Peracetic acid bleaching

Puu-19.3000

Chemistry of pulping and bleaching

Classification of bleaching agents

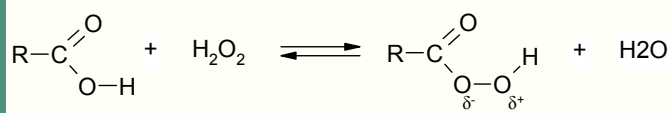
RADICALS	ELECTROPHILES	NUCLEOPHILES
O_2	Cl_2	HO_2^- (H_2O_2)
ClO_2	HOCl	ClO^-
	O_3	(Peroxyacids)
	Peroxyacids	

Peracids

- Peracids in pulping and bleaching (in mill or pilot scale production)
  - **Peracetic acid (Paa) CH_3CO_3H**
  - Performic acid (Pfa) HCO_3H
  - Caro's acid (Caa) H_2SO_5
- Laboratory scale pulp bleaching
  - Peroxypropionic acid $CH_3CH_2CO_3H$
  - Peroxybezoic acid $C_6H_5CO_3H$
  - Peroxonitric acid HNO_4

Preparation of peracids

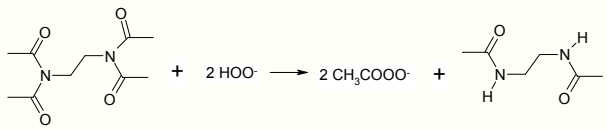
Acid + hydrogen peroxide → peracid + water



	Equilibrium Paa	Distilled Paa
CH_3COOOH	20%	34%
H_2O_2	14%	0,7%
CH_3COOH	26%	3%
H_2O	40%	62%

Alternative method

TAED* + H_2O_2 → Paa + DAED**



*Tetraacetylethylenediamine
** Diacetylethylenediamine

Peracids in water solution

In water solution peracids dissociate:

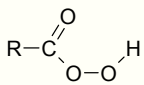
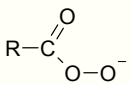
$RCOOOH + H_2O \rightleftharpoons RCOOO^- + H_3O^+$

pK_a values for acids and corresponding peracids:

HCO_2H:	**3.8**	**HCO_3H:**	**7.1**
CH_3CO_2H:	**4.7**	**CH_3CO_3H:**	**8.2**
H_2SO_4:	**-3**	**H_2SO_5:**	**9.4**

→ **Peracids are relatively weak acids ("high" pH is required to ionize peracids)**

Peracids in water solution

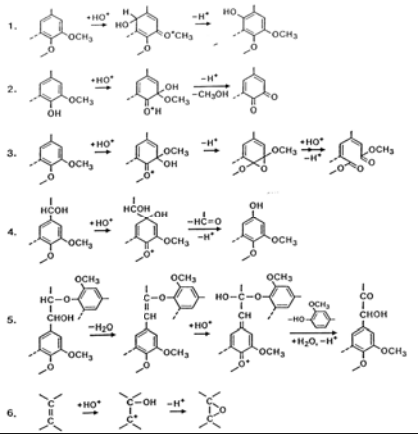
- When pH of water solution = pK_a value of acid:
  - the amount of ionized molecules is the amount of molecules in acid form
- In other words, peracids are both electrophiles and nucleophiles:
  - Electrophile:  (acid form)
  - Nucleophile:  (ionized structure)

Peracetic acid bleaching

- Usually bleaching is carried out at pH ~4,5
  - ⇨ Paa is in acid form and acts mainly as an electrophile
- Transition metal content of pulp should be relatively low in order to avoid catalytic decomposition of Paa

Reactions of peracids with lignin

(Gierer, J., Chemistry of delignification. Part 2. Reactions of lignings during bleaching . Wood Sci. Technol. 20(1986):1, 1-30)



1. **Ring hydroxylation**
2. **Oxidative demethylation**
3. **Oxidative ring cleavage**
4. **Displacement of side chains**
5. **Cleavage of β-O-4 linkages**
6. **Epoxidation**

Comparison of peracids

- Properties of the leaving group affect the electrophilicity and reactivity of peracids:
  H_2SO_5 > HCOOOH > CH_3COOOH
- H_2SO_5 is more electrophilic and it favours aromatic ring hydroxylation (reaction 1)
- CH_3COOOH is more nucleophilic and therefore it favours oxidative ring cleavage (reaction 3)

Lignin after Paa bleaching

- The structure of residual lignin changes during the peracetic acid bleaching.
- Residual lignin consists of higher amounts of phenolic hydroxyl groups.
- The amount of acid groups is increased which improves the hydrophilicity of lignin.
- Due to the cleavage of side chains the molecular mass of residual lignin is decreased which further improves the hydrophilicity.

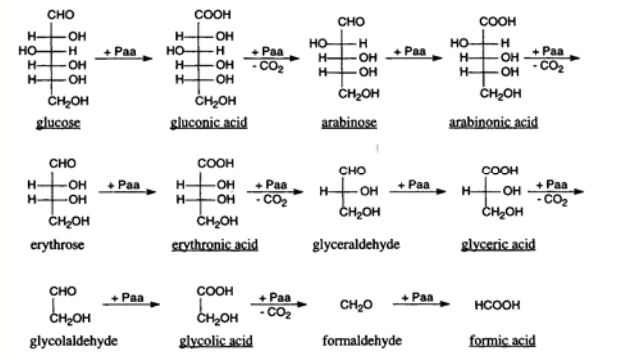
→ Due to Paa treatment the residual lignin is more easily removed in next bleaching sequences.

Reactions with carbohydrates

- Peracids are very selective chemicals and carbohydrate yield loss is limited
- However:
  - Transition metal catalysed decomposition of Paa may produce harmful radicals (e.g. hydroxyl radicals) which cause the degradation of carbohydrates
  - Low pH may lead to acid hydrolysis and degradation of carbohydrates
- Peracids react easily with reducing end groups of carbohydrates

→ high amounts of Paa could be consumed, however the amount of reducing end groups in pulp is relatively low

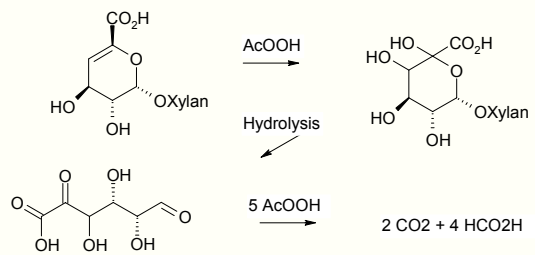
Reactions with carbohydrates - reducing end groups



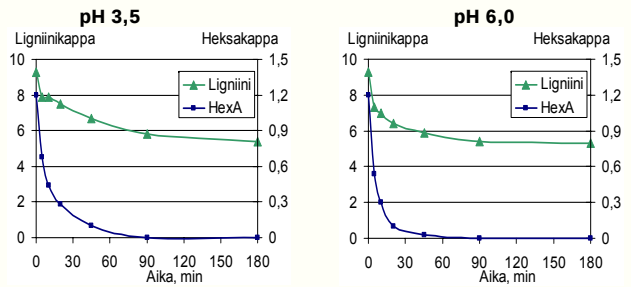
Reactions with carbohydrates - hexenuronic acid groups

- Peacids react easily with hexenuronic acid groups
- An intermediate product (5-oxohexuronic acid) is formed in the reaction.
- Peracids can further react with this intermediate product. As a result formic acid is formed.
- Reaction consumes considerable amounts of peracids and therefore it is advisable to remove HexA prior to the Paa- stage.
- The reaction is much faster in neutral pH than in low pH (HexA dissociated).

Reactions with carbohydrates - hexenuronic acid groups



Selectivity of peracetic acid bleaching (lignin vs. HexA)



Oxygen-delignified softwood pulp, 78ºC, peracid charge 2,5% on pulp.

Peracids in bleaching

- O-Q-Eop-PaaQ-PO
- O-Q-Paa-P
- O-Q-P-Paa-P
- Post-bleaching

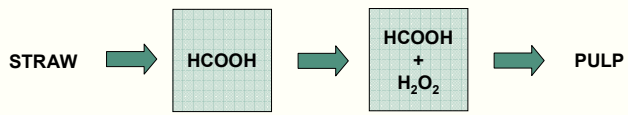
Peracids in pulping

MILOX pulping method

+ BLEACHING P - P - P

MILOX

- Modified method is applicable in the production of straw pulp:



+ BLEACHING P - P

MILOX-process

- The pulp is more easily bleached in than kraft pulp since the pulp contains minor amounts of condensed lignin structures.
- In addition lignin contains reactive phenolic hydroxyl groups.
- Due to acidic condition the hemicellulose yield is low in Milox process.
- Silica does not disturb the process (unlike in kraft process)