Alkaline Oxidation of Enzymatic Hydrolysis Lignin Using Reversibly Soluble Bases

Jacob S. Kruger, David Brandner, Camille Amador, Katherine Krouse, Daniel Wilcox, Gregg T. Beckham
National Renewable Energy Laboratory
2020 Bioenergy Sustainability Conference | 14 Oct 2020
Lignin Background

- Heterogeneous aromatic polymer
- 15-30 wt% of lignocellulosic biomass\(^1\)
- Depolymerization and further upgrading is promising valorization strategy\(^2\)

---

DMR-EH Lignin and Alkaline Oxidation

- Residue after deacetylation, mechanical refining, and enzymatic hydrolysis of biomass
- 50-60% lignin
- Native-like structure
- Alkaline oxidation produces high yields of valuable products, but separations are expensive due to excess base

![Graph showing monomer yield comparison](image)

<table>
<thead>
<tr>
<th>Component</th>
<th>Corn Stover</th>
<th>DMR Lignin</th>
<th>DAP Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucan</td>
<td>40.3</td>
<td>9.4</td>
<td></td>
</tr>
<tr>
<td>Xylan</td>
<td>25.0</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>Other Sugars</td>
<td>5.3</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td>3.9</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Lignin</td>
<td>16.1</td>
<td>53.5</td>
<td></td>
</tr>
<tr>
<td>Ash</td>
<td>3.3</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>Other/unknown</td>
<td>6.2</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
<td></td>
</tr>
</tbody>
</table>

2 M NaOH
3-5 bar O₂
130-170 °C
0.5-3 h

[Cu-based cat]
Improving Lignin Oxidation

• How can we reduce the costs and improve the sustainability of lignin alkaline oxidation?
  o Improve alkali usage by recycling excess hydroxide

\[
\text{[Cu-based cat]}
\]
Solubility of M(OH)$_2$

- Ba(OH)$_2$ and Sr(OH)$_2$ are soluble at reaction temperature, but mostly insoluble at room temperature

---

Lambert et al., Alkaline Earth Hydroxides in Water and Aqueous Solutions, *IUPAC Solubility Series, Vol 52, 1992*
Reversibly Soluble Bases Concept

• \( \text{M(OH)}_2 \) could act as *reversible* OH\(^{-}\) source, recyclable by filtering
M(OH)$_2$ could act as \textit{reversible} OH$^-$ source, recyclable by filtering
Reversibly Soluble Bases Concept

- \( \text{M(OH)}_2 \) could act as *reversible* \( \text{OH}^- \) source, recyclable by filtering.
• **M(OH)$_2$** could act as *reversible* OH$^-$ source, recyclable by filtering
NaOH vs. M(OH)$_2$ – Lignin Monomers

- Monomer yields using 2M Sr(OH)$_2$ or Ba(OH)$_2$ are similar to those using 2M NaOH.
Glucose degraded primarily to lactic acid
Cellulose mostly not degraded
Ba(OH)$_2$ vs. Sr(OH)$_2$

- Prefer Sr(OH)$_2$ in this application
  - Lower solubility of SrCO$_3$ vs. BaCO$_3$
  - Lower toxicity of Sr$^{2+}$ vs. Ba$^{2+}$
  - Lower calcination temperature for SrCO$_3$ regeneration to SrO
  - Mass of reactants lower for Sr than Ba

<table>
<thead>
<tr>
<th>Base</th>
<th>M(OH)$<em>2$ $K</em>{sp}$</th>
<th>MCO$<em>3$ $K</em>{sp}$</th>
<th>$[M^{2+}]$ after neut. (ppm)</th>
<th>Max safe $[M^{2+}]$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>$3.2 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-10}$</td>
<td>2.1</td>
<td>4*</td>
</tr>
<tr>
<td>Ba</td>
<td>$2.6 \times 10^{-4}$</td>
<td>$2.6 \times 10^{-9}$</td>
<td>7.0</td>
<td>2</td>
</tr>
</tbody>
</table>

*not federally regulated
M(OH)$_2$ Neutralization

- Neutralization equilibrates within ~5 min
- Final pH is 6-6.5, ideal for selectively extracting non-carboxylic phenolics
Monomer Recovery Through Workup

- Reaction-[sample]-Filter Sr(OH)$_2$-[sample]-Neutralize-[sample]-Filter SrCO$_3$-[sample]
  - End product is neutral/slightly acidic monomer stream ready for separations/biological upgrading

- Negligible monomer loss through workup
More than 90% of Sr can be recovered directly post-reaction (not optimized)

Preliminary TEA suggests this level of recovery makes Sr(OH)₂ economically advantageous to NaOH
Conclusions

• DMR-EH processing preserves lignin in a native-like state

• Alkaline oxidation generates high-value, biologically-available monomers from lignin

• Replacing NaOH with Sr(OH)$_2$ shows similar monomer yields, but should decrease production costs and increase process sustainability
Acknowledgements

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office under Contract No. DE-AC36-08GO28308. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

• Brenna Black
• Kelsey Kinley
• Stefan Haugen
• Nick Thornburg
• Rui Katahira
• Ally Robinson
Thank you!

Questions?

NREL/PR-2800-78152