

EXPLORING THE LABYRINTH OF CELLULOSE AND LIGNIN



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Wood comes as a finished product of nature to the hand of the builder and the craftsman. To the chemist, however, wood is no more a finished product than is a slab of coal or a field of flax. It is raw plant tissue of specialized type; its true usefulness can be determined only by a thorough discovery of its inward structure and substance. In the domain of physical and organic chemistry lie possibilities not only of converting wood into manifold new products of value, but also of adapting it more and more adequately to requirements of established use.

Wood is a definite entity; it is substantially alike in trees of all species. Its chemical make-up, however, is not simple. To say that it consists of the elements carbon, hydrogen, oxygen, and none other is a truth leading nowhere in particular; the same analysis would hold for sugar, carbolic acid, or pine rosin. Even to measure C, H, and O by quantitative methods reveals no property of wood except as a fuel. To capture its concealed values requires a far more subtle approach.

Wood is a mixture. Experimentation a century ago accomplished its separation into two main components -- a fibrous, cotton-like part comprising the cell bodies proper and designated as cellulose, and a part denominated lignin, the essentially "woody" component, appearing chiefly as an encrusting or compacting medium between the cells. There also exist in wood, in some associative pattern, a considerable group of intermediate compounds, designated in general as hemicelluloses.

Furthermore, wood is a labyrinth. It consists of parts within parts. Methods of microchemistry, recently developed, have thrown light on its inner recesses. The lignin complex has been isolated as a continuous web or honeycomb, with traces of interpenetration into the fiber walls. The fiber, a hollow body of about the size of a hair removed in shaving, has been examined throughout its range of visible structure. About it is coiled a cellulose filament of marvelous fineness, binding its parts together. Within, it is found to consist of three or more concentric layers of cellulose, each a compact of some hundreds of parallel fibrils having a slight slope or twist about the fiber axis. Composing the fibrils are still smaller spindle-shaped integers, named fusiform bodies. These, in turn, are made up of ultimate microscopic objects, units of cellulose so minute that their relation to the whole fiber is as a golf ball alongside the Washington monument.

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Taking up the search where the microscope must leave off, instrumentalities such as the ultracentrifuge and the X-ray are yielding information on the molecular dimensions and character of both cellulose and lignin. Closely related studies are exploring the maze of capillary and submicroscopic water-conducting passages throughout wood. Their fineness and manifold complexity are witnessed by the finding that, within a single cubic inch, the internal wood surface bounding them is more than 50,000 square feet.

The scientific concept thus obtained of the wood aggregate and its subdivisions, though still far from complete, has bearings on present technical problems and far-reaching implications for the future. For example, recognition that lignin forms an enveloping matrix about the fibers led to the development of the "semichemical" pulping process, the story of which, with its high yields and its successful adoption in industry, is told in another section. Structural analysis of the cellulose fiber has made clear to the papermaker the degree to which fibrillation of a pulp, produced by beating, affects the strength of paper. It has also, for the first time, given the rayon manufacturer a knowledge of the various microscopic units through which the fiber passes during dispersion of cellulose prior to its emergence through the spinnerette. In the drying of wood, successful results depend on the proper removal of water from its minute structure by diffusion after the larger cell interiors are empty. Increasing knowledge of the structure in which diffusion takes place aids in setting up efficient drying conditions, either by temperature and humidity control or by the new method of chemical seasoning elsewhere described.

To the general user, the one greatest drawback to wood in service has been its tendency to shrink or swell as its moisture environment changes. Successful antishrink treatments were unknown until, in the course of research, it was realized that moisture-excluding agents must be used which will bond with the innermost parts of the wood substance. By a new "substitution" method of impregnation with synthetic resins, the swelling and shrinking of wood can now be reduced to about one-quarter of that naturally occurring. The process is applicable to superior manufactured articles such as shoe lasts, athletic goods, brush backs, lithograph blocking, and musical instruments, and studies are now under way looking to its use in the production of a permanently weather-proofed plywood for house construction. In these and related fields of wood research -- preservative treatment, painting, gluing, decay investigations, and the rest -- the facts of wood's minute structure supply the necessary groundwork of both sound theory and improved processes.

Cellulose fiber is the acknowledged treasure of the wood labyrinth. For decades chemists have found its investigation exciting and rewarding, until today the world stands fascinated with the profusion of its products -- papers of every variety, boxes, cartons, and fancy wrappings, rich fabrics, pressed and molded articles, photographic and projection films, lacquers brilliant of hue and surface. To this great development the Forest Products Laboratory has contributed its part by

clarifying ideas as to what constitutes the cellulose part of wood and by devising means of recovering more of it in useful form.

According to common analytical procedure, wood is considered to contain about 60 percent of cellulose. A new concept, however, has arisen with the introduction of a less severe method, by which wood is found to yield a total carbohydrate fraction of 77 percent. Signifying its cellulosic character, the carbohydrate component has been given the name holocellulose. Not only does holocellulose contain substances formerly disintegrated, but its content of superior fiber, the tough alpha-cellulose of fine paper and rayon, is considerably higher than has been obtained before, either analytically or commercially. This fact points to the possibility of new and radically different pulping processes, with higher yields and less waste.

The setting up of the new body, holocellulose, has found an incidental application outside the field of forest products. Researchers in animal nutrition have wanted to find out to what extent lignin interfered with the assimilation of plant carbohydrates, but have never been able to remove the lignin without also removing part of the carbohydrates. Holocellulose, the total carbohydrate group, lignin free, was the answer to their problem.

In the recovery of pulps with high yields, the so-called hemicelluloses will play a major or minor part, according to the degree of refinement required in the final product. On the other hand, their part in hydrolytic reactions for purposes such as ethyl alcohol production is exceedingly interesting, as many of them are readily convertible into sugars. While their structure and relationships in the wood complex are not as yet fully determined, current studies indicate the close association of at least a part of them with the lignin fraction. The acetyl and certain of the methoxyl groups, however, which yield acetic acid and methyl alcohol, have been shown to be chemically attached to the cellulose.

If cellulose is the treasure of wood, lignin as hitherto regarded has been mere slag or offscouring --- dross to be purged in the winning of fiber; and it pours out from pulp mills at the rate of a million and a half tons a year, to pollute rivers and perplex the public and conservation authorities. Yet lignin, comprising one-quarter of the wood substance, was put together by nature for a definite function. It must have definite chemical characteristics, and perhaps, were these fully known and determined, products might be developed from it as useful as those now extracted from packing-house wastes or from that once valueless refuse, coal tar.

Such was the conception with which the current research on lignin was undertaken. The chemical problem has proved as hard as its past history would lead one to expect. Lignin is a stubborn material, ambiguous in its reactions and grudging of any clues to its composition or hidden values. A limited disposal of lignin-bearing pulping waste is

found in the manufacture of linoleum adhesive and in tanning operations, and its use as a road binder or a component of fertilizers offers some promise; but for lignin itself, the utilization program awaits a fuller revelation of what it is.

The unknown is at last taking shape. Paralleling the holo-cellulose separation, lignin is now segregated as a thing in itself free of all cellulose-degradation products. Considerable differences between typical hardwood and softwood have been distinguished. Five hydroxyl groups have been identified as a part of lignin, one of them being a secondary alcohol and another an enolic compound that can condense with phenols to form resins. Five methoxyl groups have likewise been identified, one of which on distillation of wood yields methyl alcohol. Another finding, which departs radically from former conceptions, is the disclosure by X-rays that lignin has a definite crystalline structure; all previous conclusions were that it was amorphous in character.

Research has lately been reinforced with the powerful aid of the hydrogenation process, the transformation by which gasoline is generated from coal, and cooking fats from vegetable oils. Under hydrogenation, lignin can be converted completely into glycols, alcohols, and a residue similar to a high-grade synthetic resin. One of the alcohols produced is propyl-cyclohexanol, a liquid of pleasant odor suitable for use as a lacquer vehicle. It is also inhibitory to wood-destroying fungi and hence gives promise as a wood preservative. Of the two glycols, one is a waxy crystal and the other a viscous liquid adapted for use as a thickening and toughening agent for varnish.

These various developments are only parts of a chemical picture which remains to be completed. But they are already opening up vistas into an economic future for lignin. A fortunate outgrowth of the research has been a vast improvement in the performance of millions of automobile batteries. No sooner had lignin been isolated in pure form than manufacturers began incorporating it as a part of negative battery plates, with a tenfold increase of current output in zero weather.

At an early stage of the lignin research it was noted that formaldehyde had a pronounced softening effect on the material, and that upon drying a hard, resinous product was obtained. This observation led directly to the development of a process for the production of a new type of molding compound. Its formation depends on the removal of part of the cellulose from wood by cooking with dilute acid, with consequent increase of the lignin content of the residue. The softening point of the lignin is lowered by the addition of plasticizers such as aniline and furfural, so that the mixture can be hot-pressed at 3,000 pounds per square inch to form a hard, dense, brilliant black molded product of low cost. A number of industries are interested in it, and its possibilities in the production of plastics from wood waste, especially sheet materials, panels, and wall boards, are very apparent.

Such, in outline, is the account of the Laboratory's exploration of the wood labyrinth to date. Facts of scientific and practical value are being brought to light, and the boundaries of the unknown are being pushed back a step at a time. The search goes hand in hand with efforts of other workers, and by this cooperative attack the time is being hastened when the inner wealth of wood will be fully at the command of society.