

Characterizing Lignocellulosics from Miscanthus Cellulose - Lignin

Poulomi Sannigrahi

A.J. Ragauskas

School of Chemistry and Biochemistry
Georgia Institute of Technology



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

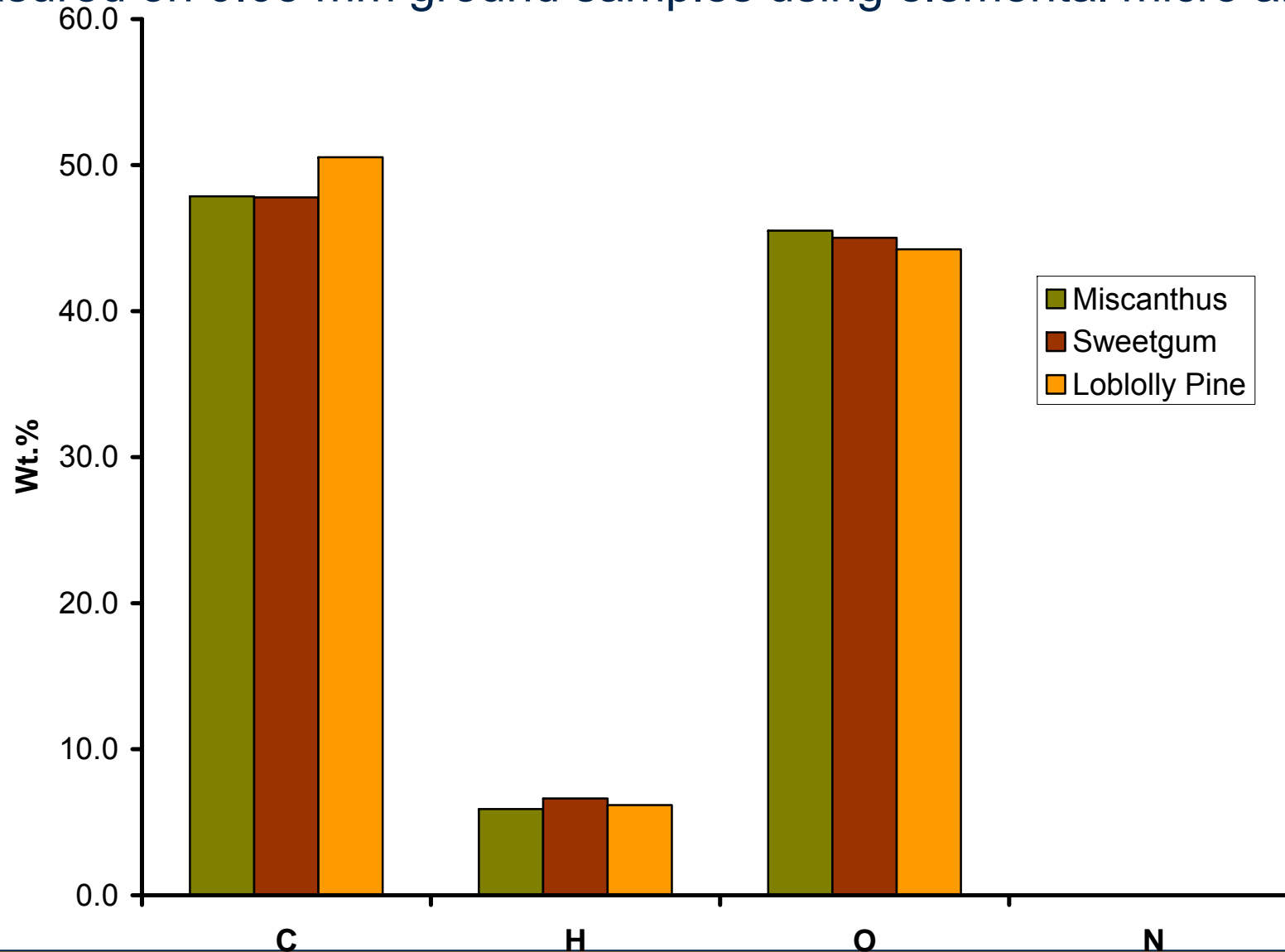
✧ 2.2%

✧ Higher than Loblolly pine (0.2 %) & sweetgum (0.8 %)



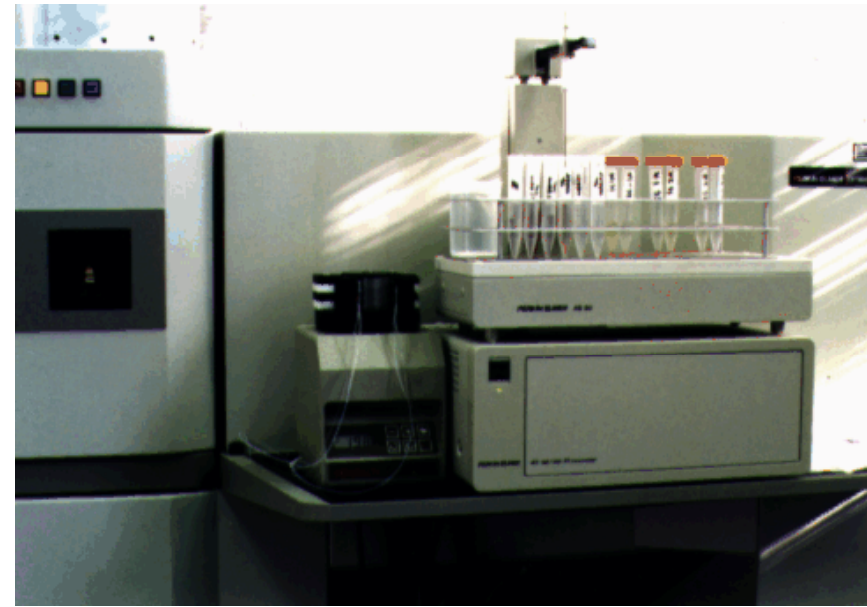
Elemental analysis

Measured on 0.05 mm ground samples using elemental micro analyzer

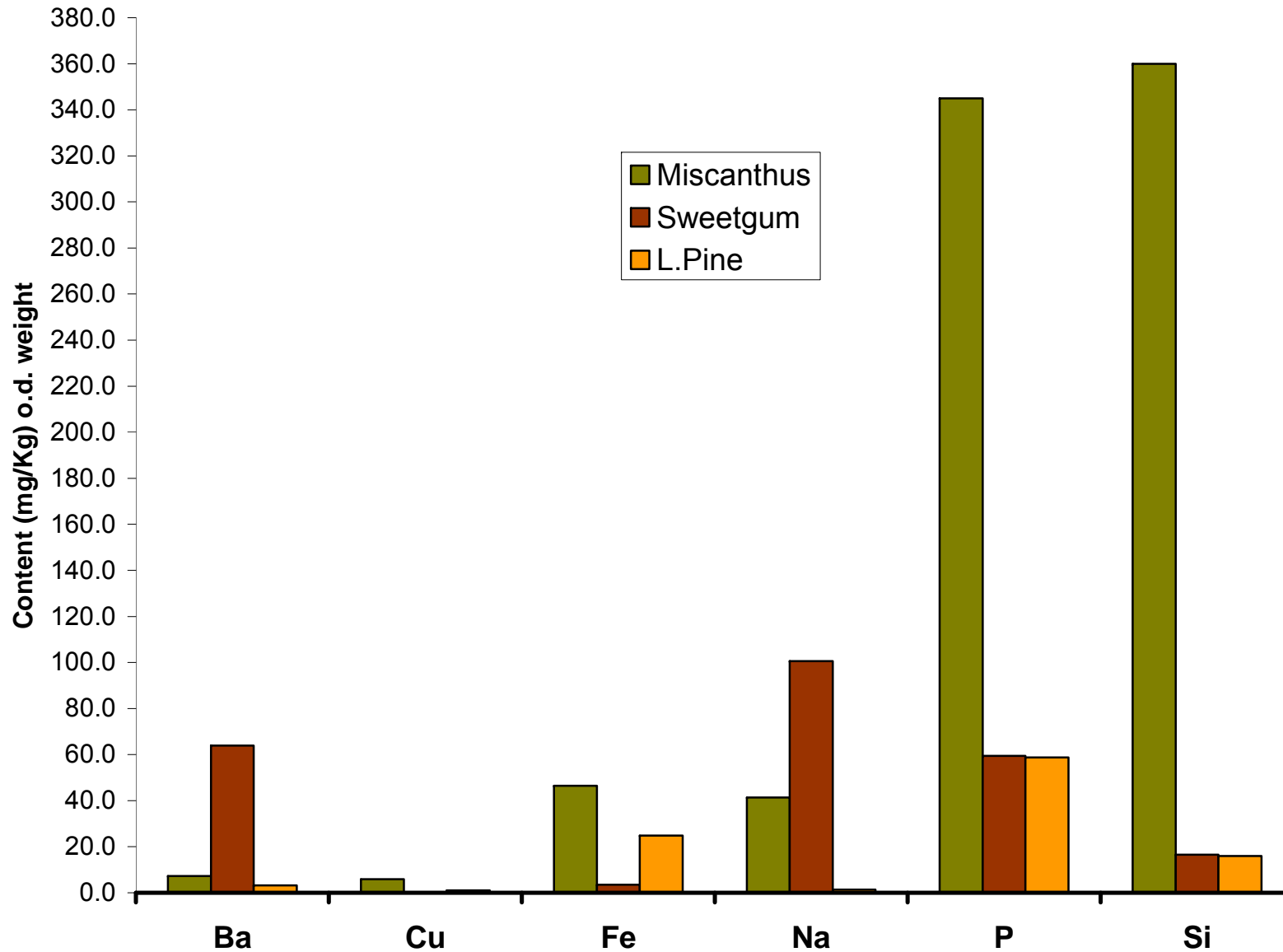


Inorganic elements

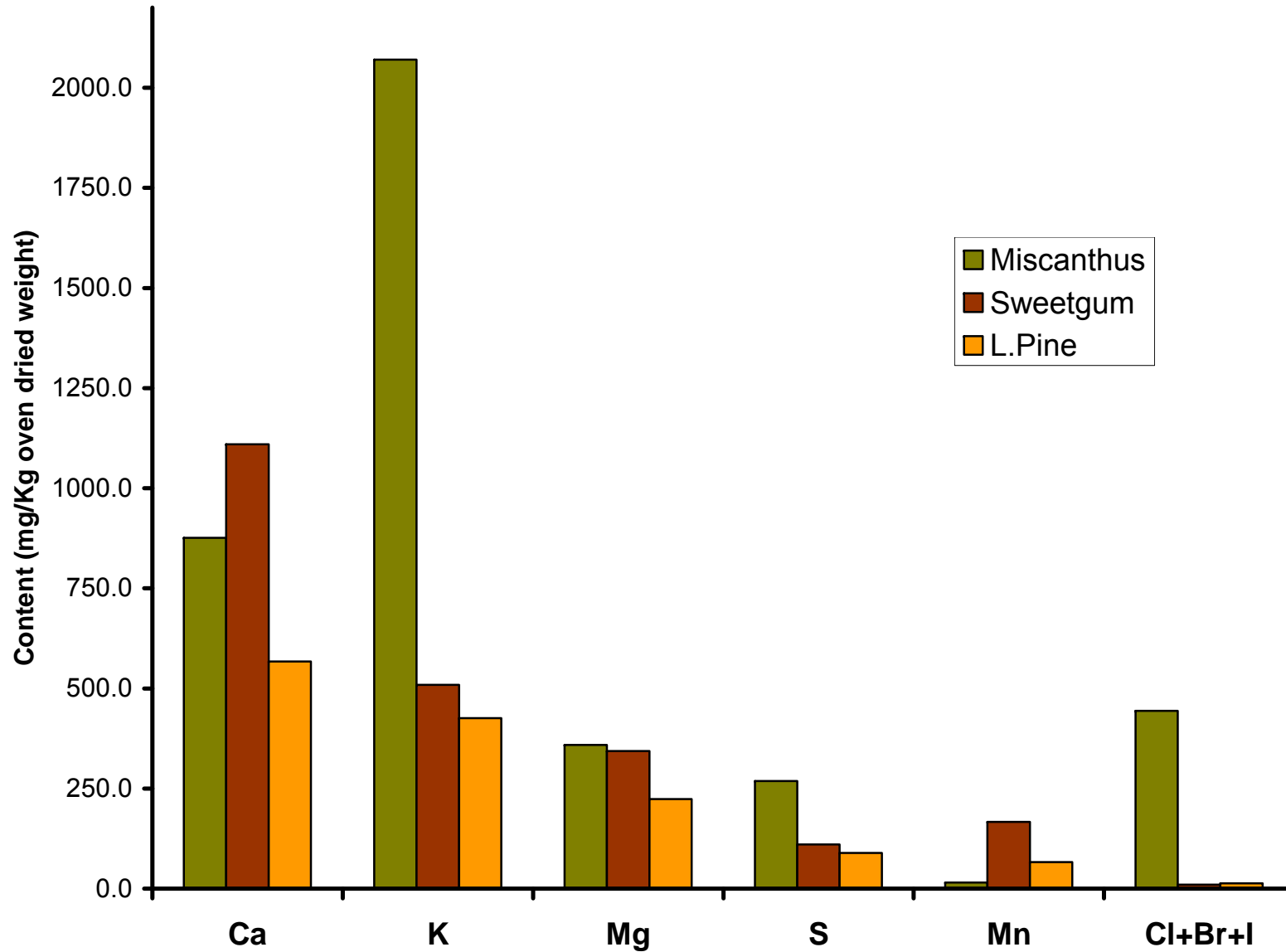
- ⌘ Analyzed in 6 mm ground samples
- ⌘ Acid digestion followed by ICP-emission spectroscopy
- ⌘ Coulometric method for total halogen (Cl+Br+I)



Inorganic elements



Inorganic elements



Acid soluble and insoluble lignin

⌘ Klason lignin

- ✦ Acid insoluble lignin isolated using NREL methods
- ✦ Extractive free (40 mesh) sample hydrolyzed using 72 % H_2SO_4

⌘ Acid soluble lignin

- ✦ Measured using UV-vis spectrophotometer
- ✦ Calculated from absorption at 205 nm



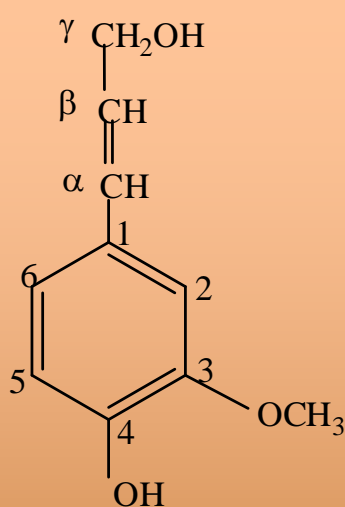
Lignin content and composition

Klason lignin

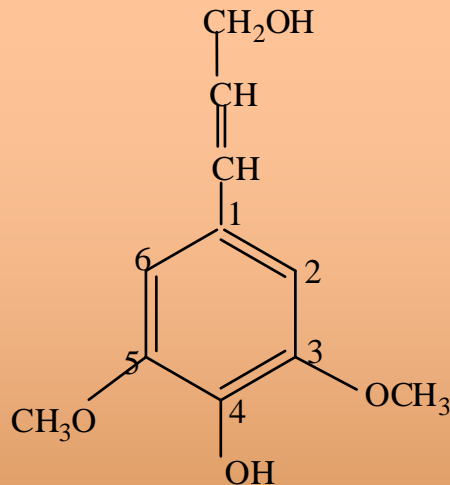
Miscanthus: 25 %
Loblolly pine: 29 %
Sweetgum: 26 %

Acid soluble lignin

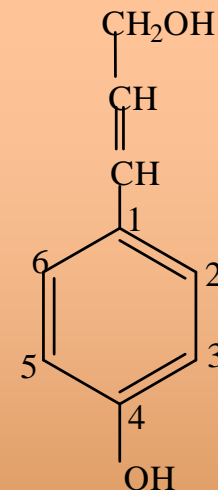
Miscanthus: 1.1 %
Loblolly pine: 0.5 %
Sweetgum: 2.6 %



Guaiacyl



Syringyl



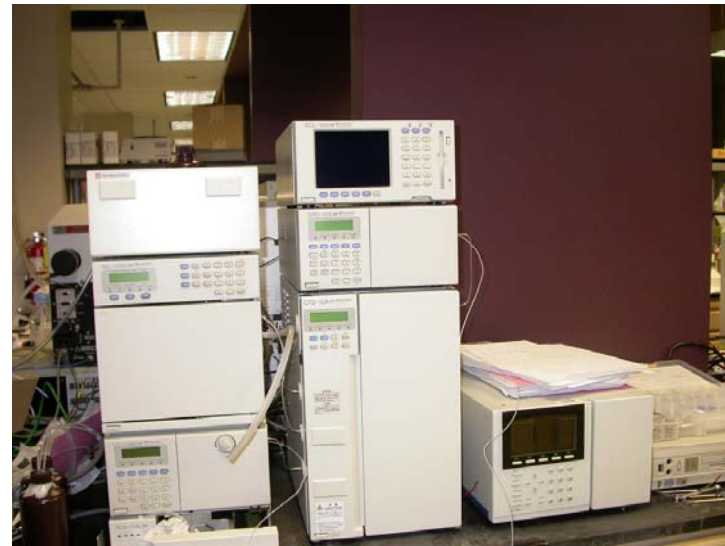
p-Coumaryl

SW	x		x
HW	x	x	x
Grass	x	x	x

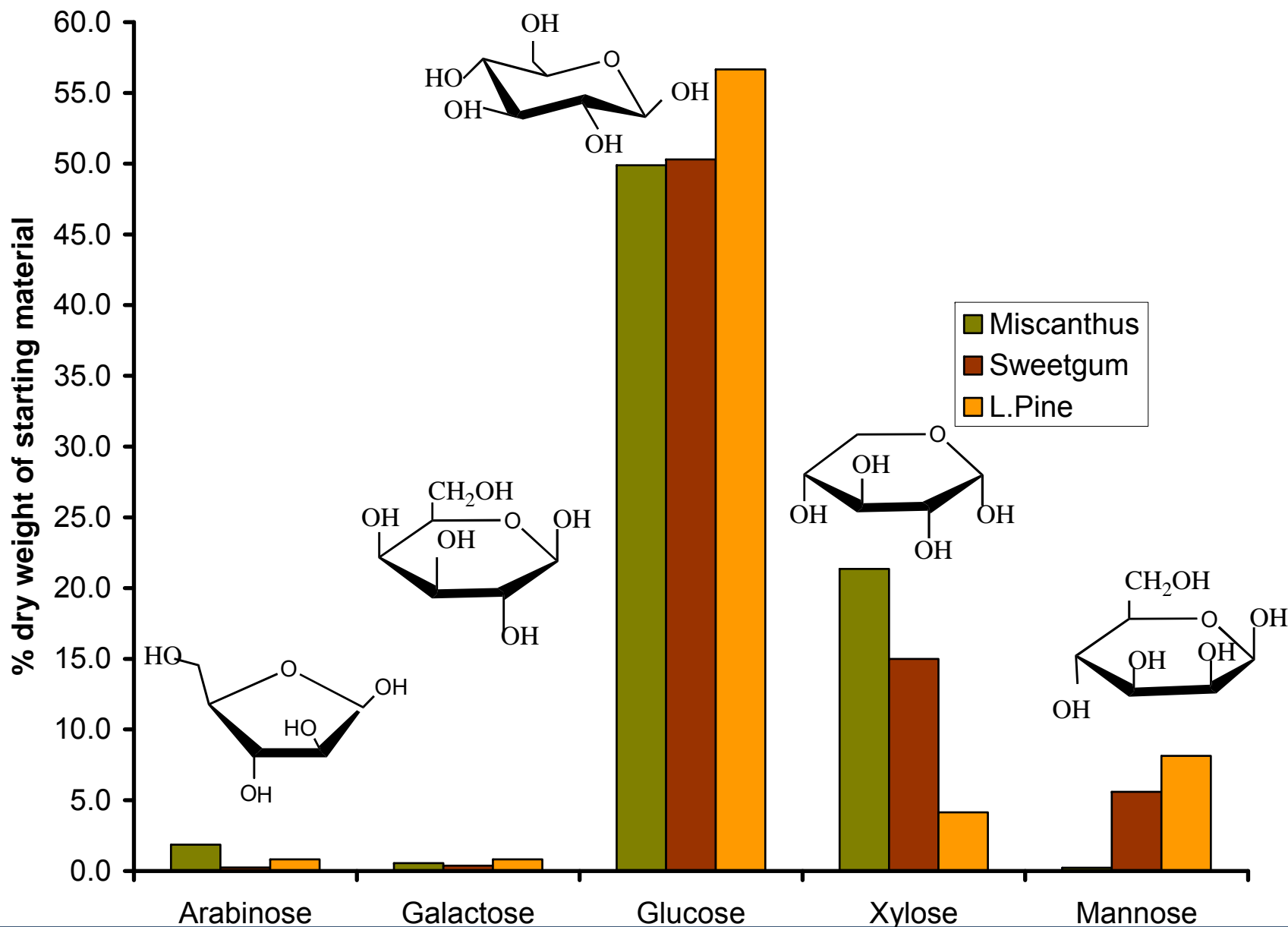


Carbohydrate analysis

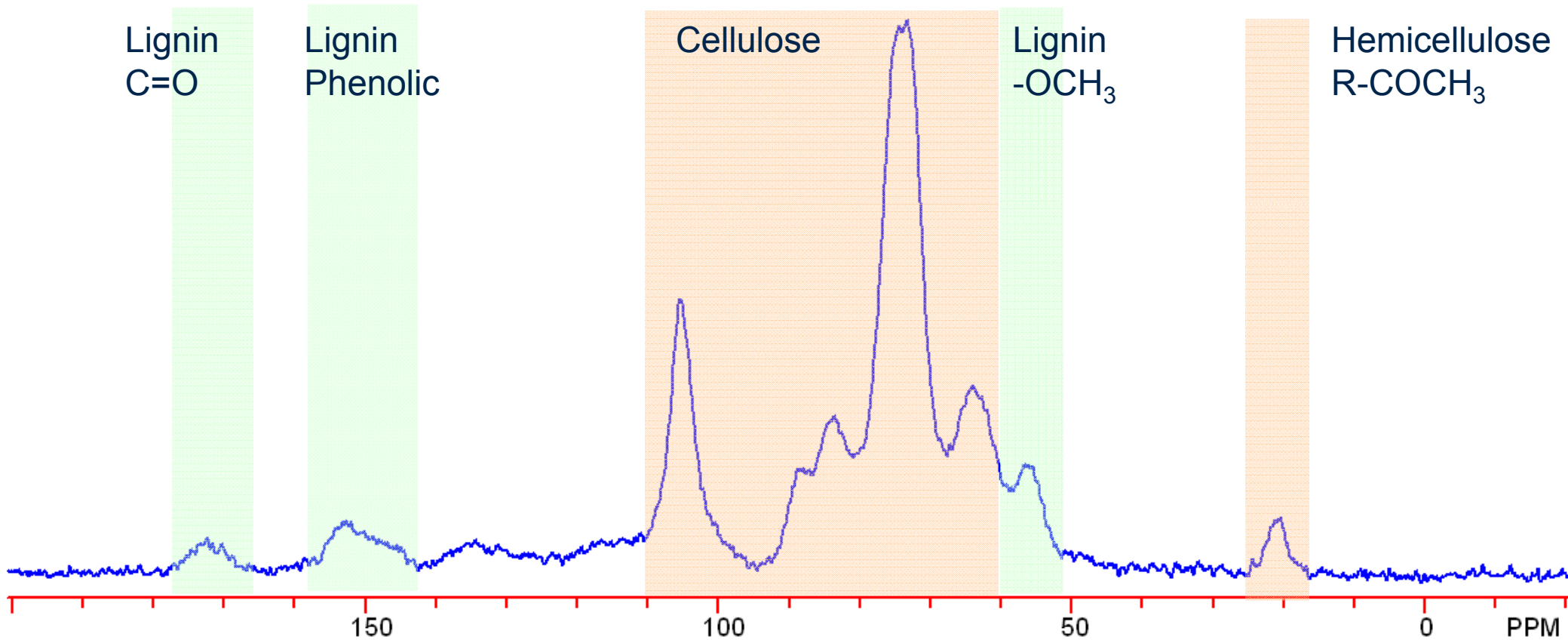
- ⌘ 40 mesh extractive free wood
- ⌘ Hydrolyzed with 72 % H_2SO_4
- ⌘ Diluted to 3% H_2SO_4 and autoclaved at 121°C for 1 hour
- ⌘ Sugars measured using HPLC with pulsed amperometric detector



Carbohydrate profile



Solid-state ^{13}C NMR of miscanthus



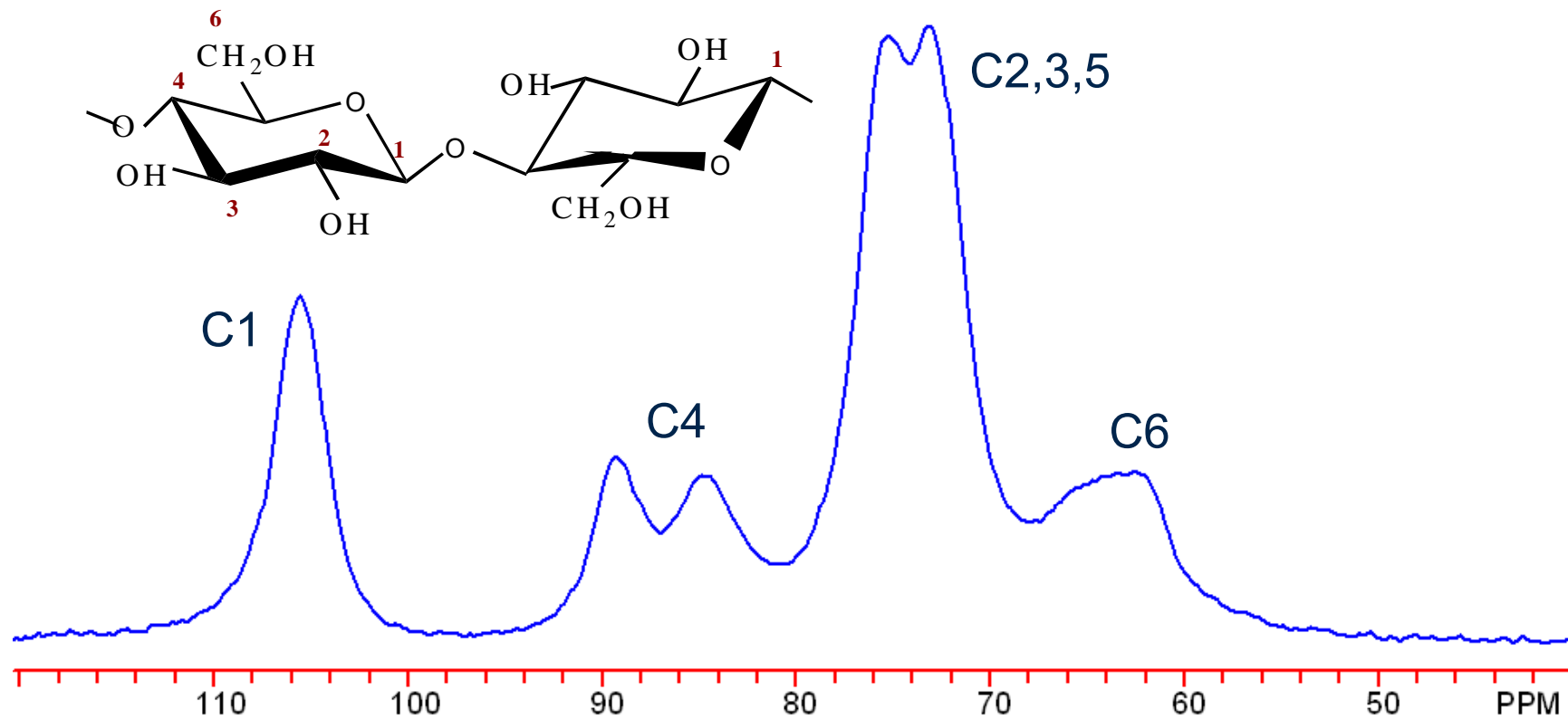
Cellulose extraction

- ⌘ 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)



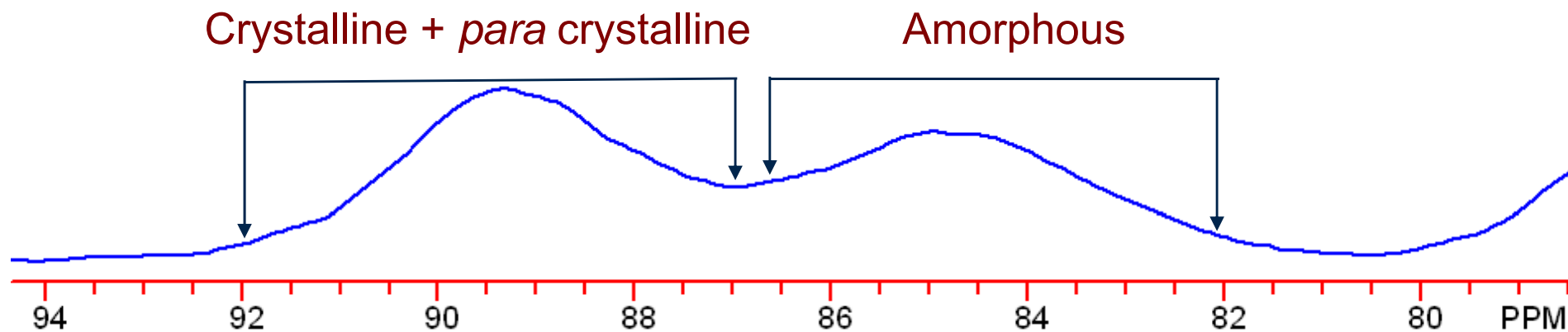
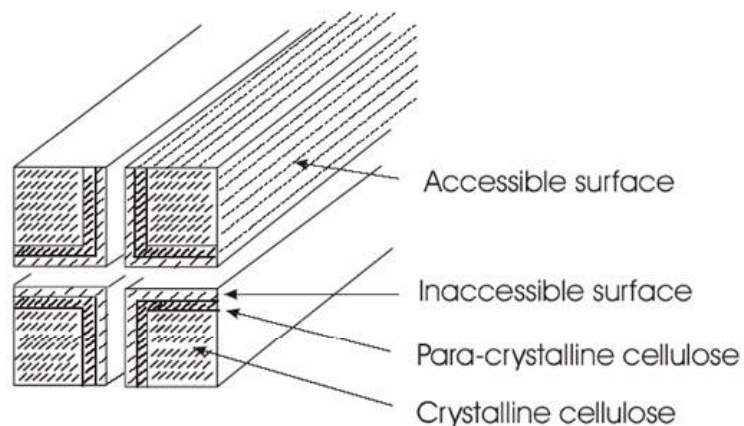
Cellulose structure and crystallinity

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



Cellulose structure and crystallinity

- ✧ Degree of crystallinity : 48.9 %
- ✧ Loblolly pine: 63 %; Sweetgum: 53.3%

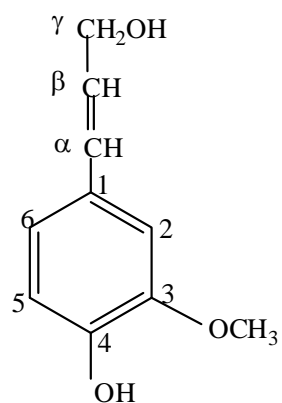


Milled wood lignin

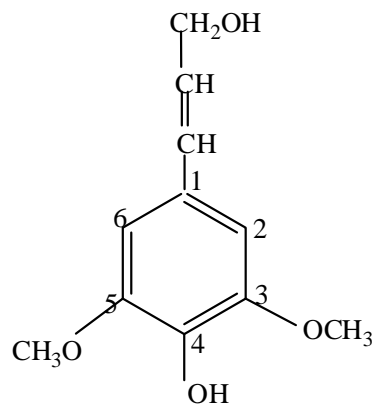
- ⌘ Purest form of lignin that can be isolated
- ⌘ Wood extracted with ethanol and ethanol/benzene
- ⌘ Milled for 130 hours
- ⌘ Extracted with 96% Dioxane for 48 hours
- ⌘ Dioxane collected, dried and lignin purified



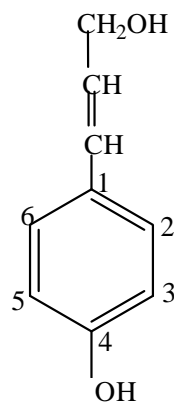
Milled wood lignin – ^{13}C NMR



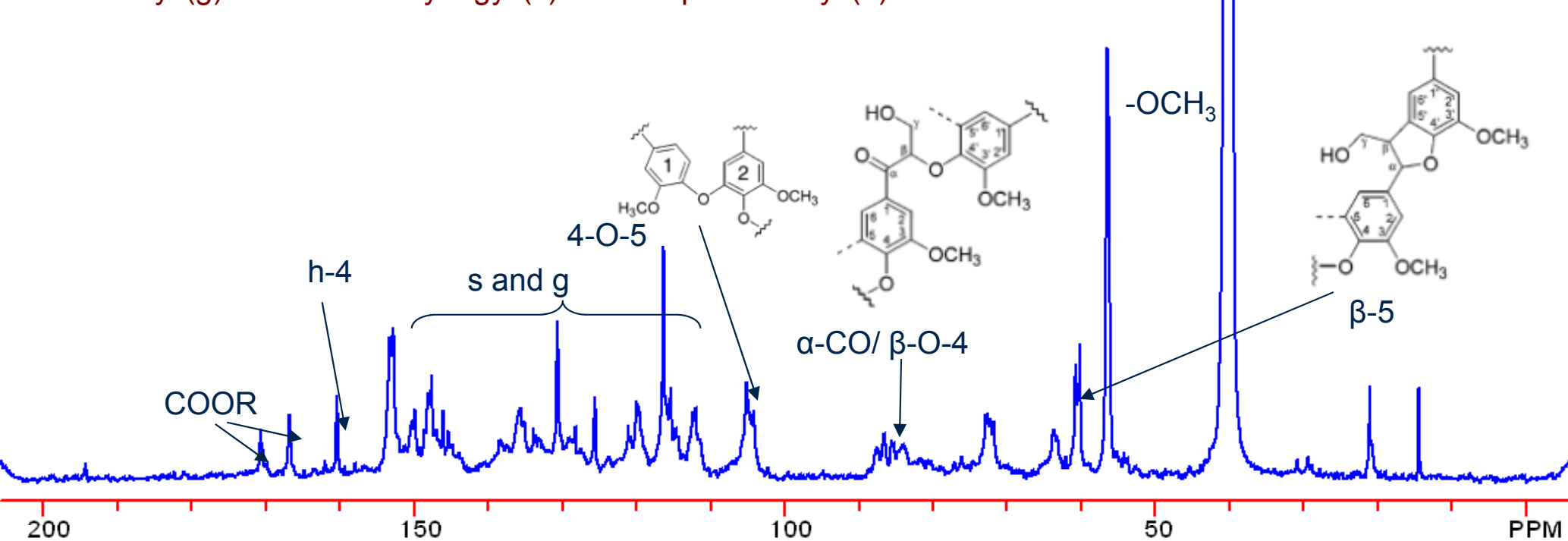
Guaiacyl (g)



Syringyl (s)



p-Coumaryl (h)



Lignin molecular weight

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

	Mn	Mw	D
Miscanthus	8.33e ³	1.38e ⁴	1.65
Sweetgum	9.41e ³	1.6e ⁴	1.70
L.Pine	7.58e ³	1.34e ⁴	1.77





Thank You!