NARA Supply Chain

FOREST RESIDUES PREPARATION
Primary feedstock targets include forest residues from logging and thinning operations. We are also considering mill residues and discarded woody material from construction and demolition, in regions where these materials are under utilized.

TRANSPORTATION
Feedstocks are transported from the collection site to a conversion facility. Chipping can take place at the loading or in a preprocessing facility.

PRE-TREATMENT
Wood chips are treated to make the sugar polymers (polysaccharides) accessible to degrading enzymes. These processes allow the lignin to be available for separation.

ENZYMATIC HYDROLYSIS
Specific enzymes are added to hydrolyze (breakdown) the polysaccharides and generate simple sugars (monosaccharides).

FERMENTATION
Specialized yeast convert the monosaccharides into isobutanol.

BIOJET & CO-PRODUCTS
Aviation fuels can be generated from the platform molecules derived from wood sugars. Lignin can be used to generate co-products such as epoxies, structural materials and bio-based plastics. As an alternative, lignin can be burned to produce renewable energy.

ONE BONE DRY TON WOODY BIOMASS + DIESEL + HEAT, WATER, & CHEMICALS = ~600 POUNDS LIGNIN AND ~59 GALLONS ISOBUTANOL OR ~42 GALLONS BIOJET

Image credit: NARA
Source of Lignin in a Biorefinery

The Need for Co-Products

Relative IPK Production Cost

- IPK total cost: 2.88
- RIN credit: 0.73
- Feedstock hauling 20% reduction: 0.04
- Pretreat yield 86% to 90%: 0.17
- Pretreat capex 20% reduction: 0.06
- IBA and IPK yield & capex improvements: 0.15
- Optimized IPK cost: 1.75

Speculative – need to be developed

Credit: Gevan Marrs, NARA
Few Commercial Uses for Lignin

• Annual lignin production:
  – 40 to 50 million metric tons?

• Annual commercial lignin consumption:
  – ≈ 1.5 million metric tons

• What is the problem? Why isn’t lignin more widely used?

• Are the chances for success in lignin utilization better today?
• Lignin is a complex molecule to begin with.

Lignin Isolation Affects its Structure and Purity

- **Commercial**
  - Kraft pulping
  - Sulfite pulping

- **Non-commercial**
  - Organosolve pulping
  - Milled wood
  - Ionic liquid pretreatment
  - Mild acid hydrolysis

Photo credit: JBEI
Drivers for Success

Near Term

• Cleaner commercial lignins
• Characterization methods are more powerful
• New market opportunities

Long Term

• Better methods to break specific lignin bonds
• Advances in biomass fractionation
• Ability to manipulate lignin biosynthesis
Many Possibilities from Lignin

- Concrete Dispersant
- Fine Chemicals
- Fuels
- Phenolic Resins
- Carbon Products
- Thermoplastics
- Energy Storage
- Adsorbents
- Rubber Reinforcement
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NARA Co-Product Streams

Wood Chips or Forest Residuals

- MBS Process
  - Spent Sulfite Liquor
  - Treated Wood
    - Enzyme Hydrolysis & Fermentation
      - Residual Solids
      - Soluble Sugars to Fermentation

- WOX Process
  - Treated Wood
    - Enzyme Hydrolysis & Fermentation
      - Residual Solids
Mild Bisulfite Pretreatment (MBS)

Process development by Johnway Gao and Dwight Anderson at Catchlight Energy and J.Y. Zhu at the Forest Products Laboratory

**Wet Oxidation Pretreatment**

Process development by Dr. Brigitte Ahring at Washington State University’s Bioproducts, Sciences & Engineering Laboratory

## Composition of Fermentation Residual Solids (FRS)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Klason Lignin</th>
<th>Total Polysaccharide</th>
<th>Ash</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock</td>
<td>34.9%</td>
<td>54.4%</td>
<td>0.2%</td>
<td>0.0%</td>
</tr>
<tr>
<td>MBS FRS as rec’d</td>
<td>70.4%</td>
<td>18.9%</td>
<td>8.9%</td>
<td>2.4%</td>
</tr>
<tr>
<td>MBS FRS washed</td>
<td>69.4%</td>
<td>23.9%</td>
<td>4.1%</td>
<td>1.8%</td>
</tr>
<tr>
<td>Wet Ox FRS as rec’d</td>
<td>53.0%</td>
<td>43.9%</td>
<td>2.0%</td>
<td>0.1%</td>
</tr>
<tr>
<td>Wet Ox FRS washed</td>
<td>53.4%</td>
<td>47.3%</td>
<td>0.5%</td>
<td>0.0%</td>
</tr>
</tbody>
</table>

% oven dry
How to Determine FRS Lignin Chemistry?

- Saccharification and fermentation residual solids are insoluble in all attempted solvents.
- Need to extract high purity, unmodified lignin from SRS and FRS samples.
- Can we simply extract lignin using dioxane/water mixture, similar to milled wood lignin?
- Not really.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBS SRS</td>
<td>2.8%</td>
</tr>
<tr>
<td>Wet Ox SRS</td>
<td>8.3%</td>
</tr>
</tbody>
</table>
Ball Milling Increases Extracted Lignin Yield

Effect of Ball Milling on Lignin Isolation from Wet Ox SRS

Isolated Yield

Ball Milling Time (h)
Enzymatic Mild Acidolysis Lignin (EMAL)


- Ball Milling: 21 days
- Enzymatic Hydrolysis: 48 hours
- Solvent Extraction: 2 hours
## Lignin Isolation Yields

<table>
<thead>
<tr>
<th>Sample</th>
<th>Enzymatic Hydrolysis Yield</th>
<th>Lignin Extraction Yield</th>
<th>Extracted Lignin Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Residuals</td>
<td>42.8%</td>
<td>52.4%</td>
<td>81.0%</td>
</tr>
<tr>
<td>Mild Bisulfite FRS</td>
<td>64.7%</td>
<td>52.5%</td>
<td>95.4%</td>
</tr>
<tr>
<td>Wet Oxidation FRS</td>
<td>86.4%</td>
<td>44.9%</td>
<td>94.2%</td>
</tr>
</tbody>
</table>
Lignosulfonate Isolation Procedure

1. Spent Sulfite Liquor + \( \text{C}_{12}\text{H}_{25}\text{NH}_3 \text{ in octanol} \)
2. Organic extraction: 
   - Organic Phase: LS/amine complex
   - Aqueous Phase: Residual sugars, salts
3. Discard

4. Back extraction: 
   - Organic Phase: Dodecylamine
   - Aqueous Phase: \( \text{Na}^+ \text{ LS} \)
5. Retain and dry

## Elemental Analysis of Isolated Lignins

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Oxygen*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Residual Lignin</td>
<td>0.032</td>
<td>61.0</td>
<td>6.0</td>
<td>0.07</td>
<td>32.9</td>
</tr>
<tr>
<td>Wet Oxidation Lignin</td>
<td>0.096</td>
<td>64.9</td>
<td>5.3</td>
<td>0.96</td>
<td>28.7</td>
</tr>
<tr>
<td>Mild Bisulfite Lignin</td>
<td>1.13</td>
<td>63.3</td>
<td>5.7</td>
<td>1.01</td>
<td>28.9</td>
</tr>
<tr>
<td>MBS Lignosulfonic acid</td>
<td>8.10</td>
<td>52.1</td>
<td>4.8</td>
<td>0.36</td>
<td>34.7</td>
</tr>
</tbody>
</table>

* Oxygen determined by difference
All values % oven dry
31P NMR Analysis of EMALs

Lignin—OH + Cl—P—O—CH₃ → Lignin—O—P—O—CH₃ + HCl

Quant. 31P NMR spectrum of forest harvest residual EMAL
## Hydroxyl Group Comparison

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aliphatic OH</th>
<th>Aromatic OH</th>
<th>C-5 Substituted OH</th>
<th>COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Residuals Lignin</td>
<td>4.31</td>
<td>1.11</td>
<td>1.45</td>
<td>0.03</td>
</tr>
<tr>
<td>Wet Oxidation Lignin</td>
<td>1.93</td>
<td>2.86</td>
<td>1.32</td>
<td>0.21</td>
</tr>
<tr>
<td>Mild Bisulfite Lignin</td>
<td>1.38</td>
<td>2.71</td>
<td>1.66</td>
<td>0.22</td>
</tr>
<tr>
<td>MBS Lignosulphonic acid</td>
<td>2.42</td>
<td>3.96</td>
<td>1.73</td>
<td>0.10</td>
</tr>
</tbody>
</table>
## Molecular Weight Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Mw</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Residuals Lignin</td>
<td>26.8 ±</td>
<td>54.6</td>
<td>1.94</td>
</tr>
<tr>
<td>Wet Oxidation Lignin</td>
<td>34.1 ±</td>
<td>45.7</td>
<td>1.34</td>
</tr>
<tr>
<td>Mild Bisulfite Lignin</td>
<td>47.5</td>
<td>56.4</td>
<td>1.19</td>
</tr>
<tr>
<td>MBS Lignosulfonic acid</td>
<td>4.7</td>
<td>28.0</td>
<td>5.92</td>
</tr>
</tbody>
</table>
Summary

• Developing value-added products from lignin-rich process residuals will be critical to large scale biorefinery commercial success.

• Different pretreatment technologies produce residuals with different properties.

• The residues from Mild Bisulfite and Wet Oxidation pretreatments contain a lot more than just lignin.

• Processes to upgrade lignin must be robust enough to handle significant impurity content and variability in the feedstock.
Summary

• High purity lignin was isolated from the Mild Bisulfite and Wet Oxidation residuals and characterized with respect to elemental content, hydroxyl group content, and molecular weight.
Acknowledgements

• Colleagues Dave Fish and Ian Dallmeyer
• NARA Summer undergraduate intern Steve Cline

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