

Lignin

Lignin is a complex, polyphenolic, amorphous polymer with a chemical structure that differs from the other macromolecular constituents of wood. Because of its amorphous nature and irregular chemical structure it's difficult to define lignin based on its morphology. Lignin is part of lignocellulose which consists of cellulose, hemicellulose, and lignin. By weight lignin constitutes approximately 15-30 % of lignocellulose present in plants, woods and industrial crops. The characteristic that makes lignin stand out amongst other natural polymers is its very high entropy and degree of heterogeneity.¹

STRUCTURE

The exact chemical structure of lignin has not been deduced to this day. Yet it is well established that lignin is primarily composed of three phenylpropane monolignols, namely p-coumaryl, coniferyl, and sinapyl alcohols as seen in Figure 1.

The core of the lignin polymer is formed by the random interlocking of these three monolignol units into a condensed amorphous matrix that embeds and surrounds the secondary cell walls of plants. The so-called non-core lignin is formed when the monolignol units bind to at least some of the hemicellulosic species via benzyl ether, benzyl ester or phenyl glycoside linkages. The core and non-core lignin can further link with each other with ether or ester bonds. The most common linkages found in softwood and hardwood lignin are shown in Figure 2.

Depending on the plant origin, the composition of lignin varies with regard to the relative abundance of its monolignol subunits. In general, lignins can be classified into three major groups: softwood, hardwood and grass lignins. Lignin obtained from wood sources are mainly composed of coniferyl and sinapyl alcohol units whereas grass and herbaceous plants contain also p-coumaryl alcohol.

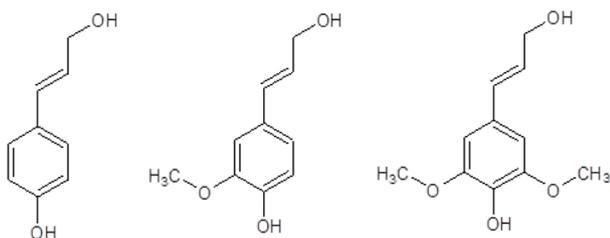


Figure 1. *trans-p-coumaryl alcohol* (left), *trans-coniferyl alcohol* (middle) and *trans-sinapyl alcohol* (right).

Table 1. The distribution of lignin in softwoods and hardwoods.

Wood species	Amount of ligning (%)	Reference
Softwood stem wood	25-35	Fengel & Grosser 1975 ²
Softwood bark	40-55	USDA 1971 ³
Hardwood stem wood	20-25	Fengel & Grosser 1975
Hardwood bark	40-50	USDA 1971

The most important functional groups in lignin are the phenolic and aliphatic hydroxyl groups, and methoxy, carbonyl and carboxy groups, which make lignin suitable as an additive in various applications such as dispersants, resins, surfactans, absorbents etc. The amount of free phenolic hydroxyl groups in lignin seems to be the factor that contributes most to the relatively high antioxidant activity of lignin.

SOURCES OF LIGNIN

Lignin can be found almost everywhere in the plant kingdom. Natural lignocellulose is the world's most abundant biomass resource and lignin, being a major part of lignocellulose, can provide a viable alternative to many nonrenewable fossil resources. Lignocellulose is easy to access, cheap and renewable. Any processing of lignocellulosic material will usually lead to lignin side streams that could be further enhanced in terms of their value. This is however yet uncommon as most "lignin waste" is still being burned for energy and only 2 % gets utilized for other applications.

BIOLOGICAL FUNCTIONS OF LIGNIN

The biological functions of lignin are fairly well understood. Lignin provides trees and plants protection against insects, fungi, microbial degradation, and

weather. Lignin allows for efficient transfer of water and nutrients in trees and plant by making their cell walls hydrophobic. Lignin also provides structural integrity to vegetal cell walls and greatly contributes to their final morphology. Lignin acts kind of like all-encompassing matrix for other polymer species by filling the space between them and crosslinking polysaccharides. This gives lignocellulose much of its strength, stiffness and rigidity. Consequently, trees and plants with more lignin are, in general, able to build up higher and stronger stem and branches.

EXTRACTION OF LIGNIN

Extraction of lignin from lignocellulosic biomass can be accomplished in multiple ways (physical, chemical or physicochemical), leading to lignin with slightly different characteristics depending on the used method. Traditional extraction ways include inorganic acid-, soda- or Kraft-extraction or ball-milling methods. More novel are organosolv, steam explosion, autohydrolysis or microwave extraction methods.

Usually the extractions are done under elevated temperature and pressure lasting for several hours. Longer reaction time is however not cost-efficient and may lead to unwanted side reactions.

Lignin that is separated in the form of "milled wood lignin" (MLW), "dioxane lignin" or "enzymically liberated lignin" is usually referred to as the "native lignin". Technical lignins are the industrial by products of chemical pulping, such as "Kraft lignin" (or sulphate lignin) and alkali lignin (or soda lignin). Other lignin kinds include "organosolv lignins", obtained via organic solvent (mainly alcohols) pulping of wood and acid hydrolysis lignins, obtained from the acid hydrolysis processes of wood.

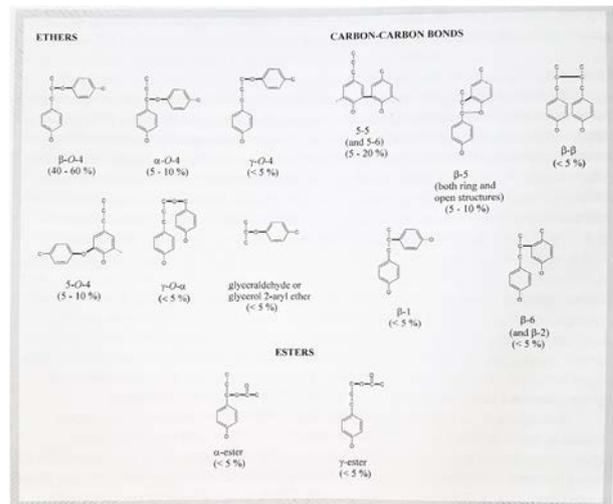


Figure 3. The most common inter-unitary linkages and structures found in native softwood and hardwood lignins.¹ The frequency of a given linkage is shown as a percentage of the total linkages.



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