen delignification than peeling reaction.
- As a result of carbohydrate reactions pulp viscosity and strength properties may decrease.

Reaction mechanism for carbohydrates

- Step 1
  - Primary oxidation by a hydroxyl radical and formation of a carbonyl intermediate at the C_2-position of a monomeric sugar unit
- Step 2
  - A cleavage of the glycosidic bond at C_4 by β-alkoxy elimination
- Step 3
  - Formation of a new reducing end group

Reaction mechanism for carbohydrates



Extractives

- Unsaturated lipophilic extractives can react with oxygen.
- Alkaline conditions with efficient washing can result in extensive deresination during oxygen bleaching.

Advantages and Disadvantages

+ Low chemical costs
+ Environmentally friendly method
  - lower chemical consumption in subsequent bleaching stages
  - ⇒ less AOX load in D and C bleaching stages
  - lower BOD and COD
  - reduced colour of pulp

- High capital costs
- Ineffective in normal state

⇒ necessary to have
- high temperature
- a reactive substrate

- Low selectivity at higher degrees of delignification

AOX = a group of halogenated organic compounds; BOD = biochemical (biological) oxygen demand, COD = chemical oxygen demand