VARIATION IN THE CELL-WALL DENSITY OF WOOD[1]

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ABSTRACT

The density of wood substance determined pycnometrically in water for 18 species was found to range from 1.508 to 1.542 g/cc. After correction for perturbation or compression of the sorbed water, wood-substance density values ranged from 1.497 to 1.517 g/cc for hardwoods and from 1.517 to 1.529 g/cc for the softwoods studied. Specific volume of wood substance ranged from 0.654 to 0.668 cc/g.

Specific volume of the dry cell walls was determined pycnometrically in toluene, using 1-mm sections and wood meal. Values obtained with wood meal were more reliable because of incomplete cell cavity penetration in 1-mm sections and ranged from 0.668 to 0.698 cc/g. Optically estimated values of specific volume based on microtome sections were usually considerably higher as a consequence of the aberrant shrinkage behavior of microtome sections as compared with blocks of wood. Calculated as the difference between specific volumes of cell wall and wood substance, voids in the dry cell walls of these 18 species occupied from 1.64 to 4.76% of cell-wall volume. Swollen cell-wall specific volumes derived by means of an optical technique, the validity of which has been questioned, ranged from 0.894 to 1.206 cc/g, implying water-filled voids in swollen cell walls ranging from 0.231 to 0.546 cc/g.

Variation in specific volume of wood substance, and particularly in specific volume of dry cell walls, accounted for significant amounts of variation in strain behavior among these 18 species. In bending, tension, and compression parallel to grain, the effect of high specific volume is to increase strain at maximum load. The increase was manifest only beyond the proportional limit. This is the region of large plastic deformation, and it may be assumed that woods having cell walls of low density are more susceptible to time-dependent effects such as creep and relaxation.

Within proportional limit, the effect of increasing specific volume of cell walls is to decrease the efficiency of the cell wall in response to stress. The ratio of proportional limit to ultimate stress, at least in bending and tension, decreases similarly as the specific volume of wood substance and cell wall increases.

The concept of density is deceptively simple. Measurements of the physical characteristics of weight and volume of a body would seem to be among the easiest physical parameters to describe. In reality, for a porous, hygroscopic, polymeric material such as wood the measurement of one of these parameters—the volume component—is extremely controversial. This is true to some degree of gross wood density measurements, but particularly so in the determination of cell-wall and wood-substance densities.

[1] A report on a study initiated at Yale University, School of Forestry, in 1966 under a cooperative research agreement with the United States Forest Service. The authors acknowledge the many valuable contributions to this work made by their coworkers, particularly Dr. George Tsoumis, now a member of the forestry faculty at the University at Thessaloniki, Greece, who was involved in the early stages of the study; David G. Briggs and Earl Marcellus, currently graduate students at the University of Washington; and George E. Woodson, now wood technologist at the Southern Forest Experiment Station, Pineville, La., who as graduate research assistants gathered most of the data on which this paper is based. Grateful acknowledgment is also due to Edward C. Childs, Great Mountain Forest, Norfolk, Conn., and to Dr. Peter Koch, Southern Forest Experiment Station, for their cooperation in supplying most of the test material.

It seems probable that many properties of wood, particularly those involving sorption, penetrability, swelling, and strain-related phenomena, are dependent upon the porosity of the cell wall. Variation in porosity might be due to the presence of physical voids or to the degree of molecular order within the cell wall. In any case, these differences should be experimentally evident as differences in cell-wall density. It is not clear, however, which of the various available techniques for density determinations yield the most significant information with respect to wood behavior.

The primary purpose of this study was to develop a foundation for meaningful relationships between cell-wall density and various wood properties. Particular interest was directed toward rationalizing the differences in optically and pycnometrically determined values of cell-wall density.

LITERATURE REVIEW

Stamm (1967) has reviewed the history of research in this field from the early work of Sachs (1879) and Hartig (1882) up to papers published in 1966. We will focus on the controversy present in the literature and interpret some of the earlier results in the light of more recent studies in a manner which will, at least to some degree, make it possible to rationalize them.

The controversy concerning wood-substance density values determined in water (Schwappach 1897; Dunlap 1914; Stamm 1929; Stamm and Hansen 1937; Wilfong 1966; Raczkowski and Stempien 1967) has come about because these values ranging from 1.50 to 1.55 g/cc are appreciably higher than those obtained with desiccated samples using helium as the displacement medium. Similar differences in density for charcoal (Harkins and Ewing 1921; Williams 1920, 1922) depending upon the displacement medium have been attributed to compression of the liquid at the liquid–solid interface or interpreted (Cude and Hewlett 1920; Howard and Hewlett 1924) as a differential ability to penetrate the charcoal. Davidson (1927) determined the density of soda-boiled cotton as 1.62 g/cc and 1.57 g/cc in water and helium, respectively. The difference between these values was suggested to be the result of adsorption–compression of water.

Stamm (1929) appears to have been the first to make helium-displacement determinations for wood. Stamm and Hansen (1937) used an improved helium-displacement technique and obtained values of 1.460 g/cc for white spruce, compared with 1.533 g/cc with water. This difference was attributed to compression of the adsorbed water in the cell wall to an average density of 1.113 g/cc. Several years earlier, Stamm and Seborg (1934) had calculated the compressive force of adsorption to be in the order of a few thousand atmospheres. In a subsequent analysis, Stamm (1950) reaffirmed the contention that reduced experimental values for specific volume of cellulose were the result of adsorption–compression of water. The compressibility of the wall substance was not taken into consideration in any of these calculations.

Heertjes (1942) rejected the hypothesis of adsorption–compression and attributed the difference in apparent densities to differences in the ability of the displacement medium to penetrate the porous structure. Hermans (1946, 1949) likewise rejected values of apparent density obtained in media which penetrate the cell wall on the basis that they are influenced by the laws of molecular packing. He viewed density as a typically macroscopic physical constant, which loses meaning when attempts are made to measure volumes at the molecular level by displacement of other molecules.

Howard and Hulett (1924) established that the adsorption of helium by charcoal was negligible at room temperature. Further work with wood has accepted the general assumption of lack of adsorption. It has, however, never been shown that helium is able to penetrate the dry cell wall. The assumption has been that, because of the small size of the helium molecule, it must be capable of penetrating the wall com-

pletely. Campbell and Russell (1935) appear to be among the few who questioned the ability of helium to penetrate completely the void structure of dry cellulose.

Pycnometric measurements of density, using non-swelling organic liquids such as benzene or toluene resulted in values slightly lower than those obtained with helium (Davidson 1927; Stamm and Hansen 1937). These differences have been attributed to the greater penetration of helium into the porous structure. Hermans (1946, 1949), however, has maintained that liquids which are "indifferent" to cellulose do not penetrate into cellulose fibers and that displacement values in non-swelling organic liquids produce density values that reflect differences in cell-wall density or order. Wilfong (1966) subsequently determined the densities of a number of species in helium and toluene and found them to be identical within the range of experimental error. They must therefore penetrate the same structure. Either they both penetrate the cell wall and are measures of wood-substance density, or they penetrate the wall not at all and therefore measure cell-wall density.

Frey-Wyssling and Speich (1942) concluded from studies of birefringence effects on ramie that liquids such as toluene and benzene fail to penetrate the fiber. Stone and Scallan (1965) and Stone, Scallan and Aberson (1966) have estimated the surface area of water-dried and solvent-exchange-dried spruce microtome sections using nitrogen adsorption and have suggested that the much lower values for the water-dried material imply the lack of pores in the cell walls. The ability of nitrogen or helium gas to penetrate any voids that might occur in the cell-wall structure was not questioned by them. Kallmes and Eckert (1964) found good agreement between the optical and nitrogen-adsorption estimates of the relative-bonded area of 2-D sheets. This could be the case only if nitrogen penetrated neither the cell wall of water-dried fibers nor the space between fibers in the bond areas. Since the nitrogen molecule has an effective diameter of 0.4 nm[2], the fiber surfaces must be close enough (0.3 nm) for hydrogen bonding to take place. If separate fibers can be drawn this close together under the action of surface tension forces during the last stages of drying, it is not difficult to imagine a compaction of similar magnitude within the cell wall itself.

A number of studies involving displacement of liquids of high molecular weight are covered in a recent review paper (Wangaard 1969). Several workers have employed the mercury porosimeter, whereby mercury is forced at high pressures (up to 15,000 psi) into the samples. At the highest pressure, it is estimated that mercury will penetrate all voids larger than 7 nm effective radius. Stone et al. (1966) reported density values as high as 1.41 g/cc for black spruce blocks, compared to 1.48 g/cc using helium displacement. By reading density values from the curves presented for Douglas-fir and birch, it would appear that the difference between the mercury and helium displacement values was even less for these species. In further work Stone (1966) reported an average value for 50 μm-thick[3] cross-sections of white spruce of 1.44 g/cc. Stayton and Hart (1965) used a mercury porosimeter technique with maximum pressures of 3000 psi. Values obtained for pine, spruce, and cedar were in the order of 1.44 to 1.45 g/cc. Wilfong (1966) found only a 1.75% difference between the highest values obtained by Stayton and Hart and those he obtained by means of toluene or helium displacement. He further noted that the difference between the 1.45 value for toluene displacement and 1.53 for water could allow for only a 5% void volume if the water within the wall was uncompressed.

Weatherwax and Tarkow (1968a) determined the cell-wall density of dry Sitka spruce samples with minimum thicknesses of 10 and 100 μm, using two silicones as the displacement fluids. The density values for the silicone with a viscosity of 0.65 centistoke ranged from 1.451 g/cc to 1.465 g/cc.

[2] Nanometer (nm) = millimicron.
[3] Micrometer (μm) = micron.

The values using the 30,000 centistoke viscosity silicone were slightly lower. The difference between these two sets of values was explained on the basis of incomplete penetration of ray cells with the high viscosity fluid. The values for the low viscosity fluid are essentially in agreement with helium displacement values. The dry cell walls must therefore be equally inaccessible to viscous silicone and helium. Weatherwax and Tarkow (1968b) also determined the density of Sitka spruce particles in water, silicone, ethanol, and hexane. The hexane was introduced into the cell wall through a solvent-exchange process. The density determined in hexane was 1.533 g/cc, only slightly less than the value of 1.546 g/cc found for water displacement. The value determined in silicone was 1.465 g/cc. Hexane introduced through solvent exchange was assumed to penetrate the residual void volume in dry wood not accessible to the non-swelling silicone. This amounted to 0.030 cc/g or about 4% on a volume basis. As a first approximation, they estimated that about 85% of the apparent loss in specific volume of wood substance in water is due to the presence of 4% residual void volume in the dry cell wall. The remaining 15% is due to adsorption–compression or perturbation. The water in the cell walls was calculated to be compressed by 1.67%, which would result in an average specific gravity of 1.014.

According to Goring (1966), the hydroxyl groups on the carbohydrate–molecule surfaces perturb the layer of water next to the surface so that the lower density (0.970 g/cc at 25 C), cluster form of water is diminished in concentration. Farther away from the surface, the proportion of clusters to unbonded liquid is envisioned as that of normal water. His argument is based on the theory of water structure as developed by Frank and Wen (1957) and further developed quantitatively by Némethy and Scheraga (1962). Ramiah and Goring (1965) determined that for a sulfite pulp with an accessibility of 26%, 0.045 gram of water per gram of fiber substance was in the perturbed state. This quantity of water would be more compact by 12% resulting in a calculated "adsorption–compression" of 0.0054 cc/g. If we assume that a gram of wood substance contains 0.300 g of water at the fiber-saturation point and that 0.045 g of this quantity is more compact by 12%, the average density of the water within the cell wall would be 1.010 g/cc at 25 C.

In further consideration of the work of Frey-Wyssling and Speich (1942), the authors interpreted their data to mean that the wall structure of dry ramie fibers contains either 4.4% disordered cellulose or complete voids. The latter case was accepted since a 12.6% density deficit had been determined between the fiber density determined optically and the density of crystalline cellulose. Even greater discrepancies have been reported with optically determined cell-wall densities. Clegg and Harland (1923) determined the density of cotton fibers based on fiber volumes gained from projected microtome cross-sections. Density values thus obtained were in the order of 1.00 g/cc. Taking 1.55 g/cc as the density of cell-wall substance for cotton fibers, a porosity of something in excess of 30% is indicated.

Similar techniques have subsequently been applied to wood by several investigators. Details of these techniques have varied slightly, but generally cell-wall density determinations have been based on gross density of the wood and per cent wall area in the cross-section as estimated by various optical techniques. Jayme and Krause (1963) studied the cell-wall density of several hardwood species and obtained values varying from 0.73 g/cc to 1.27 g/cc. Worrall (1963), working with five softwoods, measured cell-wall densities of less than 1.00 g/cc, and Tsoumis (1964) has reported a dry cell-wall specific gravity of 0.967 for eastern white pine. Comparably low cell-wall densities have been observed by Ifju and Kennedy (1962), and implied in the results of Kellogg and Ifju (1962). In a study of the apparent density of wood and pulp fibers, Yiannos (1964) reported

cell-wall densities for several coniferous woods ranging from 1.04 g/cc for eastern spruce to 1.32 g/cc for slash pine. In most of these studies, the determinations of cross-sectional area have presumably represented the wall in the dry condition; but in no case has it been established that the techniques involved in preparing the microtome sections left the wall in a state equivalent to that condition. The fact that any swelling or bulking of the wall would lead to diminished values of cell-wall density casts considerable doubt as to the precision of these optical density values.

Berlyn (1968a) has proposed an optical technique for determining cell-wall density, using interference microscopy and two-wave-length microspectrophotometry. He has applied this technique (1968b, c) to red pine samples, and the results suggest that voids within the cell wall are completely eliminated if the cell walls are carefully dehydrated.

Although a great deal of work has been concerned with the measurement and interpretation of cell-wall or cell-wall-substance density in different displacement media and with different measuring techniques, surprisingly little effort has been devoted to relating variation in these fundamental characteristics to the physical, chemical, or mechanical nature or behavior of wood. Many have suggested that cell-wall density should have an important influence on the mechanical behavior of wood, but we are unaware of any published results demonstrating the fact.

Wilfong (1966) has attributed variability in wood-substance specific gravity as determined by water displacement mainly to differences in extractive content and perhaps to some degree to the relative holocellulose content. Stamm and Sanders' (1966) suspension measurements in mixtures of toluene and carbon tetrachloride were interpreted by them to be measurements of wood-substance density. If there is some small percentage of voids in the dry cell wall and toluene does not penetrate them, these values should be interpreted as cell-wall density measurements. In any case, they have shown that the relative holocellulose–lignin content of a small sample is related to these measurements provided that the density of the chemical components is determined from the same material. Raczkowski and Stempien (1967) have reported a strong positive relationship between the density determined pycnometrically in either water or toluene and gross wood density. Worrall (1963) also found cell-wall specific gravity to be related in a positive manner to gross wood density. The data of Jayme and Krause (1963) show a similar relationship.

In summary, the literature supports the following concept of cell-wall composition. The dry cell wall has a density which, if measured with care, is approximately 1.45 g/cc in displacement media ranging from helium to a silicone polymer. These displacement media must therefore penetrate the dry cell wall equally or not at all. It is our opinion that there is sufficient experimental evidence to support the latter view. If the total difference between the density of the dry cell wall and the density of wood substance determined in water is due to the presence of "voids," they could not exceed 5% of the wall volume. Increases in the degree to which it is felt that water within the cell wall is compacted or perturbed will decrease the estimate of void volume. There is now rather convincing evidence that the water within the cell wall is compacted only slightly, compared with earlier estimates, and that the maximum void volume may be approximately 4% of the dry-wall volume.

Optical estimates of dry cell-wall density are obviously lower than those otherwise determined. No satisfactory explanation of this difference has been offered. Unfortunately, in all studies involving optical estimates of dry cell-wall density, it has not been established that the techniques involved in preparing the sample have left the wall in a state equivalent to the desiccated condition.

TABLE 1. *Density and specific volume of wood and wood substance of extractive-free sapwood of 18 species.*

Species	Wood density		Wood substance density[1]		Wood substance specific volume	
	Green vol.	O.D. vol.	By direct H_2O displacement	Corrected for densification of H_2O	Direct	Corrected
	g/cc	g/cc	g/cc	g/cc	cc/g	cc/g
1. Basswood (*Tilia americana*)	0.296	0.368	1.527	1.515	0.655	0.660
2. Eastern cottonwood (*Populus deltoides*)	0.340	0.408	1.528	1.517	0.654	0.659
3. White ash (*Fraxinus americana*)	0.423	0.499	1.508	1.497	0.663	0.668
4. Yellow poplar (*Liriodendron tulipifera*)	0.416	0.501	1.522	1.510	0.657	0.662
5. Black cherry (*Prunus serotina*)	0.430	0.523	1.520	1.508	0.658	0.663
6. Hard maple (*Acer saccharum*)	0.458	0.548	1.520	1.508	0.658	0.663
7. Red maple (*Acer rubrum*)	0.468	0.549	1.528	1.517	0.654	0.659
8. Beech (*Fagus grandifolia*)	0.497	0.602	1.514	1.504	0.660	0.665
9. Paper birch (*Betula papyrifera*)	0.492	0.616	1.521	1.510	0.657	0.662
10. Red oak (*Quercus rubra*)	0.573	0.680	1.524	1.513	0.656	0.661
11. Yellow birch (*Betula alleghaniensis*)	0.557	0.706	1.523	1.511	0.657	0.662
12. White oak (*Quercus alba*)	0.587	0.735	1.525	1.513	0.656	0.661
13. Shagbark hickory (*Carya ovata*)	0.616	0.767	1.520	1.508	0.658	0.663
14. Eastern white pine (*Pinus strobus*)	0.308	0.351	1.535	1.524	0.651	0.656
15. Red spruce (*Picea rubens*)	0.351	0.416	1.542	1.529	0.649	0.654
16. Eastern hemlock (*Tsuga canadensis*)	0.363	0.418	1.530	1.517	0.654	0.659
17. Spruce pine (*Pinus glabra*)	0.385	0.446	1.541	1.529	0.649	0.654
18. Loblolly pine (*Pinus taeda*)	0.472	0.564	1.540	1.529	0.649	0.654

[1] Density of wood substance determined by pycnometric displacement of water by 1-mm.-thick by 3-mm. square wafers.

EXPERIMENTAL PROCEDURE

Since the primary purpose of this study was to develop a foundation for meaningful relationships between cell-wall density and various properties, it was essential to employ an effective scheme of matching to insure that the samples used for determinations of density be representative of the material that was used for mechanical testing.

Green sapwood slabs of the thirteen hardwood and five softwood species listed in Table 1 were received at the laboratory directly after sawing. For each species, the material selected for testing consisted of six flatsawn units, ⅝ by 2 inches in cross section and 18 inches long, straight grained and free from defects. A transverse section ½ inch thick was immediately cut from

one end of each unit and stored in a mixture of water, glycerine, and alcohol for subsequent preparation of microtome blocks. At the same time five successive wafers, each 1 mm thick, were cut from each unit to provide material for pycnometric determination of wood-substance and cell-wall density, and three successive wafers, each 3 mm thick, were cut and set aside for later determination of wood specific gravity.

The remaining portion of each unit, reserved for mechanical testing, was then end-coated and stored in a humidity-controlled room that established an equilibrium moisture content of approximately 10%.

Extraction

All of the wafers to be used for pycnometric determination of cell-wall density and for determination of wood specific gravity were first extracted successively with benzene–alcohol (2:1), alcohol, and distilled water, employing standard Soxhlet apparatus. Extraction was continued with each solvent until the extracting solvent was colorless. Following extraction, the wafers were stored in distilled water.

Pycnometric Methods

A pycnometric method was used to determine the densities of 1) wood substance and 2) dry cell walls based on extractive-free 1-mm wafers for each sampling unit.

Density of wood substance. Determination of wood-substance density involved the usual relationship:

$$D = \frac{W_d \times g}{W_o - (W_1 - W_d)} \qquad (1)$$

in which

W_d = oven-dry weight of wood, g
W_o = weight of water to fill pycnometer, g
W_1 = weight of water + wood to fill pycnometer, g
g = density of water at 30 C, g/cc

This equation may be seen to involve simply oven-dry weight of wood, g ÷ volume of displaced water, cc, or density of wood substance, g/cc.

The determination was carried out at 30 C, using pre-weighed 25 ml pycnometer bottles filled successively with distilled water and with water plus 2–3 g (dry weight) of 3-mm square flakes cut from the 1-mm wafers following application of a vacuum of 3-mm mercury or less to remove air from the filled pycnometer bottle.

(Substitution of 1.xx W_d, where xx is moisture content (per cent) at the fiber-saturation point, for W_d in the denominator of equation 1 should permit calculation of swollen cell-wall density. Use of this relationship will be referred to later.)

Density of dry cell walls. After drying at 50 C over barium oxide desiccant in a vacuum oven, the pycnometer bottle containing the dry wood sample consisting of 1-mm-thick flakes was evacuated to a pressure of less than 3 mm for one hour while attached to a filling device. Without breaking the vacuum, the pycnometer was filled with toluene and subjected to six cycles of alternate heating and evacuation.

Determination of dry cell-wall density followed the procedure described previously for wood-substance density employing equation 1, except that g, W_o, and W_1 involve toluene as the displaced liquid. As later discussion will reveal, results obtained with this technique were questioned on the ground that penetration of cell cavities by toluene may have been incomplete.

Consequently, additional wood representative of two to four units of each species was ground in a Wiley mill to pass a 40-mesh screen. The resulting meal was enclosed in nylon bags and subjected to the extraction procedure described previously. Dry cell-wall density was determined in toluene, following the saturating and pycnometric displacement technique described previously for wafer material.

Wood Specific Gravity Methods

Determination of wood specific gravity from extractive-free 3-mm wafer material involved the maximum-moisture-content

method for green-volume specific gravity and a Breuil mercury volume meter for dry-volume specific gravity. The 3-mm wafers used for specific gravity determination had been stored in water, following removal of extractives, and required no further saturation treatment for the determination of maximum moisture content. The appropriate value for density of wood substance, directly determined previously for the same sampling unit by the pycnometric method, was used in the usual equation. After air drying in the laboratory for at least 24 hr, the wafers were oven dried at 102 C and weighed. Oven-dry volume was determined by displacement in a mercury volume meter. Average values for each species were calculated from the individual unit values for specific gravity.

Optical Method for Determination of Cell-wall Density

The optical method used for determination of cell-wall density was based on measurement of the proportionate area of cell wall from a microtome-cut cross-sectional sample of each unit. Two of the four microtome blocks to which the entire cross section of each unit had been reduced were selected at random for sectioning. Several sections of 15 μm thickness in the case of hardwoods and 25 μm thickness for softwoods were cut on a sliding microtome. Cutting was facilitated by the fact that the blocks were never dried, having been stored in a water–glycerine–alcohol solution while still green.

Immediately after cutting, the microtome sections were extracted for 1 hr in a 2:1 benzene–alcohol solution at 70 C, followed by another hour in alcohol in the same water bath. Finally, alcohol was replaced by water and extraction continued for a third hour. Extracted sections were stored in glass vials containing distilled water with 2–3 drops of formaldehyde as preservative.

Density of water-swollen cell walls. Measurement was done at 450× magnification, employing a microscope with a Zeiss integrating eyepiece with a 25-point grid. Initially two random traverses were made across the entire ⅝-inch dimension of each water-mounted section (essentially in the radial direction)—four traverses in all. For each traverse, the number of points counted as cell wall was expressed as a percentage of the total number of points in all of the fields measured.

The variance among the four traverses was calculated and, from the relationship

$$N = \frac{4S^2}{E^2}$$

where S^2 is the variance and E is the permissible error (0.05 of mean value), the number of passes (N) required to assure at the 95% probability level that the error in the mean value was less than 5% was determined. Additional traverses were run if necessary. The error of the final mean value for each unit was generally about 3% and in no case exceeded 4%.

Cell-wall density[4] in the water-swollen condition was calculated from the relationship:

$$D = \frac{G_g}{\%\ \text{cell-wall area}} \times 100 \qquad (2)$$

where

G_g = bulk specific gravity of the unit, green volume basis

Average values were calculated from the values for the six units of each species.

Density of dry cell walls. The microtome section was then dried for 48 hr at 55 C in a vacuum oven containing fresh barium oxide. Immediately upon removal from the oven, the section was flooded with toluene. At the time of microscopic examination, the section was transferred to a slide, covered with a few drops of toluene, and mounted under a cover glass.

The method of determining the proportionate amount of cell wall was identical to

[4] As determined in equations 2 and 3, cell-wall density is used as a synonym for specific gravity in order to retain comparability with equation 1. Specific gravity is, of course, dimensionless. The metric dimensions have been included in subsequent presentation of the data.

that described previously for water mounts. Dry cell-wall density was calculated as

$$D = \frac{G_u}{\%\ \text{cell-wall area}} \times 100 \qquad (3)$$

where

G_u = bulk specific gravity of the unit, oven-dry volume basis

The sampling error in this determination was held within 3.5%. Average values for each species were calculated from the six individual unit values.

Mechanical Testing and Methods for Calculating Strain

The purpose of this phase of the study was to determine various properties, particularly with respect to strain behavior, from static bending, tension, and compression-parallel-to-grain tests conducted on material closely matched to that from which cell-wall density values had been obtained. Mechanical test specimens were consequently prepared from the remaining portion of each sampling unit that had been stored in a constant humidity room, as mentioned previously. Each flat-sawn unit yielded two static-bending specimens ½ × ½ × 8 inches in size, one compression parallel to grain specimen ½ × ½ × 3 inches, and four tension parallel to grain specimens ½ × 0.020 × 6 inches in size.

Static bending. One specimen from each unit—six for each species—was tested dry at approximately 10% moisture content. Center loading was applied on the radial face of the specimens with supports placed 7 inches apart in a hydraulic testing machine. Platen speed was 0.024 inch per min, and deflection of the neutral plane at midspan was measured by means of an Ames dial. Fiber stress at proportional limit, modulus of rupture, and modulus of elasticity were calculated in the conventional manner. Strain at proportional limit and at maximum load were calculated from the relationship between deflection and strain in outermost fiber under this type of loading:

$$\varepsilon = \frac{6\ yd}{\ell^2} \qquad (4)$$

where

ε = calculated strain in outermost fiber
y = deflection, in.
d = depth, in.
ℓ = span, in.

This relationship is strictly accurate only within proportional limit. Its use here for evaluating strain at maximum load is justified on the ground that the values obtained accurately portray the relative deflection at maximum load of the test beams.

Tension parallel to grain. For all species except the oaks, the specimens for this test were cut so that the ½-inch-wide face was a radial surface. In the wide-rayed oaks, the specimens were ripped at an angle to the radial plane to minimize the possibility of failure at a cross section consisting predominantly of ray tissue. Four specimens from each unit—24 for each species—were tested in the conditioning room maintained at 10% e.m.c.

A type TT-C-L Instron tensile testing machine fitted with special air-actuated serrated steel grips was used for testing. Strain was measured with a 2-inch strain-gage extensometer. Crosshead speed was 0.01 inch per min. Load and strain were recorded continuously by means of an X-Y recorder. Fiber stress at proportional limit, ultimate tensile strength, and modulus of elasticity were calculated, and strains were read directly from the load-strain curve.

Compression parallel to grain. One specimen from each unit—six per species—was tested on the same Instron testing machine. A strain-gage compressometer of 2-inch gage length was used to measure strain. Crosshead speed was 0.01 inch per min. Load and strain were read from the chart of an X-Y recorder to obtain values for calculating fiber stress at proportional limit, maximum crushing strength, and modulus of elasticity.

RESULTS AND DISCUSSION

Wood-substance and Cell-wall Densities

Table 1 shows the 18 species involved in this study—13 hardwoods and 5 softwoods —each group arranged in order of increasing gross wood density in the oven-dry condition.

Wood-substance density determined pycnometrically by water displacement ranged from 1.508 to 1.542 g/cc for these species, in agreement with values obtained by many previous investigators. Such values are too high as the result of compaction of water used in the determination, and it has commonly been assumed that the average density of the sorbed water within the cell walls is in the order of 1.11 g/cc (Stamm 1964). Recent work by Weatherwax and Tarkow (1968b) has shown that the compaction of water is much less than this, amounting only to 0.0052 cc/g of wood substance. Assuming 0.30 g of water present in a gram of wood at fiber saturation, this reduction in volume would result in the sorbed water having a density of 1.014 g/cc. As already indicated, a similar conclusion may be reached from data presented by Ramiah and Goring (1965) on the basis of the perturbed state of water associated with cellulose. Regardless of the mechanism of compaction—adsorption–compression or perturbation—the practical consequence of the compaction of water is to underestimate the specific volume of wood substance in the pycnometric determination of density by 0.0052 cc/g.

As shown in Table 1, this correction has been applied to the direct determination of the specific volume of wood substance and, from this, corrected values for the density of wood substance have been calculated. These corrected values range from 1.497 to 1.517 g/cc for the hardwoods and from 1.517 to 1.529 g/cc for the softwoods involved in this study.

The specific volume of oven-dry cell walls was determined by three techniques with the results shown in Table 2. Determination of cell-wall density by sampling the proportionate area occupied by cell walls in dried microtome sections mounted in toluene yielded values that have been converted to specific volume (cc/g) as shown in Table 2.

TABLE 2. *Specific volume of dry cell walls as determined by three techniques.*[1]

Species	Pycnometric specific volume		Optical specific volume
	1-mm. sections	Wood meal	Microtome sections
	cc/g	cc/g	cc/g
1. Basswood	0.707	0.671*	0.865
2. E. cottonwood	0.686	0.676*	0.801
3. White ash	0.866	0.698*	0.704
4. Yellow poplar	0.757	0.679*	0.732
5. Black cherry	0.745	0.689*	0.739
6. Hard maple	0.728	0.689*	0.751
7. Red maple	0.738	0.685*	0.757
8. Beech	0.742	0.681*	0.713
9. Paper birch	0.685	0.679*	0.720
10. Red oak	0.843	0.686*	0.716
11. Yellow birch	0.692	0.686*	0.713
12. White oak	0.793	0.694*	0.706
13. Shagbark hickory	0.803	0.693*	0.689
14. E. white pine	0.672	0.669*	0.868
15. Red spruce	0.674	0.668*	0.753
16. E. hemlock	0.694	0.676*	0.796
17. Spruce pine	0.667*	0.680	0.758
18. Loblolly pine	0.667*	0.680	0.786

[1] Values indicated by * were judged to be most nearly free of error and were used in subsequent analyses.

Two sets of data were obtained by the pycnometric technique—one based upon displacement of toluene by small wafers cut from 1-mm-thick cross-sections, and one from wood meal that had been ground to pass a 40-mesh screen. It was found difficult to establish an absolute saturation endpoint in working with 1-mm sections and, with only two exceptions, specific volume as determined by this technique was larger than that obtained from wood meal. The greatest differences were encountered in species such as white ash and shagbark hickory, which are characterized by a relatively high proportion of parenchymatous tissue and, as suggested by Wilfong (1966), Stamm (1967), and Weatherwax and Tarkow (1968a), it seems probable that complete penetration of all cell cavities was not achieved by a non-swelling liquid such as toluene. It should be noted that in the soft-

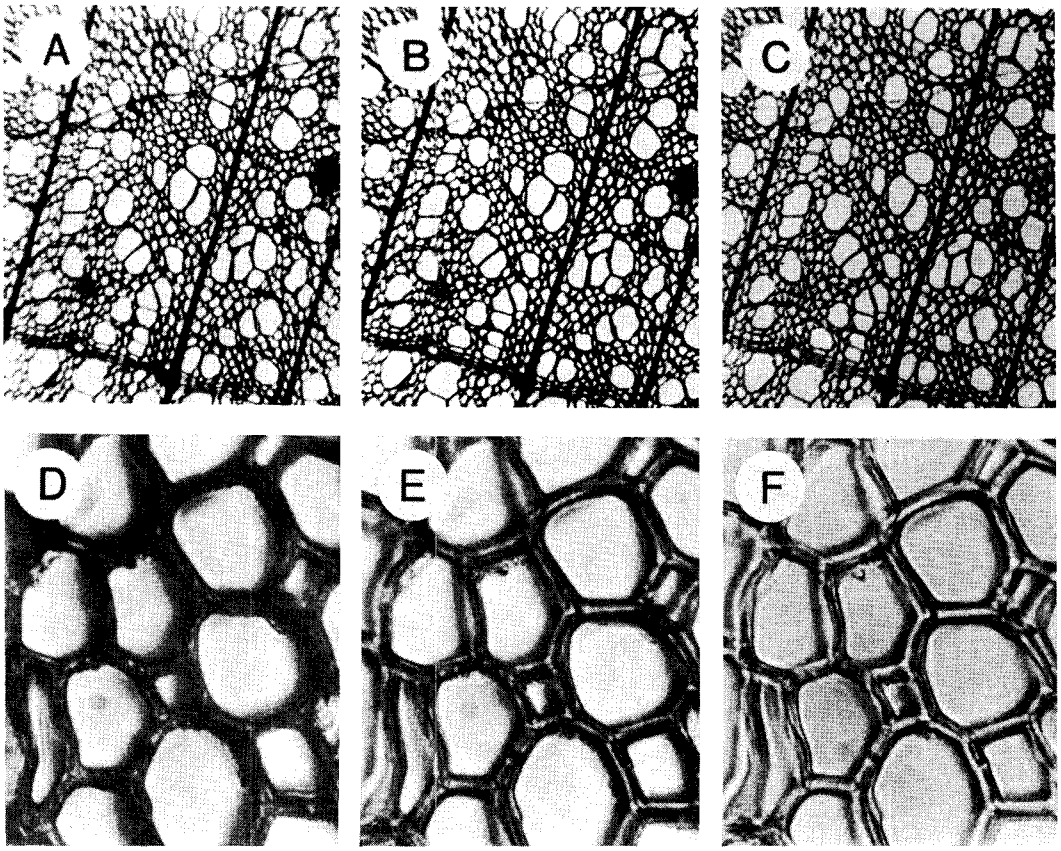

FIG. 1. Micrographs of a desiccated basswood section showing lack of swelling in toluene. A and D. photographed in air; C and F. photographed after flooding in toluene; B and E. print made from superimposed sets of negatives A and C, D and F.

woods, having a relatively small proportion of parenchyma cells, specific volumes measured from the displacement of toluene by 1-mm-thick sections were similar to values obtained from wood meal. In fact, the specific volumes obtained for spruce pine and loblolly pine from such sections were slightly lower than those obtained with wood meal.

Assuming that the smaller values of specific volume represent more nearly complete saturation of cell cavities, the values obtained with wood meal were considered to be most nearly free of error and, with the exception of spruce pine and loblolly pine, wood-meal values were selected for further analysis. In selecting these values to represent the specific volume of dry cell walls, we recognize that the true value may lie somewhere between the value obtained with 1-mm sections and wood meal because of the possibility that the grinding of meal may have exposed some internal voids in the dry cell walls to penetration by toluene. Consequently, subsequent estimates of the void volume in dry cell walls might be considered as conservatively small.

The optical estimates of dry cell-wall specific volume are inversely related to gross wood specific gravity. For the high-density woods such as hickory, the agreement between the optical and pycnometric specific volume is very good. The disparity increases with decreasing wood density until it is as great as 0.20 cc/g for white pine.

One possibility for error in the optical

TABLE 3. *Change in wall and lumen areas due to sectioning and drying, as measured in microtome sections and blocks.*

Species	Change in area with shrinkage (%)				Change in area, section relative to block (%)			
	Wall		Lumen		Wall		Lumen	
	Block	Section	Block	Section	Wet	Dry	Wet	Dry
White pine	29.4	20.4	0.3	2.8	−0.2	12.4	−3.4	−5.5
Basswood	24.2	25.2	−2.5	1.1	9.7	9.4	−3.2	−5.4
Cottonwood	32.9	25.3	−10.2	−9.1	4.0	16.0	0.2	2.2
Spruce pine	38.9	31.1	21.6	15.8	2.8	8.0	−8.0	−7.6
Black cherry	20.9	26.4	−0.7	7.6	−4.4	3.4	0.9	−7.6
Red oak	25.2	26.4	−13.7	−5.9	4.6	3.7	−4.2	−8.5
Hickory	22.5	16.8	−0.6	16.9	4.6	12.4	6.8	−12.0
Average	27.7	24.5	−0.8	−4.2	3.0	9.3	−1.6	−6.3

estimate of specific volume from sections mounted in toluene can be dismissed. That is the possibility that the cell walls had been slightly swollen by toluene penetration. Photomicrographs of desiccated microtome sections mounted in air (and sealed to prevent the possible admission of moisture) and the identical sections after flooding with toluene are shown in Fig. 1. The photomicrographs have been superimposed and offer convincing evidence that no dimensional change has occurred as the result of immersion in toluene. This evidence is supported by Frey-Wyssling and Speich (1942), who have established the inability of liquids such as xylene and toluene to penetrate the cell wall of ramie fibers.

A small sub-study was carried out in an effort to rationalize the difference between the optically and pycnometrically determined values of cell-wall density. A single air-dried block was selected from available material from 7 of the 18 species in the study. After thorough soaking, transverse microtome sections were cut from each block. The surfaces of both water-swollen block and section were examined, using near UV incident illumination. Several groups of cells which could be located in both the block and section were photographed at 882× magnification. The section was then desiccated in the same manner used in the optical method of determining cell-wall density. The block was first air-dried in the laboratory and then vacuum-desiccated over phosphorous pentoxide.

The same cell groups originally photographed were located again and rephotographed in the desiccated state at exactly the same magnification. The 35-mm negatives were first enlarged about 6 times onto Kodalith Royal Ortho film. A system of negative registration was devised to ensure exactly the same enlargement of all negatives. The lumens of the selected group of cells were delineated on the enlargements with a fine ink line. The outer limits of the cell group were delineated at the middle lamella. By weighing cutouts of these delineated areas, it was possible to calculate the change in wall and lumen areas as a result of sectioning and desiccation. The average values for these calculations are shown in Table 3.

Because considerable variation often existed between the separate measurements for one species, it seems advisable to place emphasis on the average values for the seven species. The altered shrinkage in microtome sections compared to blocks resulted in an estimation of dry cell-wall area that was 9.3% too large and of lumen area that was 6.3% too small. This combination of errors involved in equation 3 leads to an underestimate of optically determined cell-wall density and an overestimate of cell-wall specific volume. The average optically-estimated cell-wall specific volume for the

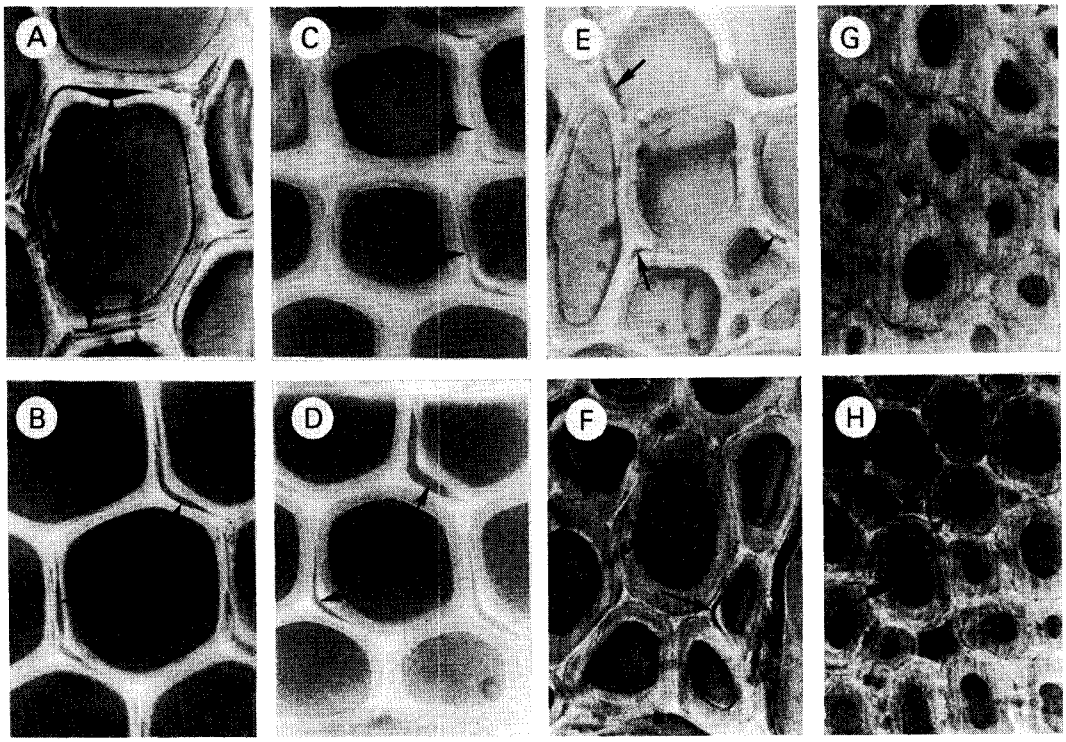

FIG. 2. Incident illumination micrographs illustrating the decreasing amount of gross cell-wall damage in wet cross-sections with increasing wall thickness. A. White pine, earlywood; B. Spruce pine, earlywood; C. White pine, latewood; D. Spruce pine, latewood; E. Basswood; F. Black cherry; G. Red oak; H. Hickory.

seven species as given in Table 2 was 0.777 cc/g. The average adjusted specific volume after correcting for these errors would be 0.704 cc/g—much closer to the pycnometric average of 0.679 cc/g for these species.

It has been observed, as illustrated in Fig. 2, that the intensity of wall damage in the microtome sections increases with decreasing wood specific gravity. To a considerable degree, this type of gross wall damage should not affect the optical estimates of cell-wall area obtained from the dot–grid technique, but it was also observed that many of the ruptures are far more difficult to see when viewed with transmitted rather than incident light. These results have convinced us that the optical estimates of dry cell-wall specific volume made with transmitted light (Table 2) are not reliable.

In Table 4 are shown average values for specific volume (cc/g) and density (g/cc) of dry cell walls that we have accepted for each species. Also shown in Table 4, reproduced from Table 1, is the corrected specific volume of wood substance. The void volume in the dry cell walls, averaged for the material tested from each species, is also shown in the table. Ranging from 0.011 for basswood to 0.033 cc/g for white oak, these values represent void volumes ranging from 1.64 to 4.76% of the volume of the dry cell wall.

Results obtained through the use of the optical technique described earlier for determination of the density of swollen cell walls for these 18 species are shown in Table 5. Swollen cell-wall densities ranged from 0.829 g/cc for basswood to 1.119 g/cc for shagbark hickory. Corresponding specific volumes for each species are also shown in this table. These values are inversely related to gross wood density, as

TABLE 4. *Density and specific volume of dry cell walls, wood substance, and void volume in dry cell walls.*

Species	Dry cell walls[1]		Wood substance[2]	Void volume in dry cell walls	
	Density	Specific volume	Corr. specific volume		
	g/cc (1)	cc/g (2)	cc/g (3)	cc/g[3] (4)	% (5)
1. Basswood	1.491	0.671	0.660	0.011	1.64
2. E. cottonwood	1.480	0.676	0.659	0.017	2.51
3. White ash	1.433	0.698	0.668	0.030	4.30
4. Yellow poplar	1.472	0.679	0.662	0.017	2.50
5. Black cherry	1.451	0.689	0.663	0.026	3.77
6. Hard maple	1.451	0.689	0.663	0.026	3.77
7. Red maple	1.459	0.685	0.659	0.026	3.80
8. Beech	1.468	0.681	0.665	0.016	2.35
9. Paper birch	1.472	0.679	0.662	0.017	2.50
10. Red oak	1.458	0.686	0.661	0.025	3.64
11. Yellow birch	1.458	0.686	0.662	0.024	3.50
12. White oak	1.440	0.694	0.661	0.033	4.76
13. Shagbark hickory	1.442	0.693	0.663	0.030	4.33
14. E. white pine	1.494	0.669	0.656	0.013	1.94
15. Red spruce	1.498	0.668	0.654	0.014	2.10
16. E. hemlock	1.480	0.676	0.659	0.017	2.51
17. Spruce pine	1.499	0.667	0.654	0.013	1.95
18. Loblolly pine	1.500	0.667	0.654	0.013	1.95

[1] With the exception of spruce pine and loblolly pine, density of dry cell walls is based on pycnometric displacement of toluene by wood meal. Data for spruce pine and loblolly pine are based on pycnometric displacement by 1-mm wafers. (In the wood meal series both of these southern pines showed identical values of 1.470 g/cc.)
[2] From Table 1.
[3] Col. 2 – col. 3.

were the optically determined dry cell-wall specific volumes. The question arises as to the validity of these optically determined values.

As a check on these optically determined values for swollen cell-wall density, the equation for determining density pycnometrically was modified by substitution of the unknown weight at fiber saturation for oven-dry weight in the denominator:

$$D = \frac{W_d \times g}{W_o - (W_1 - 1.xxW_d)} \qquad (5)$$

where xx is the moisture content (%) at the fiber-saturation point. Substituting the optically determined values for cell-wall density in this equation permits solving for the fiber-saturation moisture content. Fiber-saturation point values resulting from this calculation are included in Table 5. They range from 23.6% for shagbark hickory to 55.1% for basswood.

These values have been plotted against wood specific gravity in Fig. 3 to permit comparison with the Feist–Tarkow (1967) curve for the relationship between fiber-saturation point and specific gravity. The Feist–Tarkow data were obtained by means of the non-solvent water technique; and their curve, based on a relatively small number of species, was presented primarily to support other evidence (Vorreiter 1963) indicating that the fiber-saturation point in low-density species may be considerably higher than has been commonly recognized. The curve fitted to the present data by the method of least squares supports such a trend and, considering the scatter in both sets of data, shows rather good agreement with the curve drawn by Feist and Tarkow. Further, the fiber-saturation point of 41.9% shown for red spruce is almost identical with the value reported by Stone and Scallan (1967) for black spruce as determined by non-solvent water and porous-plate techniques. If these values for fiber-saturation

TABLE 5. *Density and specific volume of water-swollen cell walls of extractive-free sapwood.*

Species	Cell-wall[1] Density g/cc (1)	Cell-wall[1] Specific volume cc/g (2)	Fiber saturation point[2] % (3)	Wood substance Corr. sp. vol.[3] cc/g (4)	Water-filled voids[4] cc/g (5)	Av. density of sorbed H_2O[5] g/cc (6)
1. Basswood	0.829	1.206	55.1	0.660	0.546	1.009
2. E. cottonwood	0.924	1.082	42.8	0.659	0.423	1.012
3. White ash	1.058	0.945	28.2	0.668	0.277	1.018
4. Yellow poplar	1.031	0.970	31.3	0.662	0.308	1.016
5. Black cherry	1.016	0.984	32.6	0.663	0.321	1.016
6. Hard maple	1.010	0.990	33.2	0.663	0.327	1.015
7. Red maple	0.977	1.024	37.0	0.659	0.365	1.014
8. Beech	1.044	0.958	29.8	0.665	0.293	1.017
9. Paper birch	0.991	1.009	35.2	0.662	0.347	1.014
10. Red oak	1.073	0.932	27.6	0.661	0.271	1.018
11. Yellow birch	1.053	0.950	29.3	0.662	0.288	1.017
12. White oak	1.042	0.960	30.4	0.661	0.299	1.017
13. Shagbark hickory	1.119	0.894	23.6	0.663	0.231	1.022
14. E. white pine	0.906	1.104	45.3	0.656	0.448	1.011
15. Red spruce	0.936	1.068	41.9	0.654	0.414	1.012
16. E. hemlock	1.024	0.976	32.2	0.659	0.317	1.016
17. Spruce pine	0.988	1.012	36.3	0.654	0.358	1.014
18. Loblolly pine	0.999	1.001	35.2	0.654	0.347	1.014

[1] Density of swollen cell walls determined optically from microtome cross sections in water.
[2] Moisture content required to reconcile pycnometric and optical determinations of swollen cell-wall density.
[3] From Table 1.
[4] Col. 2 – col. 4.
[5] From data in col. 3 and col. 5.

point are acceptable, then by the same token the values for swollen cell-wall density shown in Table 5 can be considered reliable.

The validity of the optically estimated, swollen cell-wall specific volume may, however, be questioned on the basis of certain qualitative evidence. From Table 3 it can be seen that the microtoming process had increased the average section wall area of these seven species by 3.0% over that of the blocks from which they were cut and decreased the average lumen area by 1.6%. In the case of basswood, these errors were 9.7 and 3.2%, respectively. These errors imply an average underestimate of cell-wall density of 0.020 g/cc, principally in the species of lower gross density. Correcting for these errors would have the effect of reducing the estimated fiber-saturation point average for these species by about 2.7% and that for basswood by 9.5%. Indications from such evidence are that the fiber-saturation point shown for basswood in Table 5 is much too high and that fiber-saturation points for other low-density species as given in the same table may be too high by 2–3%. Acceptance of these corrected values would bring our fitted regression line (Fig. 3) into

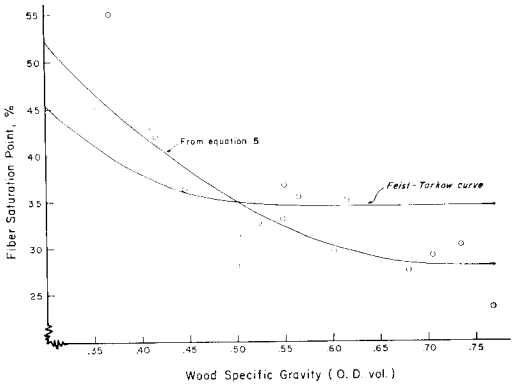

FIG. 3. Fitted regression between fiber-saturation point and gross specific gravity based on data from equation 5, compared with the Feist–Tarkow curve based on non-solvent water technique.

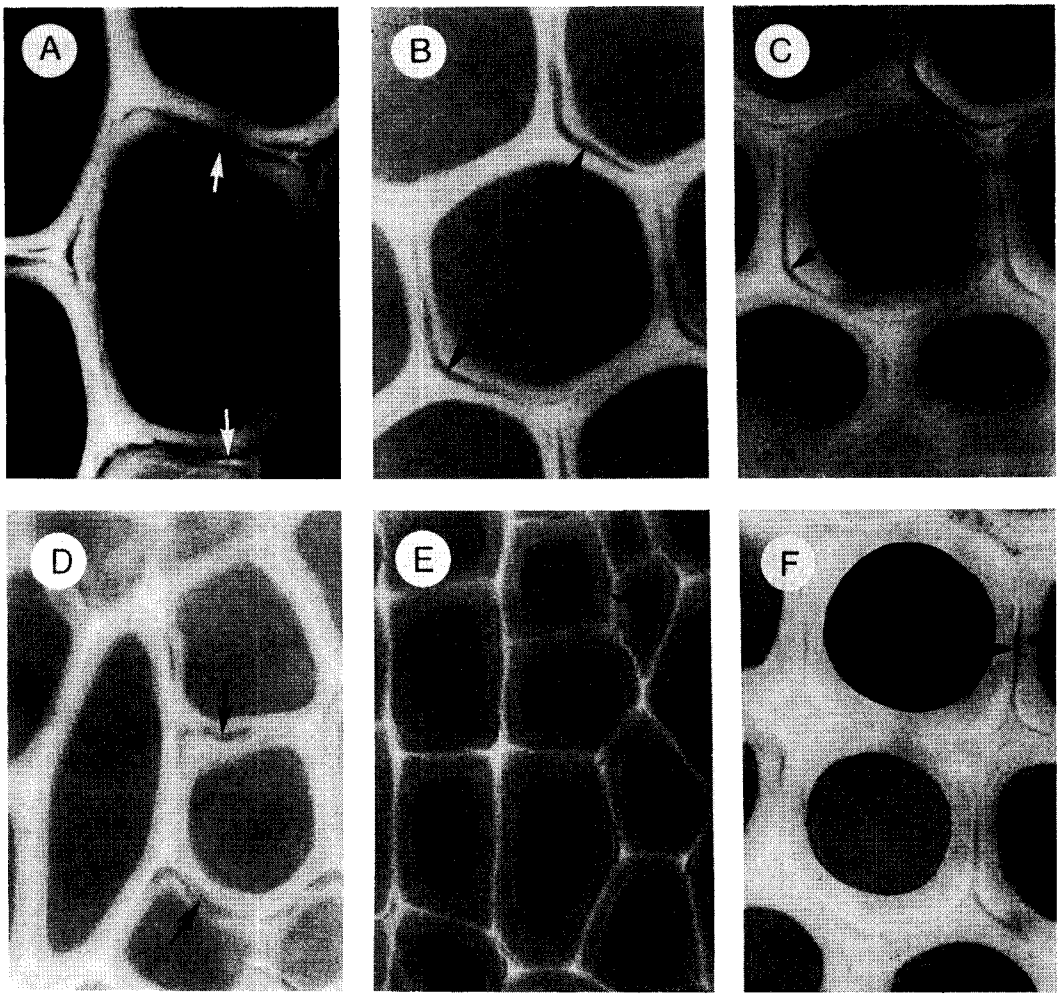

FIG. 4. Incident illumination micrographs illustrating the presence of gross cell-wall damage in microtomed surfaces of wet blocks. A. White pine, earlywood; B. Spruce pine, earlywood; C. Spruce pine, latewood; D. Basswood; E. Cottonwood; F. White pine, latewood.

closer agreement with the Feist–Tarkow curve. We must recall, however, that the differences between swollen sections and blocks reported in Table 3 are based on the cutting of resoaked blocks that had previously been dried, whereas the original sections from which the optically-determined values of Table 5 were calculated were cut from never-dried blocks that may have responded to cutting with less damage. Common experience tells us that never-dried blocks are sectioned more easily than resoaked blocks.

The foregoing discussion neglects to consider another possibility—that block surfaces too may have been altered in the microtoming process. That similar visible damage occurred at the surfaces of the resoaked blocks from which the microtome sections were cut is revealed in Fig. 4. A progressive decrease in wall damage with increasing wall thickness is shown in Figs. 2 and 4. Minute ruptures of a similar nature have been illustrated in electron micrographs in other studies (Stone et al. 1965; Fengel 1967). If the intensity of such sub-

TABLE 6. *Summary of simple linear regression relationships.*

Property	Variable	Regression Equation: Intercept a	Regression Equation: Coefficient b	Coefficient of Determination, r^2	Significance, F-ratio
1. Wood substance, sp. vol.	Wood sp. gr., o.d. vol.	+0.6513	+0.0167	0.297	6.76*
2. Dry cell wall, sp. vol.	Wood sp. gr., o.d. vol.	+0.6518	+0.0532	0.446	12.85**
3. Strain at max. load, static bending ($\times 10^{-3}$)	Wood sp. gr., o.d. vol.	+6.443	+15.176	0.482	14.91**
	Wood substance spec. vol.	−283.032	+450.780	0.400	10.68**
	Dry cell wall spec. vol.	−127.403	+208.733	0.579	22.03**
4. Strain at proportional limit, static bending ($\times 10^{-3}$)	Wood sp. gr., o.d. vol.	+5.125	+0.2871	0.006	0.10
	Wood substance spec. vol.	+0.302	+7.539	0.004	0.06
	Dry cell wall spec. vol.	+1.004	+6.285	0.018	0.30
5. Strain at max. load, tension parallel grain ($\times 10^{-3}$)	Wood sp. gr., o.d. vol.	+7.267	+5.439	0.153	2.88
	Wood substance spec. vol.	−202.233	+321.719	0.502	16.10**
	Dry cell wall spec. vol.	−66.060	+112.078	0.411	11.16**
6. Strain at max. load, compression parallel grain ($\times 10^{-3}$)	Wood sp. gr., o.d. vol.	+2.032	+11.195	0.177	3.44
	Wood substance spec. vol.	−284.945	+443.750	0.261	5.66*
	Dry cell wall spec. vol.	−132.876	+207.141	0.384	9.99**
7. E static bending ($\times 10^3$)	Wood sp. gr., o.d. vol.	+322.51	+2515.7	0.650	29.66**
8. E static bending/sp. gr. ($\times 10^3$)	Wood substance spec. vol.	+36261.5	−50168.0	0.211	4.27
	Dry cell wall spec. vol.	+18931.6	−23215.8	0.305	7.01*
9. FSPL static bending	Wood sp. gr., o.d. vol.	+1325.8	+13893.8	0.686	34.78**
10. FSPL static bending/sp. gr.	Dry cell wall spec. vol.	+84900	−100561	0.240	5.06*
11. MOR	Wood sp. gr., o.d. vol.	−1623.8	+30959.3	0.929	210.08**
12. MOR/sp. gr.	Dry cell wall spec. vol.	−9996	+55480	0.061	1.04
13. FSPL/MOR	Wood sp. gr., o.d. vol.	+0.7734	−0.32921	0.386	10.06**
	Wood substance spec. vol.	+8.177	−11.4805	0.441	12.61**
	Dry cell wall spec. vol.	+4.1169	−5.1748	0.605	24.52**

TABLE 6. Continued.

Property	Variable	Regression Equation: Intercept a	Regression Equation: Coefficient b	Coefficient of Determination, r^2	Significance, F-ratio
14. FSPL/UTS	Wood sp. gr., o.d. vol.	+0.7739	−0.28652	0.072	1.25
	Wood substance spec. vol.	+14.543	−21.086	0.369	9.35**
	Dry cell wall spec. vol.	+6.494	−8.633	0.418	11.42**
15. FSPL/MCS	Wood sp. gr., o.d. vol.	+0.7083	−0.20725	0.064	1.09
	Dry cell wall spec. vol.	+2.269	−2.458	0.057	0.96

* Denotes significant at 5% level.
** Denotes significant at 1% level.

microscopic voids increased with decreasing cell-wall thickness as the grosser ruptures appear to do, they might account for the increasing fiber-saturation point with decreasing gross wood density as shown in our data plotted in Fig. 3—but any such explanation would also have to account for the similar trend shown by Feist and Tarkow (1967) as well as the fiber-saturation point of black spruce as reported by Stone and Scallan (1967), with which our red spruce value is almost identical. These authors, as indicated previously, employed a non-solvent water technique in their determinations of fiber-saturation point. It is obvious that additional work must be done to resolve this question.

Also included in Table 5 is the volume of water-filled voids in the swollen cell wall, calculated as the difference between the specific volume of the cell wall and the corrected specific volume of wood substance, as well as the average density of the water contained in these voids. As noted previously, the data for basswood are of doubtful validity. Otherwise, the close agreement between these values for the density of sorbed water and that calculated by Weatherwax and Tarkow (1968b) is evident. The volume of water-filled voids in the swollen cell wall should be of considerable interest from the standpoint of accessibility to water-borne chemicals in pulping and other chemical reactions.

Relationships between Specific Volumes of Wood Substance and Dry Cell Wall and Other Wood Properties

As shown in Figs. 5 and 6, specific volumes of wood substance and of dry cell wall were correlated with wood specific gravity in a positive manner. In the case of wood substance, the correlation was clearly influenced by the low specific volume shown by the softwoods, the hardwood data by themselves showing only a slight trend toward increasing specific volume with increasing wood specific gravity. In the case of the dry cell walls, however, the relationship was statistically highly significant and the positive relationship between cell-wall specific volume and wood specific gravity was well demonstrated by the data for the hardwoods alone. The regression equations for the relationships and their significance are summarized in Table 6. Generalizations of these trends beyond the limits of the particular material studied may be open to question. A contrary trend has been reported by Raczkowski and Stempien (1967), who found a positive correlation between wood specific gravity and the density of wood substance as determined 1) in water and 2) in toluene. Values determined in water ranged from 1.504 to 1.540 g/cc for individual species and compared closely with those reported here. The trend with wood specific gravity was, however, just the reverse of that shown in the present study.

TABLE 7. *Mechanical properties and strain behavior of unextracted sapwood.*[1]

Species	Static bending					Tension parallel to grain				Compression parallel to grain			
	FSPL	MOR	E	ε_{pl}	ε_{max}	FSPL	UTS	ε_{pl}	ε_{max}	FSPL	MCS	ε_{pl}	ε_{max}
	psi	psi	psi $\times 10^3$	$\times 10^{-3}$	$\times 10^{-3}$	psi	psi	$\times 10^{-3}$	$\times 10^{-3}$	psi	psi	$\times 10^{-3}$	$\times 10^{-3}$
1. Basswood	5220	8160	1167	4.47	14.69	7820	12140	6.16	10.21	2900	4010	2.54	5.07
2. E. cottonwood	6990	10440	1451	4.82	14.02	10310	13780	6.08	8.46	3960	5530	2.40	5.05
3. White ash	6660	13700	1247	5.34	17.34	6840	14010	5.67	12.67	2840	5910	1.98	16.62
4. Yellow poplar	8200	14650	1564	5.24	14.13	9760	16520	6.46	11.79	3480	6280	2.09	8.99
5. Black cherry	8850	14660	1601	5.53	14.71	8280	15690	5.16	10.62	4260	6420	2.48	6.10
6. Hard maple	8940	15360	1488	6.01	15.28	10140	17630	6.74	12.84	3990	6410	2.61	9.36
7. Red maple	9390	16570	1997	4.70	14.06	13200	18180	6.30	9.07	4420	7470	2.09	5.81
8. Beech	10470	18010	1824	5.74	16.36	11370	20480	6.12	12.09	4760	8170	2.33	8.23
9. Paper birch	9850	18000	2141	4.60	11.57	15500	18230	6.53	7.82	3630	8480	1.51	6.65
10. Red oak	8200	17370	1582	5.18	17.98	9760	15340	6.33	11.64	3630	7170	2.22	14.39
11. Yellow birch	13030	21390	2525	5.16	17.34	18390	28360	6.97	11.29	6360	8810	2.44	5.71
12. White oak	9410	19110	1874	5.02	18.52	7810	14670	4.41	9.31	3950	7580	1.89	11.49
13. Shagbark hickory	13440	22820	2314	5.81	19.22	15830	28310	6.56	12.44	5780	9700	2.27	9.32
14. E. white pine	6240	9590	1134	5.50	12.48	6440	10220	5.44	9.34	3290	5010	2.46	4.99
15. Red spruce	7970	12330	1570	5.08	12.86	8880	14750	5.30	9.32	4160	6040	2.34	4.16
16. E. hemlock	7850	11720	1416	5.54	9.68	9680	12010	6.31	7.96	4120	6490	2.70	6.36
17. Spruce pine	7700	10830	1258	6.12	10.52	10200	11420	6.77	7.63	2180	5950	1.44	9.26
18. Loblolly pine	10190	16290	1968	5.18	12.38	15140	18300	7.21	9.06	5770	8400	3.00	7.57

[1] Mechanical testing followed attainment of moisture equilibrium in a room maintained at 50% relative humidity and 73 F. Actual moisture content ranged from 9.0–11.0%.

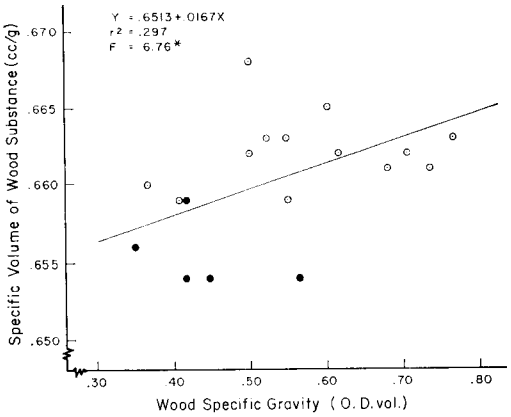

FIG. 5. Relationship between specific volume of wood substance and gross specific gravity. Open circles: hardwoods; Solid circles: softwoods.

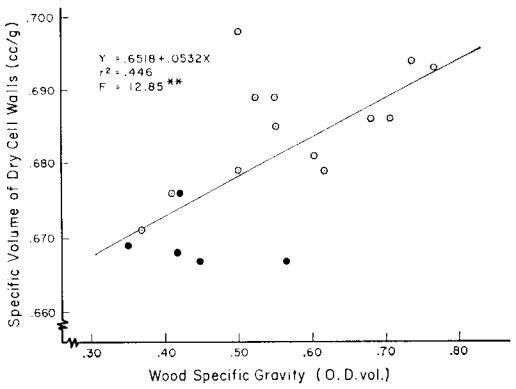

FIG. 6. Relationship between specific volume of dry cell walls and gross specific gravity. Open circles: hardwoods; Solid circles: softwoods.

Values for so-called "wood substance" determined pycnometrically on wood meal in toluene are, of course, equivalent to values interpreted in this study as descriptive of dry cell-wall density. Their values ranged from 1.420 to 1.480 g/cc, again closely comparable with the range of values reported here, but the trend of their values with wood specific gravity is clearly opposite to that shown in the present study. As a consequence of this contradiction, it would appear ill advised to attempt any broad generalization from the relationships shown in Figs. 5 and 6. Nevertheless, these relationships help to explain some of the correlations to be discussed subsequently.

Results of several tests to ascertain the mechanical properties and particularly the strain behavior of specimens taken from the same sample units as the wafers and meal used for wood substance and cell-wall density determinations are shown in Table 7. The significance of these properties lies not in how representative they are of a particular species but in the fact that they represent material matched to that used in density determinations. The particular properties shown in the table, from tests in static bending and in tension and compression parallel to the grain, were selected to illustrate the kind of mechanical behavior that may be expected to be related to the density of wood substance and of the dry cell wall.

Strain at maximum load is one of the properties most strongly related to cell-wall density. As shown in Fig. 7, strain at maximum load in static bending is positively correlated ($r^2 = 0.400$) with the specific volume of wood substance. The positive relationship with specific volume of the dry cell wall (Fig. 8) is even stronger ($r^2 = 0.579$). These relationships are consistent with the generally understood influence of the less-well-organized molecular structure within the cell-wall zones of lower packing density (amorphous zones) as compared with the more compact crystalline zones. It is logical to reason from the stronger relationship

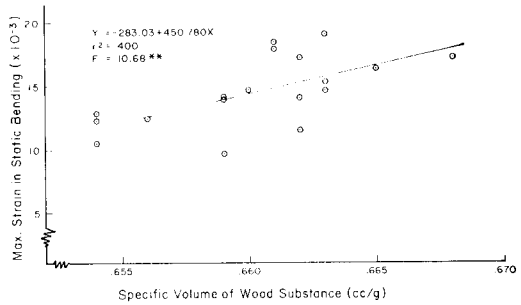

FIG. 7. Calculated strain at maximum load in static bending in relation to specific volume of wood substance.

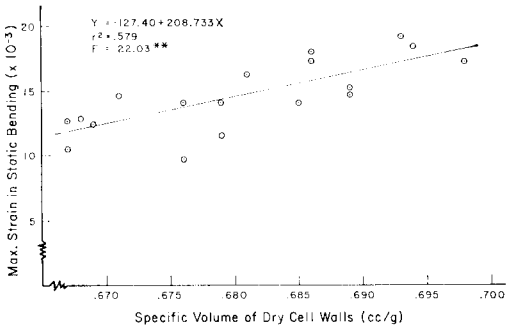

FIG. 8. Calculated strain at maximum load in static bending in relation to specific volume of dry cell walls.

shown between maximum strain and specific volume of the cell wall that voids in the cell wall which are of a size penetrable by water but not by toluene contribute to the observed increase in strain.

Although no logical explanation can be advanced for such behavior other than the coincidental correlation in these data between the specific volumes of wood substance and dry cell wall with wood specific gravity, strain at maximum load was also found to be correlated with wood specific gravity ($r^2 = 0.482$). Although many properties of wood, including most mechanical properties, are positively related to specific gravity, there is no logical reason to suppose that wood specific gravity *per se* should affect the amount of strain that can occur at failure. Our experience in the testing of many dense tropical woods cannot support such a conclusion. The regression equations involving strain at maximum load in static bending are summarized in Table 6.

Strain at proportional limit in static bending is also shown in Table 7. Regression analyses of strain at proportional limit with wood specific gravity, wood substance specific volume, and dry cell-wall specific volume failed to show any significant relationships. A summary of the regression equations and their lack of significance is included in Table 6.

Maximum strain in tension parallel to the grain was also positively correlated with specific volume of wood substance ($r^2 = 0.502$) and with the specific volume of the dry cell walls ($r^2 = 0.411$). An attempted regression between strain at maximum load in tension parallel to the grain and wood specific gravity failed to reveal any significant relationship. The constants of the regression equations and their significance are summarized in Table 6. The lower values for strain at maximum load in tension as compared with those in static bending (Table 7) are indicative of the fact that the calculated static-bending values are too high. This results from the assumption made in the calculation that the neutral axis remains at mid-depth of the beam throughout the loading. This is obviously not the case, and these data are indicative of the extent to which the neutral axis is shifted toward the tension side of the beam. Regardless of this recognized deficiency in the static-bending data, the values for maximum strain in outermost fiber as given in Table 7 accurately reflect the greater deflections at failure in those species showing the higher values for maximum strain.

Maximum strain, or strain at maximum load, in compression parallel to the grain was also shown to be correlated with specific volume of wood substance and of the dry cell walls. The correlations were not as good, however, as those shown in the other tests, probably because of greater experimental difficulties involved in the measurement of strain in the type of test specimen employed. The relationships were nevertheless statistically significant. No correlation was found between strain at maximum load in compression parallel to the grain and wood specific gravity. The regression equations and their levels of significance are summarized in Table 6.

As was to be expected, modulus of elasticity in static bending was strongly correlated ($r^2 = 0.650$) with wood specific gravity in a positive linear relationship. Specific modulus of elasticity (E/specific gravity) eliminates the effect of specific gravity by expressing modulus of elasticity in terms of unit weight. Although not significantly related to the specific volume of

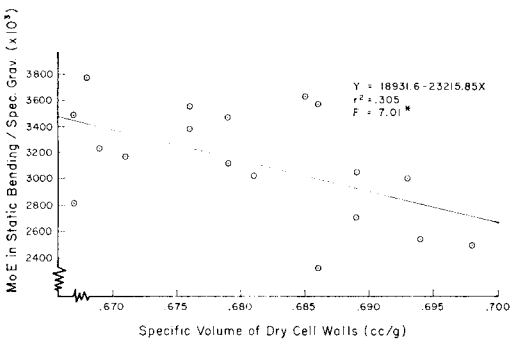

FIG. 9. Specific modulus of elasticity in relation to specific volume of dry cell walls.

wood substance, specific modulus of elasticity is shown in Fig. 9 to have a negative linear relationship with specific volume of dry cell walls ($r^2 = 0.305$). Although other factors, notably fibril angle, are known to affect specific modulus of elasticity, the negative slope of the relationship—higher specific modulus of elasticity being associated with lower values for specific volume of the cell wall—is entirely logical as it denotes the influence of the more compact crystalline cellulosic material in the cell wall in contributing to a high modulus of elasticity per unit weight. The constants of the regression equations and the significance of these relationships are summarized in Table 6.

Fiber stress at proportional limit in static bending was strongly correlated in a positive linear manner ($r^2 = 0.686$) with wood specific gravity. Specific FSPL (FSPL/specific gravity), like specific modulus of elasticity, is shown to be related to specific volume of the cell wall, although the significantly negative slope of the relationship is accompanied by considerable scatter ($r^2 = 0.240$). The regression equations and their significance are summarized in Table 6. As in the preceding relationships with modulus of elasticity, it is evident that low cell-wall specific volumes (high cell-wall densities) indicate greater efficiency of the cell wall response to stresses within the proportional limit.

The data shown in Table 7 for modulus of rupture were correlated to an unusually high degree with specific gravity. The coefficient of determination (r^2) for the linear positive regression was 0.929. Specific modulus of rupture (modulus of rupture/specific gravity), however, showed no correlation with cell-wall specific volume. The attempted regression accounted for only 6.1% ($r^2 = 0.061$) of the total variance in specific modulus of rupture. The regression equations are summarized in Table 6.

From the foregoing relationships, it is evident that the less compact cell walls with higher values for specific volume are related to high strain values at maximum load but have no influence on the amount of strain at proportional limit. The effect of high cell-wall specific volume, then, is to increase the strain occurring at stress levels beyond proportional limit. This is the region of plastic deformation, and it may be assumed that wood having cell walls with high specific volume is more susceptible to time-dependent effects such as creep and relaxation than wood having cell walls of low specific volume. Within the proportional limit, the effect of low cell-wall specific volume is to increase the efficiency of the cell wall in response to stress. From these relationships, the effects to be discussed in the following paragraphs might also be anticipated.

The ratio of proportional limit stress to ultimate stress in a particular type of loading has commonly been regarded as a relatively constant value for all species. As shown in Fig. 10, however, the ratio of fiber stress at proportional limit/modulus of rupture in static bending is related to wood specific gravity in a negative manner ($r^2 = 0.386$). This, it would seem, is the consequence of the coincidental relationship in these data between specific gravity and the specific volume of wood substance and of dry cell walls. A stronger negative relationship is shown in Fig. 11 between the ratio FSPL/MOR and specific volume of wood substance ($r^2 = 0.441$), and a still stronger relationship in Fig. 12 between FSPL/MOR

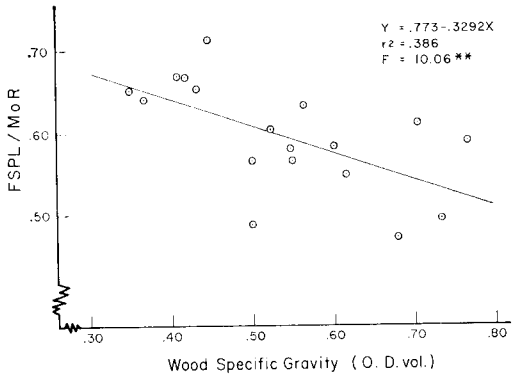

FIG. 10. FSPL/MOR in relationship to gross wood specific gravity.

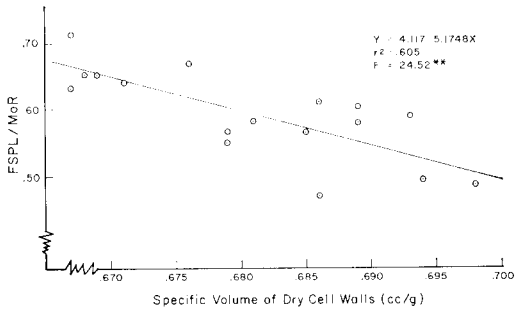

FIG. 12. FSPL/MOR in relationship to specific volume of dry cell walls.

and specific volume of dry cell walls (r^2 = 0.605). The regression equations are summarized in Table 6. As suggested in the preceding discussion, these relationships reflect the dependence of specific proportional limit stress in static bending on the specific volume of wood substance, the even greater dependence of this ratio on the specific volume of dry cell walls, and the absence of such a relationship in the case of modulus of rupture. Relatively higher stress values at proportional limit are associated with the more compact cell walls.

Similar relationships between stress at proportional limit and ultimate stress in tension parallel to the grain are shown in the summary in Table 6. The ratio FSPL/UTS in tension was not significantly correlated with wood specific gravity, but highly significant negative correlations were shown with specific volume of wood substance (r^2 = 0.637) and with specific volume of dry cell walls (r^2 = 0.418). These relationships may be interpreted in the same way that has been offered for the data derived from static-bending tests.

Similar regressions were also attempted in the case of the ratio FSPL/MCS (fiber stress at proportional limit/maximum crushing strength) in compression parallel to the grain, but no significant relationships were revealed. The constants of the regression equations and their lack of significance are indicated in summary Table 6. This inconsistency is probably the result of difficulties encountered in determining reliable proportional-limit values in the rather small specimens used in the compression parallel-to-grain test. Stress–strain diagrams were characterized by a gradual increase in curvature with increasing load rather than a sharply defined limit of proportionality between stress and strain. Eccentric bending may also have contributed to inaccuracies in the determination of maximum crushing strength. In contrast to the high correlations shown between fiber stress at proportional limit and modulus of rupture in the static-bending tests with wood specific gravity, the correlations in compression parallel to grain were relatively poor—FSPL vs. wood specific gravity (r^2 = 0.333) and maximum crushing strength vs. specific gravity (r^2 = 0.746).

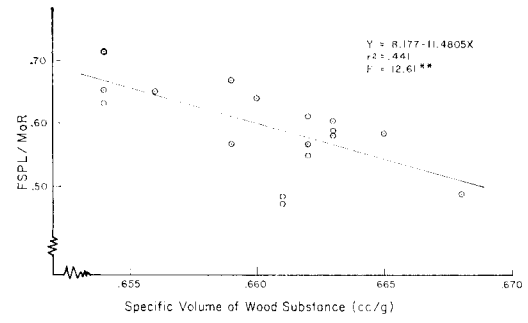

FIG. 11. FSPL/MOR in relationship to specific volume of wood substance.

REFERENCES

BERLYN, G. P. 1968a. A hypothesis of cell wall density. Forest Prod. J., **18**(2): 34–36.

———. 1968b. Biophysical investigation of free space in tracheid cell walls. Amer. J. Bot., **55**(6) Part 2: 728.

———. 1968c. Personal communication.

CAMPBELL, W. B., AND J. K. RUSSELL. 1935. What is the true density of cellulose? Quart. Rev. Can. Forest Prod. Labs., Pulp and Paper Lab. Montreal, **21**: 24–26.

CLEGG, G. C., AND S. C. HARLAND. 1923. The measurable characters of raw cotton. I. The determination of area of cross section and hair weight per centimeter. J. Textile Inst., **14**: 489–492.

CUDE, H. E., AND G. A. HULETT. 1920. Some properties of charcoals. J. Amer. Chem. Soc., **42**: 391.

DAVIDSON, G. F. 1927. The specific volume of cotton cellulose. J. Textile Inst., **18**: T175.

DUNLAP, F. 1914. Density of wood substance and porosity of wood. J. Agr. Res., **2**(6): 423–428.

FEIST, W. C., AND H. TARKOW. 1967. Polymer exclusion in wood substance; a new procedure for measuring fiber saturation points. Forest Prod. J., **17**(10): 65–68.

FENGEL, D. 1967. Ultramicrotomy, its application in wood research. Wood Sci. and Tech., **1**(3): 191.

FRANK, H. S., AND W. Y. WEN. 1957. Structural aspects of ion-solvent interaction in aqueous solutions: A suggested picture of water structure. Discussions Faraday Soc., **24**: 133.

FREY-WYSSLING, A., AND H. SPEICH. 1942. Über die Durchdringbarkeit der Cellulosefasern. Helv. Chim. Acta., **25**: 1474–1484. CSIRO Translation No. 7589 (1965).

GORING, D. A. I. 1966. The structure of water in relation to the properties of wood constituents. Pulp Paper Mag. Can., **67**(11): T-519–524.

HARKINS, W. D., AND D. T. EWING. 1921. A high pressure due to adsorption, and density and volume relations of charcoal. J. Amer. Chem. Soc., **43**: 1787.

HARTIG, R. 1882. Über die Verteilung der organischen Substanz, des Wassers und des Luftraumes in Baümen. Untersuchg. Forst-bot. Inst. München Bd. 2.

HEERTJES, P. M. 1942. The density and sorption capacity of some samples of cotton, silk and wool. Part IV. Some remarks on the sorption of water by cotton, silk and wool. Rec. Trav. Chim. Pays-Bas, **61**: 751.

HERMANS, P. H. 1946. Contributions to the physics of cellulose fibers. Elsevier, Amsterdam. 221 p.

———. 1949. Physics and chemistry of cellulose fibers. Elsevier, Amsterdam. 534 p.

HOWARD, H. C., AND G. A. HULETT. 1924. A study of the density of carbon. J. Phys. Chem., **28**: 1082–1095.

IFJU, G., AND R. W. KENNEDY. 1962. Some variables affecting microtensile strength of Douglas-fir. Forest Prod. J., **12**(5): 213–217.

JAYME, G., AND T. KRAUSE. 1963. Über die Packungsdichte den Zellwande in Laubholzern. Holz als Roh- und Werkstoff, **21**:(1): 14–19. PPRIC Translation Series #50 Woodlands Research Index No. 146 (1963).

KALLMES, O., AND C. ECKERT. 1964. The structure of paper. VII. The application of the relative bonded area concept to paper evaluation. TAPPI, **47**(9): 540–548.

KELLOGG, R. M., AND G. IFJU. 1962. Influence of specific gravity and certain other factors on the tensile properties of wood. Forest Prod. J., **12**(10): 463–470.

NÉMETHY, G., AND H. A. SCHERAGA. 1962. Structure of water and hydrophobic bonding in proteins. I. A model for the thermodynamic properties of liquid water. J. Chem. Phys., **36**: 3382.

RACZKOWSKI, J., AND C. STEMPIEN. 1967. Zur Beziehung zwischen der Rohdichte und der Reindichte von Holz. Holz als Roh- und Werkstoff **25**(10): 380–383. Canada Dept. of Forestry Translation No. 199.

RAMIAH, M. V., AND D. A. I. GORING. 1965. The thermal expansion of cellulose, hemicellulose and lignin. J. Polymer Sci., **C11**: 27–48.

SACHS, J. 1879. Über die Anordnung den Zellen in jüngsten Pflanzenteilen. Arb. Bot. Inst. Würzburg Bd. 2. S.46.

SCHWAPPACH, A. 1897. Untersuchungen über Raumgewicht und Druckfestigkeit des Holzes wichtiger Waldbaüme. Berlin.

STAMM, A. J. 1929. Density of wood substance, adsorption by wood, and permeability of wood. J. Phys. Chem., **33**: 398–414.

———, AND R. M. SEBORG. 1934. Adsorption compression in cellulose and wood. I. Density measurements in benzene. J. Phys. Chem., **39**: 133–142.

———, AND L. A. HANSEN. 1937. The bonding force of cellulosic materials for water (from specific volume and thermal data). J. Phys. Chem., **41**: 1007–1016.

———. 1950. Specific volume of native cellulose. Textile Res. J., **20**:(9): 631–636.

———. 1964. Wood and cellulose science. Ronald Press, New York. 549 p.

———, AND H. T. SANDERS. 1966. Specific gravity of the wood substance of loblolly pine as affected by chemical composition. TAPPI, **49**(9): 397–400.

———. 1967. History of two phases of wood physics. Wood Sci. and Tech., **1**(3): 186–190.

STAYTON, C. L., AND C. A. HART. 1965. Deter-

mining pore size distribution in softwoods with a mercury porosimeter. Forest Prod. J., **15**(10): 435–440.

STONE, J. E., AND A. M. SCALLAN. 1965. A study of cell-wall structure by nitrogen adsorption. Pulp Paper Mag. Can., **66**(8): T407–T414.

STONE, J. E. 1966. The cell wall. Trend, **7**: 4–9.

———, A. M. SCALLAN, AND G. M. A. ABERSON. 1966. The wall density of native cellulose fibers. Pulp Paper Mag. Can., **67**(3): T263–T268.

STONE, J. E., AND A. M. SCALLAN. 1967. The effect of component removal upon the porous structure of the cell wall of wood. II. Swelling in water and the fiber saturation point. TAPPI, **50**(10): 496–501.

TSOUMIS, G. 1964. Microscopic measurement of the amount of cell wall substance in wood and its relationship to specific gravity. TAPPI, **47**(11): 675–677.

VORREITER, L. 1963. Fasersättigungsfeuchte und höchste Wasseraufnahme der Hölzer. Holzforschung, **17**(5): 139–146.

WANGAARD, F. F. 1969. Cell-wall density of wood with particular reference to the southern pines. Wood Science, **1**(4): 222–226.

WEATHERWAX, R. C., AND H. TARKOW. 1968a. Cell wall density of dry wood. Forest Prod. J., **18**(2): 83–85.

———. 1968b. Density of wood substance: Importance of penetration and adsorption compression of the displacement fluid. Forest Prod. J., **18**(7): 44–46.

WILFONG, J. G. 1966. Specific gravity of wood substance. Forest Prod. J., **16**(1): 55–61.

WILLIAMS, A. M. 1920. Forces in surface films. Proc. Roy. Soc. London, **98A**: 223.

———. 1922–23. Two properties of powders. Trans. Faraday Soc., **18**: 87–90.

WORRALL, J. 1963. The relationship between void volume and wood quality in western Canadian conifers. Undergraduate Thesis. Univ. of B. C. Vancouver.

YIANNOS, P. 1964. The apparent cell wall density of wood and pulp fibers. TAPPI, **47**(8): 468–471.

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