

# A!

Aalto University  
School of Chemical  
Engineering

# Lignin: Structure and characterization

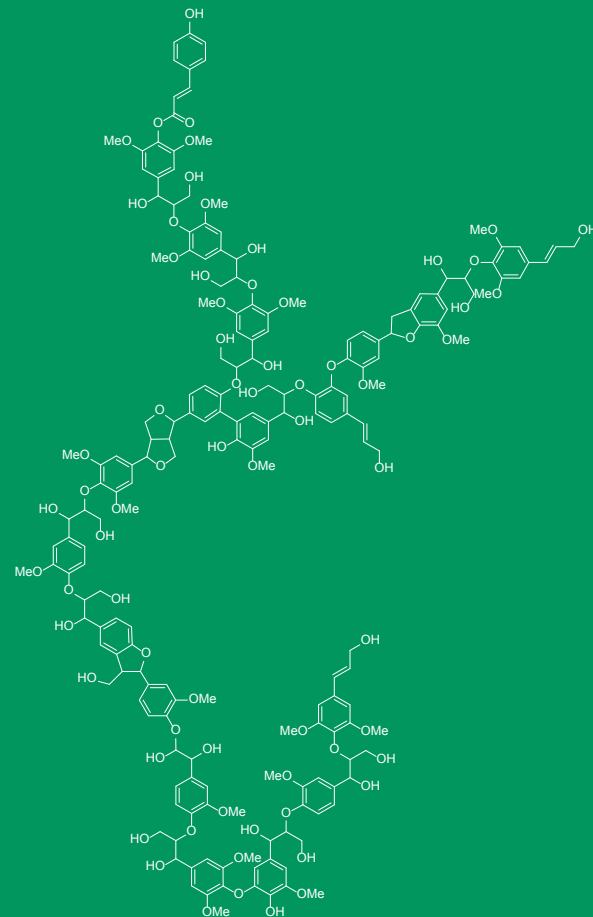
**CHEM-E2140**

**Cellulose-based fibres, 5 cr**

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School of Chemical Engineering  
Aalto University

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# Learning outcomes

## After the lecture you will know:

- Principles of lignin biosynthesis
- Classification of lignins
- Function of lignin to plants
- Distribution of lignin in plant cell walls
- Overview of reactions under thermochemical conditions
- Industrial sources & relevance
- Isolation and characterization
- Current and emerging applications

# Contents

- (1) Occurrence and functions in plants
- (2) Biosynthesis and the diversity of molecular structures
- (3) Industrial relevance
- (4) Fundamental properties and reactivity
- (5) Isolation and purification
- (6) Derivatizations
- (7) Characterization
- (8) Applications

# Lignin

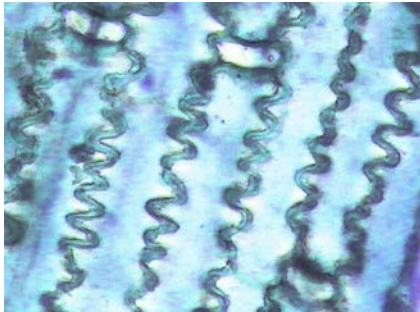
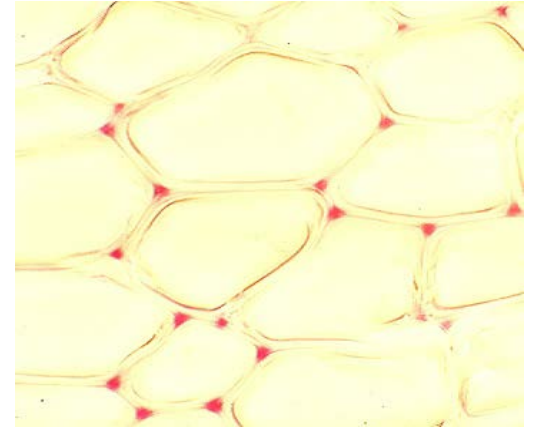
- Main component of plant biomass (in addition to cellulose and hemicelluloses)
- Makes <sup>17-</sup>25-35% of wood dry weight and 15-25% in annual plants
- Structurally, it is a polydisperse mixture of methoxylated polyphenols
- Naturally brown, hence the colour of wood
- Dissolved from wood chips in chemical pulp production: combusted for chemical recovery and heat and power production
- New uses for lignin are sought in materials and chemicals



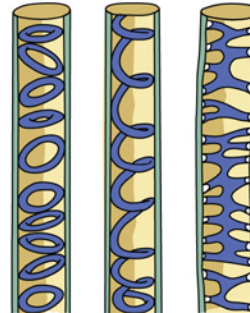


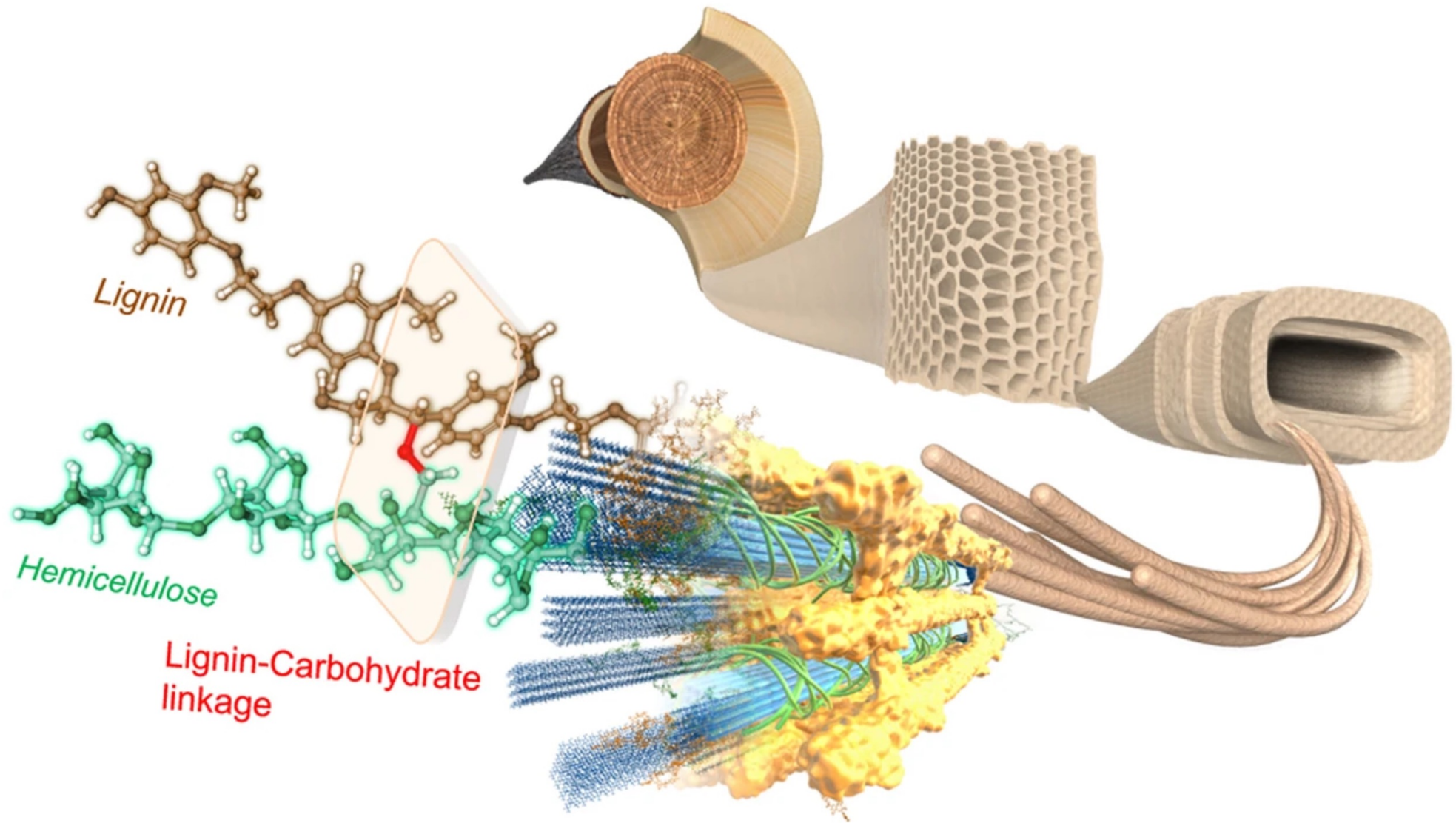
# 1. Occurrence and functions in plants

- Lignin is "natural resin" that fills spaces between plant cells and strengthens cell walls by covering cellulose microfibrils
- Functions of lignin in plants:
  - Provides strength
  - Barrier against the attack of insects and microbes
  - Enables transportation of water and ions from the soil



Wheat straw xylem tissue seen in optical microscope



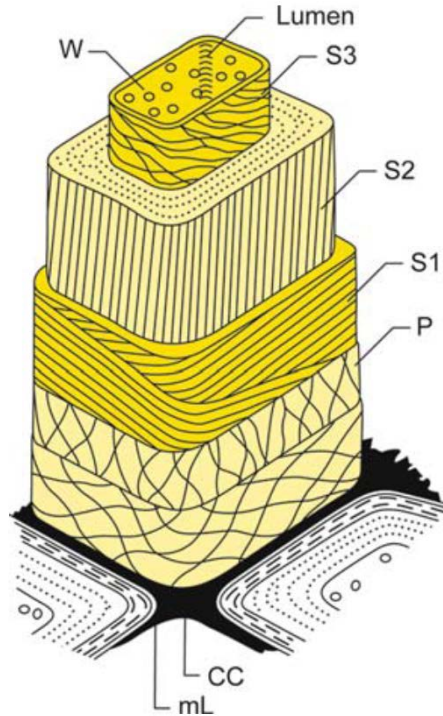


A three-dimensional view of the lignin–carbohydrate complex (LCC) in the wood cell wall. An illustration of wood cell walls and their ultrastructure focusing on the ether linkage between lignin and carbohydrate.

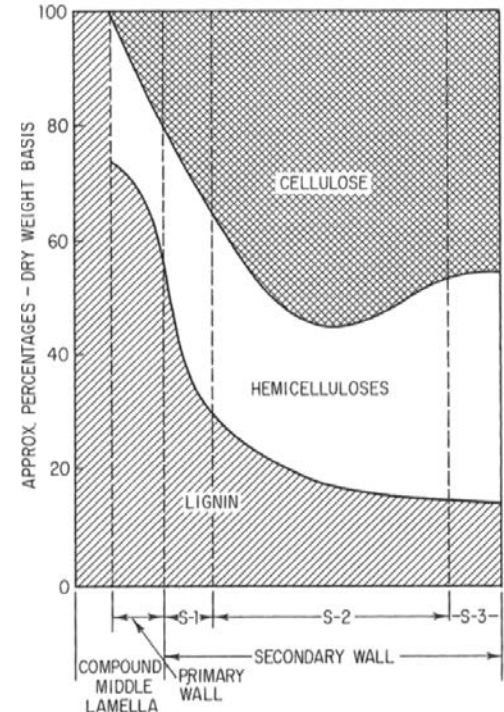
From: Scientific Reports (*Sci Rep*) ISSN 2045-2322 (online) [Direct evidence for  \$\alpha\$  ether linkage between lignin and carbohydrates in wood cell walls](#)

# Distribution of lignin in plant cell walls

- CC, ML enriched in lignin, presumably because lignification is initiated there<sup>[1]</sup>
- Secondary walls contain the largest proportion of the total lignin in cell walls
- The xylem tissue is enriched with lignin – functions in water transportation



Wood cell wall regions<sup>[2]</sup>



Distribution of lignin in cell walls<sup>[3]</sup>

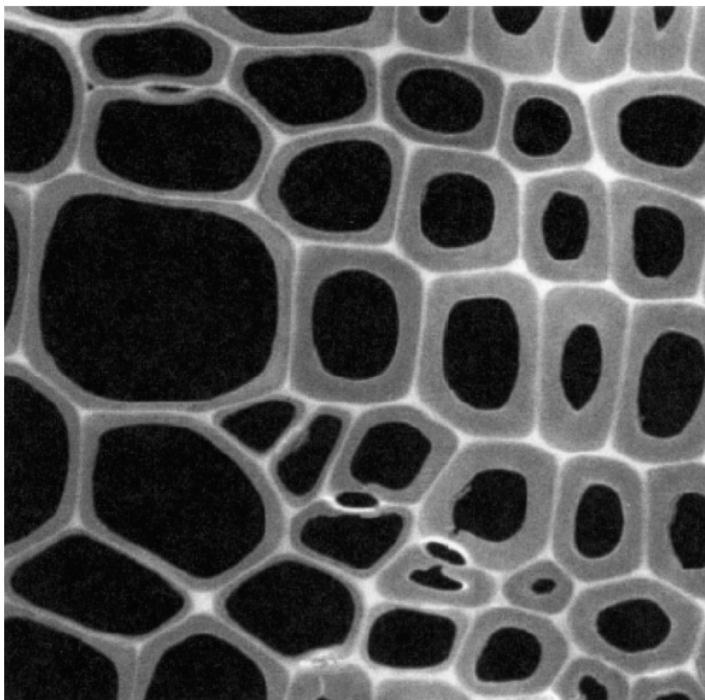
<sup>[1]</sup> Donaldson, *Phytochem.* 57 (2001) 859–873

<sup>[2]</sup> Agarwal, *Planta* (2006) 224:1141–1153 (ref. Sjöström, 1993)

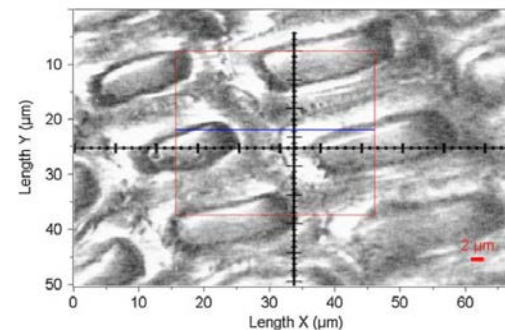
<sup>[3]</sup> Hale, 1969 "Structural and physical properties of pulpwood"



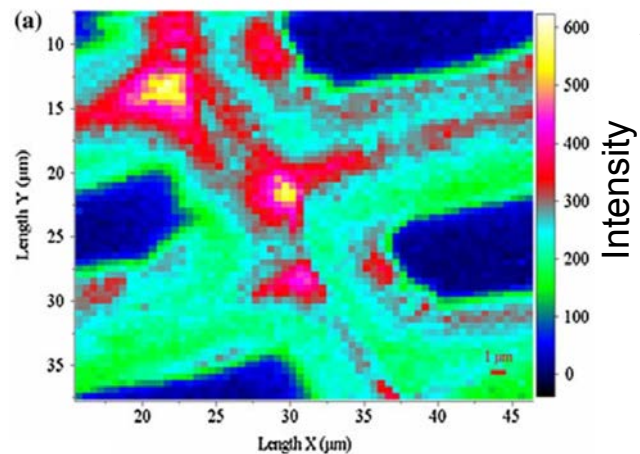
# Imaging distribution of lignin in plant cell walls



Bright areas in pine wood arise from autofluorescence of lignin<sup>[1]</sup>



Raman imaging of lignin in spruce wood at the area of six mature cells<sup>[2]</sup>

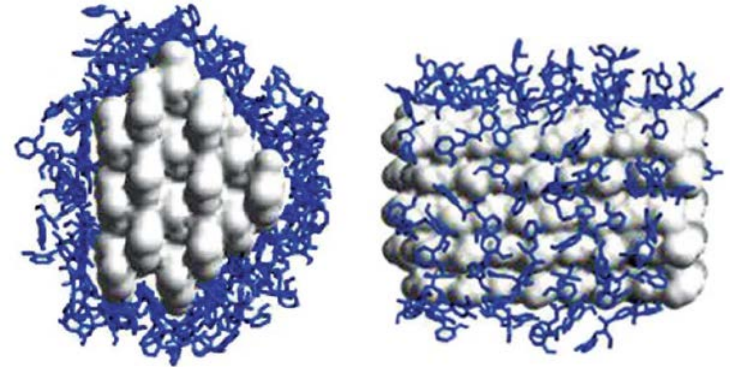


<sup>[1]</sup> Donaldson, Phytochem. 57 (2001) 859–873

<sup>[2]</sup> Agarwal, Planta (2006) 224:1141–1153

# Association of lignin with cellulose

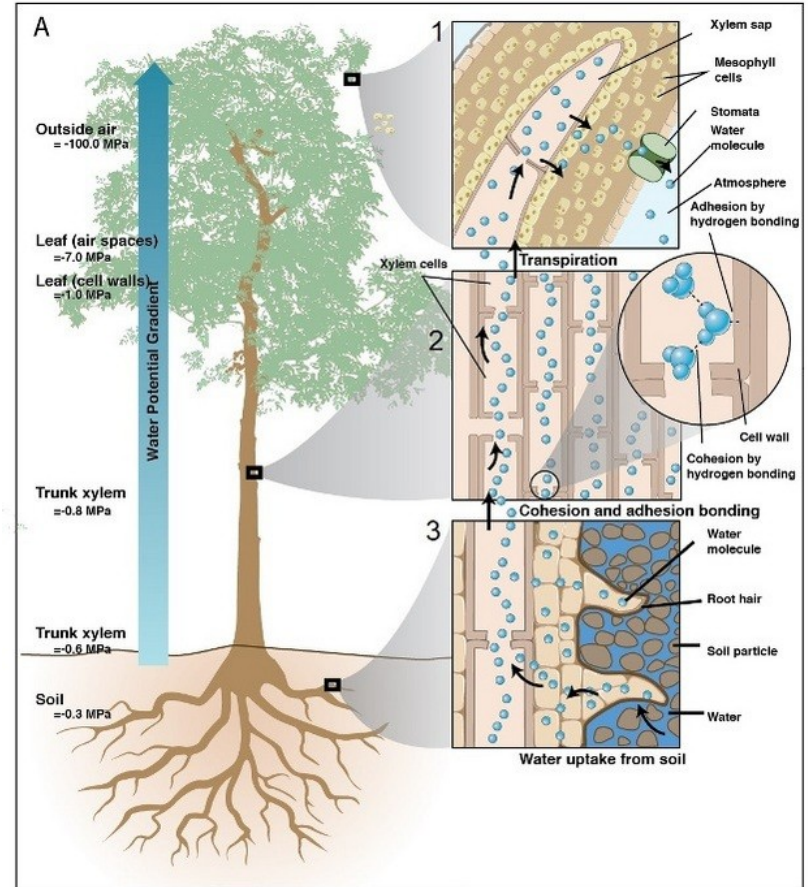
- An unresolved question that is challenging to research by direct methods
  - Lignin adsorbs on cellulosic pulp fibres, a process influenced by metal ions<sup>[1]</sup>
- Molecular modelling:
  - Aromatic rings adopt a parallel orientation with respect to aromatic rings relative to the cellulose surface<sup>[2]</sup>
  - Lignin preferably associates with crystalline regions of cellulose independent of water<sup>[3]</sup>
  - Increased molar mass and branching of lignin hinder adsorption<sup>[3]</sup>



69 lignin dimers on the 16-chain cellulose whisker <sup>[2]</sup>

# Effect of lignin on water transportation

- Enrichment of lignin in the xylem forms unwettable surfaces<sup>[1]</sup> that enable vascular plants to transport water vertically by transpiration (Cohesion-Tension Theory)
- Transpiration is a continuous dynamic process during the lifetime of the tree
- Lignin forms water-impermeable composites with cellulose and hemicelluloses
- Xylem elements are millions of conduits (microtubes) with at least some hydrophobic surfaces<sup>[2]</sup>
- Besides lignin, contain “extractives” i.e. water-insoluble lipids, including phospholipids, and proteins<sup>[2]</sup>
- Lignin also restricts water penetration into ML regions as studied by infiltration of aqueous dye solution<sup>[3]</sup>



[1] Laschimke, Thermochemica Acta, 1989, 151, 35-56

[2] Schenk et al., Plant Physiol. 2017, 173

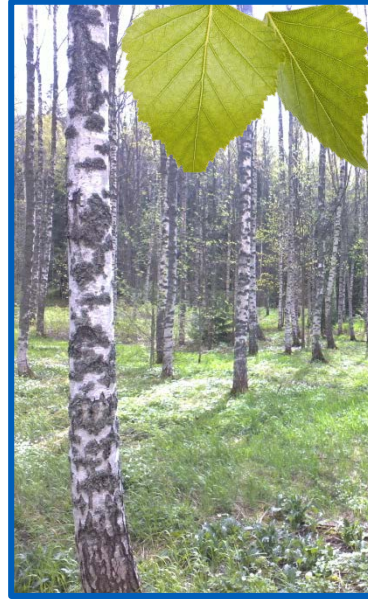
[3] Donaldson et al., 2018 DOI: <https://doi.org/10.1104/pp.18.00883>



# Botanical classification of lignins



Gymnosperms  
"Softwood"  
**G-lignin**

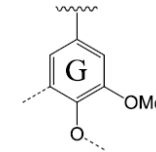


Angiosperm  
dicotyledons  
"Hardwood"  
**GS-lignin**

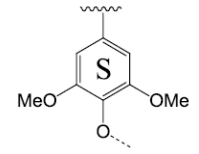


Graminoids  
"Grasses"  
**HGS-lignin**

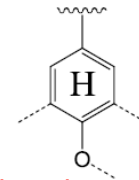
Additionally, lignin in softwood compression wood can be classified as **GH lignin**<sup>[1-2]</sup>



Guaiacyl



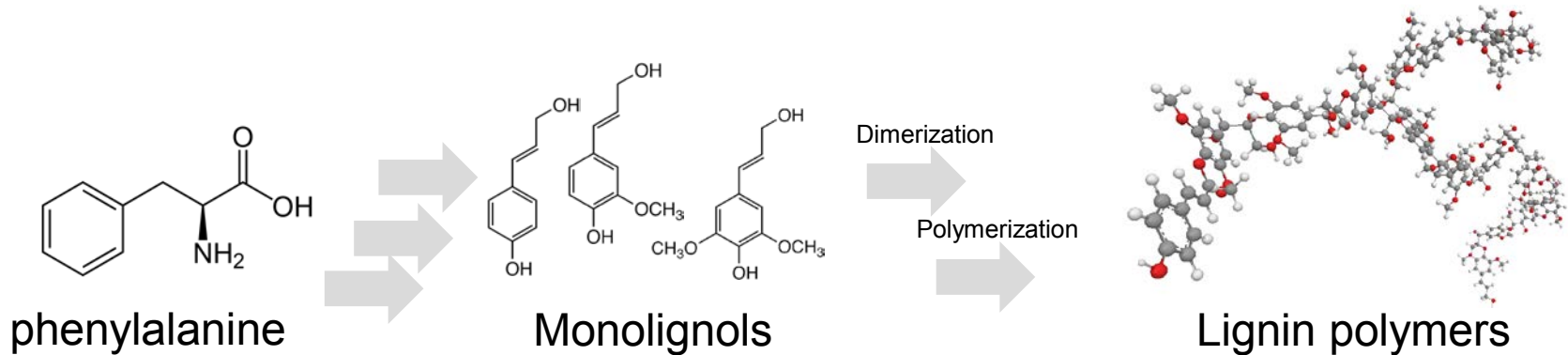
Syringyl



p-Hydroxyphenyl

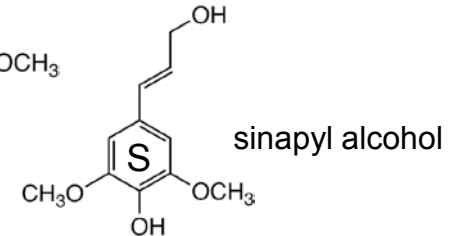
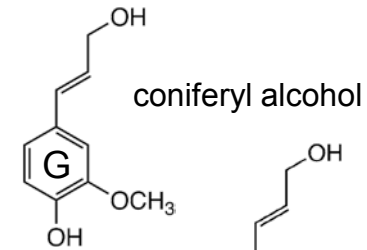
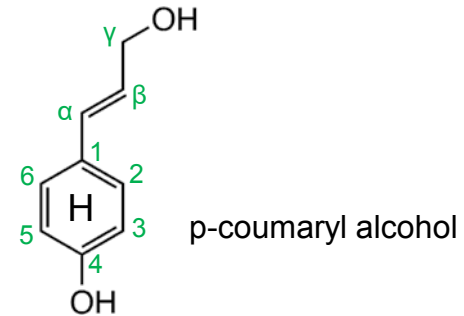
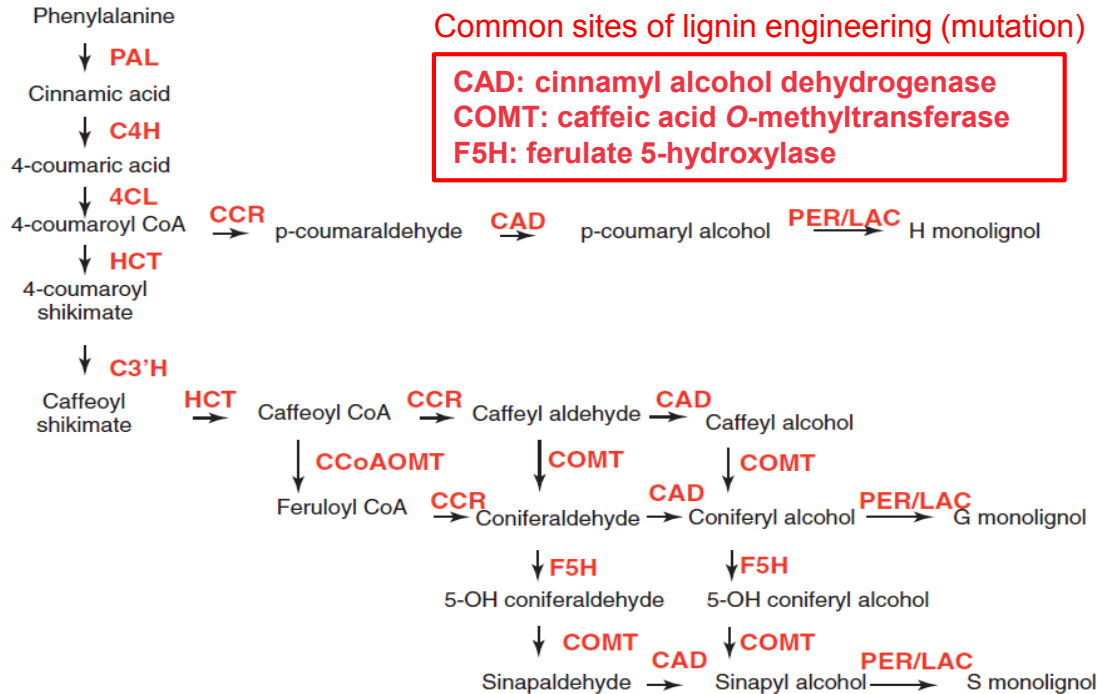
# 2. Biosynthesis and the diversity of molecular structures

- Growing trees and other plants do not "just grow" – they are living organisms with subtle control over biosynthesis
- Lignin is synthesized principally from three precursor monomers which are referred to as monolignols
- Amino acid phenylalanine is the starting point:





# Several enzymes are needed in the monolignol synthesis

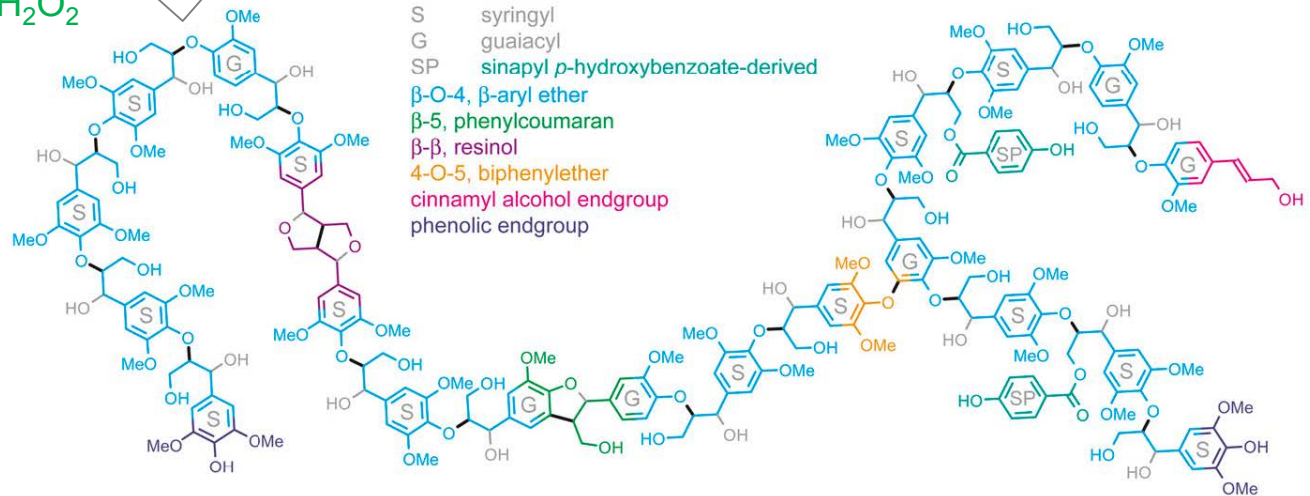
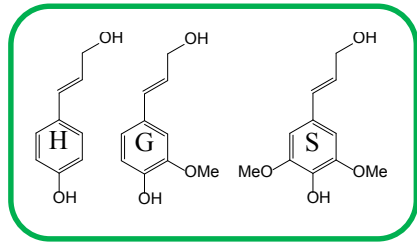


# Lignin polymer is formed from monolignols in enzyme-initiated radical polymerization

enzyme-catalyzed

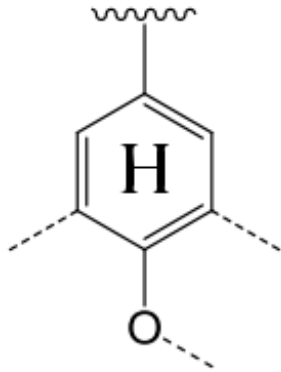
Note: lignification occurs under chemical control i.e. it does not use template control (such as in protein synthesis)

Laccase or  
Peroxidase  
+ H<sub>2</sub>O<sub>2</sub>

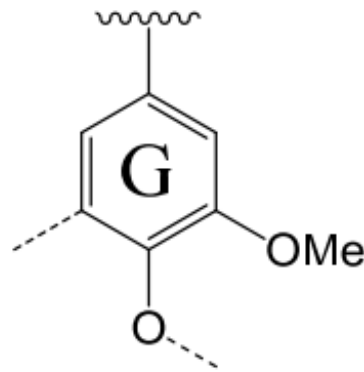


- **Result = mixtures of molecules (not one well-defined compound)**

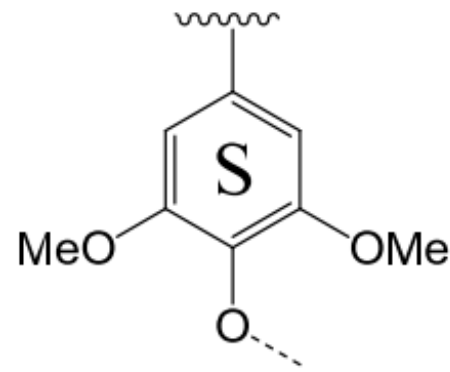
# Naming of the units in the lignin polymer



p-hydroxyphenyl (H)

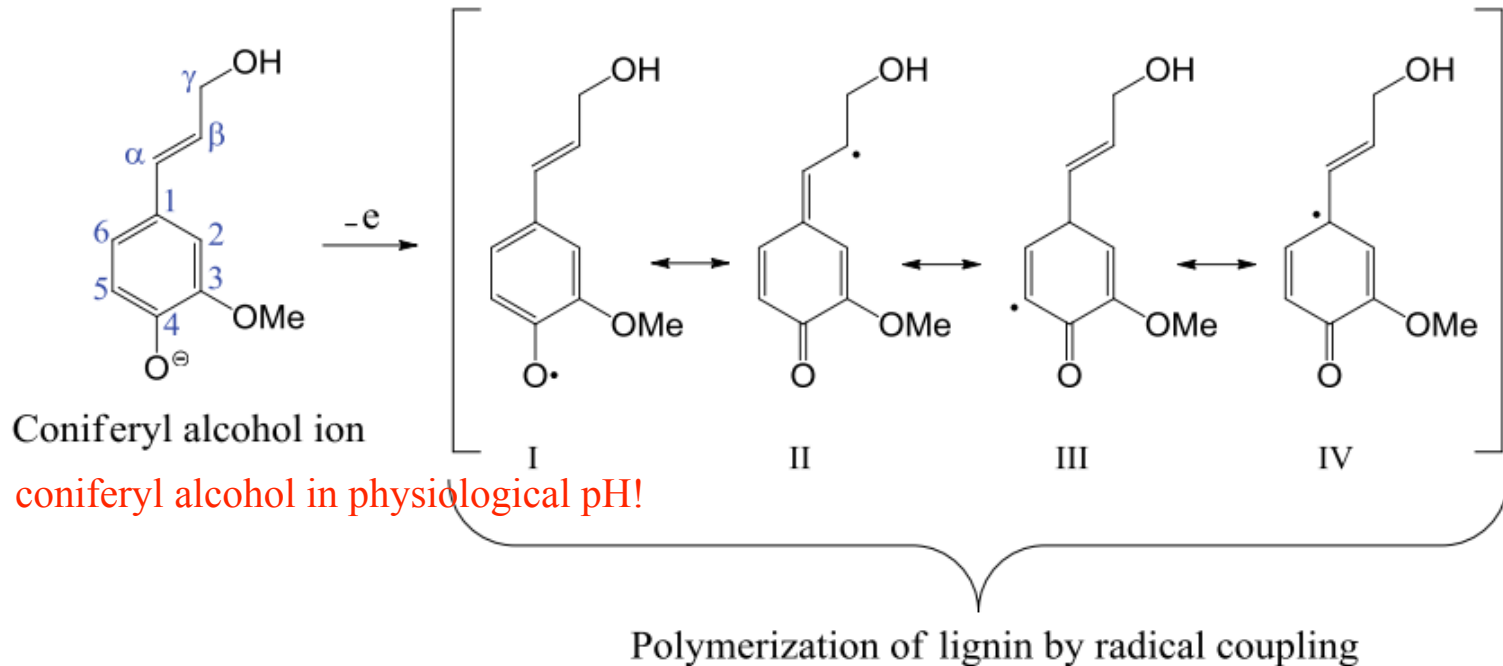


Guaiacyl (G)



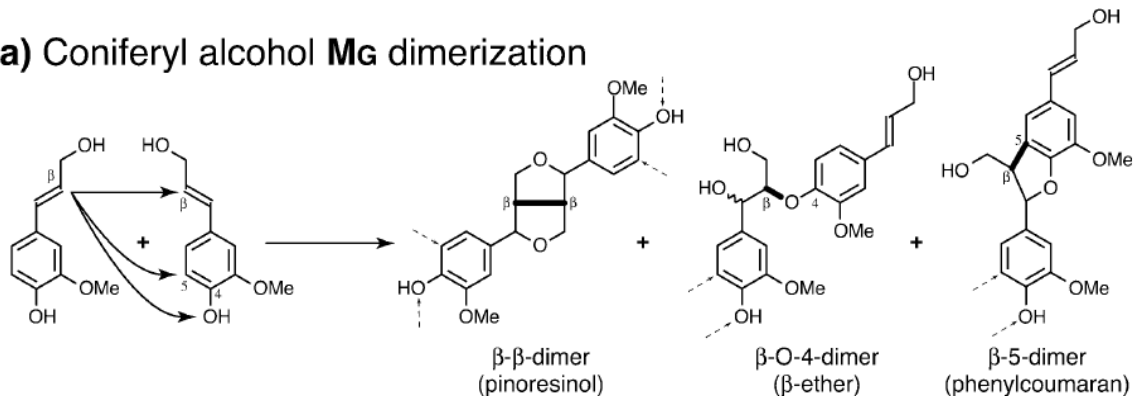
Syringyl (S)

# Example of radical delocalization



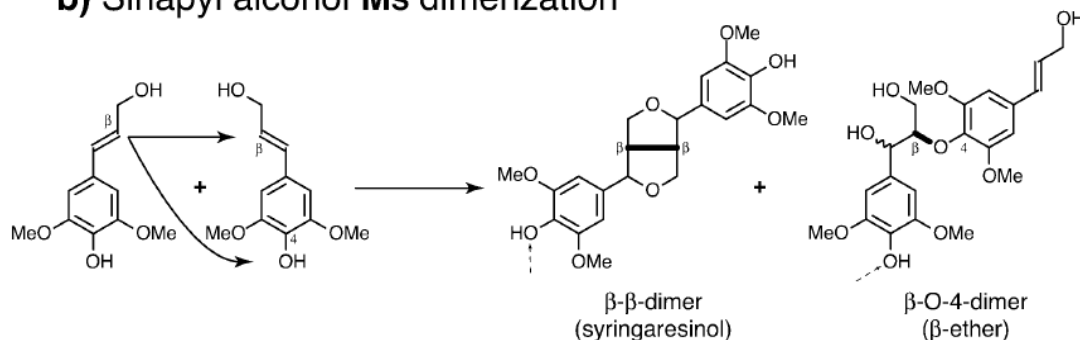
# Dimerization reactions of monolignols

## a) Coniferyl alcohol **Mg** dimerization



**G-G dimers**

## b) Sinapyl alcohol **Ms** dimerization

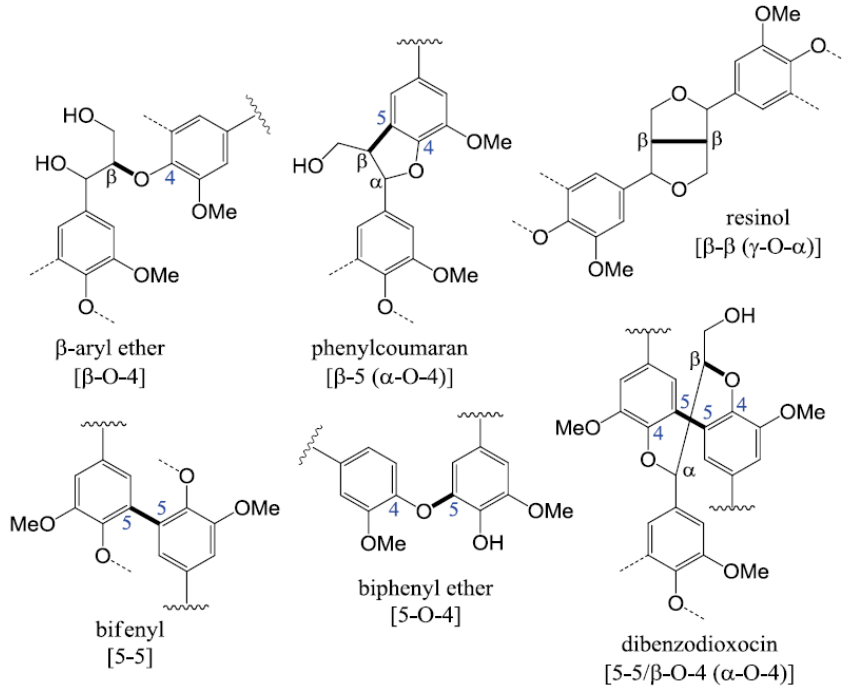


**S-S dimers**



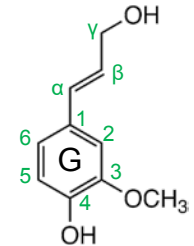
# Major structural units of lignin polymer

- Bolded bonds are formed in radical coupling and other in dimerization reactions



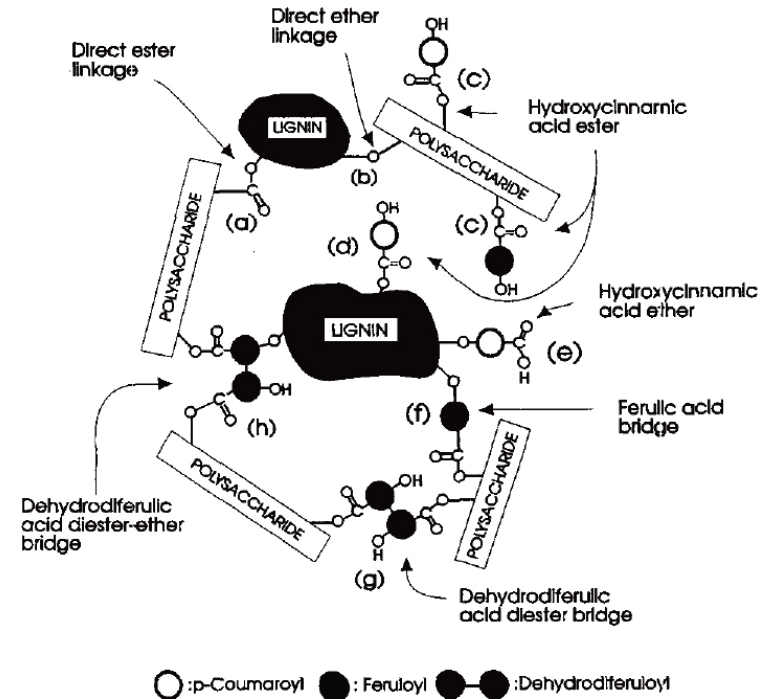
Linkage type	Dimer structure	Approximate percentage
$\beta$ -O-4	Phenylpropane $\beta$ -aryl ether	45–50
$\alpha$ -O-4	Phenylpropane $\alpha$ -aryl ether	6–8
$\beta$ -5	Phenylcoumaran	9–12
5–5	Biphenyl and dibenzodioxocin	18–25
4-O-5	Diaryl ether	4–8
$\beta$ -1	1,2-Diaryl propane	7–10
$\beta$ - $\beta$	$\beta$ - $\beta$ -Linked structures	3

- Units linked to another phenylpropane unit from the aryl ring positions 3 and 5 (~~and 6~~) are referred to as "condensed linkages"



# Covalent linkages between lignin and polysaccharides

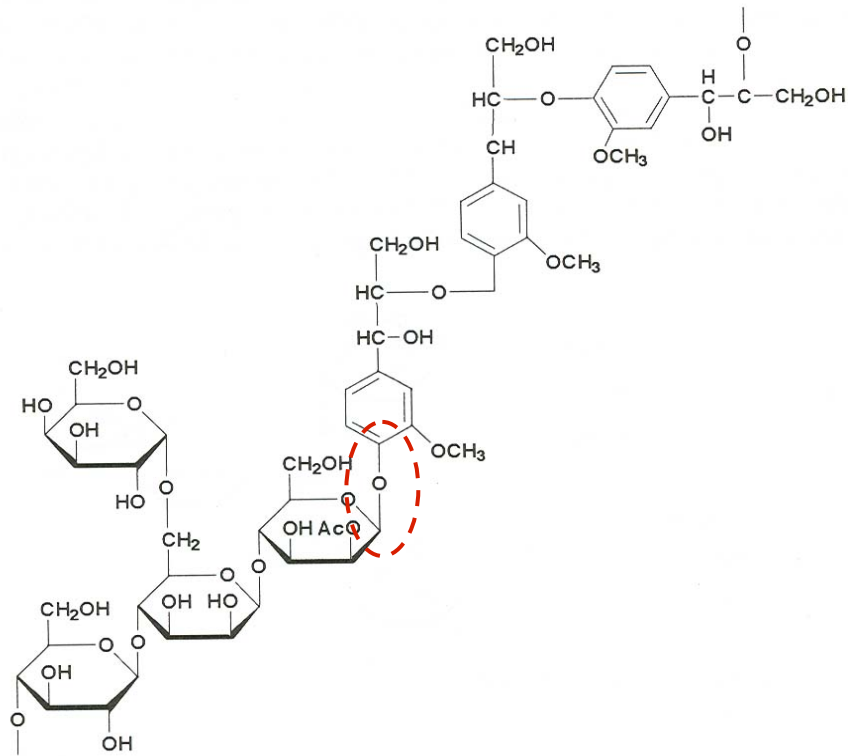
- Lignin-carbohydrate complexes (LCCs) contain ether and ester bonds
- Linkages are mainly between hemicelluloses and lignin
- LCCs contribute to the cell wall integrity and difficulty of delignifying residual lignin<sup>[1]</sup>
- Lignin carbohydrate network (LCN) must be disrupted for enzymatic saccharification of plant biomass



A schematic illustration of LC-linkages in grasses<sup>[2]</sup>



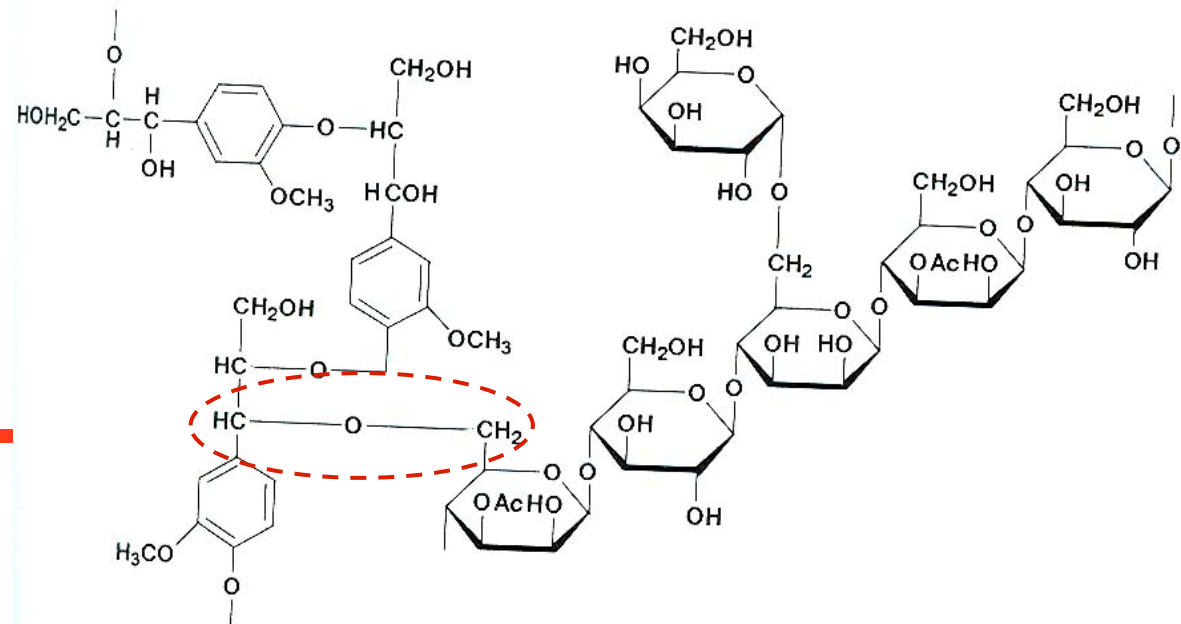
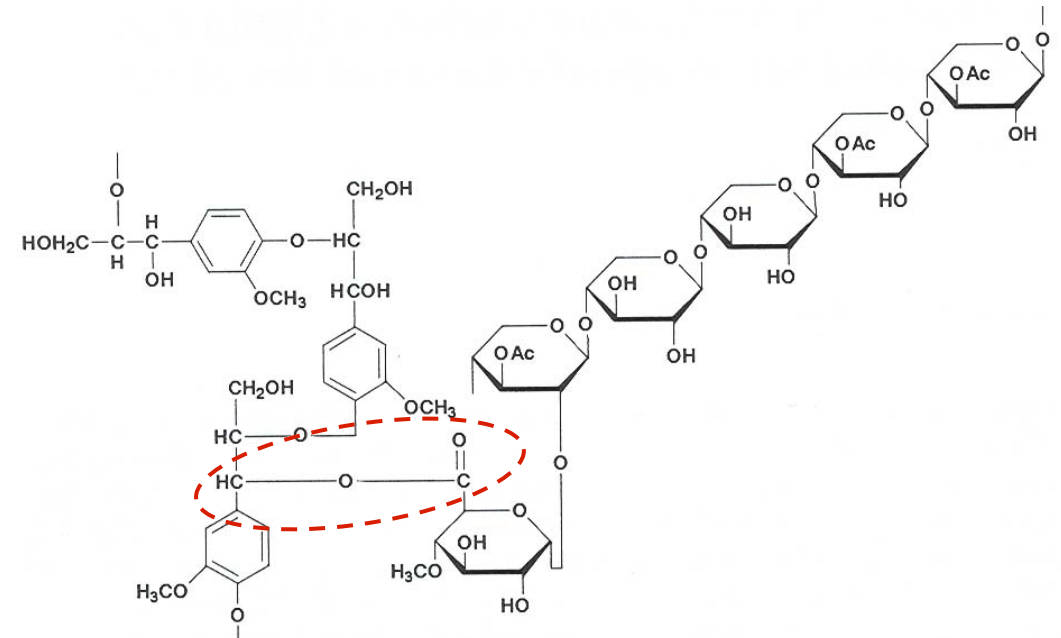
# Lignin-Carbohydrate Linkages



Phenyl glycoside

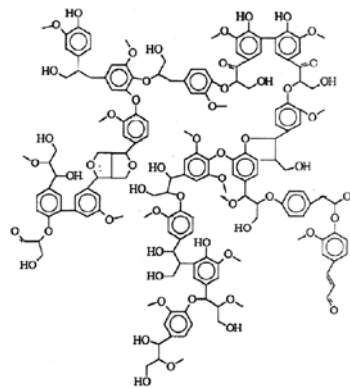
Benzyl ether

Benzyl ester

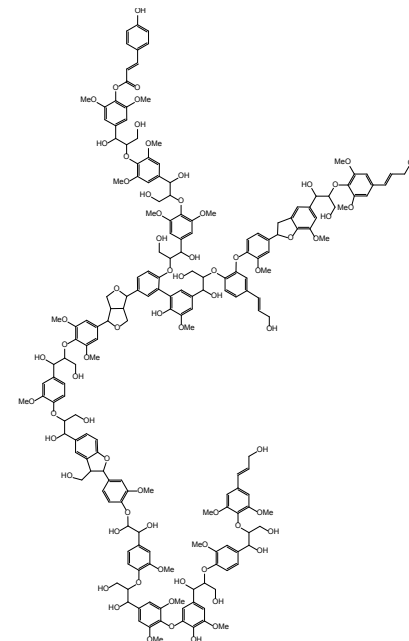


# Notes on structure and molecular weight of lignin

- Native lignins seem less branched & less cross-linked,<sup>[1]</sup> and having lower Mw than lignins from thermochemical processes
- Lignin isolated from wood using "mild" processing was oligomeric<sup>[2]</sup>
- Average molar mass of lignin varies from 2 kDa to ~50 kDa, and may be overestimated by size-exclusion chromatography<sup>[3]</sup>
- The analysis of lignin will be dealt more in-depth later in the lecture



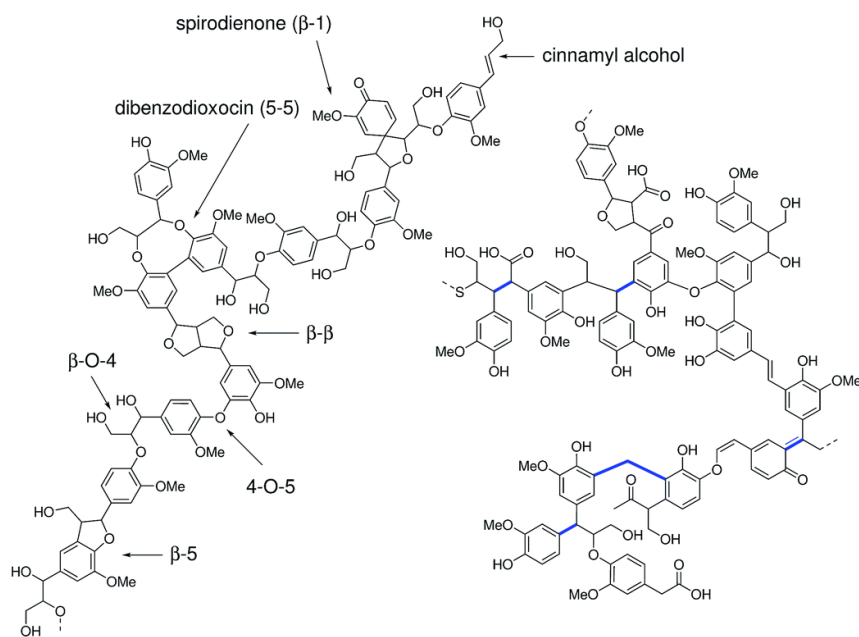
Hardwood lignin model<sup>[4]</sup>  
Softwood



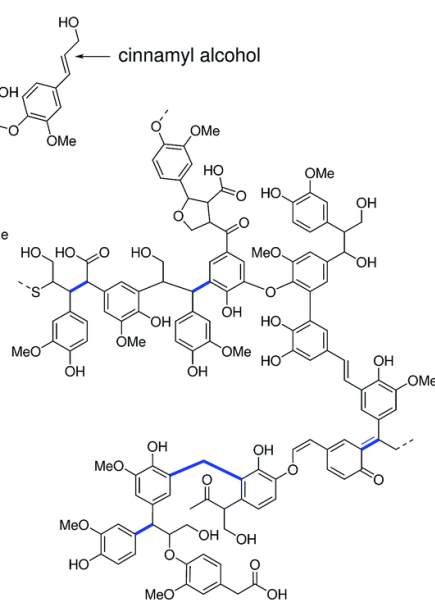
Wheat straw lignin model<sup>[5]</sup>

# Examples of Kraft lignin and native lignin structures

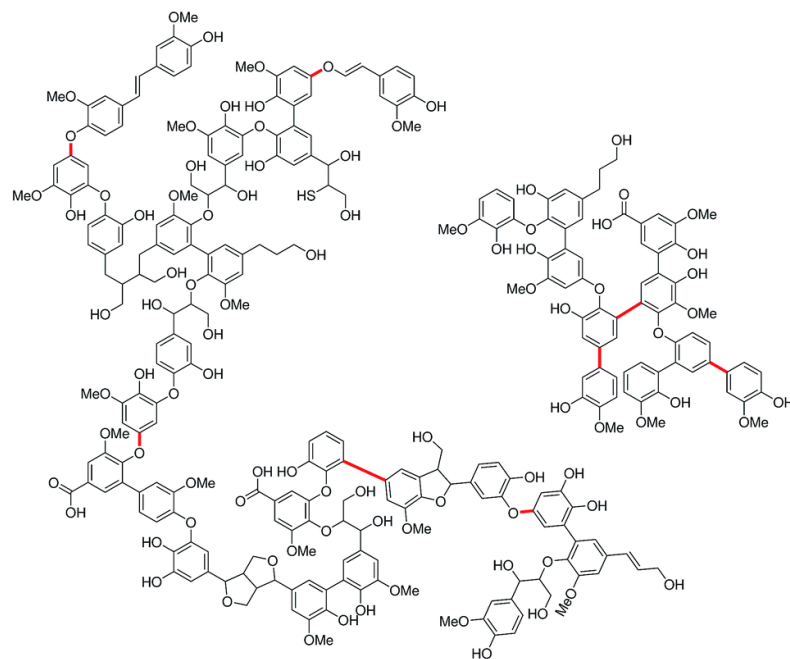
The view has changed during time



**Native Softwood Lignin**



**Marton's Kraft Lignin**



**Crestini and Argyropoulos' Kraft Lignin**

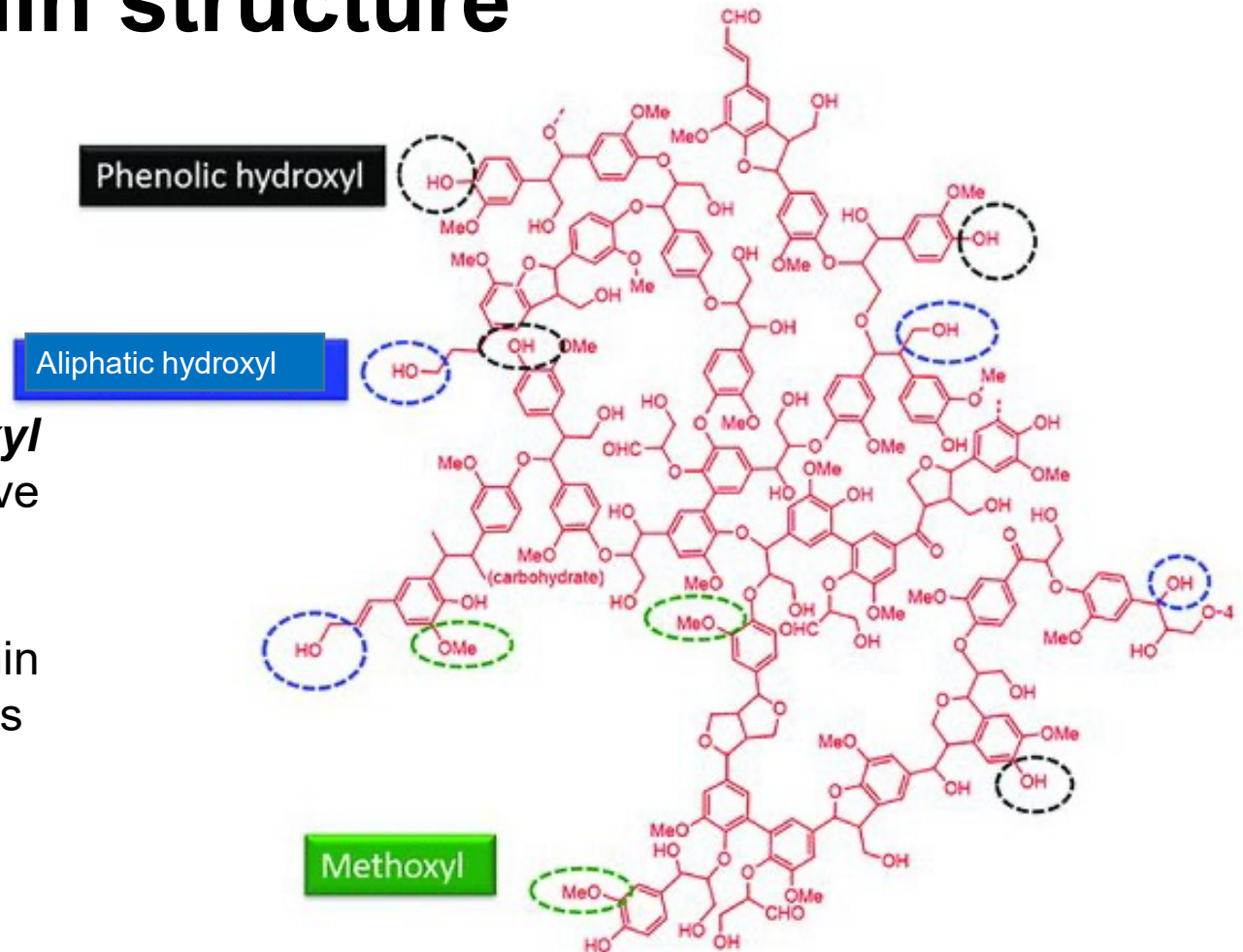
# Functional groups in lignin structure

**Hydroxyl groups** – aliphatic and phenolic

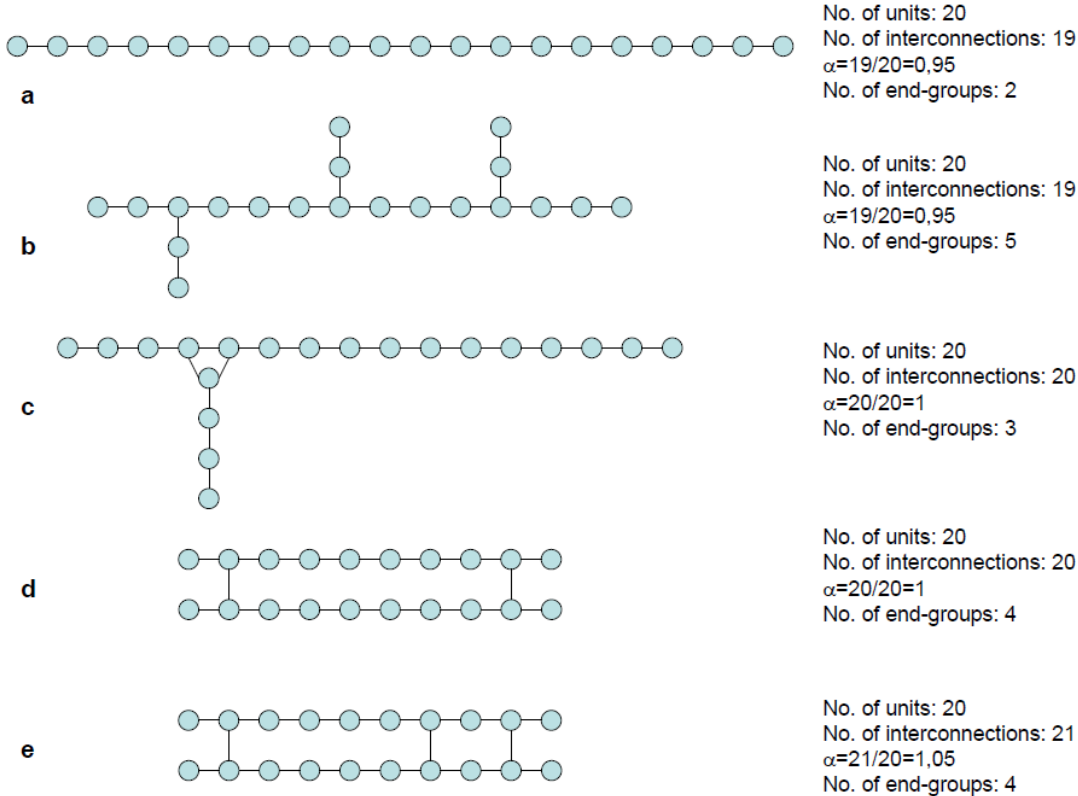
**Methoxyl groups**

**Carbonyl groups** – *aldehyde, ketone, and carboxyl groups*. **Carboxyl groups** are not intrinsic for native lignin and are formed during lignin modifications

**Sulphonic acid groups** – are not intrinsic for lignin and are formed during processing in liginosulphonates

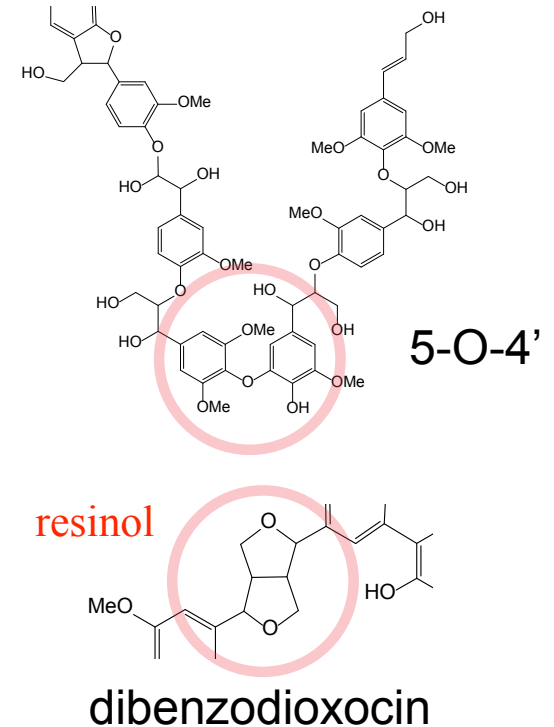


# Branching and end groups



● = lignin unit      — = inter-unit linkage

## Examples of branching points:



# 3. Industrial relevance

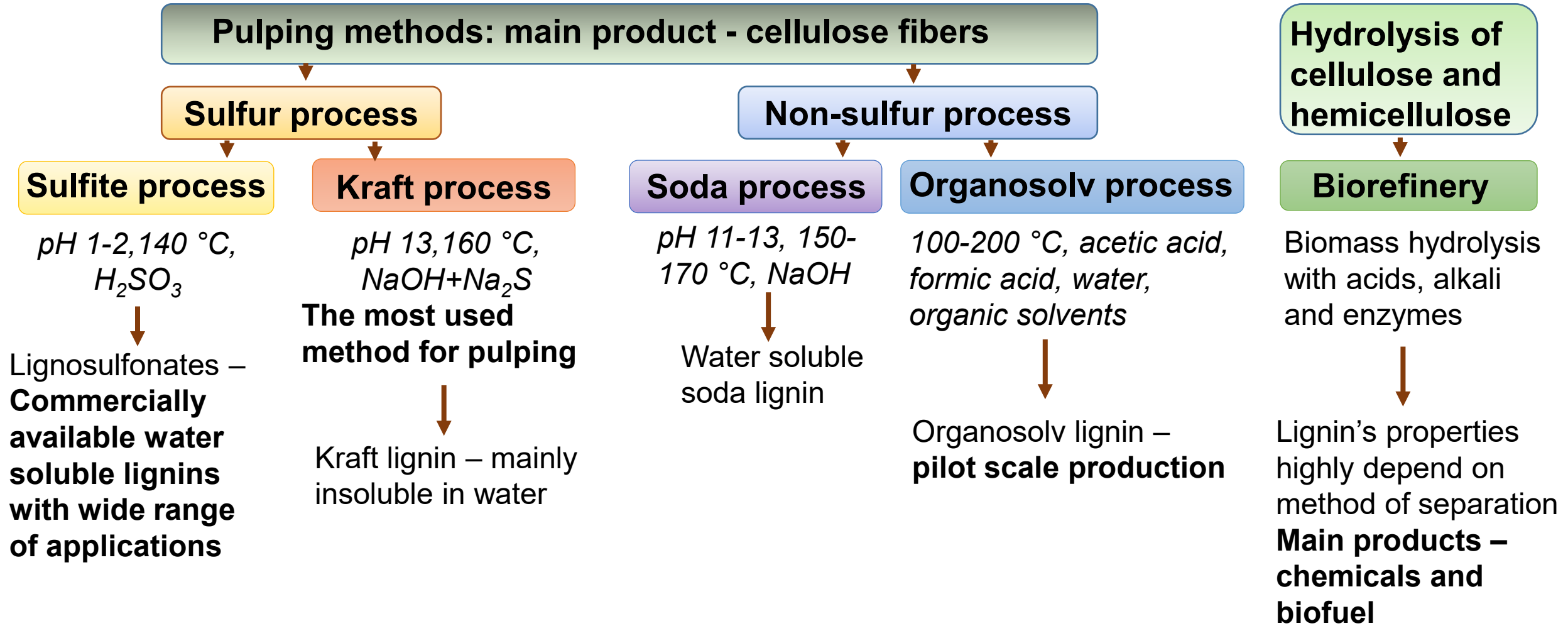
- Lignin is removed from fibers during cellulose pulp production
  - Provides surplus energy for the pulp mills
- Kraft, soda, sulfite, organosolv processes rely on different chemical reactions
- Lignin is a structural constraint and inhibitor in biochemical conversion of plant biomass into fuel ethanol
- Biorefineries produce soluble and insoluble lignin
  - A spectrum of different hydrothermal and thermochemical lignocellulose pretreatment processes are under development



<https://www.metsafibre.com/PublishingImages/ECHO/Echo-1-2015/Echo-1-2015-%C3%84%C3%A4nekoski-bioproduct-mill.jpeg?RenditionID=14>



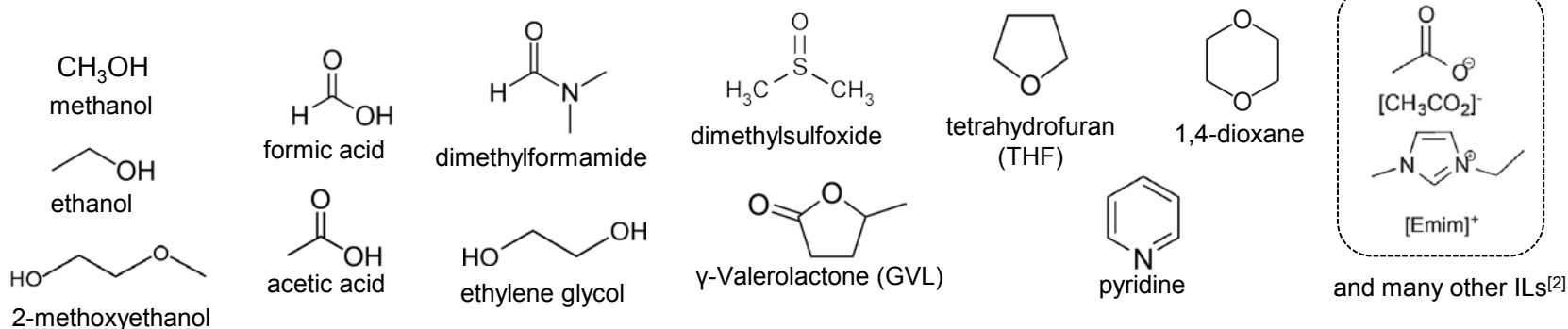
# Industrial methods of lignin production from biomass



**Note!** Industrial methods of lignin production make significant changes to lignin structure!

# 4. Fundamental properties and reactivity

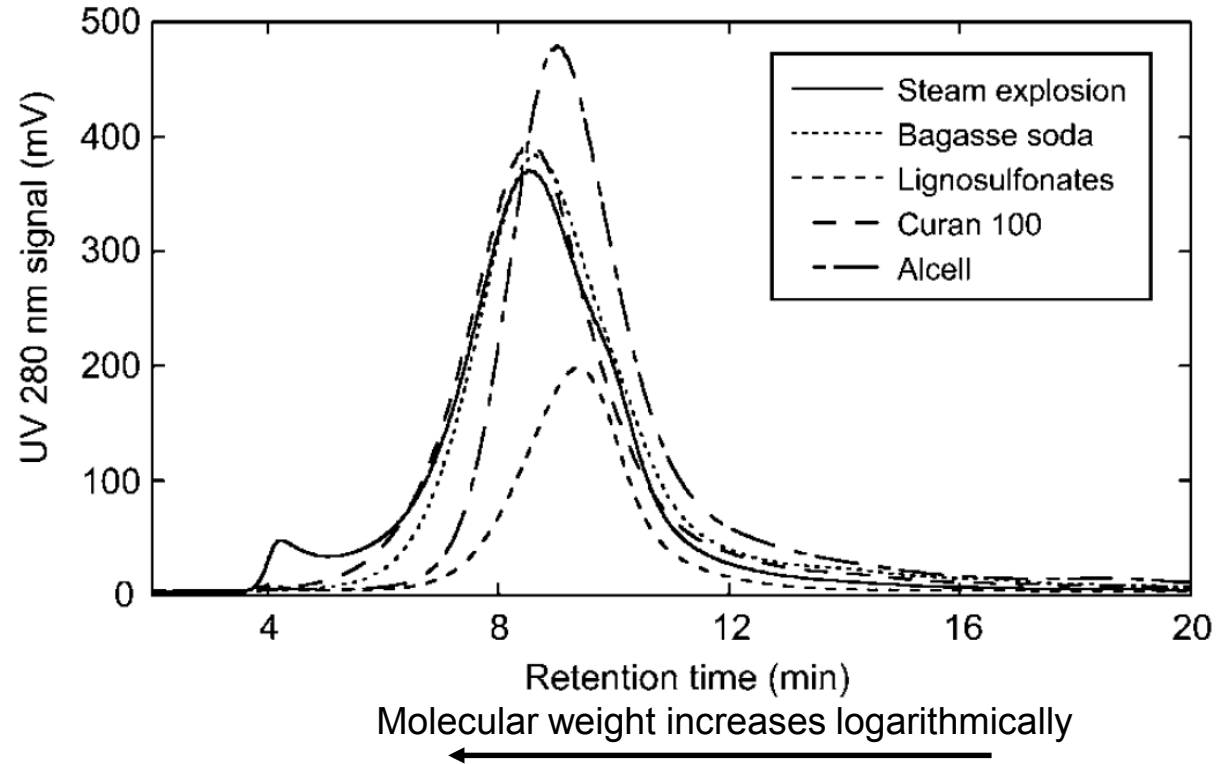
- Lignins are negatively charged in aqueous solutions (in alkaline solutions)
  - pKa of phenolic hydroxyl groups vary between (7–10,<sup>[1]</sup>) depending on the neighbouring substituents; carboxylic acids have generally pKa < 4 4-5
- Solubility of lignin is important for industrial utilization and analytical work
  - Lignins are usually soluble in alkaline water and often (but not always) also in polar organic solvents and ionic liquids such as:





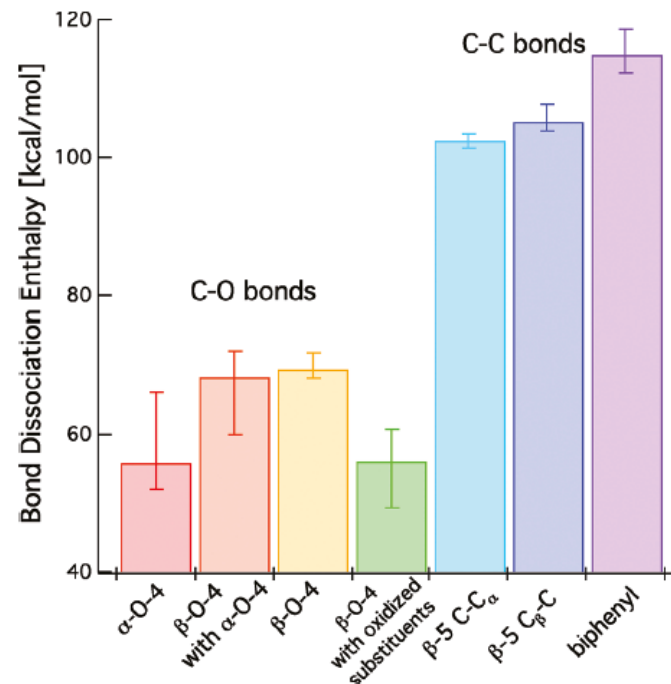
# Polydispersity of lignin

- When isolated from wood, lignin contains molecules at various molecular weights
- Small lignin oligomers are naturally present also in plant biomass



# Stability of covalent bonds in lignin

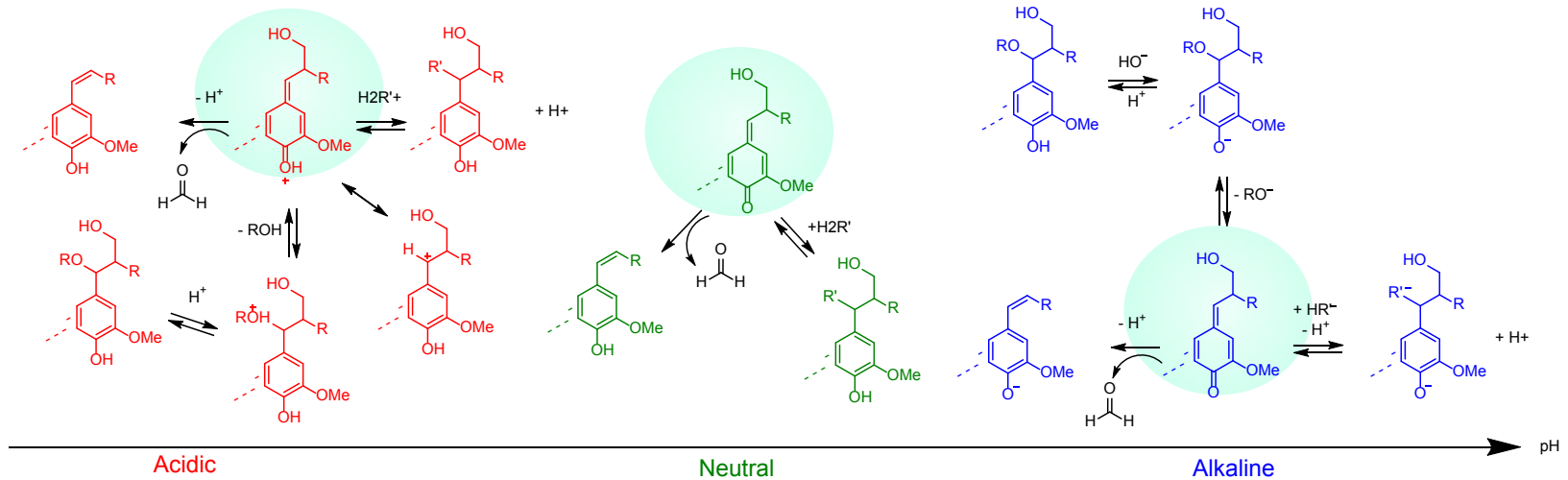
- **Bond dissociation enthalpies (BDE) based on density functional theory calculations:**
  - $\alpha$ -O-4 in GG pinoresinol, 284 kJ/mol<sup>[1]</sup>  $\beta$ -O-4 (native) HG, 292 kJ/mol<sup>[2]</sup> SS 295 kJ/mol<sup>[3]</sup>
  - C-O are weaker than C-C bonds
  - Side-chain oxidation decreases BDE
- **Note that lignin is more reactive in thermochemical conditions because of:**
  - Formation of reactive quinone methide intermediates
  - Neighbouring group participation



Kim et al., 2011

# Quinone methide intermediates are important reactive forms of lignin

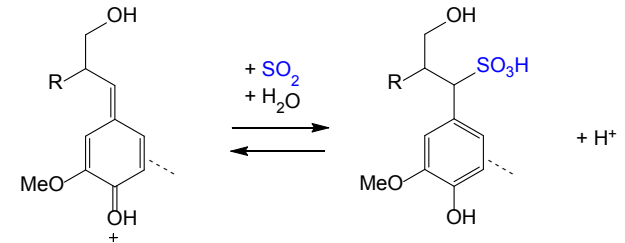
R' = O, S, SO<sub>3</sub> or internal nucleophile  
R = OAr, Ar or Alk



Reactions of lignin through the quinone methide intermediate in acidic, neutral and alkaline media.<sup>[1]</sup>

# Sulfonation of lignin

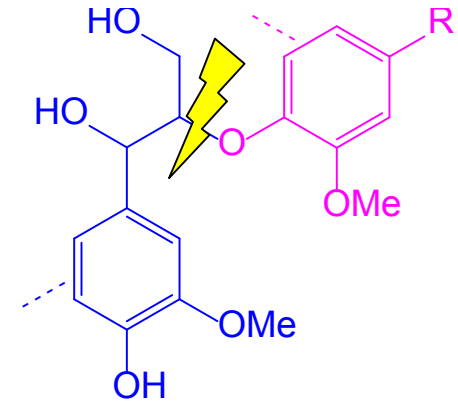
- Formation in acid sulphite pulping
- Sulfoxyl groups ( $pK_a < 2$ ) give water-solubility within a broad pH region
- Lignosulfonates are industrial chemicals:
  - Plasticizers and additives in concrete and cement production
  - Viscosity reducing additive in oil drilling mud
  - Dispersants in pesticides, dyes, carbon black
  - Vanillin production (example follows later)



Sulfonation of lignin<sup>[1]</sup>

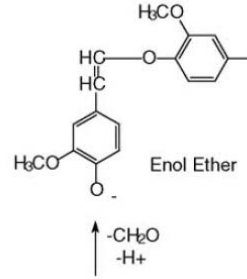
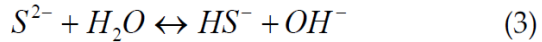
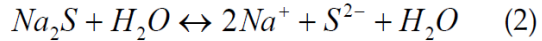
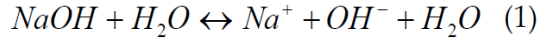
# Cleavage of $\beta$ -O-4 bonds in pulping processes

- The most important scission reaction in lignin chemistry, why?
  - Because  $\beta$ -O-4 bonds are so abundant and thermochemically labile
- Basis of delignification: depolymerisation & dissolution in cellulose pulp production
  - Increases the content of phenolic hydroxyls
  - Side reactions form new C-C bonds



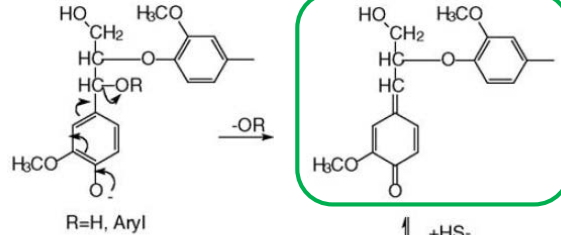
# $\beta$ -O-4 cleavage during kraft cooking

Formation of active species in kraft pulping<sup>[1]</sup>

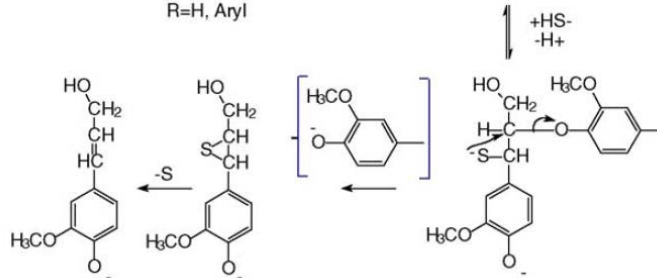


Elimination of formaldehyde

Formation of the reactive quinone methide intermediate

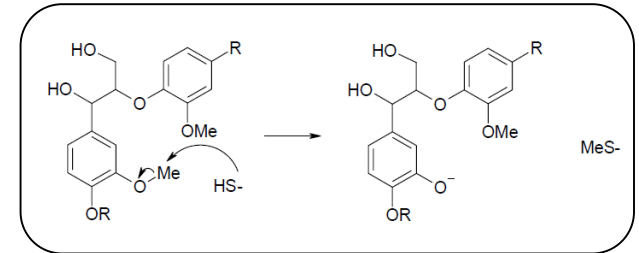


Sulfidolytic cleavage of  $\beta$ -aryl ether bonds



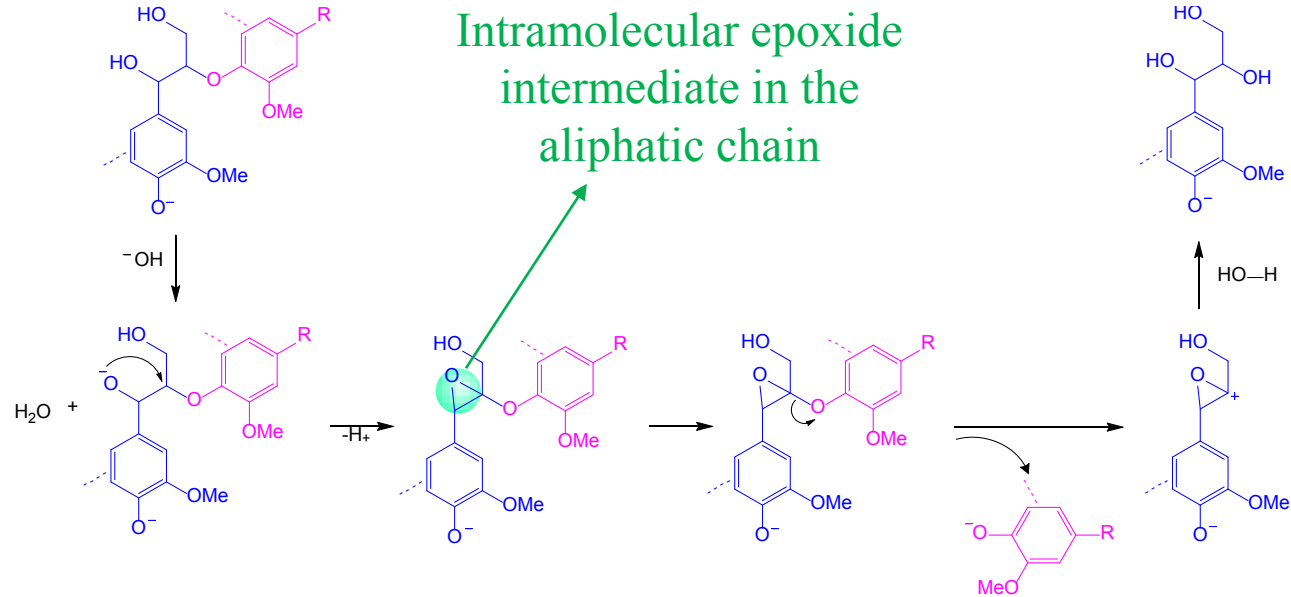
A simplified reaction scheme of kraft cooking<sup>[2]</sup>

- The cooking takes place at 160-180 °C and lasts 1-2 h
- Demethylation and condensation occur also<sup>[1]</sup>



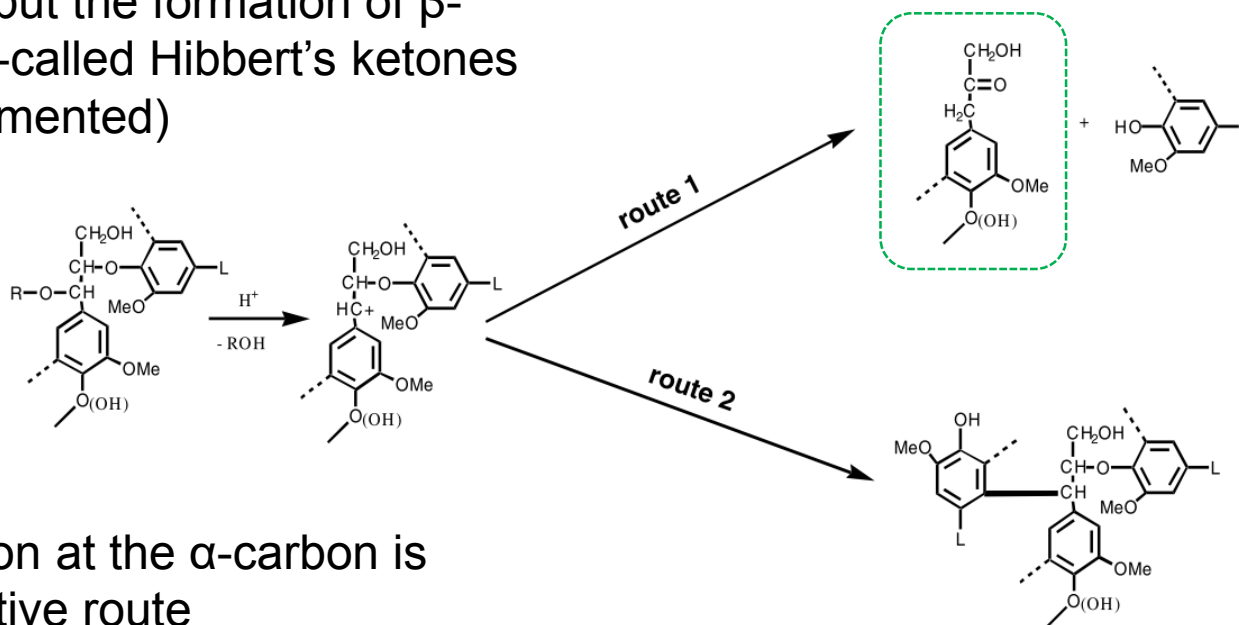
# $\beta$ -O-4 cleavage during soda (NaOH) cooking

Reaction occurs via neighbouring group participation



# $\beta$ -O-4 cleavage in acidic conditions

- Exact mechanism had not been fully elucidated, but the formation of  $\beta$ -ketones (so-called Hibbert's ketones) is well documented

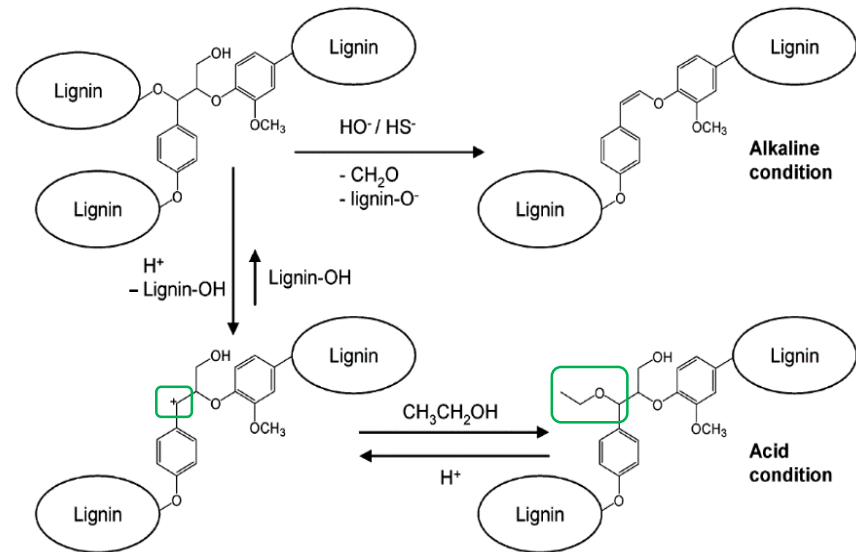


- Condensation at the  $\alpha$ -carbon is the competitive route



# Organosolv pulping: ethanol-water process as an example

- Ethylation of the carbocation at C $\alpha$  reduces formation of condensed linkages
- This is one reason why organosolv lignins have low Mw, Tg, and dissolve well in organic solvents

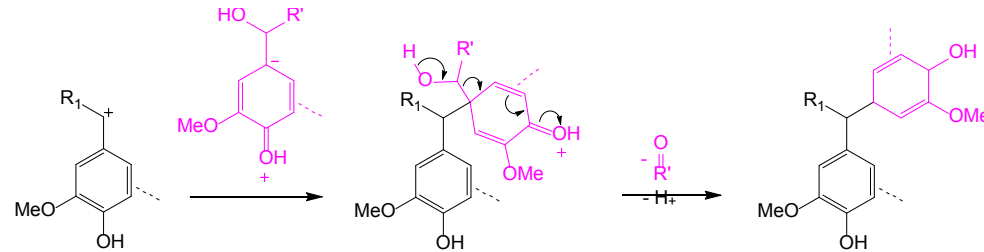


Proposed ethylation of lignin in organosolv pulping<sup>[1]</sup>

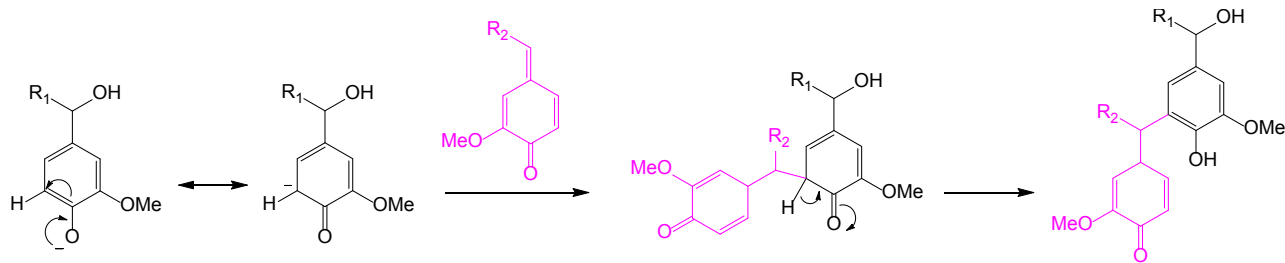
# Formation of chemically stable "condensed" linkages

- Generally, condensed linkages reduce solubility and increase molecular weight of lignin
- Occurs either in acidic or alkaline media, for example:

Acidic media:



alkaline media:



# 5. Isolation and purification of lignin

## Industrial lignin production

- Lignosulfonates (~1100 kt per year)
  - Borregaard LignoTech (Norway) is the main producer
- Kraft (sulfate) lignin (~100 kt per year)
  - WestRock (formerly MeadWestvaco) (US)
  - 2013: Domtar, North Carolina (US)
  - 2015: Stora Enso, Sunila (Finland)
  - 2016: West Fraser LignoForce 30 t/day demonstration plant

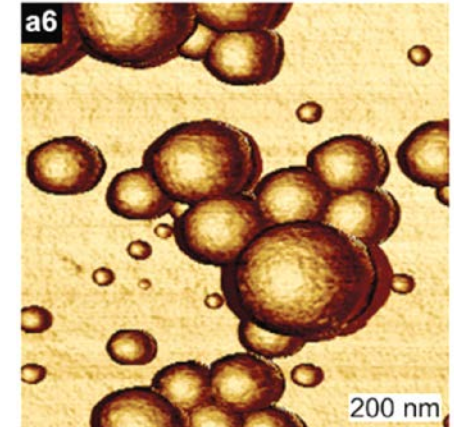


Stora Enso's Sunila mill

<http://www.hs.fi/webkuva/taysi/700/1374823934135?ts=763>

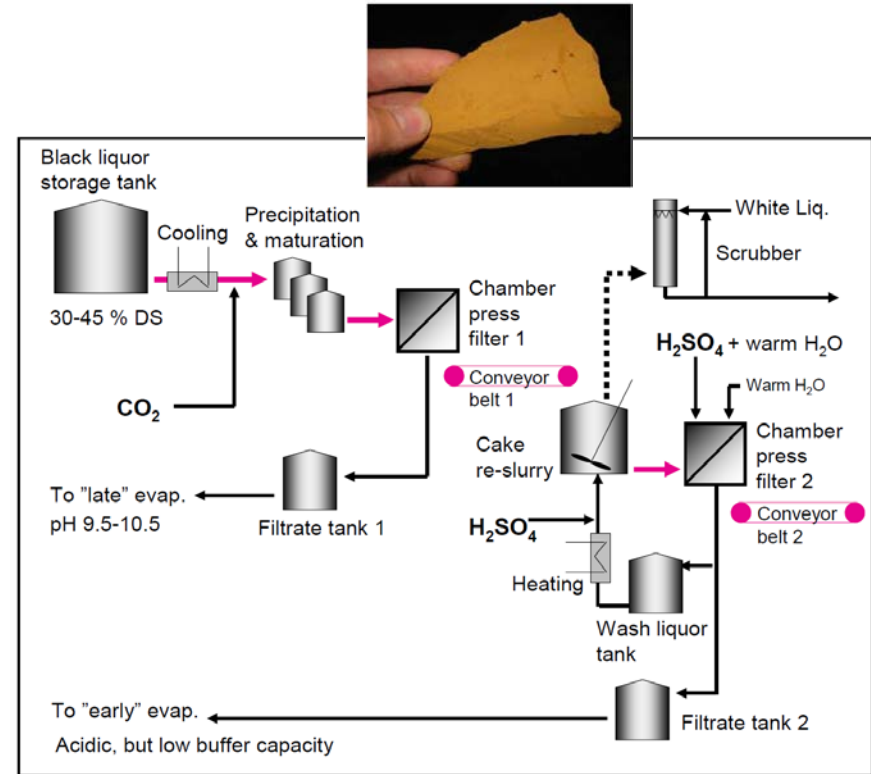
# Isolation of lignin from spent pulping liquors

- Acid precipitation from alkaline solution: recall that lignin contains acidic groups which ionize above pH 4 and pH 7–10: precipitation occurs when anionic charge is reduced so that aggregation occurs
- Complexation with metals or cationic polymers
- Solvent-exchange precipitation: lignin precipitates from organic solvent solution when mixed with water
  - Used in the formation of colloidal lignin particles<sup>[1,2]</sup>
- Membrane technology using small pore sizes ~1 kDa



# Commercial lignin isolation processes

- Based on the capacity of  $\text{CO}_2$  to reduce pH and precipitate lignin at pH 10
  - Carbon dioxide precipitation of lignin from pine kraft black liquor<sup>[1]</sup>
- Lignoboost technology was further developed by Innventia and acquired by Valmet
- LignoForce technology oxidizes lignin before  $\text{CO}_2$  precipitation<sup>[2]</sup>



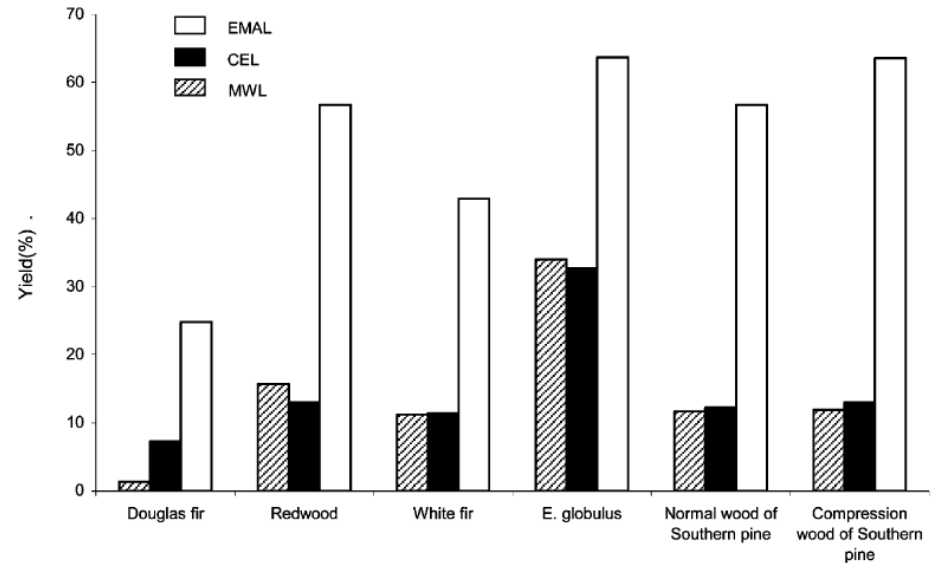
Tomani, Cellulose Chem. Technol., 44 (1-3), 53-58 (2010)

<sup>[1]</sup> Alén et al., Tappi 62: 11 (1979) 108-110.

<sup>[2]</sup> [https://www.lemaitrepapetier.ca/images/stories/documents/articles%20techniques/J-FOR\\_Vol2-issue4-ART1-The%20Lignoforce%20System.pdf](https://www.lemaitrepapetier.ca/images/stories/documents/articles%20techniques/J-FOR_Vol2-issue4-ART1-The%20Lignoforce%20System.pdf)

# Analytical lignin isolation methods

- Isolation of lignin causes always some structural alteration
- In the Milled Wood Lignin (MWL) method, wood is ground in a ball mill and subsequently extracted with aqueous Dioxane
- Cellulolytic enzyme lignin (CEL) and Enzymatic Mild Acidolysis Lignin (EMAL) procedures remove polysaccharides using hydrolytic enzymes before extraction of lignin with (acidic) aq. dioxane

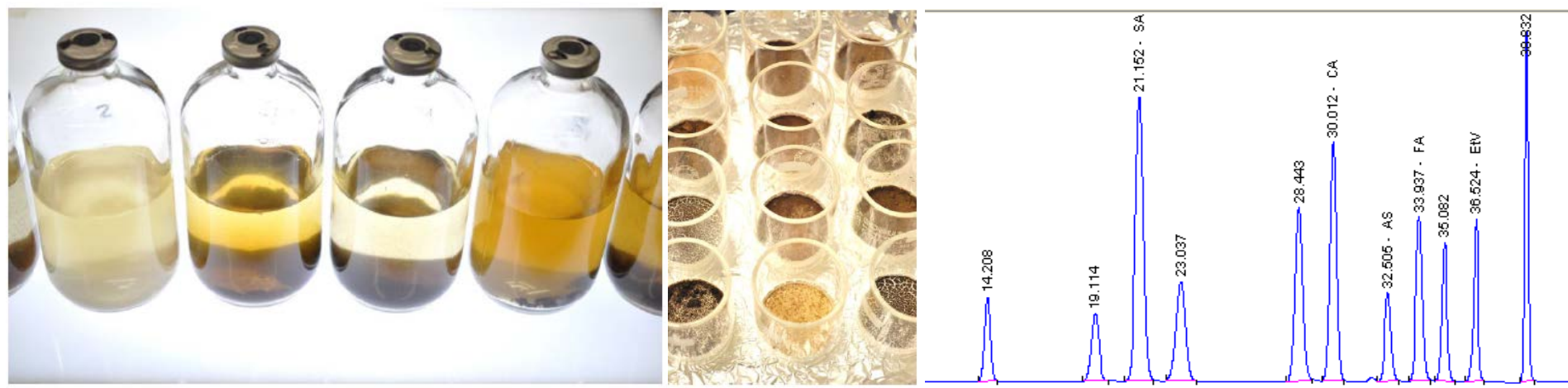


# 6. Chemical modification of lignin

- In order to analyze structure of lignin or to render it more suitable to applications, chemical or enzymatic derivatizations are used
- Some common chemical modification reactions:
  - Acetylation
  - Methylation
  - Carboxymethylation
  - Cationization
  - Cross-linking
- Various other organic compounds such as fatty acids can be grafted to lignin
- The enzyme laccase has been used to oxidize and cross-link lignins



# 7. Characterization of lignin



# Tools for characterization of lignin

- Combination of wet chemistry with spectroscopy, chromatography, and various other techniques
- Characterization in liquid or solid state?
  - **Liquid state:** functional groups, molecular weight, interunit linkages
  - **Solid state:** material properties , functional groups and elemental composition, imaging of the physical structure
- A few illustrative examples follow

# Solution-state analysis of lignin

- **Chemical degradations combined with chromatography**
  - Oxidations: ozonolysis, permanganate oxidation, nitrobenzene oxidation, **cupric oxide oxidation**
  - Reductive treatments: **thioacidolysis**, DFRC
  - Chromatography is used to quantify the products
- **NMR spectroscopy**
- **Size-exclusion chromatography**

# Wet chemistry methods

Before NMR, chemical degradation reactions were the only way to get structural information of lignin:

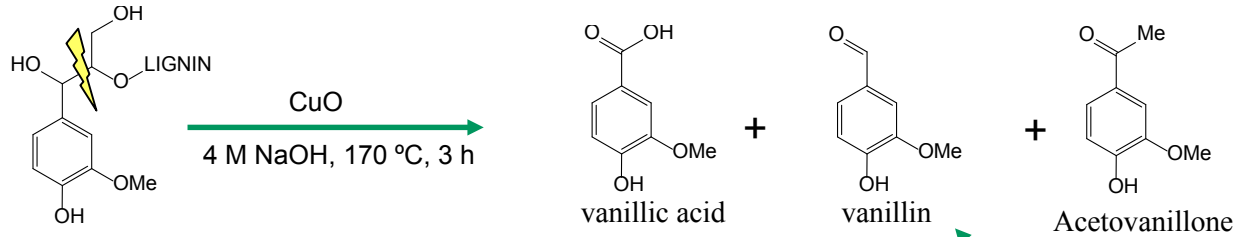
- Acidolysis, thioacidolysis and hydrogenolysis
- Alkaline nitrobenzene oxidation
- Permanganate oxidation
- Periodate oxidation
- Reductive cleavage followed by derivatization (DFRC)

Techniques are based on analyzing the degraded monomer fragments of lignin by chromatographic methods: GC-FID, GC-MS, HPLC-MS

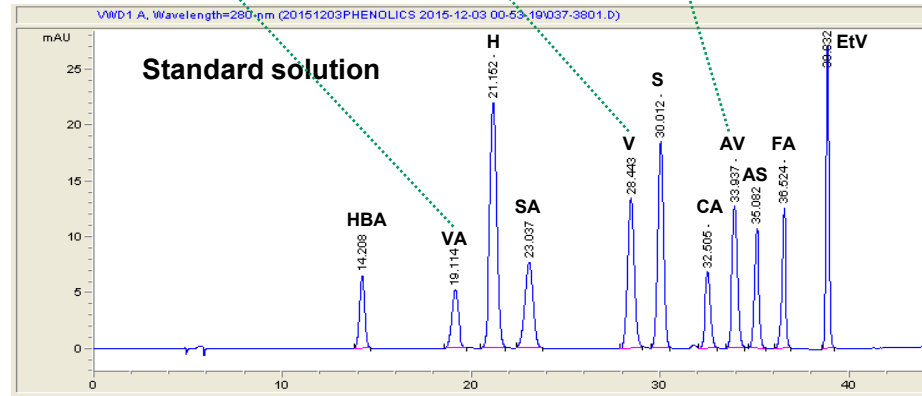
- Well established, selective, quantification
- Tedious, sample preparation and analysis costly, toxic reagents or products
- Require calibration standards

# Cupric oxide oxidation

- A classical oxidative degradation method still in use today due to its simplicity
- Reaction mechanism involves radical oxidation

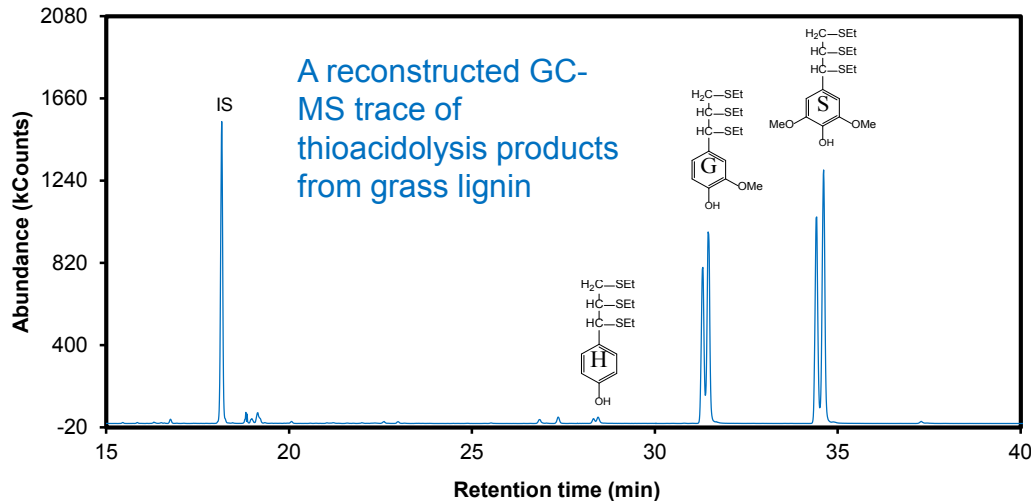


Note that regardless of the lignin source vanillin is always the main product

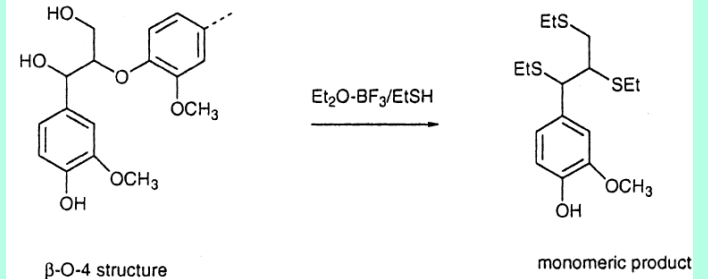


# Thioacidolysis

- Comparable information as from CuO oxidation, but more specific to  $\beta$ -O-4 cleavage and yields less degradation side-products
- Solvolytic cleavage of lignin in the presence of ethanethiol
- Malodorous (EtSH) and harmful ( $\text{Et}_2\text{O-BF}_3$ ) reagents limit applicability



## Primary reaction in thioacidolysis:



Brunow G (2001) Methods to Reveal the Structure of Lignin. In: Hofrichter M & Steinbüchel A, (ed), Lignin, Humic Substances and Coal, Vol 1 (pp. 89–116). Wiley-VHC, Weinheim.

# Spectroscopic techniques

- UV(vis)– detection of aromatics and conjugated double bonds, possibility to quantification
- FTIR – determination of functional groups
- Raman -
- NMR experiments – knowledge of structure and specifically the lignin phenylpropane interconnecting bonds
  - 1D ( $^1\text{H}$ ,  $^{13}\text{C}$ )
  - 2D (HSQC, HSQC-TOCSY, HMBC)
  - $^{31}\text{P}$
  - Qualitative
  - Quantitative
- Pyrolysis-GCMS – thermal decomposition ‘fingerprint’, aromatic unit composition, lignin-carbohydrate ratio



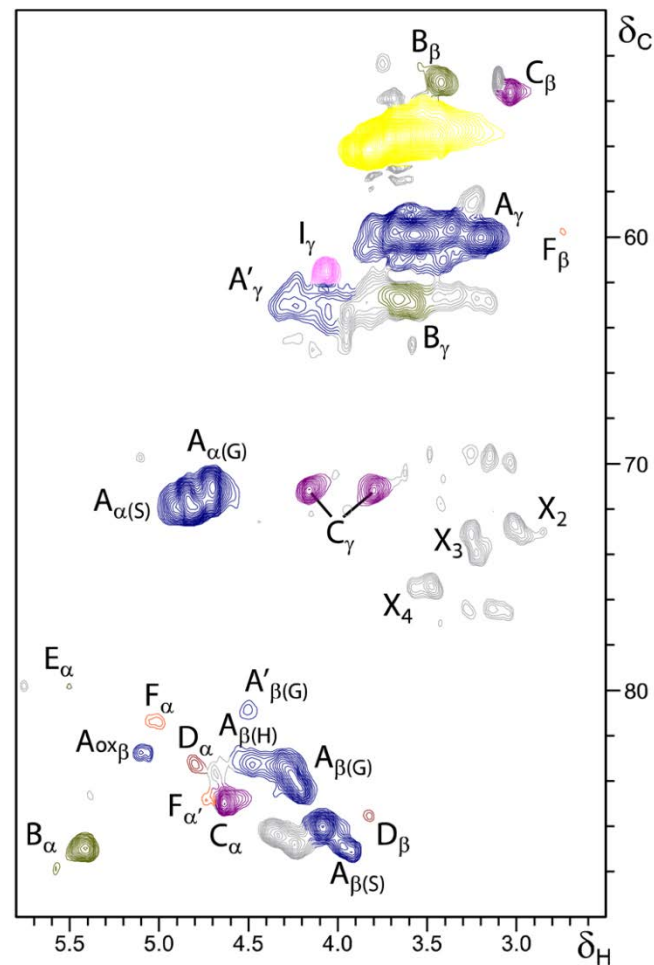
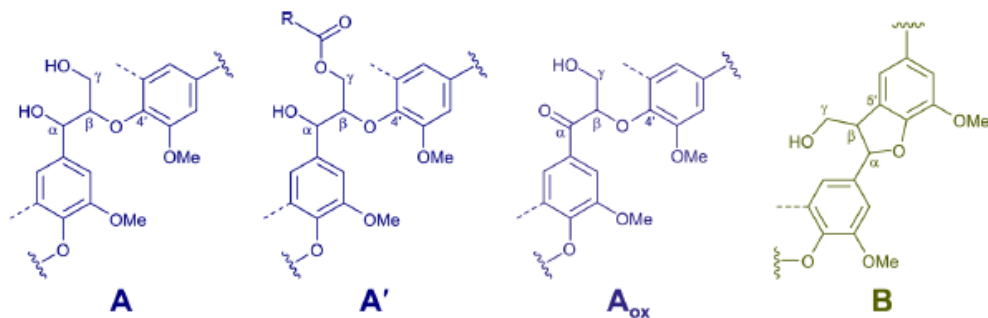
# $^{13}\text{C}$ NMR

- Nuclear Magnetic Resonance (NMR) spectroscopy measures chemical shifts (changes in frequency compared to the reference frequency) when the atom is subjected to a magnetic pulse at similar frequency as its natural resonance frequency
- $^{13}\text{C}$  NMR delivers a wealth of quantitative structural information:<sup>[1]</sup>
- However, time consuming in data collection and analysis

$\beta$ -O-4 total	
Pino/syringylresinol ( $F_\alpha$ ) <sup>b</sup>	Primary aliphatic OH
Phenylcoumarane ( $E_\alpha$ )	Secondary aliphatic OH
Sugars ( $C_1$ )	5-free phenolic OH
$S_{2,6}$	5-subst. phenolic OH
$G_2$	Ar-H
$H_4$	Oxygenated aliphatic
Degree of condensation	Saturated aliphatic
OMe	
Non-conjugated CO	EtO-
Conjugated CO	Alkyl-O-Alkyl
Non-conjugated COOR	Side chain length
Conjugated COOR	Demethylation degree
Total OH	

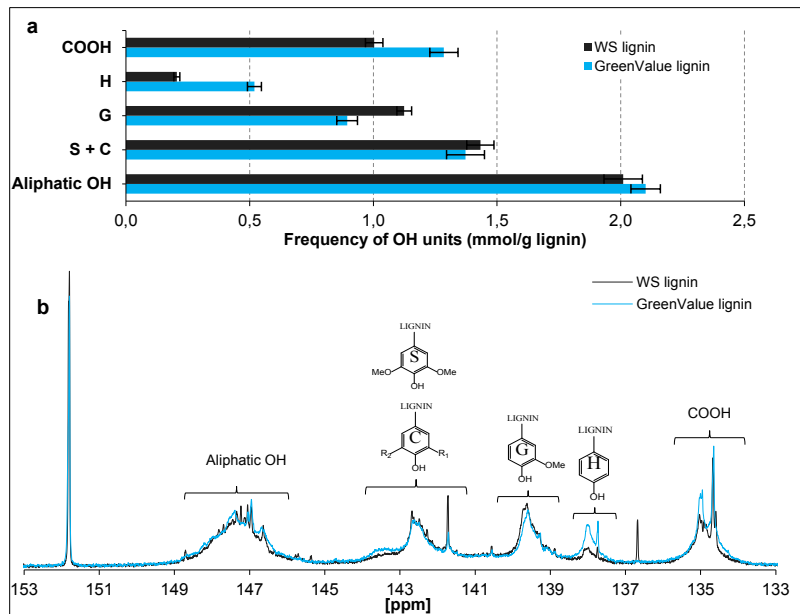
# HSQC NMR (2D NMR)

- Integration of  $^1\text{H}$  and  $^{13}\text{C}$  cross peaks gives semiquantitative information of the lignin interunit linkages as well as linkages to carbohydrates



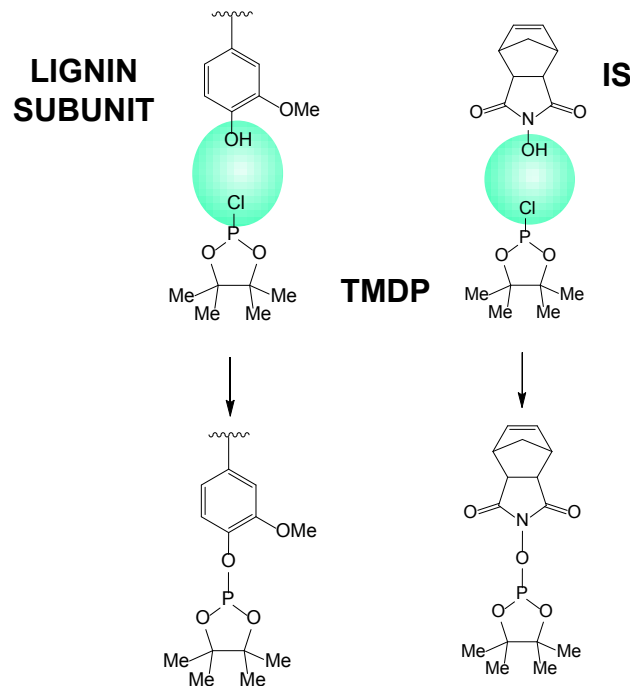
# $^{31}\text{P}$ NMR, a powerful method for OH groups

- Derivatization of lignin in solution with a P-donor which is quantitatively measured against internal standard



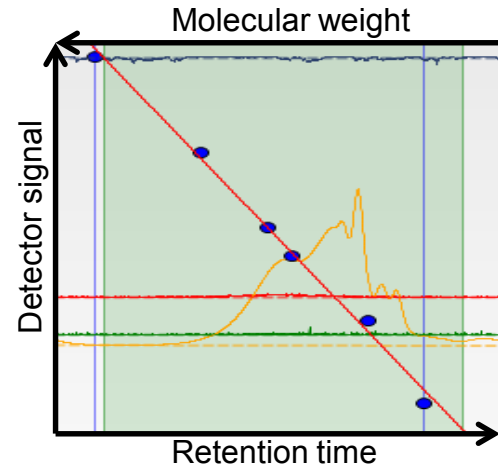
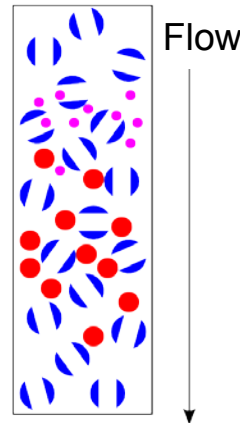
**TMDP** = 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

**IS** = N-Hydroxy-5-norbornene-2,3-dicarboxylic acid imide



# Size-exclusion chromatography (SEC)

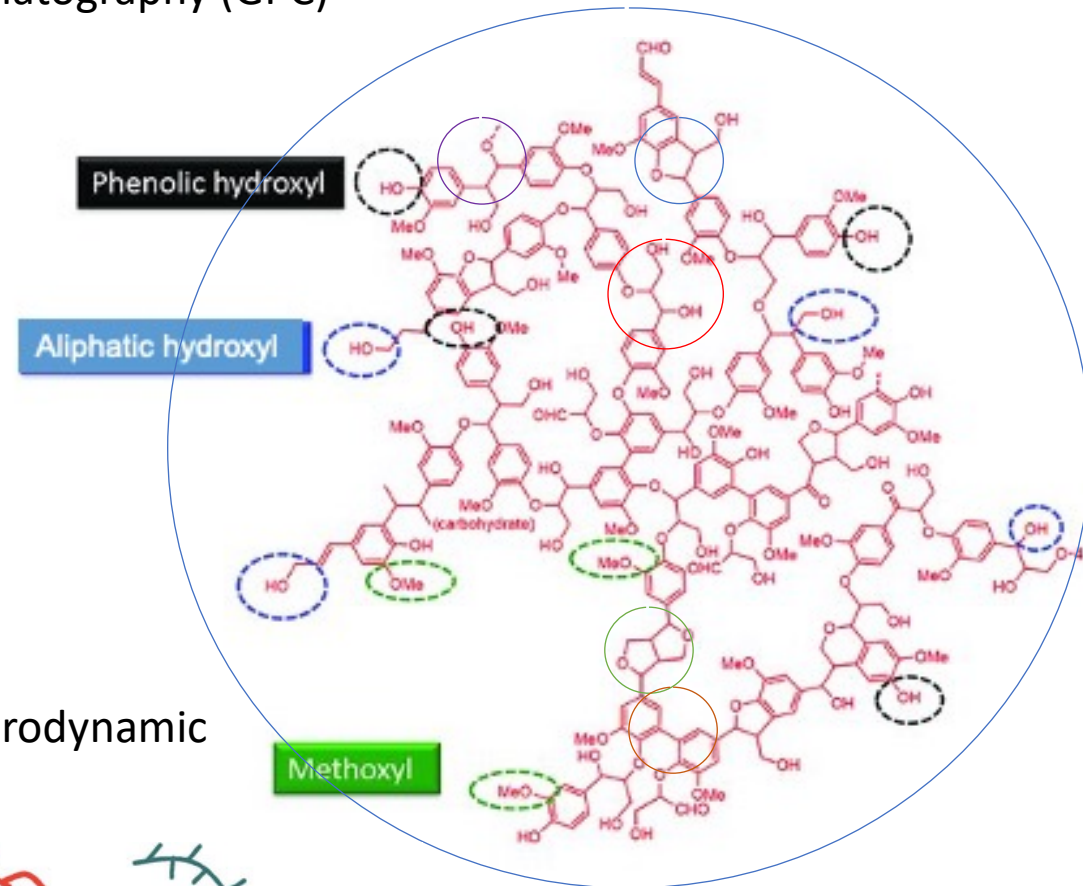
- Separation of molecules based on their hydrodynamic radii (size in solution)
- Organic and aqueous elution systems are in use
- Sample must dissolve fully and should not associate with the particles in the column packing material
- Molecular weight is calculated relative to known Mw standards or directly using laser scattering or viscometer



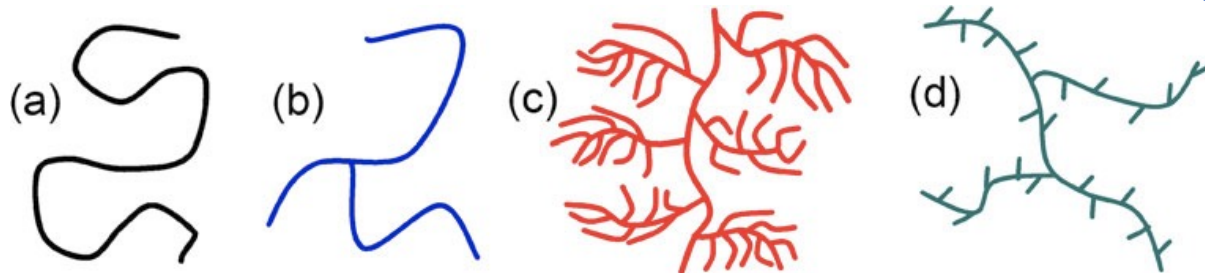
# Molecular weight determination: Size exclusion chromatography (SEC)

- Called also as gel permeation chromatography (GPC)

**Size-exclusion chromatography (SEC)**, is a **chromatographic** method in which molecules in solution are separated by their **size**, and in some cases molecular weight. It is usually applied to large molecules or macromolecular complexes. -> measure of macromolecules hydrodynamic volume!



Polymer branching shapes affecting hydrodynamic volume and molecular weight.



# Molecular weight determination of lignin

## Examples of lignin MWD

**Table 6. Average molecular weights and polydispersity indices from milled wood lignin of various biomasses.**<sup>18,27,32,45</sup>

Biomass	M <sub>n</sub> (g mol <sup>-1</sup> )	M <sub>w</sub> (g mol <sup>-1</sup> )	D
Norway Spruce <sup>a</sup>	6400	23,500	3.7
Douglas Fir <sup>b</sup>	2500	7400	3.0
Redwood <sup>b</sup>	2400	5900	2.5
White Fir <sup>b</sup>	2800	8300	3.0
<i>E. globulus</i> <sup>b</sup>	2600	6700	2.6
Southern Pine <sup>b</sup>	4700	14,900	3.2
Bamboo	5410	12,090	2.23
<i>Miscanthus</i> <sup>c</sup>	8300	13,700	1.65

<sup>a</sup>Vibratory-milled; <sup>b</sup>Ball mill for 28 days; <sup>c</sup>Values corrected from the original manuscript after a personal discussion with the author.

**Table 8. Average molecular weights and polydispersity indices from enzymatic mild acidolysis lignin of various biomasses.**<sup>27,32</sup>

Biomass	M <sub>n</sub> (g mol <sup>-1</sup> )	M <sub>w</sub> (g mol <sup>-1</sup> )	D
Norway Spruce <sup>a</sup>	8850	78,400	8.8
Douglas Fir <sup>b</sup>	7600	38,000	5.0
Redwood <sup>b</sup>	4700	30,100	6.4
White Fir <sup>b</sup>	6300	52,000	8.2
<i>E. globulus</i> <sup>b</sup>	8700	32,000	3.7
Southern Pine <sup>b</sup>	9700	57,600	5.9

<sup>a</sup>Vibratory-Milled for 48h; <sup>b</sup>Ball mill for 28 days prior

Tolbert, A.; Akinosho, H.; Khunsupat, R.; Naskar, A. K.; Ragauskas, A. J. Characterization and Analysis of the Molecular Weight of Lignin for Biorefining Studies. *Biofuels, Bioproducts and Biorefining* **2014**, *8* (6), 836–856. <https://doi.org/10.1002/bbb.1500>.

# Analysis of lignin as a product

- Complex structure, but all-inclusive analysis is not necessary
- **Key properties in relation to the application important**
- Real application tests needed also
- Distinction of a high purity lignin from a low purity one:
  - Low amounts of contaminating carbohydrates, sulphur, inorganics
  - Good solubility and material properties





# 8. Applications of lignin

- $2 \cdot 10^{10}$  tons of lignin is produced annually in Nature [1]
- Only a fraction of the total is used in products, why?
  - Lack of regular (stereochemical) structure
  - Heterogeneous repeating units (H, G, S and their linkage patterns)
  - Poor understanding of how the degree of polymerization and structure change when lignin is isolated from cell walls
- However, recent advances in lignin isolation and characterization hold promise for increased use of lignin in materials

# R&D for commercialization of lignin is undergoing rapid growth

## New kind of gold from Nordic forests



Lignin is an organic material that binds the fibres and cells of wood. The word lignin may not be familiar to many, but there is a lot of anticipation and excitement around this material. Why?

PHOTO: Vesa Laitinen

Experts say that lignin may eventually be one of the new renewable materials extracted out of the green gold of the Nordic forests. Stora Enso's Sunila Pulp Mill in Finland will, in the future, extract lignin from pine and spruce.

Following the biorefinery investment announcement made in July, there is an air of

excitement at the mill.

The first dedicated biorefinery investment is expected to be completed in early 2015. Mill Director **Olli-Pekka Reunanen** is pleased, and with good reason. Installing the new machinery in the architectural milieu that dates back to 1938 is an enjoyable challenge for the mill staff. "We won't be building new buildings; instead, the idle buildings in the mill area will be used to house the machinery required for the biorefinery," explains Reunanen.

Prior to making the 32-million-euro investment decision, Stora Enso carefully looked into areas where lignin extraction would be profitable. Sunila is Stora Enso's first, but probably not its last, biorefinery dedicated investment.

Stora Enso has been researching lignin and its attributes for more than a decade. "Lignin is a challenging and complex material; it's an honour to be a pioneer in this area. At the same time, we are taking a leap into new and previously uncharted markets, but Stora Enso is in a good position to develop commercially viable applications from lignin," says **Mikael Hannus** of the Biomaterials's Biorefinery and Bioenergy unit.

The initial markets are anticipated in, for example, the construction and automotive industries, where lignin offers a sustainable alternative to the phenols used in plywood and wood-panelling glues and the polyols used in foams. Other applications are also under development.



storaenso

## Lignin – a vast source of opportunities for innovative minds



Lignin is an ideal bio-based substitute for various petro-based products used today.

Now, for the first time, high-quality lignin is commercially available in large quantities, ready to be used in a broad range of applications.

UPM has developed profound know-how and IP regarding the chemistry of lignin from various sources as well as lignin analysis, fractionation, purification, activation, modification, and formulation. Together with our partners we are committed to develop our innovative lignin-based products further.

## Lignin works in favor of both environment and economy

Features and benefits of UPM's lignin-based products:

- 100% bio-based – UPM's lignin-based products are exclusively based on renewable raw materials
- Excellent performance – stringent quality control and a proprietary activation technology make UPM's lignin-based products reliable and effective
- Reduced dependency on fossil raw materials – lignin-based products can help to increase security of supply while enabling a smooth transition to renewable raw materials
- Cost savings – based on their outstanding performance, UPM's lignin-based products can help realize cost savings in a variety of applications;
- Versatility – lignin can be used in a broad range of applications, ranging from composites, through a broad range of resin systems, to raw material for carbon fibers



# Industry investment in lignin production is good news to R&D in this area

## BioChoice™ Description and Applications

BioChoice™ lignin is a bio-based alternative to the use of petroleum and other fossil fuels. A wide range of potential applications for BioChoice lignin exist, including in the energy, materials and chemical categories.

- Adhesives
- Agricultural Chemicals
- Carbon Products (e.g. carbon fiber, graphite, activated carbon, etc.)
- Coatings
- Dispersants
- Fuels and Fuel Additives
- Natural Binders
- Resins



## BioChoice Product Attributes

- Total Lignin > 95% of Total Solids
- Low Ash
- Low Sulphur
- Single Species - Southern Pine

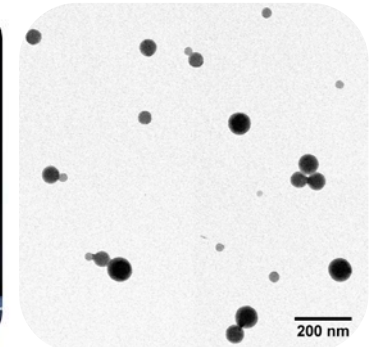


# Current and emerging applications

- Energy (it has value!) 26.7 MJ/kg (HHV)<sup>[1]</sup>
- Chemicals:
  - Pyrolysis of lignin → bio-oil (15–25%), gas (20–50%), char (30–60%)<sup>[4]</sup>
  - Aromatic chemicals (BTX)
  - Vanillin, 3% from softwood (~10% of lignin) → 20% of vanillin is produced from lignin and 80% from crude oil using the guaiacol route<sup>[2-3]</sup>
- Composites and polymer blends
- Colloidal particles and capsules
- High-performance materials such as carbon fibres are also under development



[http://www.btgworld.com/media/cms\\_block/rtd-technologies-biomaterials-and-chemicals-1.jpg](http://www.btgworld.com/media/cms_block/rtd-technologies-biomaterials-and-chemicals-1.jpg)



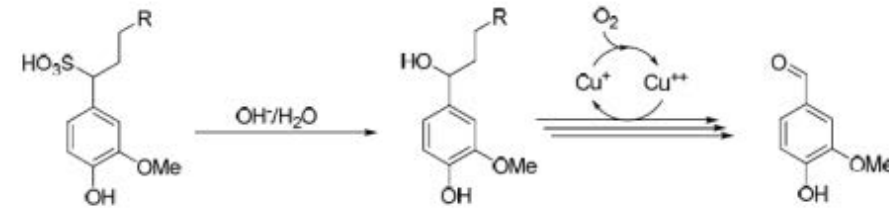
[1] <http://www.nrel.gov/biomass/pdfs/2839.pdf>

[2] Smolarski, High-Value Opportunities for Lignin: Unlocking its Potential, Frost & Sullivan, 2012

[3] [http://www.bioref-integ.eu/fileadmin/bioref-integ/user/documents/Martin\\_Lersch\\_\\_Borregaard\\_-\\_Creating\\_value\\_from\\_wood\\_-\\_The\\_Borregaard\\_biorefinery.pdf](http://www.bioref-integ.eu/fileadmin/bioref-integ/user/documents/Martin_Lersch__Borregaard_-_Creating_value_from_wood_-_The_Borregaard_biorefinery.pdf)

[4] Beis et al., Fast pyrolysis of lignins. *Bioresources* 5 (2010) 1408–1424.

# Oxidation of lignosulfonate to vanillin



Copper catalyst is recycled due to strict limitations on copper in effluent



Compare the reaction to the analytical cupric oxide oxidation presented above

# Formation of colloidal lignin particles



Dissolution (15 kg)



CLP formation (40 kg)



Ultrafiltration



Final product 1 kg



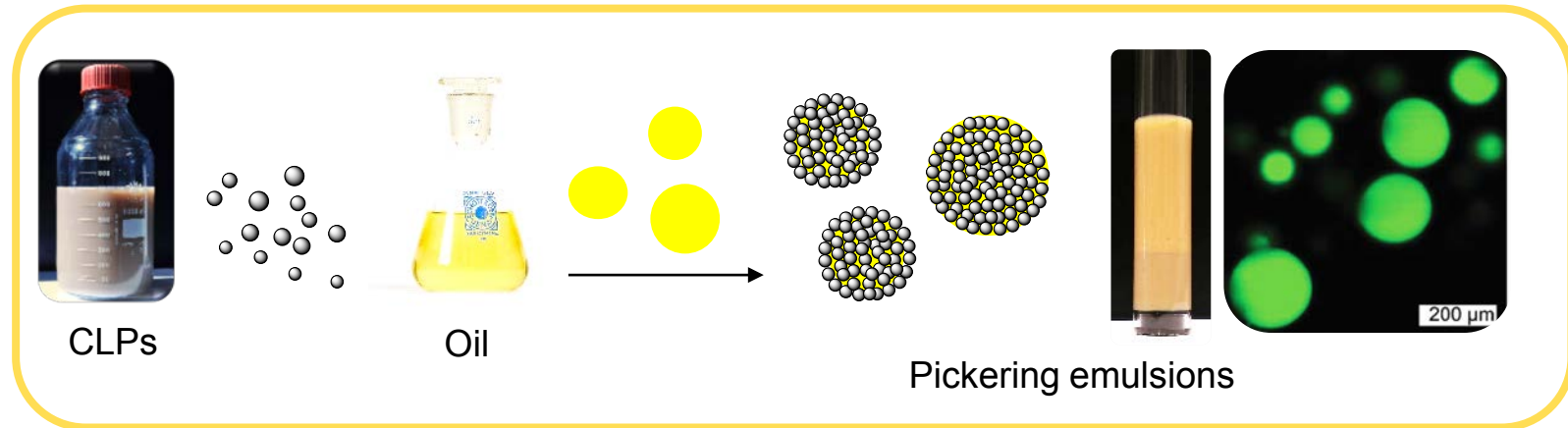
Spray-drying



Solvent evaporation

# Example of applications of colloidal lignin particles

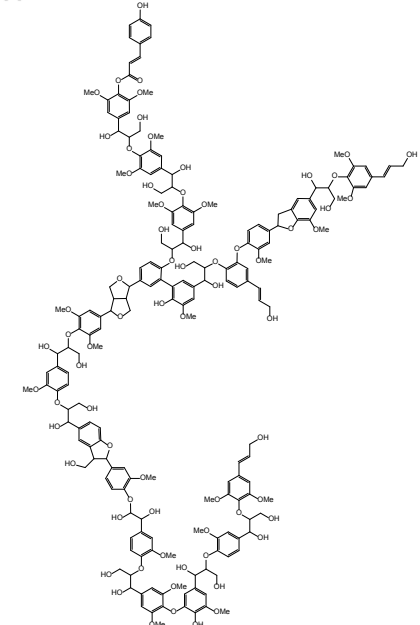
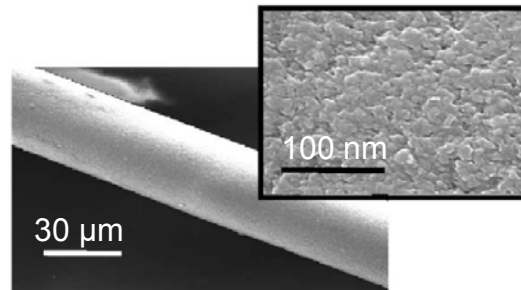
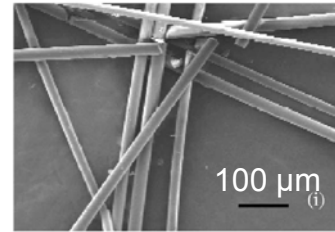
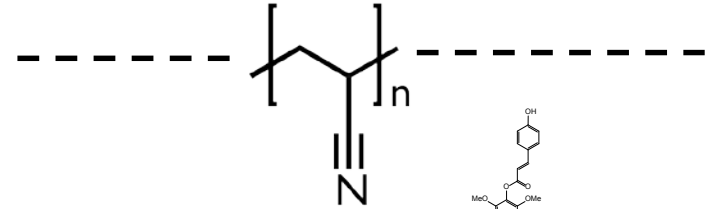
## Emulsion stabilization





# Carbon fibers from lignin

- Carbon fibers are high-value materials currently produced from polyacrylonitrile (PAN)
  - Lignin is more affordable raw material, but less linear polymer with predominant ether linkages
- Challenges the production of carbon fibres with sufficient strength properties
- Ongoing research seeks to match process and properties with in suitable applications



# Questions?

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**Room 317**

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