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EXPERIMENTAL DETERMINATION OF THE ANISOTROPIC SWELLING AND WATER SORPTION PROPERTIES OF CHESTNUT WOOD

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ABSTRACT

It was realized that the swelling rate coefficients increases significantly with extractive free chestnut wood-water systems resulting the initiation of the swelling process displaced towards shorter times, had lowering activation energies (Ea). The Ea of unextracted and extracted free chestnut was found to be 38.4 and 19.5 kj.mol^{-1}, respectively.

The measured maximum water absorption for unextracted samples was ranged from 141.8 % at 23 °C to 161.0 % at 100 °C. However, at similar temperature level, the further increased water absorption was realized for extracted samples. It ranged from 147.7 % at 23 °C to 179.1 % at 100 °C. These features could be mainly attributed to modify cell wall chemical components resulting in a greater ease of diffusion and increase potential sites for water molecules.

KEY WORDS: chestnut, transverse direction, swelling coefficient, activation energy, lignin, extractives, cellulose, water sorption

INTRODUCTION

The wetting of wood is represented water molecule bound to the cell wall. Because of the bipolar nature of water, other water molecules could be bonded to the cell wall (hydroxyl groups) and form hydrogen linkages to produce hydration layers in wood. It was reported that the average number of hydration layers and the fiber saturation point decrease as the temperature increases (Berry and Roderick 2005).

Since the various microscopic channels between cells and the anisotropic arrangement of the cell wall components, wood could be considered as a porous material. However, the flow of liquids into wood can occur by various ways such as; capillarity, pressure permeability, and diffusion, are extremely variable and depend many condition. The transport of water through wood has been intensively studied and a detailed description has provided by Albert et al. (2005), Durbak et al. (1998), Stamm (1964), Siau (1984) and Tarkow (1981).

Dimensional increase (swelling) continues until the cross banding of the cell wall polymers and this point is defined as the fiber saturation point. It was speculated that the maximum swelling of wood have mainly influenced by the solvent pH, the molar size, and the hydrogen bonding capacity of the liquids (Rowell 2005). Especially, the orientation of the cell wall components in the secondary layers (S_{1-3}) determines the extent of swelling.

In the absence of swelling stress (e.g., extremely slow swelling), the degree of swelling from the oven dry to high moisture condition can be predicted, as a first approximation, proportional to the specific gravity of the wood. The value of the slope of the linear relationship may be equal to the average fiber saturation point. However, serious deviations from the linear relationship may occur with species high in carbohydrates or extractives (Durbak et al. 1998, Siau 1984).

Knowledge about the physical and anatomical properties of wood is useful for estimating swelling but is not enough to evaluate variations because wood swelling is highly anisotropic and correlate many variables. However, those are of capital importance as for understanding anisotropic swelling/drying properties, as for the modeling of the hygroscopic behavior of woods.

The aim of this study is to bring some elements on determination the swelling rate coefficients, water retention and activation energy of unextracted and ethanol-benzene extracted (1:2 by v/v) chestnut wood (C*astanea sativa* Mill*)*. The modeling tool chain has been applied, starting from swelling profiles of chestnut samples.

MATERIAL AND METHODS

The chestnut (*Castanea sativa* Mill*)* woods were supplied from Isparta region in Turkey. The samples were cut in the form of 20×20×15 mm pieces and oven-dried for 48 hours at 50 °C prior to experiments. Only distilled water was used in the all conditions.

The treated samples had an average number of annual rings per cm four and the specific gravity was found to be 0.56 $g.cm^{-3}$.

The small wood samples were swollen in water at four temperature levels of 23, 50, 75 and 100 °C (± 3 °C), respectively. The dimensional changes in all three directions (tangential, radial and longitudinal) were measured.

All swelling measurements were made at room temperature with digital Mitutoyo-500 caliber (± 0.02 mm). In order to accurately determine the swelling coefficients (k) and activation energy (Ea), small intervals of time was used in initial wetting period. Larger intervals of time (hours) were utilized for determination of maximum equilibrium swelling and water sorption. After the termination of each experiment, the samples were air dried and then dried in oven for 24 hours at 105 °C for determination of the final weight.

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) was determined using the Tappi Test Method T-222-om-06. The extraction with 80 % ethanol-95 % benzene (1:2 by v/v) system was chosen as the most suitable since it gave the least swelling with suitable removal of the extractives (Mantanis 1994). The extractions were carried out for 6 hours by soxhlet method. The samples were then dried in an oven for 48 hours at 50 °C. The hot and cold water soluble extractives were also determined by using Tappi Test Method T-207-om-93.

Using the methodology developed by Mantanis (1994) and Sahin (2007, 2008), the activation energy for the chestnut wood was calculated with using the Arrhenious equation:

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

Where, k is the rate coefficient, A is the pre-exponential factor and R is the gas constant, E_a is the activation energy and T is the temperature (˚C).

Analysis of variance (Anova) was used for the statistical determination of swelling variations. All multiple comparisons were individually evaluated and significance differences between only the average tangential, radial and longitudinal dimension from the swollen samples were determined.

RESULTS AND DISCUSSION

Swelling properties of chestnut wood *in water*

The significant differences from the swollen samples were statistically analyzed and results presented in Tab 1. However, as expected, the tangential maximum equilibrium percent swelling averaged from 5.3 % to 7.9 % was higher than that of radial maximum equilibrium percent swelling. The longitudinal maximum equilibrium percent swelling ratio was averaged from 0.8 % to 1.99 % which lowest compare to others. Those variances are in good agreement with the results reported for chestnut wood by Bozkurt and Erdin (1989).

Tab. 1: Maximum dimensional changes and percent swelling of chestnut wood

Temp. (°C)	Tangent		Radial		Longitudinal	
	mm	(%)	mm	(%)	mm	(%)
23	1.03 (0.41)	5.3	0.99 (0.37)	5.1	0.22 (0.07)	0.8
50	1.48 (0.56)	7.7**	1.21 (0.48)	6.3	0.39 (0.39)	1.99**
75	1.46 (0.51)	7.8**	1.31 (0.58)	6.8	0.36 (0.14)	1.8**
100	1.52 (0.55)	7.9**	1.27 (0.51)	6.5	0.39 (0.15)	1.9**

Numbers in parentheses are standard deviations

** The increases of temperature are significant at 0.05 confidence level.

It was realized close relationship between dimensional increases to elevated temperature in all directions. This can be ascribed to the fact that the wood-water systems have higher average densities at increasing temperature than that of lower temperature system, resulting in various level dimensional changes.

The swelling coefficients (k) and activation energy (Ea) of chestnut samples were determined as described by Sahin (2007). The calculated swelling coefficients (k) in each direction are summarized in Tab. 2. In all cases, the higher temperature usually caused increasing k values. In the tangential direction, it ranged from 0.19 to 0.55, was greater than that of radial direction which from 0.10 to 0.28. In longitudinal direction, it was lowest among other directions, ranged from 0.09 to 0.17.

Tab. 2: Swelling rate coefficients (k) of chestnut wood at elevated temperature conditions

Temp. (°C)	Tangential	Radial	Longitudinal
23	0.19	0.10	0.09
50	0.40	0.19	0.10
75	0.42	0.24	0.12
100	0.55	0.28	0.17

The relationship between the rate of a reaction proceeds and its temperature could be quantitatively determined by the Arrhenius law (Mantanis 1994, Rowell 2005, Sahin 2007). When the Arrhenius equation is expressed in terms of natural logarithms, the activation energy (Ea) can then be determined graphically from a plot of the rate coefficient, as a function of reciprocal temperature.

The Ea was found to be 35.0 $Kj.mol^{-1}$ for tangential, 41.4 $kJ.mol^{-1}$ for radial and 22.2 $kj.mol^{-1}$ for longitudinal direction, respectively. Those suggest wood swelling is strictly dependence on temperature and direction of chestnut wood. Due to higher swelling occur in tangential and radial (transverse) direction, it is reasonable to use average Ea of transverse direction rather than longitudinal direction which have very low percent equilibrium maximum swelling (0.8-1.99 %), swelling coefficients (0.09-0.17) and activation energy (Ea: 22.2 $kj.mol^{-1}$).

In this sense, the Ea of 38.4 $kj.mol^{-1}$ was calculated for chestnut. These are in good agreement with the results reported for other woods by researchers. It was reported to be 38.9 $kj.mol^{-1}$ for Douglas fir which is softwood but specific gravity (0.59-0.60 $g.cm^{-1}$) is very close to chestnut and chemical content marginally similar (Rowell 2005). Mantanis et al. (1994) were also reported 44.7 kjmol for quaking aspen (0.48 $g.cm^{-1}$) and 47.6 $kj.mol^{-1}$ for sugar maple (0.66-0.72 $g.cm^{-1}$).

The application of an Arrhenius-kinetic approach to modelling swelling variations for woods were more completely discussed by Mantanis (1994), Rowell (2005) and Sahin (2007 and 2008). However, the activation energies obtained by the different approaches verifies the relationship between swelling and temperature.

The chemical composition of chestnut wood and its respond on swelling in water are further discussed in below.

The effects of chemical constituents and extractives on swelling and water sorption of chestnut wood

A comparative summary of the chemical composition of chestnut wood is presented in Tab. 3. The holocellulose, lignin and extractive content found to be 64.2 %, 22.2 % and 3.6 %, respectively. In general, hardwoods usually have higher carbohydrates and lower lignin compare to coniferous woods. However, chestnut has medium holocellulose and lignin, hence; it can be considered as classical example of hardwoods.

Tab. 3: Chemical composition (%) of chestnut wood (Castanea sativa Mill)

Chemical groups	Contents (%)
Holocellulose	64.2
Lignin	32.2
Ethanol-benzene extractives	3.6
Cold water extractives	0.9
Hot water extractives	1.5

It is also well known that lignin has the lowest affinity for water and hemicelluloses the highest. The affinity of cellulose is between these two (Durbak et al., 1998, Sahin 2007). Those clear evidence for considering Ea variations among woods.

The comparative swelling rate coefficients for unextracted and ethanol-benzene (1:2 by v/v) extracted chestnut samples are presented in Fig. 1. For extracted samples, it was ranging from 0.45 to 0.78 in tangential, 0.36 to 0.61 in radial and 0.19 to 0.24 in longitudinal directions, respectively. These clearly imply the ethanol-benzene extracted samples have relatively higher swelling rate (easier swelling) in all directions than the unextracted samples. It is noteworthy that increased temperature positively affects swelling rate in all directions. However, statistically not any significant differences on extracted samples were found for maximum equilibrium percent swelling. It was calculated for tangential direction ranging from 5.9 % to 7.2 %, for radial direction ranging from 5.4 % to 6.1 % and for longitudinal direction ranging from 0.9 % to 1.8 %, respectively.

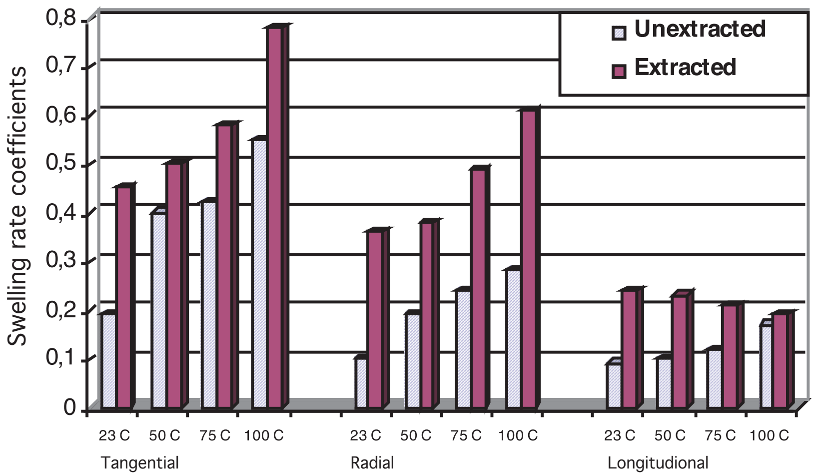

Fig. 1: Swelling coefficients of unextracted and extracted chestnut wood at different temperatures

The swelling of woods vary and closely related to the relative chemical content and morphological structures. Some variations also occur with environmental conditions such as temperature and relative humidity (Anonymous 1987, Simpson 1993). However, it has already well documented the relationships between the carbohydrates and the other components (e.g. lignin and extractives) influence on the swelling characteristics of woods. Moreover, interactions between the component fractions play an important role and do not allow a simple explanation of the component rates to be used for an evaluation of the wood swelling property. Yamamoto et al. (2001) hypotheses the hygroexpansion of wood cell wall very complex and mainly controlled by the mechanism of the reinforced matrix system. Murata and Masuda (2006) found the swelling behavior of woods was strongly influenced by the macroscopic/microscopic structure, for instance, the cell wall arrangement.

As shown in Fig. 2 by eliminating extractives, the activation energy decreases significantly. It was calculated 19.5 $kj.mol^{-1}$ for extractive free chestnut woods on transverse direction. The increase in reaction rate constant and lowering activation energy clearly implied the extractives play an important role for swelling proceeds. It was reported, woods high in extractives could have anomalous swelling behavior (Berry and Roderick 2005, Sahin 2007, Siau 1984).

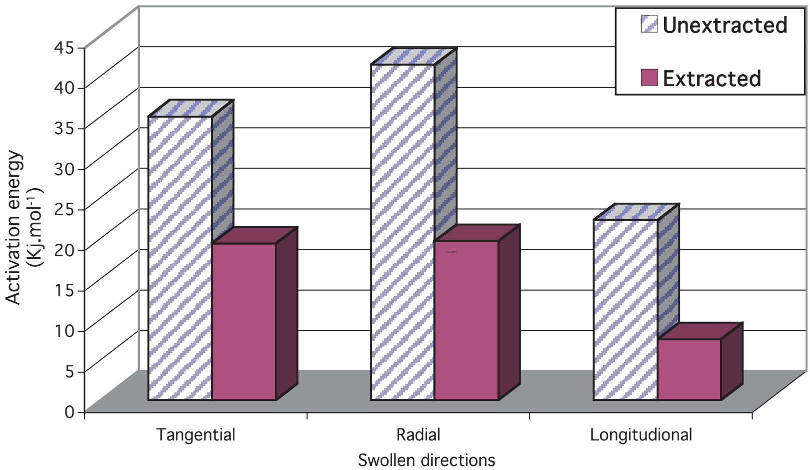

Fig. 2: The Activation energies of unextracted and extracted chestnut wood

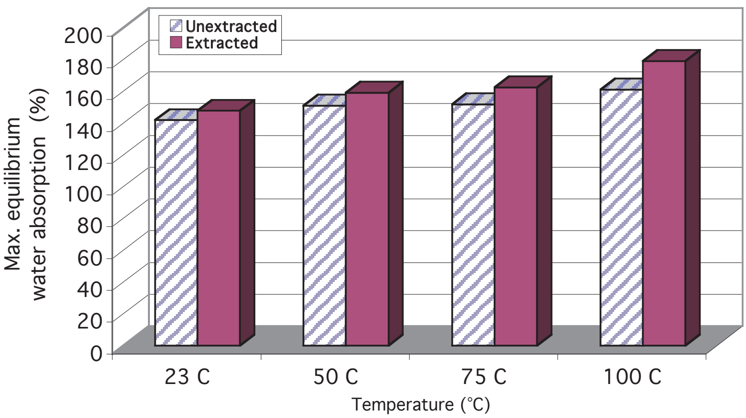

Fig. 3: Maximum equilibrium water absorption of unextracted and extracted chestnut wood at different temperatures

The comparative maximum equilibrium water adsorption of both type samples (unextracted and extracted) is presented in Fig. 3. Not surprisingly, a relatively linear relationship between water sorption and temperature was observed for all samples. The measured maximum water absorption for unextracted samples is ranging from 141.8 % at 23 °C to 161.0 % at 100 °C. Eriksson at al. (1991) suggested the increase in swelling above 75 °C has due to the softening of the lignin. Below its softening temperature, the stiff lignin restricts the swelling which was primarily promoted by water uptake in the hemicelluloses. It may be hypothesized, the sorption of water molecules in cell wall polymers can acts as a plasticizer to loosen the cell wall micro configuration. Those may allow to the better accessibility, hence, additional water penetration into wood. However, at similar temperature level, the further increased water absorption was realized for extracted samples. It is ranging from 147.7 % at 23 °C to 179.1 %

at 100 °C. These features can be mainly attributed to modify cell wall components resulting in a greater ease of diffusion and increase potential sites for water molecules. These are in good agreement with the results reported by Rowell (2005) and Mantanis (1994), and Mantanis at al. (1994). Moreover, it was proposed by Siau (1984) that the extracted wood is rather different from those of unextracted wood due to a lower degree of physically obstructs and further spaces for liquids (e.g. water) in wood.

CONCLUSIONS

The swelling rate coefficients increases significantly with extractive free chestnut wood-water systems resulting the initiation of the swelling process is displaced towards shorter times, have lowering Ea. The calculated activation energy was found to be variable in wood direction. However, considering transverse direction, it was found to be 38.4 kj.mole^{-1}. It is also clear evidence that extractives which are generally located in the lumens, and in the cell wall, have the physical obstructs for liquid diffusion into wood. It is reasonably to conclude that the temperature dependence of chestnut wood swelling in water can be predicted using Arrhenius equation.

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