WOOD

Wood is an important natural resource, one of the few that are renewable. It is prevalent in our everyday lives and the economy, in wood-frame houses and furniture; newspapers, books, and magazines; bridges and railroad ties; fence posts and utility poles; fuelwood; textile fabrics; and organic chemicals. Wood and wood products are also a store for carbon, thus, helping to minimize carbon dioxide in the atmosphere.

Wood supplies the solid raw material for products, such as lumber, plywood, and wood pallets, and the fiber for paper, paperboard, fiberboard panels, rayon, and acetate (see also LAMINATED WOOD-BASED COMPOSITES; PAPER; PULP). Many wood products can be recovered for reuse or recycling, thus extending our wood supply into the future. A large and increasing portion of the paper and paperboard products that is used, such as newspapers, magazines, and corrugated containers, are recovered for recycling 45% of the total new supply in 1995 (l). In addition, wood residues from lumber, plywood, and pulp mills are recovered and used to make new fiber products or burned to generate energy.

Production and consumption of wood products and residues are measured in various units, based on common usage and their metric equivalents (2-4). Pulpwood logs and fuelwood are commonly measured in cords. A cord refers to a stacked pile of wood, with outside dimensions of 4 by 4 by 8 ft (1.22 by 1.22 by 2.44 m) and a volume of 128 ft^3 (3.62 m^3). The weight of a cord depends on density of wood and bark and on moisture content. In the United States, it can range from 1.3 to 1.7 short tons (1.2 to 1.5 metric tons), air dried.

Sawn lumber is commonly measured in board fret. A board foot of lumber has a nominal dimension of 1 ft by 1 ft by 1 in. (30.5 by 30.5 by 2.5 cm) and volume of 1/12 ft^3 (2360 cm^3 = 0.0024 m^3). The actual board foot dimension and volume is often smaller, however. Paper and paperboard products are commonly measured in short tons (2,000 lb) or metric tons (2,204.6 lb).

Roundwood equivalent is also sometimes used. It refers to the volume of logs or other round products required to produce a given quantity of lumber, plywood, wood pulp, and other wood products (2). Roundwood equivalents may be used in assessing the overall wood resource supply and demand or in comparing wood products measured in different units.

In recent years, lumber production has accounted for close to 40% of all roundwood used in the United States (4). Pulp, paper, and board products have accounted for close to 30% of total roundwood used. Between 1965 and 1994, annual production of lumber (in board feet) increased by 26%. In contrast, production of paper and board (in tons) more than doubled (4).

The following shows production levels for selected major commodities and years (4). Lumber is given in nominal volume terms (1,000 board feet= 2.36 m^3).

	1970	1980	1990	1994
Lumber (million cubic meters)	81.7	83.3	114.5	109.5
Plywood (million cubic meters)	14.1	14.6	19.5	18.5
Paper (shipments; million metric tons)	22.9	28.6	35.7	39.5
Paperboard (million metric tons)	23.2	28.4	35.7	41.5

Structure

The anatomical structure of wood affects strength properties, appearance, resistance to penetration by water and chemicals, resistance to decay, pulp quality, and the chemical reactivity of wood (5). To use wood most effectively requires a knowledge of not only the amounts of various substances that make up wood, but also how those substances are distributed in the cell walls.

Woods are either hardwoods or softwoods. Hardwood trees (angiosperms, ie, plants with covered seeds) generally have broad leaves, are deciduous in the temperate regions of the world, and are porous, ie, they contain vessel elements. Softwood trees (conifers or gymnosperm, ie, plants with naked seeds) are cone bearing, generally have scalelike or needlelike leaves, and are nonporous, ie, they do not contain vessel elements. The terms hardwood and softwood have no direct relation to the hardness or softness of the wood. In fact, hardwood trees such as cottonwood, aspen, and balsa have softer wood than the western white pines and true firs; certain softwoods, such as longleaf pine and Douglas-fir, produce wood that is much harder than that of basswood or yellow-poplar.

Many mechanical properties of wood, such as bending and crushing strength and hardness, depend upon the density of wood; denser woods are generally stronger (6). Wood density is determined largely by the relative thickness of the cell wall and by the proportions of thick-walled and thin-walled cells present.

The cells that make up the structural elements of wood are of various sizes and shapes and are firmly bonded together. Dry wood cells may be empty or partly filled with deposits such as gums, resins, or other extraneous substances. Long and pointed cells, known as fibers or tracheids, vary greatly in length within a tree and from species to species. Hardwood fibers are ~1 mm long, and softwood fibers are ~3 to 8 mm.

Just under the bark of a tree is a thin layer of cells, not visible to the naked eye, called the cambium. Here, cells divide and eventually differentiate to form bark tissue outside of the cambium and wood or xylem tissue inside of the cambium. This newly formed wood on the inside contains many living cells and conducts sap upward in the tree, and hence, is called sapwood. Eventually, the inner sapwood cells become inactive and are transformed into heartwood. This transformation is often accompanied by the formation of extractives that darken the wood, make it less porous, and sometimes provide more resistance to decay.

Because of the great structural variations in wood (7), there are many possibilities for selecting a species for a specific purpose. Some species, like spruce, combine light weight with relatively high values for stiffness and bending strength. Very heavy woods, like lignumvitae, are extremely hard and resistant to abrasion. A very light wood, like balsa, has high thermal insulation value. Hickory has extremely high shock resistance. Mahogany has excellent dimensional stability.

Composition

Wood is a complex polymeric structure consisting of lignin (qv) and carbohydrates (qv) [cellulose (qv) and hemicelluloses], which form the visible lignocel-

Iulosic structure of wood (8-10). Also present, but not contributing to wood structure, are minor amounts of other organic chemicals and minerals. The organic chemicals are diverse and can be removed from the wood with various solvents. The minerals constitute the ash residue remaining after ignition at a high temperature.

Wood species cannot readily be determined by chemical analysis because composition is affected by many variables, including geographical location, soil and weather conditions, and location of the wood within a given tree. Some generalizations are possible to distinguish hardwood and softwood composition, eg, the average lignin content of softwood is slightly higher than that of hardwood. If the minerals and small amounts of nitrogen and sulfur (0,1 -0.2%) are ignored, the elementary composition of dry wood averages 50% carbon, 6% hydrogen, and 44% oxygen.

Lignin. Lignin is an amorphous, insoluble organic polymer and is very difficult if not impossible to isolate in a natural state. Molecular weights of isolated lignins range from the low thousands to as high as 50,000. The basic chemical structural unit is a methoxy-substituted propylphenol moiety, bonded in an irregular pattern of ether and carbon-carbon linkages. Lignin comprises 18-30% by weight of the dry wood, most of it concentrated in the compound middle lamella and the layered cell wall. It imparts a woody, rigid structure to the cell walls and distinguishes wood from other fibrous plant materials of lesser lignin content. Quantitative analysis usually involves removing the carbohydrate material by acid hydrolysis and filtering and weighing the insoluble residue (referred to as Klason lignin).

Carbohydrates.   Carbohydrates are the principal components of the cell wall, comprising 65-7570 by weight of the dry wood. Total hydrolysis yields simple sugars, primarily glucose and xylose in hardwoods and glucose and mannose in softwoods. Minor amounts of galactose, arabinose, and rhamnose are present.

Cellulose is the main component of the wood cell wall, typically 40-50% by weight of the dry wood. Pure cellulose is a polymer of glucose residues joined by 1,4-β-glucosidic bonds. The degree of polymerization (DP) is variable and may range from 700 to 10,000 DP or more. Wood cellulose is more resistant to dilute acid hydrolysis than hemicellulose. X-ray diffraction indicates a partial crystalline structure for wood cellulose. The crystalline regions are more difficult to hydrolyze than the amorphous regions because removal of the easily hydrolyzed material has little effect on the diffraction pattern.

Hemicellulose is a mixture of amorphous branched-chain polysaccharides consisting of a few hundred sugar residues. They are easily hydrolyzed to monomeric sugars and uronic and acetic acids. Many different hemicelluloses have been isolated from wood.

Extractives and Ash. The amount of extractives in wood varies from 5 to 20% by weight and includes a wide variety of organic chemicals (11). Many of these function as intermediates in tree metabolism as energy reserves or participate in the tree's defense mechanism against microbiological attack. The extractives contribute to wood properties such as color, odor, and decay resistance.

The ash content is 0.2-0.5% by weight for temperate woods and 0.5-2.0% by weight for tropical woods. The principal elemental components of wood ash are

calcium and potassium with lesser amounts of magnesium, sodium, manganese, and iron. Carbonate, phosphate, silicate, oxalate, and sulfate are likely anions. Some woods, especially from the tropics, contain significant amounts of silica.

The chemical compositions of selected North American hardwoods and softwoods are given in Table 1 (10).

Wood-Liquid   Relationship

Adsorption. Wood is highly hydroscopic. The amount of moisture adsorbed depends mainly on the relative humidity and temperature (Fig. 1). Exceptions occur with species with high extractive contents (eg, redwood, cedar, and teak). The equilibrium moisture contents of such woods are generally somewhat lower than those given in Figure 1.

In green wood, the cell walls are saturated, whereas some cell cavities are completely filled and others may be completely empty. Moisture in the cell walls is called bound, hydroscopic, or adsorbed water. Moisture in the cell cavities is called free or capillary water. The distinction is made because, under ordinary conditions, the removal of the free water has little or no effect on many wood properties. On the other hand, the removal of the cell wall water has a pronounced effect.

At equilibrium with relative humidity below 100%, the moisture in wood is present primarily in the cell walls. The moisture content at which the cell walls would be saturated and the cell cavities empty is called the fiber saturation point. Actually, such distribution is impossible. Beginning at ~90% relative humidity, some condensation may occur in small capillaries. The determination of the fiber saturation point is based on the fact that certain properties of wood (eg, strength and volume) change uniformly at first with increasing moisture content and then become independent of the moisture content (Fig. 2). The equilibrium moisture content (usually determined by extrapolation), at which the property becomes constant at 25 to 30% moisture, is represented by the fiber saturation point.

The density of wood substance is ~1.5 g/cm^3. A species with a density of 0.5 g/cm^3 (based on oven-dry weight and volume) has a void volume of 66.6%. Each 100 kg of the totally dry wood occupies 0.2 m^3 (7 ft^3) and contains 0.067 m^3 (2.4 ft^3) wood substance and 0.133 m^3 (4.7 ft^3) void. In waterlogged condition, the cell walls adsorb ~0.028 m^3 (1 ft^3) water, whereas the cell cavities contain ~0.133 m^3 (4.7 ft^3) water.

The average specific gravity of different species is given in Table 2 (6). The conventional way for expressing the specific gravity of wood is in terms of the ovendry weight and volume at 12% moisture content. The specific gravity based on the volume of the ovendry wood is ~6% higher.

At low relative humidities, adsorption is due to interaction of water with accessible hydroxyl groups. These are present on the lignin and on the carbohydrates in the noncrystalline or poorly crystalline regions. The high differential heat of adsorption by dry wood, ~1.09 kJ/g (469 Btu/lb) water, reflects a very high affinity for moisture (12-14).

At high relative humidities, adsorption is believed to occur in response to a tendency for cellulose chains and lignin to disperse (solution tendency). Complete dispersion (dissolution) is prevented because of the strong interchain

Table 1. Chemical Composition of Some North American Woods [a]

Scientific name/Common name	Glucan	Xylan	Galactan	Arabinan	Mannan	Uronic anhydride	Acetyl	Lignin	Ash
Hardwoods (Angiosperms)									
Acer rubrum L./Red maple	46	19	0.6	0.5	2.4	3.5	3.8	24	0.2
Acer saccharum Marsh./Sugar maple	52	15	<0.1	0.8	2.3	4.4	2.9	23	0.3
Betula alleghaniensis Britton/Yellow birch	47	20	0.9	0.6	3.6	4.2	3.3	21	0.3
Betula papyrifera Marsh./White birch	43	26	0.6	0.5	1.8	4.6	4.4	19	0.2
Fagus grandifolia Ehrh./Beech	46	19	1.2	0.5	2.1	4.8	3.9	22	0.4
Liquidambar styraciflua L./Sweetgum	39	18	0.8	0.3	3.1			24	0.2
Platanus occidentalis L./American sycamore									
Fast growth	44	18	2.0	0.7	2.2	5.6	5.3	20	0.8
Slow growth	43	15	2.2	0.6	2.0	5.1	5.5	23	0.7
Populus deltoides Bartr. ex Marsh./ Eastern cottonwood									
Fast growth	42	19	1.3	0.5	2.9	5.5	4.0	24	0.7
Slow growth	47	15	1.4	0.6	2.9	4.8	3.1	24	0.8
Populus tremuloides Michux./Quaking aspen	49	17	2.0	0.5	2.1	4.3	3.7	21	0.4
Quercus falcata Michx./Southern red oak	41	19	1.2	0.4	2.0	4.5	3.3	24	0.8
Ulmus americana L./White elm	52	12	0.9	0.6	2.4	3.6	3.9	24	0.3
Softwoods (Gymnosperms)									
Abies balsamea (L.) Mill/Balsam fir	46	6.4	1.0	0.5	12	3.4	1.5	29	0.2
Gingo biloba L./Ginko	40	4.9	3.5	1.6	10	4.6	1.3	33	1.1
Juniperus communis L./Common juniper	41	6.9	3.0	1.0	9.1	5.4	2.2	31	0.3

631

Table 1. *(Continued)*

Scientific name/Common name	Glucan	Xylan	Galactan	Arabinan	Mannan	Uronic anhydride	Acetyl	Lignin	Ash
Softwoods (Gymnosperms) (continued)									
Larix decidua Mill./Common larch (sapwood)	46	6.3	2.0	2.5	11	4.8	1.4	26	0.2
Larix laricina (Du Roi) K. Koch/ Tamarack	46	4.3	2.3	1.0	13	2.9	1.5	29	0.2
Picea abies (L.) Karst./Norway spruce	43	7.4	2.3	1.4	9.5	5.3	1.2	29	0.5
Picea glauca (Moench) Voss/White spruce	45	9.1	1.2	1.5	11	3.6	1.3	27	0.3
Picea mariana (Mill.) B.S.P./Black spruce	44	6.0	2.0	1.5	9.4	5.1	1.3	30	0.3
Picea rubens Sarg./Red spruce	44	6.2	2.2	1.4	12	4.7	1.4	28	0.3
Pinus banksiana Lamb./Jack pine	46	7.1	1.4	1.4	10	3.9	1.2	29	0.2
Pinus radiata D. Don/Australian radiata[b]	42	6.5	2.8	2.7	12	2.5	1.9	27	0.2
Pinus resinosa Ait./Red pine	42	9.3	1.8	2.4	7.4	6.0	1.2	29	0.4
Pinus rigida Mill./Pitch pine	47	6.6	1.4	1.3	9.8	4.0	1.2	28	0.4
Pinus strobus L. Eastern white pine	45	6.0	1.4	2.0	11	4.0	1.2	29	0.2
Pinus sylvestris L./Scots pine	44	7.6	3.1	1.6	10	5.6	1.3	27	0.4
Pinus taeda L./Loblolly pine	45	6.8	2.3	1.7	11	3.8	1.1	28	0.3
Pseudotsuga menziesii (Mirb.) Franco/Douglas-fir	44	2.8	4.7	2.7	11	2.8	0.8	32	0.4
Thuja occidentalis L./Northern white cedar	43	10.0	1.4	1.2	8.0	4.2	1.1	31	0.2
Tsuga canadensis (L.) Carr./Eastern hemlock	44	5.3	1.2	0.6	11	3.3	1.7	33	0.2

[a]The values expressed are for percent oven-dry wood and extractive-free wood.
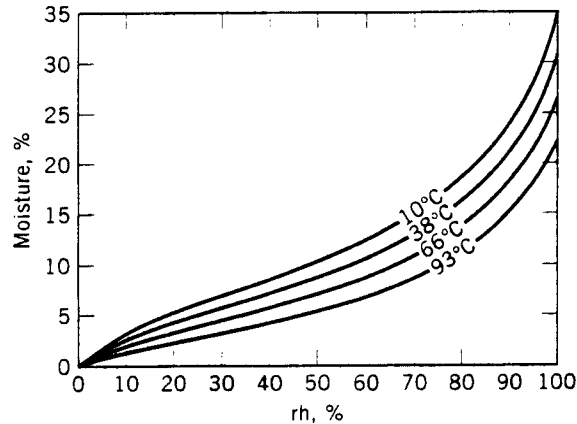[b]Australian-grown wood. Percent oven-dry wood.

Fig.1. Relationship between the moisture content of wood (% of dry wood) and relative humidity at different temperatures.
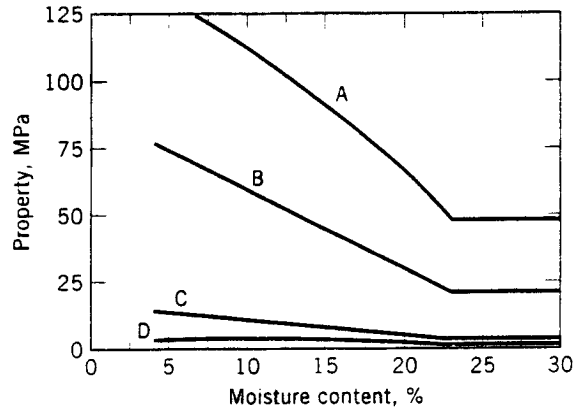

Fig. 2. Relationship between various strength properties of clear wood and moisture content. A, modulus of rupture; B, compression parallel to grain; C, compression perpendicular to grain; D, tension perpendicular to grain.

or interpolymer bonding at certain sites or regions. The differential heats of adsorption are much smaller than at low relative humidities.

Because the relative humidity of the atmosphere changes, the moisture content of wood undergoes corresponding changes. Effective protection against fluctuating atmospheric conditions is furnished by a surface coating of certain finishes, provided the coating is applied to all surfaces of wood through which moisture gains access. However, no coating is absolutely moistureproof; coatings simply retard the rate at which moisture is taken up from or given off to the atmosphere. This means that coatings cannot be relied upon to keep moisture out of wood that is exposed to dampness constantly or for prolonged periods. Coatings vary markedly in their moisture-retarding efficiencies.

For some uses, it is important to protect wood against water, eg, doors, windows, door and window frames, and the lap and butt joints in wood siding. Water repellents and water-repellent preservatives, long used in the millwork

Table 2. Specific Gravity of Some Common Woods Growing in the United States

Wood	Specific gravity[a]
aspen	0.40
birch, yellow	0.67
cottonwood, eastern	0.42
Douglas-fir, coast-type	0.51
fir, balsam	0.38
hemlock, western	0.44
maple, sugar	0.68
oak, white	0.73
pine	
lodgepole	0.43
ponderosa	0.42
longleaf	0.62
spruce, Engelmann	0.36
walnut, black	0.59

industry, provide protection from wetting. They are designed to penetrate into wood, but they leave a very thin coating of wax, resin, and oil on the surface, which repels water. However, they are not as effective in resisting water vapor (see WATERPROOFING).

Neither coatings nor water repellents alter the equilibrium moisture content or equilibrium swelling of wood. This can be accomplished only by depositing bulking agents that block normal shrinkage within the cell walls, chemically replacing the hydroscopic hydroxyl groups of cellulose and lignin with less hydroscopic groups, or forming chemical crosslinks between the structural units of wood.

Shrinking and Swelling.   The adsorption and resorption of water in wood is accompanied by external volume changes. At moisture contents below the fiber saturation point, the relationship may be a simple one, merely because the adsorbed water adds its volume to that of the wood, or the desorbed water subtracts its volume from the wood. The relationship may be complicated by the development of stresses. Theoretically, above the fiber saturation point, no volume change should occur with a change in the moisture content. Actually, owing to the development of stresses, changes in volume or shape may occur. The magnitude of such stresses is minimized by drying wood under carefully controlled and empirically established conditions (13).

In the absence of drying stress (ie, with small specimens and extremely slow drying), the degree of shrinkage from the green to ovendry condition is, as a first approximation, proportional to the specific gravity of the wood. The value of the slope of the linear relationship is equal to the average fiber saturation point of the wood. Serious deviations from the linear relationship may occur with species high in extractives.

Swelling or shrinking of wood is highly anisotropic. Tangential swelling (occurring tangent to the rings) is 1.5 to 3.5 times greater than radial swelling (occurring along a radius of the rings). Longitudinal swelling (occurring in the

direction of tree growth) is usually very small. In certain abnormal woods, however, such as compression or tension wood, longitudinal swelling or shrinking may be relatively high (up to 1-2% for tension wood and 5-6% for compression wood) (14).

Permeability. Although wood is a porous material (60-70% void volume), its permeability (ie, flow of liquids under pressure) is extremely variable. This is due to the highly anisotropic shape and arrangement of the component cells and to the variable condition of the microscopic channels between cells. In the longitudinal direction, the permeability is 50 to 100 times greater than in the transverse direction (13). Sapwood is considerably more permeable than heartwood. In many instances, the permeability of the heartwood is practically zero. A rough comparison, however, may be made on the basis of heartwood permeability, as shown in Table 3.

Transport. Wood is composed of a complex capillary network through which transport occurs by capillarity, pressure permeability, and diffusion. A detailed study of the effect of capillary structure on the three transport mechanisms is given in Stamm (13).

Drying. The living tree holds much water in its cells. A southern pine log, 5 m long and 0.5 m in diameter, for example, may weigh as much as 1000 kg and contain ~47% or 0.46 m^3(16 ft^3) water.

There are a number of important reasons for drying it reduces the likelihood of stain, mildew, or decay developing in transit, storage, or use; the shrinkage that accompanies drying can take place before the wood is put to use; wood increases in most of its strength properties as it dries below the fiber saturation point (30% moisture content); the strength of joints made with fasteners, such as nails and screws, is greater in dry wood than in wet wood dried after assembly the electrical resistance of wood increases greatly as it dries; dry wood is a better thermal insulating material than wet wood; and the appreciable reduction in weight that accompanies drying reduces shipping costs (see DRYING).

Ideally, the temperature and relative humidity during drying should be controlled; if wood dries too rapidly, it is likely to split, check, warp, or honeycomb because of stresses. If wood dries too slowly, it is subject to development of stain and mold growth.

Table 3. Relative Permeability of the Heart wood of Some Common Species, Decreasing from Group 1 to Group 4

Group 1	Group 2	Group 3	Group 4
ponderosa pine	coastal Douglas-fir	eastern hemlock	alpine fir
basswood	jack pine	Engelmann spruce	Douglas-fir[a]
red oaks	loblolly pine	lodgepole pine	tamarack
slippery elm	longleaf pine	noble fir	western redcedar
tupelo gum	western hemlock	Sitka spruce	black locust
white ash	cottonwood	western larch	red beech
	aspen	white fir	red gum
	silver maple	white spruce	white oaks
	sugar maple	rock elm	
	yellow birch	sycamore	

[a]Growing in interior regions: permeability practically zero.

Air drying is a process of stacking lumber outdoors to dry (15). Control of drying rates is limited and great care must be taken to avoid degrading the wood. Drying time is a function of climatic condition; in cold temperatures or in damp coastal areas, wood dries slowly, whereas in warm temperatures and in the arid regions of the Southwest, wood dries rapidly. Typical air drying times for 2.5-cm-thick lumber of various species are shown in Table 4.

Kiln drying is a controlled drying process widely used for drying both hardwoods and softwoods. Dry-bulb temperatures for hardwood lumber seldom exceed 87°C and then only at the end of the drying schedule. Dry-bulb temperatures for softwood lumber are sometimes as high as 115°C. In the initial stages, the relative humidity is maintained at a high level to control the moisture gradient in the wood and thus prevent splitting and checking. Modem kiln installations use forced-air circulation and are equipped with automatic controls for both dry- and wet-bulb temperatures. The kilns are vented to exhaust the moisture evaporated from the wood. Most kilns are steam heated, although furnace-type kilns fired with gas or oil are now common for certain softwood species. Many species, especially hardwoods, are first air dried to about 20% moisture content, then kiln dried to the moisture content at which they will be used (Table 4). A typical time schedule for kiln drying a softwood is shown in Table 5. Schedules for drying hardwoods are generally more complex (16).

Special drying methods, such as superheated steam, solvent, vacuum, infrared radiation, and high frequency dielectric and microwave heating, are occasionally employed when accelerated drying is desired and the species being dried can withstand severe conditions without damage. None of these methods is of significant commercial importance.

Table 4. Approximate Air-Drying and Kiln-Drying Periods for 2.5-cm Lumber

Species	Days required to	
	Air-dry to 20%	Kiln-dry to 6%[a]
baldcypress	100–300	10–20
hickory	70–200	7–15
magnolia	60–150	10–15
oak		
red	100–300	16–28
white	150–300	20–30
pine, southern	40–150	3–5
sweet gum	70–300	10–25
sycamore	70–200	6–12
tupelo	70–200	6–12
yellow poplar	60–150	6–10

Structural Material

Strength and Related Properties. In the flaming of a building or the construction of an industrial unit, where wood is used because of its unique physical properties, strength and stiffness are primary requirements. Different species of wood have different mechanical properties that relate to the amount of

Table 5. Typical Softwood Kiln-Drying Time Schedules for 2.5-cm Ponderosa Common Pine

Hours in kiln	Dry-bulb temperature, °C	Wet-bulb temperature, °C	Relative humidity, %
heartwood[a]			
1–8	54	43	52
8–16	58	44	48
16 until dry	60	44	41
sapwood[b]			
1–12	54	43	52
12–24	58	44	48
24 until dry	60	44	41

wood substance per unit volume, ie, its specific gravity. Heavy wood such as oak tends to be stronger and stiffer than a light wood such as spruce. The strength of a piece of lumber depends also upon its grade or quality. The strength values of a lumber grade depend upon the size and number of such characteristics as knots, cross grain, shakes, splits, and wane (17). Wood free from these defects is known as clear wood.

Most strength properties of clear wood improve markedly as moisture is reduced below ~30%, based on the ovendry weight (18) (Fig. 2). However, some properties (eg, tensile strength parallel and perpendicular to the grain) may be reduced if the wood is overly dried (19). In structural lumber containing defects, the improvement in mechanical properties normally associated with wood as it dries may be partially offset by degradation during drying, particularly with low grade material (Fig. 3) (20). The strength properties of wood that is conventionally kiln dried are not significantly different from those of wood that is carefully air dried. However, there is increasing interest in high temperature drying (110- 120°C) of structural lumber to reduce processing time and energy consumption. These processes may reduce strength up to 20% depending upon species and property (21).

The mechanical properties of wood tend to increase when it is cooled and to decrease when it is heated (6,18). If untreated wood heated in air is not exposed to temperatures of more than ~70°C for more than about one year, the decrease in properties with increasing temperature is referred to as immediate or reversible; ie, the property would be lower if tested at the higher temperature but would be unchanged if heated and then tested at room temperature. The immediate effect of temperature on strength and modulus of elasticity of clear wood, based on several different loading modes, is illustrated in Figures 4-6 (6).

Higher temperatures result in permanent degradation. The amount of this irreversible loss in mechanical properties depends upon moisture content, heating medium, temperature, exposure period, and, to some extent, species. The effects of these factors on modulus of rupture, modulus of elasticity, and work to maximum load are illustrated in Figures 6-9 (6). The effects may be less severe for commercial lumber than for clear wood heated in air (Fig. 10). The permanent property losses shown are based on tests conducted after specimens
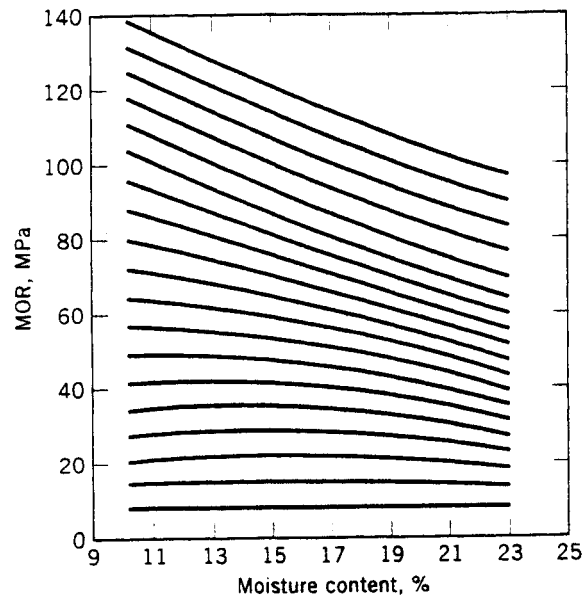
Fig. 3. Effect of moisture content on bending strength of structural lumber, MOR = modulus of rupture.
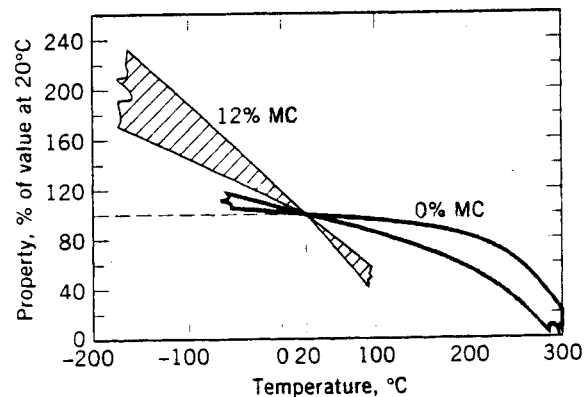

Fig.4. The immediate effect of temperature on the modtius of elasticity of clear wood, relative to the value at 20°C. The plot is a composite of studies on the modulus as measured in bending, in tension parallel to grain, and in compression parallel to grain. Variability in reported results is illustrated by the width of the bands. MC = moisture content.

were cooled to ~24°C and conditioned to a moisture content of 7- 12%. If tested hot, presumably immediate and permanent effects would be additive. Exposure to elevated temperature for extended periods has immediate and permanent effects and must be considered in the design of structures such as chemical storage tanks.
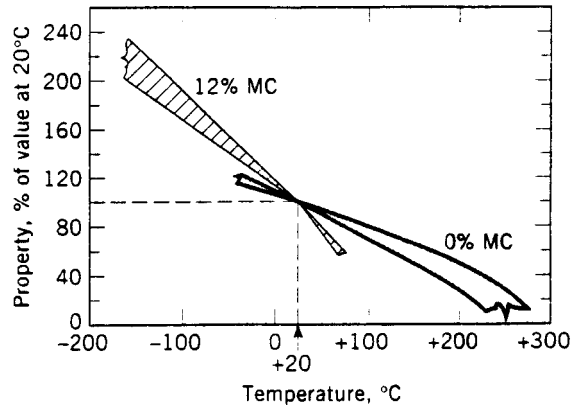
Fig. 5. The immediate effect of temperature on strength properties of clear wood, expressed as percentage of value at 20°C. Trends illustrated are composites from studies on three strength properties: modulus of rupture in bending, tensile strength perpendicular to grain, and compressive strength parallel to grain. Variability in reported results is illustrated by the width of the bands. MC = moisture content.
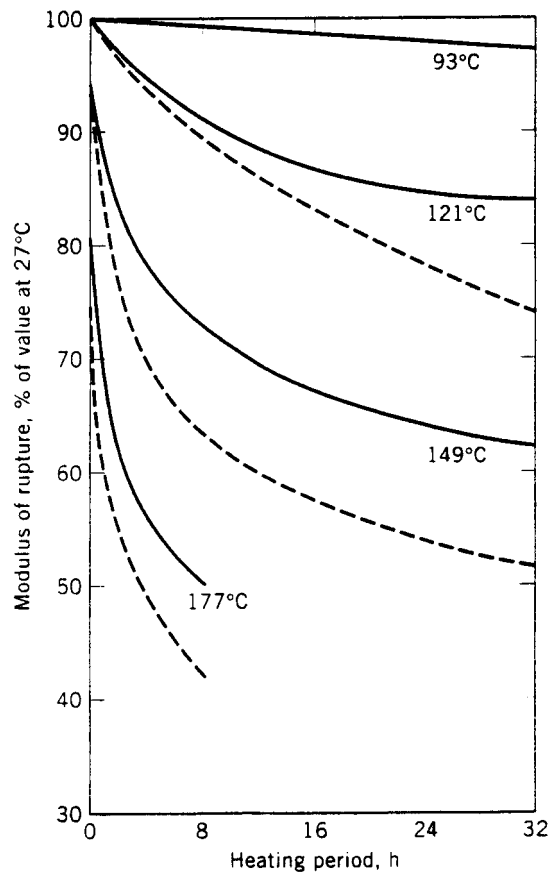

Fig. 6. Permanent effect of heating in water (—) and in steam (---) on the modulus of rupture. Data based on tests of clear Douglas-fir and Sitka spruce.
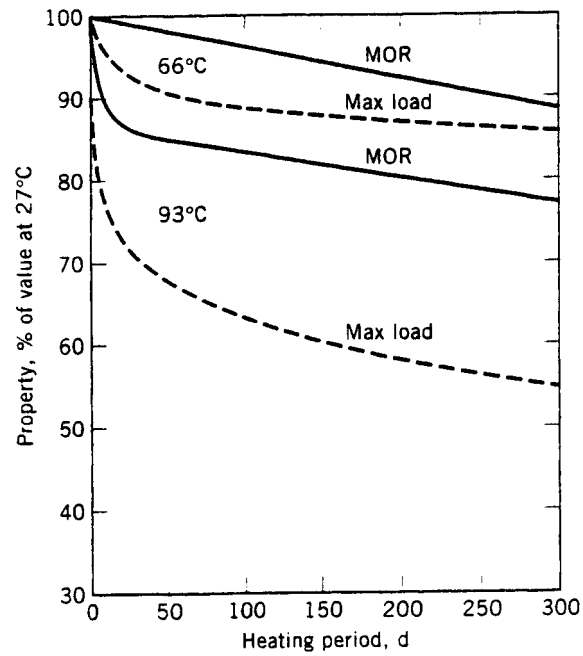
639

Fig. 7. Permanent effect of heating in water on work-to-maximum-load and on modulus of rupture (MOR). Data based on tests of clear Douglas-fir and Sitka spruce.
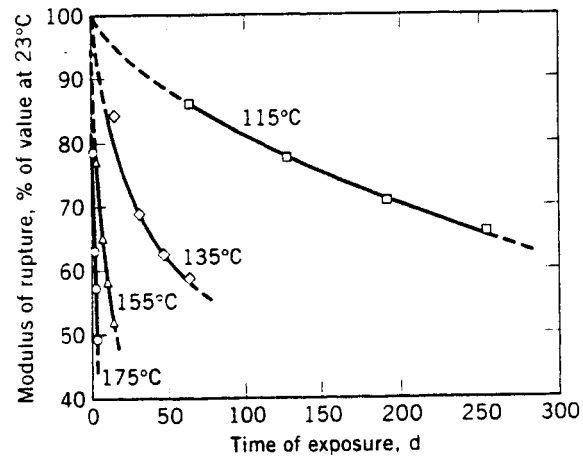

Fig. 8. Permanent effect of oven heating at four temperatures on the modulus of rupture of clear wood. based on four softwood and two hardwood species.
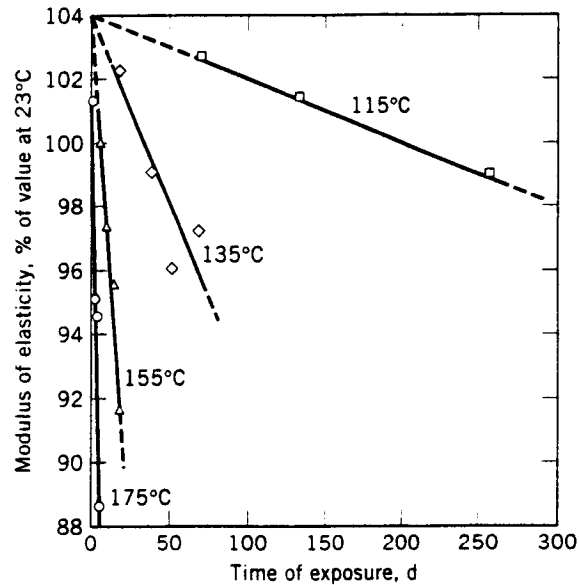
640

Fig. 9. Permanent effect of oven heating at four temperatures on modulus of elasticity of clear wood, based on four softwood and two hardwood species.
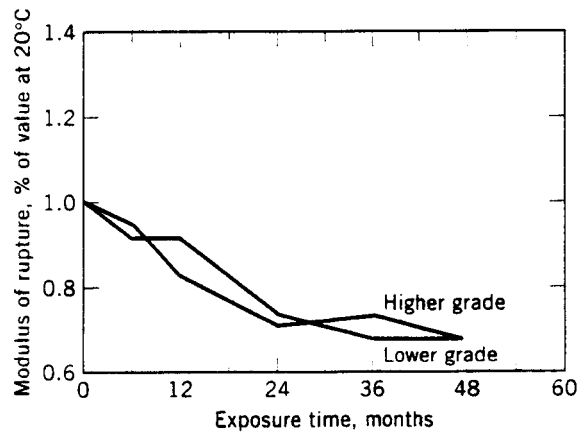

Fig. 10. Permanent effect of heating in air on bending strength of spruce–pine-fir lumber.

Repeated exposure to elevated temperature has a cumulative effect. For example, at a given set of exposure conditions, the property losses are about the same after six exposure periods of one month each and after a single 6-month period.

The shape and size of wood pieces are important in analyzing the influence of temperature. If exposure is for only a short time and the inner parts of a large piece do not reach the temperature of the surrounding medium, the immediate effect on the strength of inner parts is less than for outer parts. The type

of loading must also be considered. If the piece is to be stressed in bending, its outer fibers are subjected to the greatest load and ordinarily govern the ultimate strength; under such a loading condition, the inner part having a lower temperature may be of little significance.

For extended, noncyclic exposures, it can be assumed that the entire piece reaches the temperature of the heating medium and is, therefore, subject to permanent strength losses throughout the piece, regardless of size and mode of stress application. Because dry wood is a good insulator, it often does not reach the daily extremes in temperature of the air around it in ordinary construction; thus, estimates of long-term effects should be based on the actual wood temperatures experienced by critical structural parts.

The effect of absorption of various liquids upon the strength properties of wood largely depends on the chemical nature and reactivity of the absorbed liquid. In general, neutral, nonswelling liquids have little if any effect upon the strength properties (22,23). Any liquid that causes wood to swell causes a reduction in strength. This effect may be temporary, existing only while the liquid remains in the wood. This effect may also be permanent, as in the case of chemically reactive liquids (strong acids and bases), with the magnitude being dependent upon the time and temperature of exposure and concentration of the solution.

Wood preservatives are applied either from an oil system, such as creosote, petroleum solutions of pentachlorophenol, or copper naphthanate, or a water system. Oil treatments are relatively inert with wood material, and thus, have little effect on mechanical properties. However, most oil treatments require simultaneous thermal treatments, which are specifically limited in treating standards to preclude strength losses (24).

The mechanical properties of wood can be damaged by preservative systems. In North America, the primary waterborne preservatives are copper-based systems, which may contain chromic acid and arsenic, ammoniacal or amine-based copper systems with supplemental zinc, arsenate, or quaternary ammonium chloride. The effects of waterborne preservative treatments are directly related to key pretreatment, treatment, and post-treatment processing factors (25). Because treating standards have strict thermal limits to avoid affecting strength, few design modifications are required to allowable design stresses if waterborne preservative-treated materials are treated to standards (24). The two design exceptions involve (a) restrictions on impact-load adjustments for wood treated with waterborne preservatives and (b) adjustment for the mechanical process of making knife-like incisions, which is used with difficult-to-treat species to improve preservative penetration and distribution. Incising reduces strength; the literature supports a 5-10% reduction in MOE and a 20–30% reduction in allowable design stresses *(Fb, Ft, Fh, Fc)*.

Most commercial fire retardant treatment formulations are proprietary. Fire retardant treatments generally reduce allowable design stresses by 10–25%. The magnitude of these reductions varies depending upon the fire retardant chemical, the severity of treatment and processing conditions, and the property being considered (25). Treatment standards specifically limit thermal processing to control design adjustments to the levels stated above (24). Specific modification factors to allowable design stresses depend on the specific fire retardant

treatment. The treater should be consulted to obtain appropriate modifications factors for specific fire retardant treatments.

Another problem occurs when some fire retardant formulations are exposed to elevated temperatures (eg, when used as roof trusses or as roof sheathing); thermal-induced strength reductions can occur in-service. The thermo-chemical factors were discussed by LeVan and Winandy (26), and a kinetic degrade model was developed (27). The treater should be consulted to obtain appropriate in-service modifications for specific fire retardant treatments.

Reaction to Heat and Fire. The physical and chemical properties of wood, like those of any organic material, are subject to deterioration. The rate and extent of deterioration are governed by the interdependent factors of temperature, time, and moisture. In locations not conducive to decay or insect attack, wood is extremely stable at ordinary temperatures. However, with increasing temperature, the degradation of surface layers progresses into the interior layers. Prolonged heating at temperatures as low as 90°C may cause charring.

In general, the thermal degradation of wood and other cellulosic substances proceeds along one of two competing reaction pathways (28). At temperatures up to ~200°C, carbon dioxide and traces of organic compounds are formed, in addition to the release of water vapor. The gases are not readily ignitable, but under certain conditions, a pilot flame can ignite the volatiles after 14 to 30 min at 180°C (29). Exothermic reactions may occur near 200°C and, in situations where heat is conserved, self-ignition at temperatures as low as 100°C has been observed (30). Times and temperatures that might result in smoldering initiation can be determined (31). To provide a margin of safety, 77°C should be the upper limit in prolonged exposure near heating devices.

Temperatures in excess of 200°C lead to much more rapid decomposition. Under these conditions, the pyrolysis gases contain 200 or more different components (32-34) and the degradation is accompanied by reduction in weight, depending on temperature and duration of heating (35) (Fig. 11). Thermogravimetric analysis of wood [α-cellulose and lignin (Fig. 12)] indicates that a slow initial weight loss for lignin and wood begins at ~200°C.

Differential thermal analyses (dta) of wood and its components indicate that the thermal degradation reactions in an inert atmosphere release less than 5% of the heat released during combustion in air. The typical dta data given in Figure 13 (36) show two main exothermic peaks for wood. The peak near 320°C represents the flaming reaction resulting from combustion of the volatiles associated with cellulose pyrolysis; the other peak, near 440°C, represents glowing in place of the solid charcoal residue. The dta for α-cellulose and lignin in Figure 11 can be superimposed to approximate the curve for wood. Several extensive reviews on thermal degradation of wood are available (37-40).

Building code requirements for fire performance are mainly concerned with noncombustibility (41), fire endurance (42,43), and surface burning characteristics (44). Wood, even in its treated form, does not meet the building code requirements for a noncombustible material. However, for some specific applications where noncombustible materials are required, the codes permit the substitution of fire retardant treated wood.

Wood in its untreated form has good resistance or endurance to fire penetration when used in thick sections for walls, doors, floors, ceilings, beams, and
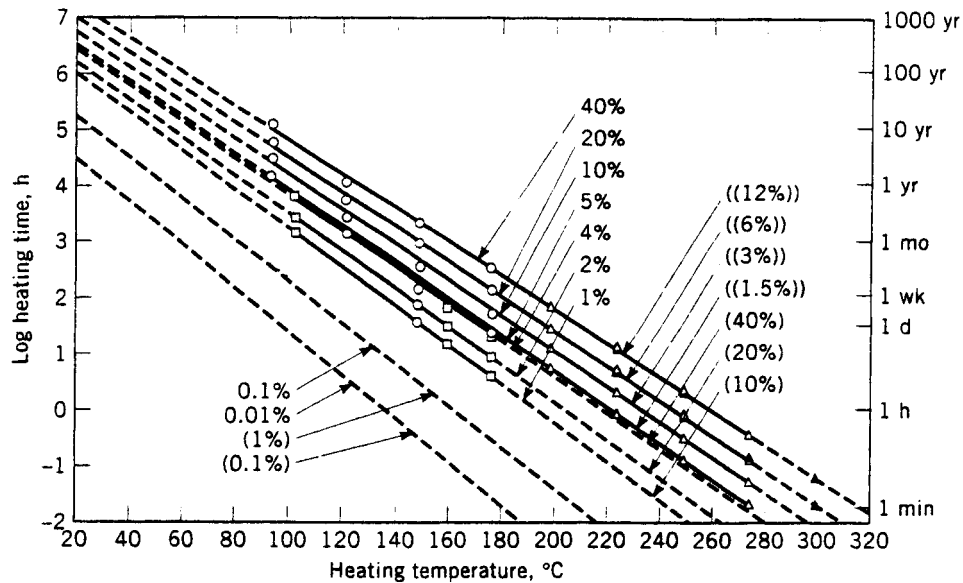
Fig. 11. Logarithm of heating time compared with temperature to attain various degrees of degradation of wood (35). No parentheses indicates weight loss on oven heating a single parenthesis indicates modulus of rupture on oven heating and double parentheses indicates weight loss on heating beneath surface of molten metal. Courtesy of *Industrial and Engineering Chemistry.*
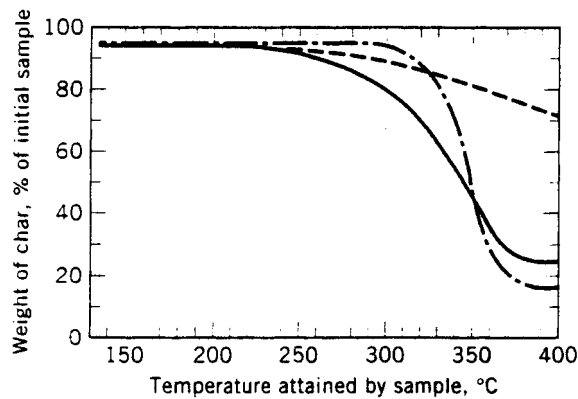

Fig. 12. Portion of dynamic thermogravimetric curves between 130 and 400°C, with temperature rising 6°C per minute for wood, lignin, and α-cellulose. — wood, --- lignin, .-·—·—· α-cellulose (36).

roofs. This endurance is due to low thermal conductivity, which reduces the rate at which heat is transmitted to the interior. Typically, when the fire temperature at the surface of softwood is 870-980°C, the inner char zone temperature is ~290°C, and 6 mm further inward, the temperature is 180°C or less. The penetration rate of this char line is ~0.6 mm/min, depending on the species, moisture content, and density (45,46). Owing to this slow penetration rate and low ther-
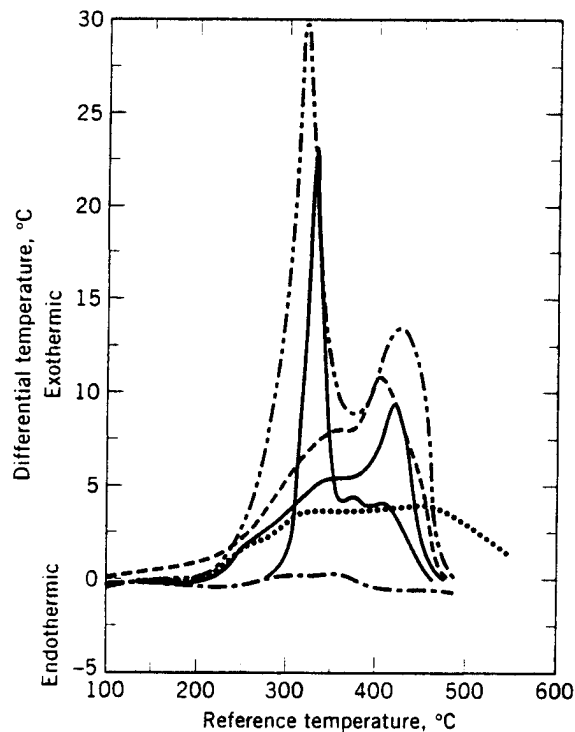
Fig. 13. Differential thermal analysis of wood and its components at a heating rate of 12°C per minute and a gas flow rate of 30 cm³ per minute. Sample weight: wood 40 mg, α-cellulose 20 mg, lignin 10 mg, charcoal 12 mg. Treated wood sample contains 9% by weight of commercial fire retardant. — untreated wood in O_2; --- untreated wood charcoal in O_2; --- untreated wood in N_2; — untreated α-cellulose in O_2; --- untreated sulfate lignin in O_2; ---- wood treated with fire retardant in O_2.

mal conductivity, large wood members retain a substantial portion of their load carrying capacity for considerable time during fire exposure (47).

The surface burning characteristics (flame spread index and smoke developed index) for wood and wood products as measured by American Society for Testing and Materials (44) can be reduced with fire retardant treatments, either chemical impregnation or coatings (48). Fire retardant treatments also reduce the heat release rate of a burning piece of wood (49,50). The heat release rates (51) of the burning materials are an important factor in fire growth.

Fire retardant chemicals, such as ammonium phosphate, ammonium sulfate, zinc chloride, guanylurea phosphate, dicyandiamide phosphate, borax, and boric acid, are often used in combinations. Borax and boric acid mixtures are moderately effective in reducing flamespread and afterglow without premature charring during severe drying operations. Although very hydroscopic, zinc chloride is an effective flame retardant; boric acid is often added to retard afterglow. Fire retardant treatments can adversely affect the strength properties of wood. Elevated temperatures in service can cause futher strength loss (52). Fire retardants such as ammonium sulfate can have a corrosive effect on metal fasteners.

In exterior applications, a treatment with resistance to weathering and leaching is important (53,54).

Solutions of these fire retardant formulations are impregnated into wood under full cell pressure treatment to obtain dry chemical retentions of 65 to 95 kg/m^3; this type of treatment greatly reduces flame-spread and afterglow. These effects are the result of changed thermal decomposition reactions that favor production of carbon dioxide and water (vapor) as opposed to more flammable components (55). Char oxidation (glowing or smoldering) is also inhibited.

Some of the chemicals mentioned above and others, such as chlorinated rubber or paraffin, antimony trioxide, calcium carbonate, calcium borate, pentaerythrithol, alumina trihydrate, titanium dioxide, and urea-melamine-formaldehyde resin, may be used to formulate fire retardant coatings. Many of these coatings are formulated in such a way that the films intumesce (expand) when exposed to fire, thus insulating the wood surface from further thermal exposure. Fire retardant coatings are mostly used for existing construction.

Resistance to Chemicals. Different species of wood vary in their resistance to chemical attack. The significant properties are believed to be inherent to the wood structure, which governs the rate of ingress of the chemical and the composition of the cell wall, which affects the rate of action at the point of contact (56).

Wood is widely used as a structural material in the chemical industry because it is resistant to a large variety of chemicals. Its resistance to mild acids is far superior to that of steel but not as good as some of the more expensive acid-resistant alloys. Wood tanks used to store cold, dilute acid have a relatively long service life. However, increasing concentration or temperature causes the wood tank to deteriorate rapidly (6).

Softwoods are generally more resistant to acids than are hardwoods because they have high lignin and low hemicellulose contents. In general, heartwood is more resistant to acids than sapwood, probably because of heartwood's higher extractive content and slower movement of liquid into the heartwood. For these reasons, the heartwood of certain conifers has been widely used in the chemical industry.

Oxidizing acids, such as nitric acid, attack wood faster than common mineral acids, although wood is frequently used in contact with dilute nitric acid. Oxidizing acids not only attack wood by hydrolysis of the polysaccharides but also degrade these polymers through oxidative reaction. Wood shows excellent resistance to organic acids, which gives it a distinct advantage compared with steel, concrete, rubber, and some plastics. Mild organic acids such as acetic acid have little effect on wood strength.

Alkaline solutions attack wood more rapidly than acids of equivalent concentrations, whereas strong oxidizing chemicals are harmful. Wood is seldom used where resistance to chlorine and hypochlorite solutions is required. These chemicals cause extensive degradation of cell wall polymers. Wood tanks are, however, satisfactory for holding hydrogen peroxide solutions and give good service on contact with strong brine. Solutions of iron salts cause degradation, particularly of the polysaccharides.

In contact with iron under damp conditions, wood may show severe deterioration within a few years (57). Species high in acidic extractives seem especially prone to such attack.

Because traces of iron reduce the brilliance of many dyes, wood tanks have long been preferred to steel in the manufacture of dyes. Similarly, vinegar and sour foodstuffs are processed in wood tanks because common metals impart a metallic taste. Ease of fabrication may be the reason for using wood tanks in less accessible areas to which ready-made tanks of other materials cannot be easily moved.

Resistance to chemical attack is generally improved by resin impregnation, which protects the underlying wood and reduces movement of liquid into the wood. Resistance to acids can be obtained by impregnating with phenolic resin and to alkalies by impregnating with furfural resin (see FURAN COMPOUNDS; PHENOLIC RESINS).

Biodeterioration. The principal organisms that degrade wood are fungi, bacteria, insects, and marine borers. Decay, molds, and stain are caused by fungi. Decay is the most serious kind of damage because it causes structural failure and consequently, tremendous economic losses. Soft rot is another type of decay that weakens wood, but it typically progresses slowly and is most often associated with very wet wood. Moisture conditions conducive to decay occur when the moisture content of the wood is above fiber saturation (~30%). The optimum temperature range for most decay fungi is about 25-30°"C, although some species grow at temperatures as low as 0°C and some as high as 45°C. The optimum pH is in the range of 4.5 to 5.5. Oxygen is essential for growth of all species. Decay can be prevented by keeping wood either too dry (below 20% moisture content) or too wet (lumens filled with water) for fungal development, by using naturally decay-resistant species, or by treating with preservatives.

Mold and stain fungi primarily attack the sapwood. Mold fungi growth occurs primarily on the surface of the wood, while stain fungi may cause a stain throughout the affected sapwood. These fungi can be controlled by dipping the lumber in a fungicidal solution immediately after cutting.

Bacterial degradation of wood generally is not a serious problem, although in some situations of extreme wetness, bacteria may increase the permeability of wood after many years or reduce the strength of the wood (58).

Termites are the most destructive insects that attack wood. Their attack can be prevented or lessened by using naturally resistant wood or by treating wood with preservatives. For subterranean termites, which generally require contact with the ground to survive, poisoning the soil around the wood structure is the principal means of preventing infestation. A promising new approach to subterranean termite control is the use of food bait with an insecticide (59). The drywood termite flies directly to the wood, bores into it, and does not require contact with the ground. Physical barriers, such as paint or screens, prevent infestation. Despite great differences between fungi and termites, chemicals that inhibit fungi usually also inhibit termites.

Marine borers inhabit saline or brackish waters where they cause serious destruction to untreated wood. The mollusks include the Teredo and Bankia borers; among the crustaceans, the Limnoria borers are the most widespread and destructive. Preservatives or borer-resistant woods deter marine borers (see COATINGS, MARINE).

For practical purposes, the sapwood of all species may be considered to be susceptible to biodeterioration. The heartwood of some species, however, contains toxic extractives that protect it against biological attack. Among the native

species that have decay-resistant or highly decay-resistant heartwood are bald cypress, redwood, cedars, white oak, black locust, and black walnut (60). Douglas-fir, several of the pines, the larches, and honey locust are of intermediate decay resistance. Species low in decay resistance include the remainder of the pines, the spruces, true firs, ashes, aspens, birches, maples, hickories, red and black oaks, tupelo, and yellow poplar. Native woods considered somewhat resistant to termite attack include close-grained redwood heartwood and resinous heartwood of southern pine (6). Although several tropical woods show resistance to marine borers, no commercial native woods are sufficiently borer resistant to be used untreated (6).

The best protection for wood against the attack of decay fungi, insects, or marine borers is obtained by applying preservatives under pressure before installation (61,62). Both oil-type preservatives, such as creosote or petroleum solutions of pentachlorophenol, and waterborne preservatives, such as copper-chrome arsenate and ammoniacal-copper arsenate, are used when wood is to be in direct contact with the ground or in the marine environments.

Where wood is to be used under low to moderate decay hazard conditions (eg, above ground), it can be protected by brushing, spraying, dipping, or steeping (62,63). Once decay is established, preservatives brushed onto the wood will not penetrate, and decay cannot be eradicated in this way. However, high vapor pressure fungicides (fumigants) penetrate deeply into wood and have successfully stopped internal decay in structural timbers. Diffusible preservatives such as boron and fluoride are also used to eradicate decay (64).

Modified Wood

In addition to preservation or fire protection, wood is modified to reduce the rate that moisture is sorbed by the wood (water repellency) and/or to reduce the shrinking and swelling that occur at equilibrium (dimensional stability) under conditions of fluctuating relative humidity. Certain species with high extractives content, especially in the cell walls, have greater water repellency and, in some cases, greater dimensional stability than species with low extractives content. This suggests a means of obtaining still greater reductions in the rate and extent of swelling and shrinking, that is, by filling the voids in the wood to reduce rate or deliberately adding large amounts of bulking agents to the cell walls to improve dimensional stability.

Low molecular weight, nonswelling vinyl-type monomers can be impregnated into woods that polymerize *in situ* into the void structure by radiation or heat and a catalyst (65). The hydroscopic characteristics of the wood substance are not altered because little, if any, polymer penetrates the cell walls. However, because of the high polymer content (70-100%), the normally high void volume of wood is greatly reduced. With the elimination of this important pathway for vapor or liquid water diffusion, the response of the wood substance to changes in relative humidity or water is very slow and moisture resistance or water repellent effectiveness (WRE) is greatly improved (66). Water repellent effectiveness

is measured as follows:

$$\text{WRE} = \frac{\text{Swelling or moisture uptake of control specimen during exposure to water fort minutes}}{\text{Swelling or moisture uptake of treated specimen during exposure to water also fort minutes}} \times 100$$

Hardness is increased appreciably. Wood-polymer composites are currently used in certain sporting equipment, musical instruments, decorative objects, and high performance flooring.

To improve dimensional stability, low molecular weight chemicals are used that penetrate the cell walls and either bond to the cell wall polymers or polymerize in the cell wall. Improvements in dimensional stability are measured by antishrink efficiency (ASE):

$$\text{ASE} = \left[1 - \left(\frac{\text{Percentage swelling of treated specimen}}{\text{Percentage swelling of control}} \right) \right] \times 100$$

ASE is a measure of the extent to which the swelling and shrinking tendency has been reduced at an equilibrium condition.

The wood cell wall can be bulked with leachable polyethylene glycol (PEG) to achieve an ASE of about 80% (67). In this case, the wood is usually treated in a green condition and the PEG is exchanged for the cell wall water. The green wood is soaked in a 30% by weight PEG-1000 solution for a length of time depending upon the thickness of the wood; two coats of polyurethane varnish are usually applied later to seal in the PEG and exclude water. Maximum ASE of 80% is achieved at PEG loadings of 45% weight gain. The strength properties of PEG-treated wood approximate those of untreated green wood (see GLYCOLS; POLYETHERS).

It is possible to react an organic moiety to the hydroxyl groups on cell wall components. This type of treatment also bulks the cell with a permanently bonded chemical (68). Many compounds modify wood chemically. The best results are obtained by the hydroxyl groups of wood reacting under neutral or mildly alkaline conditions below 120°C. The chemical system used should be simple and must be capable of swelling the wood structure to facilitate penetration. The complete molecule must react quickly with wood components to yield stable chemical bonds while the treated wood retains the desirable properties of untreated wood. Anhydrides, epoxides, and isocyanates have ASE values of 60-75% at chemical weight gains of 20–30%.

Thermosetting phenolic resins have been used successfully to penetrate and polymerize in the cell wall. The rate-determining step for successful treatment is the penetration of the resin into the cell wall. With green wood, this rate depends on the diffusion rate of the resin in the lumen-trapped water. With dry wood, pressure can be applied. In this case, the rate depends on the permeability of the wood. For both processes, the size of the object is very important; long treating times are used for large pieces and for heartwood. The sapwood of some species is sufficiently permeable to admit resin fairly uniformly and in a reasonable time. Thin veneers are generally pressure impregnated (up to 1.4 MPa = ~14 atm)

with a 30% aqueous solution of a water-soluble resin. The wood is then slowly dried and heated at ~150°C for 20 min to set the resin. Laminates are built up by gluing the individual sheets together. The product is called impreg. Its density is ~20% higher than that of the original wood, and its color is that of the original wood or slightly darker. The ASE of impreg increases with increasing content of phenolic resin and then tends to level off at ~65% when the resin content reaches 30-35%, based on original wood. Impreg generally contains 25-35% resin (67).

The mechanical properties of resin-impregnated wood are improved or not affected except for toughness, which is reduced by as much as 60% (69). Treatment with phenol-formaldehyde resins increases the decay resistance. Impreg stakes containing ~30% resin had an average service life of 12 years in ground tests (70). Biological resistance may be due to the fact that the cell walls of the treated wood resist moisture-supporting decay. It could also be due in part to toxic effects of partially polymerized phenolic resin on the destructive organism.

Heat resistance is improved markedly by resin impregnation. A block of impreg, subjected to forty-five 1-hour exposures at 204°C, showed no apparent loss in properties, although an untreated sample showed signs of deterioration after three 1-hour exposures (71).

The largest industrial application of impreg is in die models for automobile body parts and other model dies. The dimensional stability and ease of shaping are the reasons that impreg, although expensive, has wide application.

If pressure is applied to dry, resin-treated veneers while they are being heat cured, a densified product (1.35 kg/mL) is obtained. This material, called compreg, retains most of the advantages of impreg. In addition, owing to the two- to threefold increase in density, the mechanical properties are appreciably better than those of the original wood. The strength of compreg is increased in proportion to the compression. Compreg is less tough than untreated wood but more tough than impreg.

Because of the plasticizing action of the resin-forming materials. the wood can be compressed under considerably lower pressures than dry, untreated wood. For example, treated spruce, cottonwood, and aspen veneer, dried to a moisture content of ~65 but not cured, are compressed, when subjected to a pressure of only 1.72 MPa (~17 atm) at 149°C, to about half the original thickness and a specific gravity of ~1.0.

In a 24-h water soaking test, compreg has an ASE value of 95%. The rate of water pickup is so slow that complete swelling equilibrium of a 1.27-cm specimen is not achieved in a year at room temperature. Compreg is brown and acquires a high polish on buffing. It is made commercially in small quantities and is used for knife handles, gears, and certain musical instruments and decorative objects.

Bending is another treatment process. Above 80°C, green wood becomes readily deformable. The new shape persists after cooling to room temperature and drying under restraint. This is the basis for commercial bending of wood to various shapes. The deformation, however, is not a fully plastic one. An elastic component persists and produces some strain recovery at high or cyclic humidification. Ammonia is also used to bend wood (72). The wooden object is immersed in liquid ammonia for a period of time, depending on the dimensions, imparting

appreciable plasticity to the wood. The ammonia is allowed to evaporate from the deformed wood, and very little strain recovery occurs on humidification.

Chemical Raw Material

Wood is one of our most important renewable biomass resources. Unlike most biomass sources, wood is available year round and is more stable on storage than other agricultural residues. In the United States, wood residues from industrial by-products totaled 60.8×10^6 metric tons in 1993 (73). Increasingly, residues are incorporated into manufactured wood products and are used as a fuel, replacing petroleum, especially at wood-industry plants (73); some is converted to charcoal but most is used in the pulp and paper industiy. Residues are also available for manufacturing chemicals, generally at a cost equivalent to their fuel value (see FUELS FROM BIOMASS; FUELS FROM WASTE).

Wood can be pyrolyzed (heated to 400°C or higher in the absence of oxygen) to produce a variety of chemical compounds. For example, various wood species heated to 400°C yielded 31-41% charcoal, 3–7% acetic acid, 1.5-2.5% methanol, 11-19% tar, and 15-17% gases (74). The gases occurring are predominately hydrogen, carbon monoxide, carbon dioxide, and methane. Wood gasification takes place at ~l,000°C in the presence of a controlled amount of oxidizing agent. The product gas composition depends upon the starting moisture content of the wood. In addition to the above-mentioned gases, some low molecular weight aliphatic hydrocarbons are also produced.

Wood is about 65-75% carbohydrate and has been considered as a potential source of ethanol for fuel. The carbohydrate material can be hydrolyzed to monomer sugars, which in turn can be fermented to produce ethanol. However, wood carbohydrates are expensive to hydrolyze. Hydrolysis with acids and enzymes is impeded by the crystalline structure of cellulose. Lignin interferes with processing, and hydrolytic by-products such as furfural, acetic acid, and derivatives of lignin and extractives can inhibit fermentation. Research is still being conducted on wood hydrolysis to develop a process that is economically sound. Furfural is a useful chemical feedstock and results from the dehydration of pentose sugars. It can be obtained in 9 to 10% yield from the dilute acid hydrolysis of hardwoods (75).

The principal chemical industry based on wood is pulp and paper. In 1995, ~114.5×10^6 metric tons of wood were converted into ~60×10^6 metric tons of fiber products ranging from newsprint to pure cellulose in the United States (1,76). Pure cellulose is the raw material for a number of products, eg, rayon, cellulose acetate film base, cellulose nitrate explosives, cellophane, celluloid, carboxymethylcellulose, and chemically modified cellulosic material.

Most of the more than 54.5×10^6 metric tons of organic material removed from wood during pulping are burned for their energy content and to recover the inorganic pulping chemicals. Some organic chemicals are recovered from this waste stream, referred to as black liquor. A large proportion of the organic chemicals recovered from sulfite pulp mills are lignosulfonates. Lignosulfonates are used as oil-well drilling fluids, binders for animal food pellets, and as an additive to improve the structural properties of concrete. Some of the recovered lignin-derived material is used to produce vanillin, and the recovered sugars are used

to produce small amounts of yeast, ethanol, and acetic acid. The most valuable chemical by-products are isolated at kraft pulp mills. These chemicals are sulfate turpentine and tall oil (a mixture of fatty acids and rosin); dimethyl sulfide and dimethyl sulfoxide are also obtained from sulfate pulping (kraft) liquors.

There are a few minor wood-based chemical industries. After chestnut blight wiped out the American chestnut, U.S. tannin production essentially ceased. The main natural tannins, wattle and quebracho, are now imported. High U.S. labor costs and the advent of synthetic tannins make re-establishment of a U.S. tannin industry unlikely. Tannins are used in oil-well drilling muds. Tree exudates are a continuing wood-based chemical industry. Tree exudates include rubber, true carbohydrate gums (eg, acacia gum), kinos (eg, the phenolic exudates from eucalyptus), balsams (eg, Storax from *Liguidambar* spp.), and many different types of oleoresins (mixtures of a solid resin and a liquid essential oil). The most important oleoresin still collected in the United States is pine gum (rosin plus turpentine).

Wood is the raw material of the naval stores industry (77). Naval stores, so named because of their importance to the wooden ships of past centuries, consist of rosin (diterpene resin acids), turpentine (monoterpene hydrocarbons), and associated chemicals derived from pine (see TERPENOIDS). These were obtained by wounding the tree to yield pine gum, but the high labor costs have substantially reduced this production in the United States. Another source of rosin and turpentine is through extraction of old pine stumps, but this is a non-renewable resource and this industry is in decline. The most important source of naval stores is spent sulfate pulping liquors from kraft pulping of pine. In 1995, U.S. production of rosin from all sources was estimated at under 300,000 metric tons and of turpentine at 70,000 metric tons. Distillation of tall oil provides, in addition to rosin, nearly 128,000 metric tons of tall oil fatty acids annually (78).

Hydrolysis

In the acid hydrolysis process (79-81), wood is treated with concentrated or dilute acid solution to produce a lignin-rich residue and a liquor containing sugars, organic acids, furfural, and other chemicals. The process is adaptable to all species and all forms of wood waste. The liquor can be concentrated to a molasses for animal feed (82), used as a substrate for fermentation to ethanol or yeast (82), or dehydrated to furfural and levulinic acid (83-86). Attempts have been made to obtain marketable products from the lignin residue (87) rather than using it as a fuel, but currently only carbohydrate-derived products appear practical.

When concentrated acids are used, the carbohydrates are recovered in high yields, but the problem of economically recovering the large quantities of acid used has not been solved. At the present state of development, the dilute acid processes, especially percolating and two-stage, appear more promising.

A number of commercial plants using the Scholler percolation process (88) were built in Germany, Switzerland, and the former USSR, only the latter are still in operation. In general, these plants were built to produce sugars for fermentation to ethanol and yeast (qv). Except under special circumstances, however, such a process has proved to be uneconomical. In the Scholler process,

a hot dilute solution of sulfuric acid is percolated through wood chips; the solubilized sugars are carried with the solution withdrawn from the bottom of the digester. The acid concentration and temperature of the charged solution are continuously increased; the more labile hemicelluloses are hydrolyzed and removed in the early part of the cycle, whereas the resistant cellulose, yielding glucose, is hydrolyzed at the end.

A percolation process requiring less time was developed at the USDA Forest Service, Forest Products Laboratory, in Madison, Wisconsin, during World War II (89-91). For Douglas-fir, this process gives a sugar yield of 40-45%; the sulfuric acid requirement is 5% based on the dry wood weight. The concentration of the resulting sugar solution is 4-5%. Yields per 100 kg of dry wood are 20-25 L of 100% ethanol.

In two-stage processes, the hemicelluose sugars are hydrolyzed in the first stage; the solubilized material is washed from the residue, which is reimpregnated with acid and passed to the second stage where the cellulose is hydrolyzed. This process is much less energy and capital intensive than the percolation process and gives a better fractionation of the hemicellulose sugars and glucose. Enzymatic saccharification of the cellulose requires two-stage processing. Sugar yields are about the same as those obtained by percolation, but concentrations of 10-12% are reached with significantly lower acid, energy, and equipment capacity requirements. The two-stage process is not operated commercially, but during World War II, some pilot studies were done in Sweden (92). More recently, the Tennessee Valley Authority (TVA) did extensive pilot plant testing on the process with a l-ton-per-day pilot plant (93). Much of the recent work on lignocellulose use has been directed toward the development of the two-stage process with either chemical or enzymatic hydrolysis of the cellulose (94-100).

High yields of pure glucose can be obtained by enzymatic cellulose hydrolysis. However, the enzyme is expensive and does not attack lignin-encrusted cellulose. Several processes have been studied using various organisms singly and in combination after subjecting the lignocellulose to different pretreatments (94, 100-104). In the Gulf process, cellulose hydrolysis and glucose fermentation take place simultaneously in one vessel.

The Iotech steam explosion process has been used to prepare cellulosic substrates for enzymatic digestion (105, 106). Wood, or other lignocellulose material, is subjected to a short prehydrolysis at high temperature and pressure and then is rapidly decompressed. The combined chemical and mechanical treatment solubilizes the hemicellulose component in hot water and the lignin in alcohols. Freed of lignin encrustation. the cellulose is highly accessible to hydrolytic enzymes. The recovered lignin is thermoplastic and may be marketable as a resin component.

Although the hydrolysis of wood to produce simple sugars has not proved to be economically feasible, by-product sugars from sulfite pulping are used to produce ethanol and to feed yeast (107). Furthermore, a hemicellulose molasses, obtained as a by-product in hardboard manufacture, can be used in cattle feeds instead of blackstrap molasses (108). Furfural can be produced from a variety of wood processing byproducts, such as spent sulfite liquor, liquors from the prehydrolysis of wood for kraft pulping, hardboard plants, and hardwood wastes (109).

Fuel Properties

The fuel properties of wood can be summarized by ultimate and proximate analyses and determination of heating value. The analytical procedures are the same as those for coal, but with some modifications. Analytical results generally vary about as much within a species as they do between species, except that softwood species generally have a higher carbon content and higher heating values than hardwood species because of the presence of more lignin and resinous materials in softwood species (see FUELS FROM wASTE).

The higher heating value of wood and bark of softwood species is usually ~21 kJ/g (~9000 Btu/lb) and slightly less for hardwood. The higher heating value includes the heating value of the condensed steam given off. These values are within ± 5% of nearly all the values reported in the literature for specific samples. A systematic study of the heating value of a species has not been done because it requires measuring the heating value at various positions in a tree and from trees selected from the entire geographic range of the species.

Wood ash generally contains calcium, potassium, phosphorus, magnesium, and silica. Ashes recovered from burned wood are ~25% water soluble and the extract is strongly alkaline. The ash fusion temperature is in the range of to 1500°C.

The moisture content of freshly cut wood varies between species and portions of the tree. Between species, it can be 30-70% on a total weight basis (65); commonly, it is 45- 50%. Within a tree, the heartwood generally has lower moisture content than the sapwood. For hardwood species, this difference is usually small; for softwood species such as Douglas-fir, the difference can be as great as 30% for heartwood compared with 50% for sapwood.

Charcoal Production

Charcoal is produced by heating wood under limited access of oxygen. When wood is heated slowly to ~280°C, an exothermic reaction occurs. In the usual carbonization procedure, heating is prolonged to 400 to 500°C in the absence of air. The term charcoal also includes charcoal made from bark.

Charcoal is produced commercially from primary wood-processing residues and low quality roundwood in either kilns or continuous furnaces. A kiln is used if the raw material is in the form of roundwood, sawmill slabs, or edgings. In the United States, most kilns are constructed of poured concrete with a capacity of 40 to 100 cords of wood and operating on a 7-to 12-d cycle. Sawdust, shavings, or milled wood and bark are converted to charcoal in a continuous multiple-hearth furnace commonly referred to as a Herreshoff furnace. The capacity is usually at least 1 ton of charcoal per hour. The yield is ~25% by weight on a dry basis.

The proximate analysis of charcoal is ~20-25% volatile matter, 70-75% fixed carbon, and 5% ash. Charcoal briquets have lower heating values than charcoal lumps, because of additives in the briquets. The higher heating value of lump charcoal is ~28 kJ/kg (12,000 Btu/lb). The higher heating value of briquets is 23 to 25 kJ/kg (~9,900-10,800 Btu/lb).

To alleviate the air pollution problem associated with charcoal kilns and furnaces, the gases from the kiln and furnaces are burned (see AIR POLLUTION

CONTROL METHODS). They can be burned with additional fossil fuel to recover heat and steam (110, 111), or in afterburners to nearly eliminate visible air pollution and odors (112).

Charcoal was an important industrial raw material in the United States for iron ore reduction until it was replaced by coal in the early 1880s. Charcoal production increased, however, because of the demand for the by-products acetic acid, methanol, and acetone. In 1920, nearly 100 by-product recovery plants were in operation in the United States, but the last plant ceased operation in 1969.

Charcoal production has increased since the 1940s, which reflects the use of charcoal briquets for home and recreational cooking (Table 6). The charcoal currently produced is nearly all consumed as briquets for cooking. Some charcoal is used in certain metallurgical and filtration processes and horticultural uses. In Brazil, charcoal is produced in beehive-type kilns born natural and plantation-grown trees for use as a reducing agent for iron ore because Brazil does not have abundant supplies of coking coal. In many developing countries, charcoal is preferred for domestic cooking. It is made in pit-type kilns or portable sheet metal kilns (114) (see also CARBON AND ARTIFICLAL GRAPHITE).

Table 6. Charcoal Production for Selected Years [a]

Year	Production, 10^3 t
1940	227
1950	227
1960	290
1970[b]	454
1980[b]	726

[a]Ref. 113.
[b]Charcoal briquet production from all sources including wood, bark, lignite, coal, and agricultural residue.

Economic Aspects

Timber production in the United States is an important contributor to Gross Domestic Product (GDP). In 1991, timber-related activities in the United States generated ~$59,498 million (Table 7). It accounted for 2.2% of the goods and structures portion of GDP. Primary timber products production totaled $19,370; secondary timber-related products added $40,128 million of value in 1991.

Primary Timber Products. Primary timber products are roundwood products such as "logs, bolts, and other round timber generated from harvesting trees for industrial or consumer use" (116). In 1991, 17,889 million ft³ of roundwood timber products were harvested in the United States (Table 8) (116). Nearly one-half (48%) of this volume originated in one region, the South (Table 9). Just under one-fourth (23%) originated from each of two regions, the North and Pacific Coast regions. Overall, 63% of the volume harvested was softwood, 37% hardwood. Ninety percent or more of the timber harvested from the Rocky Mountain and Pacific Coast regions was softwood species. Nearly two-thirds (64%) of the

Table 7. Value of Primary and Secondary Timber Products and Gross Domestic Product (GDP) in the United States, 1991

| Product and GDP | Value | | GDP[a] | |
	Million dollars	Percent of total	Percent of goods	Percent of total
primary	19,370	32.6	0.7	0.3
secondary	40,128	67.4	1.5	0.7
Total	*59,498*	*100.0*	*2.2*	*1.0*
		GDP		
goods[b]	2,690,200	47.0		
services	3,032,700	53.0		
Total	*5,722,900*	*100.0*		

Table 8. Volume and Value of Roundwood Timber Products Harvested in the United States by Region. 1986 and 1991 [a]

| | Volume | | | | Value[b] | | | |
	Total, million ft^3	Total, %	Soft-wood, %	Hard-wood, %	Total, million dollars	Total, %	Soft-wood, %	Hard-wood, %
				1986				
North	4,079	23	22	78	1,627	13	23	77
South	8,079	46	66	34	5,110	40	77	23
Rocky Mountain	948	5	90	10	821	6	94	6
Pacific Coast	4,486	26	96	4	5,082	40	98	2
United States	17,593	100	64	36	12,640	100	79	21
				1991				
North	4,140	23	22	78	2,746	14	20	80
South	8,613	48	64	36	7,976	41	71	29
Rocky Mountain	938	5	90	10	1,320	7	95	5
Pacific Coast	4,198	23	93	7	7,328	38	97	3
United States	17,889	100	63	37	19,370	100	76	24

[a]Refs. 116–118.
[b]Market values at local points of delivery.

timber harvested in the South was softwood, whereas in the North, less than one-fourth (22%) was softwood.

Total roundwood harvested increased by less than 300 million ft^3 between 1986 and 1991 (Table 8). The value of all roundwood timber harvested in the United States in 1991 was estimated to be $19,370 million (Table 8). The value of roundwood timber is defined as the market value at local points of delivery, ie, delivered to a processing facility.

Softwood roundwood tended to be relatively higher valued than hardwood in all regions except the North in 1986 and 1991. Overall, softwood roundwood

Table 9. Regions of the United States

North	South	Rocky Mountain	Pacific Coast
Connecticut	Alabama	Arizona	Alaska
Delaware	Arkansas	Colorado	California
Illinois	Florida	Idaho	Hawaii
Indiana	Georgia	Kansas	Oregon
Iowa	Kentucky	Nebraska	Washington
Maine	Louisiana	Nevada	
Maryland	Mississippi	New Mexico	
Massachusetts	North Carolina	North Dakota	
Michigan	Oklahoma	Montana	
Minnesota	South Carolina	South Dakota	
Missouri	Tennessee	Utah	
New Hampshire	Texas	Wyoming	
New Jersey			
New York			
Ohio			
Pennsylvania			
Rhode Island			
Vermont			
Virginia			
West Virginia			
Wisconsin			

accounted for 63% of total production in 1991 but accounted for 76% of total value (Table 8).

Total value of roundwood production increased by $6,730 million between 1986 and 1991 even though production increased by less than 300 million ft^3 (118) (Table 8). Much of this increase is directly attributable to rapidly rising stumpage prices.

Secondary Timber Products.   Secondary timber products are products manufactured from primary timber products. Secondary products can be sold directly to the final consumer or can require additional processing before reaching the final consumer. The wide diversity of products manufactured from primary timber products makes it difficult to precisely define secondary products. Lumber, for example, is clearly a secondary product because it is manufactured from roundwood and typically requires further processing before reaching its final use. Wooden furniture is considered a final product, not a secondary product because it is made from lumber or other secondary timber products. In general, products made from secondary timber products were not included in this analysis.

Table 10 itemizes the specific four-digit Standard Industrial Classification (SIC) industries considered to be secondary timber products manufacturers. For more information on the SIC system, see Executive Office of the President, Office of Management and Budget (119).

In 1991, timber-related secondary products manufacturing industries added an estimated S40, 128 million of value to primary timber products (Table 11). Most of the timber-related value added (63%) originated in the paper and allied products industry. The lumber and wood products industry added

Table 10. Four-Digit SIC Secondary Timber-Related Manufacturing Industries in the United States [a]

SIC code	Description
24--	Lumber and Wood Products
242-	sawmills and planing mills
2421	sawmills and planing mills, general
2426	hardwood dimension and flooring mills
2429	special product sawmills, nec
243-	millwork, plywood, and structural members
2435	hardwood veneer and plywood
2436	softwood veneer and plywood
2439	structural wood members, nec
244-	wood containers
2441	nailed wood boxes and shook
2448	wood pallets and skids
2449	wood containers, nec
249-	miscellaneous wood products
2491	wood preserving
2493	reconstituted wood products
2499	wood products, nec
26--	Paper and Allied Products
261-	pulp mills
2611	pulp mills
262-	paper mills
2621	paper mills
263-	paperboard mills
2631	paperboard mills
28--	Chemicals and Allied Products
286-	industrial organic chemicals
2861	gum and wood chemicals

[a]Ref. 119.

Table 11. Value Added by Manufacture [a] for Timber-Related Two-Digit SIC Industries [b] by Region, 1991 [c]

	Value, 10^6 \$			
Region	Principal Group 24 (Lumber and wood products)	Principal Group 26 (Paper and allied products)	Principal Group 28 (Chemicals and allied products)	Total
North	4,067	11,385	97	15,549
South	5,367	10,846	128	16,350
Rocky Mountain	908	169	7	1,083
Pacific Coast	4,386	2,753	7	7,145
United States	14,737	25,153	238	40,128

[a]Value of industry shipments minus the cost of materials, supplies, containers, fuel, purchased electricity, and contract work.
[b]Timber-related industries include the following four-digit SIC Codes:
  24: 2421, 2426, 2429, 2435, 2436, 2439, 2441, 2448, 2449, 2491, 2493, 2499
  26: 2611, 2621, 2631
  28: 2861
[c]Ref. 120.

658

nearly 37% of total timber-related value added. Less than 1% was from chemicals and allied products.

The South and North were the two largest timber-related secondary products manufacturing regions, adding $16,350 million (41%) and $15,549 million (30%) of value, respectively, in 1991 (Table 10). The Rocky Mountain and Pacific Coast regions combined added the remaining 20%.

BIBLIOGRAPHY

"Wood" in *ECT* 1st ed., Vol. 15, pp. 72–102, by E. G. Locke, R. H. Baechler, E. Beglinger, H. D. Bruce, J. T. Drow, K. G. Johnson, D. G. Laughnan, B. H. Paul, R. C. Rietz, J. F. Saeman, and H. Tarkow, U.S. Department of Agriculture; "Wood" in *ECT* 2nd ed., Vol. 22, pp. 358–387, by H. Tarkow, A. J. Baker, H. W. Eickner, W. E. Eslyn, G. J. Hajny, R. A. Hahn, R. C. Koeppen, M. A. Millet, and W. E. Moore, U.S. Department of Agriculture; "Wood" in *ECT* 3rd ed., Vol. 24, pp. 579–611 by Theodore H. Wegner, A. J. Baker, B. A. Bendtsen, J. J. Brenden, W. E. Eslyn, J. F. Harris, J. L. Howard, R. B. Miller, R. C. Pettersen, J. W. Rowe, R. M. Rowell, W. T. Simpson, D. F. Zinkel, U.S. Department of Agriculture.

1. *1996 Statistics, Data through 1995, Paper, Paperboard & Wood Pulp*, American Forest & Paper Association, Washington, D.C., 1996.
2. *An Analysis of the Timber Situation in the United States: 1989–2040*, General Technical Report RM-199, U.S. Department of Agriculture, Forest Service, Rocky Mountain Forest and Range Experimental Station, Fort Collins, Colo., 1990.
3. *Tree Biomass—A State-of-the-Art Compilation*, General Technical Report WO-33, U.S. Department of Agriculture, Forest Service, Washington, D.C., 1981.
4. J. L. Howard, *U.S. Production, Trade, Consumption, and Price Statistics 1965–1994*, General Technical Report FPL-GTR-98, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1997.
5. A. J. Panshin and C. deZeeuw, *Textbook of Wood Technology: Structure, Identification, Uses, and Properties of the Commercial Woods of the United States*, 4th ed., McGraw-Hill Book Co., Inc.. New York, 1980.
6. *Wood Handbook: Wood as an Engineering Material*, Agriculture Handbook 72, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., revised, 1987.
7. R. L. Gray and R. A. Parham, *Chemtech* **12**(4), 232 (1982).
8. E. Sjöström, *Wood Chemistry: Fundamentals and Applications*, 2nd ed., Academic Press, San Diego, Calif., 1992.
9. D. Fengel and G. Wegener, *Wood: Chemistry, Ultrastructure, Reactions*, W. de Gruyter, Berlin and New York, 1984.
10. R. Pettersen, "The Chemical Composition of Wood," in R. Rowell, ed., *The Chemistry of Solid Wood*, American Chemical Society, Washington, D.C., 1984, Chapt. 2.
11. J. W. Rowe, ed., *Natural Products of Woody Plants. Chemicals Extraneous to the Lignocellulosic Cell Wall*, Vol. I and II, Springer-Verlag, Berlin, 1989.
12. C. Skarr and W. T. Simpson. *For. Prod. J.* **18**, 49 (1968).
13. A. J. Stamm, *Wood and Cellulose Science*, Ronald Press Company, New York, 1964.
14. F. F. P. Kollmann and W. A. Côté, Jr., *Principles of Wood Science and Technology*, Vol. 1, Springer-Verlag New York, Inc., New York, 1968.
15. R. C. Rietz and R. H. Page. *Air Drying of Lumber: A Guide to Industry Practices*, Agriculture Handbook 402. U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C., 1971.

16. E. F. Rasmussen, *Dry Kiln Operators Manual*, Agriculture Handbook 188, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C., 1961.

17. *National Design Specifications for Wood Construction*, National Forest Products Association, Washington, D.C., 1977.

18. C. C. Gerhards, *Wood Fiber* 14(1), 4 (1982).

19. D. E. Kretchmann and D. W. Green, *Wood and Fiber Science* 28(3), 320–337 (1996).

20. D. W. Green and J. W. Evans, "Moisture Content and the Mechanical Properties of Dimension Lumber: Decisions for the Future" in D. Green and co-eds., *Proceedings no. 47363, In-Grade Testing of Structural Lumber*, Madison, Wisc., April 25–26, 1988, Forest Products Society, Madison, Wisc., 1989.

21. C. C. Gerhards and J. M. McMillen, eds., *Proceedings of the Research Conference on High-Temperature Drying Effects on Mechanical Properties of Softwood Lumber*, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1976.

22. H. D. Erickson and L. W. Rees, *J. Agric. Res. (Washington, D.C.)* 60, 593 (1940).

23. W. S. Thompson, *Effect of Chemicals, Chemical Atmospheres, and Contact with Metals on Southern Pine: A Review*, Research Report 6, Forest Products Utilization Laboratories, Mississippi State University, State College, Miss., 1969.

24. *AWPA Book of Standards*, American Wood-Preservers' Association, Woodstock, Md., 1997.

25. J. E. Winandy, "Effects of Waterborne Preservative Treatment on Mechanical Properties: A Review," in *Proceedings of the 91st Annual Meeting of the American Wood-Preservers' Association*, New York, May 21–24, 1995, Vol. 91, AWPA, Woodstock, Md., 1995, pp. 17–33.

26. S. L. LeVan and J. E. Winandy, *Wood and Fiber Science* 22(1), 113–131 (1990).

27. J. E. Winandy and P. K. Lebow, *Wood and Fiber Science* 28(1), 39–52 (1996).

28. F. Shafizadeh and A. G. W. Bradbury, *J. Thermal Insulation* 2, 141 (Jan. 1979).

29. *Ignition and Charring Temperature of Wood*, Report 1464, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1958.

30. A. F. Matson, R. E. Dufour, and J. F. Breen, *Survey of Available Information on Ignition of Wood Exposed to Moderately Elevated Temperatures*, Bulletin of Research 51, Part II, Underwriters Laboratories, Inc., 1959.

31. E. L. Schaffer, *Fire Technol.* 16(1), 22 (Feb. 1980).

32. V. W. Jahnsen, Ph.D. thesis, Purdue University, West Lafayette, Ind., 1961.

33. R. W. Porter, Ph.D. thesis, Michigan State University, East Lansing, Mich., 1963.

34. J. J. Brenden, *Effect of Fire-Retardant and Other Inorganic Salts on Pyrolysis Products of Ponderosa Pine at 250° and 350°C*, Research Paper FPL 80, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1967.

35. A. J. Stamm, *Ind. Eng. Chem.* 48, 413 (1956).

36. H. W. Eickner and W. K. Tang, *Proceedings of International Union of Forest Research Organizations*, Section 41, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1963.

37. F. L. Browne, *Theories of the Combustion of Wood and its Control*, Report 2136, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1958; reviewed and reaffirmed 1963.

38. F. C. Beall and H. W. Eickner, *Thermal Degradation of Wood Components: A Review of the Literature*, Research Paper FPL 130, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1970.

39. I. S. Goldstein in D. D. Nicholas, ed., *Degradation and Protection of Wood*, Vol. 1, Syracuse University Press, Syracuse, N.Y., 1973.

40. F. Shafizadeh, *Adv. Carbohydr. Chem.* 23, 419 (1968).

41. *Standard Test Method for Behavior of Materials in a Vertical Tube Furnace at 750°C,* Standard E 136, American Society for Testing and Materials, West Conshohocken, Pa., 1994.

42. *Standard Methods of Fire Tests of Building Construction and Materials,* Standard E 119, American Society for Testing and Materials, West Conshohocken, Pa., 1995.

43. *Standard Methods of Fire Tests of Door Assemblies,* Standard E 252, National Fire Protection Association, Quincy, Mass., 1995.

44. *Standard Test Method for Surface Burning Characteristics of Building Materials,* Standard E 84, American Society for Testing and Materials, West Conshohocken, Pa., 1995.

45. E. L. Schaffer, *Review of Information Relating to the Charring Rate of Wood,* Research Note FPL-0145, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1966.

46. R. H. White and E. V. Nordheim, *Fire Technol.* **28,** 5 (1992).

47. R. H. White, in P. J. DiNenno and co-eds., *The SFPE Handbook of Fire Protection Engineering,* 2nd ed., National Fire Protection Association, Quincy, Mass., 1995, Chapt. 4, p. 217–229.

48. H. W. Eickner, *ASTM Journal of Materials* **1,** 625 (1966).

49. J. J. Brenden, *Rate of Heat Release from Wood-base Building Materials Exposed to Fire,* Research Paper FPL230, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1974.

50. H. C. Tran, in V. Babrauskas and S. J. Grayson, eds., *Heat Release in Fires,* Elsevier Applied Science, New York, 1993, Chapt. 11, Part b, pp. 357–372.

51. *Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter* Standard E 1354, American Society for Testing and Materials, West Conshohocken, Pa., 1994.

52. J. E. Winandy, R. J. Ross, and S. L. LeVan, in *Proceedings of the 1991 International Timber Engineering Conference,* 1991 Sept. 2–5, Vol. 4, London, TRADA, London, 1991, pp. 4.69–4.74.

53. S. C. Juneja and L. Calve, *J. Fire Retardant Chem.* **4,** 235–241 (1977).

54. S. L. LeVan, *Effectiveness of Fire-Retardant Treatments for Shingles after 10 years of Outdoor Weathering,* Research Paper FPL 474, U.S. Department of Agriculture, Forest Service. Forest Products Laboratory, Madison, Wisc., 1986.

55. R. S. Roberts. *Biotechnol. Bioeng. Symp.* **10,** 125 (1980).

56. R. H. Baechler. *J. For. Prod. Res. Soc.* **4,** 332 (1954).

57. R. H. Baechler and C. A. Richards, *Trans. Amer. Soc. Mech. Eng.* **73,** 1055 (1951).

58. W. E. Eslyn and J. W. Clark, *Mater. Org. Suppl.* **3,** 43 (1976).

59. G. R. Esenther and R. H. Beal, *Sociobiology* **4,** 215 (1979).

60. *Comparative Decay Resistance of Heartwood of Native Species,* Research Note FPL 0153, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1967.

61. *Wood Preservation: Treating Practices,* Federal Specification TT-W-5711, U.S. General Services Administration, Washington, D.C.

62. T. C. Scheffer and W. E. Eslyn, *For. Prod. J.* **28,** 25 (1978).

63. T. L. Highley. *For. Prod. J.* **30,** 49 (1980).

64. E. Schmidt. *First International Conference on Wood Protection with Diffusible Preservatives,* 1990. pp. 91–92.

65. J. A. Meyer, *Wood Sci.* **14**(2), 49 (1981).

66. R. M. Rowell and W. B. Banks, *Water Repellency and Dimensional Stability of Wood,* General Technical Report FPL 50, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1985.

67. R. M. Rowell and R. L. Youngs, *Dimensional Stability of Wood in Use*, Research Note FPL 0243, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1981.

68. R. M. Rowell, *Proc. Am. Wood-Preserv. Assoc.* **71**, 41 (1975).

69. E. C. O. Erikson, *Mechanical Properties of Laminated Modified Wood*, Report 1639, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1965.

70. L. F. Gjovik and H. L. Davidson, *Comparison of Wood Preservatives in Stake Tests*, Research Note FPL 02, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1979.

71. R. M. Seborg and A. E. Vallier, *J. For. Prod. Res. Soc.* **4**, 305 (1954).

72. C. Schuerch, *For. Prod. J.* **14**, 377 (1964).

73. P. J. Ince, *Recycling of Wood and Paper Products in the United States*, General Technical Report FPL-GTR-89, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1996.

74. Ref. 9, p. 338.

75. F. W. Herrick, and H. L. Hergert, "Utilization of Chemicals from Wood: Retrospect and Prospect," in F. A. Loewus and V. C. Runeckles, eds., *The Structure, Biosyntheses, and Degradation of Wood, Recent Advances in Phytochemistry*, Vol. 11, Plenum Press, New York, 1977.

76. *Annual Pulpwood Statistics Summary Report*, American Pulpwood Association Inc., Rockville, Md., 1995.

77. D. Zinkel and J. Russell, eds., *Naval Stores: Production, Chemistry, Utilization*, Pulp Chemicals Association, New York, 1989.

78. *Naval Stores Review*, New Orleans, La., 1995.

79. J. F. Harris, J. F. Saeman, and E. G. Locke inn B. L. Browning, ed., *Wood as a Chemical Raw Material, The Chemistry of Wood*, Interscience Publishers, a division of John Wiley & Sons, Inc., New York, 1973, Chapt. 11, pp. 535–585.

80. J. A. Hall, J. F. Saeman, and J. F. Harris, *Unasylva* **10**(1), 7 (1956).

81. J. F. Harris, J. F. Saeman, and E. G. Locke, *For. Prod. J.* **8**, 248 (1958).

82. G. J. Hajny, *Biological Utilization of Wood for Production of Chemicals and Foodstuffs*, Research Paper FPL 385, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1981.

83. D. F. Root and co-workers, *For. Prod. J.* **9**, 158 (1959).

84. S. W. McKibbins and co-workers, *For. Prod. J.* **12**, 17 (1962).

85. J. F. Harris and J. M. Smuk, *For. Prod. J.* **11**, 303 (1961).

86. M. S. Feather and J. F. Harris, *Adv. Carbohydr. Chem. Biochem.* **28**, 161 (1973).

87. *Chem. Eng. News*, **35** (Nov. 3, 1980).

88. J. F. Saeman, E. G. Locke, and G. K. Dickerman, *Production of Wood Sugar in Germany and its Conversion to Yeast and Alcohol*, U.S. Department of Commerce Office Technical Service PB Report 7736, U.S. Department of Commerce, Washington, D.C., 1945.

89. E. E. Harris, *Adv. Carbohydr. Chem.* **4**, 154 (1949).

90. R. A. Lloyd and J. F. Harris, *Wood Hydrolysis for Sugar Production*, Report 2029, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wisc., 1955.

91. A. J. Panshin, *Wood Saccharification in Forest Products*, McGraw-Hill Book Co., Inc., New York, 1950, pp. 403–412.

92. K. N. Cederquist, *Some Remarks on Wood Hydrolyzation, Report of a Seminar Held at Lucknow, India, 1952, on Production and Use of Power Alcohol in Asia and the Far East*, Technical Assistance Administration, United Nations, New York, 1954, pp. 193–198.

93. J. D. Broder, J. W. Barrier, K. P. Lee, and M. M. Bulls, *World Resources Review* **7**(4), (1995).

94. A. J. Baker and T. W. Jeffries, *Status of Wood Hydrolysis for Ethanol Production*, Report of U.S. Department of Agriculture, Forest Service, for U.S. Agency for International Development Support Bureau, Office of Energy (TMR Authorization No. 81-89), Washington, D.C., June 1981.

95. U.S. Pat. 4,201,596 (May 6, 1980), J. A. Church and co-workers (to American Can Co.).

96. R. D. Ziminski, *paper presented at American Institute of Chemical Engineers Meeting, New Orleans, LA*, Nov. 1981.

97. D. R. Thompson and H. E. Grethlein, *Ind. Eng. Chem. Prod. Res. Dev.* **18**(3), 166 (1979).

98. G. T. Tsao and co-workers, *Lorre Biomass Conversion Conference*, Purdue University, West Lafayette, Ind., 1981.

99. R. S. Roberts, *Biotechnol. Bioeng. Symp.* **10**, 125 (1980).

100. *Enzymatic Hydrolysis of Cellulose to Glucose—A Report on the Natick Program*, U.S. Army, Natick Research and Development Command, Natick, Mass., Sept. 1981.

101. L. Spano, *J. Coatings Technol.* **50**, 71 (1978).

102. G. H. Emert, R. Katzen, R. E. Fredrickson, and K. F. Kaupisch, *Chem. Eng. Prog.* **76**(9), 47 (1980).

103. D. M. Jenkins and T. S. Reddy, *Economic Evaluation of the MIT Process for Manufacture of Ethanol*, DSE-3992-T1, National Technical Information Service, Washington, D.C., 1979.

104. R. Brooks, T.-M. Su, M. Brennan, and J. Frick, *Proceedings 3rd Annual Biomass Energy Systems Conference, Golden, CO*, SERI/TP-33-285, National Technical Information Service, Washington, D.C., June 1979.

105. R. H. Marchessault, S. Coulombe, T. Hanai, and H. Morikawa, *Monomers and Oligomers from Wood, Transactions of Technical Section of the TR52*, 1980; published in *Pulp and Paper Canada* **81**(6), 1980.

106. L. Jurasek, *Devel. Ind. Microbiol. 1978*, **177** (1979).

107. L. A. Underkofler and R. J. Hickey, *Industrial Fermentation*, Chemical Publishing Company, Inc., New York, 1954.

108. H. D. Turner, *For. Prod. J.* **14**, 282 (1964).

109. J. F. Harris, *Tappi* **61**, 41 (1978).

110. U.S. Pat. 4,280,878 (Oct. 30, 1979), G. E. Sprenger.

111. J. Rienks, *Forest Products Research Society Proceedings No. P-75-13*, Forest Products Research Society, Madison, Wisc., pp. 104–106, 1975.

112. J. Hartwig, *For. Prod. J.* **21** (1971).

113. A. J. Baker, "Charcoal," in R. C. Davis, ed., *Encyclopedia of American Forest and Conservation History*, Vol. 1, Macmillan Publishing Company, New York, 1983, pp. 73–77.

114. D. E. Earl, *A Report on Charcoal*, Food and Agriculture Organization of the United Nations, Rome, Italy, 1974.

115. *Federal Reserve Bulletin* **79**(12):A51, Board of Governors of the Federal Reserve System, Washington, D.C., 1993.

116. D. S. Powell, J. L. Faulkner, D. R. Darr, Z. Zhu, and D. W. MacCleery, *Forest Resources of the United States, 1992*, General Technical Report RM-234, U.S. Department of Agriculture, Forest Service, Rocky Mountain Forest and Range Experiment Station, Ft. Collins, Colo., 1993, 132 pp.

117. K. L. Waddell, D. D. Oswald, and Douglas S. Powell, *Forest Statistics of the United States, 1987*, Resource Bulletin PNW-RB-168, U.S. Department of Agriculture, Forest Service, Pacific Northwest Research Station, Portland, Oreg., 1989, 106 pp.

118. D. B. McKeever and K. C. Jackson, "Economic Importance of the Timber Processing Industries," in R. W. Haynes, coordinator, *An. Analysis of the Timber Situation in the United States, 1989–2040*, General Technical Report RM-199, U.S. Department of Agriculture, Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, Colo., 1990, Chapt. 4, pp. 59–78.

119. Executive Office of the President, Office of Management and Budget, *Standard Industrial Classification Manual, 1987*, National Technical Information Service, Springfield, Va., 1987, 703 pp.

120. *1991 Annual Survey of Manufactures*, Geographic Area Series, 1987 Economic Censuses compact disk, Vol. 1, Release 1E, Data User Services Division, U.S. Department of Commerce, Washington, D.C., 1993.

IRENE DURBAK
DAVID W. GREEN
TERRY L. HIGHLEY
JAMES L. HOWARD
DAVID B. MCKEEVER
REGIS B. MILLER
ROGER C. PETTERSEN
ROGER M. ROWELL
WILLIAM T. SIMPSON
KENNETH E. SKOG
ROBERT H. WHITE
JERROLD E. WINANDY
JOHN I. ZERBE
USDA Forest Service