Peracetic acid bleaching

Puu-19.3000
Chemistry of pulping and bleaching

Classification of bleaching agents

<table>
<thead>
<tr>
<th>RADICALS</th>
<th>ELECTROPHILES</th>
<th>NUCLEOPHILES</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Cl₂</td>
<td>HO₂⁻ (H₂O₂)</td>
</tr>
<tr>
<td>ClO₂</td>
<td>HOCl</td>
<td>ClO⁻</td>
</tr>
<tr>
<td>O₂</td>
<td>(Peroxyacids)</td>
<td></td>
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</tbody>
</table>

Peracids

- Peracids in pulping and bleaching (in mill or pilot scale production)
  - Peracetic acid (Paa) CH₃CO₃H
  - Performic acid (Pfa) HCO₃H
  - Caro’s acid (Caa) H₂SO₅
- Laboratory scale pulp bleaching
  - Peroxypropionic acid CH₃CH₂CO₃H
  - Peroxybezoic acid C₆H₅CO₃H
  - Peroxonitric acid HNO₄

Preparation of peracids

Acid + hydrogen peroxide → peracid + water

\[
\begin{align*}
R-C\overset{\text{O}}{\text{O}}-H \quad + \quad H₂O₂ & \quad \leftrightarrow \quad R-C\overset{\text{O}}{\text{O}}-O-H \quad + \quad H₂O
\end{align*}
\]

<table>
<thead>
<tr>
<th></th>
<th>Equilibrium Paa</th>
<th>Distilled Paa</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COOOH</td>
<td>20%</td>
<td>34%</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>14%</td>
<td>0.7%</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>26%</td>
<td>3%</td>
</tr>
<tr>
<td>H₂O</td>
<td>40%</td>
<td>62%</td>
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</tbody>
</table>
Alternative method

TAED* + H₂O₂ → Paa + DAED**

* Tetraacetylenediamine
** Diacetylenediamine

Peracids in water solution

In water solution peracids dissociate:
RCOOOH + H₂O ⇌ RCOO⁻ + H₃O⁺

pKₐ values for acids and corresponding peracids:
HCO₂H: 3.8  HCO⁻: 7.1
CH₃CO₂H: 4.7  CH₃CO⁻: 8.2
H₂SO₄⁻: -3  H₂SO₅⁺: 9.4

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

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


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:
  - $H_2SO_5 > HCOOH > CH_3COOH$
- $H_2SO_5$ is more electrophilic and it favours aromatic ring hydroxylation (reaction 1)
- $CH_3COOH$ 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

- 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, 78°C, peracid charge 2.5% on pulp.
Peracids in bleaching
- O-Q-Eop-PaaQ-PO
- O-Q-Paa-P
- O-Q-Paa-Pa-P
- Post-bleaching

Peracids in pulping

MILOX pulping method

Wood chips $\rightarrow$ HCOOH + $\text{H}_2\text{O}_2$ $\rightarrow$ HCOOH $\rightarrow$ HCOOH + $\text{H}_2\text{O}_2$ $\rightarrow$ PULP

+ BLEACHING P - P - P

MILOX

Modified method is applicable in the production of straw pulp:

STRAW $\rightarrow$ HCOOH $\rightarrow$ HCOOH + $\text{H}_2\text{O}_2$ $\rightarrow$ 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)