WOOD RESEARCH
57 (1): 2012
69-78

EFFECT OF HOT-WATER EXTRACTIVES ON WATER SORPTION AND DIMENSIONAL CHANGES OF BLACK LOCUST WOOD

Stergios Adamopoulos
Technological Educational Institute of Larissa
Department of Forestry and Management of Natural Environment
Karditsa, Greece

Elias Voulgaridis
Aristotle University of Thessaloniki, School of Forestry and Natural Environment, Laboratory of Forest Utilisation
Thessaloniki, Greece

(Received June 2010)

ABSTRACT

The hygroscopicity and the dimensional changes of black locust heartwood were investigated in relation to the progressive removal of hot-water extractives. Extraction in the original specimen form removed only part of the total 8.434 % hot-water extractives, 3.601 % in first extraction and 4.642 % in second extraction. As a result, the adsorption and desorption behaviour of black locust wood was little affected by the extraction and only a small increase was observed in dimensional changes at every RH from 0 % to 97 %. The mean hysteresis coefficient was also little affected by extraction and increased from 0.75 at the unextracted stage to 0.77 at the second extraction. The initial dimensional change 3.76 % of unextracted black locust wood corresponding to RH changes between 43 % and 80 % increased after the first and second extraction to the respective values of 3.96 % and 3.97 %. Extraction had no effect on the significant, very strong linear relationships between swelling or shrinkage and equilibrium moisture content (EMC).

KEYWORDS: Adsorption, desorption, EMC, hysteresis, hot-water extractives, black locust.

INTRODUCTION

Extractives have profound effects on many wood properties with technological interest including wood-water relations. A vast number of experimental results have shown that the removal of extractives increases the dimensional changes of wood (Stamm and Loughborough 1942, Nayer 1948, Nearn 1955, Salamon and Kozak 1968, Choong 1969, Cooper 1974, Taylor 1974, Burmester 1989, Choong and Achmadi 1991, Militz and Homan 1993, Mantanis et al.

1995, Adamopoulos and Voulgaridis 2003). Most authors have attributed this to the class of extractives deposited in the cell wall structure and thus their bulking effect. The contribution of extractives deposited in the coarse capillary structure to wood shrinkage and swelling is negligible (Krutul 1983, Hernández 2007).

The influence of extractives on the sorption behaviour of wood has been described in detail in literature (Wangaard and Granados 1967, Ladomerský 1978, Willeitner and Schab 1981, Themelin 1998, Popper et al. 2005, 2006, 2007). However, the effect of progressive extraction on water vapour sorption has not been investigated much. In a previous investigation on black locust, radial and tangential shrinkage increased significantly after extraction with hot water in two stages (Adamopoulos 2002). In the present report, the water sorption isotherms and dimensional change of black locust wood are discussed in view of progressive removal of hot-water extractives.

MATERIAL AND METHODS

The experiments were carried out with straight grained heartwood of black locust (*Robinia pseudoacacia* L.). Sticks, 30 (R) by 30 mm (T) in cross section, with true radial and tangential faces and uniform growth rings were first conditioned at 20°C and 65 % RH and then cut to obtain specimens with a height of 5 mm (L). The perpendicular machining yielded three comparable groups of ten adjacent specimens each: A, B and C. Specimens of group A were used to investigate their sorption characteristics in the unextracted condition while specimens of groups B and C were extracted before testing.

Extraction was performed in the original specimen form in a Soxhlet apparatus with distilled hot water by modification (prolongation) of ASTM-D 1110, 1984 standards. Specimens of group B were extracted for 24 h (Extraction – Stage I) while specimens of group C were extracted for 48 h (Extraction – Stage II). Hot-water extractive content was also determined in wood flour that was prepared from material taken randomly from the sticks (ASTM-D 1110, 1984).

The specimens were exposed to a moisture sorption test, first in adsorption and subsequently in desorption, as follows: oven-drying, conditioning at six different relative humidities ranging from 8-9 % to 97 %, water wetting, partial air-drying, and conditioning at the same relative humidity but in a reverse order from 97 % to 8-9 %, oven-drying. As soon as each point of sorption was completed, the mass of the specimens was measured to the nearest 0.001 g and their dimensions (radial, tangential) were taken to the nearest 0.001 mm with a digital micrometer. Conditioning of specimens to appropriate moisture content was possible with the use of sealed enclosures in which prescribed saturated salt solutions were placed at 23 ± 1°C. The salts used in establishing various relative humidities are shown in Tab. 1. A criterion for equilibrium was established as three successive identical mass readings at 24 h intervals. Equilibrium was attained in approximately ten days and the entire sorption cycle was completed within three months.

The test results were used to obtain isotherm curves (adsorption, desorption, swelling, shrinkage), dimensional changes and EMC of black locust wood before and after extraction with hot-water. Sorption experimental data were fitted with the Hailwood-Horrobin (H-H) single-hydrate model (1946). According to H-H model, the total sorbed water is assumed to exist in two forms, water of hydration and water of solution. The cell wall is then presumed to consist of three chemical components considered to behave as an ideal solution; dry wood, hydrated wood and dissolved water. The H-H model divides total water sorbed into its monomolecular and polymolecular components with the equation for the predicted isotherm being of the form:

$U_{tot} = U_m + U_p$

$$U_{tot} = \frac{1800}{Mp} \cdot \left(\frac{\alpha \cdot \beta \cdot \mathbf{h}}{1 + \alpha \cdot \beta \cdot \mathbf{h}}\right) + \frac{1800}{Mp} \cdot \left(\frac{\alpha \cdot \mathbf{h}}{1 - \alpha \cdot \mathbf{h}}\right)$$

where: U_{tot} - total water sorbed (%),
U_m - monomolecular water sorbed (%),
U_p - polymolecular water sorbed (%),
h - relative vapour pressure,
M_p - hypothetical molecular weight of the dry wood polymer,
α - equilibrium constant of the hydrated wood,
β - equilibrium constant of the no hydrated wood.

Also, the specific area of the sorbent Σ was determined from the monolayer moisture content.

It should be noted that the process of moisture gain was the 1st adsorption for the unextracted specimens and the 2nd adsorption for the extracted specimens. The 1st adsorption for the extracted specimens (Stages I and II) occurred during their extraction with hot water. For all specimens (unextracted, extracted) the process of moisture loss was the 2nd desorption as the first one occurred during their oven-drying. For comparison purposes the values of both swelling and shrinkage were based on the initial dried dimensions. Hence, shrinkage values express how swollen is the wood at a certain relative humidity during the 2nd desorption.

Tab. 1: Relative humidity of air at constant temperature 23±1°C obtained in sealed enclosures with the use of saturated salt solutions.

Saturated salt solution	Relative humidity at 23±1°C
Potassium hydroxide KOH	9-8
Potassium acetate CH_3COOK	23-22
Potassium carbonate K_2CO_3	44-43
Sodium nitrite $NaNO_2$	66-65
Ammonium sulfate $(NH_4)_2SO_4$	81-80
Potassium sulfate K_2SO_4	97

Finally, the dry-density (based on oven-dry weight and volume) of all specimens was determined as an important parameter influencing the EMC and the magnitude of dimensional changes of wood under specific variations of temperature and relative humidity of air.

RESULTS AND DISCUSSION

The classic sigmoid adsorption and desorption isotherms in the unextracted and extracted conditions are shown in Fig. 1. These curves were drawn from the EMC data of Tab. 2 (U_{tot}), computed according to the H-H model. Also plotted are the mean moisture content points as measured from ten replicate specimens per treatment. The computed isotherms were in good agreement with the experimentally measured values. The degree of fit of the H-H isotherms to the experimental EMC results was remarkably high, with r^2 values ranging from 0.991 to 0.998. As judged from Fig. 1 and Tab. 2, the adsorption and desorption behaviour of black locust wood was very little affected by hot-water extraction in two stages. H-H values of U_m, U_p and U_{tot} at a given RH gradually increased both in adsorption and desorption with progressive removal of hot-water extractives but the differences were rather small. The specific surface Σ, being a function of monomolecular sorption U_m, also showed no marked dependence on the hot-water extractives. The EMCs U_{tot} of 21.70 % in adsorption and 23.89 % in desorption at 97 % RH were second lowest after those of *Morus alba* heartwood when compared to data of domestic hardwoods (Voulgaridis 1987).

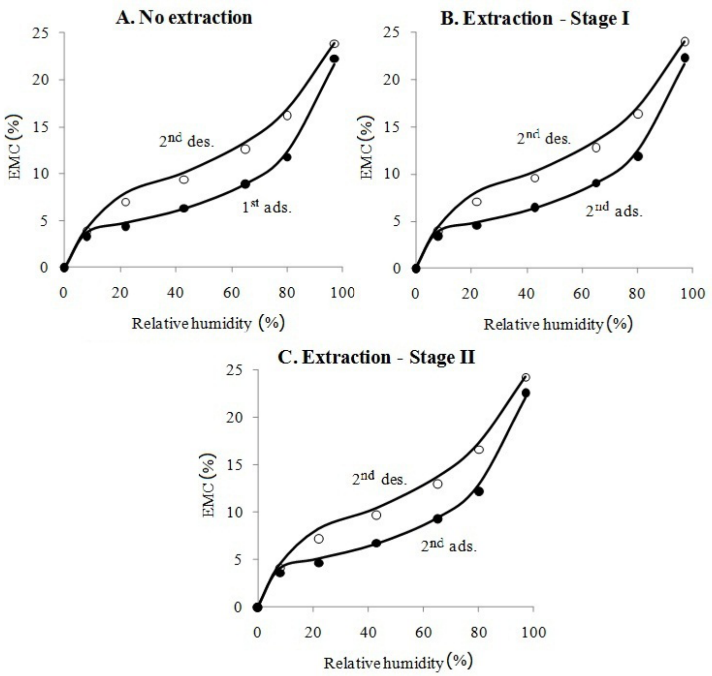

Fig. 1: Experimental adsorption (●) and desorption (○) points and fitted sorption isotherms in black locust wood specimens according to the Hailwood-Horrobin model; A) non extracted, B) extracted-stage I, C) extracted-stage II.

The swelling and shrinkage isotherms (Fig. 2) were also found to be more or less of the sigmoid type. The highest dimensional changes were noticed when RH changed between 80-81 % and 97 %. Under the same conditions of temperature and RH, the shrinkage values during the 2nd desorption appeared to be higher than the swelling values during the 1st adsorption for the unextracted specimens and during the 2nd adsorption for the extracted specimens. This is mainly due to the hysteresis of EMC during adsorption (Goulet and Fortin 1975). However, the shrinkage values measured at 0 % RH (Fig. 2, Tab. 3) imply that this hysteresis of dimensions due to loosening of wood structure might be also responsible for the shrinkage-swelling difference. Hysteresis of dimensions at 0 % RH was found to increase with extraction in both the radial and tangential directions (Tab. 3).

The hysteresis of dimensions may cause smaller dimensional changes during the 2nd desorption for certain change of RH (Fig. 2). The swelling and shrinkage in both dimensions (radial, tangential) at every RH was found to slightly increase with progressive extraction (Fig. 2).

Tab. 2: Results of the analysis of the sorption isotherms according to the Hailwood-Horrobin model of unextraxted and extracted black locust wood at various levels of relative humidity.

Treatment	**Relative humidity**					
	8 (%)	**22 (%)**	**43 (%)**	**65 (%)**	**80 (%)**	**97 (%)**
No extraction						
U_{am}/U_{dm} (%)	3.49/3.80	3.86/6.61	3.98/6.68	4.02/6.98	4.04/7.02	4.05/7.05
U_{ap}/U_{dp} (%)	0.29/0.44	0.93/1.36	2.31/3.24	4.90/6.36	8.31/9.84	16.84/17.65
U_{atot}/U_{dtot} (%)	3.78/4.24	4.79/7.97	6.29/10.12	8.92/13.35	12.35/16.87	21.70/23.89
Σa/Σd (m^2. g^{-1})	124/206	137/234	141/244	143/247	143/249	144/250
Extraction – Stage I						
U_{am}/U_{dm} (%)	3.62/3.93	3.96/6.74	4.07/7.01	4.11/7.11	4.12/7.15	4.13/7.18
U_{ap}/U_{dp} (%)	0.30/0.45	0.94/1.38	2.33/3.28	4.94/6.43	8.35/9.92	16.91/17.58
U_{atot}/U_{dtot} (%)	3.92/4.38	4.90/8.12	6.40/10.29	9.04/13.54	12.47/17.07	21.71/24.08
Σa/Σd (m^2. g^{-1})	128/210	140/239	144/248	145/252	146/253	146/254
Extraction – Stage II						
U_{am}/U_{dm} (%)	3.79/4.08	4.14/6.88	4.26/7.14	4.30/7.24	4.31/7.27	4.32/7.30
U_{ap}/U_{dp} (%)	0.31/0.45	0.97/1.39	2.41/3.31	5.08/6.49	8.54/10.00	16.99/17.69
U_{atot}/U_{dtot} (%)	4.10/4.53	5.12/8.27	6.67/10.45	9.38/13.73	12.85/17.28	22.01/24.29
Σa/Σd (m^2. g^{-1})	134/215	147/244	151/253	152/256	153/258	153/259

The small magnitude of increase in EMC and dimensional changes with progressive extraction could be explained by the fact that the extraction, although prolonged, did not remove all hot-water extractives (Tab. 3). Hot-water extractive content, based on oven-dry weight of unextracted wood flour, was 8.434 %. The first extraction (Stage I, specimens of group B) removed 3.601 % hot-water extractives (based on oven-dry weight of unextracted wood), the second extraction (Stage II, specimens of group C) 4.642 %. Extraction resulted in lowering the dry-density of specimens from 0.732 $g.cm^{-3}$ (unextracted) to 0.720 $g.cm^{-3}$ (extracted – Stage I) and 0.709 $g.cm^{-3}$ (extracted – Stage II) but, again, the differences were not substantial. The almost identical sorption behaviour of unextracted and extracted specimens is also illustrated by the mean hysteresis coefficient which is the ratio of EMCs in adsorption and desorption for every RH. The mean hysteresis coefficient was not affected considerably by extraction and it was 0.75, 0.76 and 0.77 without extraction, after first extraction and after second extraction,

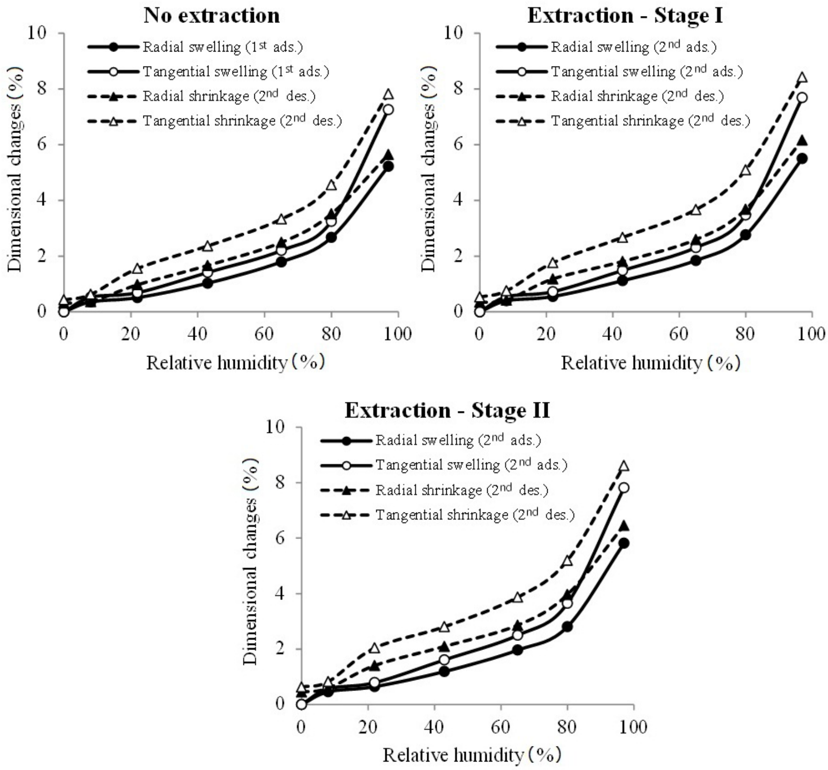

Fig. 2: Swelling and shrinkage isotherms in black locust wood specimens; A) non extracted, B) extracted-stage I, C) extracted-stage II.

respectively (Tab. 3). Extraction had a negative effect on the dimensional stability of black locust wood based on the magnitude of changes of radial and tangential dimensions corresponding to the common RH fluctuations between 44-43 % and 81-80 % in Greece. Unextracted specimens had a dimensional change of 3.76 % which increased to the respective values of 3.96 % and 3.97 % for the extracted specimens in stages I and II (Tab. 3). Other authors also reported that wood extractives contribute greatly to the dimensional stability (Torelli and Cufar 1979, Chafe 1987, Hernández 2007). The increase in dimensional change was caused by higher changes in the tangential direction after extraction as the mean radial dimensional change remained the same. This finding is in agreement with previous reports (Taylor 1974, Kryla 1980).

Relationships between dimensional changes and measured EMC were found to be linear with very high r^2 values (higher than 0.990 for both swelling and shrinkage) statistically significant at P = 95 % (Fig. 3).

Tab. 3: Influence of hot-water extractives on equilibrium moisture content (EMC), hysteresis, and dimensional changes of black locust wood.

Property	Treatment		
	No extraction	Extraction – Stage I	Extraction – Stage II
Dry density ($g.cm^{-3}$)	0.732	0.720	0.709
Extractives removed (%)	-	3.601	4.642
EMC[1] (%)	8.92	9.05	9.33
Hysteresis of dimensions (%)			
Radial	0.32	0.34	0.45
Tangential	0.43	0.53	0.63
Hysteresis coefficient[2]	0.75	0.76	0.77
Dimensional changes[3] (%)			
Radial			
Swelling	1.64	1.64	1.62
Shrinkage	1.85	1.87	1.87
Mean	1.75	1.76	1.75
Tangential			
Swelling	1.83	1.99	2.04
Shrinkage	2.20	2.42	2.40
Mean	2.01	2.20	2.22
Sum[4]	3.76	3.96	3.97

[1]during the 1st adsorption for the unextracted specimens and during the 2nd adsorption for the extracted specimens at 23±1°C and 66-65 % RH (experimental results calculated from ten replicate specimens per treatment).
[2]ratio of measured EMCs in adsorption and desorption for every RH (mean values of six determinations).
[3]for RH changes between 44-43 % and 81-80 %.
[4]sum of mean radial and tangential dimensional change.

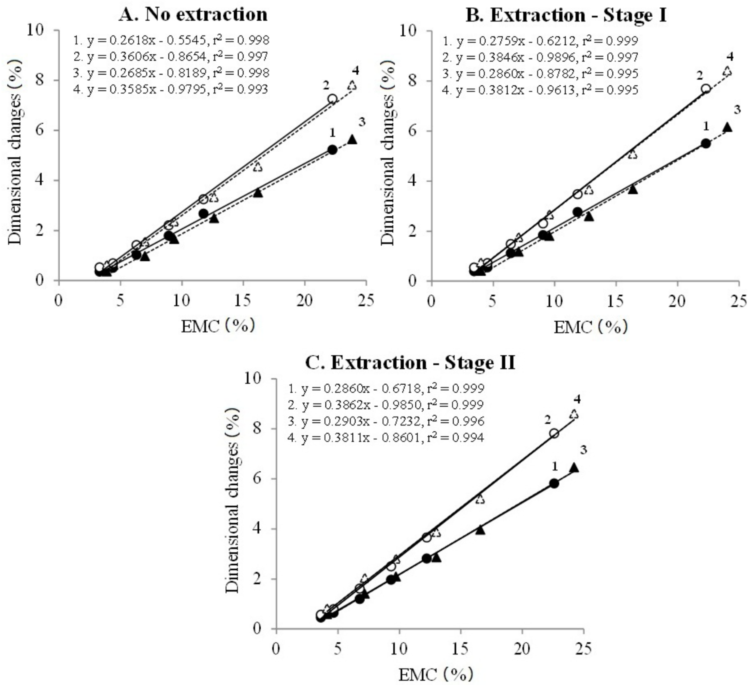

Fig. 3: Relationships between dimensional changes and EMC in A) non extracted, B) extracted-stage I and C) extracted-stage II black locust wood specimens; 1. Radial swelling (●), 2. Tangential swelling (○), 3. Radial shrinkage (▲), 4. Tangential shrinkage (Δ).

As shown in Fig. 3, progressive extraction did not alter the relationships.

CONCLUSIONS

Moisture sorption experiments were carried out with black locust wood after progressive removal of hot-water extractives. The EMC results associated with dimensional measurements led to the following conclusions:

1. Hot-water extraction in two stages caused only a small increase in equilibrium moisture contents U_m, U_p and U_{tot} at a given RH. Also, the amount of extractives removed (up to 4.642 % of the total 8.434 %) did not show noticeable influence on the specific surface Σ. The magnitude of the loop between adsorption and desorption curves remained almost unchanged after the first and second extraction as revealed by the hysteresis coefficients.
2. Extractive removal also resulted to a slight gradual increase in radial and tangential dimensional changes along the hygroscopic range of sorption. Extraction had no particular effect on the characteristic hysteresis loop between swelling and shrinkage curves as dimensional changes in both directions (radial, tangential) remained greater for desorption than for adsorption.
3. Extraction had an inverse effect on the dimensional stability of black locust wood with the

dimensional changes in the tangential direction being responsible.

4. Very strong linear relationships existed between dimensional changes and EMC in both the unextracted and extracted states.

ACKNOWLEDGMENT

This paper is dedicated to Professor Ioannis Kakaras upon his retirement from the Technological Educational Institute of Larissa, Greece.

REFERENCES

1. Adamopoulos, S., 2002: Influence of hot-water extractives on radial and tangential shrinkage of black locust wood (*Robinia pseudoacacia* L.). Holz als Roh- und Werkstoff 60(5): 377-378.
2. Adamopoulos, S., Voulgaridis, E., 2003: Dimensional changes of extracted and non-extracted small wood specimens of black locust (*Robinia pseudoacacia* L.). Holz als Roh- und Werkstoff 61(4): 264-268.
3. ASTM D-1110, 1984: Standard test methods for water solubility of wood.
4. Burmester, A., 1989: Dimensionsstabilisierung von Buchenholz durch Extrakte aus Rinden, Nadeln, Blättern und Sägespänen. Holz als Roh- und Werkstoff 47(1): 33.
5. Chafe, S.C., 1987: Collapse, volumetric shrinkage, specific gravity and extractives in eucalyptus and other species. Part 2: The influence of wood extractives. Wood Sci. Technol. 21(1): 27-41.
6. Choong, E.T., 1969: Effect of extractives on shrinkage and other hygroscopic properties of ten southern pine woods. Wood Fiber 1(2): 124-133.
7. Choong, E.T., Achmadi, S.S., 1991: Effect of extractives on moisture sorption and shrinkage in tropical woods. Wood Fiber Sci. 23(2): 185-196.
8. Cooper, G.A., 1974: The effect of black walnut extractives in sorption, shrinkage, and swelling. Wood Sci. 6(4): 380-385.
9. Goulet, M., Fortin, Y., 1975: Measurements of swelling of sugar maple in a cycle of moisture sorption at 21°C. (Mesures du gonflement de l'érable à sucre au cours d'un cycle de sorption d'humidité à 21°C). Note de recherches N°12, Département d'exploitation et utilisation des bois, Université Laval, Québec, 49 pp. (in French).
10. Hernández, R.E., 2007: Swelling properties of hardwoods as affected by their extraneous substances, wood density, and interlocked grain. Wood and Fiber Science 39(1): 146-158.
11. Krutul, D., 1983: Influence of the isolation of extractives substances and carbohydrates soluble in alkalien on some hygroscopic properties of spruce wood. Drevársky výskum 28(2): 1-12.
12. Kryla, J.M., 1980: Characteristics of carbonized wood affected by extraction. Wood Sci. 13(1): 18-25.
13. Ladomerský, J., 1978: Über den Einfluss der Extraktstoffe auf das Sorptionsgleichgewicht des Holzes. Drevársky výskum 23(3): 145-168.
14. Mantanis, G.I., Young, R.A., Rowell, R.M., 1995: Swelling of wood. Part III: Effect of temperature and extractives on rate of maximum swelling. Holzforschung 49(3): 239-248.
15. Militz, H., Homan, W.J., 1993: The use of natural and synthetical tannins to improve the dimensional stability and durability of beech wood (*Fagus sylvatica*). 24. Annual Meeting - International Research Group on Wood Preservation, Doc. No. IRG/WP 93-300316, Orlando (USA), 16-21 May 1993, 16 pp.

16. Nayer, A.N., 1948: Swelling of wood various organic liquids. Ph.D Thesis. University of Minesota, Minneapolis.
17. Nearn, W.T., 1955: Effect of water soluble extractives on the volumetric shrinkage and equilibrium moisture content of eleven tropical and domestic woods. Bulletin 598. Agricultural Experiment Station, Pennsylvania State University, University Park, Pennsylvania.
18. Popper, R., Niemz, P., Torres, M., Croptier, S., 2005: Einfluss der Extraktstoffe ausgewählter fremdländischer Holzarten auf die Gleichgewichtsfeuchte. Interner Bericht, ETH Zürich, Institut für Baustoffe.
19. Popper, R., Niemz, P., Torres, M., 2006: Einfluss des Extraktstoffanteils ausgewählter fremdländischer Holzarten auf deren Gleichgewichtsfeuchte. Holz als Roh- und Werkstoff 64(6): 491-496.
20. Popper, R., Niemz, P., Eberle, G., Torres, M., 2007: Influence of extractives on water vapour sorption by the example of wood species from Chile. Wood Research 52(1): 57-68.
21. Salamon, M., Kozak, A., 1968: Shrinkage of sapwood and heartwood of young Douglas-fir trees. Forest Prod. J. 18(3): 90-94.
22. Stamm, A.J., Loughborough, W.K., 1942: Variation in shrinkage and swelling of wood. Trans. Amer. Soc. Mech. Eng. 64(4): 379-386.
23. Taylor, F.W., 1974: Effect of extraction on the volume dimensions and specific gravity of solid wood blocks. Wood Sci. 6(4): 396-404.
24. Themelin, A., 1998: Comportement en sorption de produits lingo-cellulosiques. Bois et forèts des tropiques 256(2): 55-64.
25. Torelli, N., Cufar, K., 1979: Shrinkage, swelling and sorption characteristics of 43 Mexican tropical hardwoods. Dep. Wood Sci. and Technol., Edvard Kardelj University, Ljubljana, SFR, Yugoslavia, 55 pp.
26. Voulgaridis, E., 1987: Sorption and movement studies of thirty Greek woods. Aristotelian University of Thessaloniki, Scient. Ann. Dep. For. Nat. Environ. 30(2): 63-131.
27. Wangaard, F.F., Granados, L.A., 1967: The effect of extractives on water-vapour sorption by wood. Wood Sci. Technol. 1(4): 253-277.
28. Willeitner, H., Schwab, E., 1981: Holz- Aussenanwendung im Hochbau. Verlagsanstalt Alexander Koch, Stuttgart.

Stergios Adamopoulos
Technological Educational Institute of Larissa
Department of Forestry and Management of Natural Environment
Laboratory of Forest Utilization & Wood Technology
Terma Mavromihali Str.,
431 00 Karditsa
Greece
Phone: + 302441064706
Corresponding author: adamopoulos@teilar.gr

Elias Voulgaridis
Aristotle University of Thessaloniki
School of Forestry and Natural Environment
Laboratory of Forest Utilisation
541 24 Thessaloniki
Greece