

## Wood-Water Interactions as Affected by Chemical Constituents of Woods

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The results indicate that the chemical constituents of woods have considerable effects on wood-water interactions. Pine, poplar and eucalyptus woods show more or less expected swelling properties. However, cedar, which has the highest density, shows considerably less swelling (6.3 %) and very low activation energy (21.4 KJ/mol) compared with other woods. This clearly reveals cedar's chemical composition contributes to its anomalous swelling behaviour in water. The results prove the potential use of the chemical constituents of wood in predicting the swelling and water-sorption properties on the basis of its both density and chemical composition. However, cellulose content can be better predicted by the activation-energy relationship of different woods. A significant increase in the water sorption and swelling properties was observed in the four different wood species after the removal of their extractives.

**Key Words: Poplar, Cedar, Pine, Eucalyptus, Activation energy, Swelling, Cellulose, Extractives.**

### INTRODUCTION

Woods are composed of cellulose, lignin, hemicelluloses and minor amounts of extraneous materials (1-10 %) within a cellular structure. Variations of these components and differences in their structure are reflected in the anisotropic properties of wood. However, important cell-wall constituents are hygroscopic in nature and their moisture sorption capacity depends on their hydrophilic properties as well as accessibility of water to the polymer chains. Because hygroscopic expansion of the cell wall (swelling) occurs between the chains, it has no influence on the lengths of the polymer chains<sup>1</sup>.

In general, hydroxyl sites in hemicelluloses and lignin are easily accessible to water molecules because of their branched structure. This is also the case for the amorphous part of cellulose, but the crystalline part is not accessible by water<sup>2,3</sup>.

Water entering the cellulose forces the chains apart causing swelling. The  $S_2$  layer has the most dominant influence on dimensional changes, because it has *ca.* 60-80 % of the cell wall by volume. However, woods usually swell more in the transverse than in the longitudinal direction. These variations can be attributed to the  $S_2$  layer microfibril arrangements and the modification of the  $S_1$  and  $S_3$  layers with their transverse microfibril angles<sup>4,5</sup>.

Siau<sup>1</sup> presents the following equation to estimate the per cent volumetric swelling of wood:

$$\Delta S = S_o G_o (0.01 R_a) \quad (1)$$

where  $\Delta S$  = total swelling,  $S_o$  = oven-dry volume,  $G_o$  = oven-dry specific gravity,  $R_a$  = moisture content.

For any moisture content, the eqn. 1 can be rewritten as

$$S_1 = S_o (1 + 0.01 R_a G_o) \quad (2)$$

At fiber-saturation point, the maximum swollen volume ( $S_f$ ) may then be calculated as

$$S_f = S_o (1 + 0.01 R_f G_o)$$

or

$$S_f = S_o (1 + 0.28 G_o) \quad (3)$$

where  $S_1$  = volume at any moisture content,  $G_o$  = oven-dry specific gravity,  $R_f$  = fiber-saturation point (assumed as 28 %),  $S_f$  = volume at fiber-saturation point.

The eqns. 1-3 clearly show that the swelling of wood is closely related to its specific gravity, assuming constant fiber-saturation point and lumen size. However, these equations are based on theoretical considerations and the assumptions are only partially true. Moreover, the swelling of wood represents a phenomenological parameter, which is not exclusively characterized by its physical properties alone but also by its chemical reactions<sup>2,6,7</sup>.

Wood-wetting phenomena may be defined as molecular interactions at the interface between liquids and solids (wood) in direct contact with each other. Because wood is a cellular structure having many openings such as lumens and pits, it can be considered a porous, capillary medium. Hence, the primary routes for liquid penetration into wood are by these openings (lumens and pits). Rowell<sup>3</sup> has proposed that water moves through wood by forcing cell-wall polymers apart as in a 'zipper'. Ishimaru *et al.*<sup>7</sup> found that the radical group, hydrophobic nature and steric factor of the molecules in the swelling agents affect the swelling anisotropy of wood to some extent.

The objective of this study is to discuss some of the most common concepts of wood-water interactions in the context of the chemical constituents and swelling properties of woods. Simplifications and assumptions

can not always predict the swelling properties of woods. Because the chemical constituents of the cell wall have considerable effects on wood-water relationships, their importance in predicting the wood-water interactions of four different species are discussed herein.

### EXPERIMENTAL

Black pine (*Pinus nigra*, Arnold), cedar (*Cedrus libani*, A.Rich), poplar (*Populus canadensis*) and eucalyptus (*Eucalyptus camaldulensis* Dehn) woods were selected for investigation. The eucalyptus woods were obtained from the Tarsus-Karabucak Forests and other wood samples were acquired from the Isparta region in Turkey. The samples were cut in the small pieces and dried in an oven at 50 °C before the experiments. The oven-dry density of woods was calculated as 0.39, 0.48, 0.58 and 0.60 for poplar, eucalyptus, black pine and cedar, respectively.

The chemicals used in this study were purchased from Carlo Erba Co. (Spain) with a purity of 95-99 %, otherwise noticed. The lignin content (klason lignin) of wood samples was determined using the Tappi Test method T-222-om-06. Extraction with 80 % ethanol-95 % benzene (1:2 v/v) system was chosen for the determination of extractive contents. The extractions were carried out for 6 h. The hot water-soluble and cold water-soluble extractives were determined using the Tappi Test Method T-207-om-93.

The swelling measurements were made with a digital Mitutoyo-500 calliper, accurate to  $\pm 0.02$  mm. After the termination of each experiment, the woods were dried in an oven for 48 h at 105 °C ( $\pm 5$  °C) for determination of the final weight.

The activation energy (tangential) (EA) for the individual species was calculated using the method developed by Mantanis<sup>8</sup> and Sahin<sup>9,10</sup>. With this approach, the Arrhenius equation was used to predict the EAs of wood samples in water.

The surface hydrophobic properties of wood samples were evaluated by the sessile droplet method. In this approach, 5  $\mu$ L of deionized water was placed on the tangential surface and the shapes of the droplets indicated the surface-energy level. A sustaining 1 min angle ( $\theta$ ) between the water and wood surfaces was indicative of good hydrophobic characteristics.

### RESULTS AND DISCUSSION

The comparative chemical composition of two hardwood (poplar and eucalyptus) and two softwood (pine and cedar) species are shown in Table-1. It is observed that poplar and eucalyptus have marginally similar chemical constituents, whereas cedar has considerably higher lignin (35.7 %) and lower holocellulose (52.4 %) content than others. However, pine and cedar also have considerably higher extractive content (10.7 and 11.9 %, respectively)

than poplar and eucalyptus woods (2.5 and 2.6 %, respectively). It has already been predicted by a number of researchers that wood having different chemical constitutions could influence water-wood interactions<sup>3,6,7</sup>. Hence, it is assumed that the chemical variations might influence the wood-water interactions to some degree in addition to affecting the physical characteristics (density) of woods.

TABLE-1  
CHEMICAL COMPOSITION (%) OF WOODS

Woods	Holo-cellulose	Cellulose	$\alpha$ -Cellulose	Lignin	EtOH-Benzene extract	Cold water extract	Hot water extract
Poplar	78.6	49.2 <sup>a</sup>	42.8 <sup>a</sup>	18.9	2.5	N/A	< 0.5
Eucalyptus	77.5	–	41.0 <sup>b</sup>	19.9	2.6	0.6	1.2
Black pine	65.5	55.7 <sup>c</sup>	46.8 <sup>c</sup>	23.8	10.7	3.0 <sup>c</sup>	4.7 <sup>c</sup>
Cedar	52.4	48.5 <sup>c</sup>	37.9 <sup>c</sup>	35.7	11.9	4.0 <sup>c</sup>	8.7 <sup>c</sup>

Data from <sup>a</sup>Ref. [11], <sup>b</sup>Ref. [12], <sup>c</sup>Ref. [13].

The per cent maximum equilibrium swelling (MES) of woods in the tangential direction at four different temperature levels are shown in Fig. 1. It can be realized that increasing temperature usually effects swelling positively on all woods. It is likely cell-wall chemicals undergo modification at elevated temperatures and affects swelling positively. These are good agreement with the results reported swelling properties for various woods by Mantanis and coworkers<sup>14</sup> and Sahin<sup>10</sup>. However, the highest MES (average) occurred in pine (10.5 %) followed by eucalyptus (9.7 %), poplar (7.6 %) and cedar (6.3 %), respectively. But, this is not expected because cedar has the highest density (0.60 g/cm<sup>3</sup>) but showed the lowest dimensional changes compared to others. Although a number of researchers have already reported a definite relationship between swelling and specific gravity of woods<sup>1,15</sup>. This information may be true only for poplar, eucalyptus and pine woods, as realized in this study.

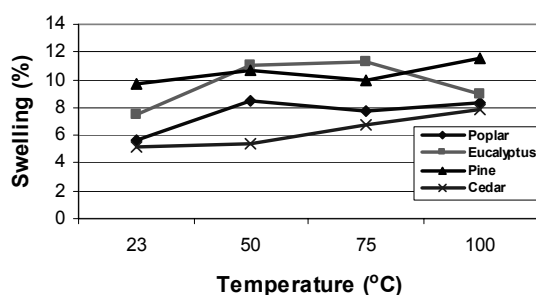


Fig. 1. Maximum equilibrium swelling of woods at different temperatures

As stated in the introduction section, the swelling of wood represents a phenomenological parameter, which is characterized by both its density and chemical interactions. Hernandez<sup>16</sup> reported that after wood density, the extracted fraction was the most significant variable and that it negatively affects the tangential swelling of tropical hardwoods. This may also be the case for other woods that have a very high extractive content, such as cedar. However, it is also well known that lignin and extractives are less hydrophilic than carbohydrates. It has been reported that the bulky methoxyl groups obstruct water from accessing the hydroxyl regions in lignin, where hydrogen bond formation is anticipated and this further lowers the water penetration<sup>17</sup>. This information can be useful in the case of cedar, which has the highest extractive (11.7 %) and lignin (35.7 %) content and these variations might make cedar swell less in water. It was speculated that the anomalous wood swelling primarily on extractives<sup>1,3</sup>. The results found for cedar clearly consisted with this information.

It has been proposed by Mantanis<sup>8</sup> and Sahin<sup>10</sup> that the rate of wood swelling with temperature could be quantitatively determined and that the activation energy (EA) may be obtained from the Arrhenius equation.

Fig. 2 shows the EAs of woods determined according to the Arrhenius kinetic model. Pine has the highest EA of 31.3 kJ/mol followed by poplar (30.7 kJ/mol), eucalyptus (29.3 kJ/mol) and cedar (21.8 kJ/mol), in that order.

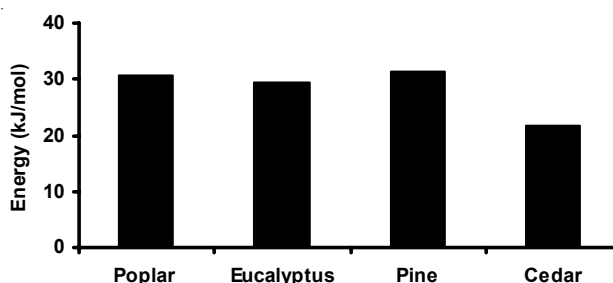


Fig. 2. Activation energies of woods in water

This suggests that maximum equilibrium swelling and activation energy are independent of each other and that swelling in the case of pine is more difficult than in other species, whereas cedar swells most easily. It has been predicted that hardwoods and more dense woods usually have higher activation energy than lower density woods and softwoods<sup>3,8</sup>. However, experimental results indicate more-or-less similar findings for all woods except cedar, which has a higher density but still has the lowest maximum equilibrium swelling and activation energy compared to the other woods. This is probably related to its chemical structure, especially its high

extractive and lignin content. Hence, a number of researchers suggest that density is not always useful for determining the swelling properties of woods with high extractive contents and other properties should also be considered, especially chemical constituents and morphological heterogeneity<sup>2,6</sup>. The extractives deposited in the cell-wall structure may have an influence on the rate of swelling. Siau<sup>1</sup> and Rowell<sup>3</sup> have reported that woods high in extractive content usually show anomalous swelling properties. The results found for cedar correlated with this information.

A number of researchers have reported that the quantification of cell-wall constituents might be useful for evaluating the wood-water phenomenon<sup>8,10</sup>. In this respect, The calculated activation energies vs. chemical constituents of different woods are presented in Figs. 3-5.

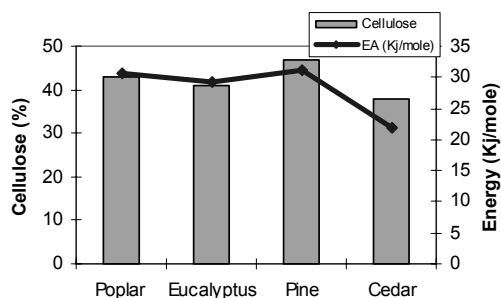


Fig. 3. Cellulose content and activation energy relations of woods

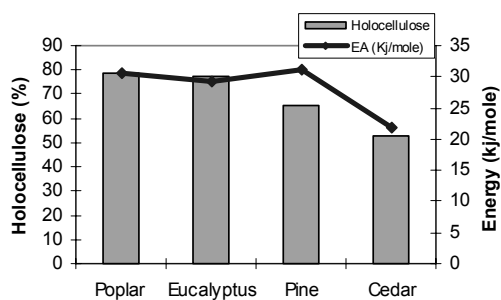


Fig. 4. Holocellulose content and activation energy relations of woods

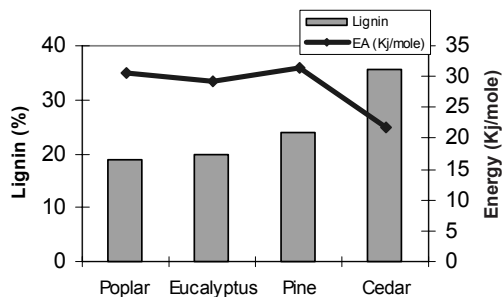


Fig. 5. Lignin content and activation energy relations of woods

It appears that cellulose (Fig. 3) has better swelling and activation energy properties compared to holocellulose (Fig. 4), because holocellulose contains, in addition to cellulose, various short-chain pentoses and hexoses of hydrophilic nature. Moreover, the chemical composition and types of hemicellulose vary, depending on the species and isolation process. Hence, the determination of all carbohydrate compounds is very complicated and not easy to evaluate. In addition, the main hemicellulose in softwoods is galactoglucomannan (20 %), with a small amount of arabinoglucuronoxylan (5-10 %) and arabinogalactan. However, the main hemicelluloses in hardwoods are glucuronoxylan (15-30 %) and a little amount of glucomannan (2-5%)<sup>18,19</sup>. Moreover, some wood polysaccharides are extensively branched and readily soluble in water. This is also another reason for the variations in the sorption properties of wood in water. Because variations in structures, such as the position of the glycosidic bonds and the substituted groups on the main chain, can influence interactions with water.

Lignin, which is less hydrophilic than hemicellulose and cellulose, shows variable relations and appears negatively correlated with the activation energies (Fig. 5).

It was reported by Dourado *et al.*<sup>20</sup> that cellulose/water/cellulose free-energy interactions were positive, regardless of the crystallinity of cellulose. This implies that the cellulose surfaces have a hydrophilic character. Sakai and Ishimaru<sup>21</sup> found that the sorption sites of cellulose were almost homogeneous; therefore, adsorption onto cellulose could not be affected by surface heterogeneity. With this information, it is reasonable to predict the EAs and swelling properties of woods with cellulose rather than holocellulose and lignin.

It has already been well predicted that extractives could have an important role during wood swelling. They might influence the surface energy of the cellular structure (fibers). For verifying this assumption, sessile droplet contact angle method was used to determine the surface hydrophobic properties (Fig. 6). The poplar, eucalyptus and cedar wood surfaces are very hydrophilic and did not show a measurable angle. However, pine shows a sustaining angle around 30° (Fig. 6b). It can be explained by the presence of some resinous compounds in pine, which accounts for the fact that resinous, extractive generated fiber surfaces are more-or-less hydrophobic in character. However, the change in dimensions by exposure to water is complicated, as also the solubility of the extractives in water. This is another clear evidence that wood-water interactions are not only related to the species and the density of the corresponding woods but also to the chemical constituents.

Fig. 7 shows the comparative water absorption of wood samples at four different temperature levels. As expected, there is no correlation between swelling and water absorption. However, carbohydrate content

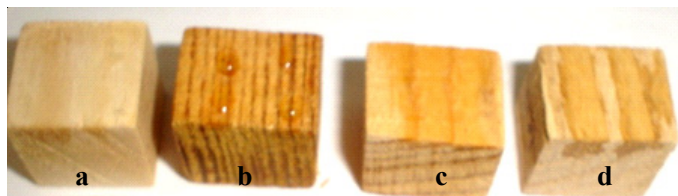


Fig. 6. Surface hydrophilic properties of woods (a: poplar, b: pine, c: cedar, d: eucalyptus)

and water-sorption properties of woods appear closely related. It has already been stated above that the holocellulose content is the highest in poplar followed by eucalyptus, pine and cedar. A similar trend is observed for the water-sorption properties of woods excluding cedar. The highest water sorption at room temperature is found in poplar (177.2 %) followed by eucalyptus (116.1 %), cedar (101.4 %) and pine (90.0 %). Pine shows less water-sorption properties probably due to the presence of resinous compounds in its cellular structure. Avramidis and Iliadis<sup>22</sup> have reported that the chemical composition affects the wood-moisture interaction. Hence, it is clear that chemical constituents and water sorption have a close relationship.

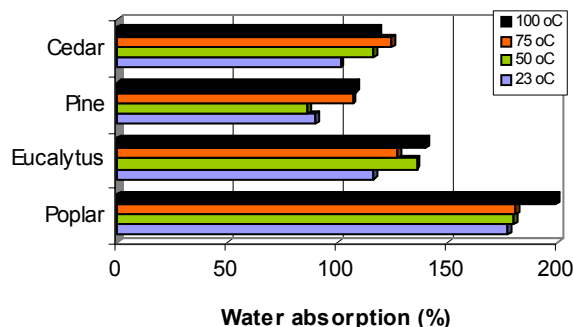


Fig. 7. Water absorption (%) of woods at different temperatures

However, it is observed that increasing temperature usually increases water sorption of woods (Fig. 7). The maximum water sorption usually occurs at 100 °C and is *ca.* 10-23 % higher than room temperature absorption. The increase of wood water sorption on the temperature clearly suggests a chemical mechanism occurring during the water-wood interaction. These can be attributed to the creation of new adsorption sites that are created with heat. Moreover, other phenomena such as structural modifications and chemical changes of extractives, lignin and carbohydrates might make available further H-bonding sites for water. The data from previous research and the experimental findings in this study support this suggestion<sup>9,10</sup>.



Fig. 8 indicates water sorption of unextracted and extracted samples at 100 °C. Apparently removing extractives causes considerable variation in the water sorption of woods. The water absorption further increases approximately by 18 % for poplar, 31.5 % for eucalyptus, 44 % for pine and 16.9 % for cedar, respectively.

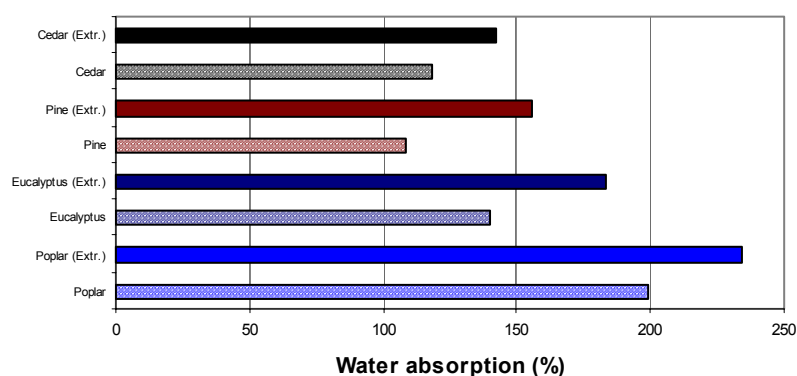


Fig. 8. Water absorption (%) of unextracted and extracted woods at 100 °C

It is reasonable to conclude that wood constituents considerably effects on wood-water sorption variations. The removing extractives in cell wall cavities make easy to water molecules diffusing into wood, creating further binding sites. The increased water sorption with temperature and further sorption with extracted free woods verify this assumption.

### Conclusion

The experimental findings showed that wood density alone can not be used for predicting the swelling and EAs of woods. Other phenomena such as structural modifications and chemical changes of the cell-wall constituents also play an important role. Increasing of wood swelling and water sorption with increasing temperature can be attributed to the cell-wall modifications. This increase is probably related to the creation of new adsorption sites simultaneously with lignin softening as well as hemicellulose and extractive solubility in water.

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