Forest BioRefinery
Lignin

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Kraft Digester: Cooking Liquors

Black Liquor
Contains Valuable
Hemicelluloses
Lignin
Profiling Biomass Resources
Kraft Lignin

Relative Amount of $\beta$-O-aryl Ether Structures

Degree of Delignification % on Wood

Gellerstedt

Ragauskas
Profiling Biomass Resources
Kraft Lignin

C-5 Condensed Lignin From Conventional Kraft Cook and MWL

<table>
<thead>
<tr>
<th>Lignin Sample</th>
<th>% Delignification</th>
<th>Condensed C-5 Lignin (mmol/g lignin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWL</td>
<td>0</td>
<td>0.36</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td>16.5</td>
<td>0.87</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td>22.1</td>
<td>0.91</td>
</tr>
<tr>
<td>Kraft Lignin</td>
<td>39.1</td>
<td>1.31</td>
</tr>
</tbody>
</table>

MW: SW kraft lignin 2,000-3,000
**Profiling Biomass Resources**

**Kraft Lignin Isolation**

**Assorted Possibilities**

*Ultra-filtration*

*Low MW Lignin*

*High MW Lignin*

*Acid Precipitation*

*LignoBoost*

- Weak black liquor tank
- Evaporators
- Black liquor
- To recovery boiler
- Washed lignin
- "Re-slurry" tank
- Wash liquor
- Dewatering
- Precipitation vessel

**KBL**

19% Solids
Solids Composition:
- Lignin: 30%
- Other organics: 20%
- Inorganics: 50%

**Filtrate**

11.5% Solids
Solids Composition:
- High molecular lignin: 15%
- Other organics: 25%
- Inorganics: 62%

**Concentrate**

25% Solids
Solids Composition:
- High molecular lignin: 75%
- Other organics: 7%
- Inorganics: 18%
Bark for Biofuels/Biochemicals

Conversion Chemistry
- Cat. Pyrolysis Chemistry

Green Diesel/Gasoline

Phenolics Feedstocks
10% of U.S. kraft lignin is sufficient to produce enough carbon fiber to replace half of the steel in all domestic passenger transport vehicles.

<table>
<thead>
<tr>
<th>Lignin/PEO</th>
<th>HWKL (°C)</th>
<th>Alcell (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>195-228</td>
<td>138-165</td>
</tr>
<tr>
<td>95/5</td>
<td>189-198</td>
<td>153-172</td>
</tr>
<tr>
<td>87.5/12.5</td>
<td>191-200</td>
<td>138-172</td>
</tr>
<tr>
<td>75/25</td>
<td>150-182</td>
<td>120-157</td>
</tr>
</tbody>
</table>

Alcell and Hard Wood Kraft Lignin (HWKL) were spun continuously into satisfactory fibers. Alcell/PEO blends: inter-fiber fusing SWKL: formed chars instead of fibers.
Profiling Biomass Resources
Kraft Lignin Application

- Phenols, Cresols
- Substituted Phenols

HYDROGENATION

- Phenol, Acetic Acid
- Substituted Phenols, CO, CH₄

PYROLYSIS

- Acetylene
- Ethylene

FAST PYROLYSIS

- Phenolic Acids
- Catechols

HYDROLYSIS

- Phenol
- Substituted Phenols

ALKALI

- Vanillin, Ferulic
- Coumaric/other
- Acids

OXIDATION

- Vanillin, MeS₂
- MeSH, DMSO
- Lignin with Increased
- Polymerization

MICROBIAL

- Vanillic, Ferulic
- Coumaric/other
- Acids

OXOREDUCTASE

- Oxidized Lignin
- Coating/Paint
- Additive
Profiling Biomass Resources
Kraft Lignin Application: Pellet Binder

Drivers for Wood Pellets
- Investment Tax Credit
- Capital Grants
- Consumer Rebates
- Excise Tax Exemptions
- Tax Credits
- Targets/Quotas with Penalties
- Subsidies
  - Production of Green Electricity
  - Consumption

Lignin: Binder for Wood Pellets

District Heating
## Profiling Biomass Resources

**Kraft Lignin Application: Resin/Adhesive**

- **Strength Properties of OSB-panels Produced with Combination of Phenolic Resin and Lignin**

<table>
<thead>
<tr>
<th>Binder</th>
<th>Property</th>
<th>100% Phenolic</th>
<th>80% Phenolic/20% Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder Resin</td>
<td>MOR/psi</td>
<td>3456</td>
<td>3654</td>
</tr>
<tr>
<td></td>
<td>IB/psi</td>
<td>59.4</td>
<td>60.1</td>
</tr>
<tr>
<td></td>
<td>D-4/lbs</td>
<td>144</td>
<td>143</td>
</tr>
<tr>
<td></td>
<td>D-5/lbs</td>
<td>115</td>
<td>141</td>
</tr>
<tr>
<td>Liquid Resin</td>
<td>MOR/psi</td>
<td>5204</td>
<td>4866</td>
</tr>
<tr>
<td></td>
<td>IB/psi</td>
<td>83</td>
<td>295</td>
</tr>
<tr>
<td></td>
<td>D-4/lbs</td>
<td>276</td>
<td>97</td>
</tr>
</tbody>
</table>
Novel Oxidative Lignin Fragmentation Chemistry

$\sim C_{800} - C_{900}$

$C_6 - C_{24}$
Novel Fragmentation Chemistry for Lignin

Aromatic Production (10^9 lb)

- Benzene: 20
- Xylene: 13
- Terephthalic acid: 11
- Toluene: 11
- Phenol: 5
- Total: 60

Lignin required (10^9 lb)

- BTX: 91
- Terephthalic acid: 13
- Phenol: 10
- Total: 114
BioChemical: Lignin as A Chemical Precursor

Lignin As Chemical Precursors

New technology

Sulfite waste liquor → CuO/CeO/NaOH → Oxalic, succinic, benzenepentacarboxylic, isophthalic, phthalic acid
pine lignin

24 hrs. 230° C →
40 atm. air → Terephthalic acid
Catalytic Conversion of Biomass to Biofuels

Biofuel precursor:

\[ \sim C_{800} - C_{900} \]

Cracking Biopolymer

\[ C_9 - C_{18} \]

Viable Biodiesel or Biogasoline Component

Current Research Activities:
- Utilization of conventional heterogeneous hydrogenation catalysts
- Development of homogenous aqueous phase catalysis chemistry for hydrogenation cleavage of:
  - Aryl-O-Aryl
  - Aryl-O-Aliphatic Ethers
BioChemical: Novel Reductive Catalytic Chemistry

BioMaterial Precursors

\[ \sim C_{800} - C_{900} \]

Current Research Activities

Develop heterogeneous/homogenous aqueous phase catalysis chemistry hydrogenation cleavage

<table>
<thead>
<tr>
<th></th>
<th>Non-water-soluble hydrogenation complexes</th>
<th>Water-soluble hydrogenation complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ruthenium</strong></td>
<td>[Ru(Cl)(_2)(PPh(_3))(_3)]</td>
<td>[Ru(Cl)(_2)(TPPTS)(_3)]</td>
</tr>
<tr>
<td></td>
<td>[Ru(H)(Cl)(PPh(_3))(_3)]</td>
<td>[Ru(H)(Cl)(TPPTS)(_3)]</td>
</tr>
<tr>
<td></td>
<td>[Ru(H)(_2)(PPh(_3))(_4)]</td>
<td>[Ru(H)(_2)(TPPTS)(_4)]</td>
</tr>
<tr>
<td><strong>Rhodium</strong></td>
<td>[RhCl(PPh(_3))(_3)]</td>
<td>[RhCl(TPPTS)(_3)]</td>
</tr>
</tbody>
</table>
Ethanol Organosolv Lignin Process

1/ **Soxhlet Extraction:**
Loblolly pine (*Pinus taeda*)
Benzene/Ethanol $\rightarrow$ Extractives
Experimental Setup

- 4560 Mini Parr reactor equipped with a 4842 temperature controller.
- Pressurized with UHP Hydrogen gas.
- Under on-line controlled time and pressure.
Ethanosolv Lignin Hydrogenation

Mass Balance lignin Hydrogenolysis RuCl2(PPh3)3

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Charred</th>
<th>Unsolluble Phase</th>
<th>Solluble Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schlenk</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 C Parr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 C Parr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>175 C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Lignin Hydrogenation

<table>
<thead>
<tr>
<th>Reaction conditions</th>
<th>Solubility in ethanol (% dry wt.)</th>
<th>$M_n$ (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOL *</td>
<td>52.1</td>
<td>1191</td>
</tr>
<tr>
<td>Blank *</td>
<td>65.0</td>
<td>1026</td>
</tr>
</tbody>
</table>

**Heterogeneous catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solubility</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/Mo</td>
<td>54.3</td>
<td>1075</td>
</tr>
<tr>
<td>Raney-Ni *</td>
<td>71.8</td>
<td>1148</td>
</tr>
<tr>
<td>Pd/C</td>
<td>69.8</td>
<td>995</td>
</tr>
<tr>
<td>Pt/C</td>
<td>76.5</td>
<td>953</td>
</tr>
</tbody>
</table>

**Homogeneous catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solubility</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH$_4$/I$_2$ *</td>
<td>72.4</td>
<td>404</td>
</tr>
<tr>
<td>RhCl(PPh$_3$)$_3$</td>
<td>76.3</td>
<td>787</td>
</tr>
<tr>
<td>Ru(Cl)$_2$(PPh$_3$)$_3$ *</td>
<td>96.4</td>
<td>893</td>
</tr>
<tr>
<td>Ru(H)(Cl)(PPh$_3$)$_3$</td>
<td>77.2</td>
<td>837</td>
</tr>
<tr>
<td>Ru-(PVP)</td>
<td>58.1</td>
<td>902</td>
</tr>
</tbody>
</table>
Future Lignin Applications

• Green Antioxidant
• Co-polymer
• Green Diesel
• Carbon Fibers
• Thermal Stabilization Additive
• Polyurethanes
• Green Coatings
• Source of Green Chemicals
It can be produced with success in labs, but according to Arthur Ragauskas, a biofuels expert at Georgia Tech, bringing it to market, namely cost and efficiency. While converting a starch like corn or sugar to ethanol is relatively simple, cellulosic matter poses a greater challenge because it requires "pretreatment" to make the material more reactive to the deconstruction enzymes that turn starch to glucose, which is easily turned into ethanol. Make this cost effective. Ragauskas says new technology looks promising, but many experts believe it's unlikely that the fuel will go from zero to 20 billion in 10 years. It took the corn industry more than a decade to get to 1 billion gallons of ethanol capacity.
W.J. Bryan
Destiny is not a matter of chance, it is a matter of choice, it
is not a thing to be waited for, it is a thing to be achieved

Thank You!