Lignin Macromolecule

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Lignin is an important constituent of plant materials. Over 95% of Lignin is used presently as an energy source. 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.

Introduction:-

Most of the physical and chemical properties of the plants are determined by it's main constituent called "Lignin". The word Lignin has been derived from the Latin word "lignum" which means wood. Lignin is the substance that makes trees woody and is present mostly in cell walls. 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 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. 5-36% of biomass of both softwood and hardwood is lignin.

Lignin and cellulose (including hemicellulose) are the main structural components of almost all the plants. 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 fuel.

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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 secondary wall. 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, e.g. Rice Husk- 4%, Coconut Shell- 39.9%.

Biogenesis of Lignin:-

On the basis of recent observations, the theory which appears to be the most probable is that the lignin is a polymer of some compounds with a phenylpropane skeleton. The biochemical pathway for the process of 'Lignification' includes the formation of lignin monomers. These monomers are converted into lignin.

Process of lignification is initiated when phenolic hydrogen atom is removed by the enzyme peroxidase to form a phenoxy free radical. The radical centre can be delocalized to aromatic and side-chain carbons. Extensive coupling occurs between phenoxy radicals and radicals localized 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.

The phenoxy radical and the β radical are not the only ones that couple. Other linkages include carbon-carbon bonds. The formation of these type of linkages, including bonds to other phenylpropane unit 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.

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Nature of Lignin:-

Lignin of softwood species is quite different from that of hardwood species. Softwood-gymnosperms, Hardwood-angiosperms.

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. Angiosperm lignins have a greater number of β-O-4 ether bonds, a few phenolic hydroxyls and a few cross links. Easier chemical and biological degradation of angiosperm lignin when compared to gymnosperm lignins when compared to gymnosperm lignins.

Another type of wood lignin is the one that contains a relatively large amount of p-hydroxyphenyl units. 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'. There are many differences between normal wood and compression wood. It contains a significant amount of p-hydroxyphenyl units. Compression wood is more lignified than normal wood.

Isolation of Lignin:-

The pulp and paper industries produce a large number of quantity of lignin by 'Kraft and Sulfite process'. Spent liquor from these industries is the main source of lignin, because the pulp is exclusively made of cellulose and hermicellulose. The solid precipitation of the black liquor is obtained. This precipitated compound is then thoroughly washed with water and treated for successive chemical extraction, e.g. with ether, we get,

- Fat and Fatty acids, alcohol-benzene
- Dyes and Colouring Materials.
- Pure lignin.

Isolating lignin from the plant tissue and using it as new source for many aromatic and aliphatic compounds. A new lignin era will soon emerge with an integral and total use of the lignocellular materials.

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Lignin Reaction for Industrial Application:-

Lignin molecule contains a no. of functional groups and reactions, such as additional derivatisation, oxidation, reduction, condensation and depolymerisation are possible for synthesising 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.

Lignin when heated with nitrobenzene in alkaline medium at 160^{o}c degrades to other lower molecular compounds.

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

The versatility of lignin applications and the incentive to use it as a renewable resource is great. Lignin is noted for it's 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.

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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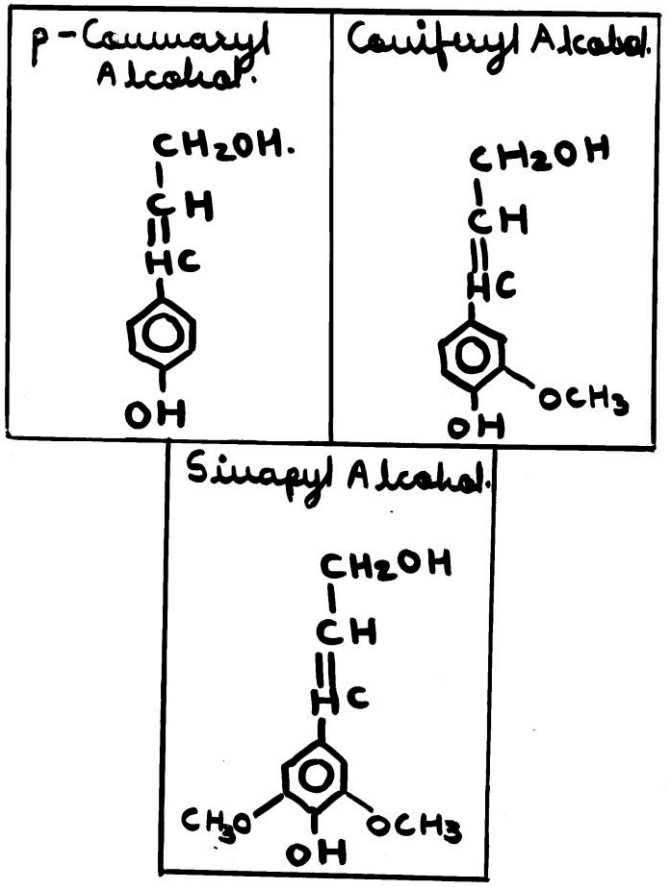
TYPE OF PLANT.	LIGNIN %.
RICE HUSK.	4.
CORN COBS.	13.
WHEAT STRAW.	13·9.
JUTE.	14·2.
OAT STRAW.	14·22.
BARLEY STRAW.	16·22.
JUTE STICK.	19·6.
EUCALYPTUS (Tension).	16.
BAGASSE.	20·3.
EUCALYPTUS (Normal).	22.
SPRUCE WOOD (Normal).	26.
BAMBOO.	29–35.
PEANUT SHELLS.	28.
SPRUCE WOOD (Compression)	38.
COCONUT SHELLS.	39·9.

THREE BASIC MONOMER UNITS OF LIGNIN.



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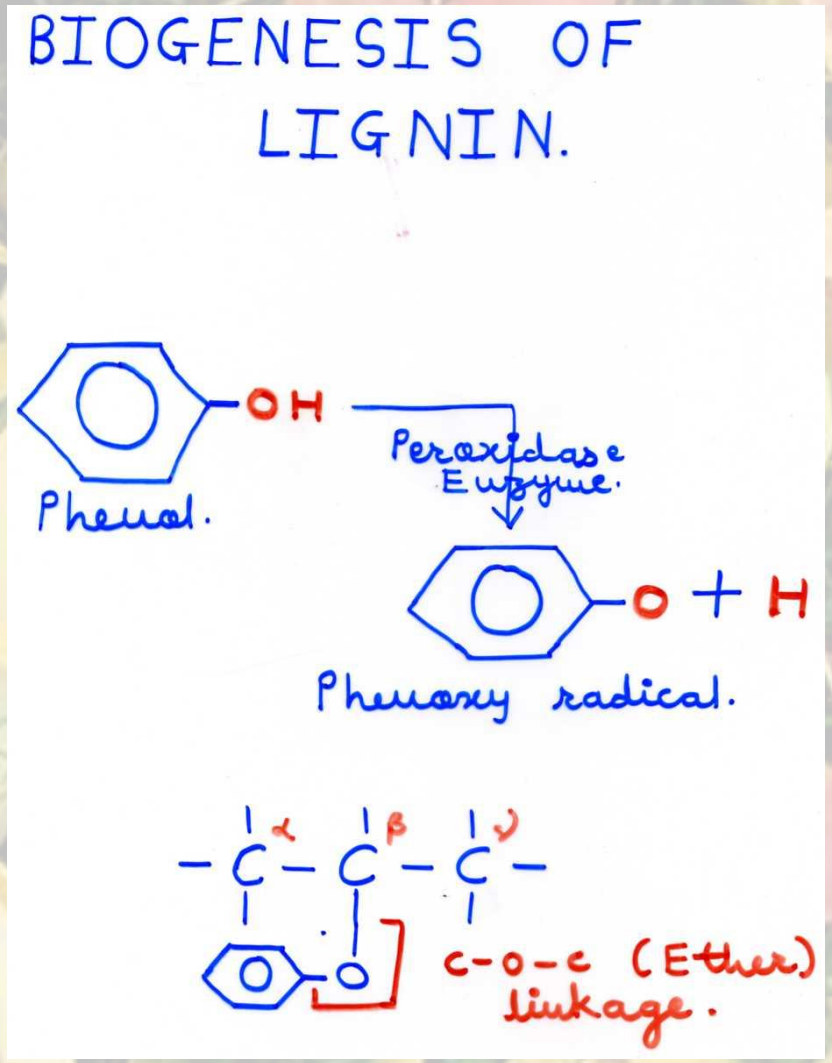

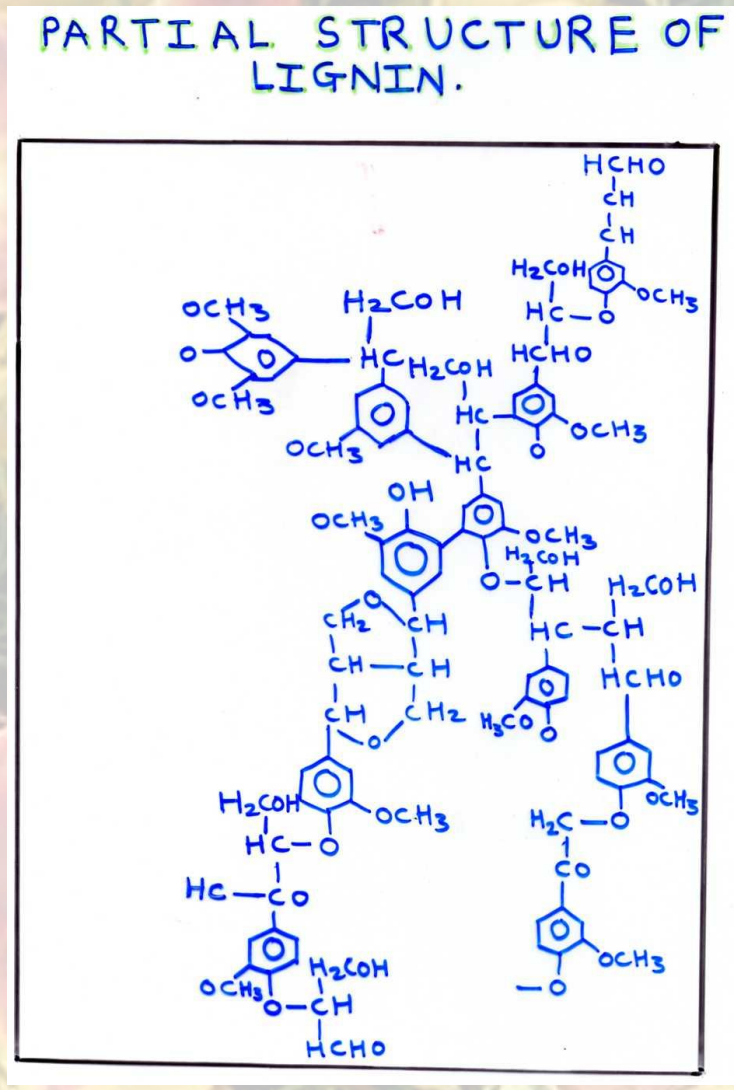

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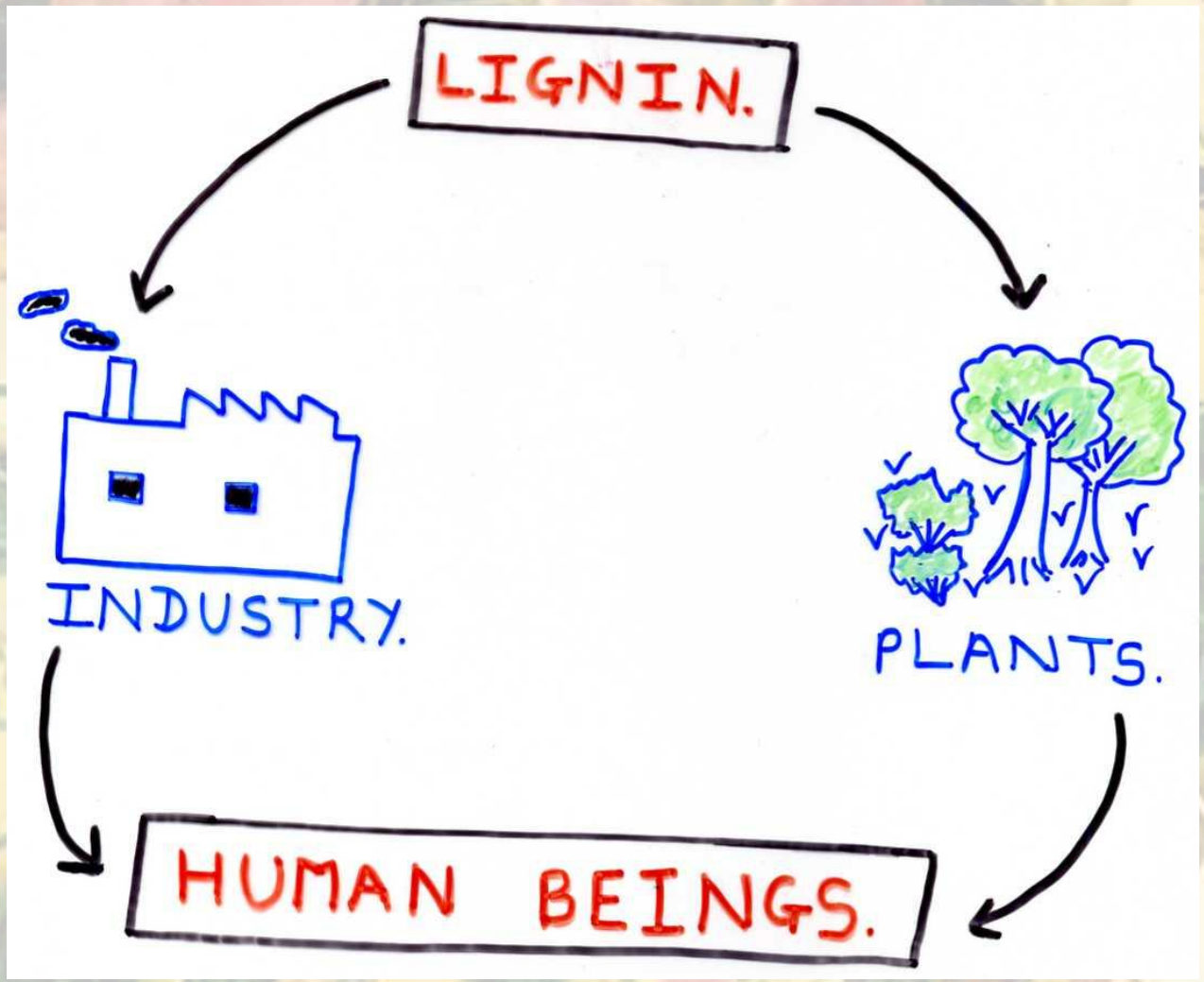

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Thank you
for your attention!