

Chapter 2

Lignin

Abstract Information on lignin is presented in this chapter.

Keywords Lignin • Hardwood • Softwood • Phenylpropane • Guaiacyl • Syringyl • Lignin isolation • Lignin sources

The term lignin is derived from the Latin word *Lignum* for wood and was first mentioned by Augustin Pyramus de Candolle, a Swiss botanist in 1819 (de Candolle and Sprengel 1821). Lignin is a complex organic polymer that forms important structural materials in the support tissues of vascular plants. It is highly polymerized and is particularly common in woody plants. The cellulose walls of the wood become impregnated with lignin. This process is called lignifications. It greatly increases the strength and hardness of the cell and imparts necessary rigidity to the tree. This is essential to woody plants in order that they stand erect (Rouhi and Washington 2001). It is one of the most abundant organic polymers on Earth after cellulose. Natural lignin is a three-dimensional polymer that occurs in many plants at levels from 15 to 32 wt% (Table 2.1). It has a complex structure containing both aromatic and aliphatic entities (Nordström 2012). Knowledge of lignin has evolved over one hundred years and the importance of lignin has been widely recognized since the early 1900s (Glasser et al. 2000). Our understanding of lignin is limited due to its complex structure. In the recent years, through the application of modern methods of chemical analysis, the lignin field has developed dramatically. This has led to the knowledge of the structure of lignin and also to the applications of lignin. Lignin has been described as a random, three-dimensional network polymer comprised of variously linked phenylpropane units. Lignin comprises 15–25% of the dry weight of woody plants. This macromolecule plays a vital role in providing mechanical support to bind plant fibres together. Lignin also decreases the permeation of water through the cell walls of the xylem, thereby playing an intricate role in the transport of water and nutrients. Finally, lignin plays an important function in a plant's natural defense against degradation by impeding penetration of destructive enzymes through the cell wall (Sarkanen and Ludwig 1971; Sjöström 1993). Although lignin is necessary to trees, it is undesirable in

Table 2.1 Composition of biomass

Biomass	Cellulose	Hemicellulose	Lignin	Extractives
Softwood	45 ± 2%	30 ± 5%	20 ± 4%	5 ± 3%
Hardwood	42 ± 2%	27 ± 2%	28 ± 3%	3 ± 2%
Switchgrass	37 ± 2%	29 ± 2%	19 ± 2%	15 ± 2%

Based on Sjöström (1993) and Mani et al. (2006)

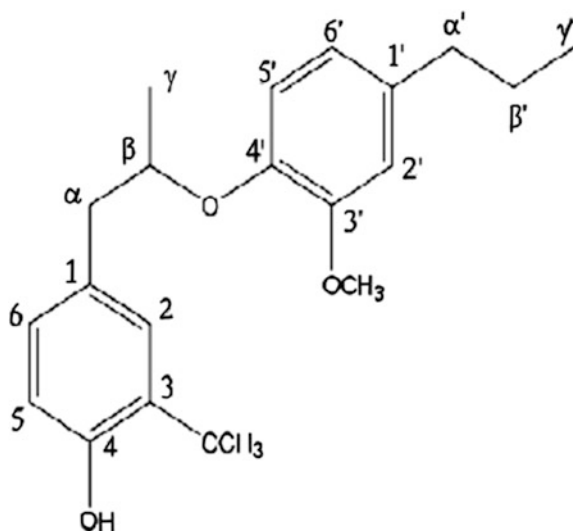
most chemical papermaking fibres and is removed by pulping and bleaching processes.

Plant lignins can be broadly divided into three classes: softwood (gymnosperm), hardwood (angiosperm) and grass or annual plant (graminaceous) lignin (Pearl 1967). Three different phenylpropane units, or monolignols, are responsible for lignin biosynthesis (Freudenberg and Neish 1968). Guaiacyl lignin is composed principally of coniferyl alcohol units, while guaiacyl-syringyl lignin contains monomeric units from coniferyl and sinapyl alcohol. In general, guaiacyl lignin is found in softwoods while guaiacyl-syringyl lignin is present in hardwoods. Graminaceous lignin is composed mainly of p-coumaryl alcohol units.

Lignins are particularly important in the formation of cell walls, particularly in wood and bark, because they impart rigidity and do not rot easily. Lignin fills the spaces in the cell wall between cellulose, hemicellulose and the pectin components, particularly in xylem tracheids, sclereid cells and vessel elements. It is linked to hemicellulose by covalent bonds and so it crosslinks different plant polysaccharides, imparting mechanical strength to the cell wall and by extension the plant as a whole. It is especially abundant in compression wood but is rare in tension wood which are types of reaction wood. Lignin plays a very important role in conducting water in plant stems and also plays a significant role in the carbon cycle and sequesters atmospheric carbon into the living tissues of woody perennial vegetation. Lignin slowly decomposes components of dead vegetation and contributes a major fraction of the material that becomes humus as it decomposes. Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u. It is relatively hydrophobic and aromatic in nature. Lignin is polymers of phenylpropane units. Several aspects in the chemistry of lignin is still not clear.

Wood consists of 20–35% of lignin, and lignin is an important factor making wood an extraordinary material (Henriksson 2007). It is a hydrophobic material, making the cell wall impermeable to water, and thus ensuring an efficient water- and nutrition transport in the cells. The compact lignin-rich structure of wood also protects the polysaccharides from harmful microorganisms (Henriksson 2007). Wood lignin is a branched three-dimensional macromolecule mainly built up from two monolignolic units, coniferyl alcohol and sinapyl alcohol (Brodin 2009). These units give two different types of phenyl propanes in the macromolecule; guaiacyl and syringyl, respectively, which are connected with ether and carbon–carbon bonds (Sjöström 1993). Softwood lignin only contains guaiacyl units in which one of the ortho positions next to the phenol is free. The distribution of linkages in the

Fig. 2.1 Common bond in lignin. The most important bond in lignin is the β -o-4. Based on Henriksson (2007)



lignin structure appears to be random and no contrary evidence has been reported (Fig. 2.1) (Henriksson 2007; Brodin 2009).

Hardwood lignin contains syringyl units in addition to guaiacyl, which contributes to retaining a more linear structure during technical delignification and isolation processes thereof, whereas lignins originating from softwoods are more easily branched and/or cross-linked (Kubo et al. 1997; Brodin 2009). The lignin yield and the final chemical structure are also affected by the isolation methods (Sjöström 1993) and therefore affect the thermal behaviour of lignins. About two-thirds of the lignin bonds are of ether type and about one-third is carbon–carbon linkages. The most common linkage is the β -o-4' linkage, which represents 50–60% of the total linkages depending on the tree type (Sjöström 1993; Henriksson 2007). The β -O-4' linkage is susceptible for pulping and bleaching and biodegrading reactions whereas the covalent carbon–carbon bonds are more stable. The functional groups in lignin are mainly methoxyl groups, phenolic hydroxyl groups and some terminal aldehyde groups. The free phenols represent only 10–13% of the total amount of aromatic rings (Henriksson 2007).

In order to use lignin as raw material, lignin has to be isolated from lignocellulose. Lignin can be derived from various sources such as cereal straws, bamboo, bagasse and wood. In terms of weight, the lignin content in wood is the highest, roughly 20–35% while other sources only contain around 3–25% (Smolarski 2012).

Around 50 million tonnes of lignin are produced annually from the pulping process; however, only approximately 1 million tonnes are isolated and sold each year for industrial applications. In general, these markets are low volume niche applications (Lucintel Market Report 2011; Luo 2010). They can be divided in three main groups, Biofuel, macromolecules and aromatics (NNFCC 2009; Chapple et al. 2007; Smolarski 2012).

Table 2.2 Types of lignin and their use

Low purity Energy, Refinery (carbon cracker)
Lignosulphonates Energy, Refinery (carbon cracker)
Kraft Bitumen, Refinery (carbon cracker) , Cement additives, Biofuel, High-grade lignin, BTX (Benzene, Toluene and Xylene), Phenolic resins, Carbon fibres, Vanillin, Phenol
Organosolv Activated carbon, Phenolic resins, Carbon fibres, Vanillin, Phenol derivatives
Based on Smolarski (2012)

The price of lignin depends on the type of feedstock and the degradation and purification process adopted, as they determine the lignin structure, purity and consistency. Typically, kraft and organosolv lignins are suitable candidates for high-value applications whereas lingosulphonate lignin most likely is used for lower value products, Table 2.2. Additionally, kraft lignin covers several applications, including the high-value ones, and is considered mid-range in terms of price. It is also readily available in sufficient quantity from pulp and paper manufacturers to start meeting the industrial demand and is considered a good intermediate between lignosulphonates and organosolv lignin.

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