FUNDAMENTAL DELIGNIFICATION CHEMISTRY OF HIGH- LIGNIN CONTENT KRAFT PULPS BY LACCASE-MEDIATOR SYSTEMS
Mediators - 1st generation

ABTS:

- 1-First mediator used to demonstrate that a laccase-mediator system can delignify kraft pulps.

Not ideal >> low delignification levels and cost prohibitive.
Mediators - 2nd generation

- **HBT**: 1-hydroxybenzotriazole (Call, 93)

- High delignification levels and selectivity.

Still not ideal >> formation of benzotriazole, interference with the enzyme, and cost prohibitive.
**Kappa**

- Constant kappa in the absence of laccase.
- VA superior mediator in comparison to HBT and NHAA
- As expected, further drop in kappa after E stage

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|| Treatment | Kappa |
|-----------|--------|
| MS        | Brownstock NHAA HBT VA |
| LMS       | Brownstock NHAA HBT VA |
| LMS-E     | Brownstock NHAA HBT VA |

Std. dev. = 0.31
Typical $^{31}$P NMR spectrum

Cyclohexanol: Internal standard
Trimethylphosphite Chemistry: Reaction with Ortho-Quinone Structures

Ramirez et al., Sidky et al., & Medvecz

$R = PO(OCH_3)(OH)$ or $H$
A typical $^{31}$P NMR-TMP Spectrum

Quinone Adduct

Internal Standard
Carboxylic acid groups

- No effect in the absence of laccase
- Increase in carboxyl moieties during LMS: largest with VA
- Enrichment after E stage

Carboxylic acid (mmole/g lignin)

95% LSD=0.032
Non-condensed lignin structures at C5

- Depletion with all mediators.
- Largest decrease with VA.
- Decrease greater with NHAA than HBT

95% LSD = 0.088
**Condensed lignin structures at C5**

- Decrease with VA
- Overall, resistance observed towards condensed structures with HBT and NHAA

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<th>Treatment</th>
<th>Condensed at C5 (mmole/g lignin)</th>
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<tr>
<td>MS</td>
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<td>LMS</td>
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<td>LMS-E</td>
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95% LSD=0.023
Quinone content (mmole/g lignin)

- Quinone formation is evident with NHAA, VA, HBT.

- Trend suggest a decrease after E stage.

- Possible explanation for significant increase in brightness after Ep