Mini Oxygen Stages for SW Kraft Pulps
More Delignification with Less Capital

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Evolution of Oxygen Delignification

- **1960/70s**
  - Basic engineering
  - General chemistry

- **1980/early 1990s**
  - Process variables, energy, environmental, pretreatments
  - Fundamental chemistry & pulp properties

- **Late 1990s/2000**
  - Yield, selectivity, process parameters,
  - Lignin/carbohydrate chemistry, catalysis
Application in North American Bleach Plants

- Chlorine
- Chlorine Dioxide
- Oxygen Delignification

Graph showing the application of bleach agents from 1983 to 2000.
Increased Selectivity, Yield, and Environmental Performance

Chemistry of Oxygen
Delignification
## Oxidative Agents

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxidative Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superoxide ($O_2^-$)</td>
<td>Addition to ring</td>
</tr>
<tr>
<td>Hydroperoxide ($O_2H^-$)</td>
<td>Addition to ring, ketones, aldehydes</td>
</tr>
<tr>
<td>Hydroxyl (OH·)</td>
<td>Severe oxidation and fragmentation</td>
</tr>
<tr>
<td>Oxoanion (O$^-$)</td>
<td>Attack of rings and carbohydrates</td>
</tr>
</tbody>
</table>
Oxidation of Lignin

Free Phenolic

Canonical Resonance Structure

Muconic Methyl Ester
Research Attention

APPLIED

- Oxygen delignification addresses the top P&P research need for increased mill closure (TAPPI Workshop Paper Industry Research Needs, 1996)

- Mini oxygen systems have not been as thoroughly investigated as warranted by capital cost effectiveness and performance

FUNDAMENTAL

- The number of citations has risen to over 100/year

- The chemical mechanisms are controversial
Research Objective 1

Examine the chemical similarities and differences in typical SW kraft pulp after standard O and mini O stages

- % Delignification
- Viscosity
- Fundamental lignin structures
Experimental Design

Bleaching Conditions

- **O Stage**: 10% cn., 90°C, 60 min., 2.5% NaOH odw
- **D Stage**: 2 kappa factors used – 0.05 and 0.20 \((D_0)\) at 10% cn., 70°C, 30 min.
- **(E+O)**: 10% cn., 90°C, 20 min., 1.25% NaOH odw
- **(E+O)***: 10% cn., 90°C, 40 min., 2.5% NaOH odw
Oxygen Delignification Results
(E+O) provides up to 25% delignification

At low caustic, the mini-O, (E+O)D(E+O), performs within 5% as well as a standard O

By splitting caustic charge in mini-O, the interstage D stage enhanced performance of subsequent (E+O)
Delignification from Mini O

- Splitting caustic charge is not as effective as one dose in \((E+O)^*\)
- Placement of low kappa factor charge impacts the final delignification level
- \((E+O)\) strongly complements the \(D_0\)
Viscosity from Mini O Trials

Viscosity/cP

Brownstock, Do(E+O), (E+O)*, (E+O)(E+O), (E+O)Dkf:0.05(E+O), Dkf:0.05(E+O)

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A mini O stage is less sensitive to base induced pulp degradation than a full O
Selectivity of Mini O

- (E+O) stage provides more selectivity than a full O
- The D stage placement is critical to the overall performance of the mini O

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Influence of Washing and Carryover
Effect of Washing on Selectivity

- (E+O) stage provides much more selectivity than a full O
- The D stage placement is important to the overall performance of the mini O
Washing was done between the first and second stage.

Carryover appears to slightly enhance the delignification of the stage.

A slight increase in delignification obtained when D stage is after (E+O) in mini O.

Interstage Washing Effect on Kappa

- No Interstage Washing
- Interstage Washing
Interstage Washing Effect on Viscosity

In this case, washing slightly improves the viscosity of the pulp.

Loss in selectivity is therefore compensated by increase in delignification.
The level of carryover does not have a pronounced effect on the levels of delignification obtained in the trials.

A slight drop in delignification does not have a major impact on viscosity.
In this case, the higher levels of carryover appear to reduce the delignification levels slightly.

Viscosity changes are not as pronounced as expected.
Increasing the number of (E+O) stages may have an impact on the overall selectivity.
$^{31}\text{P} \text{ NMR Structural Elucidation}$
All differences are based on a normalized selectivity (1) change.

Higher consistency pulps have lower selectivity trends as demonstrated from the literature.

Rates in stirring are based on a 5, 15, and 30 hz rate for 10 seconds every 5 minutes for one hour.

Basis of effect was investigated by NMR interrogation of effluents.
Typical Phenolic Structures

5,5'-Condensed Phenolic Subunits of Lignin

Non-condensed (free) Phenolic Subunits of Lignin
Lignin Structural Differences Observed in O Effluent

- Free Phenolics
- 5,5'-Condensed Phenolics

Change From BS

- 10% cn, low stirring
- 10% cn, med stirring
- 10% cn, high stirring
- 18% cn, low stirring
- 18% cn, med stirring
- 18% cn, high stirring

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Important Structural Differences

- $^{31}$P NMR was used to evaluate the chemical differences.
- Acid concentration did not change between the O and mini O.
- Changes in phenolics are not as pronounced in mini O as in O.

![Bar chart showing the concentration of different compounds in Brown Stock and O with mini O.](chart.png)
Conclusions

- Mini O systems have some inherent pulp property benefits over full O
- Placement of D stage is important to the selectivity obtained
- The NMR studies from O and mini O systems suggest that the concentration of the condensed and non-condensed phenolics may not directly correlate with bleachability
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