Wood Chemistry

Wood Chemistry
PSE 406 / Chem E 470

Lecture 11
Lignin Structure

Wood Chemistry

Class Agenda

- Functional groups
  - » Methoxyl, phenolic hydroxyl, aliphatic hydroxyl, carbonyl
- Lignin structures
- Lignin – carbohydrate complexes
- Lignin analytical procedures
- Lignin trivial facts
- Appendix

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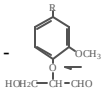
Lignin Functional Groups
Phenolic Hydroxyl

- 15-30 free phenolic hydroxyl/100C9: Softwood
- 10-15 free phenolic hydroxyl/100C9: Hardwood
- Reactivity
  - » Units containing free phenolic hydroxyl groups much more susceptible to cleavage reactions - hydrolysis of α and β aryl ether linkages
  - » Structures much more reactive towards modification reactions

Free Phenolic Hydroxyl



Etherified Phenolic Hydroxyl

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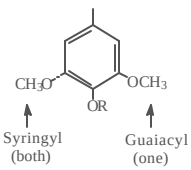
Lignin Functional Groups
Methoxyl

- ~0.95/C9 in softwoods
- ~1.5/C9 in hardwoods
- Generally resistant to acid and alkali
- HS cleaves to form thiols, mercaptans (Kraft mill odor)



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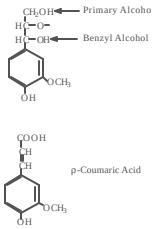
Lignin Functional Groups
Aliphatic Hydroxyl

- Majority of aliphatic hydroxyl groups are primary: on γ carbon
  - » Site relatively non-reactive
  - » In some species, γ carbon oxygen linked through ester linkage to ρ-coumaric acid, etc
- Benzyl alcohols
  - » Debated amount: 16- 40/100 C9 in spruce
  - » Play dominant role in delignification reactions



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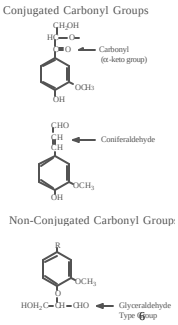
Lignin Functional Groups
Carbonyl Groups

- Total carbonyl groups 20/100C9 in spruce
  - » 1/2 Conjugated Structures
    - – Coniferaldehyde and α-keto structures
    - – Play important role in delignifcation reactions
  - » 1/2 Non-conjugated Structures
    - – Glyceraldehyde from β-1 coupling
- Larger amount in certain hardwoods and grasses due to esters.



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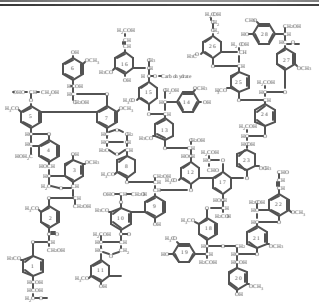
Lignin Structure
Sakakibara



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Lignin-Carbohydrate Complex

- All purified holocellulose materials contain a certain amount of lignin
- All purified lignin fractions contain a certain amount of monosaccharides
- LCCs have been enzymatically prepared from lignin and monosaccharide model compounds
- Significant work studying isolated LCCs
  - » No definitive information on exact covalent bonding patterns
  - » Generally accepted bonding patterns

Lignin-Carbohydrate Complex
Proposed Linkages

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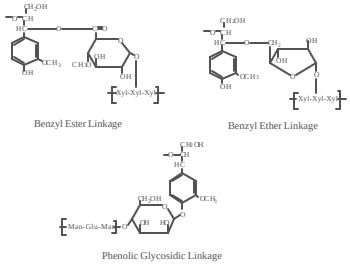

Benzyl Ester Linkage

Benzyl Ether Linkage

Phenolic Glycosidic Linkage

Lignin-Carbohydrate Complex
General Information

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- Mw of isolated LCCs 600→15,000
- LCC linkage stability
  - » Esters: alkali labile, acid labile
  - » Ethers: selectively alkali labile, mildly acid labile
  - » Glycosides: mildly alkali labile, acid labile
- Formation during pulping processes possible
- LCCs: residual lignin and bleaching
  - » Removal of that last little bit of lignin
  - » Enzyme assisted bleaching

Lignin Structure
Analytical Procedures

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- All analysis require model compound studies!
- Linkages
  - » Enzymatic dehydrogenation (test tube studies)
  - » Degradation studies (see appendix)
  - » NMR
- Functional groups
  - » Wet Chemistry techniques
  - » Spectroscopy

Lignin Trivial Facts I

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- Solubility
  - » Native lignins: limited/no solubility in all solvents without modification
- Molecular Weight
  - » Average Mw for softwood ~20,000, lower for hardwoods
  - » Polydispersity ~ 2.5-3.0
  - » Mw measured for lignosulfonates as high as 1,000,000

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Lignin Trivial Facts II

- Elemental Composition MWL
  - » Spruce $C_9H_{7.92}O_{2.40}(OCH_3)_{0.92}$ $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$
  - » Beech $C_9H_{8.50}O_{2.86}(OCH_3)_{1.43}$ $C_9H_{7.93}O_{2.95}(OCH_3)_{1.46}$
- UV Absorption
  - » Strong adsorption at 205 and 280nm
  - » Carbohydrates do not adsorb at 280nm
- Compression Wood (Softwoods)
  - » High % lignin (~40%), high % of ρ-hydroxy units (to 70%)
- Tension Wood (Hardwoods)
  - » Reduced lignin content

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Appendix

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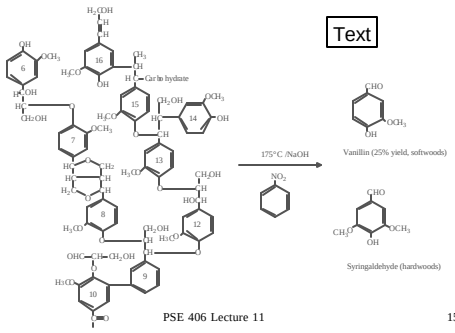
Lignin Structure Elucidation Studies
Nitrobenzene Oxidation



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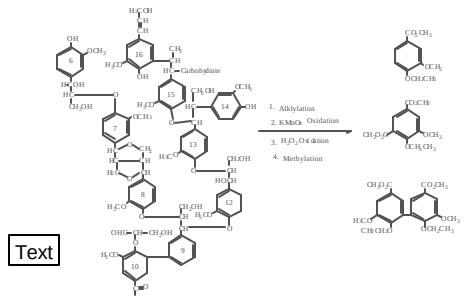
Lignin Structure Elucidation Studies
Permanganate Oxidation



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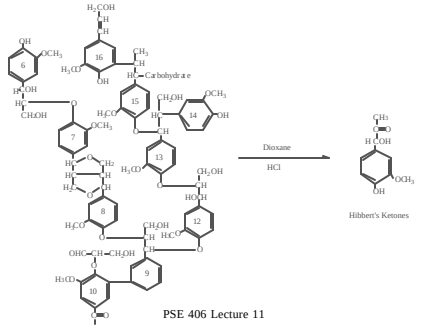
Lignin Structure Elucidation Studies
Acidolysis



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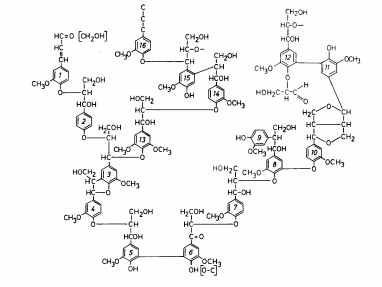
Lignin Structure: Adler



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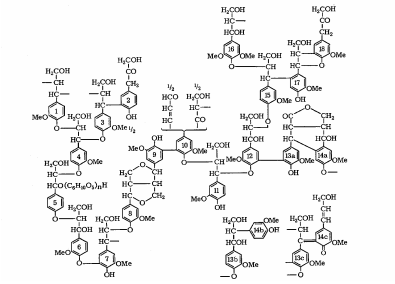
Lignin Structure: Freudenberg



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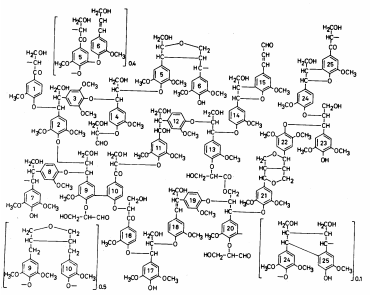
Lignin Structure: Nimz



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Lignin Structure: Forss