

Lignin Macromolecule

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Lignin is an important constituent of plant materials and the second most abundant renewable polymeric component of biomass. Over 95% of lignin is used presently as an energy source or disposed of as waste. On the other hand, it seems to be an attractive material for modification and use for purposes that increase environmental sustainability. It can provide a number of aromatic chemicals for use in paints, food industry and agriculture. This cheaply available resource must be fully exploited to generate extra revenue for sustainable industrial development and eco-friendly industrial products.

Introduction

Trees are considered to be the highest form of plant life on earth. They are the oldest of living individuals and are unsurpassed in height and mass on land. Most of the physical and chemical properties of the plants are determined by its main constituent called 'lignin'. The word lignin has been derived from the Latin word *lignum* which means wood (see *Box 1*).

Lignin is the substance that makes trees woody and is present mostly in cell walls of the vascular plants, ferns and club mosses. However, lignin is not present in mosses, algae and micro-organisms. It is a phenyl-propanoid structural polymer which binds the fibres and cell walls together and gives plants the required rigidity. It also decreases permeation of water across the cell walls of the xylem tissue and makes the wood resistant to attack by micro-organisms. The lignin content in the plants varies from about 18% to 35% of the total wood content. About 10^{10} tonnes of terrestrial biomass is produced annually through photosynthesis, and 5-36% of this lignocellulosic biomass of both softwood (gymnosperm) and hardwood (angiosperm) is

Box 1

The term lignin is understood differently in different disciplines. To a natural-product chemist, lignin is a three dimensional polymeric compound which permeates the polysaccharides and the spaces between the cells and thereby strengthens the plant tissues. To a botanist, it is a metabolite of a growing plant or a structural component of a mature plant which is detected by certain colour reactions. An enzymologist has termed lignin as the end product of a series of enzymatically controlled dehydrogenation reactions of the monomers of a phenyl-propanoid structure. A soil chemist considers lignin to be the residue of plant decay while for an analytical chemist, lignin is the insoluble substance of plant material when treated with 72% sulfuric acid. Finally for a pulp and paper manufacturer, lignin is the unwanted constituent of wood which must be removed for making good quality paper!

lignin. Softwood species have a higher lignin/cellulose ratio than hardwood species.

Lignin and cellulose (including hemicellulose) are the main structural components of almost all the plants. Natural decay or biodegradation of plant tissues is therefore the key process of the carbon cycle in nature. Interspersed with hemicellulose microfibrils, the lignin results in a heterogeneous composite aromatic polymer having biologically stable carbon to carbon and ether (C-O-C) linkages. This makes wood a good and lasting building material as well as a fuel. Plant cells can be viewed as a chemical factory wherein a large variety of highly sophisticated chemical compounds are synthesized from simple raw materials with the help of enzymes. Plants are thus the source of many important renewable chemicals, industrial compounds and energy. The utilisation of wood is therefore very extensive, being equivalent to twice the total steel and about 27 times the plastics produced all over the world.

Distribution of Lignin in Plants

Lignin is closely associated with cellulose and hemicellulose and is mostly bound to plant polysaccharide. However, the distribution of lignin, cellulose and hemicellulose is not uniform throughout the plant body. The concentration of lignin is generally higher in the middle lamella and lower in the secondary

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Type of plant	Lignin percent	Type of plant	Lignin percent
Rice husk	4	Eucalyptus (tension)	16
Clover	4-8	Bagasse	20-3
Corn cobs	13	Eucalyptus (normal)	22
Wheat straw	13-9	Spruce wood (normal)	26
Jute	14-2	Bamboo	29-35
Oat straw	14-22	Peanut shells	28
Barley straw	16-22	Spruce wood (compression)	38
Jute stick	19-6	Cocunut shells	39-9

Table 1 *Lignin content in various types of plants.*

wall. It has also been noticed that the lignin content in young plants is relatively low, but increases as the plant matures. Further, the distribution of lignin in plants varies from one type of plant to another (see *Table 1*). Note the exceptionally high lignin content in coconut shells.

Biogenesis of Lignin

Although a large number of plant constituents have been postulated as lignin precursors, in most cases the evidence supporting these hypotheses has been meagre. On the basis of recent observations, the theory which appears to be the most tenable is that lignin is a polymer of some compounds with a phenylpropane skeleton. The biochemical pathway for the formation of lignin in plants, or the process of *lignification* includes the formation of lignin monomers, or primary lignin building blocks. These (differing only in their number of methoxyl substituents) are p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, shown in *Figure 1*. These monomers are then converted into lignin.

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The process of lignification is initiated when a phenolic hydrogen atom is abstracted or removed by the enzyme peroxidase to form a phenoxy free radical. The radical centre can be delocalized to aromatic and side chain carbons. Such radicals then couple together, leading to polymerization. Extensive coupling occurs between phenoxy radicals and radicals localised at the b or

second from the ring side chain carbon. The resultant ether linkage, a β -O-4 bond, is the most common inter-unit linkage in lignin and is shown in *Figure 2*. If it were the only linkage, then lignin would be a linear polymer similar to many other natural and synthetic polymers.

The phenoxy radical and the β radical are not the only ones that couple. Delocalization of the unpaired electron to other carbon atoms or formation of other radicals by hydrogen abstraction can also lead to other linkages including carbon-carbon bonds. The formation of these types of linkages, including bonds to more than one other phenylpropane unit, may result in a rather complicated polymer having a cross-linked and three dimensional character. Additionally, the lignin-polysaccharide bonds may be formed by free radical coupling or by addition reactions to quinone methides.

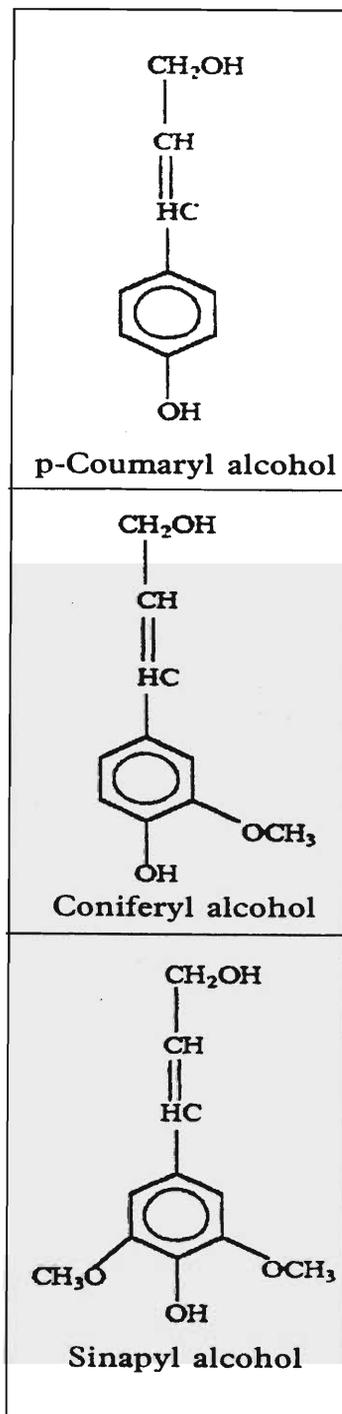
Nature of Lignin

Lignin of softwood species is quite different from that of hardwood species. The terms 'softwood' (evergreen) and 'hardwood' (deciduous broad leaved tree) do not necessarily refer to the hardness of wood, but to the botanical classifications. They are aptly called *gymnosperms* and *angiosperms* respectively.

The major differences between the gymnosperm and angiosperm lignins are discussed below. Almost all the aromatic units of softwood lignin and about half the aromatic units of hardwood contain one methoxyl group, while the rest have two methoxyl groups. As a result, angiosperm lignins have a greater number of β -O-4 ether bonds, a few phenolic hydroxyls and a few cross links. Some of these chemical differences are often cited as the reason for an easier chemical and biological degradation of angiosperm lignins when compared to gymnosperm lignins.

The lignin units arising from the monomers p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are usually referred to as p-hydroxyphenyl, guaiacyl and syringyl units respectively.

Figure 1 Three basic monomer units of lignin.



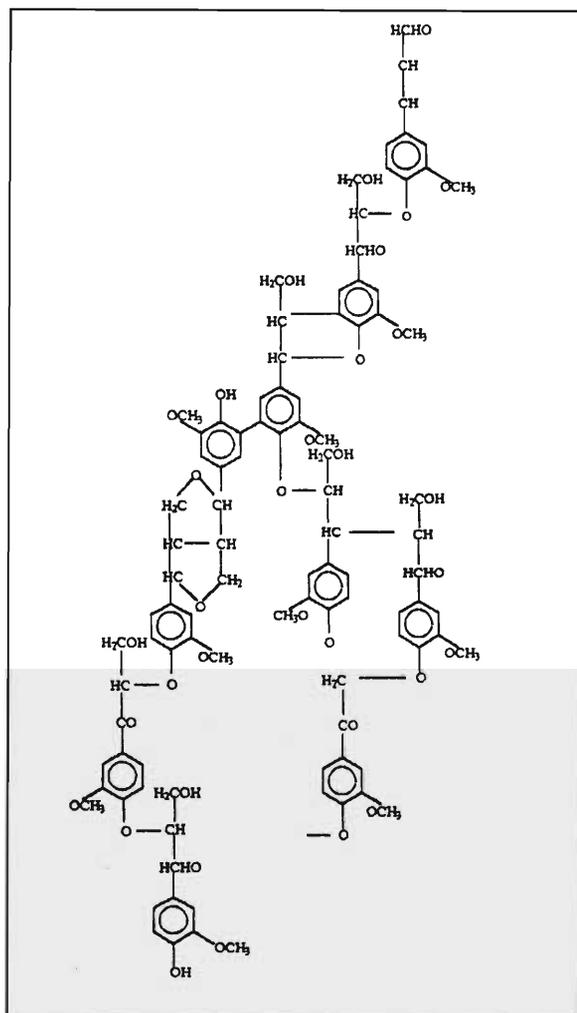


Figure 2 A partial structure of lignin macromolecule.

Gymnosperm lignins are all quite similar and they are classified as guaiacyl lignins that contain a small amount of p-hydroxyphenyl units. Angiosperm lignins are usually mixtures of syringyl and guaiacyl units, but their ratio varies widely among different species. Most temperate zone angiosperm woods have a syringyl to guaiacyl ratio of about 1:1. However, there is no such thing as typical angiosperm wood or lignin. The variety among angiosperm trees is overwhelming, and this variety extends to their lignin composition as well. Among temperate angiosperms, the syringyl to guaiacyl ratio ranges from 0.1 (for box elder, *Acer negundo*) to over 2.5 (for madrone, *Arbutus menziesii*). Most of the angiosperms grow in the tropics and many of them have very low syringyl contents.

Another type of wood lignin is the one that contains a relatively large amount of p-hydroxyphenyl units (derived from p-coumaryl alcohol). *Reaction wood* is formed when trees react to external forces such as

wind, mechanical stress, gravity, injury and disease. In gymnosperms, the reaction wood is called *compression wood*. While there are many differences between normal wood and compression wood, the major chemical difference in compression wood is that it contains a significant amount of p-hydroxyphenyl units. In addition, compression wood is more lignified than normal wood.

Isolation of Lignin

Pulp and paper industry is one of the major industries which produces large quantities of wood polymeric wastes enriched in

lignin. The only use of lignin until recent times from spent liquor, was to burn it in recovery boilers. Burning of lignin from this liquor, at best, can give only marginal returns. But lignin on the other hand, can become a replenishable and renewable resource for a series of aromatic chemicals.

A new lignin era will soon emerge with an integral and total use of the lignocellulosic materials.

The pulp and paper industries produce a large quantity of lignin by *Kraft and Sulfite process*. Spent liquor from these industries (otherwise known as black liquor) is the main source of lignin, because the pulp is exclusively made of cellulose and hemicellulose. The solid precipitation of the black liquor, otherwise called Lignin Related Compounds (LRC) is obtained by lowering the pH of the liquor to 2.5 - 3.0 by a suitable mineral acid. This precipitated compound is then thoroughly washed with water and treated for successive chemical extraction, e.g. with ether to extract the fat and fatty acids, alcohol-benzene to extract the dyes and colouring materials from the compound. Finally it is dried and powdered to yield pure lignin. Various analytical techniques are now available to verify and estimate the purity, molecular weight, dielectric constant and other physico-chemical properties of lignin so produced.

Isolating lignin from the plant tissue and using it as a new source for many aromatic and aliphatic compounds vis-a-vis environmental management and sustainability is the predominant field of current research and development. It is expected that a new lignin era will soon emerge with an integral and total use of the lignocellulosic materials.

Lignin Reactions for Industrial Applications

Lignin molecule contains a number of functional groups and reactive sites as shown in *Figure 2*. The functional groups include primary and benzyl alcohol, phenols, aldehydes, ketones, olefins and ethers, while the reactive aromatic sites include ortho- and para- positions relative to phenoxy and methoxy substituents. Therefore, a number of interesting chemical reactions, such as addition, derivatisation, oxidation, reduction,

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condensation and depolymerisation are possible for synthesizing many newer and value added products.

Lignin is degraded chemically at present, but the conditions needed are severe, i.e., high temperatures and pressures, and concentrated and powerful oxidants. Under these conditions, the more reactive degradation products tend to be destroyed. Lignin degradation by alkaline hydrolysis/chemical oxidation usually yields a wide variety of monomeric products.

Lignin when heated with nitrobenzene in alkaline medium at 160°C degrades to other lower molecular compounds such as vanillin, aceto-vanillin, etc. Vanillin, a monocyclic aldehyde-phenol containing a methoxy group, is a well known aroma chemical.

Lignin molecule on degradation by solvolysis in alkaline medium offers technically viable ways for the production of low molecular weight industrial chemicals like Dimethyl sulfide (DMS) and Dimethyl sulfoxide (DMSO). Alkali fusion products of lignin include phenol, carboxylic acid, etc.

Research efforts have recently been initiated for utilising lignin in thermosetting resins and graft-polymers, such as polyurethanes, polyesters, polyamines and epoxies.

The versatility of lignin applications and the incentive to use it as a renewable resource is great. However, the actual utilisation of lignin as a replacement for synthetic polymers has still remained low. Lignin is noted for its inertness toward chemical or biochemical degradation processes. New technologies need to be developed that can bring about the successful degradation of lignin macromolecule to low or intermediate molecular weight aromatic feedstocks. The importance of this goal becomes apparent when it is realised that about 95% of all synthetic polymers are derived from only three materials, ethylene, butadiene and phenol. Therefore, extensive R & D work in the field of lignin modification for valuable lignin based chemicals and other industrial products is necessary.

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