Characterization of LignoBoost lignin to predict possible utilization

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OUTLINE

• The need for biofuels
• Lignin as a potential source, biosynthesis
• Kraft-cycle, LignoBoost, 2nd gen. bioethanol pretreatment.
• Results (so far): Purification, GPC, NMR
WHY BIOFUELS?

• Unpredictable nature of fossil fuel prices?
• Global warming, CO2 emissions…
• Energy Independence!

M. Meinshausen et al, *Nature*, 2009, **458**: 1158-1163
PHENYLPROPANOID PATHWAY

Laurence B. Davin et al, *Natural Product Reports*, 2008, **25**: 1015-1090
LIGNIN POLYMERIZATION

Laurence B. Davin et al, *Natural Product Reports*, 2008, **25**: 1015-1090
KRAFT CYCLE-LIGNOBOOST

ORGANOSOLV PROCESS

T. J. McDonough
TAPPI
Solvent Pulping Seminar
1992
SAMPLE PURIFICATION

Preliminary Research Results

LIGNIN

“weak” BL = F

LignoBoost

Filtrate (F)

Precipitate (P)

Filtration

Precip. vessel

CO₂

Resturry washing

Composition of given sample: C H O S NM

BL

P 9.5

F 9.5
GPC

<table>
<thead>
<tr>
<th>Samples analyzed by us</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>BL</td>
</tr>
<tr>
<td>P 10.5</td>
</tr>
<tr>
<td>F 10.5</td>
</tr>
<tr>
<td>P 9.5</td>
</tr>
<tr>
<td>F 9.5</td>
</tr>
<tr>
<td>P 10.5</td>
</tr>
<tr>
<td>P 9.5</td>
</tr>
</tbody>
</table>

- Moosavifar et al. no data on pH

<table>
<thead>
<tr>
<th>Wallmo et al. at pH 9.5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
</tr>
<tr>
<td>-----------------</td>
</tr>
<tr>
<td>BL</td>
</tr>
</tbody>
</table>

<sup>*</sup> using 264 g mol<sup>-1</sup> as the hypothetical average weight of acetylated monomers


$^{13}$C-NMR

Peak assignments:

1.
2. OH
3. H
4. OCH$_2$
5. N or C
6. 2
7. 1
8. 4
9. 9
10. 10

ppm
**$^1$H-NMR**

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Carboxylic acid ppm</th>
<th>Formyl ppm</th>
<th>Phenolic ppm</th>
<th>Aromatic, Vinyl ppm</th>
<th>Aliphatic ppm</th>
<th>Methoxyl ppm</th>
<th>Aliphatic ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL</td>
<td>13.50-10.50</td>
<td>10.10-9.35</td>
<td>9.35-8.00</td>
<td>8.00-6.00</td>
<td>6.00-4.05</td>
<td>4.05-3.45</td>
<td>2.25-0.00</td>
</tr>
<tr>
<td>P 10.5</td>
<td>1.3</td>
<td>1.5</td>
<td>6.7</td>
<td>20.2</td>
<td>8.4</td>
<td>45.8</td>
<td>14.4</td>
</tr>
<tr>
<td>F 10.5</td>
<td>0.8</td>
<td>1.0</td>
<td>3.7</td>
<td>19.7</td>
<td>8.2</td>
<td>49.2</td>
<td>16.0</td>
</tr>
<tr>
<td>F 9.5</td>
<td>1.2</td>
<td>1.7</td>
<td>5.7</td>
<td>19.6</td>
<td>6.8</td>
<td>44.6</td>
<td>16.9</td>
</tr>
<tr>
<td>P 9.5</td>
<td>1.1</td>
<td>0.9</td>
<td>4.2</td>
<td>18.7</td>
<td>5.9</td>
<td>52.4</td>
<td>16.7</td>
</tr>
<tr>
<td>F 9.5</td>
<td>1.7</td>
<td>1.6</td>
<td>6.2</td>
<td>19.8</td>
<td>7.9</td>
<td>41.2</td>
<td>17.4</td>
</tr>
</tbody>
</table>

F samples contain significantly higher amounts of –OH groups of all examined types causing possibly their better solubility.
### Derivatization of phenolic structures with 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP).

#### 31P-NMR

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Total –OH content (mmol g⁻¹)</th>
<th>Hydroxyl content of selected groups (mmol g⁻¹)</th>
<th>Carboxylic hydroxyl (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>149.0-133.8 ppm</td>
<td>149.0-145.6 ppm</td>
<td>136.0-133.8 ppm</td>
</tr>
<tr>
<td>BL</td>
<td>6.37</td>
<td>1.49</td>
<td>2.46</td>
</tr>
<tr>
<td>P 10.5</td>
<td>3.18</td>
<td>0.91</td>
<td>1.03</td>
</tr>
<tr>
<td>F 10.5</td>
<td>5.76</td>
<td>1.22</td>
<td>2.2</td>
</tr>
<tr>
<td>P 9.5</td>
<td>4.3</td>
<td>1.11</td>
<td>1.47</td>
</tr>
<tr>
<td>F 9.5</td>
<td>6.74</td>
<td>1.27</td>
<td>2.55</td>
</tr>
</tbody>
</table>

**Chemical Equations**

- **Derivatization**
  - **Equation 1**: 
    \[
    \text{Phenolic structure} + \text{2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP)} \rightarrow \text{Phenolic derivative} + \text{Cl}^- + \text{H}^+
    \]
- **Equation 2**: 
  - **Phenolic in G position**: 
    \[
    \text{Phenolic structure} + \text{2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP)} \rightarrow \text{Phenolic derivative} + \text{Cl}^- + \text{H}^+
    \]
- **Phenolic @ G position**: 
  - **Equation 3**: 
    \[
    \text{Phenolic structure} + \text{2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP)} \rightarrow \text{Phenolic derivative} + \text{Cl}^- + \text{H}^+
    \]
- **Aliphatic hydroxyl**: 
  - **Equation 4**: 
    \[
    \text{Phenolic structure} + \text{2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP)} \rightarrow \text{Phenolic derivative} + \text{Cl}^- + \text{H}^+
    \]
- **Carboxylic hydroxyl**: 
  - **Equation 5**: 
    \[
    \text{Phenolic structure} + \text{2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane (TMDP)} \rightarrow \text{Phenolic derivative} + \text{Cl}^- + \text{H}^+
    \]
PYROLYSIS

- O/C and H/C molar ratios of purified LignoBoost precipitate lignin and of its pyrolysis oil show promising results

<table>
<thead>
<tr>
<th>Pyrolysis [wt%]</th>
<th>Gasoline</th>
<th>P 9.5 (pur) lignin</th>
<th>P 9.5 (pur) pyrolysis oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>sample</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BL crude</td>
<td>oil</td>
<td>char</td>
<td>gas</td>
</tr>
<tr>
<td></td>
<td>33.16</td>
<td>64.14</td>
<td>2.71</td>
</tr>
<tr>
<td>P 9.5 crude</td>
<td>31.53</td>
<td>67.55</td>
<td>0.92</td>
</tr>
<tr>
<td>P 9.5 purified</td>
<td>42.98</td>
<td>42.25</td>
<td>14.78</td>
</tr>
<tr>
<td>O/C molar ratio</td>
<td>0</td>
<td>0.34</td>
<td>0.26</td>
</tr>
<tr>
<td>H/C molar ratio</td>
<td>1-2</td>
<td>1.12</td>
<td>1.34</td>
</tr>
</tbody>
</table>
FURTHER ANALYSIS

- Repeating GPC measurements with smaller Mw standards
- Analysis of sugars and possibly short chain fatty acids still present
- Analysis of LignoBoost final products when the process is in equilibrium with Kraft cycle

EXPERIMENTAL

- alkane
- EDTA
- ethers, alcohols
- conjugated and non conjugated acids and esters

References:

- Raimo Alen et al, Cellulose Chemistry and Technology, 1985, 19: 537-541
POSSIBLE UTILIZATION

• Pyrolysis showed promising results meaning that further analysis can be fruitful

• Complete analysis and comparison of the outcome of different lignin degrading enzymes and converting microorganisms are ongoing
Thanks for listening!

Questions?