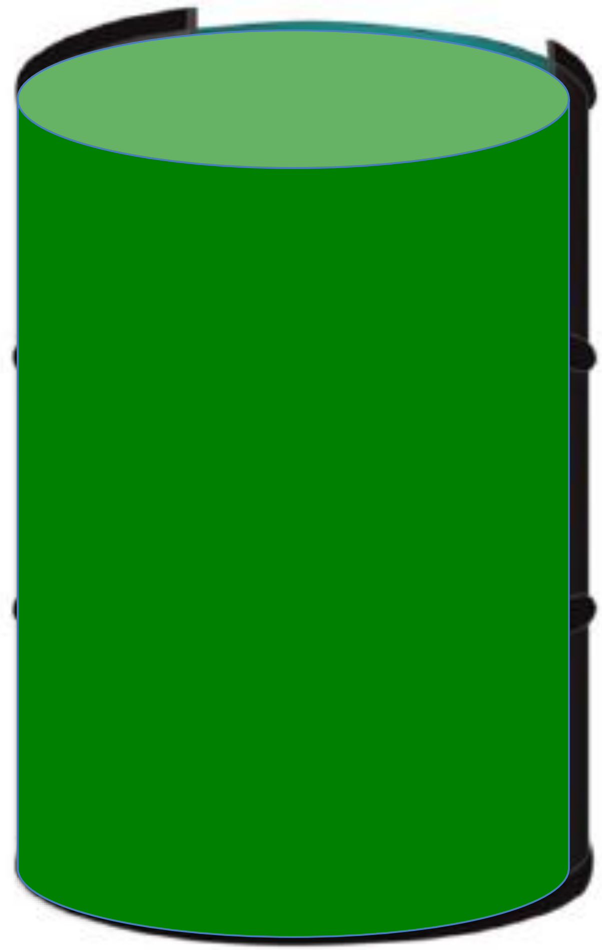
Plant Cell Wall Structure and Polymers

Lecture 6
Biofuels and Bioproducts

Bronx Community College - 2017
Chemistry and BioEnergy Technology for Sustainability NSF ATE 1601636

What is meant by the term Biomass?



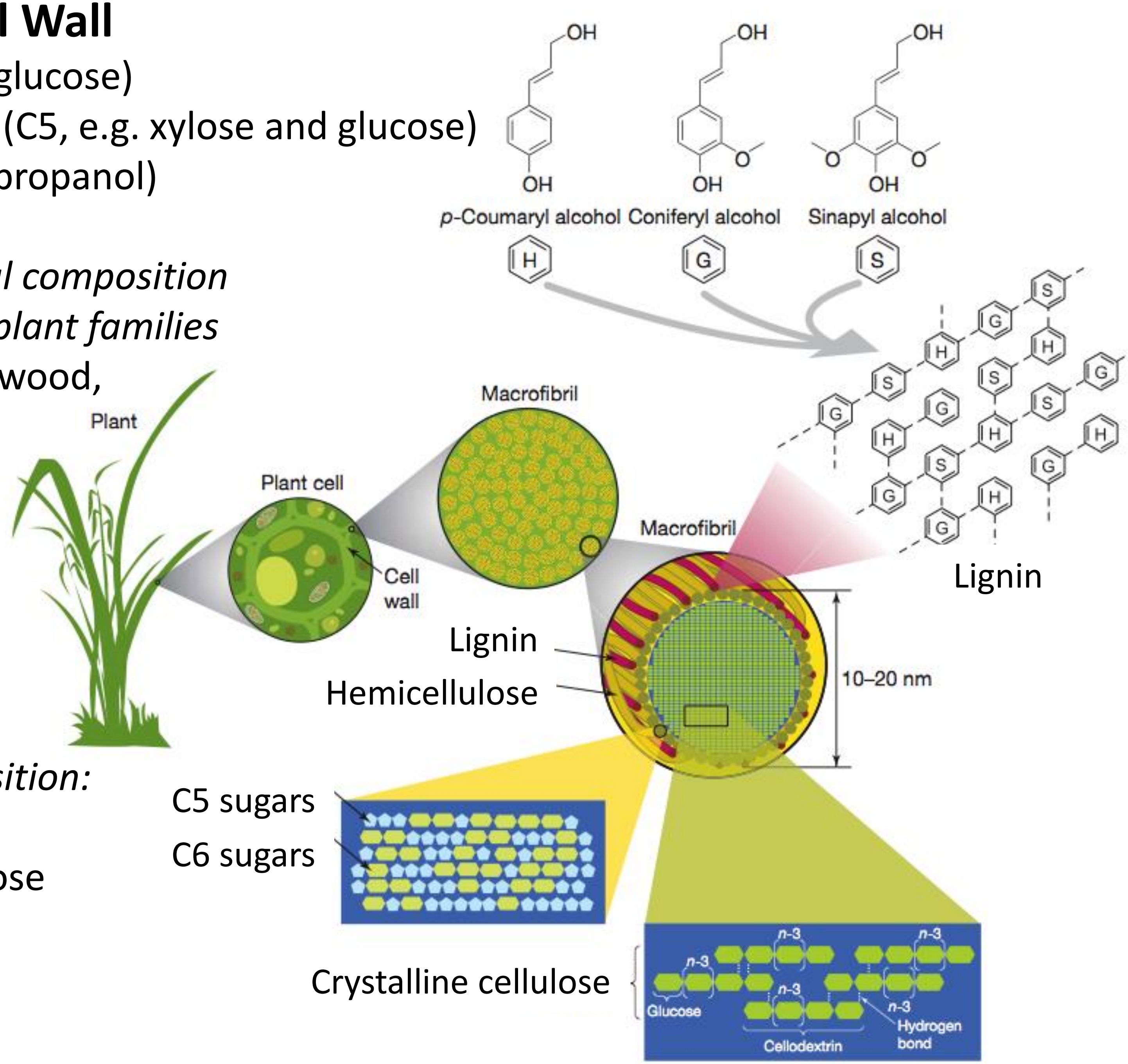
- Carbohydrates (a.k.a. polysaccharides, sugars)
- Lignin
- Lipids
- Proteins/amino acids
- Nucleic acids
- Chitin

What is meant by the term "fiber"?

The Plant Cell Wall

- Cellulose (C6, glucose)
- Hemicellulose (C5, e.g. xylose and glucose)
- Lignin (phenylpropanol)

Specific chemical composition varies between plant families (hardwood, softwood, grasses)



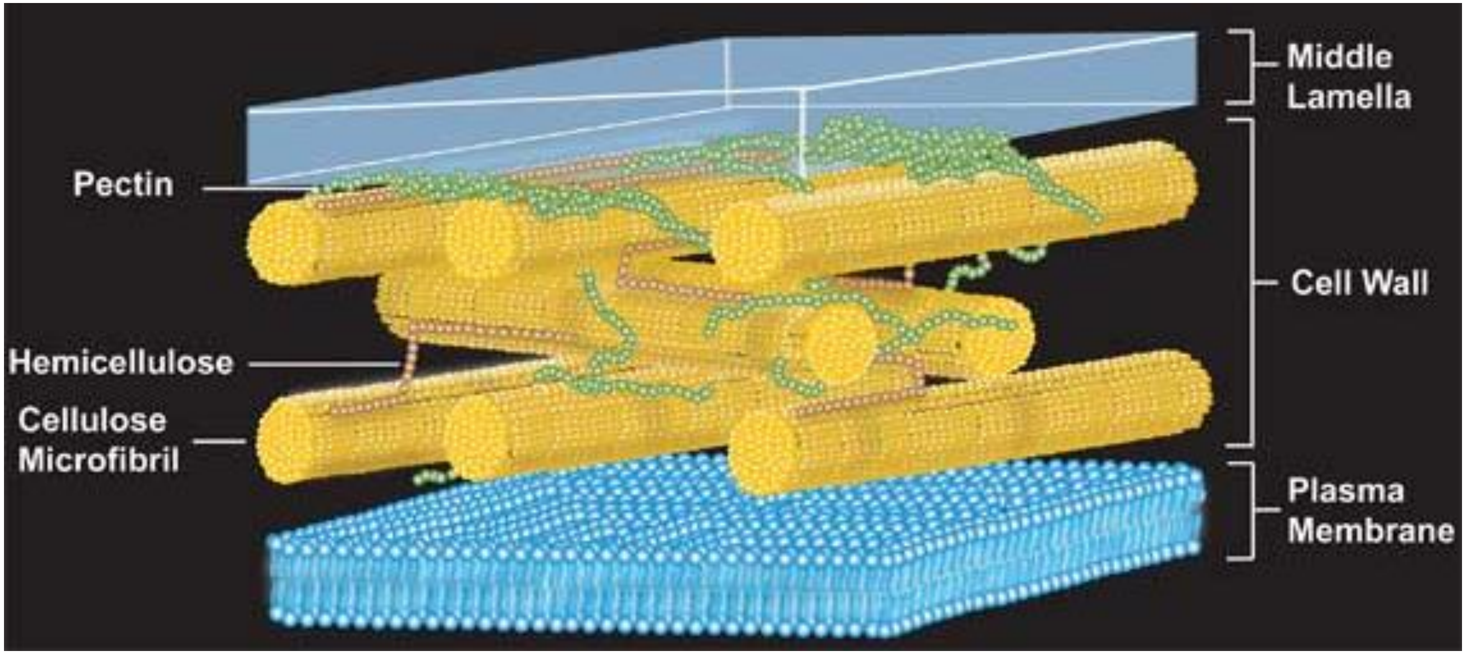
General Composition:
45% Cellulose
25% Hemicellulose
25% Lignin
5% Protein

Image: Rubin EM. *Nature* **2008** (454) 841

Polysaccharides in the Primary Plant Cell Wall

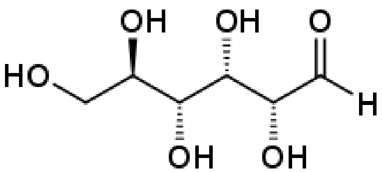
- Associated with ***growing and dividing*** cells (e.g. ripening of fruits)
- Primarily comprised of:
  - *Cellulose* (1,4-linked β-D glucose, a hexose)
  - *Hemicellulose* (1,4-linked β-D hexosyl residues)
    - Primary cell wall hemicellulose is xyloglucan
  - *Pectin* (1,4-linked α-D galactouronic acid)

The organization of the cell wall is often debated and several models exist to allow for cell to expand and grow, while still providing mechanical strength

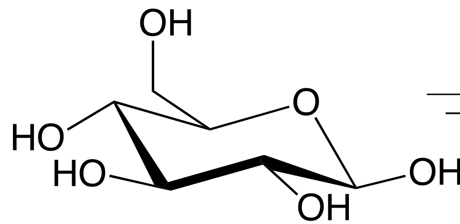


https://www.ccrc.uga.edu/~mao/cellwall/main.htm

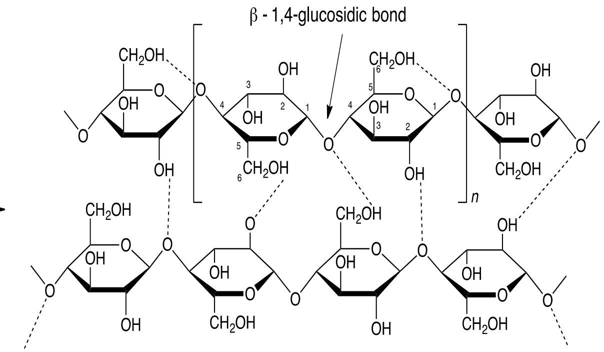
Glucose, Xylose
Glucan, Xylan
Cellulose, Hemicellulose



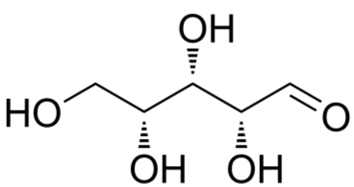
D-Glucose



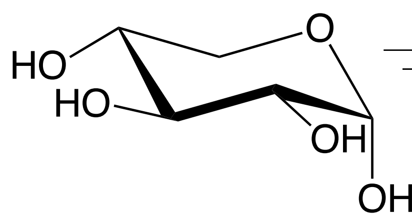
β-D-Glucose



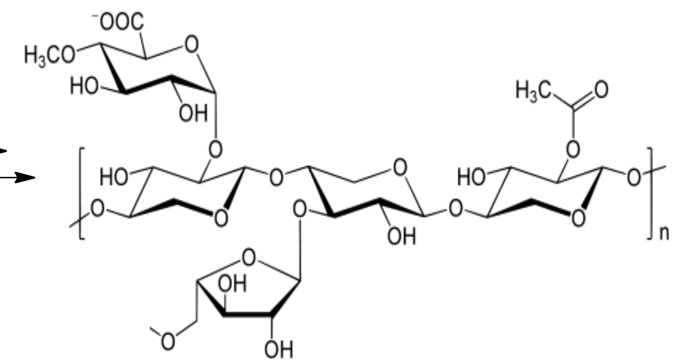
Cellulose (β-glucan)



D-Xylose



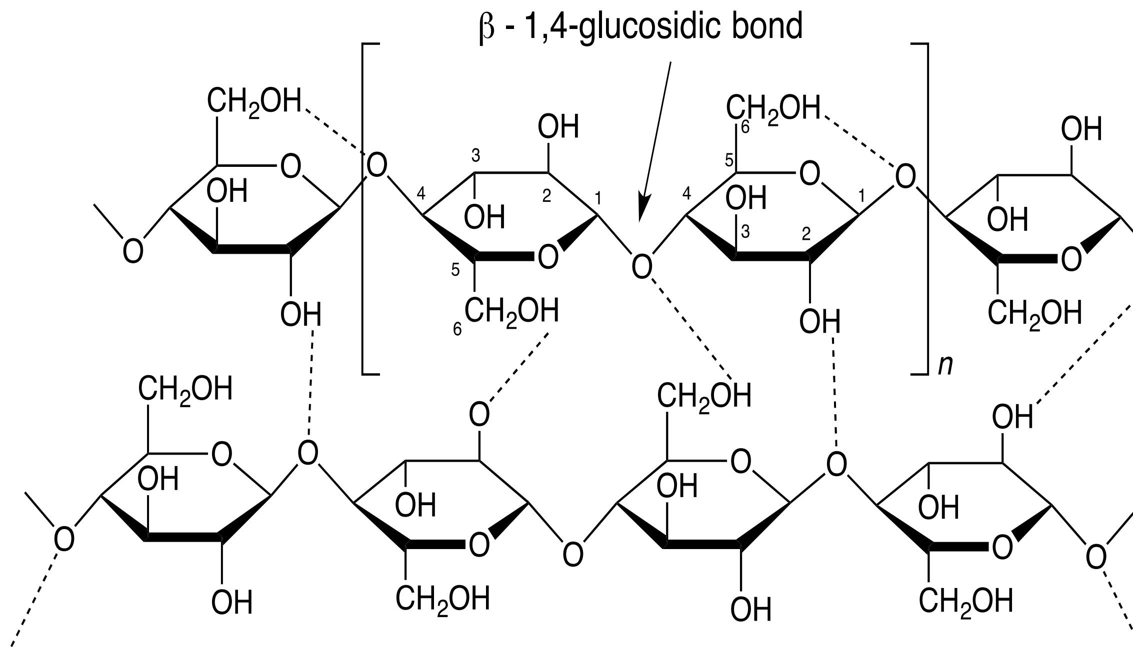
α-D-Xylose

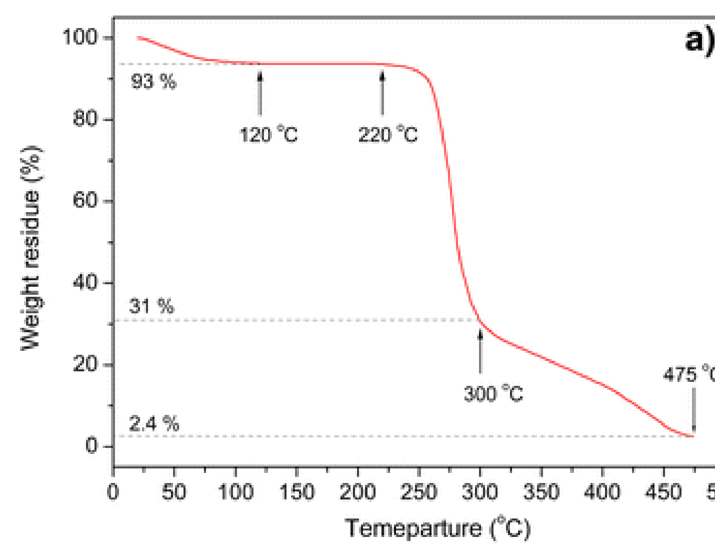


Hemicellulose (glucan + xylan)

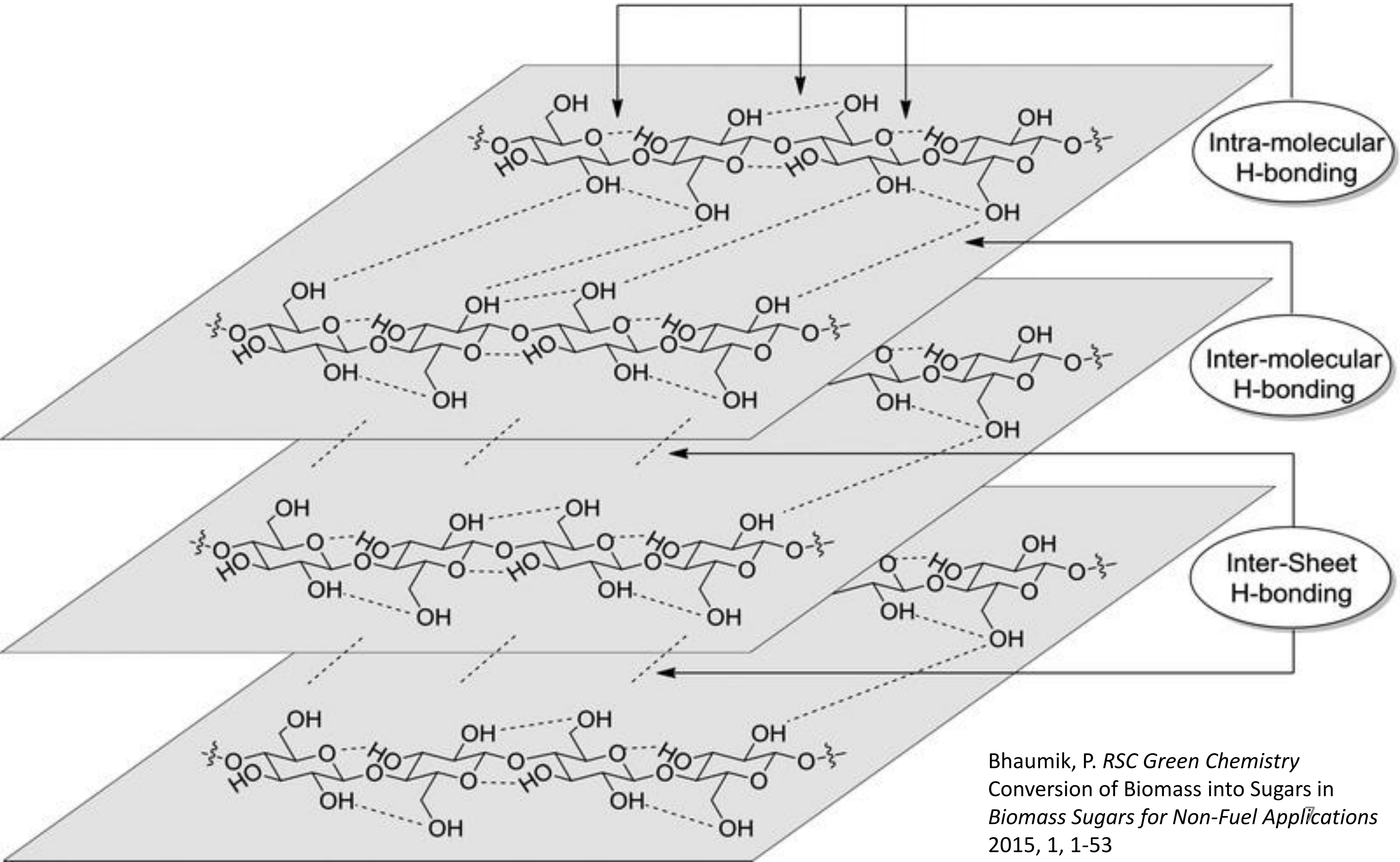
Cellulose: a β glucan polymer

- Polymer of 100% D-glucose
- β-1,4 linkages
- Crystalline (T_g cotton = 250°C)
- Wood pulp = 300-1700 units
- Cotton, other plants and bacteria = 800-10,000 units
- Insoluble in water and most organic solvents
- Soluble in NMMO, LiCl/dimethylacetamide, ionic liquids





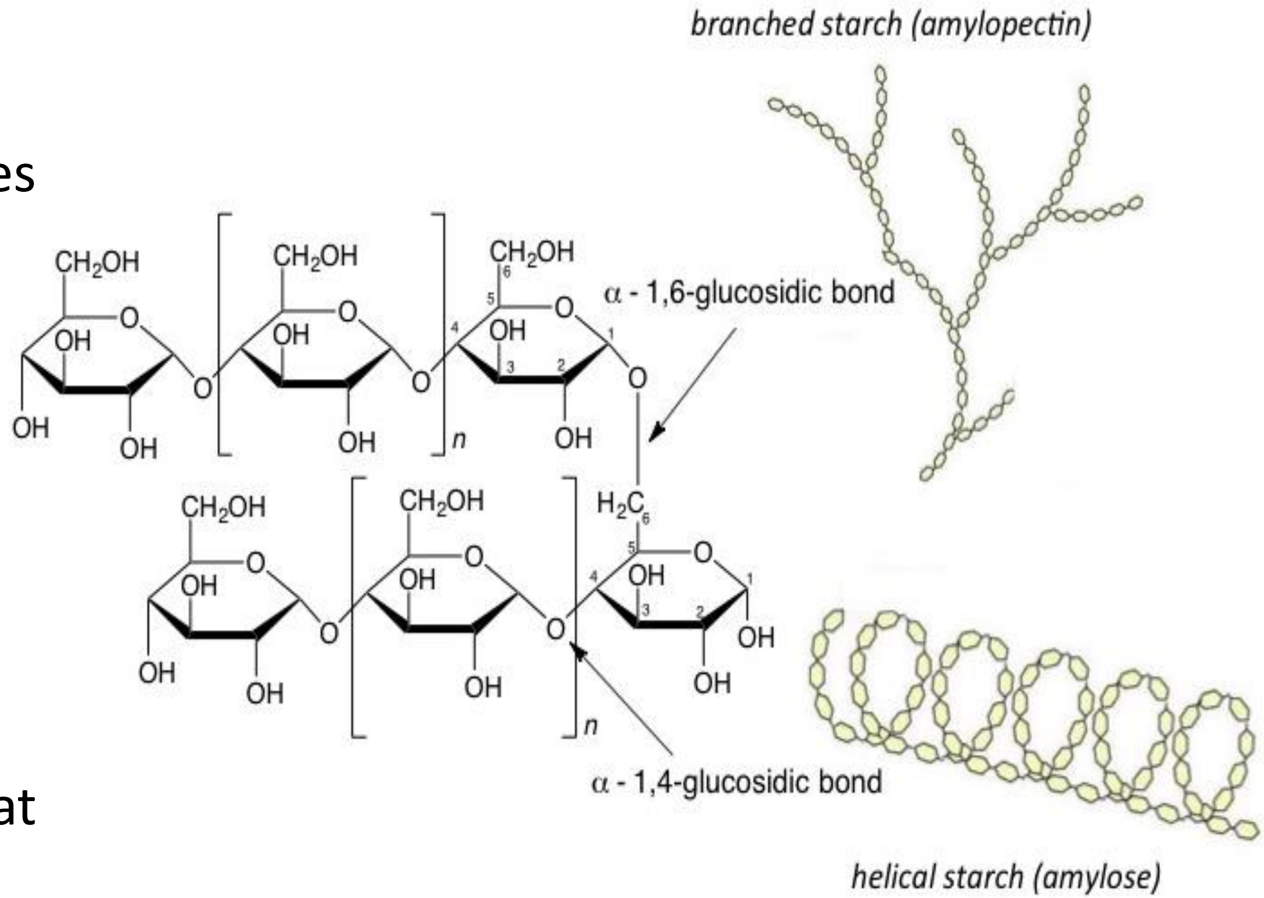
Cellulose Crosslinking *via* H-Bonding

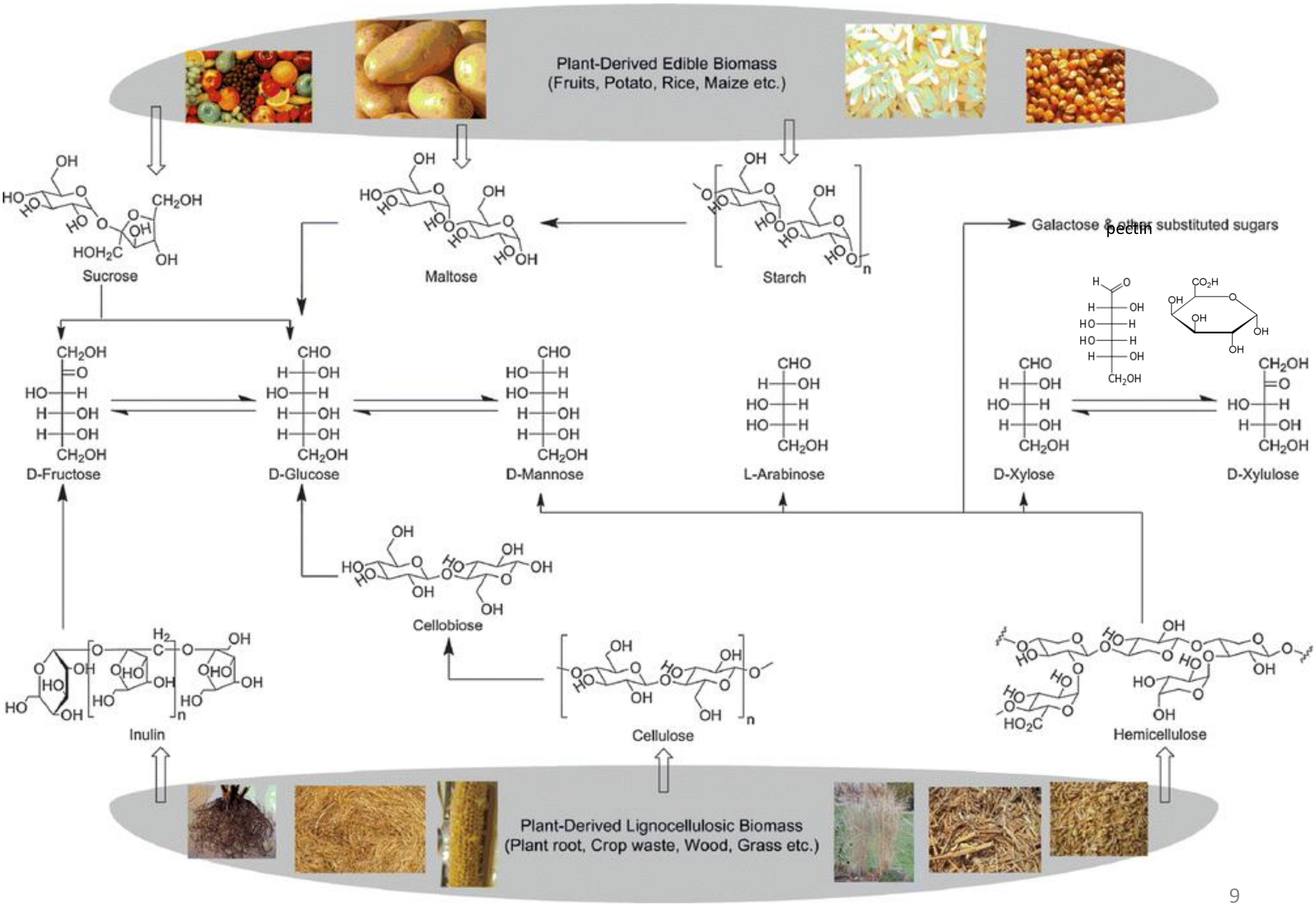


Bhaumik, P. *RSC Green Chemistry*
Conversion of Biomass into Sugars in
Biomass Sugars for Non-Fuel Applications
2015, 1, 1-53

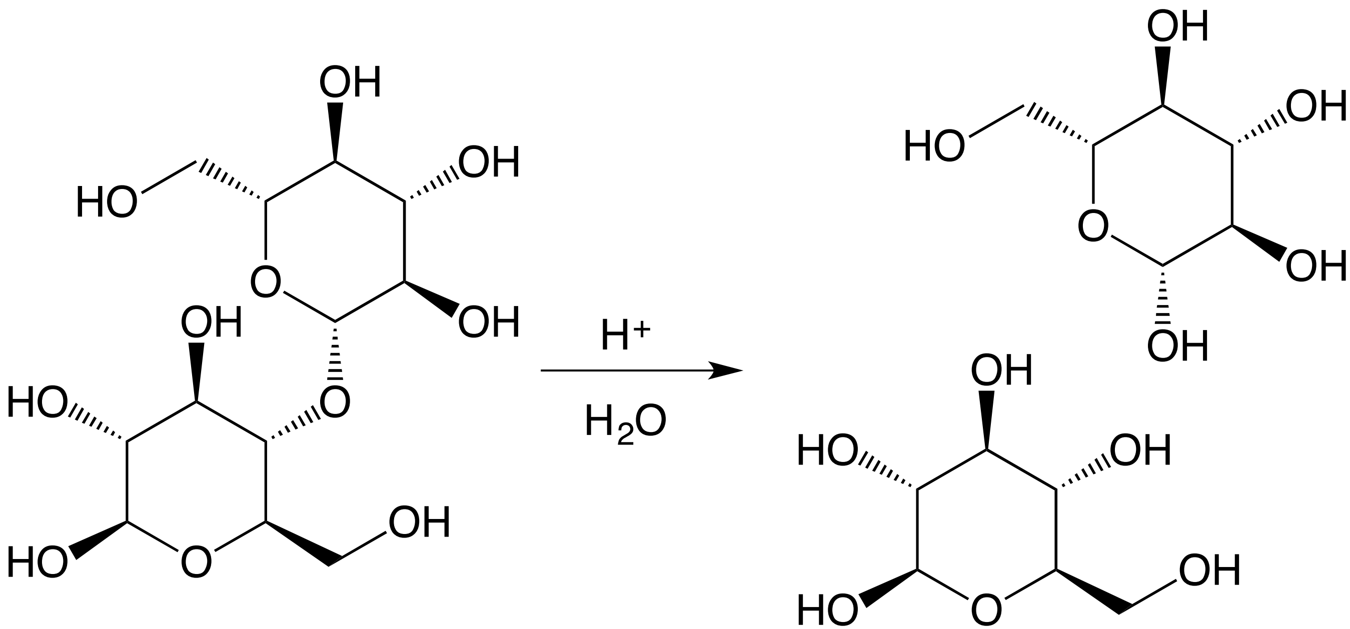
Starches: "Complex Carbohydrates"

- α-1,6 branched linkages (amylopectin)
- α-1,4 helical linkages (amylose)
- non-crystalline (T_g starch = 70^{o}C)
- Water soluble with heat




Plant-Derived Edible Biomass
(Fruits, Potato, Rice, Maize etc.)
Sucrose
Maltose
Starch
Galactose &
substituted sugars
pectin
D-Fructose
D-Glucose
D-Mannose
L-Arabinose
D-Xylose
D-Xylulose
Cellobiose
Inulin
Cellulose
Hemicellulose
Plant-Derived Lignocellulosic Biomass
(Plant root, Crop waste, Wood, Grass etc.)

Acid catalyzed hydrolysis of cellobiose, a disaccharide

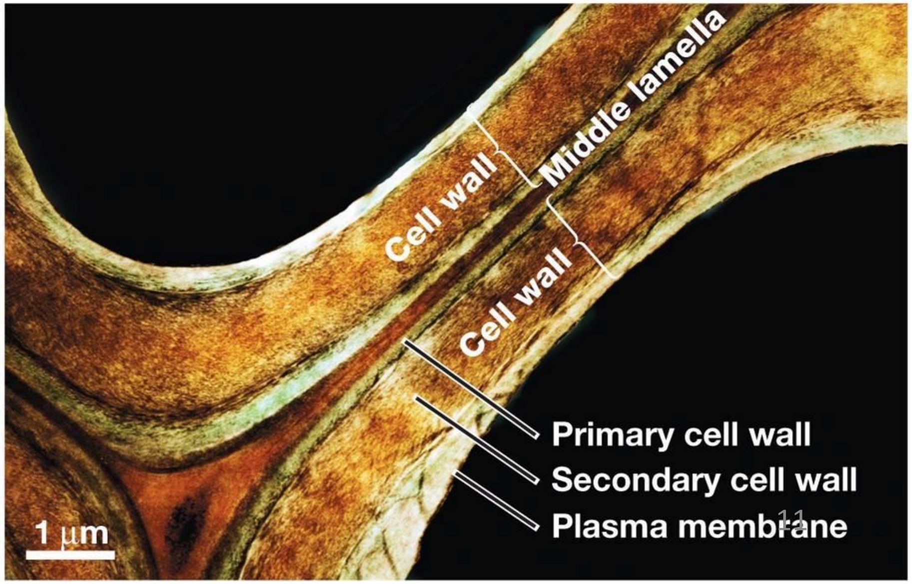


- Same mechanism for cellulose and hemicellulose hydrolysis
- Add 1 eq of water (18 g/mol) for every monomer (e.g. 162 g/mol for dehydroglucose)
- What is the mass (g) of glucose obtained from complete hydrolysis of 100 g of cellulose?

Secondary Plant Cell Walls

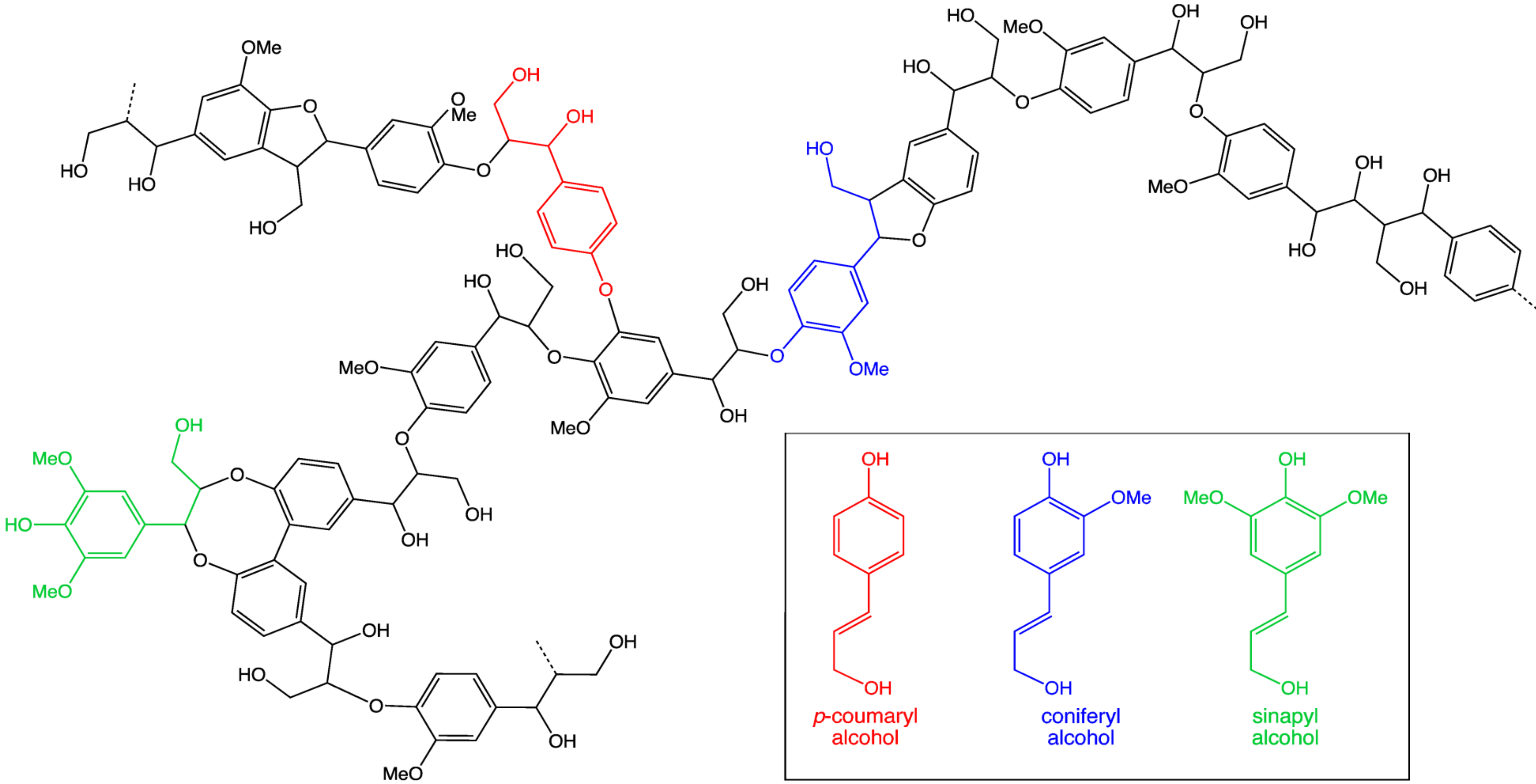
- Much thicker and stronger wall, providing ***bulk*** of the biomass
- Deposited when cell *stops growing*

- Primarily comprised of:
  - *Cellulose* (1,4-linked β-D glucose, a hexose) – *approximately 45% of mass*
  - *Hemicellulose* (1,4-linked β-D hexosyl residues) – *approx 25% of mass*
    - Primary and secondary cell walls contain glucuronoxylan, arabinoxylan, glucomannan and galactomannan
  - *Lignin* – *approx 30% of mass*
    - Polydisperse (MW range 300-600,000)[1]
    - Branched, 16+ linkages
    - Phenylpropanoid monomers
    - The challenge of 2nd Gen Biofuels



http://biorefinery.utk.edu/pdf/Molecular_Weight_Distribution_of_Lignin.pdf

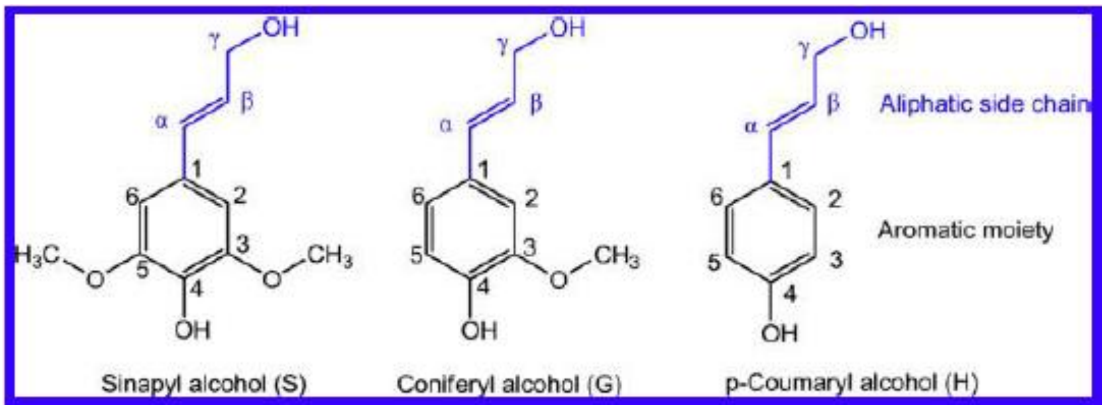
Lignin: A phenylpropanoid polymer

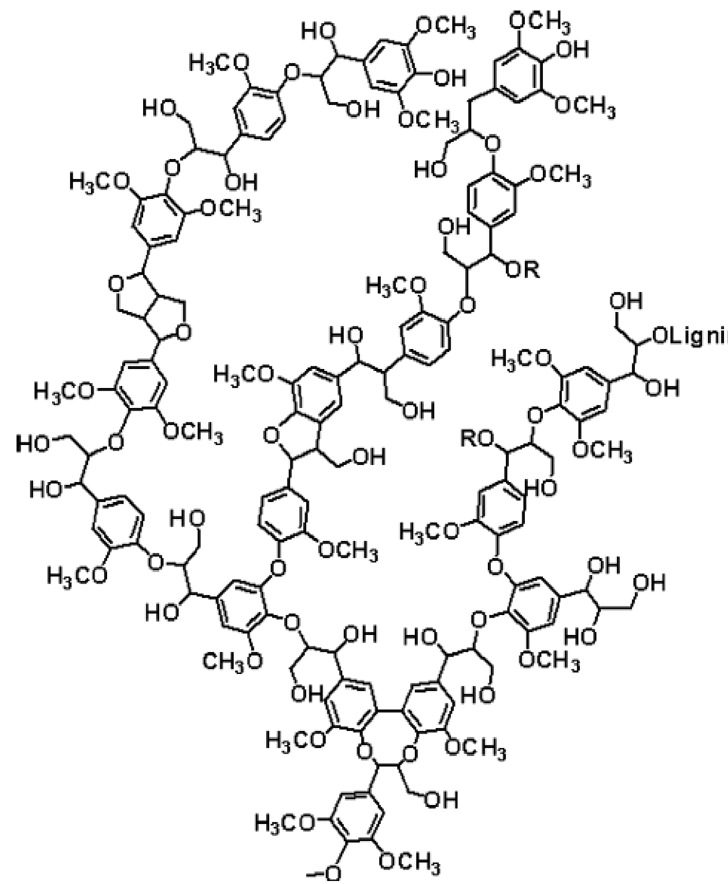


- Heterogeneous and polydisperse therefore difficult to work with (chemically)
- Commonly dehydrated & burned in pulp/paper mills
- Low heating value
- Other high volume/low value applications include additives (for e.g. asphalt, gypsum)

The Lignin Macromolecule: a Wicked Mistress

Monolignol	Grass	Conifer wood	Broadleaf wood
Sinapyl alcohol (S)	25–50%	0–1%	50–75%
Coniferyl alcohol (G)	25–50%	90–95%	25–50%
p-Coumaryl alcohol (H)	10–25%	0.5–3.4%	Trace

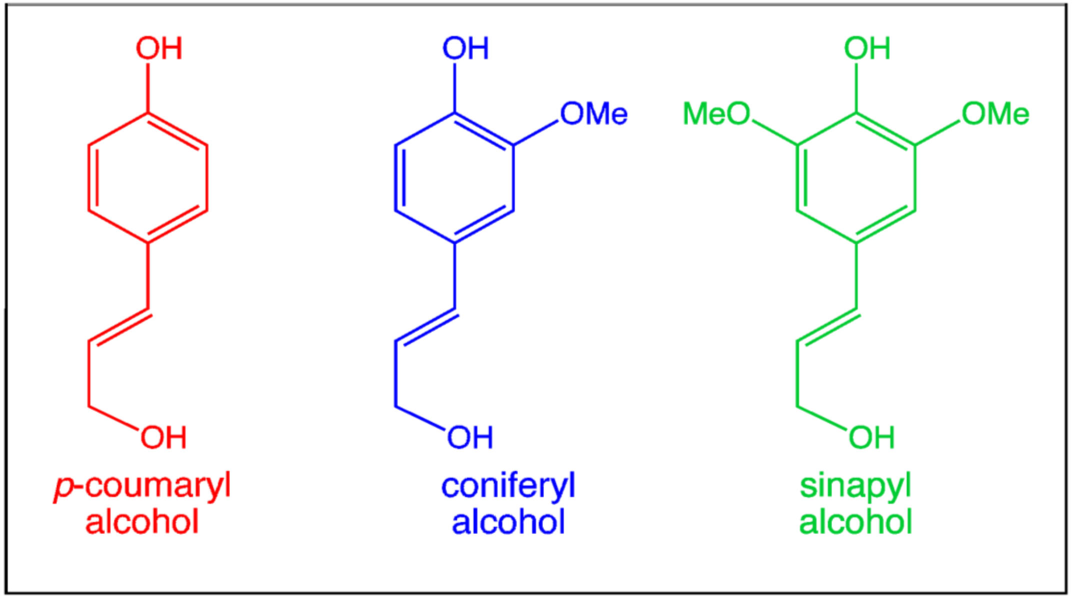




- Heterogeneous, phenolic monomers
- Variation of aromatic ring substitution between species (hardwoods have more methoxyl groups)
- Metabolic engineering has produced plant variants that are more S or G

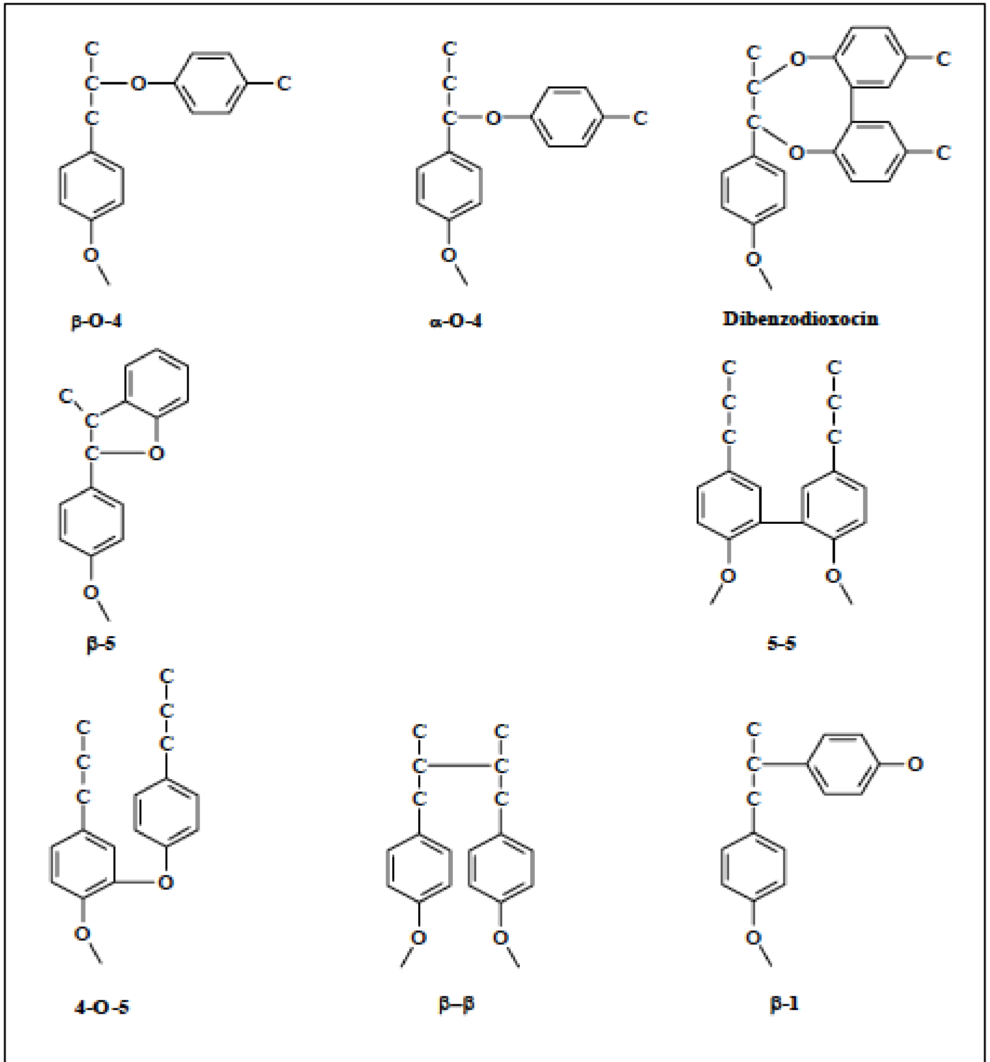
Diversity in Monolignols that Comprise Lignins

Lignin Monomer	Softwood	Hardwood	Grasses
p-coumaryl alcohol	0.5-3.5%	Trace amounts	10-25%
coniferyl alcohol (G)	90-95%	25-50%	25-50%
sinapyl alcohol (S)	0-1%	50-75%	25-50%

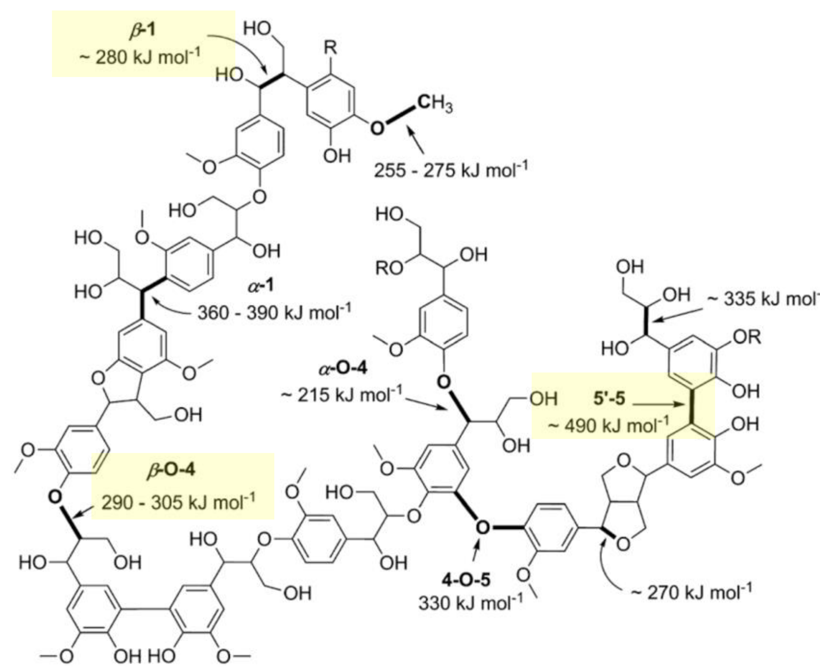


P -type G - type S - type

Diversity and Occurance of Lignin-Lignin Linkages

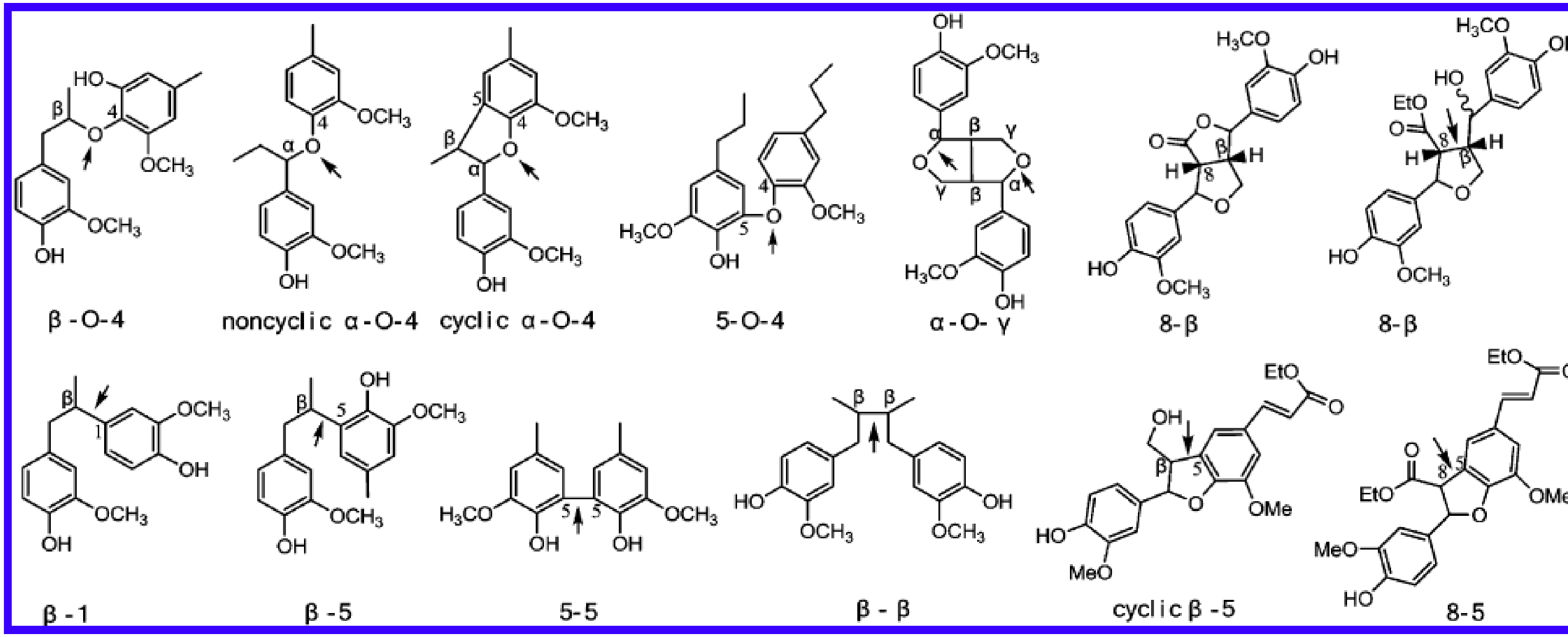


Linkage Type	Dimer Structure	Percent of Total Linkages (%)
β-O-4	Phenylpropane β–aryl ether	45-50
5-5	Biphenyl and Dibenzodioxocin	18-25
β -5	Phenylcoumaran	9-12
β-1	1,2-Diaryl propane	7-10
α-O-4	Phenylpropane α–aryl ether	6-8
4-O-5	Diaryl ether	4-8
β - β	β-β-linked structures	3



Rinaldi, R. *Catalytic Hydrogenation for Biomass Valorization*

Lignin Bonding Patterns



- Major linkage is β-O-4 ether
- Relatively labile bond can be broken with acid or base catalysis, heat

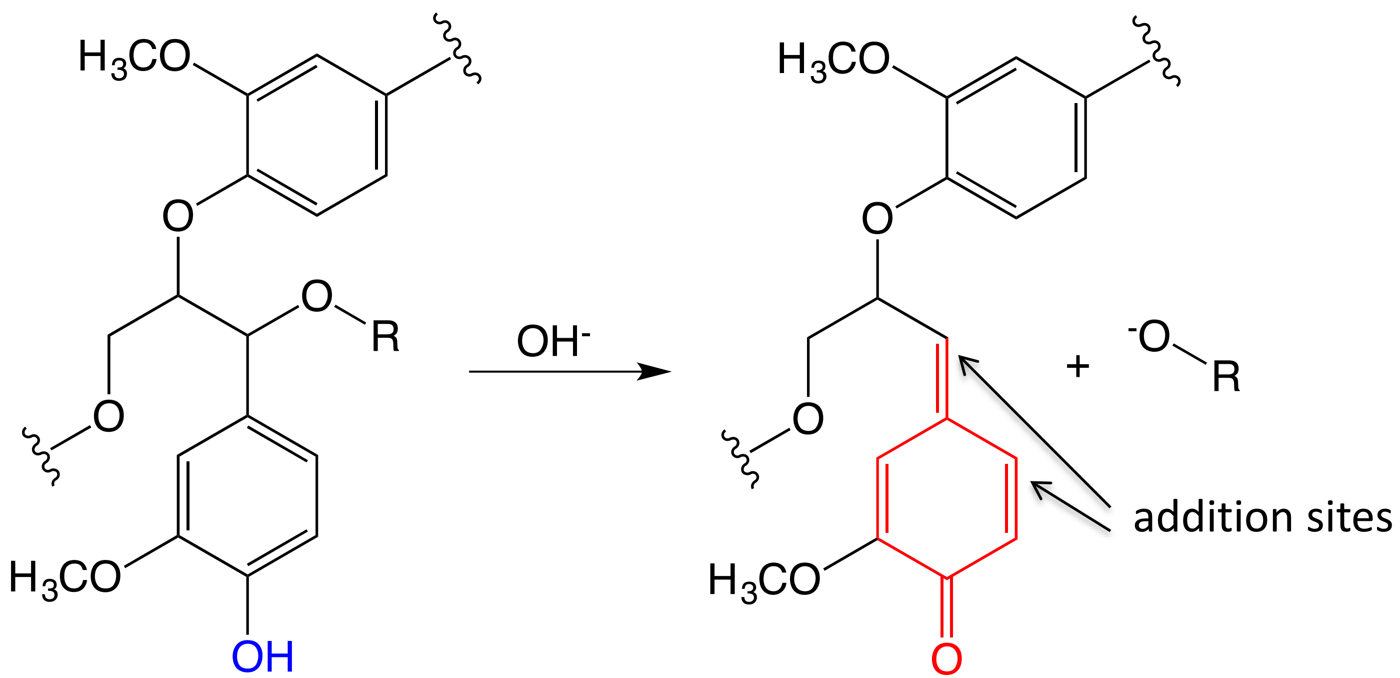
	Number/100 ppu	
Linkage	Softwood	Hardwood
β-O-4	43–50	50–65
β-5	9–12	4–6
α-O-4	6–8	4–8
β–β	2–4	3–7
5–5	10–25	4–10
4-O-5	4	6–7
β-1	3–7	5–7
Others	16	7–8

Li, Huber, et al. *Chem Rev* 2015 , 115, 21

Lignin Depolymerization via Soda Pulping

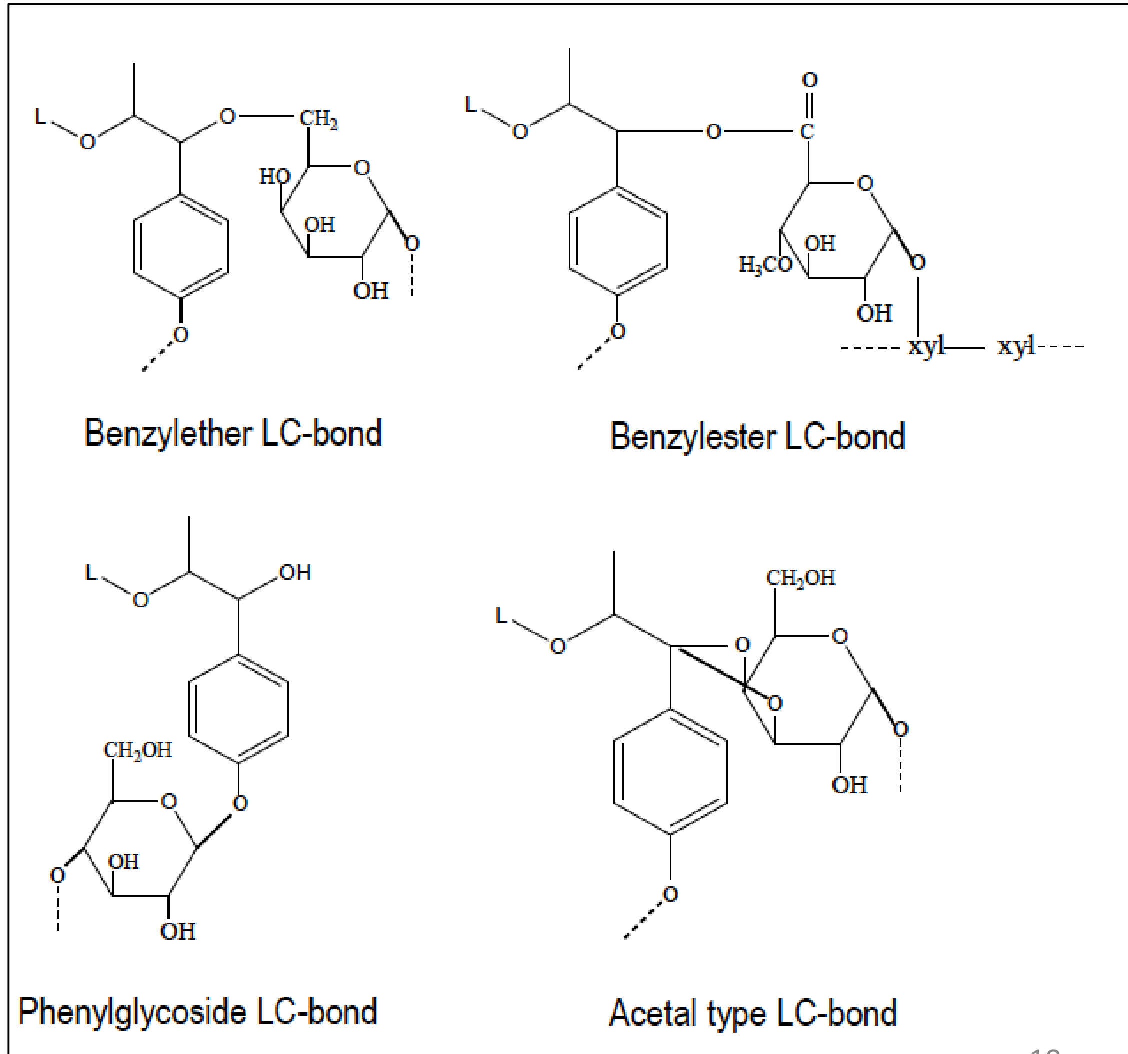
- Soda pulping is one of many lignin depolymerization techniques
- Base removes phenolic proton (pKa ~ 9)
- α ether cleavage reaction
- Reactive quinone methide is formed with loss of $^{-}$OR
- Repolymerization possible as quinone methide is non-aromatic
- (Michael-type) Conjugate Addition disrupts conjugation stability.

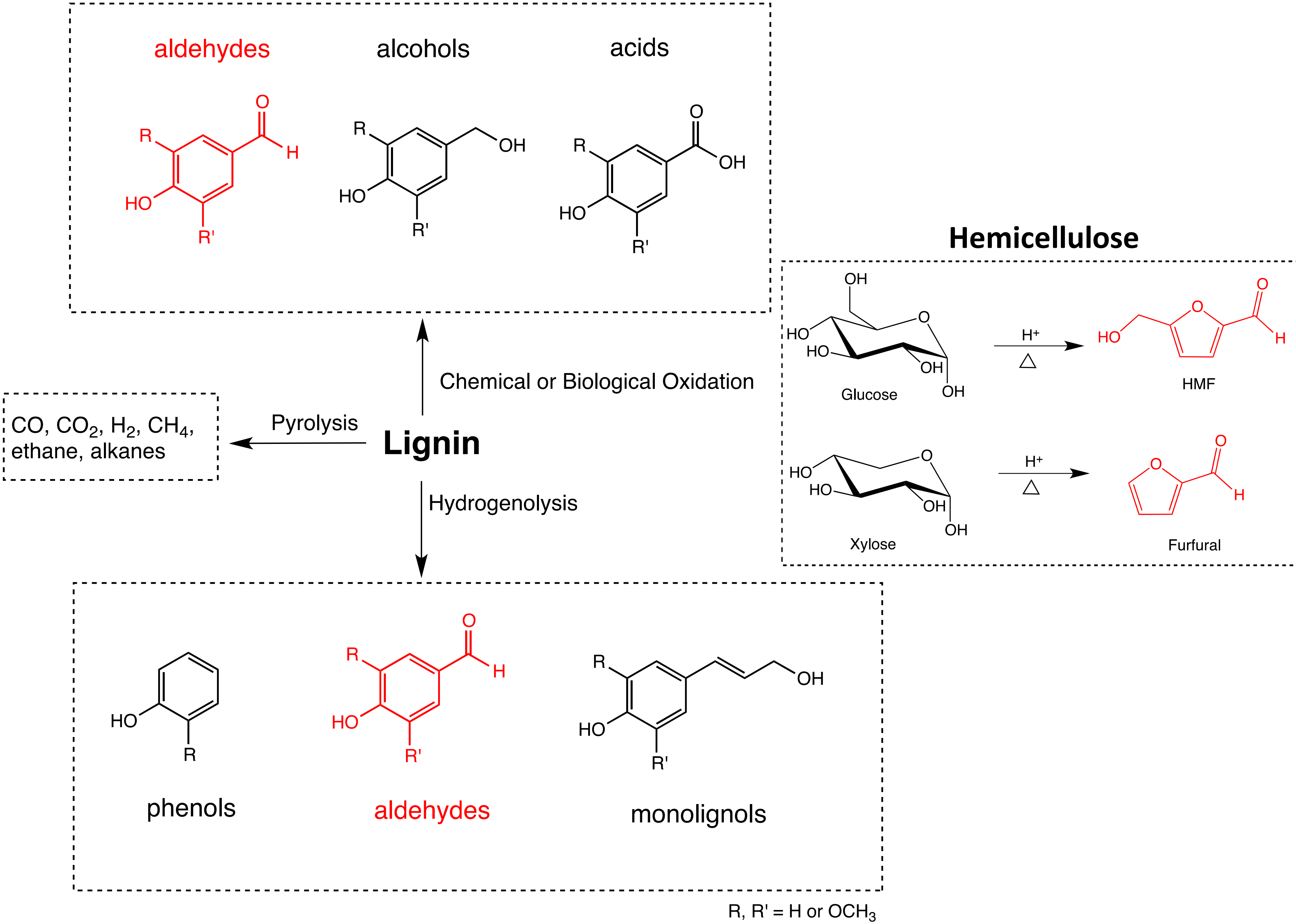
Are hardwood lignins less susceptible to repolymerization?



Lignin-Carbohydrate Linkages

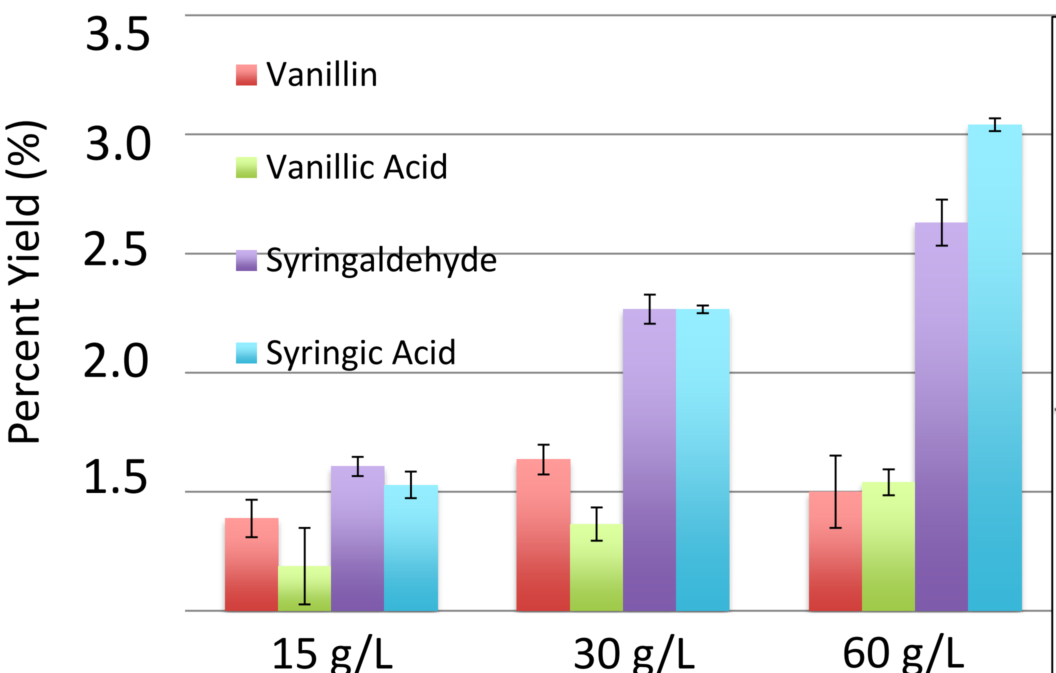
- Can be cleaved by acid or base (e.g. soda pulping)
- Klason procedure measures acid insoluble lignin

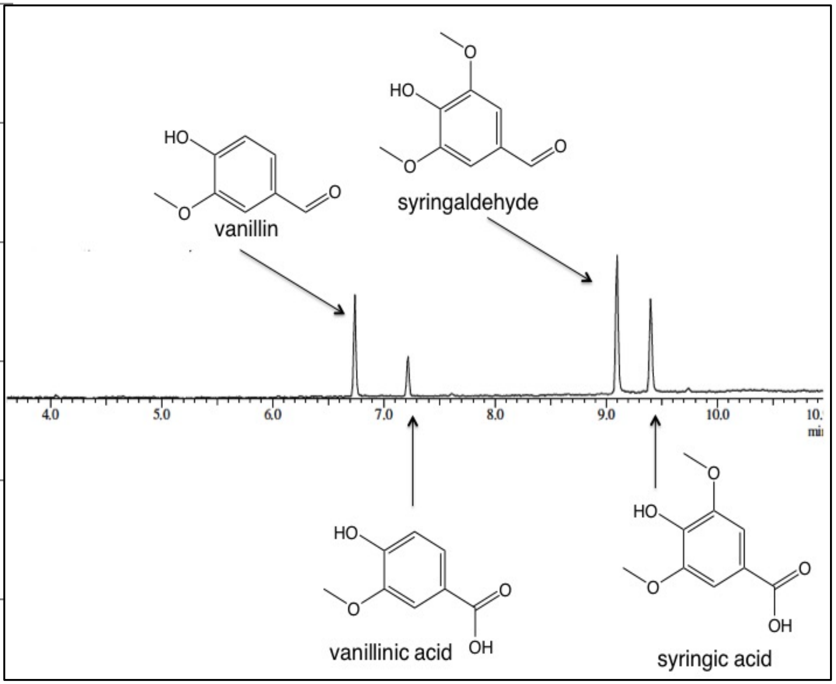



aldehydes
alcohols
acids
Chemical or Biological Oxidation
CO, CO_2, H_2, CH_4, ethane, alkanes
Pyrolysis
Lignin
Hydrogenolysis
phenols
aldehydes
monolignols
R, R' = H or OCH_3
Hemicellulose
Glucose
HMF
Xylose
Furfural
H^+
△

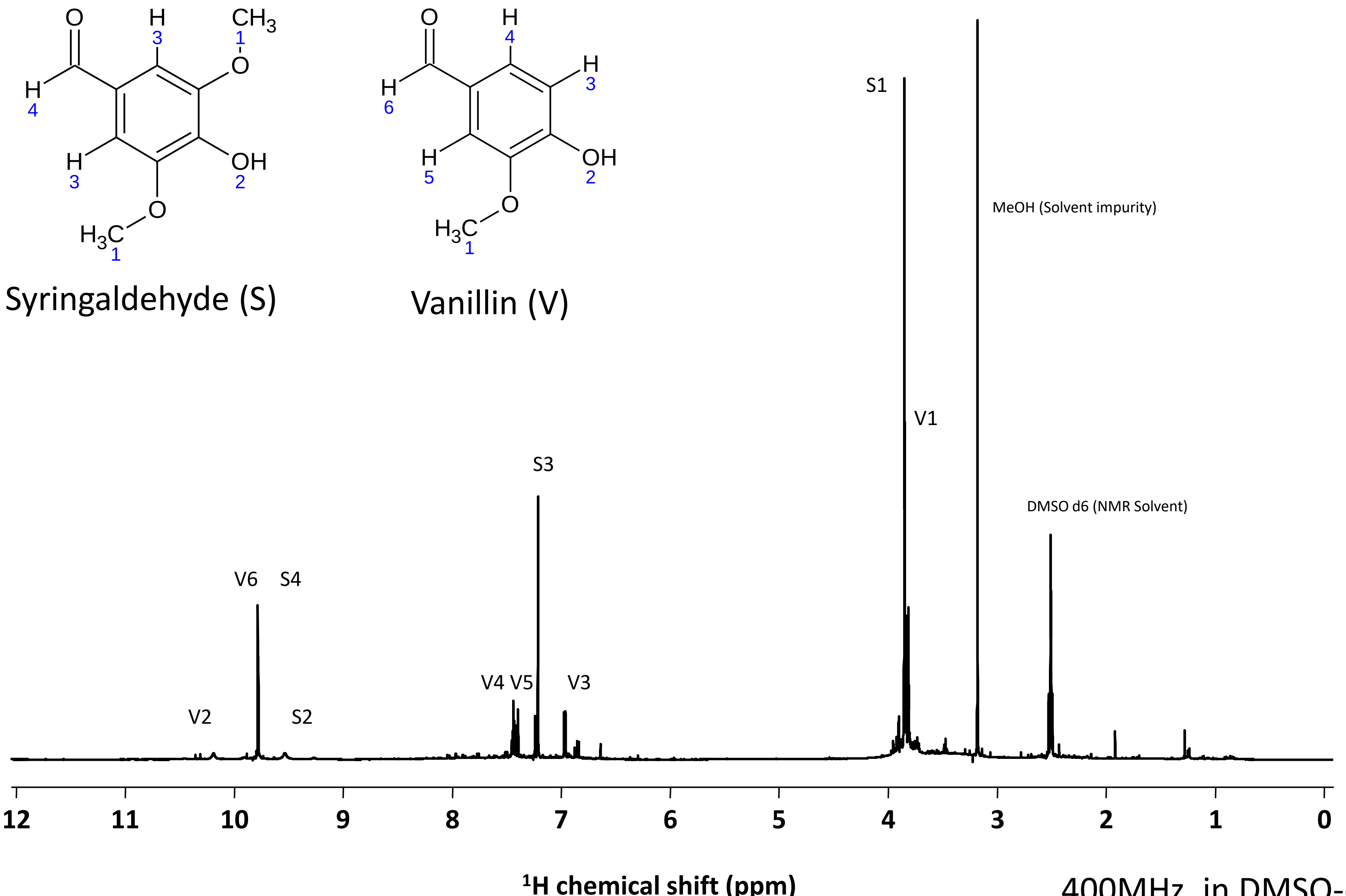
Typical Yields and GC-MS Spectrum of Depolymerized Lignin

- Softwood Lignin sourced from steam explosion (Sweetwater Energy, Rochester NY)
- 2M NaOH, 170^{o}C, 1h, 120psi, air, 800RPM
- Yields need improvement
- Lignin fragments are likely repolymerizing
- Separation of acids from aldehydes can be achieved with acid/base extraction





^{1}H NMR Spectrum of Depolymerized Lignin Extract

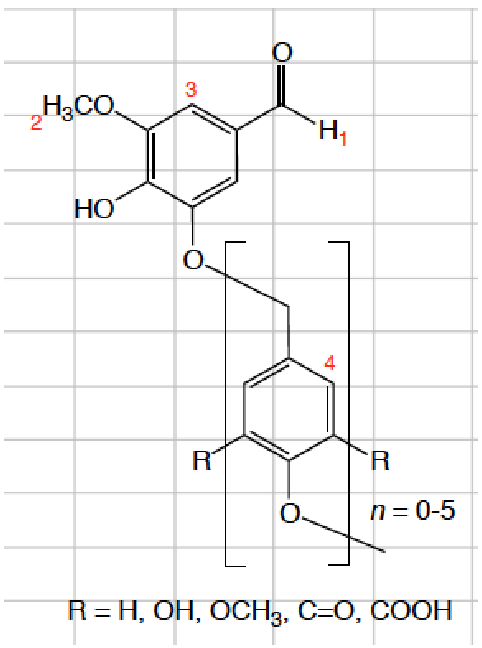


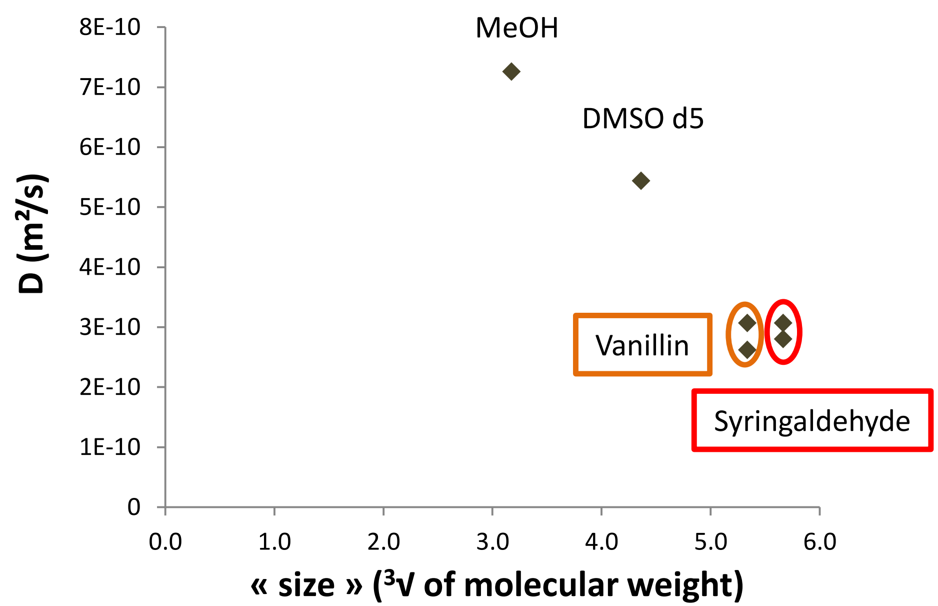
400MHz, in DMSO-d6

^{1}H NMR Diffusion Spectroscopy (DOSY)

Are we forming aldehyde oligomers that will react to make poly-cationic ammonium?

No





Stokes-Einstein Equation

Diffusion of spherical particles in a liquid

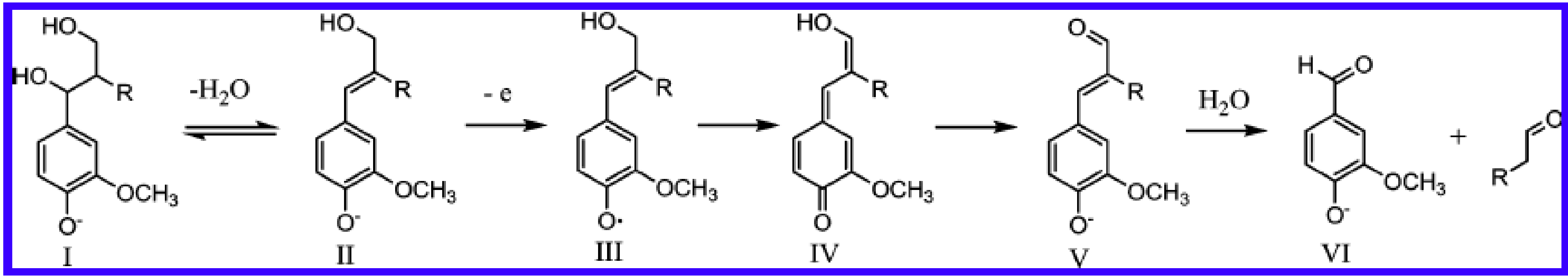
$D = kT/6\pi\eta r_h$

η is the viscosity

r_h is the hydrodynamic radius (~size)

Mallory Gobet and Dorian Whyte *Unpublished*

Vanillin Formation Mechanism

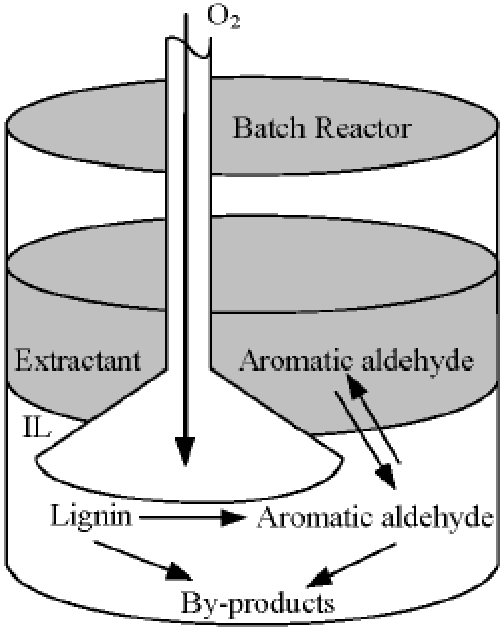


- Typical aldehyde yields are reported between 10-20% [1]
- Repolymerization of intermediate III via radical coupling
- Oxidants = O_2, H_2O_2, air, MOFs, metals (Cu, Al, Fe, Pd, etc.)
- *Alkylammonium dihydrogen phosphate ionic liquids* dissolve lignin and facilitate oxidative depolymerization (30% mixed aromatic aldehyde yields reported) [2]

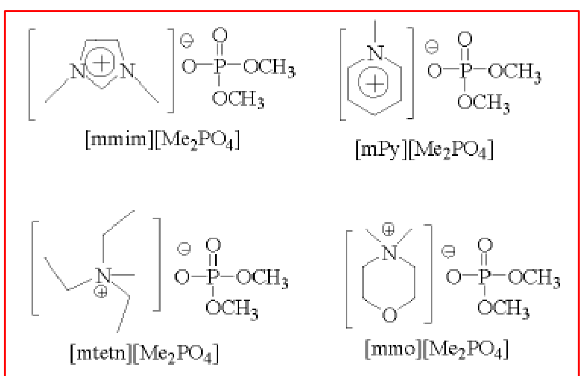
[1] Pandley et al. *Chem. Eng. Technol*. **2011**, 34, No. 1, 29–41

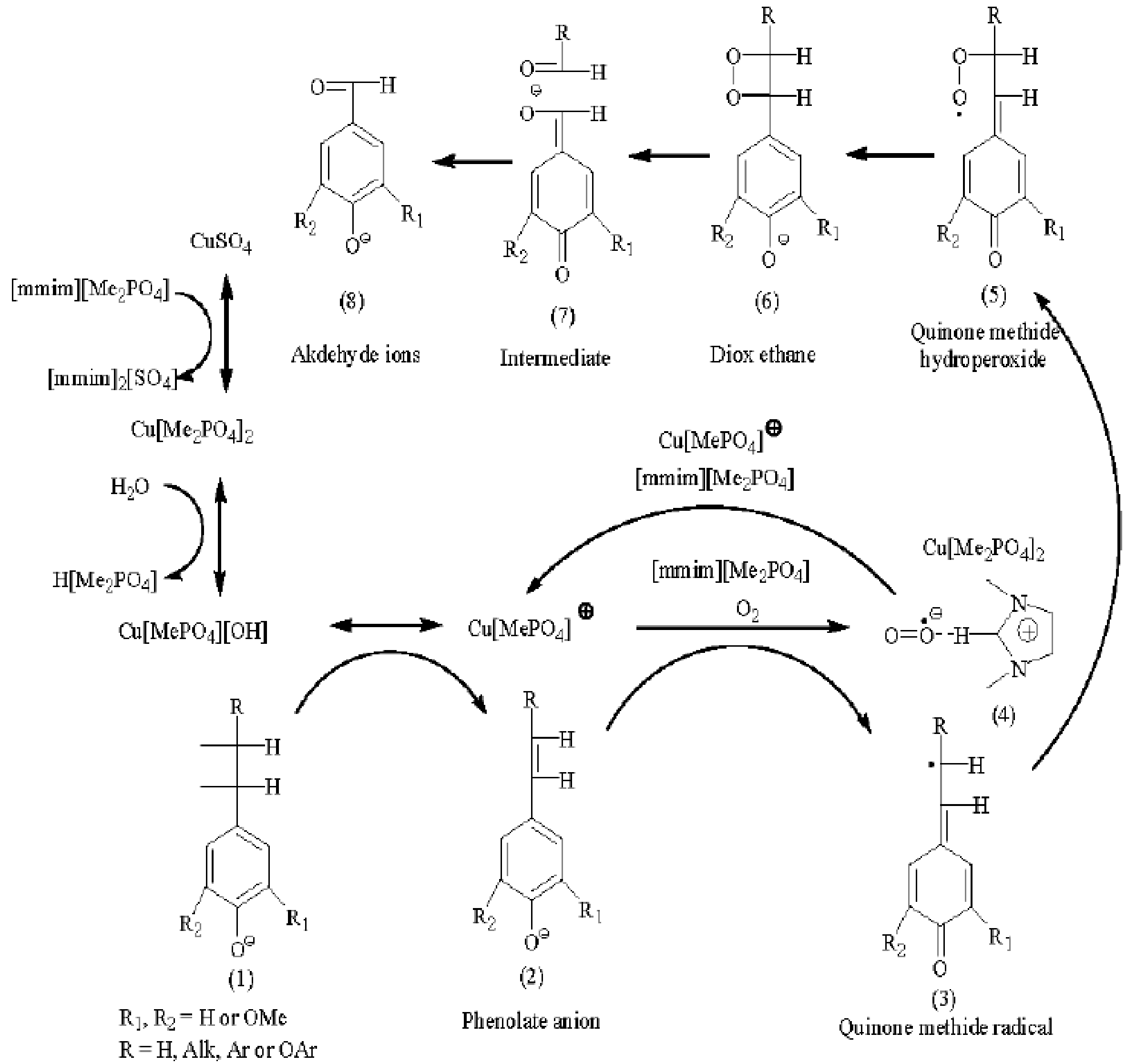
[2] Liu, S., et al., Process of lignin oxidation in ionic liquids coupled with separation. RSC Adv, 2013. **3**(17): p. 5789-5793

Proposed mechanism of lignin oxidation with Ionic Liquid + $CuSO_4$ + O_2



ILs tested





Liu S. et al. *RSC Adv,* 2013 3 (17)