Lignin

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Lignin or **lignen** is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants[1] and some algae.[2] The term was introduced in 1819 by de Candolle and is derived from the Latin word *lignum*,[3] meaning wood. It is one of the most abundant organic polymers on Earth, exceeded only by cellulose, employing 30% of non-fossil organic carbon[4] and constituting from a quarter to a third of the dry mass of wood. As a biopolymer, lignin is unusual because of its heterogeneity and lack of a defined primary structure. Its most commonly noted function is the support through strengthening of wood (xylem cells) in trees.[5][6][7]

Biological function

Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in tracheids, sclereids and xylem. It is covalently linked to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole.[8] It is particularly abundant in compression wood but scarce in tension wood.

Lignin plays a crucial part in conducting water in plant stems. The polysaccharide components of plant cell walls are highly hydrophilic and thus permeable to water, whereas lignin is more hydrophobic. The crosslinking of polysaccharides by lignin is an obstacle for water absorption to the cell wall. Thus, lignin makes it possible for the plant's vascular tissue to conduct water efficiently.[9] Lignin is present in all vascular plants, but not in bryophytes, supporting the idea that the original function of lignin was restricted to water transport. However, it is present in red algae, which seems to suggest that the common ancestor of plants and red algae also synthesised lignin. This would suggest that its original function was structural; it plays this role in the red alga *Calliarthron*, where it supports joints between calcified segments.[2]

Lignin is indigestible by animal enzymes, but some fungi and bacteria are able to secrete ligninases which can biodegrade the polymer. The details of the biodegradation are not well understood. The pathway depends on the type of wood decay - in fungi either brown rot, soft rot or white rot. The enzymes involved may employ free radicals for depolymerization reactions.[10] Well understood lignolytic enzymes are manganese peroxidase, lignin peroxidase and cellobiose dehydrogenase. Furthermore, because of its cross-linking with the other cell wall components, it minimizes the accessibility of cellulose and hemicellulose to microbial enzymes. Hence, lignin is generally associated with reduced digestibility of the overall plant biomass, which helps defend against pathogens and pests.[9]

Lignin peroxidase (also "ligninase", EC number 1.14.99) is a hemoprotein from the white-rot fungus *Phanerochaete chrysosporium* with a variety of lignin-degrading reactions, all dependent on hydrogen peroxide to incorporate molecular oxygen into reaction products. There are also several other microbial enzymes that are believed to be involved in lignin biodegradation, such as manganese peroxidase, laccase and Cellobiose dehydrogenase (acceptor).

Ecological function

Lignin plays a significant role in the carbon cycle, sequestering atmospheric carbon into the living tissues of woody perennial vegetation. Lignin is one of the most slowly decomposing components of dead vegetation, contributing a major fraction of the material that becomes humus as it decomposes. The resulting soil humus generally increases the photosynthetic productivity of plant communities growing on a site as the site transitions from disturbed mineral soil through the stages of ecological succession, by providing increased cation exchange capacity in the soil and expanding the capacity of moisture retention between flood and drought conditions.

Economic significance

Highly lignified wood is durable and therefore a good raw material for many applications. It is also an excellent fuel, since lignin yields more energy when burned than cellulose. Mechanical, or high yield pulp used to make newsprint contains most of the lignin originally present in the wood. This lignin is responsible for newsprint yellowing with age.[3] Lignin must be removed from the pulp before high quality bleached paper can be manufactured from it.

In sulfite pulping, lignin is removed from wood pulp as sulfonates. These lignosulfonates have several uses:[11]

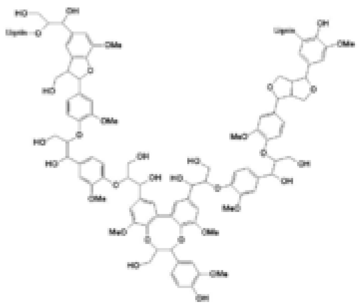
- Dispersants in high performance cement applications, water treatment formulations and textile dyes
- Additives in specialty oil field applications and agricultural chemicals
- Raw materials for several chemicals, such as vanillin, DMSO, ethanol, xylitol sugar and humic acid
- Environmentally sustainable dust suppression agent for roads

The first investigations into commercial use of lignin were reported by Marathon Corporation in Rothschild, Wisconsin (USA), starting in 1927. The first class of products which showed promise were leather tanning agents. The lignin chemical business of Marathon was operated for many years as Marathon Chemicals. It is now known as LignoTech USA, Inc., and is owned by the Norwegian company, Borregaard, itself a subsidiary of the Norwegian conglomerate Orkla AS.

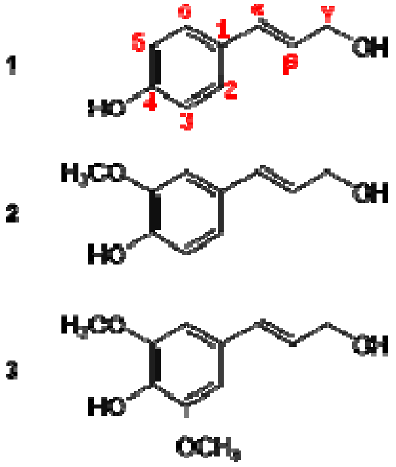
Lignin removed via the kraft process (sulfate pulping) is usually burned for its fuel value, providing more than enough energy to run the mill and its associated processes.

More recently, lignin extracted from shrubby willow has been successfully used to produce expanded polyurethane foam. [12]

In 1998, a German company, Tecnaro, developed a process for turning lignin into a substance, called Arboform, which behaves identically to plastic for injection molding. Therefore, it can be used in place of plastic for several applications. When the item is discarded, it can be burned just like wood.[13]



A small piece of lignin polymer



The three common monolignols: paracoumaryl alcohol (1), coniferyl alcohol (2) and sinapyl alcohol (3)

Lignin is a cross-linked racemic macromolecule with molecular masses in excess of 10,000 u. It is relatively hydrophobic and aromatic in nature. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures which appear to repeat in a haphazard manner. Different types of lignin have been described depending on the means of isolation.[14]

There are three monolignol monomers, methoxylated to various degrees: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol[15] (Figure 3). These lignols are incorporated into lignin in the form of the phenylpropanoids *p*-hydroxyphenyl (H), guaiacyl (G), and syringal (S) respectively.[4] Gymnosperms have a lignin that consists almost entirely of G with small quantities of H. That of dicotyledonous angiosperms is more often than not a mixture of G and S (with very little H), and monocotyledonous lignin is a mixture of all three.[4] Many grasses have mostly G, while some palms have mainly S.[*citation needed*] All lignins contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants.[16]

Biosynthesis

Lignin biosynthesis (Figure 4) begins in the cytosol with the synthesis of glycosylated monolignols from the amino acid phenylalanine. These first reactions are shared with the phenylpropanoid pathway. The attached glucose renders them water soluble and less toxic. Once transported through the cell membrane to the apoplast, the glucose is removed and the polymerisation commences.[*citation needed*] Much about its anabolism is not understood even after more than a century of study.[4]

The polymerisation step, that is a radical-radical coupling, is catalysed by oxidative enzymes. Both peroxidase and laccase enzymes are present in the plant cell walls, and it is not known whether one or both of these groups participates in the polymerisation. Low molecular weight oxidants might also be involved. The oxidative enzyme catalyses the formation of monolignol radicals. These radicals are often said to undergo uncatalyzed coupling to form the lignin polymer, but this hypothesis has been recently challenged.[17] The alternative theory that involves an unspecified biological control is however not widely accepted.

Pyrolysis

Pyrolysis of lignin during the combustion of wood or charcoal production yields a range of products, of which the most characteristic ones are methoxy phenols. Of those, the most important are guaiacol and syringol and their derivatives; their presence can be used to trace a smoke source to a wood fire. In cooking, lignin in the form of hardwood is an important source of these two chemicals which impart the characteristic aroma and taste to smoked foods.