Characterizing Lignocellulosics from Miscanthus Cellulose - Lignin

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Agro-energy feedstock: Miscanthus

- **Perennial crop**
  - Grows to 11-14 ft in height/year

- **High biomass yields**
  - C4 grass with high rate of carbon fixation
  - 14 – 17 tons/acre (up to 27 tons/acre in trials)
  - Crop stands survive 25-30 years without significant loss in biomass yields

- Presently used in Europe for power and heat generation
Moisture and Ash content

- Moisture content of air dried miscanthus sawdust (6 mm)
  - 4.6%

- Ash content
  - Measured by ramped heating to 525 °C in a muffle furnace
  - 2.2%
  - Higher than Loblolly pine (0.2 %) & sweetgum (0.8 %)
Elemental analysis

Measured on 0.05 mm ground samples using elemental micro analyzer

Biomass to Bioethanol
Inorganic elements

- Analyzed in 6 mm ground samples
- Acid digestion followed by ICP-emission spectroscopy
- Coulometric method for total halogen (Cl+Br+I)
Inorganic elements

Biomass to Bioethanol
Inorganic elements

Biomass to Bioethanol
Acid soluble and insoluble lignin

- Klason lignin
  - Acid insoluble lignin isolated using NREL methods
  - Extractive free (40 mesh) sample hydrolyzed using 72 % $\text{H}_2\text{SO}_4$

- Acid soluble lignin
  - Measured using UV-vis spectrophotometer
  - Calculated from absorption at 205 nm
Lignin content and composition

Klason lignin
- Miscanthus: 25%
- Loblolly pine: 29%
- Sweetgum: 26%

Acid soluble lignin
- Miscanthus: 1.1%
- Loblolly pine: 0.5%
- Sweetgum: 2.6%

Guaiacyl
- SW: x
- HW: x
- Grass: x

Syringyl
- SW: x
- HW: x
- Grass: x

p-Coumaryl
- SW: x
- HW: x
- Grass: x
Carbohydrate analysis

- 40 mesh extractive free wood
- Hydrolyzed with 72% H$_2$SO$_4$
- Diluted to 3% H$_2$SO$_4$ and autoclaved at 121°C for 1 hour
- Sugars measured using HPLC with pulsed amperometric detector
Carbohydrate profile

% dry weight of starting material

- Arabinose
- Galactose
- Glucose
- Xylose
- Mannose

Miscanthus
Sweetgum
L.Pine

Biomass to Bioethanol
Solid-state $^{13}$C NMR of miscanthus

- Lignin C=O
- Lignin Phenolic
- Cellulose
- Lignin -OCH$_3$
- Hemicellulose R-COCH$_3$
Cellulose extraction

- **Holocellulose = Cellulose + Hemicellulose**
  - Obtained by treating extractive free wood repeatedly with acetic acid and sodium chlorite
  - Yield: 74% (by dry wt. of miscanthus)

- **Cellulose**
  - Boil holocellulose with 2.5 M HCl at 100 °C for 4 hours
  - Yield: 55% (by dry wt. of holocellulose)
Cellulose structure and crystallinity

- Solid-state $^{13}$C CP/MAS NMR of cellulose
- Cellulose structure and crystallinity

![Cellulose structure diagram](image)

Biomass to Bioethanol
Cellulose structure and crystallinity

- Degree of crystallinity: 48.9%
- Loblolly pine: 63%; Sweetgum: 53.3%
Milled wood lignin

- Purest form of lignin that can be isolated
- Wood extracted with ethanol and ethanol/benzene
- Milled for 130 hours
- Extracted with 96% Dioxane for 48 hours
- Dioxane collected, dried and lignin purified
Milled wood lignin – $^{13}$C NMR

Guaiacyl (g)  
Syringyl (s)  
p-Coumaryl (h)

COOR

h-4  
s and g  
4-O-5  
α-CO/ β-O-4  
β-5

Biomass to Bioethanol
Lignin molecular weight

- Lignin acetylated and dissolved in THF
- Molecular weight distribution measured using gel permeation chromatography

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<th>Mn</th>
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<td>Miscanthus</td>
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<td>Sweetgum</td>
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<td>L. Pine</td>
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Thank You!