DETERMINATION OF LIGNIN CONTENT FOR EXTRACTS OBTAINED BY PRESSURISED HOT WATER

Risto Korpinnen, Andrey Pranovich, Stefan Willför

COST meeting 2012, Espoo
Acknowledgements
Background

- Purity of hemicellulose-rich extracts is important for their further usage
- The major impurity in GGM/xylan is usually **lignin**
  - Can be **reactive** when extracts are produced into new products
  - Gives **undesired colour** and lignin-derived products may emit **odour**
- The accurate lignin content of the extracts must be known
Raw materials

- Industrial spruce and birch sawdusts
- PHW extracted at Metla
  - Flow-through technique
- Ultrafiltered at LUT
  - Regenerated cellulose membrane
  - 10 kDa cut-off
Mass balance on the ultrafiltration

<table>
<thead>
<tr>
<th></th>
<th>Amount extract, kg</th>
<th>Dry solids content, %</th>
<th>Amount dry solids, kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce feed</td>
<td>1570</td>
<td>1.02</td>
<td>16.01</td>
</tr>
<tr>
<td>Spruce concentrate</td>
<td>30</td>
<td>19.16</td>
<td>5.75</td>
</tr>
<tr>
<td>Spruce permeate</td>
<td>1540</td>
<td>0.69</td>
<td>10.63</td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td></td>
<td>-0.36</td>
</tr>
<tr>
<td>Birch feed</td>
<td>1570</td>
<td>1.57</td>
<td>24.65</td>
</tr>
<tr>
<td>Birch concentrate</td>
<td>30</td>
<td>25.00</td>
<td>7.50</td>
</tr>
<tr>
<td>Birch permeate</td>
<td>1540</td>
<td>1.05</td>
<td>16.17</td>
</tr>
<tr>
<td>Difference</td>
<td></td>
<td></td>
<td>0.98</td>
</tr>
</tbody>
</table>
Lignin determination methods

- Determination of chlorine consumption, “Chlorine number“
  - ISO 3260 or SCAN-C 29
- Acetyl bromide
- Acid-insoluble & acid-soluble lignin
  - KCL N:o 115b:82
  - TAPPI Test Method T 222 and TAPPI Useful Methods UM 250
  - National Renewable Energy Laboratory, Laboratory Analytical Procedure (LAP)
  - TAPPI and Goldschmid UV lignin
Chlorine number

- Acidification of sample by 4 M HCl
- NaClO addition → formation of Cl₂-gas
- Reaction 15 min at 25 °C
- Addition of 1 M KI
- Titration with 0.2 M Na₂S₂O₃ starch as indicator
- Result g Cl₂/100 g sample
- Lignin content, % = 0.9 * Chlorine number
Acetyl bromide

- Sample treatment with 25% w/w AcBr in glacial acetic acid + HClO$_4$ (catalyst)
- Heating at 70 °C during 30 min
- Reaction mixture poured into flask containing NaAc-buffer
- Volume adjusted with AcOH to 50 ml
- UV at 280 nm
- Calibration curve done with softwood and hardwood milled wood lignin
Sample treatment with 72% $\text{H}_2\text{SO}_4$ for 2 hours

Addition of water and wait for 4 hours

Addition of water and wait overnight

Refluxing for 4 hours

Filtering, washing and drying the solid lignin

Acid-soluble lignin by UV
TAPPI T 222 and UM 250 (and Goldschmid)

- Sample treatment with 72% H₂SO₄ for 2 hours
- Addition of water and boiling in open flask for 4 hours
- Filtering, washing and drying of solid lignin
- Acid-soluble lignin by UV
Laboratory analytical procedure (LAP)

- Sample treatment with 72% H$_2$SO$_4$ for 1 hour
- Addition of water and autoclavage at 121 °C for 1 hour
- Filtering, washing and drying of solid lignin
- Acid-soluble lignin by UV
## Wavelengths and extinction coefficients for Klason lignin

<table>
<thead>
<tr>
<th>Method</th>
<th>Wavelength</th>
<th>Absorbance</th>
<th>Extinction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCL</td>
<td>203 nm</td>
<td>0.2–0.7</td>
<td>128 L/gcm for SW</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>110 L/gcm for HW</td>
</tr>
<tr>
<td>LAP</td>
<td>240 nm</td>
<td>0.7–1.0</td>
<td>12 L/gcm for SW</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25 L/gcm for HW</td>
</tr>
<tr>
<td>Tappi</td>
<td>205 nm</td>
<td>0.2–0.7</td>
<td>110 L/gcm for SW and HW</td>
</tr>
<tr>
<td>Golschmid*</td>
<td>215 and 280 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ c_L = \frac{4.53 \cdot A_{215 \text{ nm}} - A_{280 \text{ nm}}}{300} \]
Lignin content in spruce raw extract and filtrates
Lignin content in **birch** raw extract and filtrates
Furfural and HMF content in Klason lignin hydrolysates (spruce)
Furfural and HMF content in Klason lignin hydrolysates (birch)
Chlorine number and AcBr

- **Cl number**
  - Chlorine gas can react with altered carbohydrates, lipophilic extractives and low molar mass phenolics

- **AcBr**
  - Isolated MWL used for calibration
    - Less oxidised and degraded compared to lignin release from wood at high temperature
  - Pentose degradation products formed during the analysis
Lignin mass balance of spruce extract filtration

Difference = Feed - (Concentrate + Permeate)
Lignin mass balance of birch extract filtration

\[
\text{Difference} = \text{Feed} - (\text{Concentrate} + \text{Permeate})
\]
Spruce concentrate

Chemical composition (% on TDS)

Lignin
Acetyl
Hemi-cellulose
Birch concentrate

Chemical composition (% on TDS)

- Lignin
- Acetyl
- Hemi-cellulose

CI number  AcBr  KCL  TAPPI  LAP  Goldschmid
Summary

- Klason lignin (solid) for extracts obtained at relatively mild conditions up to 170 °C was the most accurate and repeatable
  - Most of variation due to acid-soluble lignin
- In case of spruce extracts all methods tested can be used for monitoring lignin balance during ultrafiltration
THANK YOU!