Uncatalyzed Lignin Solvolysis
Utilizing Water-Solvent Mixtures as a Reaction Medium

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This Is What I Will Tell You

Lignin: opportunities and challenges!
Water-solvent mixtures (solvolysis) provide remarkably small char formation and are good solvents for depolymerized lignin (bio-oil)

- 15.8 w-% char (related to the feedstock lignin) in pure water at 270 °C
- Respective values for 1:1 mixtures of water with methanol, ethanol, and 2-MTHF: 2.4, 1.2, and 1.8 w-%
- Solvolysis at 310 °C; water:2-MTHF ratio 1:1
  - 88.6 w-% depolymerized lignin, 0.3 w-% char
  - Hydrothermolysis (pure water): 13.1 and 12.6 w-%, respectively

Improving the degradation techniques, analytics, and purification methods provides substantial work in the future!
What Did We Know?
Lignin – Opportunities!

Availability

• Global kraft pulp production (2013): ~131 million Adt
• 350-500 kg lignin/Adt of pulp dissolves ⇒ 46-66 million t/a
• Assuming 50% needed for pulp mills’ process energy ⇒ ~25 million t kraft lignin available as a feedstock for e.g. chemical industry

Hydrolysis lignin from bioethanol production?

E. Sjöström, Tappi 60(9):151 (1977)
Lignin – Challenges!

Amorphous, cross-linked polymer
- Difficult to dissolve
- Many types of linkages
- Structure depends on source & isolation method
- Chemical modification (e.g. depolymerization) requires harsh conditions, special equipment
- Complex analyses
  - NMR, UV, FTIR, GC-MS, GPC, etc.

Lignin (esp. kraft) important as energy source at pulp mills

Why Depolymerizing?

Current applications for lignin polymers

- Lignosulfonates
  - \textit{global consumption} ~1 million t
- Resins, binders, adhesives, polyurethane formulations, carbon fibers, \textit{etc.}
  - \textit{global consumption minute}

Lignin: \textit{green source of aromatics}

- Successful depolymerization yields valuable building blocks for chemical industry
- Bio-oils have higher energy content than \textit{e.g.} bioethanol
What Did We Do?
Reaction Scheme

Lignin + water + solvent → Reaction mixture

- **Ethyl acetate extraction**
  - Bio-oil & solvent → Bio-oil in ethylacetate
  - Residual lignin & char
  - Residual lignin & NaOH

- **Dissolving in NaOH, filtration**
  - Bio-oil in ethylacetate
  - Residual lignin & NaOH

- **Filtration**
  - Ethyl acetate extraction

- **Solvent removal**
  - Water waste

- **Char**
  - Residual lignin

Note: ethylacetate extraction only performed when pure water used as solvent.
Reactor

Stainless steel (T316)
Parr 4575 batch reactor

- 4848 reactor controller
- Volume 500 ml
Materials and Methods

Initial experiments

- 5 g lignin, 200 ml H2O and H2O-solvent mixtures (1:1, volume basis)
- Solvents: methanol, ethanol, **2-methyl tetrahydrofuran (2-MTHF)**
- Solvolysis at 270 °C
- Fractions separated (residual lignin, char, depolymerized lignin, gases, water solubles)
- Material balance
- Molar mass distribution of the depolymerized lignin determined (GPC)

Experiments with 2-MTHF

- Water-solvent ratios (1:3, 1:1, 3:1)
- Reaction temperatures 270, 290, 310 °C
- Reaction products analyzed as described above
Organosolv Beech Lignin

Elemental composition (wt.% dry lignin)
- 62.54% C, 5.91% H, 0.25% N, 30.85% O, 0.00% S

β-O-4 linkages
- 0.27 per aromatic ring

<table>
<thead>
<tr>
<th>Ash</th>
<th>Sugars</th>
<th>Mw</th>
<th>Mn</th>
<th>PD</th>
<th>Moisture</th>
<th>Heating Value</th>
<th>S / G Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>wt.%</td>
<td>g mol(^{-1})</td>
<td>g mol(^{-1})</td>
<td></td>
<td>wt.%</td>
<td>kJ g(^{-1})</td>
<td></td>
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<tr>
<td>0.05</td>
<td>2.4</td>
<td>3428</td>
<td>606</td>
<td>5.66</td>
<td>4.39</td>
<td>24.12</td>
<td>1.29</td>
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</tbody>
</table>

Number-average (Mn) and weight-average (Mw) molecular weights; Polydispersity (PD); Syringyl to guaicyl units (S/G)
Gel Permeation Chromatography (GPC)

Agilent HPLC-system

- Phenogel (5 µm – 5 nm and 100 nm) columns
- UV detector (280 nm)
- THF eluent, rate of 1.0 mL min⁻¹; room temperature
- Calibration: syringol and polystyrene standards (76,600 g mol⁻¹ to 154.2 g mol⁻¹)

Organosolv lignin sample acetylated prior to analysis
Depolymerized lignin samples analyzed without acetylation
What Did We Achieve?
Material Balance
Solvent/water: 1/1; 270 °C; 60 min; weight %

<table>
<thead>
<tr>
<th></th>
<th>RL</th>
<th>Char</th>
<th>DL</th>
<th>Gas Phase</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol / Water</td>
<td>51.2</td>
<td>2.4</td>
<td>40.0</td>
<td>1.8</td>
<td>3.3</td>
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<tr>
<td>Ethanol / Water</td>
<td>34.4</td>
<td>1.2</td>
<td>57.4</td>
<td>1.8</td>
<td>3.3</td>
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<tr>
<td>2-MTHF / Water</td>
<td>86.8</td>
<td>1.2</td>
<td>1.8</td>
<td>3.3</td>
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</table>
Molar Mass Distribution – Solvent Effect
Material Balance
2-MTHF/water: varied; 270 °C; 60 min; weight %

<table>
<thead>
<tr>
<th>Pure water</th>
<th>150 / 50</th>
<th>100 / 100</th>
<th>50 / 150</th>
</tr>
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<tbody>
<tr>
<td>RL</td>
<td>10.0</td>
<td>15.7</td>
<td>2.3</td>
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<tr>
<td>Char</td>
<td>54.5</td>
<td>75.8</td>
<td>57.7</td>
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<tr>
<td>DL</td>
<td>10.4</td>
<td>3.1</td>
<td>23.7</td>
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<tr>
<td>Water Solubles (TOC)</td>
<td>1.8</td>
<td>3.3</td>
<td></td>
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<tr>
<td>Other</td>
<td>10.0</td>
<td>50.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Gas Phase</td>
<td>20.0</td>
<td>30.0</td>
<td>40.0</td>
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</table>
Molar Mass Distribution
Water/Solvent Ratio

Detector Response (mAU)

Log Molar Mass

- 150 ml 2-MTHF / 50 ml Water
- 100 ml 2-MTHF / 100 ml Water
- 50 ml 2-MTHF / 150 ml Water
- Acetylated Lignin
Material Balance
2-MTHF/water: 1/1; 270, 290, 310 °C; 60 min; weight %

<table>
<thead>
<tr>
<th>Temperature</th>
<th>RL</th>
<th>Char</th>
<th>DL</th>
<th>Water solubles (TOC)</th>
<th>Other</th>
<th>Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 270</td>
<td>10</td>
<td>16</td>
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<tr>
<td>270</td>
<td>55</td>
<td>1.8</td>
<td>3.3</td>
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<tr>
<td>W 290</td>
<td>11</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>290</td>
<td>87</td>
<td>1.8</td>
<td>3.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 310</td>
<td>13</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310</td>
<td>89</td>
<td>0.3</td>
<td>3.2</td>
<td></td>
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</tbody>
</table>
Molar Mass Distribution
Varying Temperature

\[
\begin{align*}
\text{Mw} &= 956 \text{ g/mol, Mn} = 456 \text{ g/mol} @ 270 \degree C \\
\text{Mw} &= 886 \text{ g/mol, Mn} = 428 \text{ g/mol} @ 290 \degree C \\
\text{Mw} &= 756 \text{ g/mol, Mn} = 392 \text{ g/mol} @ 310 \degree C
\end{align*}
\]

What Did We Learn?
Lignin and “Bio-Oil” Are Versatile

”Bio-oil”: a mixture of mono-aromatics or a complex mixture of mono-, di-, tri-, oligo-, and polymers or something in between

• Degraded lignin (a.k.a. bio-oil) at 310 °C, 1:1 water:2-MTHF, is a rubber-like substance

While lignin solubility increases, the yield of small molecule substances (e.g. monoaromatics), as well as char, decreases
Schematic Reaction Pathways
Hydrothermolysis & Solvolysis

Water Solubles

Residual Lignin

Lignin

Gas

Char

Reaction Intermediates Phase

Syringol → 3-Methoxycatechol

Guaiacol → Pyrocatechol → Phenol

Di, tri and oligomers

Bio-Oil

Much Remains to Be Done

Via hydrothermalysis nearly 10 w-% yield of monoaromatics can be obtained

- Containing valuable compounds, e.g. catechols
- Yield of char ~25% at the same time
- Isolating the pure compounds challenging

Lignin dissolves much more readily in water-solvent mixtures than in pure water

- Less char formation
- Less depolymerization to small molecules
- The resulting “bio-oil” is an interesting mixture of lignin oligomers and polymers

Improved degradation, purification and analytical methods & equipment

- Catalysts!

Who Helped Us?
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