Foams from Lignin

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• 6.3 Billion barrels of oil
• ~50% used for gasoline
• ~20% for chemicals and products
• Improved efficiency = record profits
• Operate at >90% capacity
• Product price mix fixed (3.5% margin)
• Top products for chemicals
• Sulfuric acid, BTX, olefins, etc.
• Feed stocks for products
• Plastics, carbon fibers, etc.
So... What's the problem?

- Heterogeneous
- Chemistry depends on...
  - Feedstock
  - Extraction method
- $M_w$?
  - High polydispersity
  - Off-gassing during processing
- Thermoplastic/thermoset
  - Small processing window above melt flow but below fusing and degradation
Lignin Processing
Tune the Lignin to the Product

- **Lignin**
- **Extraction**
- **Foam**
- **Low Polydispersity**
  - **Carbon fibers**
  - **Composites, electrodes, filters**
- **High Mw**
  - **Nanofibers**
  - **Electrodes, filters, composites**
- **Insulation, structural cores, filters, electrodes**
Materials

- Indulin AT Kraft Lignin MeadWestvaco Corporation
- Hot water washed (60°C) until water is clear
- Extracted with methanol and subsequently 70/30 methanol/methylene chloride at room temperature
- Switchgrass organosolv lignin
- MIBK/EtOH/H$_2$O; 16/34/50 wt% with 0.05M H$_2$SO$_4$ @ 160°C for 120min
- Blowing agent (BA) – Azodicarbonamide
- Lautan Otsuka Chemical, Indonesia
<table>
<thead>
<tr>
<th>Lignin</th>
<th>$T_g$ (°C) +/- 2</th>
<th>ΔCp (J/g.°C) +/- 0.010</th>
<th>Melting temperature (°C) +/- 5</th>
<th>5% Mass loss in TGA (°C) +/- 1</th>
<th>DTGA peak (°C) +/- 1</th>
<th>Char (%) +/- 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWKL</td>
<td>148</td>
<td>0.311</td>
<td>184*</td>
<td>267</td>
<td>356</td>
<td>43.0</td>
</tr>
<tr>
<td>SWKL-1 (MeOH)</td>
<td>117</td>
<td>0.418</td>
<td>150</td>
<td>282</td>
<td>374</td>
<td>41.5</td>
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<tr>
<td>SWKL-2 (70/30)</td>
<td>182</td>
<td>0.398</td>
<td>230</td>
<td>295</td>
<td>381</td>
<td>46.0</td>
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<tr>
<td>SG-organosolv</td>
<td>121</td>
<td>0.384</td>
<td>190</td>
<td>256</td>
<td>375</td>
<td>36.7</td>
</tr>
</tbody>
</table>

*No full melt
Foam Production
Stabilization

Center for Renewable Carbon
UT The University of Tennessee Institute of Agriculture

Heat

Temperature (°C)
Softwood Foams
Softwood foams

<table>
<thead>
<tr>
<th>Blowing Agent (%)</th>
<th>Temperature (°C) +/-2</th>
<th>Density (g/cm³) +/- 0.01</th>
<th>Pore size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>225</td>
<td>0.77</td>
<td>90.2</td>
</tr>
<tr>
<td>0</td>
<td>250</td>
<td>0.63</td>
<td>72.4</td>
</tr>
<tr>
<td>10</td>
<td>225</td>
<td>0.34</td>
<td>68.2</td>
</tr>
<tr>
<td>10</td>
<td>250</td>
<td>0.20</td>
<td>71.1</td>
</tr>
<tr>
<td>20</td>
<td>225</td>
<td>0.19</td>
<td>64.7</td>
</tr>
<tr>
<td>20</td>
<td>250</td>
<td>0.14</td>
<td>64.4</td>
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Carbon Foams
Carbon Foam Micrographs

Softwood

Switchgrass
## Carbonization Conditions

<table>
<thead>
<tr>
<th></th>
<th>Temperature (°C)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonization</td>
<td>1000</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ramp (°C/min)</td>
<td>10</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Thermostatic</td>
<td>15 min</td>
<td>Nitrogen</td>
</tr>
</tbody>
</table>
## Density of Carbon Foams

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C) +/-2</th>
<th>Pressure (kPa) +/-35</th>
<th>Density (g/cm³) +/- 0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td>250</td>
<td>1379</td>
<td>0.464</td>
</tr>
<tr>
<td>Lignin</td>
<td>250</td>
<td>1724</td>
<td>0.464</td>
</tr>
<tr>
<td>Lignin</td>
<td>250</td>
<td>2069</td>
<td>0.481</td>
</tr>
<tr>
<td>Lignin + BA</td>
<td>250</td>
<td>1379</td>
<td>0.274</td>
</tr>
<tr>
<td>Lignin + BA</td>
<td>250</td>
<td>1724</td>
<td>0.256</td>
</tr>
<tr>
<td>Lignin + BA</td>
<td>250</td>
<td>2069</td>
<td>0.306</td>
</tr>
</tbody>
</table>

Foams produced at 1517 kPa and 0 or 20% BA
Foam with BA Mechanical Behavior

Carbonized

Stress (kPa) vs. Strain

- LBA–200
- LBA–250
- LBA–300

Stress (kPa) vs. Strain

- LBAC–200
- LBAC–250
- LBAC–300
Compressive Modulus

L = no blowing agent; BA = blowing agent; C = carbonized; # = pressure
Compressive Strength

L = no blowing agent; BA = blowing agent; C = carbonized; # = pressure
## Switchgrass Foams

**Sample** | **Temperature (°C)** | **Pressure (kPa)** | **Density (g/cm³)**
---|---|---|---
Lignin | 250 | 793 | 0.070
Lignin | 200 | 2586 | 0.418
Lignin | 200 | 2586 | 0.369
CARBON | 200 | 2586 | 0.362
Lignin | 250 | 931 | 0.095
Lignin | 250 | 931 | 0.157
Lignin | 200 | 1207 | 0.285
Lignin | 200 | 1379 | 0.438
Lignin | 200 | 1379 | 0.446
Lignin | 200 | 1724 | 0.448
Lignin | 200 | 1724 | 0.468
<table>
<thead>
<tr>
<th></th>
<th>PUF*</th>
<th>Styrofoam Highload Extruded Polystyrene Foam Insulation **</th>
<th>Carbon Foam***</th>
<th>Lignin Based Carbon Foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength</td>
<td>0.13 - 0.25</td>
<td>0.275 – 0.69</td>
<td>0.1 -0.52</td>
<td>2.3</td>
</tr>
<tr>
<td>(Mpa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus (Mpa)</td>
<td>3 - 7.23</td>
<td>9.65 – 25.51</td>
<td>30.3</td>
<td>12.5</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>.0435 – 0.046</td>
<td>0.068</td>
<td>0.040 0.20</td>
<td>0.070-0.46</td>
</tr>
</tbody>
</table>


***ERG Aerospace Duocel Foam
Conclusions

• Lignin can be tuned to produce a variety of products.
• We can take advantage of volatile materials and oxidation to produce rigid foams.
• Blowing agents help produce consistent, low density foams.
• Low density ≠ low properties
• Still a lot of testing and optimization to do…
• Thermal properties, consistent cell size, lower density, higher processing temperatures, larger foams, reducing environments, low Mw biomaterials as BA, etc.
Acknowledgements

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Questions?