

LIGNIN

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Wood Chemistry

Start Course

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For over 20 years, I have been a lecturer at Poznań University of Life Sciences. I mostly deal with lignocellulose biomass chemistry, wooden cultural heritage as well as instrumental methods while investigating lignocellulose biomass.

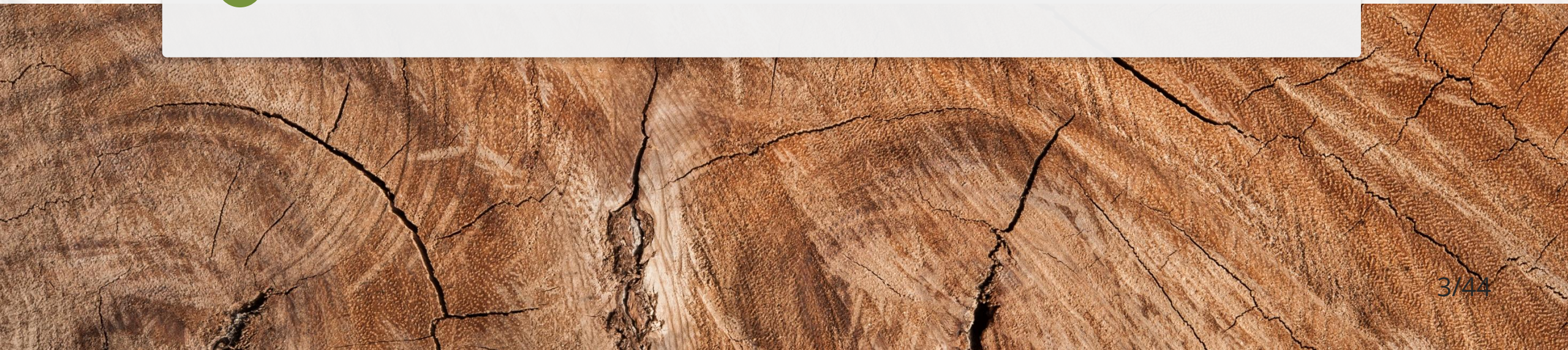
I’m the author of more than 100 scientific publications and a participant of numerous international conferences.

I’m also a keen cyclist and keeper of mixed breed dogs.



Lignin

1. Occurrence, structure and bonds of lignin
2. Reactivity
3. Application
4. Lignin-Carbohydrate complex (LCC)





Lignin

Occurence, structure, bonds

Lignin – occurrence 1/2

Lignin is the second most abundant biopolymer on the Earth, comprising 15 to 30% of biomass and being exceeded only
by polysaccharides. Worldwide, more than 50 million tonnes of lignin is generated every year as a by-product from pulp and paper-making industries.

Lignin's complexity, the degree of polymerization and diversity are so great that there may be no two identical lignin macromolecules with the same primary sequence of phenyl units. Therefore, it is more appropriate to refer to these biopolymers in the plural as "lignins".

Lignin is derived from the Latin term lignum, meaning wood. Lignin is a precursor to the fossil fuel, coal.



softwood 25-30%



hardwood 20-25%



grass less than 20%

Check your knowledge

How do you think does the percentage of lignin change as the tree grows?



You should already know the answer.

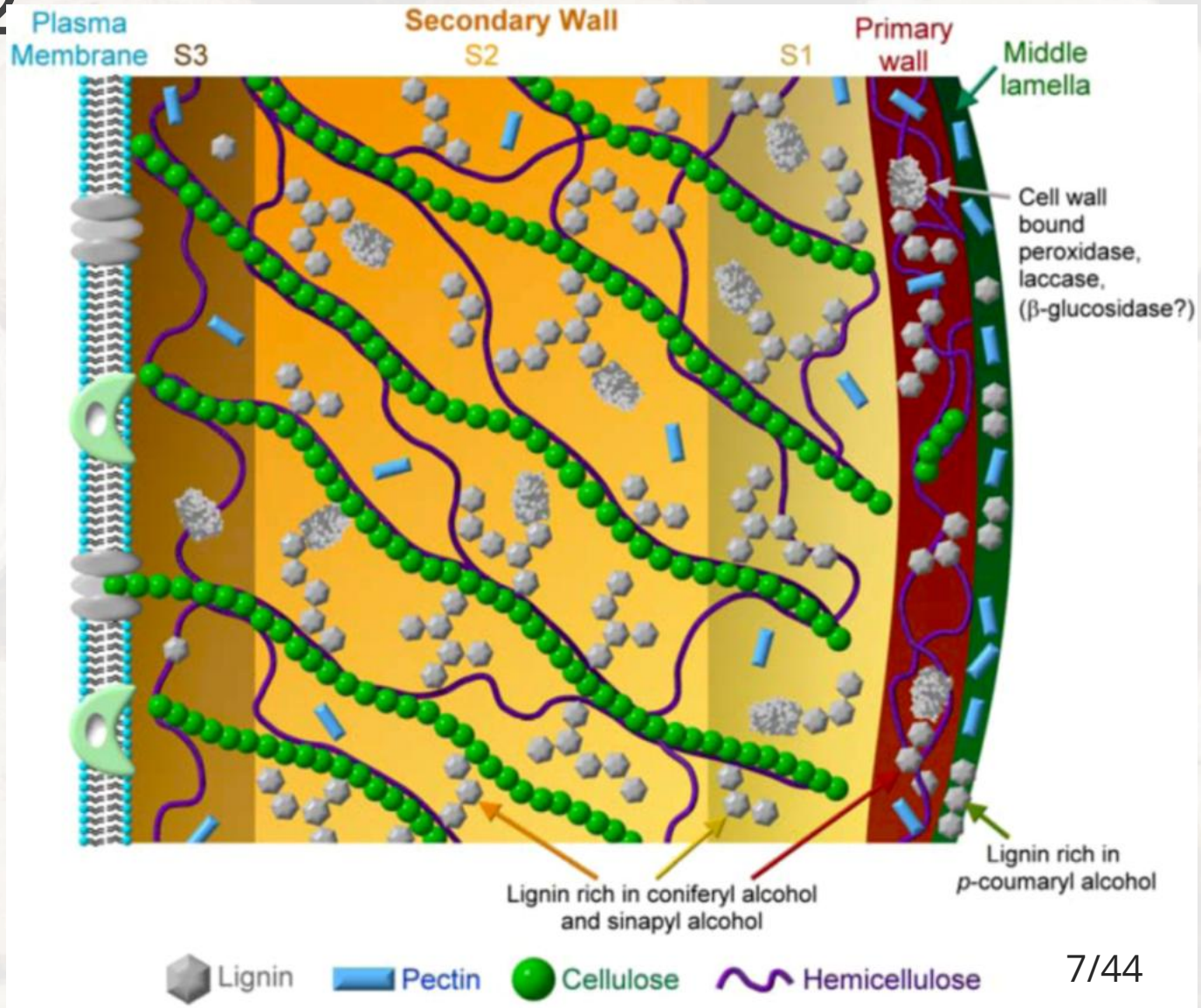
However if you don’t, please repeat the course.

Lignin – occurrence 2/2

Lignin is mainly found in the middle lamella but also, in a minor amount, in the primary and secondary cell walls of xylem vessels and fibres that strengthen plants.

Its structure differs in different zones of a cell wall.

It is also found in epidermal and occasionally hypodermal cell walls of some plants.



Check your knowledge

Which structure is dominant in the middle lamella?



You should already know the answer.

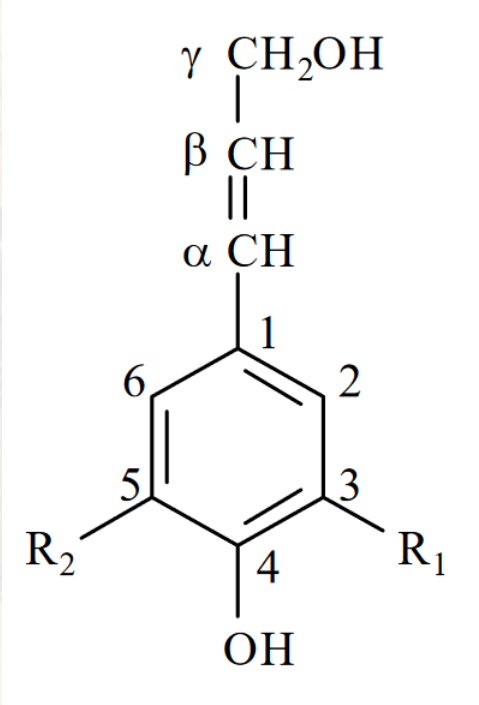
However if you don’t, please repeat the course.

Lignin - structure

Lignin is frequently described as a random, complex, irregular, heterogeneous, 3D, varyingly branched network of crosslinked, phenolic (aromatic) biopolymer.

It is composed of three main phenylpropane units (hydroxycinnamyl alcohols) that vary in their degree of methoxylation:

- coniferyl alcohols,
- sinapyl alcohols,
- *p*-coumaryl alcohols.



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Lignin - bonds

Only a small proportion of the phenolic hydroxyl groups is free since most are occupied in linkages to neighboring phenylpropane linkages.

The dominant bonding pattern of lignin is ether linkages. The abundance varies widely.

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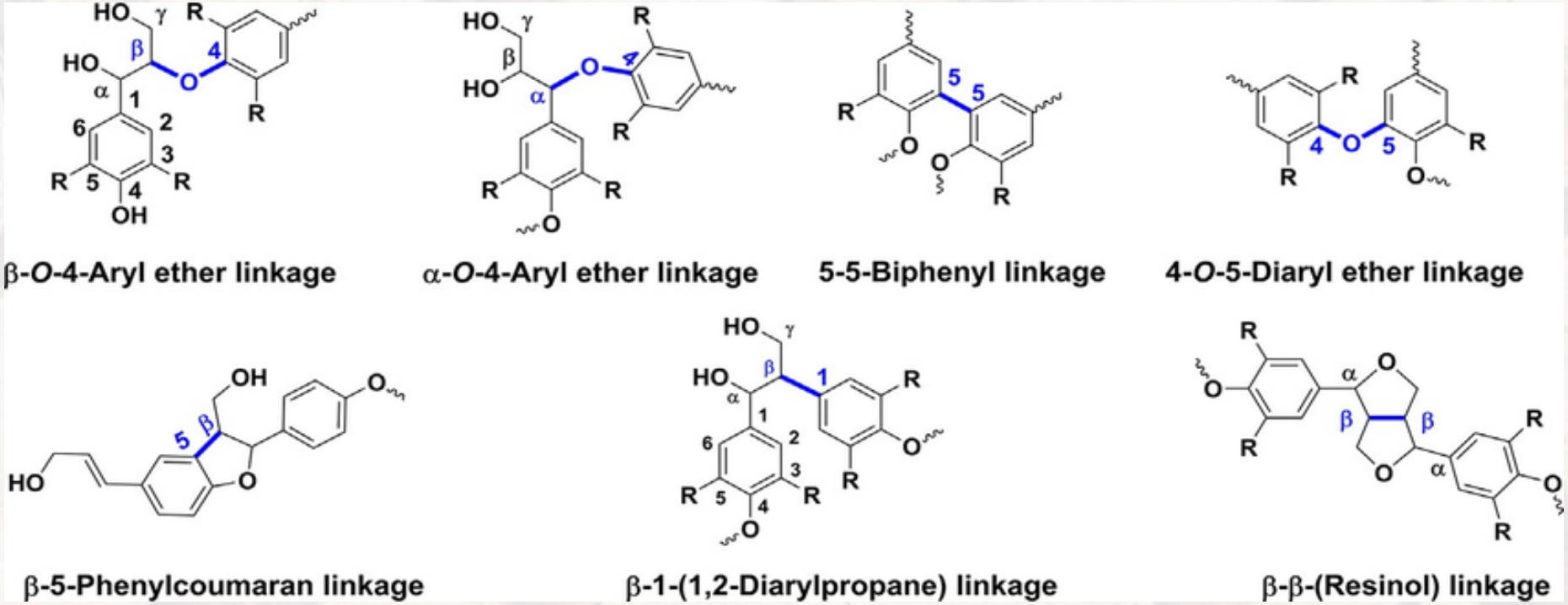
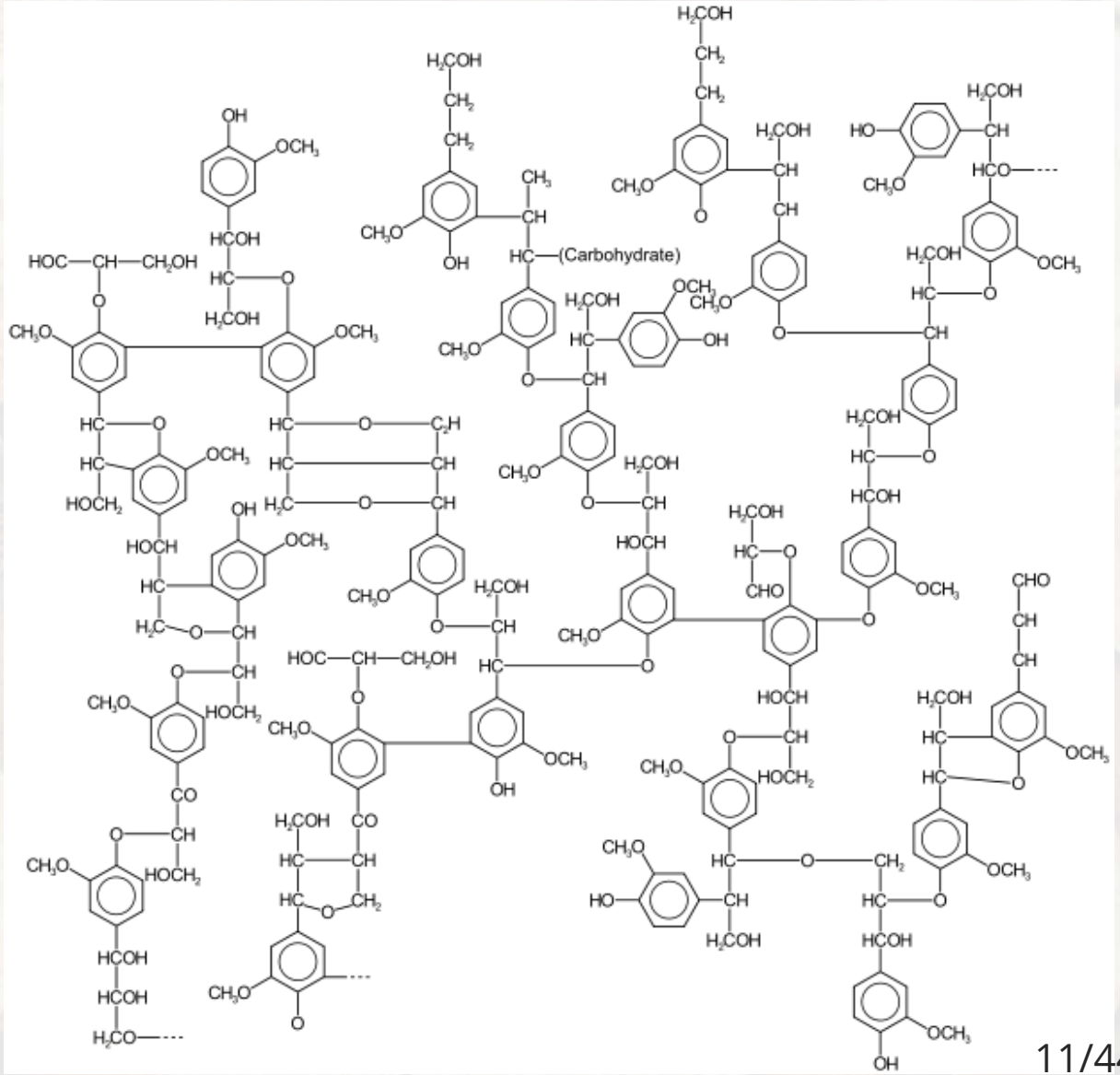


Lignin – structural model

As the lignin macromolecule cannot be described by a simple combination of one or a few monomeric units by one or a few types of linkages as in the case of cellulose or polyoses, a lignin structure is still a matter of model

The degree of polymerisation depends on source but also the method of lignin isolation. It ranges form 18 to 100.



Softwood vs. hardwood lignin

feature	softwood	hardwood
lignin content	25-30%	20-25%
lignin type	G-lignin (80% coniferyl alcohol)	GS-lignin (depends on species, average 50% coniferyl 50% sinapyl alcohol)
molecular mass	larger	lower
branching	higher	lower, more linear
cross–links	greater	fewer
C-C bonds	greater	fewer
ß-O-4 ether bonds	lower (aprox. 40%)	higher (aproc. 70%)
ß-ß and ß-5 bonds	higher	fewer
flexibility	lower	higher
-OCH3 content	15-17%	20-22%

Check your knowledge

List the differences in the structure of softwood and hardwood lignin. Which of them is more reactive?



You should already know the answer.

However if you don’t, please repeat the course.



Lignin

Lignin reactivity
Reactions in acid medium

Lignin – sulphate pulping 1/2

The sulphite pulping produces chemical wood pulp
by treating wood chips with solutions of sulphite
and bisulphite ions.

These chemicals cleave the bonds between the
carbohydrates
and lignin components of the lignocellulose.

A variety of sulphite/bisulphite salts is used, including
sodium (Na^+), calcium (Ca^{2+}), potassium (K^+), magnesium
(Mg^{2+}),
and ammonium (NH_4^+).

The lignin is converted to lignosulphonates, which are
soluble
and can be separated from the cellulose fibres.



Lignin – sulphite pulping 2/2

Typically, delignification occurs under acidic or neutral conditions during sulphite cooking. The occurring reactions are both sulphonation and condensation. The reaction mechanism is as follows:

- Quinone methide intermediates are formed by loss of the hydroxyl group or cleavage of the α-ether linkage. Under neutral conditions, the reaction proceeds with phenolic-type substrates (1), whereas under acidic conditions it proceeds with phenolic and non-phenolic-type substrates
  via a benzylic carbocation (2).
- Sulphite ions add to the quinone methide intermediates at the α-position
  to produce benzyl sulphonic acid units (3).
- When the sulphonation reaction proceeds under neutral conditions, the electron withdrawing effect of the α-sulphonic acid group of the β-O-4 moiety facilitates the nucleophilic attack by the sulphite
  on the β-carbon atom resulting in the sulphitolytic cleavage of the β-aryl ether bond (4).

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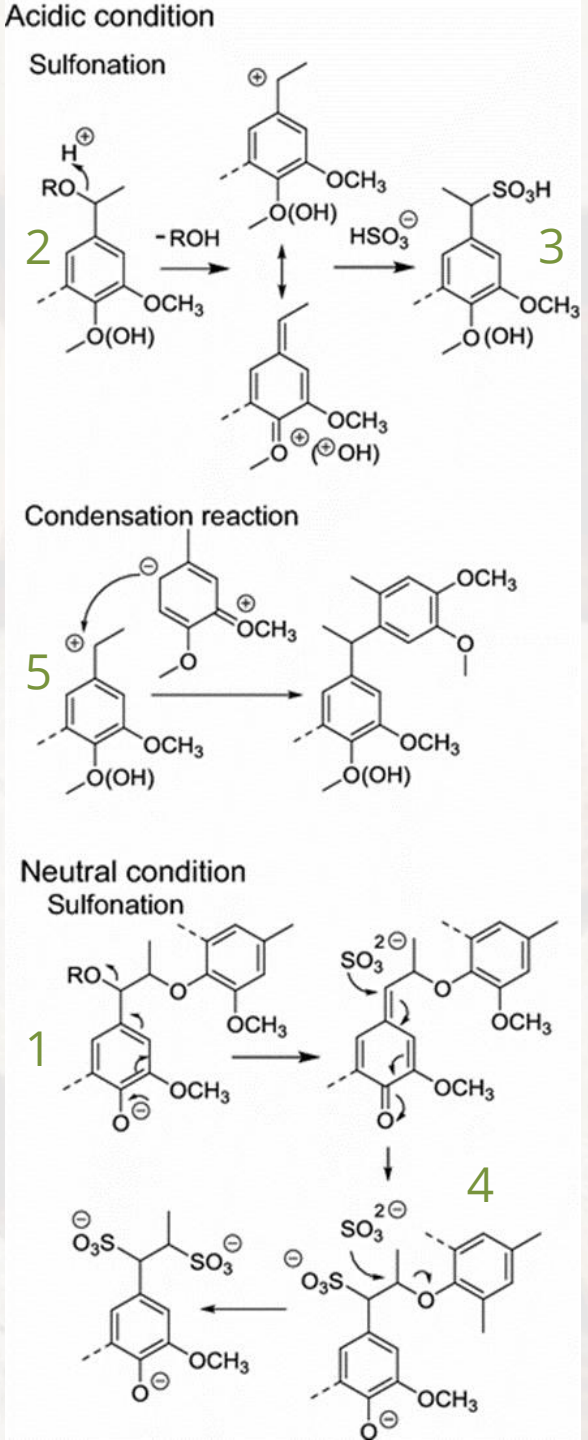
ons, a condensation reaction occurs between the benzylic carbon and the carbon in the 6-position of another nuclei owing to the benzylic cation (5).



Check your knowledge

Do you think the lignin condensation reactions are favorable or unfavorable for pulping?



You should already know the answer.

However if you don’t, please repeat the course.

Lignin – acidic bleaching

Bleaching wood pulp is the chemical processing of wood pulp to lighten its color and whiten the pulp.

Wood pulp may contain more or less (depending on a pulping process) lignin (5-40%).
The goal in bleaching pulps is to remove essentially all of the residual lignin,
hence the process is often referred to as delignification.

Acidic bleaching procedures include treatment with:

- chlorine,
- chlorine dioxide,
- hydrogen peroxide,
- peroxyacetic acid,
- ozone.



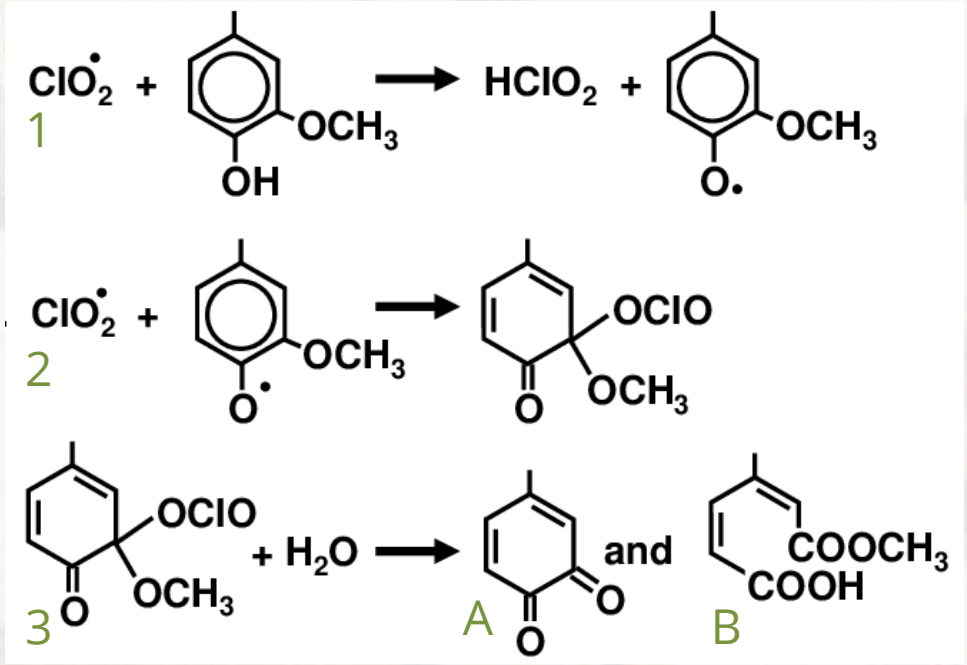
Lignin – acidic bleaching with chloride dioxide

Chlorine dioxide, which is often used in combination with chloride, causes a more efficient delignification.

This mainly results from the fact that in the contrast to chlorine, the reactions of chlorine dioxide with lignin are exclusively oxidative reactions of phenolic lignin units.

The reactions are as follows:

- the phenol is oxidized to a phenoxyl radical (1), chlorine dioxide is thereby reduced to chlorite,
- the phenoxyl radical is then oxidized to the monomethyl ester of the muconic acid derivative (2+3B) or to an ortho-quinone (2+3A).



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Lignin reactivity
Reactions in alkaline medium

Reactions in alkaline medium

- sulphate (kraft) pulping;
- alkaline bleaching;
- mild and selective oxidative;
- hydrogenolysis.



Lignin – sulphate (kraft) pulping

Kraft pulping is the predominating process for the production of chemical pulp.

The pulping treatment involves the heating of wood chips in an aqueous solution of sodium hydroxide and sodium sulphide from approximately 70°C to cooking temperature (about 170°C followed by a 1-2h cooking period.

During this treatment, lignin is extensively degraded and the degradation products are dissolved. Carbohydrates in particular hemicelluloses undergo partial degradation and dissolution. Extractives are, to a large extent, removed.



Lignin – kraft pulping 1/2

The various reactions of lignins during kraft pulping can be divided into two categories:

- degradation reactions which lead to the realize of lignin fragments and ultimately to their dissolution,
- condensation reactions which increase the molecular size of lignin fragments and may result in their precipitation.

Although having an opposite effect, these two types of reactions are closely connected with each other by proceeding via common intermediates.

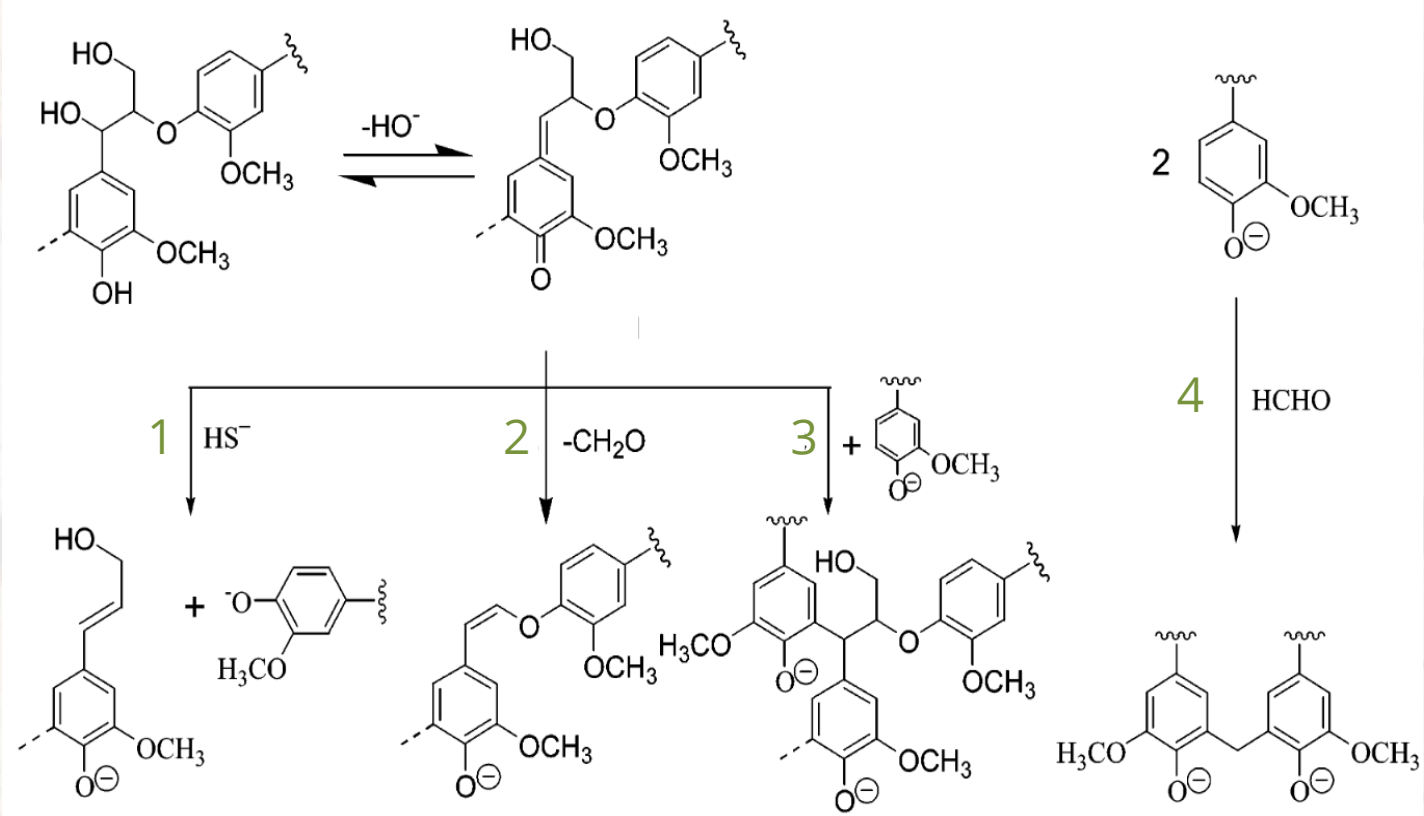


Lignin – kraft pulping 2/2

degradation reactions	condensation reactions
the ether bonds (upper half): only those belonging to the aryl-alkyl ether type (e.g. ß-O-4, α-O-4) can be cleaved during kraft pulping, whereas diaryl ether bonds (e.g. 4-O-5) are stable	so-called diarylmethane moieties of the 5-CH_2-5 and α-5 types have been considered to be the main condensed structures formed during alkaline pulping
the carbon-carbon bonds: only those belonging to the aryl–alkyl and dialkyl type (e.g. ß-5, ß-ß) can be cleaved during kraft pulping, whereas diaryl carbon-carbon bonds remain essentially unaffected	

Reactions of phenolic lignin moieties during kraft pulping

- the formation of a quinone methide structure from lignin in alkaline medium
- the sulphidolytic cleavage of ß-aryl ether bonds in sulphate pulping (1)
- the elimination of side-chains and formation
  of vinyl ether structures (2); they are believed to be stable under the conditions of kraft pulping and might be expected to accumulate in lignin
- the condensation between quinone-methide intermediates and other phenol moieties (3)
- the condensation with formaldehyde with the 5-position in phenolic units (4)



Lignin – sulphite pulping vs. sulphate (kraft) pulping

The current global production of sulphite pulps is much smaller (<4 %) than that of kraft pulps.
Sulphite pulps are used mainly as specialty pulps rather than being an alternative market grade to kraft pulps.

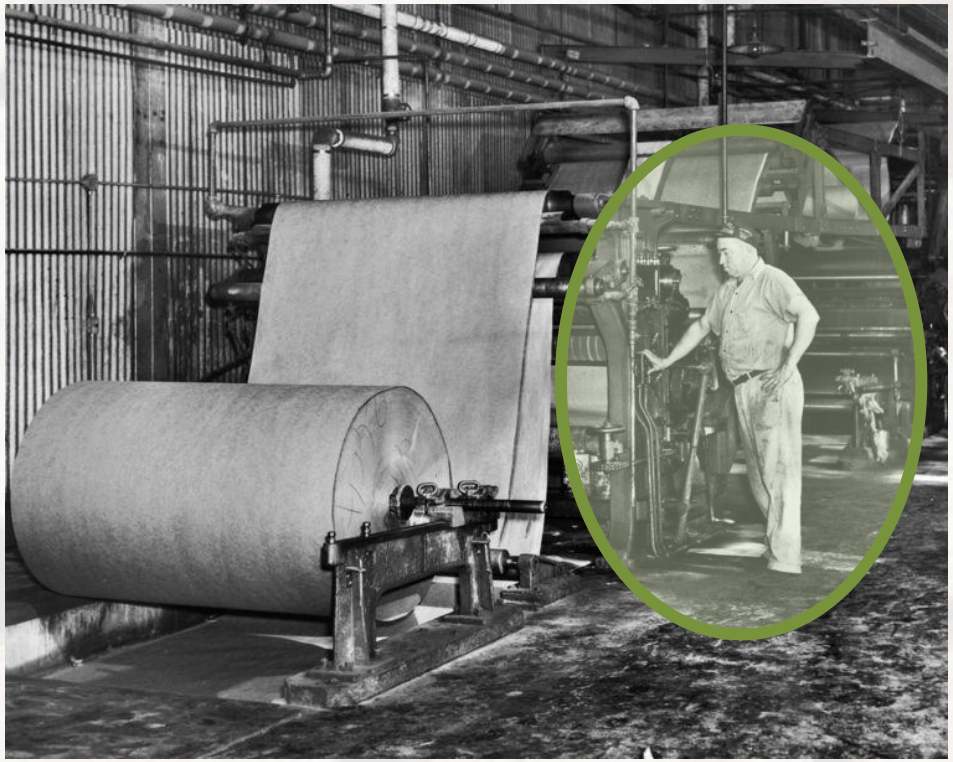
The main reasons for more limited applicability of sulphite pulps may be summarized as follows:

- It is not possible to use pine and other resinous wood raw material in a single stage acid cooking process due to the high risk of occurring lignin condensation reactions, which limits the raw material base of sulphite pulping.
- The strength of sulphite pulps is generally poorer than that of kraft pulps.
- Reducing air pollution, as required by legislation, is more costly than for a kraft mill. Also, with the exception of the magnesium-based sulphite process, it is either very costly or not possible to recover cooking chemicals.

But sulphite pulping has some advantages:

- The main characteristic of the sulphite process is its high degree of flexibility: e.g. it has a selective removal of hemicelluloses, and the entire pH range can, in principle, be used whereas kraft pulping requires an alkaline pH. Thus, the use of sulphite pulping permits the production of different types and grades of pulps suitable for a broad range of applications.
- The biorefinery approach is therefore appropriate for sulphite pulp mills, as the spent liquors are easily fermentable, and the dissolved lignin from the spent liquor can be recovered as lignosulphonates.

Paper production – the same idea, different scale



1946



nowadays

Lignin – mild and selective oxidate

A mild and selective oxidation reaction of lignin is applied to the characteristics of lignin.

The most important techniques are the following:

- alkaline nitrobenzene oxidation,
- metal oxide oxidation,
- permanganate oxidation.



Lignin – alkaline nitrobenzene oxidation

The major reaction products of lignin units are aldehydes and acids:

- for softwood lignin: vanilin;
- for hardwood lignin: mixture of vanillin syringaldehyde;
- for grass lignin: p-hydroxybenzaldehyde.

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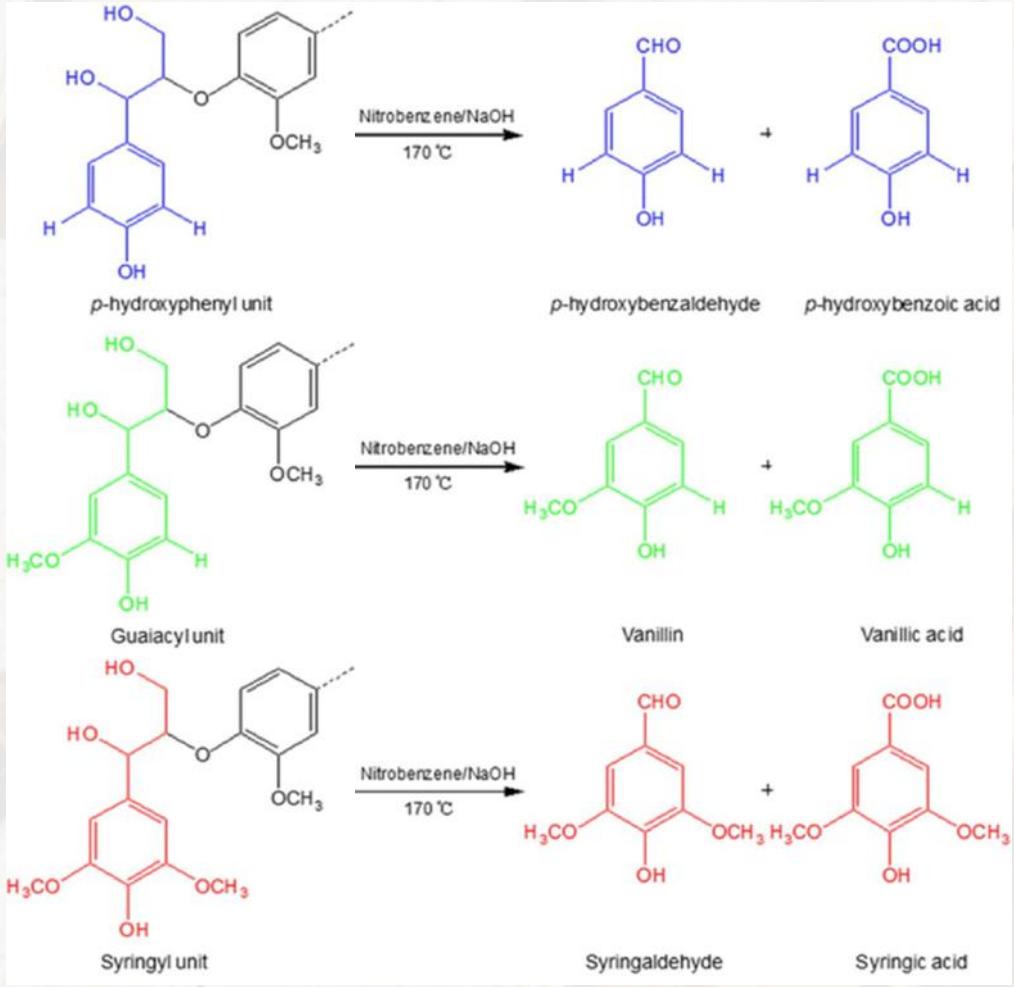
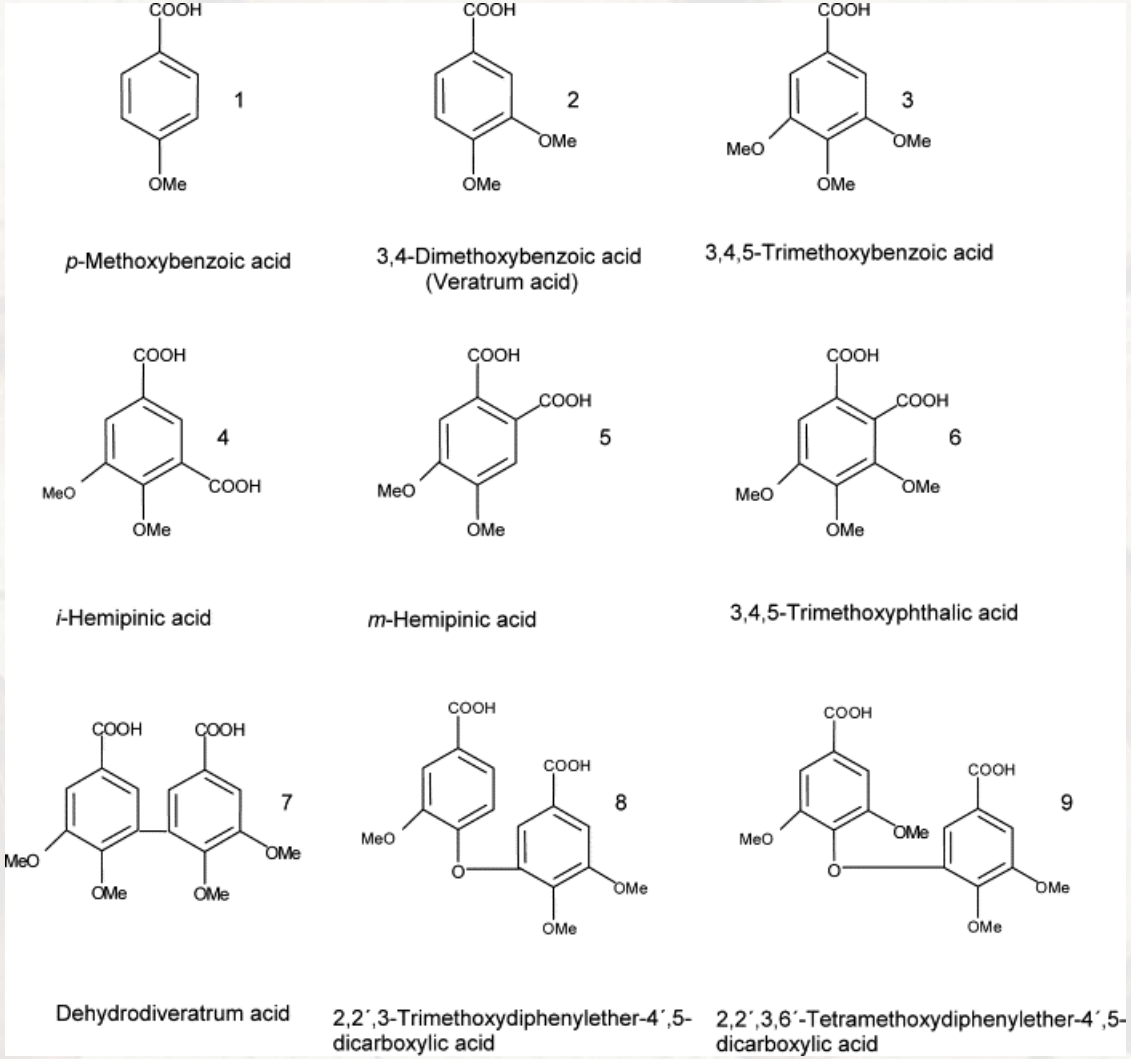


Lignin – permanganate oxidation

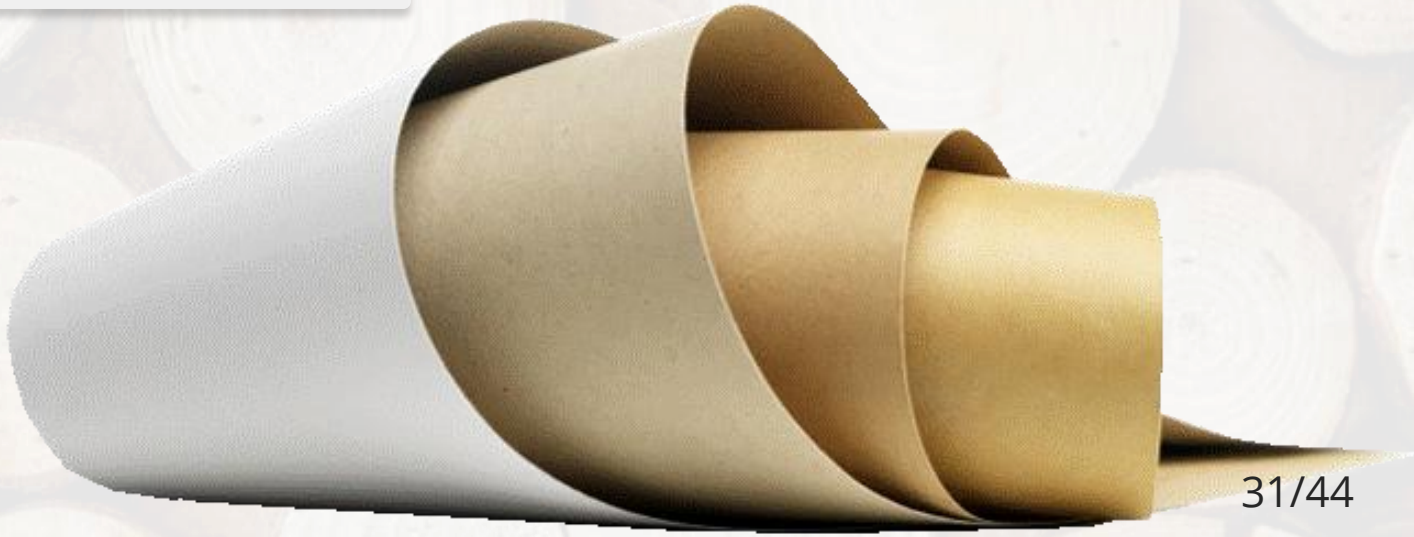
The major reaction products of softwood and hardwood
lignin units are acids.



Lignin – application 1/6

Why is lignin attractive and valuable as an industrial raw material?

- lignin accounts for 30% of all non-fossil organic carbon on the Earth;
- worldwide, more than 50 million tons of lignin is produced each year as a by-product from the pulp and paper industry;
- it is an excellent compound for chemical modifications due to the large number of functional groups (e.g. phenolic and aliphatic hydroxyl groups).



Lignin – application 2/6

Less than 2% of the lignin is actually recovered for use as a chemical product, with the remains being waste and energy recovery from combustion.

The possibility of using lignin for production depends on its structure and purity.



Check your knowledge

Why can’t lignin be used to a greater extent?

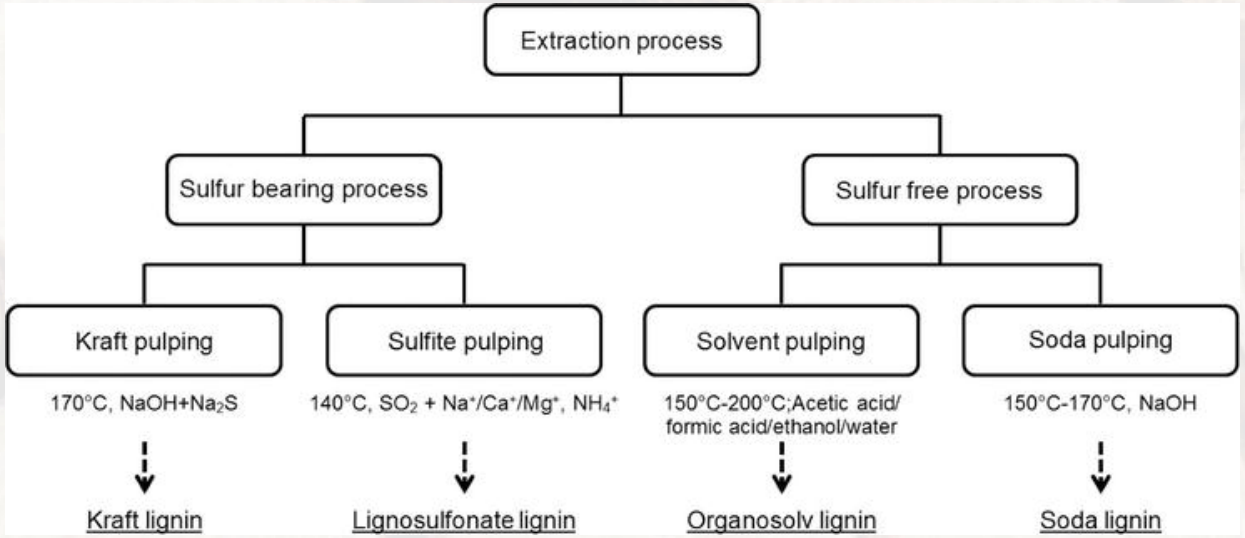


You should already know the answer.

However if you don’t, please repeat the course.

Lignin – application 3/6

The extraction processes to separate lignin from lignocellulosic biomass and the corresponding technical lignins are as follows:



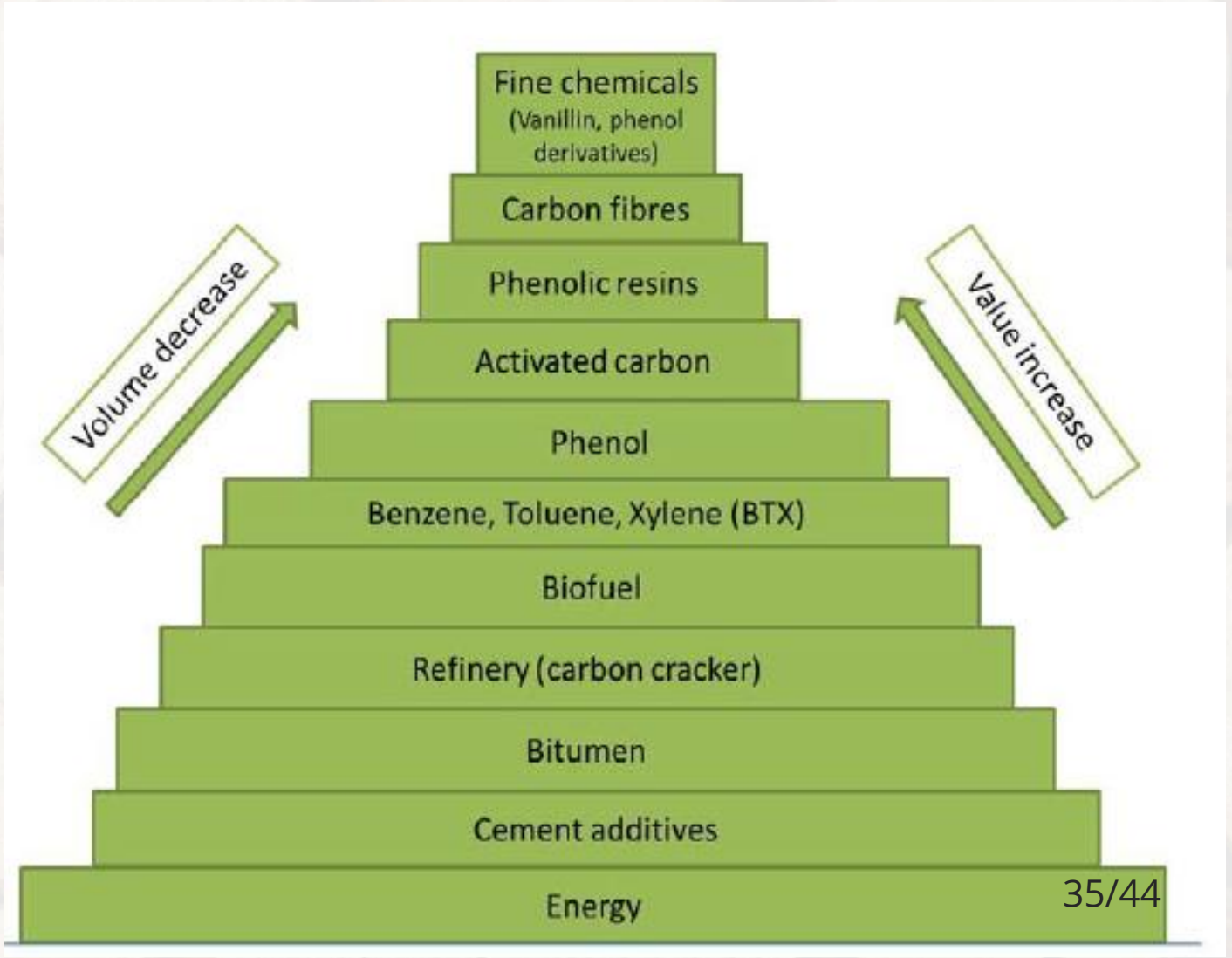
Classification of technical lignins is as follows:

Lignin type	Scale	Chemistry	Sulphur content	Purity
Kraft	Industrial	Alkaline	Low	High
Lignosulphonate	Industrial	Acidic	High	Low
Organosolv	Industrial/Pilot	Acidic	Free	High
Soda	Industrial/Pilot	Alkaline	Free	Moderate

Lignin – application 4/6

Numerous products are now obtained from lignin on an industrial scale. However, these are low market value products (energy, cement additives, bitumen, etc.).

Products such as carbon fibres, fragrances, the production of which is not large or the production
is not yet refined, have a much higher market value.

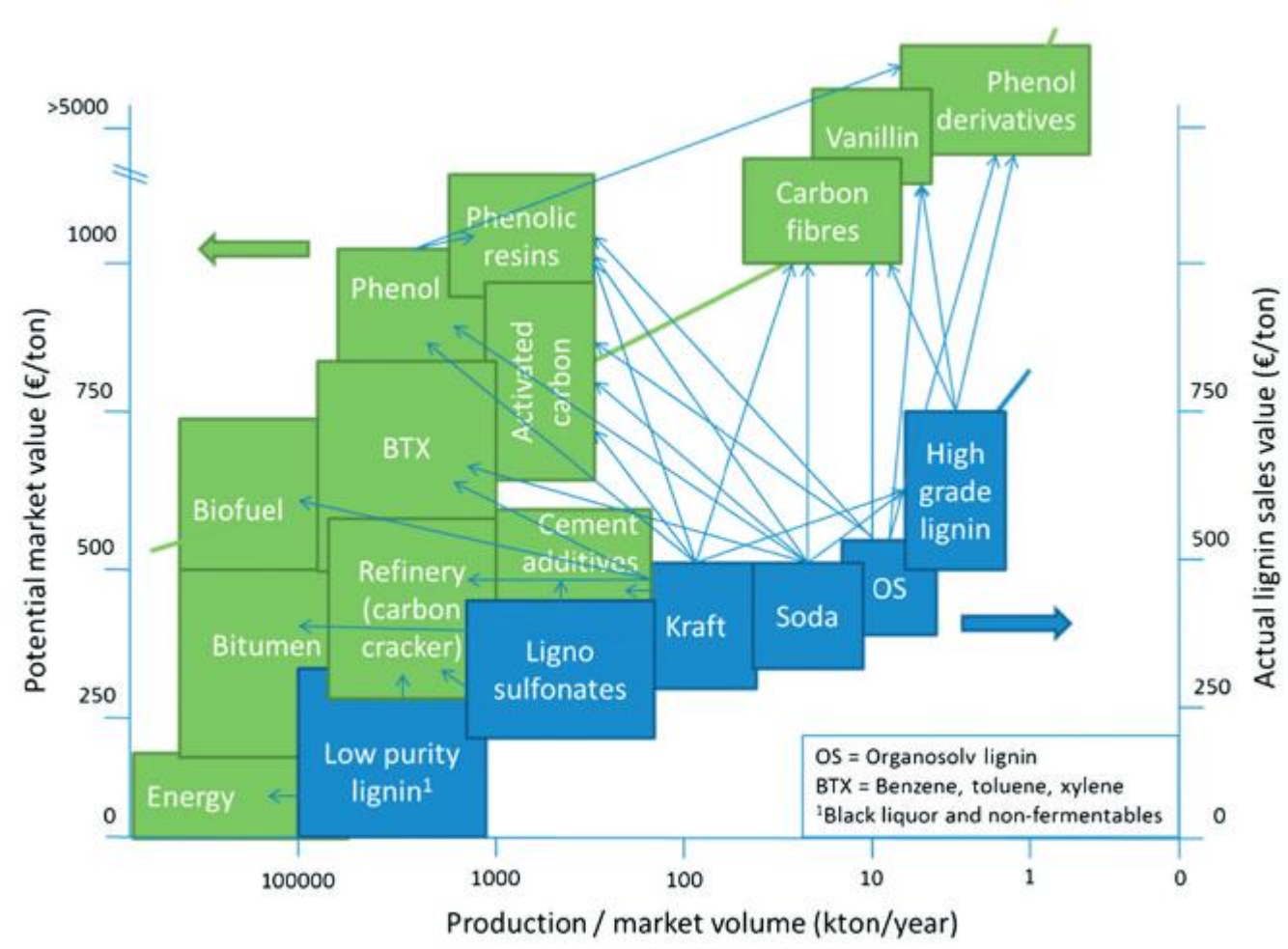


Lignin – application 5/6

Low market value products are made of low purity lignin, the production and consumption of this lignin is the greatest.

High market value products are made of high-quality lignin, the production and consumption of this lignin is much lower.

At present, lignin is definitely not used to a degree adequate to its full potential!



Lignin – application 6/6

Lignin is a fascinating molecule where established paradigms are constantly being overturned by new discoveries.

Perhaps you will contribute to decipher the structure of lignin and increase its value.





Lignin

Lignin-Carbohydrate Complex (LCC)

Lignin-Carbohydrate Complex (LCC) 1/3

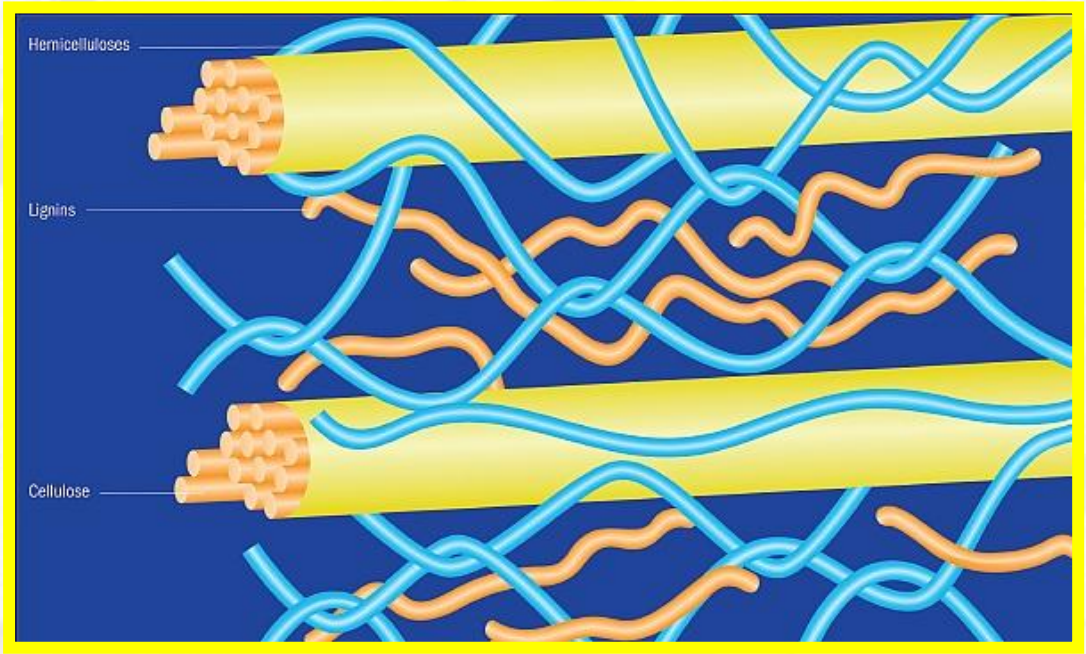
It is generally accepted today that lignin is not simply deposited between cell wall polysaccharides but it is linked and associated with at least part of them.

Studies confirmed that:

- lignin exists in a complex with hemicellulose through covalent and other non-covalent bonds;
- lignin is bound to cellulose only through non-covalent bonds.

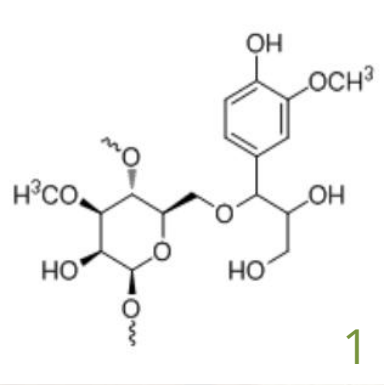
From a practical point of view, this means that the individual components
of the wood cannot be completely extracted from the wood, despite the selective chemical or cleaning action.

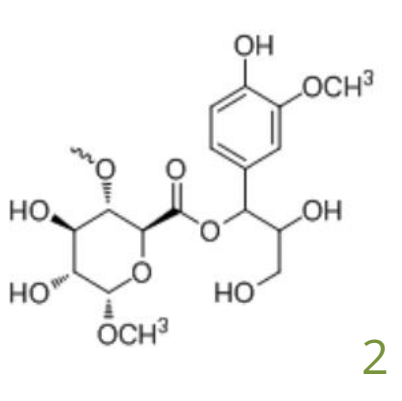
The nature and amount of LCC linkages and lignin substructures affect the efficiency of pulping, hydrolysis, and digestibility of biomass.

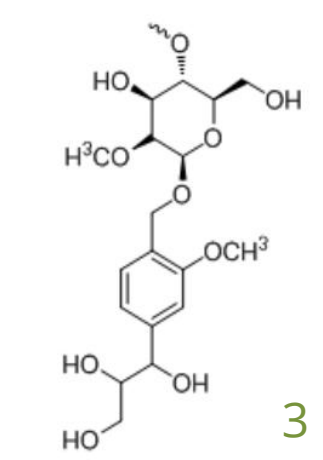


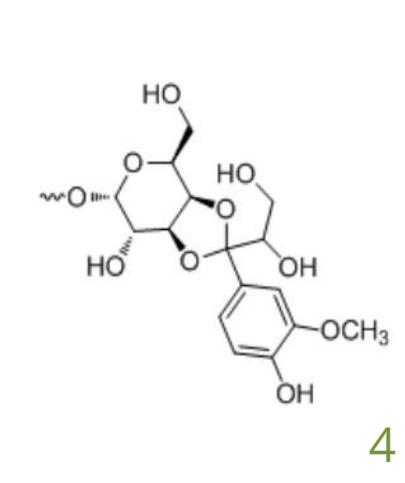
Lignin-Carbohydrate Complex (LCC) 2/3

Four major types of covalent linkages were proposed to exist between lignin and carbohydrates. These are the benzyl ether (1), benzyl ester (2), phenyl glycosidic (3) and acetal (4) bonds.









Lignin-hemicellulose complex surrounds the cellulose with which it is bound through extensive hydrogen bonding to form a supramolecular structure that protects the cellulose and is the reason for biomass recalcitrance.

Check your knowledge

List the types of bonds between lignin and carbohydrates



You should already know the answer.

However if you don’t, please repeat the course.

Lignin-Carbohydrate Complex (LCC) 3/3

Different types and proportions of lignin and polysaccharides present in biomass lead to the formation of LCC with a great variety of compositions and structures:

- in softwoods, all lignin moieties are involved in LCC and the dominant bond is the benzyl ether;
- in hardwoods and herbaceous plants, LCC constitutes 47–66% and 16–35% of total lignin, respectively, the dominant bond being the benzyl ester and phenyl glycosidic.

A high amount of benzyl ether and phenyl glycosidic bonds negatively affect kraft pulping and the delignification performance due to alkali resistance of these linkages, while the ester bonds are alkali-liable.

Summary

In this course you've learnt about:

- Occurrence, structure and bonds of lignin
- Reactivity
- Application
- Lignin-Carbohydrate complex (LCC)



Congratulations!

You've finished Lignin course.

