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Swelling of wood

Part 1. Swelling in water

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Summary. The rate and maximum swelling of several North American wood species in water have been obtained with a computer interfaced linear variable displacement transformer. Since wood swells extremely fast in water even at room temperature, this apparatus made it possible for the first time, to obtain accurate rate data on the swelling of wood in water. The strict linear dependence of swelling on the temperature suggests a chemical mechanism. The activation energies obtained from Arrhenius plots ranged from 32.2 KJ/ mole for sitka spruce to 47.6 KJ/ mole for sugar maple. Although the two hardwoods exhibited greater maximum tangential swelling compared with the two softwoods, the maximum swelling appears to be correlated with the wood density. Generally both the rate and maximum swelling of the woods were increased by removal of extractives and the activation energies were reduced.

Introduction

The phenomenon of swelling is characteristic of all elastic materials but differs somewhat for different types of materials. A solid is said to swell when it takes up a liquid and at the same time fulfills the following 3 conditions (Nageli C. Von, 1854): (a) Its dimensions are increased with an accompanying thermal change as a result of the taking up of another phase, (b) It retains its homogeneity in a microscopic sense (c) Its cohesion is diminished but not eliminated, that is, it becomes soft and flexible instead of hard and brittle. The swelling of wood with liquids is of fundamental significance to a wide range of commercial and experimental processes. It is encountered whenever a substance is added or removed from the cell wall in a wide variety of applications of wood. These include such diverse processes as pulping, preservation, removal of extractives, dimensional stabilization and chemical modification. Future uses of wood for modified products now under development will necessarily involve some type of chemical modification of wood. Also further developments in the new solvent pulping processes will require more detailed information on the effect of organic liquids on wood. Surprisingly, accurate kinetic data on water swelling of wood has not yet been reported. We plan to ascertain important factors to wood swelling in water and organic liquids.

The swelling of wood as manifested by the external dimension changes vary with the species, structure, density, drying conditions, etc. The swelling of wood in both liquid water and water vapor has been studied extensively for the past 50 years. A number of scientists have made attempts to determine the factors that influence wood swelling in liquid water and organic solvents. The most extensive work on swelling of wood in liquid water was carried out by Stamm and coworkers (1964). They found a definite correlation of shrinking and swelling of wood with specific gravity and demonstrated this can be predicted by the following qualitative relationship:

$$S = f g \qquad (1)$$

where S is the total volumetric shrinkage from green to the oven-dry condition on a percentage basis, f is the fiber-saturation point on a percentage volume per unit weight basis, and g is the specific gravity of the wood on a swollen volume basis.

Woods high in water-soluble extractives were found to invariably shrink less than predicted by Eq. (1) (Stamm 1964). This is due to the bulking effect of the extractives which are left deposited in the cell walls. For example, unextracted redwood has a low apparent f value of about 18; but after extraction with water it rises to 25, which is almost the normal value (Stamm 1964). Other species high in extractives such as eastern red cedar, juniper and yew also showed this anomalous behavior due to extractives.

Stamm and coworkers (Stamm 1935, 1964; Stamm, Tarkow 1950) also evaluated the swelling of oven-dry white pine sections with a variety of organic liquids which had been carefully freed of water. Their results obtained with a series of aliphatic alcohols, esters and fatty acids demonstrated that the size of the molecule of the swelling liquid is an important consideration. An in crease in size not only decreased the swelling rate but the swelling equilibrium was also decreased due to the greater difficulty for the larger molecules to diffuse into the fine capillary structure of wood and cellulose.

Nayer (Nayer 1948; Nayer, Hossfeld 1949) performed the most thorough investigation on swelling of wood in organic liquids. He evaluated various possible predictive factors for wood swelling. He tried to correlate the volumetric swelling of thin-sections of wood in a large number of dry organic liquids against the dielectric constant, the dipole moment and the surface tension of the liquids. In general, poor correlations were obtained with the exception of benzene derivatives.

In early work, Hasseblatt (1926) also measured the maximum swelling of dried birchwood veneers in a variety of solvents. However, the organic liquids used by Hasseblatt were not free of water, and therefore, he reported erroneously high swelling values for birchwood. The presence of water has been found to significantly influence the swelling of wood in many organic solvents. Ishimaru and Sakai (1988) explained the enhanced swelling of wood in binary liquid mixtures from the standpoint of the activity of each constituent, that is, a positive deviation of the activity of a constituent from the ideal solution means the molecules have a higher secedeability from the cohesion force in the mixture compared to the pure liquid. Thus the constituent has a greater chance to attack adsorption sites responsible for the swelling of wood than that expected in pure concentration.

Gordy (1939, 1941) made some of the best correlations for swelling of wood in organic liquids. These were based on the tendency of the liquid to form hydrogen bonds with methanol. The tendency for the various compounds to form hydrogen bonds was determined by measuring the amount of shift of the characteristic vibration of the hydroxyl group in methanol by infrared absorption. Thus, solvents representative of the classes – nitrocompounds, esters, aldehydes, ketones, ethers, nitriles and amines – were employed and the results gave proof of the correlation of hydrogen bonding to wood swelling.

Rowell and Ellis (Rowell 1984; Rowell, Ellis 1984), in an investigation on the reaction of epoxides with wood, observed the dramatic effect of temperature on wood swelling for a series of organic solvents. Some solvents which did not swell wood at room temperature were found to dramatically swell wood at elevated temperatures.

Banks and West (West 1988; Banks, West 1989) measured rates of swelling of wood with temperature in a limited number of organic liquids. They assumed that the swelling was a bimolecular reaction merely requiring the collision of the solvent molecules with wood. They found that the rate of swelling in organic liquids showed a strong dependence on temperature which closeIy obeyed the classical Arrhenius equation (1889). Wood (Scots pine) swelling activation energies were calculated for a few solvents (KJ/mole): pyridine (46), acetone (48), quinoline (86) and pentanol (145). West proposed a “zipper” model for the movement of liquid water and organic liquids (associated) such as pyridine into wood structure to cause swelling. However, application of their technique with liquid water proved very difficult because of the very rapid swelling in water even at room temperature.

Ashton (1973), determined the effectiveness of dimethyl sulfoxide, dimethyl formamide, N-methyl pyrolidone and pyridine to swell yellow birch, beech, white pine and Douglas-fir wood. He found that birch was swollen the most by these solvents and pine the least, in relation to their densities. Also, beech and pine swelled more rapidly than Douglas fir, which was the most resistant. Dimethylsulfoxide (DMSO) caused the greatest final swelling but dimethylformamide (DMFA) swelled wood more rapidly. To swell wood effectively with DMSO required a vacuum impregnation process.

Ma and coworkers (1991) explored the empirical correlations between the mechanical properties of solvent-treated wood and solvent parameters. Wood beams of birch and Douglas-fir were soaked in five solvents (benzene, dioxane, methanol, DMSO, water) for 4 months at 23°. Acoustic emision (AE), modulus of rupture (MOR), and modulus of elasticity (MOE) of the specimens were correlated with the solvent strength parameter through acceptor number (AN), donor number (DN), and molar volume (MV). A linear correlation of the AE energy of the specimens with the solvent parameter $(AN + DN)^{1/2}$ was verified. All these observations reflect the changes in mechanical properties and microstructure of wood that take place throughout the process of wood swelling.

Only limited data are available for the cross-sectional swelling of cellulose fibers because of the time consumed in making a single accurate measurement and the need to measure a large number of fibers to obtain a reasonable average. Reported values of percent swelling of cotton, corrected for lumen area, ranged from 31 – 33% for cotton of different varieties and maturity and 65% for viscose rayon fibers (Stamm 1964; Moore et al. 1950; Welo et al. 1952). No such data has been obtained for wood pulp. These results are much lower than that for swelling of cellophane, which swelled 137% in volume in water. Essentially all of the water that enters voids results in swelling in this case (Stamm 1964, 1956).

Another method for determination of swelling of cellulose fibers is by measurement of the centrifuged water retention value (Hopner et al. 1955). This empirical method is frequently used because of simplicity, but it gives values which are too low for highly swollen pulps (Scallan, Caries 1972). The solute exclusion technique, introduced by Aggebrandt and Samuelsen (1964), has been the most widely utilized method in recent years. Stone and Scallan et al. (Stone, Scallan 1967; Stone et al. 1969; Scallan 1977) have applied the technique to determine the fiber saturation point of wood pulps using sugars and dextrans as the porous probe molecules. By measuring concentration changes for a series of solutions comprised of the molecules of different sizes, they were able to determine the amount of accessible and inaccessible water. They found a wide range of swelling for both rayon and cellophane samples with textile rayon swelling to a greater extent than tire cord rayon, but both much less than cellophane (Stone et al. 1969). Sulfite wood pulps were found to swell to a greater extent than kraft pulps. However, it is important to note that the large increases in the amount of water within the cell wall that accompanies pulping is not necessarily followed by a concomitant increase in swelling (Scallan 1977).

Robertson (1964) in Canada carried out an investigation on cellulose-liquid interactions and based his swelling interpretations on accessibility measurements of the cellulose using a technique of solvent exchange with thallous ethylate in benzene. He evaluated the effects of molar volume, volubility parameter and liquid dipole interactions on swelling of cellulose fibers. He concluded that molar volume is important to swelling. None of the experimental liquids having a molar volume greater than 100 cc increased the swelling of cellulose to any appreciable extent, even though, some of the liquids are capable of strong hydrogen bonding. Liquids which are strongly associated by the Bottcher (1952) or Pauling (1950) criterion (dipole interactions) do not increase the swelling of cellulose fibers appreciably if they are not capable of participating in hydrogen bonding. He found that hydrogen bonding liquids which are not associated (proton acceptors which do not have proton donor properties) form a second series of correlations in which the fiber swelling is correlated with cohesive energy density (volubility parameter). The remaining non-associated, non-hydrogen bonding liquids did not swell cellulose appreciably. Robertson noted with fibers, as did Nayer (Nayer, Hossfeld 1949) with wood, that some binary mixtures of liquids can produce more swelling than either component alone. This synergistic effect is particularly notable when water is one of the liquids.

Chitumbo and Brown (1974) found that temperature had a significant influence on the swelling of cellulose gels. The temperature increased cellulose swelling with some liquids, but decreased the swelling with others. Particularly notable was the dramatic effect of temperature on the swelling of cellulose gels in DMSO.

Lignin

The effect of lignin swelling on the swelling of wood has been given only cursory treatment by previous investigators (Saechtting, Zocher 1934). Schuerch (1952) found that the swelling and volubility of isolated lignin preparations could be fairly well predicted on the basis of volubility parameters. He found that those organic liquids with a volubility parameter close to 11.0 gave maximum swelling (solubility) in a particular solvent.

Stone and Scalan (1967), using the solute exclusion technique, noted that the cumulative pore volume (inaccessible water) for spruce pulps increased substantially as the wood was delignified up to 44% yield. Erickson et al. (1991) reported that the swelling of lignin containing pulps increased rapidly above 60 – 75°C while, lignin free samples of cotton and holocellulose showed no effect. They suggested that the increase in swelling above 60– 75 °C was due to the softening of the lignin, the flow of which makes additional swelling possible.

Obviously, the swelling of wood and wood polymers in liquids is a complex process influenced strongly by both the solvent and the wood substrate. Our broad investigation on swelling of wood is intended to ascertain the important factors to swelling in both water and organic liquids. In our work we plan to evaluate the influence of a wide variety of solvent factors such as molar volume, dipole interactions, surface tension, basicity, solvent strength parameters, etc. Substrate properties also to be evaluated include density, swelling contributions of cellulose, hemicelluloses, lignin and extractives, early/latewood effects, and interracial surface free energy. In this first paper we report on our initial studies of wood swelling in water. We have obtained, for the first time, accurate rate constants and activation energies for wood swelling in water by use of a computer interfaced linear variable displacement transformer with a controlled temperature sample vessel. The effects of species, density and extractives have been evaluated. In future publications we will report on the factors affecting the swelling of wood in organic liquids.

Materials and methods

Materials

Distilled water was used in the swelling experiments, Heartwood samples of Sitka spruce, Douglas-fir, sugar maple and quaking aspen were selected for the investigation. The samples were cut in the form of 25 (tangential) × 25(radial) × 5(longitudinal) mm pieces and oven-dried for 24 hours at 65 °C.

Sitka spruce *(Picea sitchensis)* had an average number of annual rings per cm of 10 in the air-dry state. The average specific gravity was 0.40. Sugar maple *(Acer* *saccharum)* had an average number of annual rings per cm from 5 to 10 in the air-dry state and the specific gravity varied from 0.66 to 0.72; the average was 0.68. Douglas-fir *(Pseudotsuga menziensii)* had an average number of annual rings per cm from 3 to 8 in the air-dry state. Note that with Douglas-fir two different experiments were carried out; the first (Douglas fir I) for wood samples having low densities (0.47 – 0.49) with an average of 3 rings/cm and another (Douglas-fir II) for wood samples having higher densities (0.56 to 0.61) with 10 rings/cm; quaking aspen *(Populus tremuloides)* had 12 annual rings per cm and the average specific gravity was 0.48.

Only tangential swelling was measured. The longitudinal direction was chosen to be the shortest one (5 mm) to accomplish complete penetration of water in a short time.

Methods

Five cross-sections each of spruce, fir, maple and aspen, prepared as described above, were swollen in distilled water at five different temperatures (23, 40, 60, 80 and 100 °C). All initial measurements were made at room temperature with a jaw-type vernier caliper, accurate to ±0.05 mm and with jaws sufficient to cover the full 25 mm block side of each wood sample. The ovendry cross-sections were transferred from the oven and cooled in a dessicator. The cooled ovendry weights and tangential dimensions were measured as quickly as possible. The samples were then inserted into the swelling apparatus which was a stainless steel vessel immersed in a constant temperature oil bath. The wood sample was placed in a stainless steel holder in the center of the vessel and contacted with the sensor of a computer interfaced linear variable displacement transformer (Fig. 1).

Water was preheated to the desired temperature for introduction into the preheated apparatus which was maintained at temperature throughout the experiment. Small intervals of time (1 – 6 seconds) were used in order to accurately determine the rate of swelling. Larger intervals of time were utilized for determination of equilibrium swelling. After the termination of each experiment, the wood cross-sections were air dried and then dried in oven for 48 hours at 65 °C for determination of the final weight.

The percentage swelling was calculated by the use of the equation:

$$\text{Percentage swelling} = \frac{(\text{Swollen Dim.} - \text{Oven Dry Dim.})}{(\text{Oven Dry Dimension})} \times 100$$

The rate and maximum swelling of extracted wood in water was also evaluated. A series of extractions were done to determine the best extraction procedure. An extraction with 80% ethanol was chosen as the most suitable since it gave the least swelling with suitable removal of the extractives. The ethanol extractions were carried out for 2 hours by immersion of the samples in the solvent. The wood samples were then dried in an oven for 48 hours at 65 °C. For sugar analysis the ethanol extracts were dried, hydrolyzed with 2 ml of 3% sulfuric acid and analyzed by high pressure liquid chromatography (HPLC).

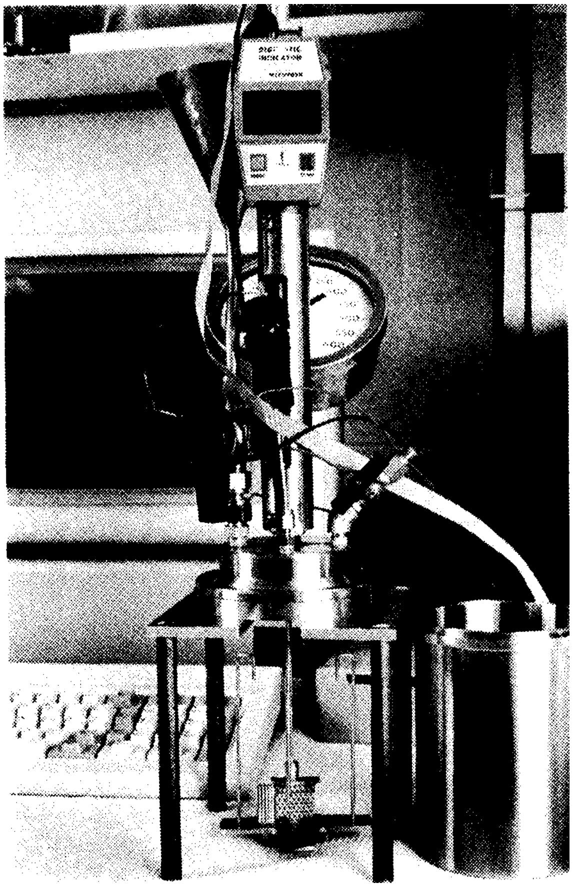

Fig. 1. Swelling apparatus with computer interfaced linear variable displacement transformer

Results and discussion

Figure 2 is a graph of a swelling profile of Sitka spruce. The increase in the tangential dimension in mm is plotted against time (min). A very small induction period is noted on the graph. This induction period was also noted by West (1988) in his study of the swelling of wood in organic solvents. The induction period is probably related to the time necessary for the initial diffusion of the liquid into the cell wall structure of the wood, however, West (1988) has suggested that the induction period reflects a gradual increase in the number of cell wall capillaries that participate in the swelling process as the liquid moves from the lumen into the cell wall and progresses slowly along in the fiber direction. To accommodate this induction period, Banks and West (1989) calculated a time to one-half swell (t 1/2). The maximum equilibrium swelling is reached after about six hours of swelling in water at 23 °C.

Figure 3 is a typical plot of the percent tangential swelling versus time (hrs) for quaking aspen. Even at room temperature (23 °C), there is a very rapid swelling of wood in water as noted in the initial linear portion of the plot. Figure 4 is

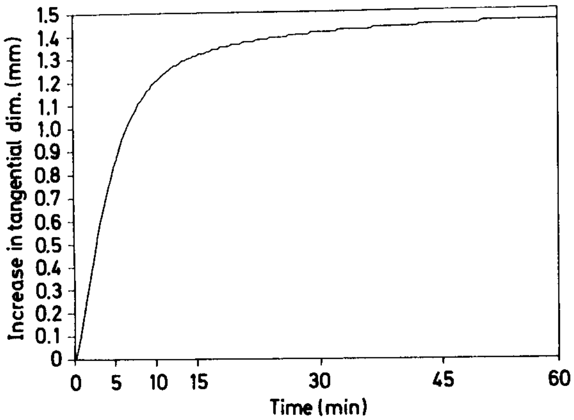

Fig. 2. Swelling of Sitka spruce in water at 23 Celsius

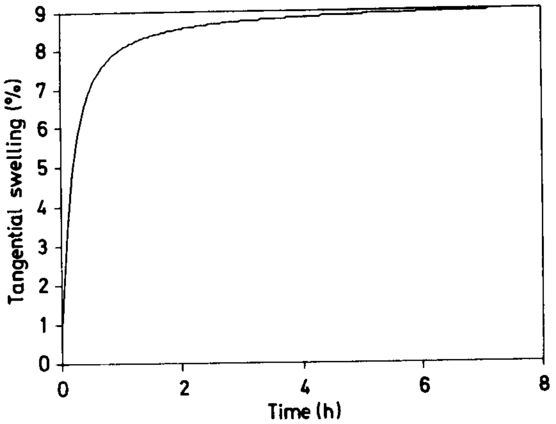

Fig. 3. Swelling of quaking aspen in water at 23 Celsius

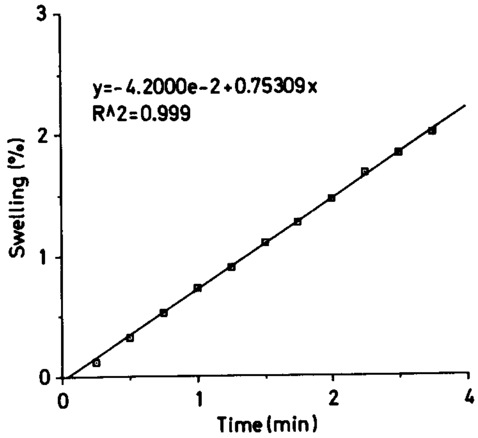

Fig. 4. Initial linear swelling of quaking aspen in water at 23 Celsius

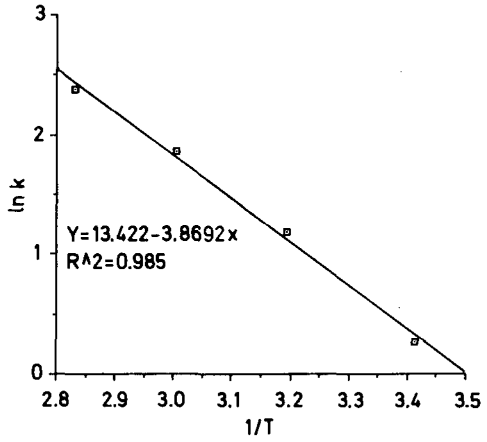

Fig. 5. Plot of ln k vs. 1/T for calculation of activation energy of swelling of Sitka spruce in water

a detailed plot of this initial linear portion of the plot but at an interval time of fifteen seconds. A swelling rate constant, k, is then derived from the slope of this curve. The activation energies, Ea, are calculated from the standard Arrhenius equation:

$$k = Ae^{-Ea/RT}$$

where A = constant,
R = gas constant,
T = temperature, degrees Kelvin

with a typical plot shown Fig. 5, in this case for Sitka spruce in water.

Swelling of unextracted wood in water

The results in Table 1 show the maximum tangential swelling, the rate of swelling, and the activation energies of unextracted wood in water at various temperatures. The total time of swelling is the time required to reach an apparent equilibrium and is presented in the parentheses. The results show the tremendous increase in the rate of swelling of wood that takes place as the temperature is increased up to 100 °C. The temperature dependence of wood swelling in water very closely obeyed the Arrhenius equation which strongly suggests that the phenomenon of wood swelling is an activated process similar to a classical chemical reaction. The strong correlation between the hydrogen bonding ability of a liquid and its swelling capacity for wood noted previously by Stamm (1964), suggests a hydrogen bond breaking mechanism for wood swelling. A bimolecular process is most likely, whereby the liquid forms a transition state with the hydrogen bonded hydroxyl groups in wood (West 1988). The transition state then collapses to give a molecule of liquid attached by a hydrogen bond to wood. Therefore liquids with strong hydrogen bonding potential would be expected to swell wood to the greatest extent. Evaluation of surface free energies of various wood species with a variety of liquids should provide valuable information for interpretation of swelling mechanisms of wood.

Table 1. Rate of swelling and maximum tangential swelling of wood in water

Maximum Tangential Swelling, %, (time, hrs)	Sitka spruce	Douglas fir I	Douglas fir II	Sugar maple	Quaking aspen
23	6.5 (1)	7.6 (8)	8.7	10.0 (2)	9.1 (8)
40	6.9 (1)	7.7 (5)	8.8	10.8 (1)	8.9 (3)
60	6.9 (1/2)	7.7 (3)	9.0	11.5 (2/3)	9.4 (2)
80	7.2 (1/3)	8.0 (2)	9.1	11.5 (1/2)	9.6 (1)
100	7.3 (1/5)	8.1 (2)	9.3	12.3 (1/3)	10.1 (2/3)
Swelling Rate, k					
23	1.3	0.3	0.7	0.3	0.8
40	3.3	0.9	1.4	1.1	2.1
60	6.5	1.8	3.1	3.6	5.9
80	10.8	4.7	4.2	6.6	14.4
100	14.8	6.9	5.8	7.6	20.4
Activation Energy Ea, kJ/mole	32.2	38.9	33	47.6	44.7

The equilibrium time significantly decreases as the temperature is raised, for instance, with aspen, it decreased from 8 hours at 230 to 40 minutes at 1000. The data show that the equilibrium swelling of hardwoods in water was greater than that of softwoods (spruce averaged from 6.5 to 7.3%, Douglas fir from 7.3 % to 9.3%; sugar maple varied from 10.0 to 12.0% and aspen from 9.1 to 10.0%). This is very likely due to the higher density of hardwoods. A relatively linear relationship is shown for plots of the maximum tangential swelling both within (Fig. 6) and between (Fig. 7) wood species versus wood density at 23 °C. This is consistent with Stamm's earlier work (Stamm 1964). Also, the higher density hardwoods had much greater activation energies for swelling in water than those of the low density softwoods (Table 1). The Ea for the hardwoods ranged from 44 – 47.6 KJ/ mole,

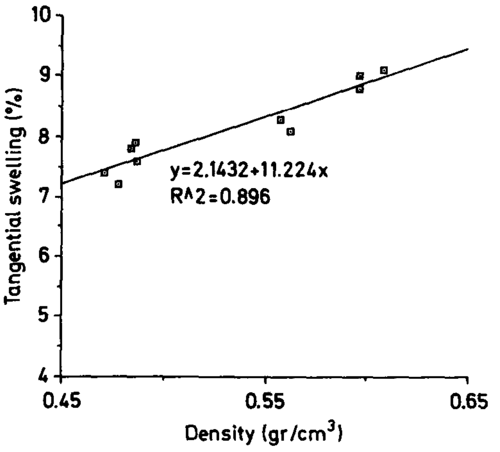

Fig. 6. Maximum tangential swelling of Douglas fir in water at 23 Celsius versus wood density

while the Ea for the softwoods was in the range of 32.2 – 38.9 KJ/mole. Using some of Stamm's earlier published data on swelling of Sitka spruce in water, we calculated an Ea of 36.4 KJ/mole (Stamm 1952) in good agreement with the results reported in this work. In another study by Stamm (1959) on the related process of bound water diffusion in wood, an Ea of 50.2 KJ/mole was calculated from the variation of the diffusion coefficient with temperature in the range of 3.5 – 56.5 °C. The reasonable agreement of the activation energies obtained by the different methods verifies the relationship between diffusion and swelling.

It should also be noted that the maximum tangential swelling increases slightly as the swelling temperature is increased as shown in Fig. 8. This may be linked to minor changes in the cell wall structure when wood is treated with high temperature liquids. This will be further discussed in the next section.

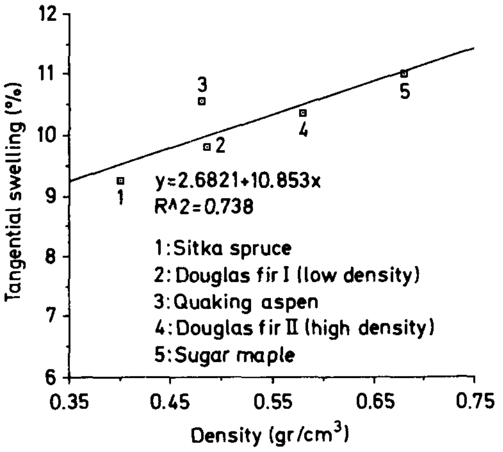

Fig. 7. Maximum tangential swelling of wood in water at 23 Celsius versus wood density

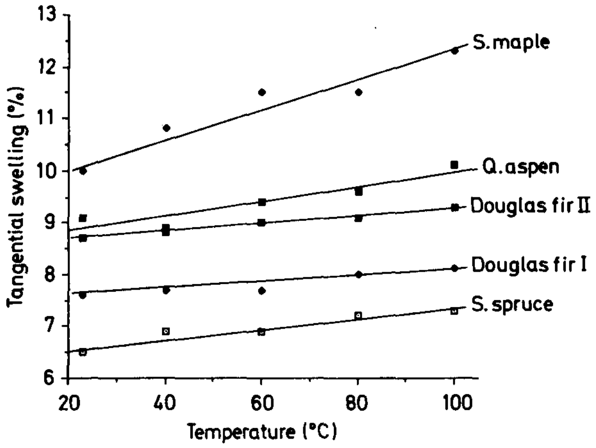

Fig. 8. Maximum tangential swelling of wood in water versus temperature

Effect of extractives

An attempt was made to evaluate the relative influence of extractives on the swelling of wood. In general, removal of extractives has been found to enhance swelling significantly especially in species which have a large percentage of extractives (i.e., pines and other conifers). Extractives (terpenes, fats, phenols, fatty acids, tannins, etc.) are not considered to be structural components of wood. Generally, the overall percent of the extractives in wood varies from 2 to 10% with the exception of some tropical wood species (20 – 25%). In this work a series of extractions were performed to determine which procedure provided the least modification to the wood structure with a reasonable removal of the extractives. We decided to avoid an extraction procedure which involved a boiling water step. Apparently, boiling water causes significant changes in wood structure since hemicellulosic substances are removed from the cell wall.

Tables 2 and 3 present the results obtained from the extractions. Table 2 shows the weight losses and the tangential dimensional changes that took place in the wood samples after the extractions. Six different extraction procedures were utilized. The results are the average of five wood cross-sections for each extraction procedure. Table 3 presents the results obtained after an extraction with 80% ethyl alcohol for two hours. This is the extraction procedure we selected because the extractive removal, 2 – 4% for all species, was sufficiently large to be representative of the range of extractives in the wood but the dimensional changes were minimal.

Table 2. Extraction of wood by different methods

Extraction Procedures:	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)	6 (%)
Weight Losses:						
Sitka spruce:	−6.9	−6.9	−3.8	−1.1	−0.1	−1.6
Douglas fir:	−2.5	−3.5	−2.2	0.4	−0.6	0.3
Sugar maple:	−5.8	−5.1	−0.6	0.5	−0.4	−0.1
Quaking aspen:	−3.2	−4.1	−1.5	−0.2	−0.1	−1.8
Tangential Dm changes:						
Sitka spruce:	−2.8	−1.9	−0.5	−0.6	0.4	−0.3
Douglas fir:	−1.1	0.6	0.6	0.2	0.5	0.1
Sugar maple:	−2.7	1.6	1.7	0.9	0.3	0.8
Quaking aspen:	−0.9	−0.7	−0.3	0.2	0.7	0.4

***Notice: (+, positive): % of swelling or weight gain
(−, negative): % of shrinkage or weight loss

1: Extraction with Benz/EtOH(2:1), boiling Water, Acet/Water (9:1), 4 + 4 + 4 hrs
2: Extraction with Benz/EtOH(2:1), boiling Water, 4 + 4 hrs
3: Extraction with Benz/EtOH(2:1), 95% EtOH, boiling Water, 4 + 4 + 3 hrs
4: Extraction with Benz/EtOH(2:1), Acet/Water (9:1), 4 + 4 hrs
5: Extraction with Benz/EtOH(2:1), 4 hours
6: Extraction with Benz/EtOH(2:1), 95% EtOH, 4 + 4 hours

Table 3. Extraction of wood with 80% ethanol for two hours

Wood species	Weight	Tangential Dimension	Radial Dimension	Longitudinal Dimension
	change (%)	change (%)	change (%)	change (%)
Sitka spruce	−3.6	−1.2	−1.1	1.3
Douglas-fir	−2.5	−0.6	−0.9	1.1
Sugar maple	−2.4	−0.6	−0.8	1.2
Quaking aspen	−2.1	−0.2	−0.7	2.4

Notice: (−, negative): weight loss or % shrinkage
(+, positive): % swelling

Table 4. Relative sugar composition (HPLC) of ethanol (80%) extracts from wood

Species	Glucose	Mannose	Galactose	Xylose	Arabinose[a]
Quaking aspen	38.2	4.0	8.5	9.1	40.1
Sugar maple	76.0	3.3	3.2	2.8	54.3
Sitka spruce	2.6	1.6	9.0	2.2	84.6
Douglas-fir	4.3	4.7	22.0	14.7	14.8

[a] Rhamnose was not resolved from the arabinose peak but rhamnose is less than 10% of the combined arabinose/rhamnose total

Table 5. Rate of swelling, maximum tangential swelling and activation energies of swelling of unextracted and extracted wood

	Sitka spruce		Douglas-fir I		Douglas-fir II		Sugar maple		Quaking aspen	
	Unextr.	Extr.	Unextr.	Extr.	Unextr.	Extr.	Unextr.	Extr.	Unextr.	Extr.
Swelling Rate, k (Temp., C)										
23	1.3	7.2	0.3	0.16	0.7	0.28	0.3	0.9	0.8	0.8
40	3.3	14.9	0.9	1.2	1.4	0.8	1.1	4	2.1	2.6
60	6.5	25.8	1.8	1.4	3.1	1.5	3.6	7.1	5.9	5.4
80	10.8	32.4	4.7	3.2	4.2	3.7	6.6	16.7	14.4	8.7
100	14.8	36.2	6.9	3.4	5.8	5.5	7.6	20.7	20.4	13.8
Maximum Tangential Swelling, (%)										
23	6.5	7.4	7.6	9	8.7	9.7	10	10.7	9.1	9.5
40	6.9	7.5	7.7	9.1	8.8	9.7	10.8	11.6	8.9	9.4
60	6.9	7.7	7.7	9.1	9	9.8	11.5	11.4	9.4	9.5
80	7.2	7.7	8	9.1	9.1	9.8	11.5	11.2	9.6	9.5
100	7.3	7.7	8.1	9.2	9.3	9.9	12.3	11.3	10.1	10
Activation energy, Ea, KJ/mole	32.2	23.3	38.9	41.5	33	35.4	47.6	42.3	44.7	36.9

However, as shown in Table 4, there still was a significant quantity of sugars removed in the procedure. It appears that the sugars are derived primarily from the hemicelluloses in the cell wall; which implies that the cell wall structure has been disrupted in the extraction procedure.

According to Stamm and Loughborough (1942) extractives present in wood may be divided into two classes: (a) extractives deposited in the coarse capillary structure and (b) extractives deposited in the cell wall structure. Extractives belonging to class (b) would have a definite influence on the swelling and shrinking of the cell wall, and therefore, would affect the swelling and shrinkage of wood as evidenced by the changes in external dimensions. It is evident that the extractives and their removal can considerably influence the rate and maximum swelling of wood. Indeed, as shown in Table 5 and Fig. 9 and 10, the rate of swelling of wood considerably increased after removal of extractives and the maximum equilibrium swelling generally increased on the average by 5 – 10%. Additionally, it was found that removal of extractives from wood caused a large decrease in the activation

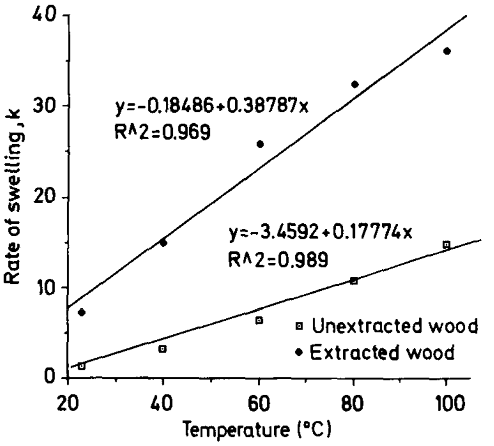

Fig. 9. Swelling rate versus temperature for Sitka spruce in water for unextracted and extracted wood

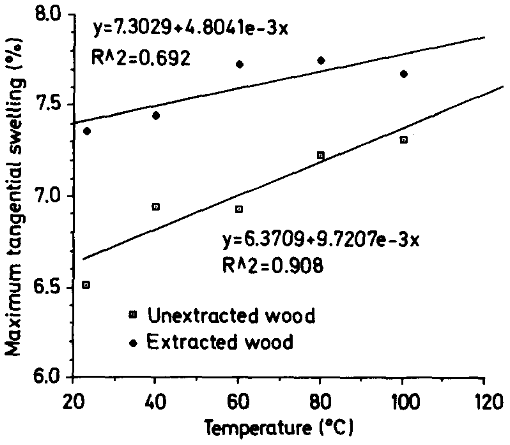

Fig. 10. Maximum tangential swelling versus temperature for Sitka spruce in water for unextracted and extracted wood

energy, that is, the swelling of extracted wood was much more facile. Since the activation energy, Ea, mainly represents the energy required to break the wood hydrogen bonds, it appears that the removal of the extractives, even with mild procedures, disrupts the internal structure of the cell wall, decreasing the network of secondary bonds, such that the cell wall structure is in a more loosely bonded state. This further suggests that either the extractives serve a role in the cell wall structure or the solvent used for removal is itself disruptive to the cell wall; probably both effects are operative. This interpretation is consistent with the observation that cell wall sugars are also removed in the extraction procedure (Table 4). However, a part of this energy is contributed from the energy required to pull a solvent molecule momentarily away from the bulk of the liquid (West 1988).

Conclusions

Activation energies for the swelling of wood in water have been accurately evaluated for the first time. Raising the water temperature above room temperature significantly increased the rate of swelling of wood. Also, an increase in water temperature caused an increase in the maximum equilibrium swelling of wood. It was ascertained once again that a removal of extractives caused an increase in the maximum equilibrium swelling of wood in water. It was also found that removal of extractives caused a large decrease in the swelling activation energy, Ea, for spruce, maple, and aspen.

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