Ligning depolymerisation
Introduction

- Introduction
- Background
- Lignin depolymerisation
- Conclusions
Motivation

- Less consumption of finite resources
- Lower climate and environment impact
- Improved competitiveness of Swedish/Nordic industry
Introduction

“In the future, mankind will make greater demands on renewable resources to satisfy needs for energy and carbon-based chemicals.”

E. Glesinger, *The Coming Age of Wood*, 1949
Introduction

“In view of the limited and diffuse availability of renewable resources, they should generally be regarded as auxiliary fuels and chemical feedstocks rather than as direct substitutes for fossil fuels.”

Introduction

“Now is the time to initiate vigorous, broad-based programs to substitute biomass-derived chemicals for petrochemicals.”

E. Lipinsky, Chemicals from biomass: petrochemical substitution options, Science, 1981
Introduction

- Lignin is a complex macromolecule
- Branched and interconnected
- Aromatic alcohol building blocks
- Bonds between lignin and hemicellulose

Proposed configuration of lignin.
Introduction

- p-hydroxyphenylpropane
- guaiacylpropane
- syringylpropane
Introduction

• Lignin is ...
  – The second most abundant natural polymer
  – Amorphous
  – Impossible to isolate in native state
  – The only natural source to aromatic structures
  – Brown
  – The concrete of nature – highly resistant!
Introduction

Macro molecule

Lignin Fragments

$M_w > 20000 \text{ u}$

$M_w 200 - 400 \text{ u}$
Introduction

• Deplymerisation needed in most cases
  – Fuel applications
  – Chemicals
  – Microbial feedstock

• Final product determine depolymerisation strategy
Background

<table>
<thead>
<tr>
<th>Structure</th>
<th>Norway Spruce [%]</th>
<th>Pine [%]</th>
<th>Birch [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>42</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>28</td>
<td>28</td>
<td>34</td>
</tr>
<tr>
<td>Lignin</td>
<td>27</td>
<td>27</td>
<td>21</td>
</tr>
<tr>
<td>Extractives</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

Softwoods > Hardwoods > Grasses
Background
<table>
<thead>
<tr>
<th>Bond types and functional groups</th>
<th>Share in spruce lignin [%]</th>
<th>Share in beech lignin [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-O-4</td>
<td>39–48</td>
<td>32–37</td>
</tr>
<tr>
<td>α-O-4</td>
<td>11–16</td>
<td>28–32</td>
</tr>
<tr>
<td>β – 5</td>
<td>6–10</td>
<td>8</td>
</tr>
<tr>
<td>β – β</td>
<td>7–10</td>
<td>6.4</td>
</tr>
<tr>
<td>5–5</td>
<td>7–9</td>
<td>2</td>
</tr>
<tr>
<td>4-O-5</td>
<td>6–7</td>
<td>2</td>
</tr>
<tr>
<td>β – 1</td>
<td>2</td>
<td>16</td>
</tr>
<tr>
<td>α – 5</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>α – β</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Aliphatic OH</td>
<td></td>
<td>92–98</td>
</tr>
<tr>
<td>Benzylic OH (α –OH)</td>
<td>18</td>
<td>4</td>
</tr>
<tr>
<td>Phenolic OH</td>
<td>29.4</td>
<td>16</td>
</tr>
<tr>
<td>Ketone groups</td>
<td>13.8</td>
<td>16</td>
</tr>
<tr>
<td>Aldehyde groups</td>
<td>2.8</td>
<td>4</td>
</tr>
<tr>
<td>Methoxy groups</td>
<td>91.7</td>
<td>136</td>
</tr>
</tbody>
</table>

**Elementary composition of C₉ units**

<table>
<thead>
<tr>
<th></th>
<th>Spruce lignin</th>
<th>Beech lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formulae of structural schemes</strong></td>
<td>C₉H₇.82O₂.4(OCH₃)₀.92</td>
<td>C₉H₇.16O₂.44(OCH₃)₁.36</td>
</tr>
<tr>
<td><strong>Formulae of milled wood lignin</strong></td>
<td>C₉H₇.95O₂.4(OCH₃)₀.92</td>
<td>C₉H₇.10O₂.41(OCH₃)₁.36</td>
</tr>
</tbody>
</table>
Depolymerisation of lignin

• Strategy determined by desired end-product
• Example: chemical feedstock production
• Classified the reactions into 5 categories
  – Pyrolysis
  – Cracking/hydrocracking
  – Hydrogenolysis
  – Hydrolysis
  – Super-critical solvents
Depolymerisation of lignin

- **Pyrolysis**
  - Thermal degradation
  - No oxygen
  - Differs with lignin preparation method
  - Non-distinct peaks
  - H/C ratio important factor for gas formation (CO and \( \text{H}_2 \))
Depolymerisation of lignin

- Pyrolysis
  - Influenced by cat-ion impregnation (e.g. Na\(^+\), NH\(_4\)^+ and Ca\(^{2+}\))
  - NH\(_4\)^+ decrease char formation
  - Ca\(^{2+}\) cause SO\(_2\) evolution
  - Char formation drawback of the technology
Depolymerisation of lignin

• Pyrolysis
  – Degradation of the propanoid side occur at 503-533 K
  – The β-β and C-C bonds in-between the monomeric units cleave at 548-623 K
  – Also the heating rate influence the product spectra
    • low heating-rates favour the formation of oxygen-containing compounds
    • alkyl-phenol derivatives are formed at fast heating-rates
Depolymerisation of lignin

• Pyrolysis
  – Reactor design and operating conditions are of great significance
    • heating rate
    • vapour residence time
    • particle size
    • reactor pressure and atmosphere
    • biomass origin
Depolymerisation of lignin

• Summary
  – Associated with char-formation
  – Cation-assisted pyrolysis (NH₄⁺)
  – Hydrogen source required to avoid char
Depolymerisation of lignin

- Cracking
  - Two types
    - Cracking
    - Hydrocracking
  - Cracking for lignin challenging due to aromatic structures
  - Hydrocracking of lignin possible but will saturate aromatics
Depolymerisation of lignin

• Cracking
  – Temperature dependent
  – Rather low pressure
  – Use zeolite catalysts
  – C9+ fraction most interesting
Depolymerisation of lignin

Hydrocracking

– Liquid phase
– 573-673 K
– $\text{H}_2$ pressure 1 to 10 Mpa
– NiMo or NiW/silica-alumina
– Used as second part in lignin-to-gasoline processes
Depolymerisation of lignin

• Summary
  – Inability of traditional cracking to treat aromatics
  – Diffusion resistance of the larger complex of lignin
  – Unsuitable for carbon black feedstock preparation
  – Hydrocracking saturate aromatic
  – New catalysts will probably be required.
  – Due to these reasons both cracking methods appear difficult to implement in the near term
Depolymerisation of lignin

• Hydrogenolysis
  – Three sections
    • Gaseous hydrogen
      – Heterogeneous catalysts
      – Homogeneous catalysts
    • Hydrogen donor solvents
    • Electro-catalysis
  – Severity (T,P):
    Heterogeneous > Homogeneous ≥
    Donor Solvent > Electro-Catalysis
Depolymerisation of lignin

• Heterogenous catalysts
  – Largest area of research
  – High pressure
  – Low solubility of hydrogen in solvent
  – Low mobility of lignin in solvent
  – Large selection of catalysts:
    Rh or Pd/C > NiO/MoO₃ > Raney Ni > Fe₂O₃ > No catalyst
  – Hydrogen pressure significantly influence carbon formation
Depolymerisation of lignin

• Homogeneous catalysts
  – Medium severity (0.1-5 Mpa, room temperature to 378 K)
  – Low solubility of hydrogen in solvent
  – High mobility of catalyst in solvent
  – Ni, Co, Fe and Mo salts used or Rh-based complex with various organic anions or colloidal rhodium
  – 98% deoxygenation by using a salt of Mo at 20 MPa and 623 K
Depolymerisation of lignin

- Rh-catalysts have maximum in performance
- Catalyst choice important

![Graph showing depolymerisation of lignin with different catalysts and temperatures.](chart.png)
Depolymerisation of lignin

- Donor solvents
  - Tetralin
  - Hydrogenated anthracene and pyrene
  - Tetrahydroflouroanthene
  - Flouroanthene
  - Dihydroanthracene
  - Tetrahydroquinoline and indoline
## Depolymerisation of lignin

<table>
<thead>
<tr>
<th>Products isolated</th>
<th>Mass share in tetralin [%]</th>
<th>Mass share in naphthalene [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>9.7</td>
<td>38.5</td>
</tr>
<tr>
<td>Non-volatile neutrals</td>
<td>3.3</td>
<td>5.9</td>
</tr>
<tr>
<td>Acetone-insoluble lignin</td>
<td>2.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Acetone-soluble lignin</td>
<td>37.8</td>
<td>18.0</td>
</tr>
<tr>
<td>Ether-soluble phenols</td>
<td>37.4</td>
<td>7.4</td>
</tr>
<tr>
<td>Acids</td>
<td>2.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adjusted reaction time [min]</th>
<th>Lignins [%]</th>
<th>Phenols [%]</th>
<th>Acids [%]</th>
<th>Neutrals [%]</th>
<th>Char [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone-insoluble</td>
<td>Acetone-soluble</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>60.2</td>
<td>38.2</td>
<td>2.5</td>
<td>0.6</td>
<td>0.7</td>
</tr>
<tr>
<td>15</td>
<td>2.6</td>
<td>37.8</td>
<td>37.4</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>75</td>
<td>2.8</td>
<td>13.4</td>
<td>31.0</td>
<td>1.9</td>
<td>5.3</td>
</tr>
<tr>
<td>255</td>
<td>2.2</td>
<td>12.6</td>
<td>26.7</td>
<td>1.5</td>
<td>8.0</td>
</tr>
<tr>
<td>615</td>
<td>2.4</td>
<td>5.8</td>
<td>22.7</td>
<td>1.2</td>
<td>7.0</td>
</tr>
</tbody>
</table>
Depolymerisation of lignin

• Electro-catalysis
  – The catalyst also works as electrode in the system
  – Most commonly Raney Ni, but also Pd supported on carbon and alumina
  – Conversions in the 70-100% range at 323 K
  – The current is in the 5-20 mA range and 2-18 F/mol of substrate is used.
  – Small field, difficulties with hydrogen evolution
Depolymerisation of lignin

• Summary
  – Heterogeneous catalysts most investigated
    • Work well with smaller molecules
    • Require high hydrogen pressure
  – Homogeneous catalysts interesting due to low severity
  – Electro-catalysis probably not viable
Depolymerisation of lignin

• Hydrolysis
  – Catalysts suppress carbon formation
  – Alkali interrupt condensation reaction normally occurring between unstable lignin fragments

Carbon formed from initial lignin (%) vs NaOH (%)

- Water Soluble
- Oil
- Gas
- Residue

Water RbCO3 CsCO3
Depolymerisation of lignin

• Summary
  – Plausible from a technical standpoint
  – Require some kind of catalyst to lower carbon formation
  – Also require after-treatment to reduce oxygen content
Depolymerisation of lignin

• Supercritical fluids
  – Used at very high severity (P,T)
  – Catalysts may influence performance
  – Not viable concept due to reaction engineering considerations
## Conclusions

<table>
<thead>
<tr>
<th>Method</th>
<th>Severity</th>
<th>Suitability</th>
<th>Process complexity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>medium</td>
<td>Low-medium</td>
<td>Low-medium</td>
</tr>
<tr>
<td>Cracking</td>
<td>Low to medium</td>
<td>low</td>
<td>Low</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>Low to high</td>
<td>High</td>
<td>Medium-high</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Medium</td>
<td>High as pre-treatment</td>
<td>Medium</td>
</tr>
<tr>
<td>Super-Critical</td>
<td>High</td>
<td>Low</td>
<td>High-very high</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method</th>
<th>Char</th>
<th>Liquid</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>30-40%</td>
<td>50%</td>
<td>15%</td>
</tr>
<tr>
<td>Cracking</td>
<td>16%</td>
<td>30%</td>
<td>54%</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>10%</td>
<td>82%</td>
<td>8%</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>0-10%</td>
<td>40-80%</td>
<td>10-50%</td>
</tr>
<tr>
<td>Supercritical</td>
<td>40%</td>
<td>30%</td>
<td>30%</td>
</tr>
</tbody>
</table>
## Conclusions

<table>
<thead>
<tr>
<th>Method</th>
<th>Liquid Fraction</th>
<th>C</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignin</td>
<td></td>
<td>64%</td>
<td>6%</td>
<td>28%</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td></td>
<td>55%</td>
<td>7.5%</td>
<td>37.5%</td>
</tr>
<tr>
<td>Cracking</td>
<td></td>
<td>85%</td>
<td>15%</td>
<td>0%</td>
</tr>
<tr>
<td>Hydrogenolysis</td>
<td>Highly varying with operating conditions and catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrolysis</td>
<td></td>
<td>73%</td>
<td>5%</td>
<td>21%</td>
</tr>
<tr>
<td>Supercritical</td>
<td>Less interesting due to low liquid production and high process complexity</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

Macro molecule

Mw > 20,000 u

Gases
CO2, H2O, CO, H2

Lignin Fragments

Mw 200 - 400 u

H2O

Polyaromatic Compounds
Conclusions

• The above valid for a specific end-product application
• Changing the end-product will most likely change the application
• Specifics to be determined from case to case
  – Severity accepted
  – Side-products to be avoided