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LIGNIN AND ITS USES

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Summary

The role of lignin in plant structure, its nature, and methods of extraction are discussed. A review of current uses of chemically modified lignin, primarily the lignosulfonates, indicates a variety of applications and a challenge to scientists to find new uses.

Introduction

Lignin is the stuff that makes plants “woody.” The name comes from the neuter Latin noun “lignum” meaning “wood.”

Most, but not all, plants contain lignin. The lignin in lignified plants may also differ more or less in distribution and type among parts of the same plant, such

as leaves, shoots, stalks, branches, trunk, and roots, as well as among plants of different species. This article attempts to explain simply why plants contain lignin and why it is important to people.

Lignin's Role in Plant Structure

When plants such as seaweed or watercress grow under water, their parts are supported firmly on all sides by uniform hydrostatic pressure. There is not much difference in density between the plant cells and their surrounding liquid environment. Such plants do not therefore require very strong structural tissues; their cell walls contain only the polysaccharides, cellulose and hemicellulose. These polymers are made up of thousands of sugar molecules attached together end to end in a line, like strings of pearls. Bundles of such chains form plant fibers, which are then loosely matted together like felt to form the cell wall.

When a plant grows on land, the part above ground is surrounded by a medium of much lower density--air--and is subject to many mechanical stresses such as rain, snow, and strong winds, from which aquatic plants are protected by their watery surroundings. Nevertheless, herbaceous land plants such as some grasses, rhubarb, parsley, or lettuce manage to get along with cell walls made up only of cellulose and hemicellulose. The pressure of the cell sap keeps their cells turgid, that is, blown up like a balloon, so that the blades of grass can stand up straight and the lettuce or rhubarb is "crisp." Loss of moisture of course, causes such plants to wilt and droop.

However, for plants that tend to grow a higher distance from the ground, this type of structure becomes too weak. One cannot build skyscrapers out of felt. Sunflowers or wheat could not raise their heavy heads toward the life-giving sun unless their stalks were reinforced in some way. This reinforcement is provided by lignin, which is a light brown amorphous "cement" that fills up the gaps between the long thin polysaccharide fibers in the cell walls and binds them together. The role of lignin in cementing the plant fibers together in this way can be compared to that of the polyester resin strengthening the fiberglass webbing in boat hulls, gliders, or car bodies.

The resultant cell structure is a system of very strung and elastic tubes or vessels. Lignin also fills up the spaces between neighboring cells. Most land plants thus develop two kinds of lignified tissue: conducting tissue--a kind of plumbing system to transport sap from one part of the plant to another; and supporting tissue--to held the plant upright and glue the pipelines together. This design applies the well-known engineering principle of the bending resistance of hollow tubes.

Lignin is mainly encountered in wood plants such as trees and bushes, but it is also found in such things as cornstalks, sugar or bamboo canes, ferns, straw, peanut husks, and nutshells. It sometimes also occurs as a nuisance (to man) in some useful produce such as alfalfa, asparagus, beets, carrots, and turnips, making them "woody."

Detection and Measurement

One can detect lignin in plant material by swabbing with a 2 percent solution of phloroglucinol in alcohol and then with concentrated hydrochloric acid; this produces a fiery red color in lignified matter. The amount of lignin present can be determined by weighing the residue that can be filtered off from an aliquot after treatment with 72 percent sulfuric acid, dilution and boiling, a procedure which degrades and dissolves out the polysaccharide skeleton.

Varied Aspects of Lignin

Scientists in different disciplines are interested in different aspects of lignin. The organic chemist is challenged by its intricate structure. Botanists view it as a vital factor in the metabolism of the growing plant and as a structural component of the nature plant cell wall. Plant pathologists, microbiologists, and soil scientists know lignin as the crumbly residue transformed into valuable humus in the soil after wood is attacked by fungi or bacteria. But to the chemical engineer in the pulpmill, lignin is a bothersome wood constituent that must be removed from his chips before a good grade of paper can be made. It is this last aspect that makes lignin of such great economic importance, for every American now uses over a quarter of a ton of paper per year!

Lignin in Papermaking

Paper is a thin, nonwoven fabric made by draining off the water from a slurry of plant fibers, compressing the resultant felt into a thin sheet between rollers, and drying it. If there is too much lignin within the fibers, as for example in a groundwood pulp for newsprint manufacture-- made by simply tearing the fibers out of the wood with a rough grinding stone--they will not bond well together, so the resulting paper is very weak, especially when wet. It also becomes discolored on standing, owing to chemical changes caused in the lignin by light. So pulp manufacturers prefer to dissolve most of the lignin out of the wood by cooking it with chemical solutions. This leaves them with vast amounts of chemically spoiled lignin as a byproduct.

There are two main methods in use for removing lignin from wood. In the sulfite process, wood is cooked with salts of sulfurous acid; in the kraft process, it is cooked with a solution (white liquor) containing sodium hydroxide and sodium sulfide. The dark solutions of the degraded lignin dissolved out of the wood--called spent sulfite liquor in the sulfite process and black liquor in the kraft process--can now be concentrated economically for use as fuel, in order to prevent major water pollution. This approach also provides for the recovery of the alkali needed to prepare the cooking liquors, and furnishes heat, steam, and electrical power for the pulpmill.

Environment Pollution

Unfortunately, all water pollution at pulpmills cannot be avoided in this way. Older mills do not have chemical recovery furnace installations or use unsuitable kinds of alkali salts. Besides, the pulp must be rinsed free from residues of the liquors, and the resultant washings are too dilute to be economically concentrated for burning. They must be discarded from the mills and, after ponding or similar simple preliminary treatments, are generally run off into local streams or rivers. In addition, the pulping processes are not efficient enough to remove all of the lignin from the wood, so the crude pulp is pale brown and must be bleached (for example, with chlorine or chlorine dioxide) if it is to be used for white papers. The dilute spent bleaching solutions and washings are also released into local waterways, where they are very troublesome because of the chlorinated lignin fractions they contain. In efforts to reduce water pollution, researchers are trying to find better ways of pulping wood and bleaching methods that avoid chlorine or yield washings concentrated enough to be amenable to purification. Inefficient old pulpmills are being closed.

Air pollution in the form of obnoxious odors has also been associated with kraft mills. The sulfur chemicals in the cooking liquor combine with parts of the lignin to form evil-smelling mercaptans and organic sulfides. The modern trend toward the use of continuous digesters instead of the older batch digesters is doing much to alleviate this situation, in addition to creating the possibility of using some wood wastes such as sawdust and planer shavings for making finer fibers for some paper stocks. Many batch-type pulpmills are also attempting to clean up their smelly digester relief gases and recovery furnace flue gases by scrubbing or oxidation treatments in order to reduce air pollution.

True Lignin Structure

Only with great effort and by using extremely mild methods can the chemist remove some true lignin in unchanged form from wood. This lignin is a buff-colored amorphous powder which, like cellulose and hemicellulose, is made up of only carbon, hydrogen, and oxygen, but in different proportions and combined in different ways. The plant fibers contain about 45 percent carbon, 6 percent hydrogen, and 49 percent oxygen; lignin has about 65 percent carbon, 6 percent hydrogen, and 29 percent oxygen.

Cellulose and hemicellulose are carbohydrates; they belong to the class of polysaccharides or sugar polymers. Lignin is also a giant polymer molecule but it has both aliphatic and aromatic portions. Its basic unit is derived from phenylpropane--a six-carbon benzene ring attached to a straight side chain of three carbon atoms. These units are interconnected in a large variety of ways by carbon-carbon or carbon-oxygen-carbon (ether) bonds, giving lignin a complicated three-dimensional structure. There are so-called methoxyl groups (H_3CO -) attached to many of lignin's aromatic rings. Some of these are split off by sulfur during kraft pulping to give the smelly vapors associated with the process. The higher a plant stands in evolutionary development, the higher the methoxyl content of its lignin. Lignin from ferns or straw has under 10 percent methoxyl, that from other "grasses" like bamboo or sugarcane and that from coniferous wood species has about 14 to 16 percent, that from hardwoods up to 23 percent. The lignin content of woody plant material also varies widely. For instance, softwoods have some 25 to 50 percent and hardwoods some 20 to 25 percent lignin.

Natural lignin is plastic when hot and wet; this explains why wood can be bent and formed by steaming.

There is no practical use for isolated natural lignin--it is only used to study the structure and properties of that component of wood. In any case, the extraction process is far too tedious and expensive.

Uses of Lignin

Although spent pulping liquors contain, in addition to lignin, lots of simple sugars and sugar acids that result from degradation of part of the cellulose and hemicellulose during aggressive pulping cooks, it is possible to isolate large quantities of lignin from them quite inexpensively. Pulped lignins have undergone considerable chemical modification and are generally dark brown brittle resins of bakelite-like appearance and properties. Nevertheless, many ingenious uses for some of these materials, or even for the crude pulping liquors, have been found. Unfortunately, the amounts disposed of profitably remain small, and it is mainly only lignosulfonates--from the now minor sulfite pulping process--that are used (about 2,000 tans per year). Worldwide, there are about 3,000 patents covering uses of lignin.

Lignosulfonates

Sugar-free lignosulfonates from softwoods (conifers) serve as starting material to make vanillin--a flavoring for food, ice cream and bakery goods. Although this product has now ousted the natural vanillin essence extracted from vanilla beans from the market, the concentration of vanillin needed for flavoring is so small that the output of one Canadian and two United States manufacturers fills the needs of the North American and much of the foreign market. A few other fine organic chemicals used as food preservatives, in suntan lotions, or as pharmaceuticals are also made from vanillin or softwood lignosulfonates. Hardwood lignin also yields vanillin, but it is contaminated with a similar compound called syringaldehyde that contains an additional methoxyl group. Because the two are too difficult to separate economically, hardwood lignosulfonates are not used as a source of vanilla.

Because the organic lignin molecule combines with strongly polar sulfonic acid groups during sulfite pulping, lignosulfonates are readily soluble in water

in the form of their sodium, calcium, or ammonia salts, which have soap- or detergent-like properties. Just as soaps loosen dirt, so also lignosulfonate solutions can disperse and suspend inorganic particles. This makes them valuable for numerous uses.

One major application is for mud viscosity control during deep oil well drilling. The diamond-studded borer head must be slightly lubricated and cooled, otherwise it will either burn away or jam, and the powdered rock produced by the drill must be removed from the shaft. A solution of lignosulfonates or even crude spent sulfite liquor in water does this job well by forming a stable thin mud that will not coagulate or foam but can ooze out of the hole. Similarly, lignosulfonates also help to control the viscosities of particle suspensions in making bricks, tiles, or gypsum boards, in grinding and polishing (for example, terrazzo floors), in spraying pesticides, in distributing carbon black during rubber masterbatching, and in textile dyeing. Another use is in the preparation of smooth clay slips for ceramics; on firing the pieces, the organic lignin simply burns away, Lignin is also said to reduce breakage and chipping of dried unfired bodies of pottery and porcelain.

Many uses of lignosulfonates and spent sulfite liquor as a binder rely on the ability of these materials to couple smooth dispersion with tackiness. In this capacity, lignin finds outlets in preparing insulation boards, linoleum and floor tile pastes, animal feed pellets (the Food and Drug Administration permits 4 percent), coal dust briquettes, and foundry sand casting form. It is also used for dust control in ceramic manufacture, synthetic fertilizer production and application, cement clinker milling, and concrete mixing. In concrete mixing, lignosulfonates also reduce the water requirement of the mix through the slurry thinning caused by their dispersant properties. This accelerates setting and can be used to control air entrainment in the concrete. Lignosulfonates are also used as soil stabilizers on soft shoulders or unfinished roads; here, too, they exert considerable dust control.

Lignosulfonates are also strong sequestering agents, that is, they enclose certain metal ions and keep them in soluble form. They form soluble complexes readily with iron, calcium, copper, nickel, tin, aluminum, and zinc. This property leads to their use in treatment of poor soils--either to add deficient minerals or to remove detrimental ones--in industrial cleaning compositions, in hard water treatment and in boiler-scale control.

They also find applications in metallurgy. Specific mineral dispersing and depressant effects plus sequestering power make lignosulfonates effective in slime

control and improving separation during tabling or flotation of ores. By counteracting electrode polarization, they are valuable additives for galvanizing baths or in the electrolytic refining of ores. Lignin is also incorporated into the negative electrode coating pastes of lead storage batteries.

The anionic charges (negatively charged ions) in lignosulfonates make them good emulsifying agents or auxiliaries for preparing or stabilizing oil-in-water or wax-in-water emulsions (for example, in polishes and furniture creams or sprays). As wetting agents, they are used in tar or asphalt emulsions or as stabilizers in some emulsion paints.

Lignosulfonates are also included in some adhesives. They act as extenders for the phenolic resins used in manufacturing particleboard, nonwoven fiber padding, and molding powders. They are also compounded into poly-vinyl alcohol and polyvinyl acetate glues and used for rewettable gummed tapes.

Lignosulfonates also have tanning properties because of their phenolic and sulfonic acid groups. However, being water soluble, their effect is not permanent; they are therefore only used as extenders for vegetable or chrome tannins. This ability to coagulate and precipitate proteins is also exploited in water clarification. Effluent from meat and fish canneries or milk processing plants can be advantageously treated with carbohydrate-free lignosulfonates and the protein-rich precipitate deposited then incorporated into animal feeds or protein-based glues. Thus, though lignin can cause water pollution in some places, it helps to abate it in others!

Kraft Lignins

Uses of kraft or alkali lignins are not as numerous or significant as those of lignosulfonates, mainly because they are less soluble in water. Applications similar to those for lignosulfonates (for example, in ceramics or tire manufacture) are sometimes possible. In addition, kraft lignins are used in some foam fire extinguishers to stabilize the foam and in printing inks for high speed rotary presses. Once company sulfonates kraft lignin to give it properties like those of lignosulfonates.

Some kraft lignin is used for making a high grade of activated charcoal. The methoxyl groups in kraft lignin are split off with sulfides by another company to make methyl thiol, dimethyl sulfide, and dimethyl disulfide. The dimethyl disulfide can be oxidized to dimethyl sulfoxide, a powerful organic solvent and useful

chemical reagent. The other three sulfur compounds are, of course, the smelly materials that cause air pollution around kraft mills. However, addition of the pure compounds as odorants to combustible and explosive gases provides a safeguard for the detection of dangerous leaks. This puts even the air pollutants to a useful purpose!

Such clever applications resulting from intelligent planning and scientific research may one day turn lignin from a troublemaker into a treasure trove. Lignin holds out a great challenge to those willing to persevere in efforts to unravel its final mysteries and thus vastly improve our environment and contribute to the wise use of our forest resources.

Suggestions for Further Reading

Irwin A. Pearl. Lignin Chemistry: A Century-Old Puzzle. Chemistry and Engineering News, July 6, 1964, pp. 81-93. Reprints available at \$1 per copy from Reprint, Department, ACS Applied Publications, 1155 Sixteenth Street, NW., Washington, D.C. 20036.

Irwin A. Pearl, The Chemistry of Lignin. Marcel Dekker, Inc., 95 Madison Ave, New York, N.Y, 10016. 1967, 355 pp. \$15.75.

Karl Freudenberg and Arthur C. Neish. Constitution and Biosynthesis of Lignin, Springer-Verlag, New York, Inc., 175 Fifth Ave., New York N.Y. 10818. 1968, 129 pp. \$7.

Kyosti V. Sarkanen and Charles H. Ludwig (editors). Lignins. Two volumes due for publication 1969/70 by Interscience (John Wiley Sons, Inc., 605 Third Ave., New York, N.Y. 10016), approx. 850 pp.

