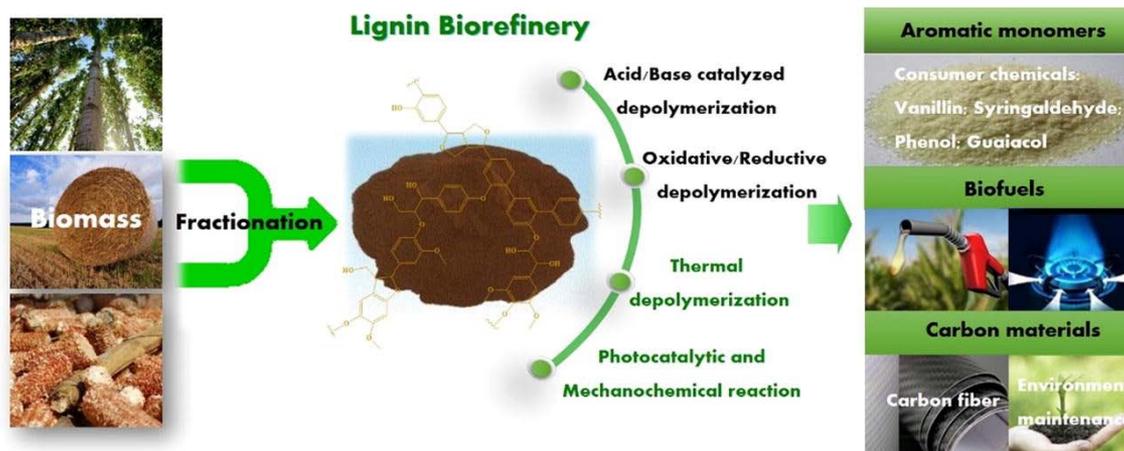
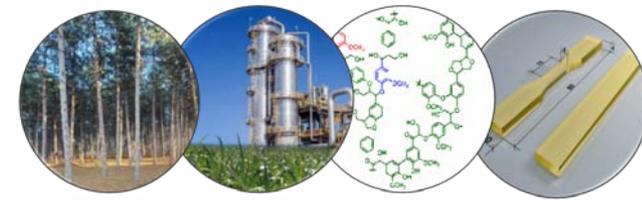


Lignin depolymerization methods – From Lignin to Valuable Oligomers/Monomers for Polymer Materials Preparation

Dr Milica Rančić

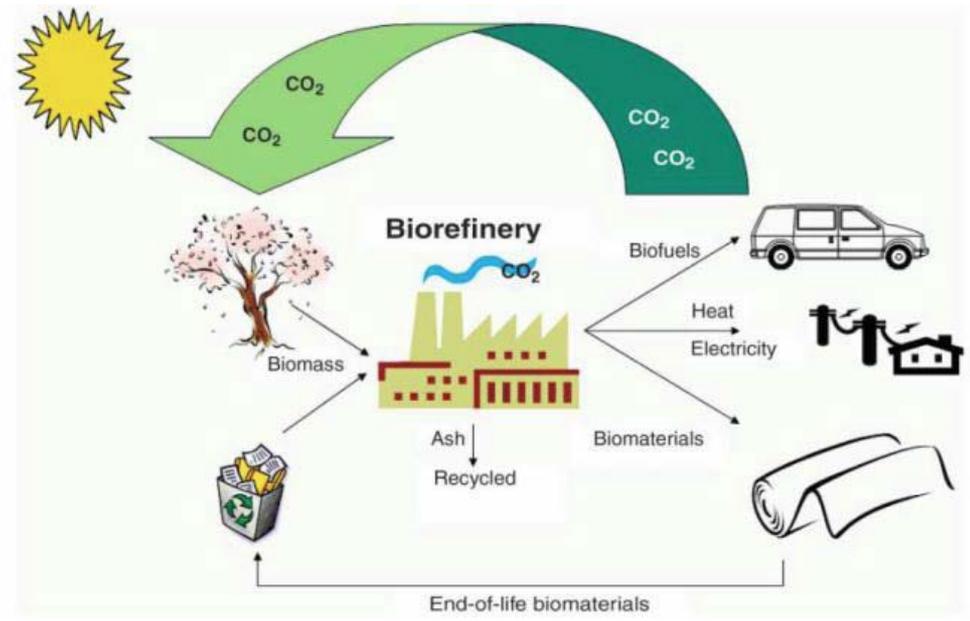
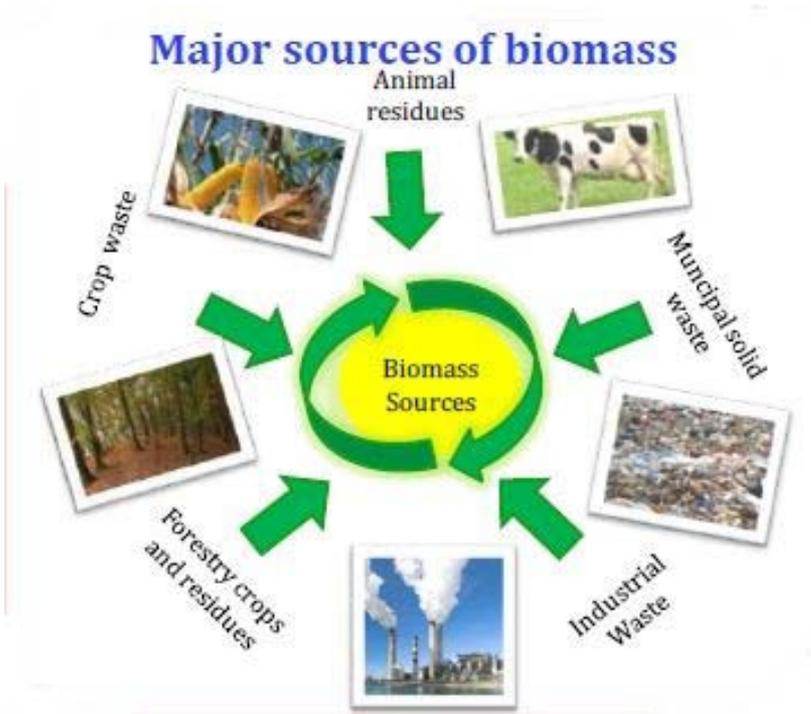
*University of Belgrade-Faculty of Forestry
Department for Wood Technologies*





Biorefinery

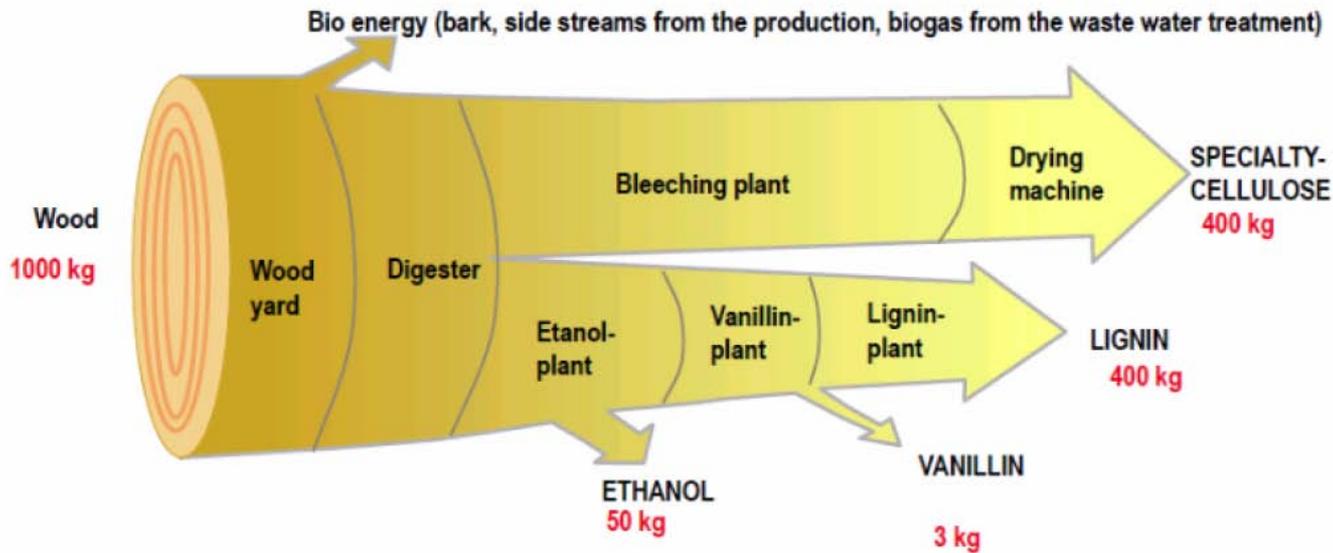
- Biomass can be converted into high energy fuels and chemicals similar to those obtained from fossil feedstock
- Less expensive
- Produced on renewable basis can reduce the net CO₂ in the atmosphere thereby reducing global warming



Biorefinery



- An example of such an industrial biorefinery is the well established sustainable biorefinery operated by Borregaard in Norway
- In this way more than 90% of the wood input is used as marketable products.



Applications (end products)

Cellulose

Construction materials
Cosmetics
Food
Tablets
Textiles
Filters
Paint / varnish

Lignin

Concrete additives
Animal feed
Dyestuff
Batteries
Briquetting
Mining

Vanillin

Food
Perfumes
Pharmaceuticals

Ethanol

Car care
Paint/ varnish
Pharmaceutical industry
Bio Fuel



- Second-generation biomass, in which waste products are used as raw material (world annual production of lignocellulosic biomass is ca. $1-5 \times 10^{10}$ MT (metric tons))
- Second-generation biofuels and chemicals are usually made from lignocellulosic biomass
- Lignocellulosic biomass can be divided into three organic components with the following representative fractions by dry weight: cellulose (40-50 wt. %), hemicellulose (25-35 wt. %) and lignin (15-40 wt. %) depending on biomass type.

Cellulose (glucose)

Hemicelluloses (xylose and arabinose)

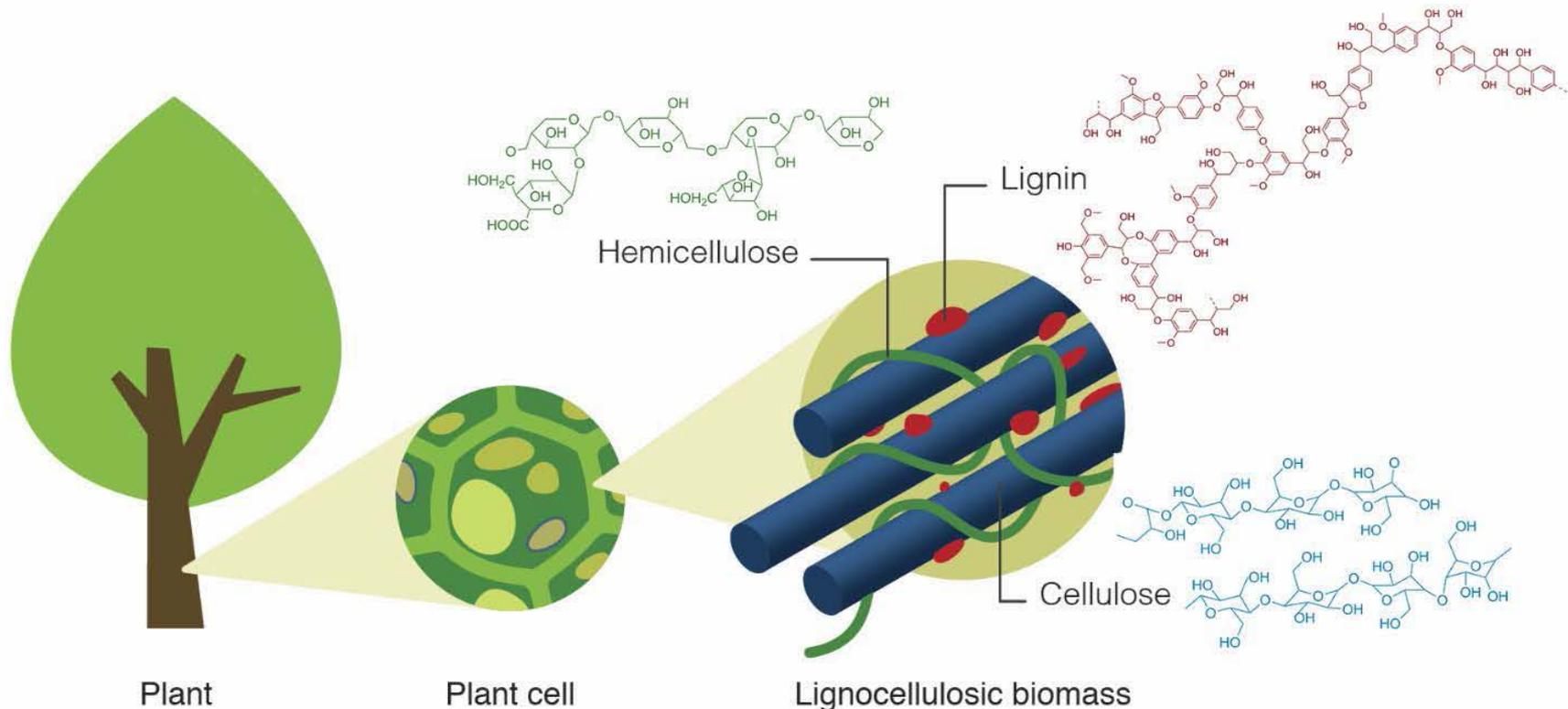


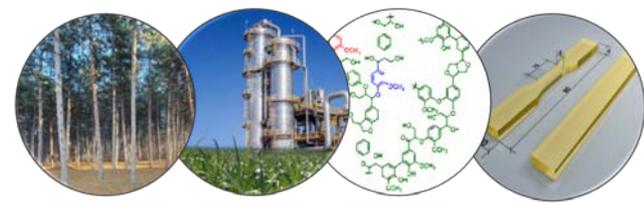
Lignins

Lignocellulosic biomass



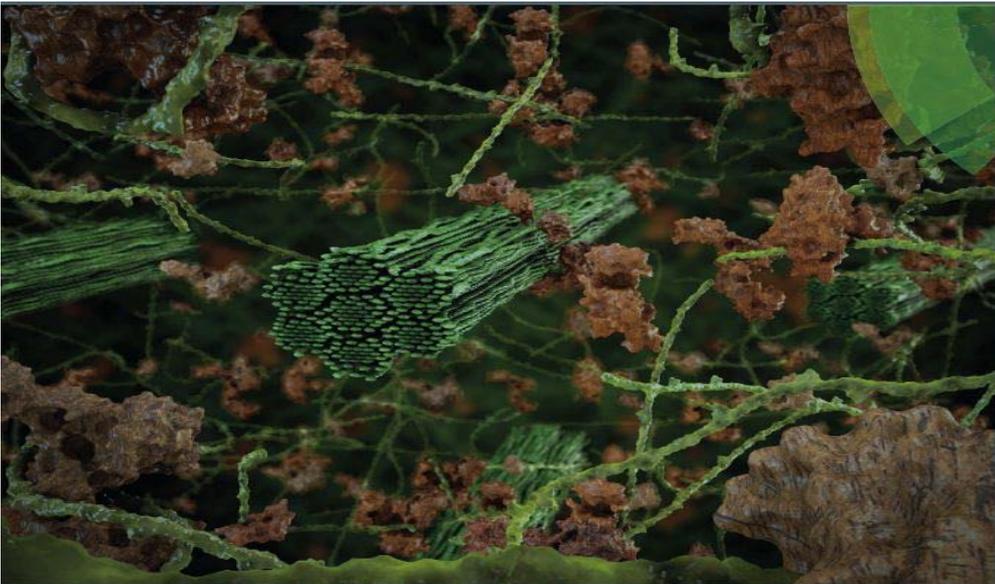
- Lignocellulose is the most abundant form of biomass, mainly composed of varying portions of lignin, hemicellulose, and cellulose.
- A number of other minor components are also found: proteins (3-10 wt. %), lipids (1.5 wt. %), soluble sugars called extractives (10.5wt. %) and minerals often referred to as “ash”.





Lignin

- Lignin is the **second abundant** and important organic substance in the plant world.
- The incorporation of lignin into the cell walls of plants gave them the chance to **conquer the Earth's land surface**.
- Lignin increased the mechanical strength properties to such an extent that huge plants such as trees with heights of even more than 100 m can remain upright.



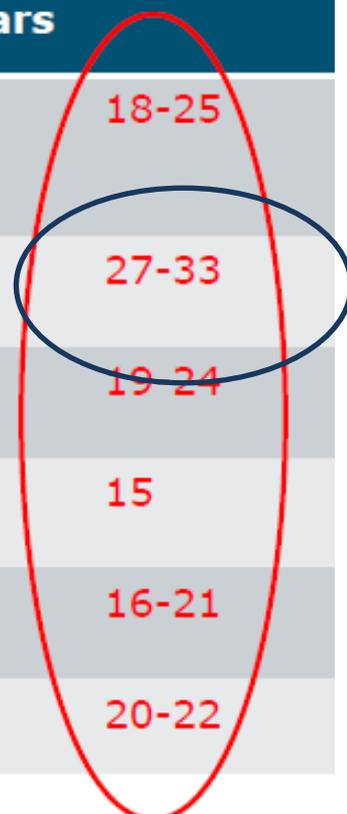
Ultra-structural view of lignocellulosics

(Brian H. Davison et al. 2014)



Composition of lignocellulosic (LC) feedstocks (wt% dm)

Origin	Species	Carbo- hydrates	C6 sugars		Lignin
			C6 sugars	C5 sugars	
Hardwoods	Mixed (stem)	60-75	40-50	16-20	18-25
Softwoods	Mixed (stem)	60-67	40-50	15-18	27-33
Grasses	Sugar cane bagasse	60-70	33-36	20-25	19-24
Agricultural residues	Corn cobs	75	40	30-34	15
	Wheat straw	55-60	30-35	20-23	16-21
	Rice husks	50-55	30-35	20-22	20-22



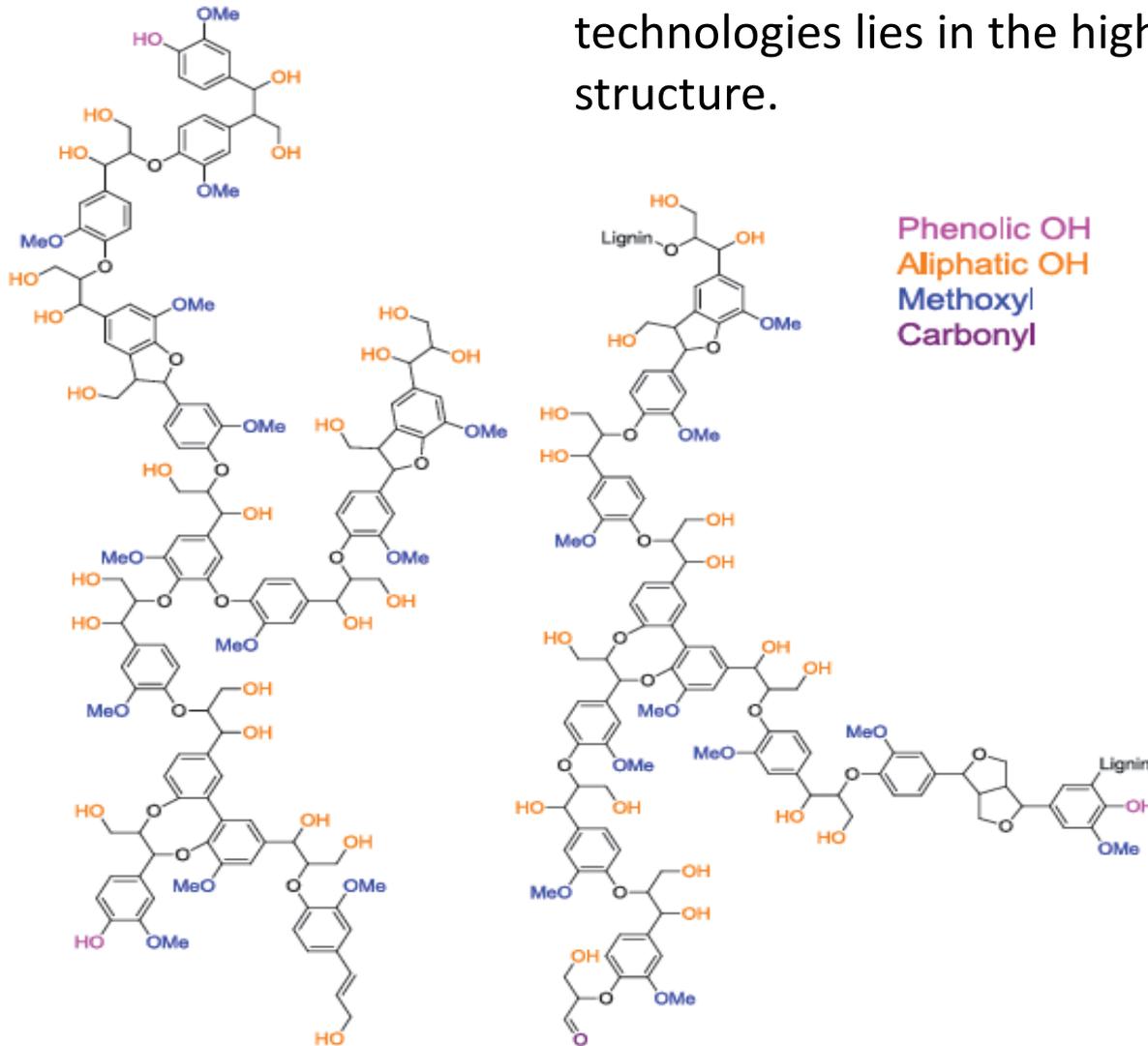


- Lignin is derived from the Latin word for wood (**lignum**)
- The largest renewable source of aromatics biopolymer on Earth, however, is mostly regarded as a low-value by-product in most biorefinery processes.
- One major source of lignin is provided by the pulp and paper manufacturer, where only 5% of waste lignin has been employed for low-grade fuel for heat and power applications through combustion.
- Lignocellulosic biomass offers many possibilities as feedstock for the energy sector but also for the chemical industry due to its chemical composition, abundant availability and relative low costs when the conversion to products can be carried out in an economic and sustainable manner.

Lignin structure



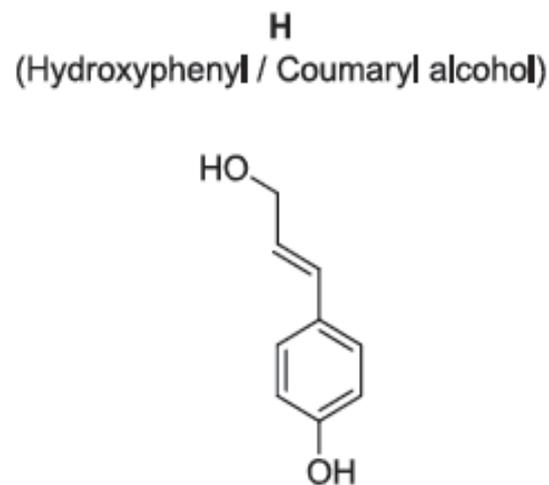
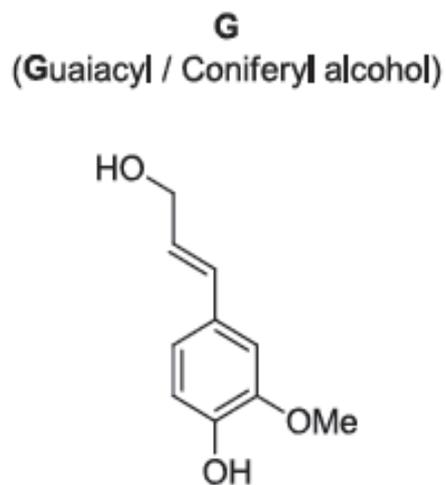
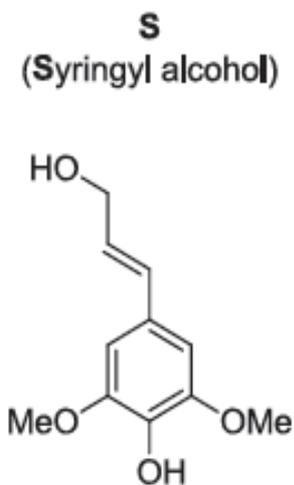
➤ The greatest challenge for the lignin-conversion technologies lies in the highly irregular polymeric structure.





Lignin structure

- Lignin may be defined as an amorphous, polyphenolic material arising from an enzyme-mediated dehydrogenative polymerization of three phenylpropanoid monomers: syringyl, coniferyl, and *p*-coumaryl alcohols.

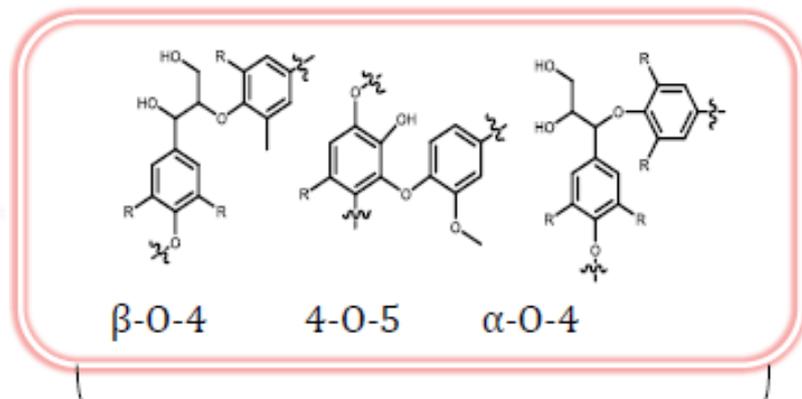
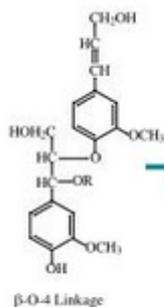




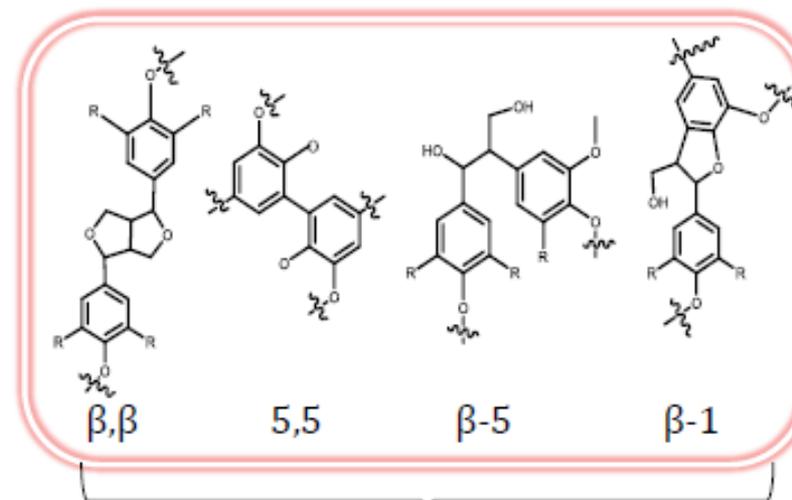
Major linkages

Lignin structure

	Linkage	Softwood	Hardwood
γ C			
β C			
α C			
1	β -O-4	50%	60%
2	α -O-4	2-8%	7%
3	β -5	9-12%	6%
4	5-5	10-11%	5%
5	4-O-5	4%	7%
6	β -1	7%	7%
	β - β	2%	3%



C-O-C linkages: 60-70 %



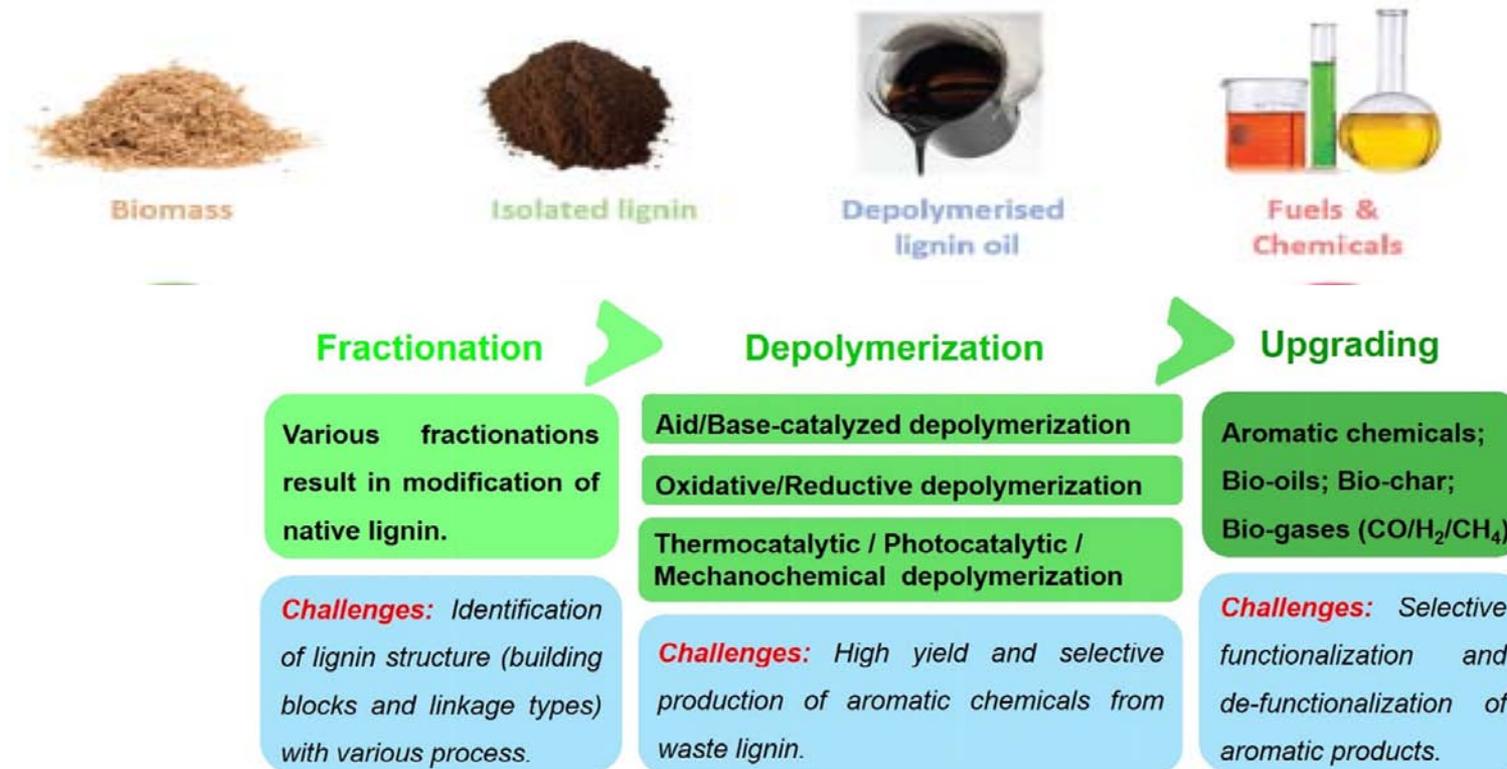
C-C linkages: 30-35 %

➤ Very irregular, **randomly cross-linked polymer** of **phenylpropanoid** units joined by many different linkages.



➤ **Valorization of lignin** often required organosolvolytic pretreatment of lignocellulosic biomass or enzymatic processing to isolate native lignin followed by hydrogenation/dehydrogenation to produce the desired aromatic products such as monomers, dimers, oligomers and bio-oil.

➤ **The lignin isolated from different processes is varied in terms of molecular weight, polydispersity, solubility, abundance in functional groups, and type of inter-subunit linkages.**





Lignin isolation

➤ Mechanical vs. Chemical Processes

- Lignin can be isolated in a variety of methods

➤ Methods can be grouped into two Major Pathways

- Cellulose and hemicelluloses are removed by solubilization, leaving lignin as insoluble residue

Ex. Lignin available as by-product from a lignocellulosic ethanol fuel biorefinery

- Methods involving dissolution and removal of lignin, leaving cellulose and hemicelluloses as insoluble residues, followed by the recovery of lignin from the solution

Ex. Kraft and sulfite lignin

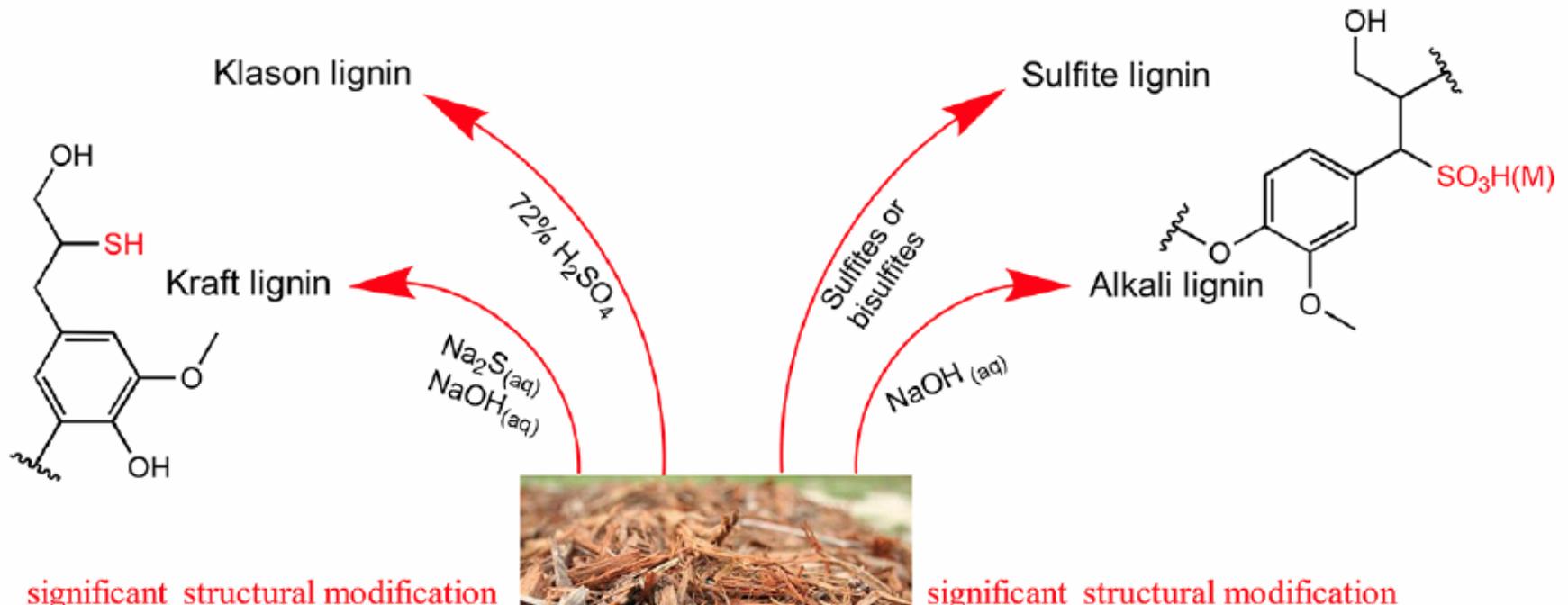
➤ Isolation method has an influential role in determining the nature and structure of lignin

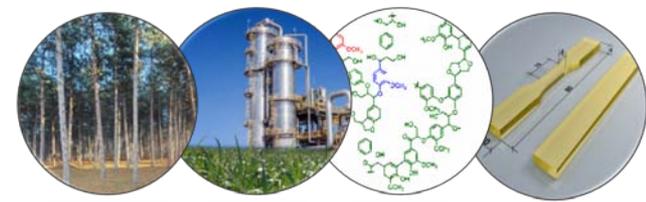


Lignin isolation

➤ Two main categories related to the extent of structural modification induced in lignin by the fractionation conditions, an important aspect when considering valorization of any lignin feed

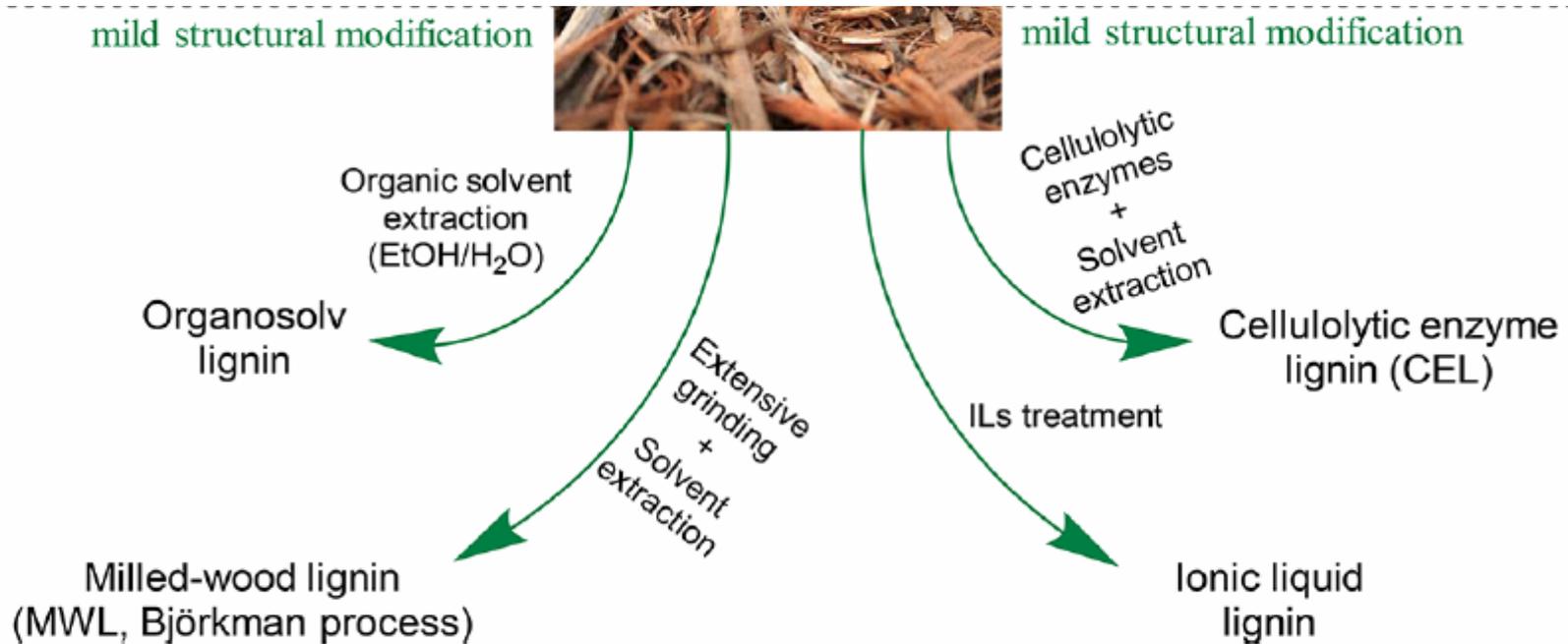
1) Methods Resulting in Significant Structural Modification.





2) Methods Resulting in Mild Structural Modification

Employment of neutral and mild conditions in extraction facilitates the isolation of native lignin.



➤ The aromatic monomers yield from direct hydrogenolysis of native lignin in biomass can reach up to 40%–50%, which is 3–10 times higher than that of the extracted lignin with the significantly modified structure

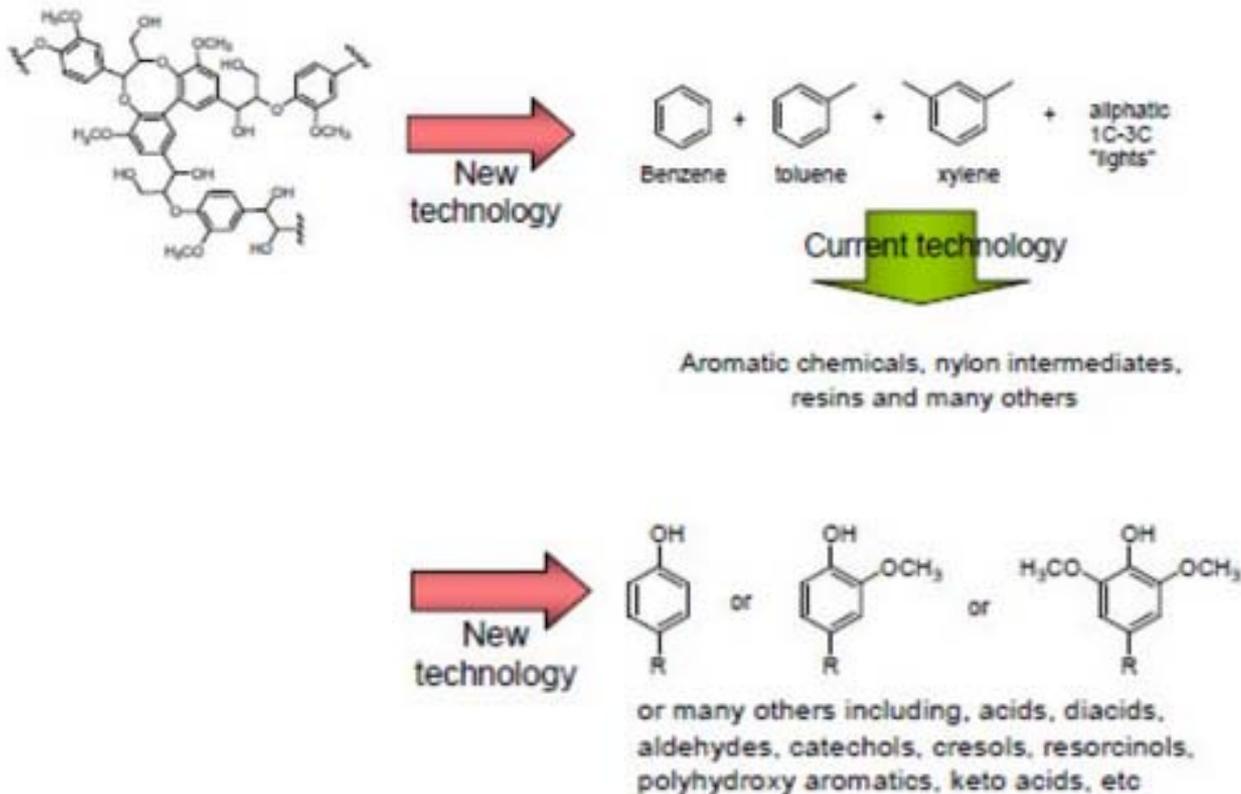
lignoCOST

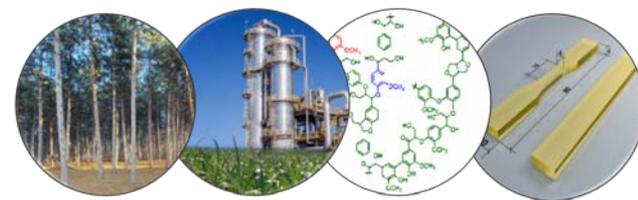
Depolymerisation of lignin



➤ An important starting point for many lignin valorization strategies, because it could generate valuable aromatic chemicals and/or provide a source of low-molecular-mass feedstocks suitable for downstream processing

➤ Commercial precedents show that certain types of lignin (lignosulphonates) may be converted into vanillin and other marketable products, but new technologies are needed to enhance the lignin value chain

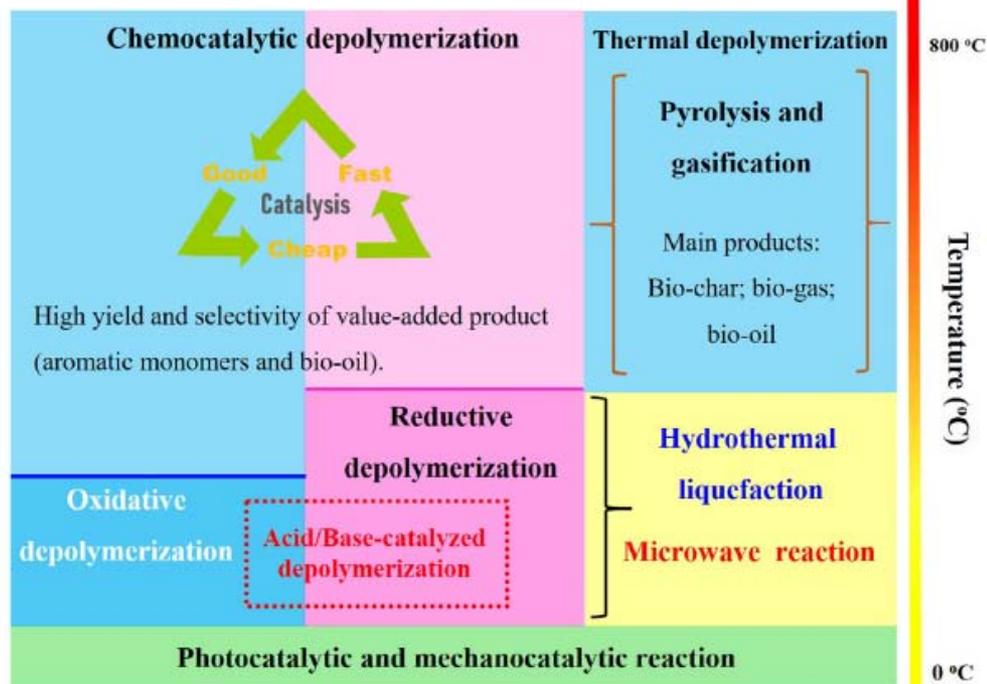




An overview of depolymerization methodologies of lignin

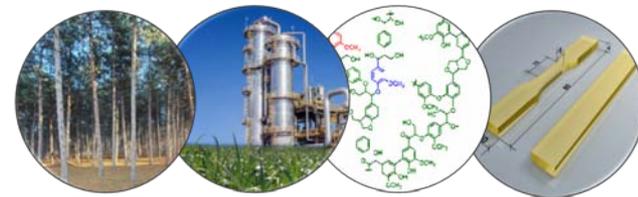
- In any biomass or lignin processing method, the lignin structure is altered through a combination of de- and repolymerisation reactions.
- The outcome strongly depends on the underlying mechanism of the processing method:

- base-catalysed,
- acid-catalysed,
- reductive,
- oxidative, or
- thermal.

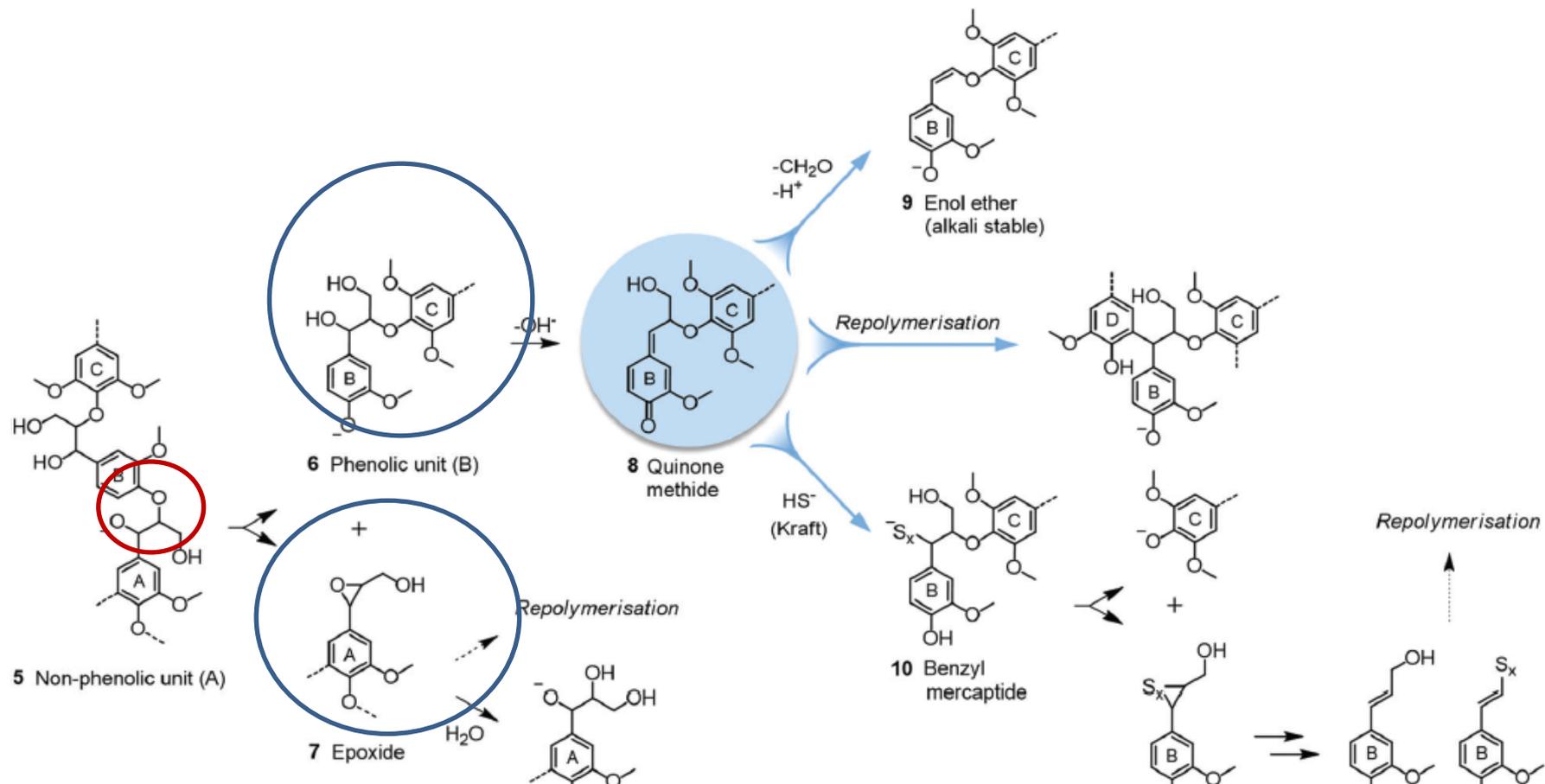


- β -O-4 reactive linkages largely dictate the lignin reactivity as they are the most abundant and overall the most reactive inter-unit linkages, and often form the primary target in biomass fractionation and depolymerisation.

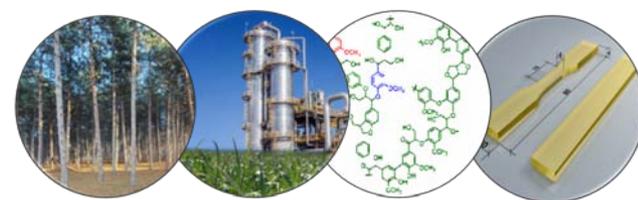
Base-catalysed lignin chemistry



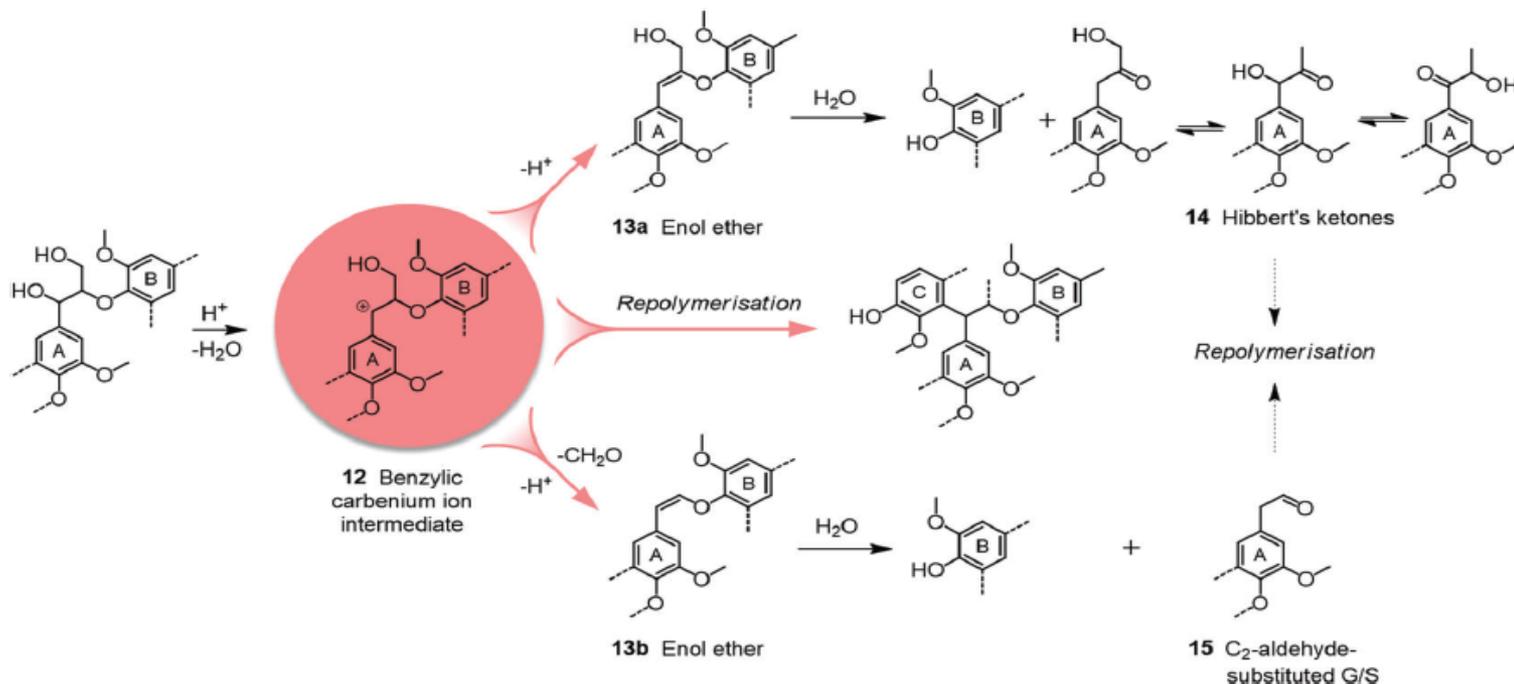
➤ Alkaline media enable the cleavage of lignin–carbohydrate bonds, the fragmentation of lignin via cleavage of the β -O-4 motifs, the solubilisation of the resulting fragments, and eventually lignin degradation/repolymerisation.

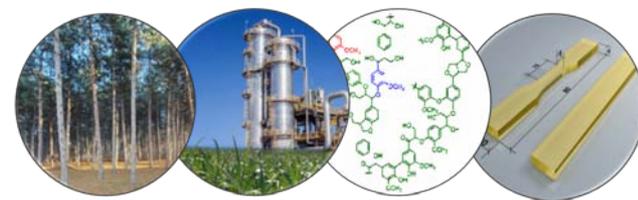


Acid-catalysed lignin chemistry



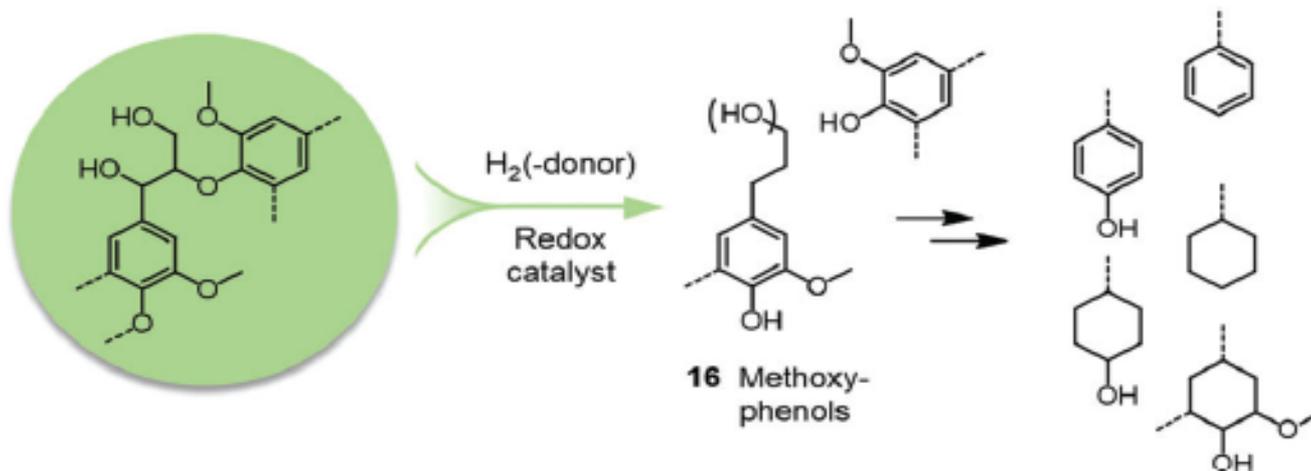
- Acidic conditions are known to promote hydrolysis of ether bonds in the carbohydrate polymers, and are therefore often applied to depolymerise and solubilise the hemicellulose and/or cellulose fraction.
- Unlike alkaline conditions, acidic environments do not necessarily promote the solubilisation and extraction of lignin.
- Acidic media affect the lignin structure by facilitating both depolymerisation (i.e. acidolysis) and repolymerisation.
- The most prominent event in acid-catalysed lignin chemistry is the cleavage of β -O-4 ether bonds

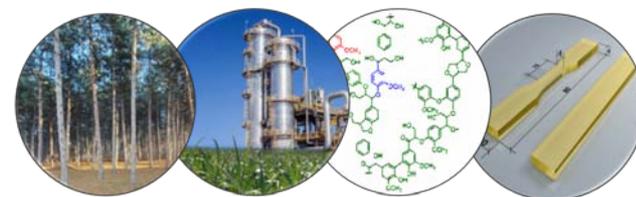




Reductive lignin chemistry

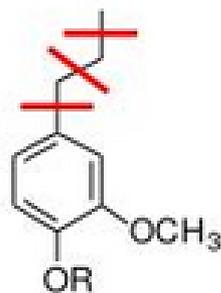
- Reductive conditions have been frequently applied in depolymerisation processes of isolated lignins.
 - To this end, a redox catalyst in combination with H₂ or a H-donor is essential.
 - Reductive processing primarily targets the inter-unit ether bonds (β -O-4 , α -O-4) and sidechain hydroxyl groups.
 - The net result in all cases is:
 - hydrogenolysis of ether bonds,
 - removal of benzylic OH α -groups,
 - possible removal of OH γ -groups
 - reductive conditions can avoid repolymerisation
 - However, on the downside is the inability of most reductive processes to cleave carbon–carbon linkages.
- Consequently, the degree of depolymerisation is typically linked to the relative amount of cleavable inter-unit ether bonds present in the lignin polymer before processing.



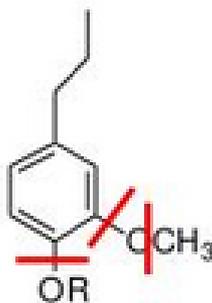


Hydrogenolysis

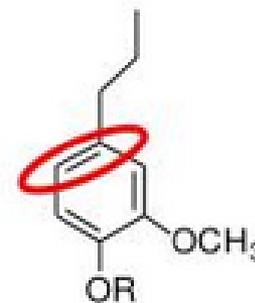
- Reactions:
 - Hydrocracking – reductive cleavage of carbon-carbon bonds
 - Hydrodeoxygenation – reductive cleavage of carbon-oxygen bonds
 - Hydrogenation – addition of hydrogen to unsaturated carbon-carbon or carbon-oxygen bonds



Hydrocracking



Hydrogenolysis



Hydrogenation

- Reactions via initial hydrolysis and/or thermolysis → fragments which are stabilised by addition of H atoms at catalyst surface

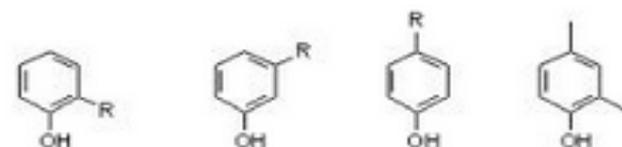


Noguchi/Crown Zellerbach process

- Hydrogenolysis of desulfonated lignosulfonate in phenolic liquid medium using a S-resistant catalyst
 - 100-200 Atm H₂, 370-430°C

Product yields from Noguchi process, wt% of lignin charged (83).

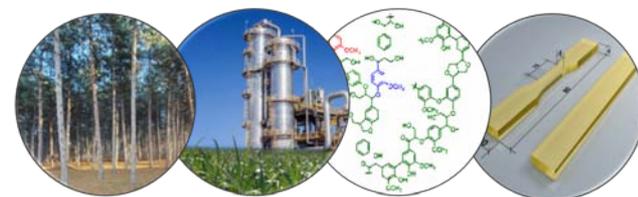
Product	Yield, wt%
Gas	17.5
Water	27.5
Light oils	5.0
Monophenols	21.0
phenol	3
<i>o</i> -cresol	4
<i>m,p</i> -cresol	6
<i>o</i> -ethylphenol	1
<i>p</i> -ethylphenol	3.25
<i>p</i> -propylphenol	2
2,4,-xylenol	1.25
unidentified	0.5
Neutrals	9.0
Excess paste oil (boiling point >240°C)	20.0



R = CH₃

R = C₂H₅

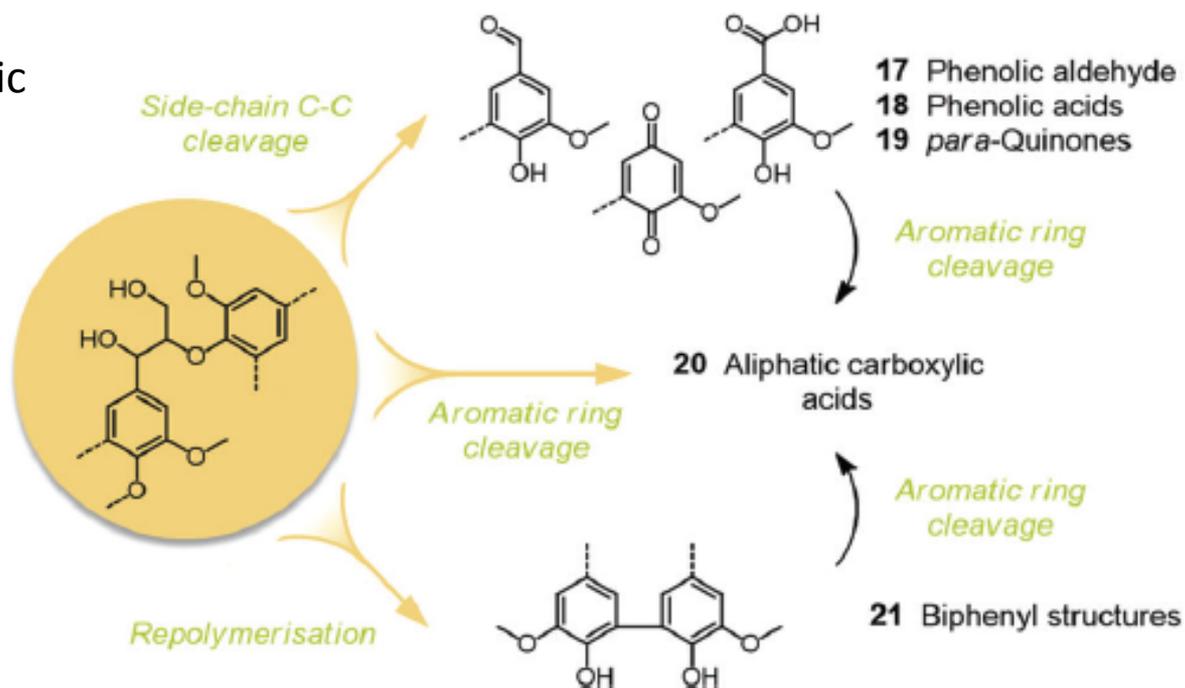
R = C₃H₇



Oxidative lignin chemistry

- Various oxidants are available, such as chlorine, chlorine dioxide, oxygen, hydrogen peroxide, ozone, and peroxyacids.
- Most oxidation mechanisms are initiated by electrophilic reactions, such as Cl^+ (from chlorine), OH^+ (from peroxyacids), or oxygen.
- The oxidative cracking reaction includes the cleavage of the β -O-4 bonds, C-C bonds, aromatic rings, or other linkages within the lignin.

in contrast to reductive processing, the generated phenolic products are not generally stable under oxidative conditions

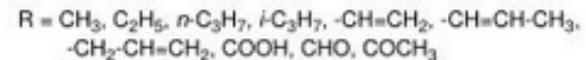
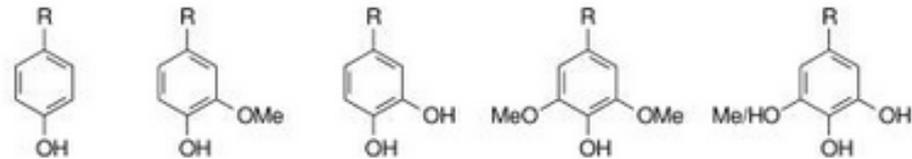
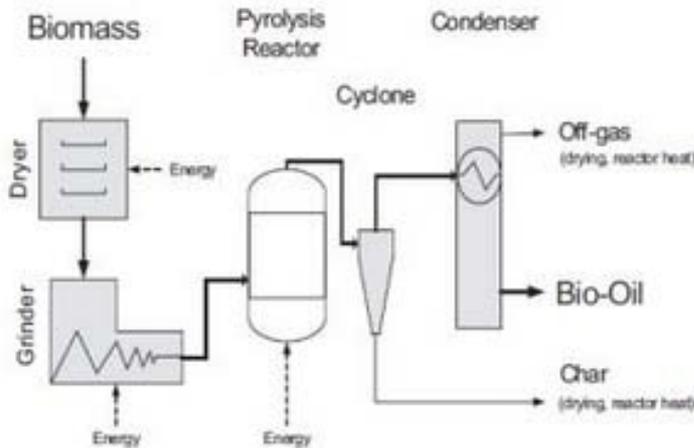




Thermal lignin depolymerisation

1. Pyrolysis and gasification
2. Hydrothermal liquefaction
3. Microwave reaction

- Main monomeric lignin pyrolysis products in bio-oil



➤ **Pyrolysis and gasification** are two of the most commonly used thermochemical methods for the conversion of biomass, lignin, and other residual waste into syngas, bio-oil, and biochar.

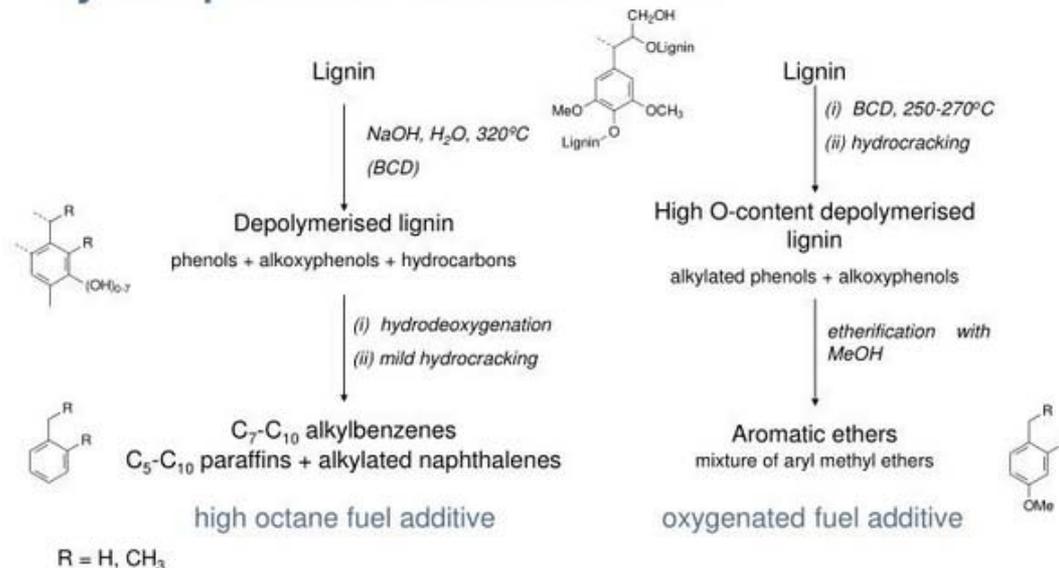
➤ Pyrolysis is often carried out in a range of 400 °C to 800 °C in the absence of oxidizing agents (oxygen or air).

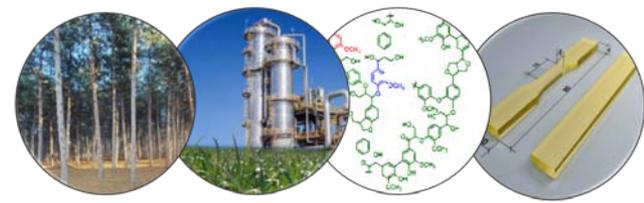
➤ The product distribution is greatly influenced by the temperature and time of pyrolysis.



2. Hydrothermal liquefaction

- Hydrothermal liquefaction (HTL) of biomass comprises the thermochemical conversion of a broad range of bio-based materials into a liquid product using water, the greenest solvent, as the reaction media, thus representing a promising and sustainable option for biomass valorization.
- This process is typically conducted under subcritical conditions: moderate temperatures (150–350 °C) and relatively high pressures (0.5–25 MPa).
- Thermochemical route allows the conversion of biomass into bio-oil.
- The HTL is a superior process than pyrolysis because bio-oil produced using the HTL process has relatively low oxygen content (i.e., high energy density bio-oil) than pyrolysis oil.

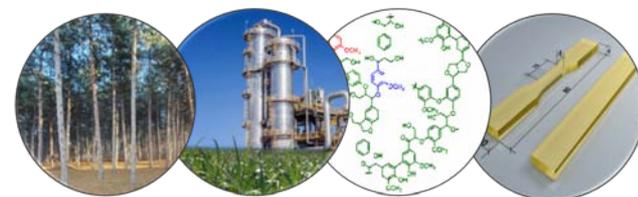




Supercritical conditions

Supercritical solvent

- Solvents in supercritical conditions behave differently than in subcritical conditions
 - Ex. They have ability to dissolve nonpolar organic molecules and inorganic solvents
- Decomposition of lignin in supercritical water occurs first by hydrolysis and then by dealkylation yielding low molecular weight fragments
- Conversion of lignin in supercritical water has been studied
 - Yield of monomers is low due to repolymerisation into char
 - Yields can be increased by introducing phenols.



Catalysis

➤ **Catalysts used in lignin depolymerisation should promote high conversion and suppress char formation and condensation**

- Conditions are not severe,
- Selective bond cleavage can be achieved leading to high selectivity for particular compounds.

Various catalysts are used for different processes and substrates.

➤ **Zeolites and amorphous silica-alumina catalysts**

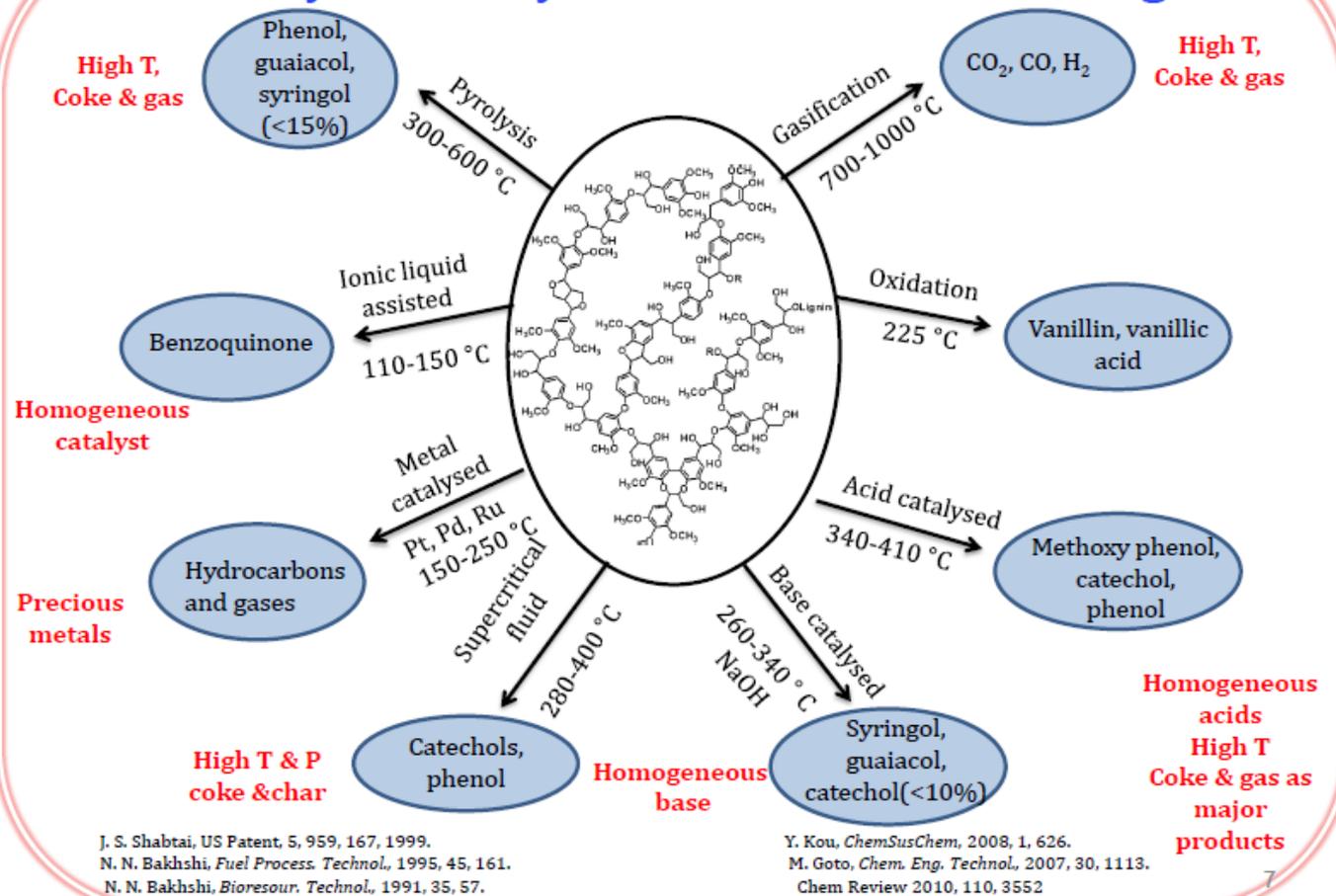
- Disrupting lignin polymer by cracking and upgrading pyrolysis oils,
- Zeolites produce more aromatic hydrocarbons,
- Silica-alumina favors aliphatic hydrocarbons,

➤ **Base catalysts (KOH, NaOH) are effective in lignin hydrolysis**

➤ **Hydrogenation catalysts (Co, W, Pd, Pt, Ni, Ru..) increases the yield and promotes hydrodeoxygenation.**

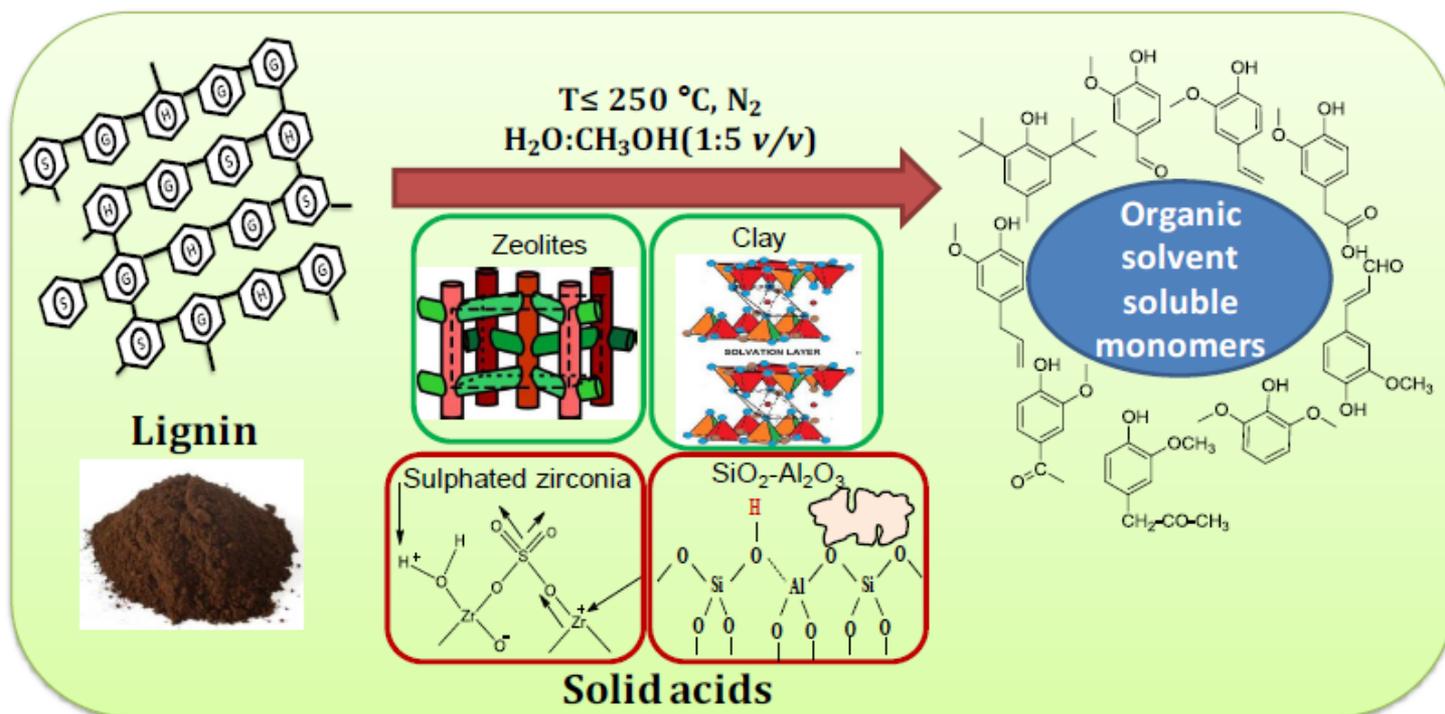


Summary on catalytic transformations of lignin



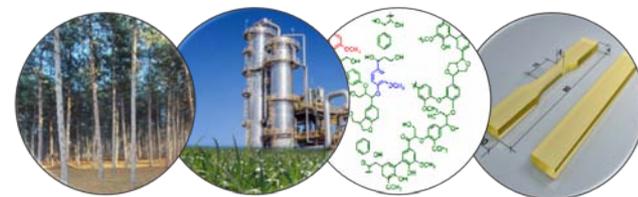


Depolymerization of lignin over solid acid catalysts



Deepa *et. al*, *ACS Catalysis*, 2015, 5, 365–379

Deepa *et. al*, Patent Application no: IN 2889 DEL 2010, US 13/467,128, AU 2012202602, BR 102012017987-3, ES 201300399



Upgrading towards desired chemicals

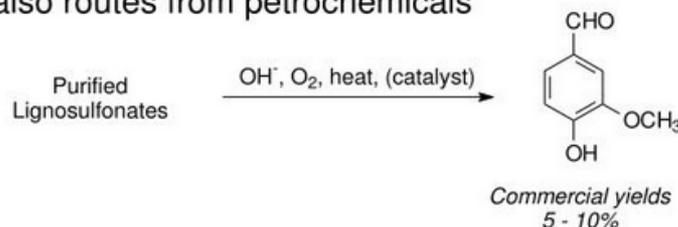
- A variety of useful products can be produced from lignin depolymerization, which includes aromatic monomers, bio-oil, biochar, syngas, heat, and energy.
- Syngas can be further processed using the Fischer-Tropsch process into methanol, dimethyl ether, and other chemical feedstocks.
- A few of the monomeric compounds obtained from various depolymerization approaches can be applied as such in end-use applications.

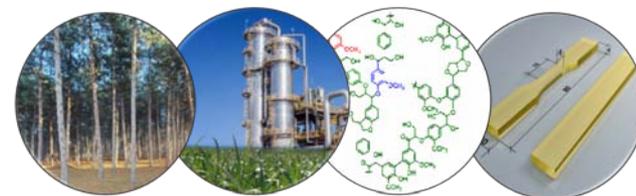
- **Vanillin** is the most available monoaromatic phenol currently produced at industrial scale from lignin.

Around 20,000 tons of vanillin is produced per year, 15% from lignin

Alkaline oxidation to vanillin

- A current commercial process
 - also routes from petrochemicals

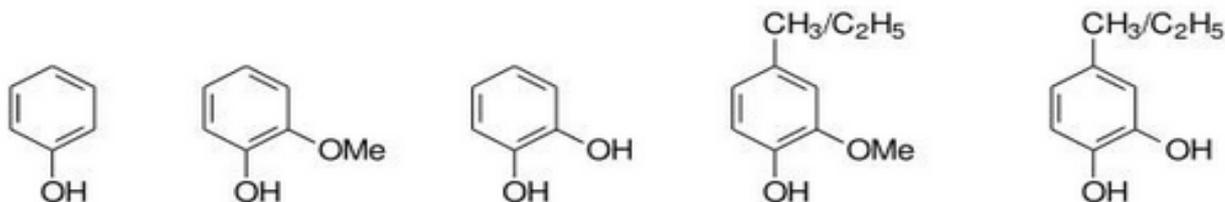


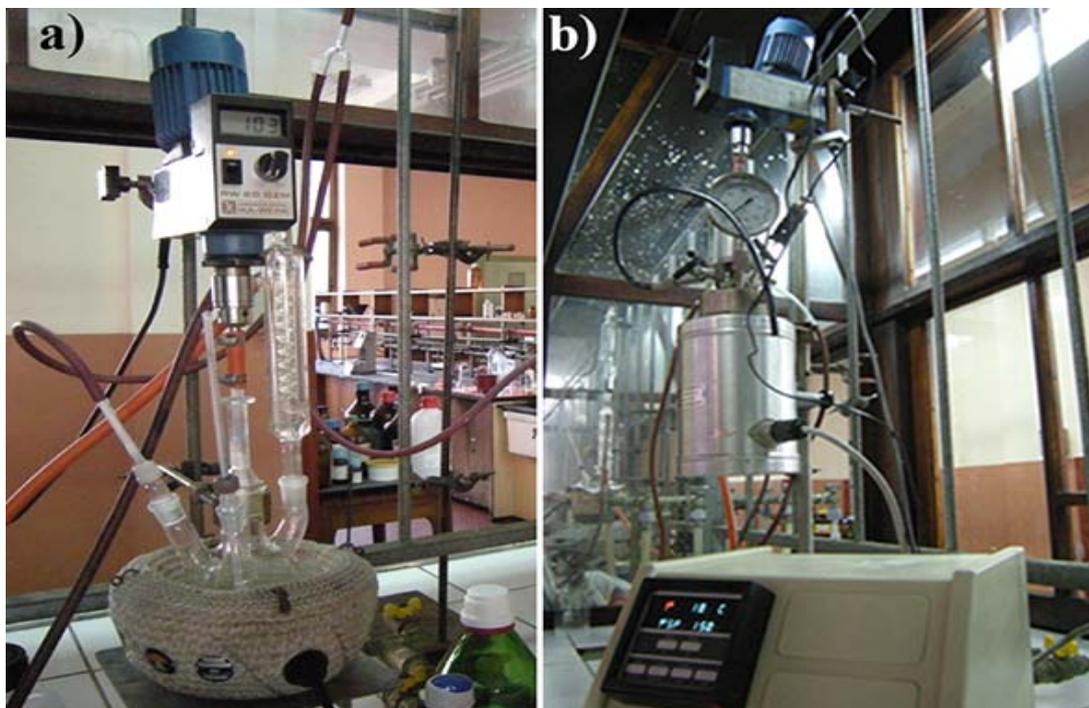


- Many depolymerization methods give rise to substituted **phenolic compounds** that require additional transformation route to marketable chemicals

Alkaline degradation of lignin

- Heat isolated lignin with aqueous alkali at 250-350°C
 - up to 33% phenolics & 11% monomeric phenols



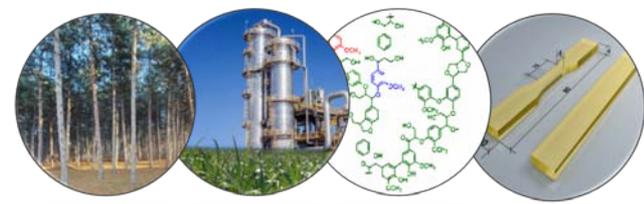


Lignin depolymerization was performed in a 0.5 L stainless steel reactor (Paar high pressure reactor; Paar Instrument Company, Moline, IL)

Alcell or Indulin lignin
10% (w/w) KOH in MeOH at 290°C
Boric acid as catalyst



oligomers



Thank you!