INFLUENCE OF WOOD EXTRACTIVES ON MOISTURE SORPTION AND WETTABILITY OF RED OAK (*QUERCUS RUBRA*), BLACK CHERRY (*PRUNUS SEROTINA*), AND RED PINE (*PINUS RESINOSA*)

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ABSTRACT

Red oak (*Quercus rubra*), black cherry (*Prunus serotina*), and red pine (*Pinus resinosa*) wood samples were soxhlet extracted with various combinations of organic solvents including ethanol, toluene, and water according to ASTM 1110-96, ASTM D1107-96, TAPPI T207 OM-88 and TAPPI T204 om-88 standards.

Contact angle and sorption isotherms of extracted and unextracted specimens were determined to evaluate the role of wood extractives on the wettability and sorption properties of these wood species.

Extracted specimens adsorbed more water than unextracted specimens at high relative humidity in agreement with the literature. The contact angle decreased with increased extraction due to the removal of hydrophobic extractives. However, the absorption rate of water, estimated as the decrease in contact angle over time suggests physical modification of the wood surface by solvent extraction due to the migration and redistribution of hydrophobic extractives.

Keywords: Extractives, equilibrium moisture content, sorption, contact angle, durability properties.

INTRODUCTION

Extractives are chemical compounds naturally occurring in woody plants (Panshin and DeZeeuw 1980). Hillis (1970) defined extractives as nonstructural constituents of plants. They have lower molecular weights than other polymeric constituents of wood and are distributed in the lumen or other specific tissues in plants. The term *extractive* covers a large number of compounds of different classes, which can be extracted from wood with polar and nonpolar solvents (Hillis 1987).

According to Koch (1972), softwood extractives comprise a heterogeneous group of compounds present in low concentrations. Among the most important are terpenes and wood resins, both of which are composed of isopropene units, polyphenols such as flavonols, anthocyanins, quinones, stilbenes, lignans and tannins, tropolones, glycosides, sugars, fatty acids, and inorganic constituents (Kollman and Côté 1984).

The description of the chemical composition of most northern hardwood extractives has been conducted (Rowe and Conner 1979). In most hardwoods, hydrolyzable gallotannins and ellagitannins are the predominant compounds. The sapwood also contains leucoanthocyanins and possibly pinoresinol. In addition, coumarin and lignans are usually present. How wood extractives affect the water properties and the dimensional stability of wood depends on their chemical composition and location in the wood structure. The chemical constitution of extractive components, their size and molecular weight, and their affinity to the ligno-cellulosic wood complex, will dictate

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their location within the wood structure. Low molecular weight monomers are found in voids in cell walls, while high molecular weight components will be located mostly in the lumen of vessels, tracheids, or fibers.

Aromatic compounds derived from glucose—such as flavonoids and condensed tannins—usually have free hydroxyl groups and are water-soluble. Consequently, they will be more susceptible to absorbing water and inducing greater dimensional change. This can also be applied to terpenoids, which usually have hydrophilic functional groups attached to the hydrocarbon moiety. To the contrary, pure hydrocarbons such as terpenes are volatile and will not affect dimensional stability.

The dimensional stability of wood, when exposed to various humidity conditions, is the main obstacle for its efficient use. It has been reported that wood-water relationships are affected by the type and total extractive content in the wood. For example, Nearn (1955) reported early work that concluded that the increased shrinkage in samples of *Acacia melanoxylon* was due to the increase of the fiber saturation point (fsp) of that species caused by the influence of water-soluble extractives. This was later confirmed by Wangaard and Granados (1967), when they showed that one of the principal effects of extractives is to depress the sigmoid isotherm in the upper range of relative humidity.

Recent publications are in line with these views (Choong and Achmadi 1991; Chen and Chong 1994). Stamm (1952) investigated the anti-shrink efficiency of wood treated with organic salts, sugars and water-soluble phenol-formaldehyde resins. He observed that extractives rich species do not conform to the usual shrinkage-specific gravity relationship and concluded that water-soluble extractive solutes reduce the shrinkage of wood in proportion to the fraction of transient cell-wall capillary structure that is occupied by the solute.

Nearn (1955) focused on the effect of extractives on the volumetric shrinkage of 15 tropical and temperate species. He found that wood with low fiber saturation points have lower than normal equilibrium moisture contents at high relative humidity due to the bulking action of extractives. The removal of extractives caused an increase in equilibrium moisture content at higher relative humidities. Chong (1969) observed wide variations in hygroscopic properties related to extractive content in ten southern pine woods samples. Cooper (1974), working on black walnut, also observed a lower fiber saturation point on extracted samples. He obtained higher swelling at low relative humidity, attributed to the fact that some of the sites formerly blocked by extractives were made available for water, consistent with the theory of extractives functioning as bulking agents in the cell wall.

Wood extractives are also known to affect the wettability of wood surfaces (Maldas and Kamdem 1999). Polar and hydrophilic extractives might increase wetting, and nonpolar extractives might decrease wetting. Chen (1970) observed increased wettability in all 70 tropical woods used in his study. To the contrary, Jordan and Wellons (1977) observed decreased wettability with keruing (*Dipterocarpus* spp.) and attributed that finding to extractives present in veneer samples tested. Maldas and Kamdem (1999) also observed decreased wettability. In their experiment, wood extracted with an ethanol-toluene solvent exhibited higher contact angle (lower wettability) compared to unextracted samples. They suggested that the high contact angle was due to the hydrophobic nature of the extracted wood surface promoted by the migration of hydrophobic extractives to the wood surface. They suggested that the more hydrophobic extractives such as waxes and long chain hydrocarbons are present in a wood species, the less water this species will absorb.

From measurement of the contact angle and moisture adsorption properties, the surface free energy of the wood surface can be calculated. The surface free energy of solids is known to govern their wettability and coatability by liquids. It controls their propensity to absorb liquids from adjacent fluid phases, and influences their catalytic activity (Sun and Berg 2002).

Most studies on sorption and wettability properties have been focused on tropical woods known for their high extractives content. Several temperate woods possess limited amount of extractive compared to tropical woods (Spalt

1957). We are hypothesizing that they would affect in a similar way most water properties of wood surfaces. How significant is the influence of wood extractives on sorption and equilibrium moisture content? How is the free energy change and contact angle affected? What are implications of these property changes on the dimensional stability of some temperate woods? These are all areas that need to be investigated further.

The goal of this study is to investigate the influence of wood extractives on the sorption and wettability behavior of northern red oak, black cherry, and red pine.

MATERIALS AND METHODS

Materials

Three wood species were selected for this study: black cherry (*Prunus serotina*), red oak (*Quercus rubra*), and red pine (*Pinus resinosa*). All three species are largely available resources in the Northeast. Oak and red pine are largely used in outdoor conditions where wood is susceptible to variations in moisture content. Cherry is mainly used in indoor applications. However, due to its specific color (due to its extractive content), it was a potentially interesting hardwood species for comparison with red oak.

Black cherry and red oak logs measuring 1.2 m (4 ft) with top diameters larger than 35 cm were randomly selected from the lumberyard at the Devereaux sawmill in Pewamo, Michigan. Red pine logs measuring 3.5 cm in diameter and 2.4 m (8 ft) in length were obtained from the Kellogg forest in Augusta, Michigan.

The logs were sawn in a traditional flat-sawn scheme to obtain exterior boards with the main face in tangential direction and boards closer to the pith in radial direction. The thickness of each cut was set at 2.5 cm (1 in.), and 14 to 16 boards were obtained from each log, with approximately seven to eight boards for each half of the cross section. Care was taken to keep track of the position of each board from pith to bark. From each half section, the first two to three boards were flat-sawn, and the last four to five boards were quarter-sawn.

All boards were dried in a laboratory kiln following drying schedules recommended by the Forest Products Laboratory (Anon 1999). Drying schedule T8-B4 was used for black cherry, T4-C2 for red oak, and T12-B4 for red pine. The final moisture content was between 6 and 8%. The boards were then stored in a conditioned room maintained at 20°C and 65% relative humidity to an equilibrium moisture content of 12 $\pm 2\%$ before further use.

The densities of samples from each log determined according to ASTM standard D2395-93-(1999)-were 393 kg/m^3 for red pine, 624 kg/m^3 for red oak, and 540 kg/m^3 for black cherry.

Samples preparation

Boards, numbers 4 and 5 (heartwood), measuring 2.5 cm $\times$ 40 cm $\times$ 120 cm from areas of the log at least 30 mm away from the pith, and 50 mm from the bark, therefore not including any sapwood material, were selected to prepare the samples.

The samples measured 4 mm $\times$ 44 mm $\times$ 80 mm (T $\times$ W $\times$ L). Attention was paid to keep the radial face as the main surface to be exposed.

The samples were then planed and successively sanded with 60-, 100-, 150-, and 220-mm grit sanding paper. Sanded specimens were conditioned to equilibrium moisture content of 12 ± 2 % before extraction.

Removal of extractives

The samples were extracted with various combinations of solvents including ethanol, toluene, and water according to modified ASTM and TAPPI standards.

Toluene is a nonpolar solvent and is traditionally believed to be capable of opening up and penetrating wood cell walls. Thus when used for extraction, it would be expected to merely recover the extractable materials located within the cell lumen (Ajuong and Breese 1998). Previous reports indicate such substances as consisting of long chain fatty acids, fats, resins, waxes, terpenes, and phytosterols (Anon 1999; Laks 1991).

Ethanol is a good bulking agent and can swell wood structure by 83% more than swelling caused by water (Laks 1991; Ajuong and Breese 1998). Thus ethanol would be expected to remove materials from within the wall structure, including among others, condensed tannins, flavonoids, and phenolics (Laks 1991). When applied, hot water extraction recovers condensed tannins and water-soluble low molecular weight carbohydrates (Ajuong and Breese 1998). Water extraction was conducted according to ASTM 1110-96 (ASTM 1999) and TAPPI T207 OM-88 (TAPPI 1993). Solvent extractions were conducted according to TAPPI T204 om-88 (TAPPI 1993) and ASTM D1107-96 (ASTM 1999). The main modification was related to the fact that solid wood samples were used in the extraction process instead of wood (powder) as recommended in the standards. The extraction time was consequently increased to remove more extractives from the specimens. Preliminary tests to determine the appropriate extraction time suggested that an extraction cycle of 72 h was sufficient.

Conditioned samples were divided into five groups. The first group was extracted with a mixture of ethanol: toluene (1:2 by volume) (Eth-Tol), the second group was extracted with ethanol: toluene for 72 h and then extracted with water for 72 h (Eth-Tol + Water), the third group was extracted with ethanol (Eth), the fourth group was extracted with ethanol for 72 h and water for 72 h (Eth + Water), and the fifth group was kept unextracted as a control (control). Twenty-four samples were extracted for each treatment from each species.

The total amount of extractives removed (Table 1) was calculated by the weight difference of the moisture-free samples before and after extractions as recommended by the standard (ASTM 1999; TAPPI 1993). Extracted specimens were stored under dark in the conditioning room for further tests.

Sorption test

From each treatment, four samples were used for the sorption test. Specimens were divided into two matching halves measuring 4 × 22 × 40 mm each (tangential, radial, longitudinal). One half was used in adsorption, and the matching half was used in desorption. Four specimens for each extraction type were exposed at various relative humidity conditions in saturated salt solutions (Table 2) in a conditioning room maintained at 20ºC according to ASTM E104-85 (ASTM 2000).

Samples were considered to have reached equilibrium at any given humidity when the daily weight changes were less than 0.1mg. The equilibrium moisture contents (EMC) were calculated on the basis of the oven-dried weight of the samples.

Contact angle

The left and right contact angle between each specimen's surface and a drop of distilled water was measured using a VCA 2000 system from AST Inc. Wood specimens were set on a stage, and a droplet of 5μl of water was placed on the specimen with a syringe. The mean values of the contact angles of 8 measurements for left and right contact angle (CA) between the droplet and wood surface at 1-s intervals were collected. The initial contact angle (t_o) was described as the

TABLE 1. *Percentage of extractives removed[1] (dry weight basis).*

	Eth-Tol	Eth-Tol +Water	Eth	Eth +Water
Red Pine	2.7 (0.5) [2]	3.5 (0.4)	3.3 (0.7)	4.6 (0.64)
Black Cherry	2.0 (0.5)	3.1 (1.2)	3.2 (1.0)	4.8 (0.5)
Red Oak	2.0 (0.6)	2.8 (0.1)	1.6 (0.1)	4.1 (0.4)

[1] Mean of four replicas.
[2] Numbers in parenthesis are standard deviation.

TABLE 2. *Relative humidity values for selected saturated salt solutions (ASTM E104-85).*

Salt	Relative Humidity (%) at 20°C
Lithium Chloride (LiCl.H_2O)	11±1
Magnesium Chloride (MgCl$_2$.6H_2O)	33±1
Magnesium Nitrate (Mg(NO$_3$).6H_2O)	54±1
Sodium Chloride (NaCl)	75±1
Potassium Chloride (KCl)	85±1
Potassium Nitrate (KNO$_3$)	94±1
Distilled Water	100±1

point where the regression line of contact angle values over time crossed the Y-axis (Maldas and Kamdem 1999; Nzokou and Kamdem 2002).

The rate of decrease of the contact angle was computed as an indication of the absorption rate of the water on the wood surface (Maldas and Kamdem 1999). The following Eq. (1) was used to calculate the rate:

$$R = \frac{d\Theta}{dt} \qquad (1)$$

where:

R = Rate of decrease of the contact angle
$d\Theta$ = Variation of the contact angle
dt = variation of the time

Data analysis

Adsorption and desorption moisture contents were plotted against the various relative humidities, and the hysteresis ratio (A/D) was calculated at each condition. The Hailwood-Horrobin (1946) equation was applied to the data, and the free energy was calculated. The statistical significance of the difference between the various extraction types and control specimens was evaluated using the one-way analysis of variance procedure in SigmaStat version 2.0 for Windows (SPSS Inc. 1997). Tukey's multiple comparisons test (95% confidence) was employed to determine differences between average CA values for the various extractions.

RESULTS AND DISCUSSION

Sorption

Adsorption and desorption EMC for each species and extraction type are summarized in Table 3. Desorption EMC were consistently higher than adsorption EMC as result of hysteresis. Hysteresis ratio data (Table 4), calculated by dividing adsorption EMC to the desorption EMC showed that ethanol-extracted samples had higher hysteresis than control samples. According to the Urquhart theory, hysteresis is believed to be caused by the development of hydrogen bonds be-

tween hydroxyl groups on adjacent cellulose molecules upon initial drying (Spalt 1957). Consequently, higher hysteresis in ethanol-extracted samples is an indication that extractives removed by ethanol prevent some of the Urquhart type hydrogen bonding reactions from occurring.

Adsorption data comparing extracted and unextracted specimens for each species are presented in Figs. 1 to 3.

For black cherry, ethanol-toluene extracted samples had an adsorption curve similar to that of control samples (Fig. 1). However, when ethanol-toluene extraction was subsequently followed by water extraction, adsorption curve for extracted samples was higher than the curve for unextracted specimens especially in the higher range of the relative humidity values. Samples extracted with ethanol and ethanol + water had
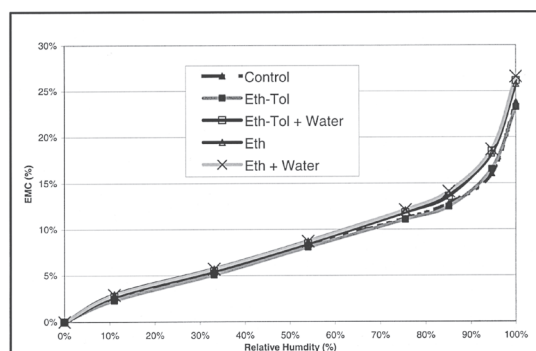

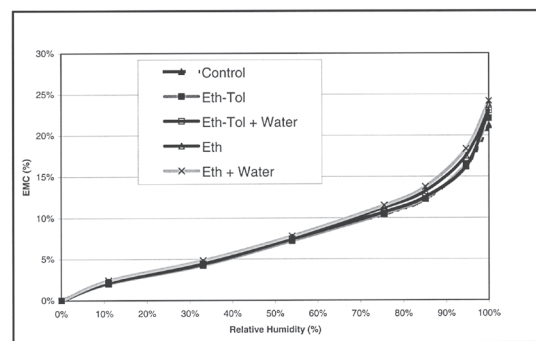FIG. 1. Adsorption curves of extracted and nonextracted black cherry specimens.

FIG. 2. Adsorption curves of extracted and nonextracted red oak specimens.

TABLE 3.   *Adsorption and desorption EMC of extracted and unextracted specimens.*

		Black cherry								
	Control		Eth-Tol		Eth-Tol+ Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11.0	2.5	4.9	2.3	4.8	2.7	4.8	2.9	5.0	2.9	4.8
33.1	5.3	6.1	5.1	6.4	5.5	6.4	5.7	7.0	5.7	6.5
54.0	8.3	9.1	8.1	9.4	8.5	9.4	8.7	10.0	8.7	9.5
75.5	11.2	14.3	11.1	15.4	11.8	15.8	12.1	15.3	12.1	15.6
85.1	12.8	15.1	12.5	16.4	13.6	17.0	13.9	16.4	14.1	16.8
94.6	16.1	18.7	16.6	20.0	18.5	20.7	18.2	19.9	18.7	20.5
100.0	23.8	24.5	23.3	25.3	26.1	26.9	25.8	25.5	26.6	26.8
		Red oak								
	Control		Eth-Tol		Eth-Tol+ Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11.0	2.1	4.5	2.0	4.2	2.2	4.4	2.3	4.2	2.4	4.4
33.1	4.5	5.6	4.3	5.7	4.4	5.7	4.6	5.6	4.8	5.8
54.0	7.5	9.8	7.2	9.7	7.5	9.7	7.6	9.6	7.8	9.7
75.5	10.5	15.5	10.5	16.1	10.7	15.9	11.2	16.2	11.5	16.0
85.1	12.3	18.0	12.3	19.1	12.5	19.0	13.2	18.9	13.8	19.2
94.6	16.3	20.5	16.5	21.4	16.2	21.7	17.5	22.0	18.4	22.3
100.0	21.2	26.4	22.1	26.6	23.0	27.2	23.7	27.1	24.2	27.3
		Red pine								
	Control		Eth-Tol		Eth-Tol+ Water		Eth		Eth + Water	
RH	Ads	Des	Ads	Des	Ads	Des	Ads	Des	Ads	Des
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11.0	2.5	4.8	2.7	5.0	2.7	4.8	2.6	4.9	2.7	4.7
33.1	5.2	7.6	5.5	7.7	5.5	7.5	5.5	7.6	5.5	7.4
54.0	8.2	9.5	8.5	9.8	8.5	9.4	8.5	9.5	8.5	9.3
75.5	12.4	16.3	13.1	16.8	13.2	16.4	12.9	16.6	13.1	16.4
85.1	14.4	17.2	15.3	17.7	15.2	17.3	15.0	17.3	15.4	17.2
94.6	17.7	18.0	19.7	18.7	18.7	18.3	18.7	18.4	19.1	18.3
100.0	26.8	27.6	28.0	27.9	29.7	29.3	28.8	29.0	30.4	29.6

Ads: Adsorption
Des: Desorption
Eth: Ethanol extraction
Eth +Water: Ethanol + Water extraction
Eth-Tol: Ethanol-Toluene extraction
Eth-Tol + Water: Ethanol-Toluene + Water extraction

consistently slightly higher EMC than control samples. A similar trend was observed in red oak (Fig. 2). For red pine (Fig. 3), the adsorption curves for all extraction treatment were consistently higher than the curve for unextracted specimens. From these observations, it can be concluded that extracted samples generally adsorbed more water than unextracted samples at high relative humidity. This conclusion is in agreement with previously published data on tropical and domestic hardwoods by Spalt (1957), Wangaard and Granados (1967), and

Chong and Achmadi (1991). The higher EMC in extracted samples is explained by the increased availability of moisture sites previously occupied by extractives, which became available to water once extractives were removed (Nearn 1955; Spalt 1979).

Analysis of adsorption data by the Hailwood-Horrobin sorption model

The Hailwood-Horrobin (1946) model considers that part of the sorbed water forms a hy-

TABLE 4. *Hysteresis ratio of specimens at various relative humidity.*

| | Black cherry | | | | |
	Control	Eth-Tol	Eth-Tol + Water	Eth	Eth + Water
11.0%	0.51	0.48	0.56	0.59	0.60
33.1%	0.87	0.79	0.86	0.82	0.87
54.0%	0.92	0.86	0.90	0.87	0.91
75.5%	0.78	0.72	0.75	0.79	0.77
85.1%	0.85	0.76	0.80	0.85	0.84
94.6%	0.86	0.83	0.89	0.92	0.91
100.0%	0.97	0.92	0.97	1.01	0.99
	Red oak				
11.0%	0.48	0.48	0.49	0.54	0.54
33.1%	0.80	0.75	0.77	0.82	0.84
54.0%	0.78	0.75	0.77	0.80	0.80
75.5%	0.69	0.65	0.67	0.69	0.72
85.1%	0.68	0.64	0.66	0.70	0.72
94.6%	0.80	0.77	0.75	0.80	0.82
100.0%	0.80	0.83	0.84	0.87	0.89
	Red pine				
11.0%	0.52	0.54	0.57	0.53	0.57
33.1%	0.68	0.71	0.74	0.72	0.75
54.0%	0.86	0.86	0.91	0.89	0.92
75.5%	0.76	0.78	0.80	0.78	0.80
85.1%	0.84	0.86	0.88	0.86	0.89
94.6%	0.98	1.02	1.02	1.02	1.04
100.0%	0.97	1.00	1.02	0.99	1.02
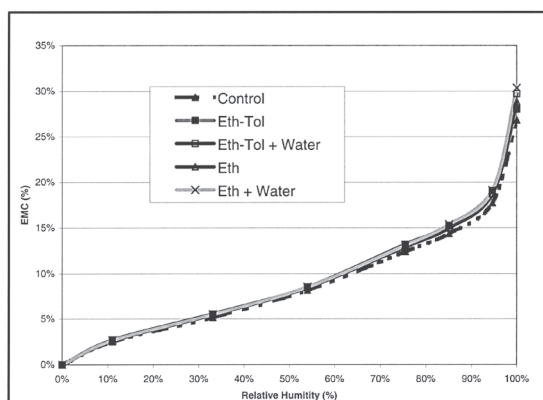
FIG. 3.   Adsorption curves of extracted and nonextracted red pine specimens.

where h is the relative vapor pressure
m is the equilibrium moisture content
A, B, and C are empirical constants.

A, B, and C are obtained by fitting the h/m values to Eq. (2) by the least square method, and the physical constants α, β, and W can be derived.

α is the equilibrium constant between the free dissolved water and the hydrated water,

β is the equilibrium constant between the dissolved water and the external vapor pressure,

W is the molecular weight of wood substance necessary to be associated with one molecular weight of water molecule (mol/mol).

α, β, and W be calculated using Eq. (3), Eq. (4), and Eq. (5) (Spalt 1958).

drate with wood, and the balance forms a solid solution in the cell wall (Spalt 1958, 1979; Cao and Kamdem 2003). Water therefore exits in two states, hydrated water and dissolved water. The sorption Eq. (2) of the Hailwood-Horrobin model is expressed as:

$$h/m = A + bh - Ch^2 \qquad (2)$$

$$\beta = \frac{\left(2 + \frac{B^2}{AC}\right) + \sqrt{\left(2 + \frac{B^2}{AC}\right)^2 - 4}}{2} \qquad (3)$$

$$\alpha = \frac{B}{A(\beta - 1)} \qquad (4)$$

$$\frac{W}{1800} = A(\beta+1)\alpha \qquad (5)$$

The free energy change for hydrated water can be calculated using Eq. (6).

$$\Delta G_h = -RT1n(\beta) \qquad (6)$$

Parameters from the Hailwood-Horrobin model are listed in Table 5. From that table, it can be observed adsorption data for all three species had a good fit with the model with R^2 values above 80% for all the treatments. The data also show that α and β equilibrium constants were consistently higher for all red pine extracted samples resulting in lower values for W and ΔG_h. ΔG_h is the energy required to swell the wood structure, and lower values of ΔG_h mean less energy is required to swell the wood structure. Therefore, lower values obtained for extracted red pine specimens are indications that the wood structure requires less energy to swell, due to the increase of hydrophilic sites. Similar trends were observed for red oak specimens (Table 5) and for cherry samples extracted with ethanol. The ΔG_h value for black cherry samples extracted with ethanol-toluene (664 j/mol) was higher than that of control samples (643 j/mol). However, this value decreased to 588j/mol when ethanol-toluene extraction was followed by water extraction. The reason

for the variation is unknown; however, it could be hypothesized that this is the result of the migration and relocation of some hydrophobic extractives not removed by the extraction process, but washed out by the subsequent water extraction.

Contact angle

The average contact angle values and standard deviations of eight replicate for each treatment are reported in Table 6. Extracted samples had contact angle values consistently lower than control samples for all three species, and the difference analyzed by one-way ANOVA (95% confidence level) was statically significant between all extraction types and control samples. In addition, the results also show that following organic solvent (ethanol or ethanol-toluene) extraction by water extraction resulted in slightly lower contact angles values. Lower contact angles for extracted samples confirm observations of the sorption experiment and reinforce the hypothesis of removal of hydrophobic compounds during the extraction process. This result is in agreement with results from Chen (1970) and Maldas and Kamdem (1999), who also obtained increased wettability in eight tropical woods and southern yellow pine. However, Nussbaum and Sterley (2002) obtained a more complex relationship between the contact angle, total extrac-

TABLE 5. *Parameters of the Hailwood-Horrobin sorption model.*

		A	B	C	R^2	β	α	W	ΔG_h
	Control	0.069	0.082	0.111	0.92	2.48	0.80	347	527
	Eth-Tol	0.060	0.095	0.118	0.91	2.94	0.81	348	490
Red pine	Eth-Tol + Water	0.060	0.093	0.117	0.90	2.88	0.81	346	487
	Eth	0.064	0.085	0.112	0.92	2.63	0.81	341	503
	Eth+Water	0.061	0.093	0.119	0.92	2.84	0.83	350	467
	Control	0.034	0.171	0.156	0.96	7.32	0.78	405	578
	Eth-Tol	0.038	0.168	0.158	0.94	6.57	0.79	411	550
Red oak	Eth-Tol + Water	0.034	0.173	0.160	0.91	7.34	0.80	409	548
	Eth	0.032	0.164	0.152	0.95	7.46	0.80	388	548
	Eth + Water	0.030	0.162	0.148	0.97	7.74	0.80	377	545
	Control	0.027	0.169	0.146	0.87	9.23	0.77	379	643
	Eth-Tol	0.025	0.173	0.147	0.85	9.96	0.76	382	664
Black cherry	Eth-Tol + Water	0.024	0.170	0.148	0.88	10.16	0.79	373	588
	Cherry Eth	0.021	0.165	0.139	0.87	11.37	0.77	355	638
	Eth + Water	0.021	0.167	0.144	0.88	11.11	0.78	361	601

TABLE 6. *Average (left and right) advancing contact Angle (degrees).*

	Red oak	Black cherry	Red pine
Control	88.1 (7.2)*	89.2 (4.1)	116.2 (6.5)
Eth-Tol	49.4 (7.5)	50.1 (6.2)	103.3 (6.9)
Eth-Tol + Water	48.3 (9.2)	42.4 (6.3)	45.6 (7.9)
Eth	62.1 (9.1)	57.6 (11.0)	80.4 (17.3)
Eth + Water	50.8 (9.2)	54.6 (6.6)	53.1 (6.5)

*Numbers in parenthesis are standard deviations.

TABLE 7. *Rate of change in contact angle (R) in degrees per second (deg/sec).*

	Control	Eth-Tol	Eth	Eth-Tol + Water	Eth+ Water
Red oak	2.75 (0.64)*	1.44 (0.38)	2.54 (0.65)	2.34 (0.75)	2.77 ().84)
Black cherry	1.62 (0.81)	0.82 (0.18)	0.69 (0.25)	2.82 (0.71)	3.16 (0.96)
Red pine	5.19 (0.91)	6.95 (1.45)	2.78 (0.73)	3.66 (1.02)	3.31 (0.86)

*Numbers in parenthesis are standard deviations.

tives, and storage time. They explained the variability in their results by the migration of extractives spreading on the wood surface and causing chemical changes to the surface.

Computed values of the water absorption rate-estimated as the decrease in contact angle of the water drop overtime are summarized in Table 7. Results presented show a tendency to a lower absorption rate of the water drop after initial solvent extraction. However, subsequent water extraction induced a higher absorption rate, similar or higher to the values for control samples. This can be explained by the migration phenomenon suggested by Nussbaum and Sterley (2002) during the first solvent extraction. Migrates are subsequently washed out during the following water extractions, resulting in wood surfaces with more affinity to water.

trend was not verified for black cherry samples extracted with ethanol-toluene mixture. This observation is probably due to the migration of some extractives to the wood surface following ethanol-toluene extraction.

The contact angle was found to decrease with increased extraction. The absorption rate, after an initial increase due to the modification of the wood surface caused by extractive migration, decreased following water extraction.

These results suggest that the increased ability of wood surfaces to absorb water due to their extractive content could lead to increased dimensional instability and eventually lead to more cracks and checks in extracted wood. Further studies are underway to test this hypothesis.

CONCLUSIONS

The influence of wood extractives on sorption and wettability of two hardwoods and one softwood species was investigated in this project. Results showed that wood extractives lowered the equilibrium moisture content of wood at high relative humidity. The difference between extracted and unextracted specimens was less pronounced when toluene was included in the solvent system. This was explained as a result of the migration and redistribution of hydrophobic extractives following the extraction, resulting in lower hysteresis.

Analysis of data using the Hailwood-Horrrobin sorption model showed that extracted red pine and ethanol-extracted cherry and oak had more adsorption sites available and needed lower energy to absorb water. However, this

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