Wood and Cellulosic Chemistry

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Preface

It may reasonably be said that the foundation of wood chemistry was laid in 1838 when Anselme Payen, a French botanist, derived cellulose and lignin from wood. Nonetheless, the systematic study of wood chemistry did not begin until the early 1900s. The classic textbooks of Schorger (1926), Hawley and Wise (1926), and Hagglund (1928) provide good summaries of the early years of wood chemistry research.

Although the concepts of wood, cellulose and lignin chemistry have received enormous impetus and development through systematic studies over the past 60 years, the whole concept of the chemical aspect of wood utilization was brought sharply into focus late in 1973 when the Western world and Japan were faced with the issue of oil and material shortage, which resulted in immense increases in oil prices and, on occasions, actual shortfalls in oil supplies. Because of wood's renewability, wood chemistry research since then has received increased emphasis in industry, government and the academic community. The field of wood chemistry has moved from a largely empirical body of accumulated practical knowledge to an increasingly sophisticated science, employing the most advanced techniques of physics and chemistry. The literature of wood chemistry has proliferated in the past 10 years at an almost geometric rate, and a number of important changes and developments in the chemistry and technology of wood, cellulose, and lignin have taken place throughout the world, particularly in Japan.

Japan, despite its limited natural resources, has become a leader in science and technology in recent years. A tremendous surge of interest and activity in wood chemistry research and development has occurred in Japan during the last two decades. Conferences and meetings dealing with cellulose, paper, lignin, and wood have attracted attention from both the academic and industrial communities. Many excellent research papers and books have been published in Japanese. Ironically, because of the language barrier, not many Western scientists have had the opportunity to become acquainted with the establishment and development of wood chemistry in Japan. This has made it desirable to review Japanese approaches on wood chemistry research in some depth in the English language. Accordingly, when we were asked to organize a book on wood and cellulosic chemistry, with major contributions from Japanese wood chemists, we agreed to do it because we believe that this type of book would fill a definite need. Further, we also believe the Japanese approach to research and interpretation of data, from different points of view, will stimulate future research in the field.

After numerous discussions with colleagues in the U.S. and Japan, the major topics thought desirable for a contemporary approach to wood chemistry were enumerated. It is hoped that this book will provide an inside view of the developments in wood chemistry in Japan. As editors, we feel pleased to have been able to recruit some of the best talent in the field, American as well as Japanese, to this endeavor.

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I. GENERAL STRUCTURE OF WOOD AND WOOD CELLS

A. Wood

1. Softwood and Hardwood

In introduction it should be understood that the term "wood" refers to the secondary xylem formed by cell division in the vascular cambium of both *gymnosperms* (softwoods) and *angiosperms* (hardwoods), and especially in *Ginkgo*. Similar secondary xylem may be produced by plants of a different form and structure such as vines and shrubs, the xylem of which may be an important resource of pulping material. The structure and formation of the secondary xylem are discussed in this chapter.

Both softwoods and hardwoods are widely distributed on earth, ranging from tropical to arctic regions. The xylem of those species present in moderate-temperate to arctic regions is characterized by distinct growth rings, in which some anatomical difference can be noted. In the softwoods consisting mainly of tracheids (approximately 90% of wood volume), the latewood (summer wood) can be distinguished from the earlywood (spring wood) in its smaller radial dimensions and thicker cells walls. These anatomical differences are reflected in the higher density of the latewood compared with the earlywood. In softwoods growing in tropical or warm areas, growth rings cannot be distinguished due to the indistinct boundary between earlywood and latewood.

As with the softwoods, hardwoods are also present in tropical to arctic regions. In colder regions, hardwood species are deciduous, whereas in tropical regions, they are predominantly evergreen and their growth rings are difficult to recognize. The macroscopic characteristics of hardwoods are reflected in the distribution and number of different cell types such as vessels (pores), parenchyma, and fibers. Although fibers may account for only 25% of wood volume, in some cases, for hardwood, it may be as high as 50 to

70%. In contrast to the tracheid as the main cell in softwoods, hardwoods have a variety of cells.

Some deciduous hardwoods such as oak or elm have very large vessels concentrated at the beginning of annual rings. Such woods are called "ring porous wood," whereas other deciduous species and almost all evergreen hardwoods in which the vessels are evenly dispersed over the annual ring are called "diffuse porous wood." The above distinctions represent extremes and many intermediate arrangements of the vessles. Variations in arrangements of these vessels with other xylem tissues such as parenchyma are reflected in the "figure" and "grain" of the wood itself when it is cut from the tree. The physical properties of wood such as density also result from such arrangements of the cells.

2. Sapwood and Heartwood

When a tree stem is cut transversely, a portion of "heartwood" can be seen frequently as a dark-colored zone near the center of the stem. This portion is surrounded by a light-colored peripheral zone called "sapwood." The sapwood or at least the outer part of the stem conducts water through the tissue where the water is transpired, and mineral nutrients are also carried with water from the roots into the wood. In addition, the sapwood has living parenchyma tissue, which often plays some physiological role such as the storage of starch or fat. From this point of view, the sapwood is considered an active xylem tissue.

In contrast to sapwood, heartwood is a dead xylem. As the tree matures, all parenchyma cells of the sapwood die, and other types of cells such as tracheids or fibers become occuluded with pigment composed of polyphenols and flavanoids supplied mainly from the ray parenchyma. The bordered pits of *gymnosperms* become aspirated, whereas the vessels are blocked by tyloses or gum in *angiosperms*. Thus, heartwood does not participate in water conduction. Although the conducting and physiological functions are lost in heartwood, the durability of wood against rot or insect decay is remarkably improved due to an addition of such pigments. Moreover, these pigments confer a variety of beautiful color on wood.

3. Reaction Wood

Reaction woods that appear on branches or a leaning stem by any force such as a landslide or snow-fall have a peculiar nature. Once reaction wood is formed as a biological response, the living tree tries to preserve the original position of its stem or branches. For the practical use of woods, the reaction woods have not been appreciated very much because of their different characteristics from normal wood in both a physical and chemical sense.

The occurrence and nature of reaction woods contrast quite a bit for softwood and hardwood. In softwood trees, the reaction wood forms at the lower side of a leaning stem or branches where the compression stress reacts on the xylem. Therefore, this reaction wood is generally called "compression wood." Compression wood is heavy and appears dark brown on account of its highly lignified tracheid walls (see Sec. II), which seem to adapt to compression stress. Thus, compression wood is easily distinguished from normal wood by its dark color. The cambial activity at the lower position of a leaning stem or branches accelerates very quickly and develops a wider compression area than normal wood on the opposite side. Through the accumulation of compression wood tracheids for many years, leaning stem will return gradually to the vertical position. The annual rings of such a stem, however, are conspicuously eccentric.

To the contrary, reaction wood in many species of hardwoods is formed at the upper side of a leaning stem or branches where the xylem loads the tensile stress. Therefore, such reaction woods are called "tension wood." Fibers at the tension wood have a slightly lignified cell wall (see Sec. II) that is adapted to the tensile stress just like a bowstring. It is not so easy to distinguish this area from a normal one on account of its slightly pale tone, in comparison to the case of compression wood.

In fact, the occurrence of both reaction woods is a very troublesome problem in the area of wood utilization. These reaction woods, however, are interesting material for the examination of wood structure and formation, as will be referred to often in the following sections.

B. Wood Cells

Wood cells are produced in the vascular cambium from two types of meristematic cells: the fusiform initial and the ray initial (Fig. 1). Since cells derived from the fusiform initials that are upright in the stem occupy a major part of xylem, woods show remarkable anisotropism. The principal functions of xylem tissue are water conduction from roots to shoots, the mechanical support of a huge tree body, and a physiological role such as the storage of starch. Although these functions are common in both softwoods and hardwoods, the xylem of the latter is more evolved than that of the former, being adapted to each function.

In softwoods and Ginkgo, tracheids being major cells of xylem are considered relatively underevolved because they have both conductive and mechanical properties. Bordered pits, the occurrence of which defines a cell as a tracheid, are very important to the regulation of water flow. On the other hand, cell wall thickness is related directly to the strength of tracheids. The earlywood tracheids, therefore, seem to be well adapted to the conducting function, whereas the latewood tracheids are loaded with the mechanical property judging from their peculiar shapes. On the earlywood tracheids, well-developed pit pairs are distributed abundantly between the neighboring tracheids, and the cell wall of latewood tracheids is very thick.

Only a small number of fusiform cells are subdivided into strand cells by horizontal partitions and compose an axial parenchyma. These parenchymatous cells survive in the sapwood for many years, being different from the tracheid in which the protoplast is lost soon after differentiation (see Sec. III), and are part of some physiological functions. In some genera of Pinaceae, axial resin canals surrounded by epitherial cells are constructed. The occurrence and structure of resin canals are often used in the identification of softwoods, although the volume of such resin canals is very slight in wood.

Ray cells are derived from the ray initials and elongated radially. A series of these ray cells make a ray parenchyma. Needless to say, these parenchyma cells are alive in the sapwood and are tied to the storage of nu-

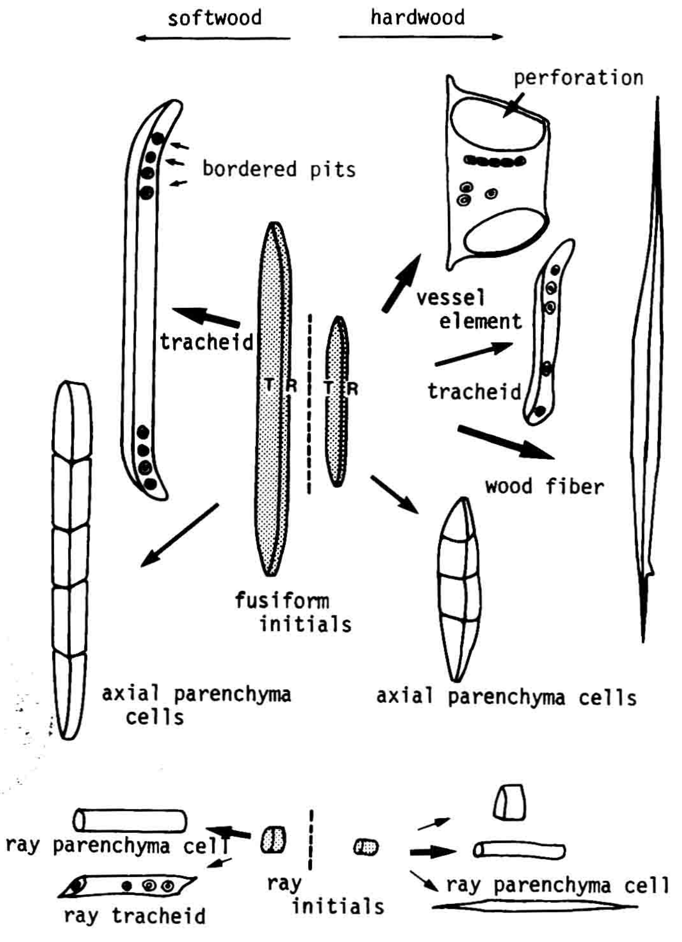

FIGURE 1 Shapes of major wood cells from the fusiform and ray initials in softwood and hardwood.

trients such as starch or fat and also the transportation of some metabolites between the phloem and the heartwood. As a result, they must be related to the secretion of heartwood substance into the tracheids. Also in some genera of Pinaceae, radial resin canals surrounded by epitherial cells are formed in many ray tissues, and more ray tracheids occur in the ray tissues.

Hardwood xylem can be characterized by the development of vessel elements and wood fibers are specialized for water conduction and the mechanical property, respectively. The vessel elements construct a very long and thick tube, namely, a vessel, being joined vertically with one another by a performation that has a more developed style compared with the bordered pit pairs between tracheids. The occurrence of perforation distinguishes the vessel elements form the tracheids. Wood fibers elongate remarkable and possess a very thick cell wall. The most developed type of cells having simple pits (see Sec. II) is called libriform wood fiber. On the other hand, there are some intermediating cells from the tracheids to the vessel elements or wood fibers, i.e., vascular tracheids, vascentric tracheids, and fiber tracheids. The fiber tracheids are often included in the category of wood fibers, because there is no need to separate them from the libriform wood fibers in the practical use of wood. Vessel elements, wood fibers, and various types of tracheids in the hardwoods lose their protoplast just after the development of their secondary wall. However, in some hardwood species specialized wood fibers that remain alive for several years and often store starch grains are formed, they are called "living wood fibers."

Axial parenchyma cells, which are dispersed on the transverse section of softwoods, are clustered at the vessel periphery or form a group often linked tangentially. Resin canals that are surrounded by epitherial cells are formed in many genera of Dipterocarpaceae and a few of Leguminosae.

Ray parenchyma cells aggregate sometimes and develop a so-called "broad ray." The broad rays strike a peculiar figure on a board, especially on the radial surface, as observed in oak or beech. Cells contained in the ray also vary in their anatomical features. Some of them are upright or square at the marginal position. These variations are used for the identification of hardwoods [1]. Both axial and ray parenchyma cells are apparently concerned with the physiolgoical function—for instance, the storage of nutrients or heartwood formation. Radial resin canals or latex tubes are formed in the ray tissue of some tropical hardwoods.

II. ULTRASTRUCTURE OF WOOD CELL WALL

Wood is a natural composite material and a chemical complex of cellulose, lignin, hemicelluloses, and extractives [2]. Cellulose is the framework substance comprising 40 to 50% of wood in the form of cellulose microfibrils, whereas hemicelluloses are the matrix substances present between cellulose microfibrils. Lignin, on the other hand, is the encrusting substance solidifying the cell wall associated with the matrix substances. The significance of lignin as the encrusting substance can be demonstrated by examination of the lignin skeleton created by the acid removal of carbohydrates (Fig. 2).

The roles of these three chemical substances in the cell wall are compared to those of the constructing materials in the structures made from the reinforced concrete in which cellulose, lignin, and hemicelluloses correspond, respectively, to the iron core, cement, and buffering material to improve their bonding.

A. Cellulose Microfibrils

The crystalline nature of cellulose in wood has been demonstrated by studies with X-ray diffractometry and polarization microscopy. This crystalline nature was also confirmed by the electron diffraction patterns of the secondary wall of wood cells in selected areas [3]. Figure 3a is a transmission electron micrograph of a longitudinal section of latewood tracheids of *Pinus densiflora*, showing the intercellular layer (I), and the S_1, S_2, and S_3 layers. The electron diffraction diagram is of a selected area in S_2 (Fig. 3b), that is