Soluble lignin and its relation to Klason lignin, acid-detergent lignin and digestibility of NDF

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The Detergent Analysis System
Sequential Analysis - Option 1.
Van Soest, 2015
Lignin Assays (Quantitative)
Lupoi, et.al., 2015

- Wet chemistry
  - Acetyl Bromide
  - Acid-Insoluble
- Klason
- Permanganate oxidation
- TAPPI
- Van Soest
- Thermo-chemical
  - pyGC/FID
  - pyMBMS
  - TGA
- Spectroscopy
  - Fluorescence
  - FTIR
  - FT-Raman
  - NIR
  - NIR
  - Photoacoustic
  - UV-Raman
  - UV-vis
  - Visible (image analysis)

\[ \Delta L = KL - ADL \]

- Where:
  - \( \Delta L \) = Acid Detergent Soluble Lignin, %DM
  - KL = Klason Lignin, %DM
  - ADL = Acid Detergent Lignin, %DM

Lignin

- One example of a possible lignin structure.
  - 28 monomers (mostly coniferyl alcohol)
  - \( C_{196}H_{286}O_{63} \)

Fig. 1. Three fundamental lignin monomers (and their respective phenylpropanoids): sinapyl alcohol (syringyl (S)), coniferyl alcohol (guaiacyl (G)), and p-coumaryl alcohol (p-hydroxyphenyl (H)).
Lupoi, et.al., 2015

https://en.wikipedia.org/wiki/Lignin
The Data

- Cornell
  - 39 Forages
    - 7 C₃ grasses
    - 17 C₄ grasses
    - 13 maize plants
    - 4 corn silages
    - 15 Legumes
    - 15 alfalfa hays

- Jung
  - 36 Forages
    - 16 C₃ grasses
    - 8 C₄ grasses
    - 12 Legumes
    - 6 alfalfas
    - 6 other legume species

Results

Table 2: Mean values of Klason, acid detergent lignin, ∆L/KL, and their ranges.

<table>
<thead>
<tr>
<th>Component</th>
<th>N</th>
<th>KL</th>
<th>ADL</th>
<th>∆L/KL (%)</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cornell Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grasses</td>
<td>7</td>
<td>13.8</td>
<td>6.4</td>
<td>55</td>
<td>42 – 73</td>
</tr>
<tr>
<td>Maize Plants</td>
<td>13</td>
<td>6.4</td>
<td>2.8</td>
<td>56</td>
<td>47 – 70</td>
</tr>
<tr>
<td>Maize Silage</td>
<td>4</td>
<td>7.7</td>
<td>3.2</td>
<td>59</td>
<td>53 – 65</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>15</td>
<td>11.3</td>
<td>6.6</td>
<td>41</td>
<td>25 – 52</td>
</tr>
<tr>
<td>Jung et al. (1997)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃ Grasses</td>
<td>16</td>
<td>9.9</td>
<td>3.3</td>
<td>67</td>
<td>49 – 83</td>
</tr>
<tr>
<td>C₄ Grasses</td>
<td>8</td>
<td>8.5</td>
<td>3.4</td>
<td>59</td>
<td>46 – 70</td>
</tr>
<tr>
<td>Alfalfas</td>
<td>6</td>
<td>12.0</td>
<td>8.4</td>
<td>30</td>
<td>22 – 36</td>
</tr>
<tr>
<td>Other Legumes</td>
<td>6</td>
<td>12.2</td>
<td>7.1</td>
<td>43</td>
<td>28 – 54</td>
</tr>
</tbody>
</table>

KL = Klason lignin
ADL = Acid detergent lignin
∆L/KL = Acid detergent soluble lignin divided by Klason lignin (%)
Results

Figure 5: Relationships of KL and ∆L with ADL for C3 forages from Van Soest and Robertson and Jung et al. (1997) – Two perspectives.

Distribution of ADL and ∆L in KL

Cornell

Jung

Linear (Cornell)

Linear (Jung)

Figure 2: Relation of acid-detergent soluble lignin as a percent of Klason lignin with acid-detergent lignin as a percent of dry matter. Combined data for forage grasses from Robertson (Cornell) and Jung et al. 1997.

Figure 3: Relation of acid-detergent soluble lignin as a percent of Klason lignin with acid-detergent lignin as a percent of dry matter for C4 mature plants. Combined data from Robertson (Cornell) and Jung et al 1997 ±5.

Table 3: Correlation between acid-detergent soluble lignin expressed as percentage of Klason lignin (∆L/KL) with acid-detergent lignin (ADL) on a dry matter basis and with in-vitro digestibility of neutral detergent fiber (NDFD48).

<table>
<thead>
<tr>
<th>Forage Class</th>
<th>N</th>
<th>∆L/KL * ADL</th>
<th>∆L/KL * NDFD48</th>
<th>ADL * NDFD48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cornell</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grasses</td>
<td>7</td>
<td>-0.85 *</td>
<td>+0.76 *</td>
<td>-0.95 **</td>
</tr>
<tr>
<td>Maize Plants</td>
<td>17</td>
<td>-0.64 **</td>
<td>+0.44</td>
<td>-0.78 **</td>
</tr>
<tr>
<td>Alfafas</td>
<td>15</td>
<td>+0.07</td>
<td>+0.12</td>
<td>-0.55 *</td>
</tr>
<tr>
<td>Jung</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3 Grasses</td>
<td>16</td>
<td>-0.90 **</td>
<td>+0.83 ***</td>
<td>-0.79 **</td>
</tr>
<tr>
<td>C4 Grasses</td>
<td>8</td>
<td>-0.41</td>
<td>+0.73 *</td>
<td>-0.59</td>
</tr>
<tr>
<td>Legumes</td>
<td>12</td>
<td>-0.81 **</td>
<td>+0.58 *</td>
<td>-0.69 *</td>
</tr>
<tr>
<td>All Legumes Combined</td>
<td>27</td>
<td>-0.48 *</td>
<td>+0.34</td>
<td>-0.53 **</td>
</tr>
</tbody>
</table>
Results

Figure 4: Relation between the in vitro digestibility of NDF (NDFD48) with acid-detergent soluble lignin as a percent of Klason lignin (ΔL/KL). Combined data for forage grasses (n=23).

Conclusions

• Klason Lignin is a heterogeneous mix
  • KL = ΔL + ADL
• ΔL is soluble in the rumen but is unfermentable
• ΔL dilutes energy of solubles
• ΔL has no effect on NDFD
• ADL (insoluble) is the main factor limiting NDFD

Proposed Collaborative Fiber Study?

• Standard reference forages
  • 12 each of:
    • Corn Silage
    • Alfalfa
    • Grass
• Multiple Sites
  • USDFRC
  • Miner
  • Cornell
  • Texas A&M
• Analyses
  • NDFom
  • ADFom
  • ADL
  • Klason
  • Acetyl Bromide Lignin
  • uNDF48
  • uNDF240
• Spectral Scans of all samples & filtrates
  • UV
  • NIR
  • MIR?
“The objectives of statistical efficiency and mechanistic understanding are sometimes incompatible.”

Then again, sometimes not.

Shameless Plug
Available NOW from Cornell CALS
Contact Heather Darrow for details

Thank You
"Hey, wait a minute! This is great! We've been eating grass!"