Effects of Acid Pre-Treatments on the Swelling and Vapor Sorption of Thermally Modified Scots Pine (*Pinus sylvestris* L.) Wood

Reza Hosseinpourpia,[a,b,]* Stergios Adamopoulos,[b] and Carsten Mai [a]

Scots pine sapwood samples were pre-treated with a Lewis acid ($AlCl_3$) and a combination of Lewis and protonic acids ($AlCl_3$ and H_2SO_4), and were subsequently exposed to respective temperatures of 180 °C and 120 °C for establishing a comparable mass loss with those impregnated with demineralized water and solely thermally modified at 220 °C. Water impregnated samples dried at 120 °C also served as controls. The swelling behavior of all wood samples was examined with respect to maximum swelling in water, anti-swelling efficiency (ASE), shrinkage, and dynamic water vapor sorption at relative humidity ranges of 0% to 95%. The thermal modification at 220 °C diminished swelling and moisture adsorption, and also reduced moisture increment and decrement compared with the unmodified control. However, it was less obvious than both acid pre-treated samples. Excess surface work and Hailwood-Horrobin results calculated from water vapor sorption studies demonstrated that, at comparable mass loss, the available sorption sites were reduced to a greater extent by Lewis acid and combination of Lewis and protonic acids pre-treatment than the sole thermal treatment. This was attributed to more pronounced degradation of polysaccharides, mainly hemicelluloses and amorphous parts of cellulose, and to cross-linking of cell wall polymers due to the acid pre-treatments.

Keywords: Dynamic vapor sorption; Anti-swelling efficiency; Lewis acid; Protonic acid; Hailwood-Horrobin; Excess surface work; Thermal modification

Contact information: a: Wood Biology and Wood Products, Burckhardt Institute, Georg-August-University Göttingen, Büsgenweg 4, 37077 Göttingen, Germany; b: Department of Forestry and Wood Technology, Linnaeus University, Lückligs Plats 1, 351 95 Växjö, Sweden;
** Corresponding author: reza.hosseinpourpia@lnu.se*

INTRODUCTION

Thermal modification improves wood properties by reducing the hygroscopicity, improving the dimensional stability, and enhancing the resistance to biological degradation (Kim *et al*. 1998; Kamden *et al*. 1999, 2000). Property enhancement is influenced by both the modification (*e.g.*, treatment atmosphere, temperature, duration, and medium of heat transfer) and the chemical composition of wood (Militz and Altgen 2014). The chemical composition of wood is altered due to degradation of the cell wall compounds, mainly hemicelluloses, by the high treatment temperatures between 160 °C and 260 °C (Rowell *et al*. 2009; Kasemsiri *et al*. 2012; Mahnert *et al.* 2013; Xing and Li 2014). The equilibrium moisture content (EMC) of wood decreases mainly by a decreased number of accessible hydroxyl groups of the cell wall to water molecules due to degradation of carbohydrates, and also by cross-linking reactions of the cell wall polymers (Jämsä and Viitaniemi 2001; Wikberg and Liisa 2004; Bhuiyan and Hirai 2005; Tjeerdsma and Militz 2005; Boonstra and Tjeerdsma 2006; Esteves *et al*. 2008; Esteves and Pereira 2009). Such cross-linking reactions result in a reduced available volume for the adsorbed water between adjacent wood polymers in the cell wall. In combination with loss of hemicelluloses, this creates a stiffer matrix restraining the expansion of the cell wall nano-pores upon water adsorption (Tjeerdsma *et al*. 1998; Jalaludin *et al*. 2010; Hosseinpourpia and Mai 2016), and, subsequently, results in an increased dimensional stability of wood (Yan and Morell 2014; Čermák *et al.* 2015).

Like thermal modification, acid modification can also change the moisture-related properties of wood. Sulphur dioxide and hydrochloric acid degrade the cell wall polysaccharides, and thus reduce the water vapor adsorption (Stevens and Parameswaran 1981a; Stevens and Parameswaran 1981b). A previous study demonstrated a slight reduction in EMC of wood treated with Lewis acid due to a reduced flexibility of the cell wall matrix (Himmel and Mai 2015). Although there have been some studies describing the water-related properties of thermally modified wood, such information is quite limited when wood is acid pre-treated. Stamm (1959) studied the improvement of wood dimensional stability by heat treatment in the presence of a range of catalysts. Catalysts reduced the time of heating required to cause a given increase in dimensional stability, but they did not change the correlation between mass loss and anti-swelling efficiency (ASE) compared with heat treatment alone. The use of acidic catalysts combined with heat treatment increased the yield of furfural and furan derivatives (Fengel and Wegener 1989). A more recent study reported that, at comparable mass loss, the pre-treatment of wood with protonic acid caused a strong reduction in hygroscopicity and significant improvement in dimensional stability as compared to solely thermal modification (Hosseinpourpia *et al*. 2017).

Numerous mathematical models have been derived to describe the sorption isotherms of hygroscopic polymers, *i.e.*, the graphical representations of the relationship between the equilibrium moisture content and the relative humidity at a given temperature. Some of them have been applied to wood with success (Simpson 1980; Skaar 1988), such as the BET (Dent 1977) or GAB (Van den Berg 1984) models, by mainly using a multilayered adsorption concept or chemical reactions. Another approach according to the Hailwood-Horrobin (H-H) single-hydrate model is the assumption that the sorption process is a water–polymer solution (Yasuda *et al*. 1994, 1995; Hill 2008; Zaihan *et al*. 2009; Hill *et al*. 2010). The H-H model considers the state of equilibrium existing between a vapor phase, a liquid phase (monolayer water bonded to the cell wall polymeric hydroxyl groups), and a solid solution or dissolved water (polylayer water) corresponding to water molecules that are less constrained, and located, however, within the cell wall nano-pores (Hailwood and Horrobin 1946). The H-H model gives an appropriate agreement with experimental analysis over a wide range of relative humidity, although this model is only suited to explain the adsorption part of the isotherm (Hill 2008; Jalaludin *et al*. 2010). Adolphs and Setzer (1996) suggested another thermodynamic model of sorption isotherms called “excess surface work” (ESW), to assess the monolayer capacity and the related characteristic energy. Hosseinpourpia *et al.* (2017) have recently used the ESW model to describe the monolayer capacity and related characteristic energy of proton acid pre-treated wood at relatively low temperatures.

Sorption analysis of modified wood by the dynamic vapor sorption (DVS) technique has been used previously (Hill *et al*. 2010; Jalaludin *et al*. 2010; Himmel and Mai 2015; Himmel and Mai 2016; Hosseinpourpia *et al.* 2016, 2017). The aim of the present study was to determine the water vapor sorption and swelling behavior of thermally modified wood pre-treated with Lewis acid and combination of Lewis and protonic acids. The results were compared with only thermally modified samples or unmodified samples at comparable mass loss. The water vapor sorption data were analyzed by a DVS apparatus and explained by applying the H-H and ESW models.

EXPERIMENTAL

Wood and Chemicals

Wood samples cut from Scots pine (*Pinus sylvestris* L.) sapwood blocks measuring 25 × 25 × 10 mm^3 (R × T × L), with an average density of 0.50 g cm^{-3}, originating from one log, which had straight grain and was free of knots and decays. Sulfuric acid (H_2SO_4) and aluminum chloride ($AlCl_3$) were purchased from AppliChem GmbH (Darmstadt, Germany) and Acros Organics (Geel, Belgium), respectively.

Wood Treatments

Wood samples were vacuum-impregnated (100 mbar, 60 min) with an aqueous solution of Lewis acid (1 mol L^{-1} $AlCl_3$) and a combination of protonic and Lewis acids (0.5 mol L^{-1} H_2SO_4 and 1 mol L^{-1} $AlCl_3$). A set of samples was impregnated with demineralized water. After impregnation, the excess solution was blotted off the samples with filter paper. Water impregnated and acid treated samples were wrapped in aluminum foil and pre-heated (120 °C) for 60 min. Heat treatment was performed at atmospheric pressure for all samples in an oven starting at 60 °C and gradually increasing the temperature (30 °C h^{-1}) up to 100 °C. Subsequently, the acid pre-treated samples were exposed for 120 min to the target temperature of 120 °C for the combined acid treatment and 180 °C for the $AlCl_3$ treatment. The water treated samples were exposed to 120 °C (untreated controls) and 220 °C (thermally treated) for the same time period. All samples were subsequently leached with demineralized water for 14 days following the standard EN 84 (1997) until the leaching water reached pH 5 to 6. After leaching, samples were stored at 20 °C and 65% relative humidity (RH) for 7 days and were subsequently oven dried at 103 °C for 24 h and weighed prior to any further measurements.

Dimensional Stability

Dimensional change (shrinking) due to treatments, considered to be equivalent to “negative” bulking, was assessed with respect to the area changes, in radial and tangential directions, of oven-dried samples before and after treatments, using a micrometer with a precision of 0.001 mm, as follows,

$$Shrinkage = -\left(\frac{A_t}{A_u} - 1\right) \times 100 \tag{1}$$

where A_t is the area of oven-dried sample after treatment and A_u is the area of oven-dried sample before treatment. Maximum swelling ($Swell_{max}$) and anti-swelling (shrinkage) efficiency (ASE) in water were determined according to the Xiao *et al*. 2010 by using the following equations,

$$Swell_{max} = \left(\frac{A_w - A_d}{A_d}\right) \times 100 \tag{2}$$

$$ASE = \frac{S_u - S_t}{S_t} \times 100 \tag{3}$$

where A_w is the water saturated area of sample; A_d is the area of oven-dried sample; S_u is the maximum swelling of untreated sample, and S_t is the maximum swelling of treated sample. Twelve samples for each of the treatments were used for the measurements.

Dynamic Water Vapor Sorption

The water vapor sorption behavior was determined using a DVS apparatus (DVS Advantage, Surface Measurement Systems, London, UK) as reported previously (Himmel and Mai 2015; Hosseinpourpia *et al*. 2016, 2017). Approximately 20 mg of wood powder (passed through a 20-mesh sieve) was used, and the sorption process was run at a constant temperature of 25 °C. The RH range started from 0% and increased stepwise by 5% increments up to 95%, decreasing to 0% RH in a reverse order. The instrument maintained a constant RH until the mass change of the sample (dm/dt) was less than 0.002% per min over a 10 min period. As there were considerable differences in the adsorption isotherms between the first and subsequent sorption cycles of thermally modified wood (Hill *et al.* 2012b), only the equilibrium moisture content (EMC) values of the second cycles were analyzed.

The EMC-ratio of the treated samples was calculated by dividing their EMC with the EMC of the respective untreated controls (120 °C) at each RH step throughout the adsorption and desorption process (Hosseinpourpia *et al.* 2016). The EMC increments and decrements for the respective adsorption and desorption stages were calculated according to Himmel and Mai (2015) and Hosseinpourpia *et al*. (2016).

Hailwood-Horrobin (H-H) Model

The adsorption behavior of treated wood was assessed by fitting the experimental data using the H-H model as reported previously (Hill *et al*. 2008; Zaihan *et al*. 2009; Jalaludin *et al*. 2010),

$$M = M_h + M_s = \frac{1800}{W}\left[\frac{K_1K_2H}{100 + K_1K_2H}\right] + \frac{1800}{W}\left[\frac{K_2H}{100 - K_2H}\right] \tag{1}$$

where M is the EMC at each given relative humidity (RH), M_h is the moisture content attributable to monolayer sorption, M_s is the moisture content due to polylayer sorption, W is the molecular weight of the cell wall polymer per mole of water sorption sites, and K_1 and K_2 are equilibrium constants and determined by plotting RH M^{-1} against RH. The detailed theory of the H-H model can be found in the literature (Skaar 1988; Hill 2008).

Excess Surface Work (ESW)

The water vapor adsorption isotherm for nano-porous materials was assessed by the ESW model (Adolphs and Setzer 1996; Adolphs and Setzer 1998; Churaev *et al*. 1998; Hosseinpourpia *et al.* 2017) as follows,

$$\mathrm{ESW} = \mathrm{n_{ads}} \times \Delta\mu \tag{2}$$

where n_{ads} is the amount of adsorbed water molecule (surface excess amount, mol g^{-1}), and $\Delta\mu$ is the change in chemical potential (J mol^{-1}), which can be computed as,

$$\Delta\mu = \mathrm{RT} \times \ln({}^{\mathrm{p}}/_{\mathrm{p_s}}) \tag{3}$$

where R is the gas constant with 8.31447(15) J mol^{-1} K^{-1} (Mohr *et al.* 2008), T is the temperature (in Kelvin), and (p/p_s) = (RH/100), the equilibrium partial pressure of the sorptive vapor to saturation vapor pressure. As the chemical potential was negative, the

ESW must be negative when the adsorbed amount was defined as positive. The ESW became zero both at zero coverage and infinite coverage when there was no change in the chemical potential (Adolphs and Setzer 1996). Below the ESW minimum, the surface-free energy dominated; in contrast, the work of sorption was prevalent at higher sorption capacities, meaning that after completion of a monolayer the adsorbent-adsorbate interaction changed to an adsorbate-adsorbate interaction, which could be defined as a multilayer sorption (Adolphs 2007; Himmel and Mai 2016; Hosseinpourpia *et al.* 2017).

RESULTS AND DISCUSSION

Dimensional Stability of Treated Wood

The treatments caused mass loss (ML) of wood samples and enhanced dimensional stability (Table 1). The ML could be explained mainly by degradation of hemicelluloses (Weiland *et al*. 1998; Alén *et al*. 2002). Thermal treatment at 220 °C decreased maximum swelling ($\text{swell}_{\text{max}}$) to 10.9% compared with the $\text{swell}_{\text{max}}$ of 17.8% of the unmodified control samples (120 °C). A comparable $\text{swell}_{\text{max}}$ of 11.2% was noticed for the wood samples subjected to $AlCl_3$ pre-treatment at 180 °C, while $\text{swell}_{\text{max}}$ was further decreased in the case of combined H_2SO_4 and $AlCl_3$ pre-treatment at 120 °C (8.6%). At comparable ML, the solely thermally treated (220 °C) and $AlCl_3$ pre-treated samples (180 °C) also had similar shrinkage (2.8% and 3.3%) and ASE (38.4% and 41.7%) values. Combination of H_2SO_4 and $AlCl_3$ at 120 °C, however, displayed a considerably higher shrinkage and ASE of 4.1% and 51.8%, respectively. It can be hypothesized that the combination of protonic and Lewis acids (H_2SO_4-$AlCl_3$) caused a greater cross-linking of the cell wall as compared to solely thermally treated samples at 220 °C and $AlCl_3$ pre-treated ones (180 °C). A very recent study reported a comparable dimensional stability of wood pre-treated with protonic acid at relatively low temperatures (up to 180 °C), and interpreted that the degradation of amorphous polysaccharides and cross-linking of the cell wall's polymer constituents resulted in a stiffer matrix, which had a low swell-ability upon water absorption (Hosseinpourpia *et al.* 2017).

Table 1. Mass Loss, Shrinkage, $\text{Swell}_{\text{max}}$, and Anti-Swelling Efficiency (ASE) of Treated Wood

Treatment	Mass Loss (%)	Shrinkage (%)	$\text{Swell}_{\text{max}}$ (%)	ASE (%)
Control (120 °C)	-	-	17.8 ± 1.0[a]	-
Thermal (220 °C)	10.5 ± 0.4[a]	2.8 ± 0.6[a]	10.9 ± 0.3[a]	38.4 ± 2.2[a]
$AlCl_3$ (180 °C)	9.8 ± 0.4[a]	3.3 ± 0.8[a]	11.2 ± 1.5[a]	41.7 ± 6.4[a]
H_2SO_4-$AlCl_3$ (120 °C)	10.2 ± 0.7[a]	4.1 ± 1.1[a]	8.6 ± 2[a]	51.8 ± 10.3[a]

[a] Standard deviation

Dynamic Vapor Sorption Behavior of Treated Wood

The adsorption and desorption curves of the unmodified and modified wood (Fig. 1a; Fig. 1b) showed the characteristic sigmoidal shape described for cellulose-based materials (Skaar 1988). EMC increased with increasing RH due to the abundant hydroxyl groups and the new sorption sites created upon swelling of cell wall polymers (Malmquist and Söderström 1996). The sharp increment of the adsorptive isotherms at approximately 60% to 70% RH was previously explained as a result of the softened hemicelluloses, which leads to increased elastic swelling of cell walls, and subsequently to more accommodation possibility for water molecules (Vrentas and Vrentas 1991; Olsson and Salmén 2004; Engelund *et al*. 2013). Compared with unmodified wood, the EMC of thermally and acid pre-treated wood was reduced over the whole range of RH in the adsorption and desorption isotherms (Fig. 1). The reduction in EMC was more obvious in the case of pre-treated samples with Lewis acid alone and with combination of Lewis and protonic acids. Decreasing the EMC of thermal and acid pre-treated wood might be attributed to the a) hydrolysis of polysaccharides, particularly hemicelluloses (Stevens and Parameswaran 1981a, b; Mburu *et al*. 2008); and/or b) reduction in swell-ability of the wood matrix due to cross-linking of the cell wall polymers (Tjeerdsma *et al.* 1998). Above 20% RH, the sigmoidal shape of desorption isotherms of modified samples became linear (Fig. 1b). This may be explained by the increased matrix stiffness due to the thermal and acid modification. The additional created bonds, by condensation reaction involving lignin, furfural and other degradation products, within the polymeric network most likely reduce the polymer mobility (Altgen *et al.* 2016) and cause a stiffer matrix. The latter, limits the accessibility of the remaining hydroxyl groups upon moisture adsorption and favors the rearrangement of the matrix polymer during desorption process.

The EMC ratio for adsorption and desorption (Fig. 2) was almost constant for the solely thermally modified samples at 220 °C. $AlCl_3$ pre-treated wood at 180 °C demonstrated a higher decreasing slope than H_2SO_4-$AlCl_3$ pre-treated ones (120 °C) in the EMC adsorption ratio. A similar trend was observed in EMC ratio of modified samples during desorption stages (Fig. 2b). A lower, but almost constant, EMC ratio of the samples pre-treated with H_2SO_4-$AlCl_3$ at 120 °C might have been related to the stronger degradation of amorphous polymers. A decreasing slope of the EMC ratio of $AlCl_3$ pre-treated wood with increasing RH was attributed to increased cell wall stiffness due to cross-linking of cell wall polymers (Himmel and Mai 2015; Hosseinpourpia *et al*. 2016, 2017). Cross-linking limits the ability of the cell wall to swell (Xie *et al*. 2011) and reduces the EMC ratio with increasing degree of swelling upon higher RHs.

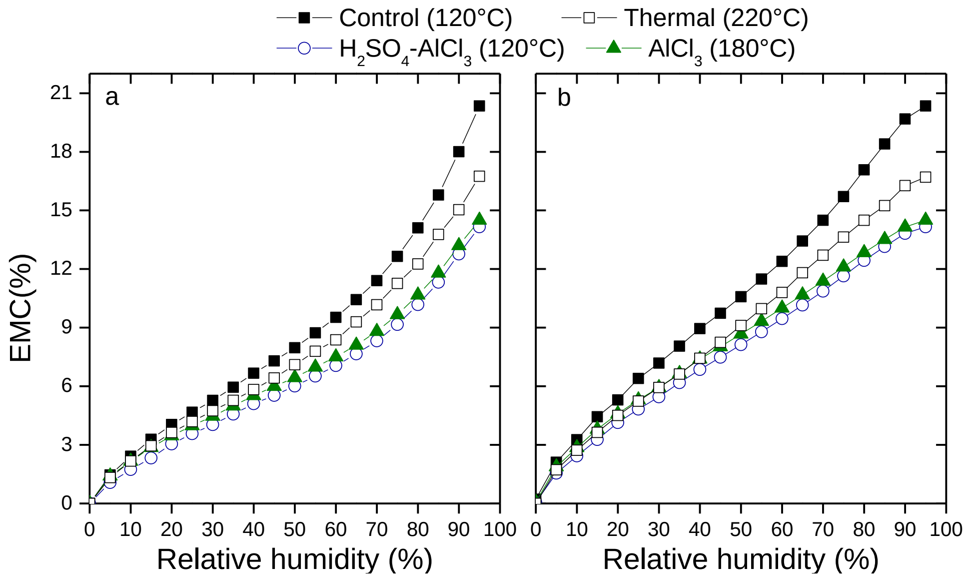

Fig. 1. Adsorption (a) and desorption (b) isotherms of untreated wood (120 °C), thermally-treated wood at 220 °C (10.5% ML), $AlCl_3$ pre-treated wood at 180 °C (9.8% ML), and H_2SO_4-$AlCl_3$ pre-treated wood at 120 °C (10.2% ML)

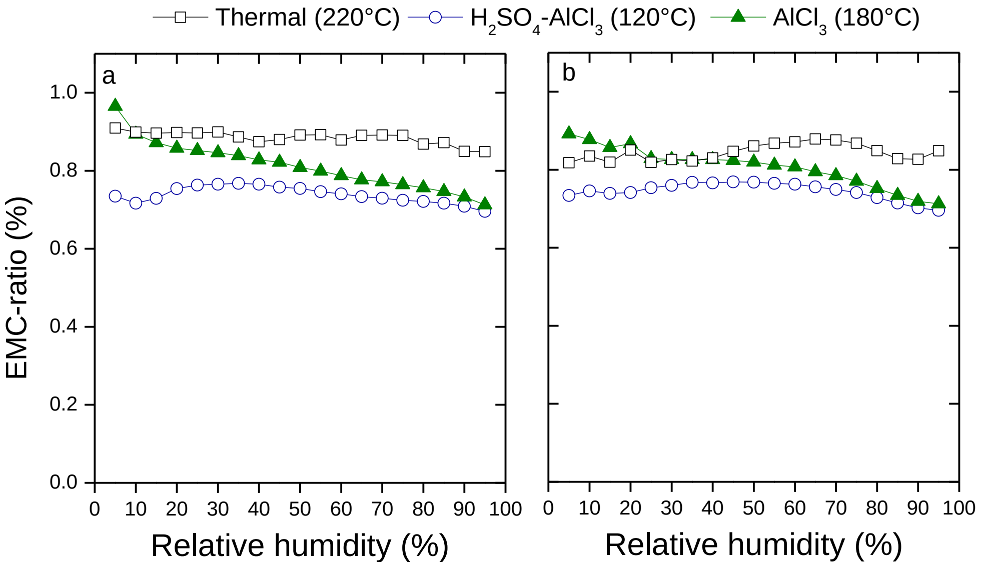

Fig. 2. EMC-ratio at adsorption (a) and desorption (b) of thermally-treated wood at 220 °C (10.5% ML), $AlCl_3$ pre-treated wood at 180 °C (9.8% ML), and H_2SO_4-$AlCl_3$ pre-treated wood at 120 °C (10.2% ML)

The moisture changes of unmodified and modified samples decreased below 20% RH during adsorption; by increasing the RH from 30% to approximately 60%, the moisture remained almost constant (Fig. 3a).

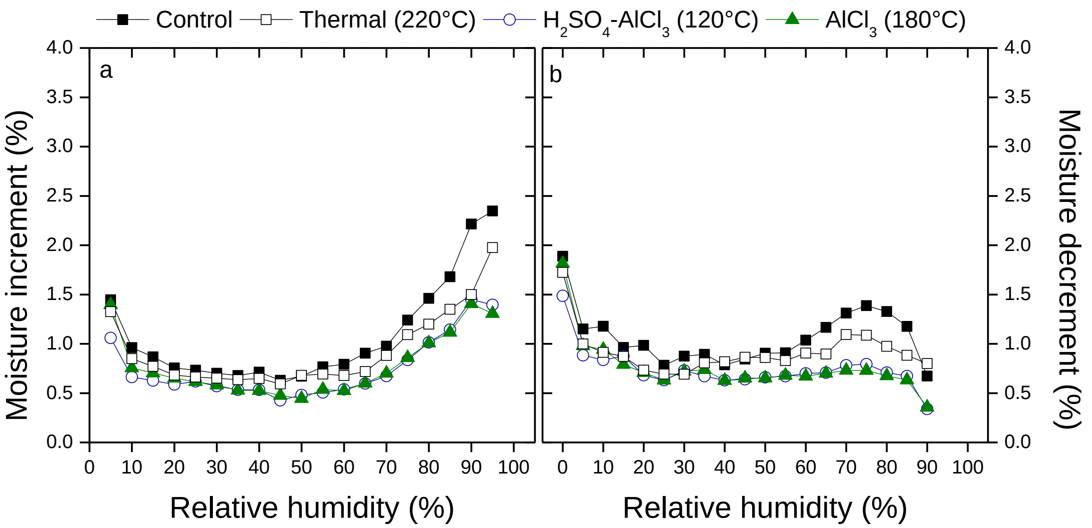

Fig. 3. Moisture increment during adsorption (a) and decrement during desorption (b) of untreated wood (120 °C), thermally-treated wood at 220 °C (10.5% ML), $AlCl_3$ pre-treated wood at 180 °C (9.8% ML), and H_2SO_4-$AlCl_3$ pre-treated wood at 120 °C (10.2% ML)

Above 60% RH, the moisture increment strongly and gradually increased. This result implied an increased swelling of the wood matrix due to softening of its amorphous polymers, particularly hemicelluloses, at the higher RHs (Siau 1995). As the concentration of bound water increases, the water vapor sorption process is dominated by the relaxation of swelling stresses generated by the sorbate (Christensen 1965; Engelund *at al*. 2013). The lower moisture increment of the samples pre-treated with Lewis acid and with combination of Lewis and protonic acids could be explained by the reduction of the amorphous polysaccharide content in wood and the increase of matrix stiffness due to cross-linking.

During the desorption process, the moisture content decrement of the unmodified and modified wood slightly increased from 95% to approximately 70% RH, remained stable with decreasing RH, and finally sharply increased at the RH range from approximately 20% to 0% (Fig. 3b). Higher moisture decrement of thermally and acid-treated wood than unmodified controls might be due to the fast egress of water molecules from the newly generated sorption sites that have been created through the adsorption process at higher RH (Himmel and Mai 2016). Fast desorption could be associated with the increased stiffness as wood became drier (Hill *et al*. 2012a). The increase in moisture desorption rate at the RH range below 20% could be related to the fact that shrinking and relaxation processes rarely occur and that water molecules are desorbed from easily accessible sorption sites (Hosseinpourpia *et al.* 2016).

Thermal modification and acid pre-treatments reduced the sorption hysteresis of wood compared with unmodified controls (Fig. 4). Hysteresis has been explained previously by swelling behavior of glassy-like matrix below the glass transition temperature (Lu and Pignatello 2002; Hill *et al*. 2010). When the matrix relaxation to a thermodynamic equilibrium state is kinetically hindered, adsorption and desorption occur in different physical environments (Lu and Pignatello 2002). Hosseinpourpia *et al*. (2017) reported that the extent of these physical differences decreases with increasing matrix stiffness, and thus hysteresis reductions in thermally modified and acid pre-treated wood as compared to unmodified ones were not merely attributed to the polysaccharide degradation, but also to enhanced matrix stiffness. The latter could be enhanced due to the polymerization of lignin at higher temperatures (Tjeerdsma *et al*. 1998). However, it was previously reported that the presence of lignin increases the sorption hysteresis (Hosseinpourpia *et al*. 2016). Therefore, it was assumed that lignin polymerization might enhance sorption hysteresis of thermally modified and acid pre-treated wood, but this was offset by polysaccharide degradation and whole matrix stiffness.

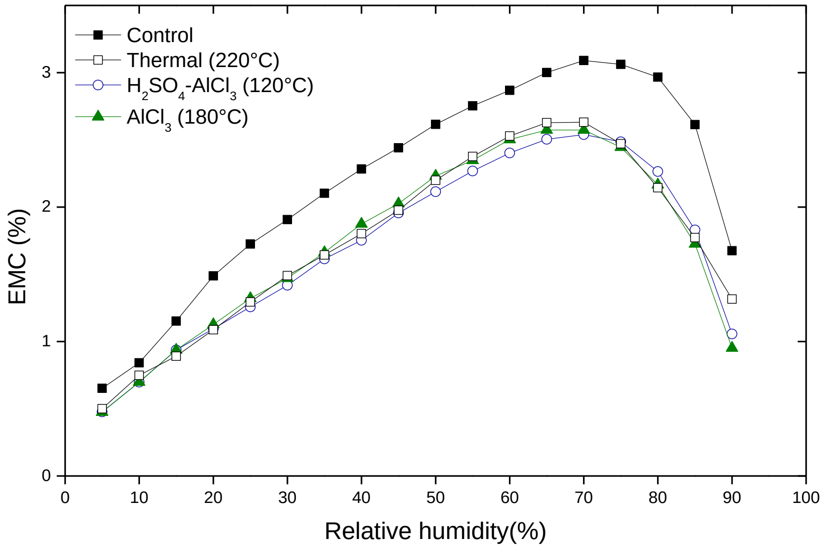

Fig. 4. Sorption hysteresis of untreated wood (120 °C), thermally-treated wood at 220 °C (10.5% ML), $AlCl_3$ pre-treated wood at 180 °C (9.8% ML), and H_2SO_4-$AlCl_3$ pre-treated wood at 120 °C (10.2% ML)

Analysis Based on the Hailwood-Horrobin (H-H) Model

The H-H model described the water sorption of wood by separation into hydrate water (M_h) and into dissolved water (M_s) (Fig. 5a). The experimental data from the adsorption isotherm of unmodified control, thermally, and acid pre-treated wood were appropriately fitted with the H-H model (Fig. 5b). The sorption value could be extrapolated to 100% RH, which is often interpreted as being the fiber saturation point (FSP) of the material (Hill 2008; Jalaludin *et al*. 2010). The projected FSP for the control wood (120 °C) was 24.6%, whereas the reduced respective values for solely thermally-treated (220 °C), $AlCl_3$ pre-treated (180 °C), and H_2SO_4-$AlCl_3$ pre-treated (120 °C) were 19.5%, 16.2%, and 17.0%, respectively.

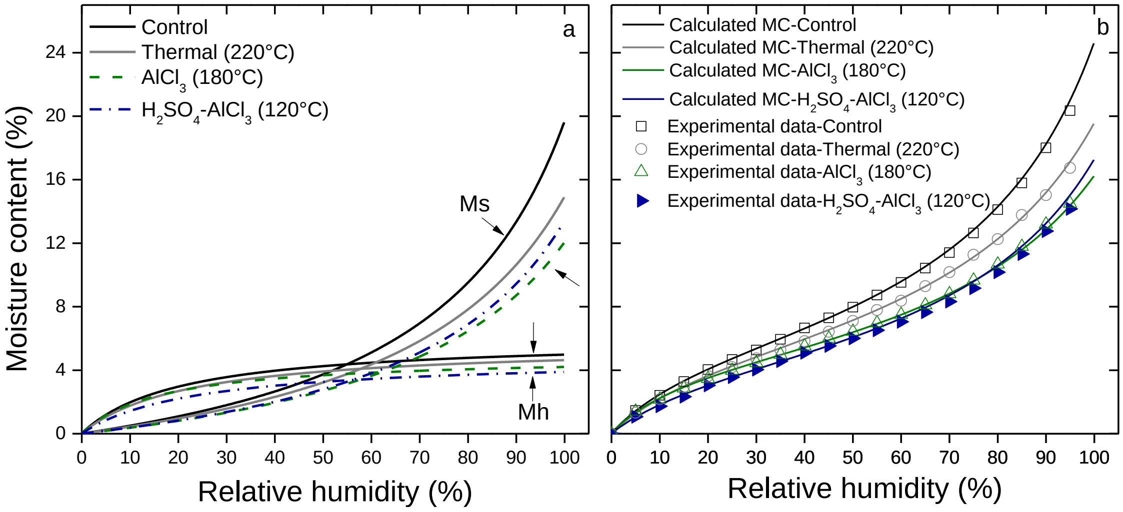

Fig. 5. Comparison of monolayer (Mh) and polylayer (Ms) water using the H-H model for the untreated, thermally and acid pre-treated wood (a). The sum of monolayer and polylayer (calculated total MC) adsorption isotherms through the RH run compared with experimental MC for the untreated, thermally and acid pre-treated wood (b)

Compared with the control, the H-H model showed a reduction in the monolayer and the polylayer sorption after the treatments. At comparable ML, the pre-treatments with Lewis acid and with combination of Lewis and protonic acids caused further reduction in M_h and M_s compared with thermal treatment alone. This result indicated that the acid pre-treatments resulted in less available sites for monolayer sorption than the thermal treatment and the controls. The reduction in M_s presumably reflected the decreased capacity of expansion of the cell wall owing to increased matrix stiffness due to lower proportion of swellable polymer (hemicelluloses) and/or due to cross-linking of the cell wall polymers (Jalaludin *et al*. 2010). The combined acid pre-treated wood samples demonstrated a slight reduction in monolayer (M_h) sorption than Lewis acid pre-treated ones, which may be related to the stronger degradation of polysaccharides. However, the lower polylayer (M_s) sorption of Lewis acid pre-treated wood can be explained by higher degree of cross-linking. This is in accordance with the negative slope obtained in EMC ratio curve (Fig. 2a).

Analysis Based on the Excess Surface Work (ESW) of Wood

The minimum value of ESW was attributed to the completed monolayer or the sum of the areas of adsorbed molecules at the maximum of interaction with the adsorbent (Adolphs and Setzer 1996; Adolphs 2007; Himmel and Mai 2016). H_2SO_4-$AlCl_3$ pre-treated wood at 120 °C and $AlCl_3$ pre-treated wood at 180 °C exhibited almost equal ESW minima, but minor decrease relative to solely thermally modified wood at 220 °C (Fig. 6a). These results were in accordance with the monolayer sorption calculated by the H-H model (Fig 5a). After formation of a completed monolayer, the ESW of acid pre-treated wood samples deceased with a somewhat steeper slope as the solely thermally modified and unmodified wood with increasing amount of adsorbed water (Fig. 6a).

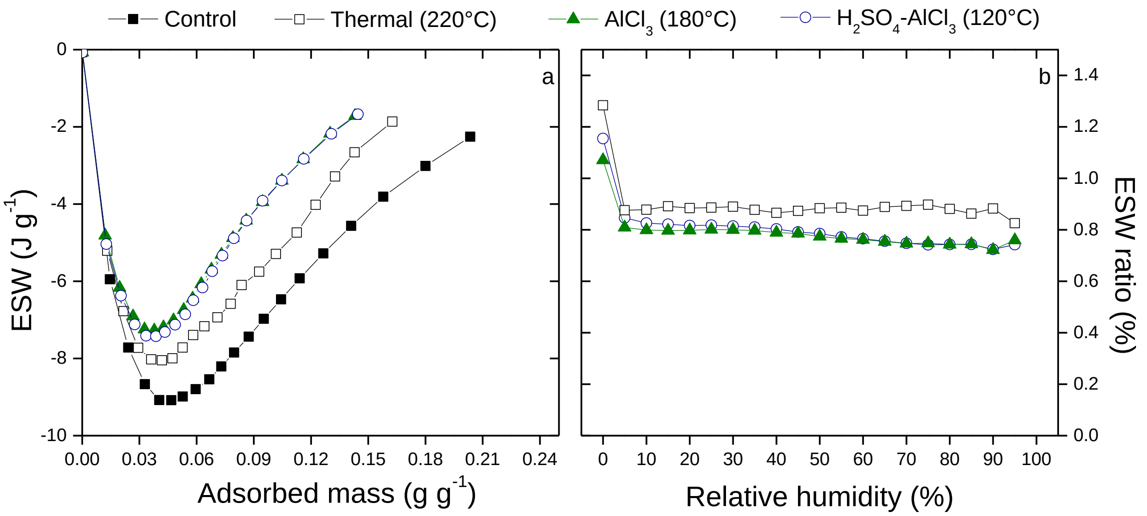

Fig. 6. Excess surface work (ESW) calculated as a function of the adsorbed mass of water (a) and ESW ratios related to the untreated wood (120 °C) (b) of thermally-treated wood (220 °C), $AlCl_3$ pre-treated wood (180 °C) and H_2SO_4-$AlCl_3$ pre-treated wood (120°C)

The slope of the ESW branch at RH above the ESW minimum indicates the resistance of the matrix to swelling; a greater slope reflects higher resistance to swelling, *i.e.* higher matrix stiffness (Himmel and Mai 2016; Hosseinpourpia *et al.* 2017). Pre-treatment of wood samples with Lewis acid and a combination of Lewis and protonic acids resulted in a slight declining course in ESW ratio, while it was almost constant in solely thermally modified wood at 220 °C. These results were in line with the polylayer sorption (M_s) assessed by the H-H model (Fig 5a), which may indicate a greater matrix stiffness in acid treated samples than thermally modified ones.

This study showed that the pre-treatment of wood with Lewis acid and combination of Lewis and protonic acids improved the dimensional stability and reduced the swell-ability of the wood cell wall to a greater extent than those of solely thermally modified wood. Combination of Lewis and protonic acids is assumed to contribute to stronger polysaccharides degradation and reduction of the available sorption sites in the wood cell wall, as observed in monolayer adsorption (M_h), while cross-linking is presumed to be slightly pronounced in Lewis acid pre-treated wood, as indicated in polylayer adsorption (M_s).

CONCLUSIONS

1. Thermal modification and acid pre-treatment improved the dimensional stability and altered the swelling behavior of Scots pine sapwood.

2. Lewis acid and combination of Lewis and protonic acids pre-treatments reduced the equilibrium moisture content (EMC), EMC-ratio, and moisture increment and decrement of wood more strongly than the solely thermal treatment at comparable mass loss (ML).
3. Application of the Hailwood-Horrobin (H-H) model showed good fitting with experimental data obtained from the adsorption isotherms. Monolayer and polylayer sorption were more strongly reduced in acid pre-treated samples than in solely thermally treated samples. Reduced polylayer sorption was attributable to the reduction in swell-ability of the cell wall upon higher RHs.
4. The calculated excess surface work (ESW) minimum was lower in the case of acid-treated wood than solely thermally treated and untreated samples, which indicated that, at comparable ML, fewer sites for monolayer sorption existed after acid pre-treatment than after sole thermal treatment.
5. The obtained results from H-H and ESW models suggested that the improvement in dimensional stability of thermally modified and Lewis acid and combination of Lewis and protonic acids pre-treated wood can mainly be attributed to the reduction of available sorption sites, and also the slight enhancement of the matrix stiffness due to the cross-linking.

ACKNOWLEDGMENTS

Dr. Reza Hosseinpourpia acknowledges the financial contribution of German Academic Exchange Service (DAAD), and also VINNOVA, Swedish Governmental Agency for Innovation Systems (VINNMER Marie Curie Incoming project 2015-04825).

REFERENCES CITED

Adolphs, J., and Setzer, M. J. (1996). “Energetic classification of adsorption isotherms,” *J. Colloid. Interf. Sci*. 184, 443-448. DOI: 10.1006/jcis.1996.0639

Adolphs, J., and Setzer, M. J. (1998). “Description of gas adsorption isotherms on porous and dispersed systems with the excess surface work model,” *J. Colloid. Interf. Sci*. 207, 349-354. DOI: 10.1006/jcis.1998.5786

Adolphs, J. (2007). “Excess surface work – A modeless way of getting surface energies and specific areas directly from sorption isotherms,” *Appl. Surf. Sci*. 253, 5645-5649. DOI: 10.1016/j.apsusc.2006.12.089

Altgen, M., Hofmann, T., and Militz, H. (2016). “Wood moisture content during the thermal modification process affects the improvement in hygroscopicity of Scots pine sapwood,” *J. Wood Sci*. 50, 1181-1195. DOI: 10.1007/s00226-016-0845-x

Alén, R., Kotilainen, R., and Zaman, A. (2002). “Themochemical behaviour of Norway spruce (*Picea abies*) at 180-225°C,” *Wood Sci. Technol*. 36, 163-171. DOI: 10.1007/s00226-001-0133-1

Bhuiyan, T. R., and Hirai, N. (2005). “Study of crystalline behavior of heat-treated wood cellulose during treatments in water,” *J. Wood Sci*. 51, 42-47. DOI: 10.1007/s10086-003-0615-x

Boonstra, M. J., and Tjeerdsma, B. (2006). "Chemical analysis of heat treated softwoods," *Holz Roh. Werkst*. 64, 204-211. DOI: 10.1007/s00107-005-0078-4

Čermák, P., Rautkari, L., Horáček, P., Saake, B., Rademacher, P., and Sablík, P. (2015). "Analysis of dimensional stability of thermally modified wood affected by re-wetting cycles," *BioResources* 10(2), 3242-3253.

Christensen, G. N. (1965). "The rate of sorption of water vapor by thin materials," in: *Humidity and Moisture. Volume Four: Principles and Methods of Measuring Moisture in Liquids and Solids,* P. N. Winn (ed.), Reinhold Publishing Corporation, New York. pp 279-293.

Churaev, N. V., Setzer, M. J., and Adolphs, J. (1998). "Influence of surface wettability on adsorption isotherms of water vapor," *J. Colloid. Interf. Sci*. 197, 327-333. DOI: 10.1006/jcis.1997.5292

Dent, R. W. (1977). "A multilayer theory for gas sorption. I. Sorption of a single gas," *Text. Res. J*. 47, 145-152. DOI: 10.1177/004051757704700213

EN 84. (1997). "Wood preservatives - Accelerated aging of treated wood prior to biological testing-Leaching procedure," European Committee for Standardization, Brussels, Belgium.

Engelund, E., Thygesen, L., Svensson, S., and Hill, C. A. S. (2013). "A critical discussion of the physics of wood-water interactions," *Wood Sci. Technol.* 47, 141-161. DOI: 10.1007/s00226-012-0514-7

Esteves, B., Graca, J., and Pereira, H. (2008). "Extractive composition and summative chemical analysis of thermally treated eucalypt wood," *Holzforschung* 62, 344-351. DOI: 10.1515/HF.2008.057

Esteves, B. M., and Pereira, H. M. (2009). "Wood modification by heat treatment: A review," *BioResources* 4, 370-404.

Fengel, D., and Wegener, G. (1989). *Wood: Chemistry, Ultrastructure, Reactions*, Walter De Gruyter, Berlin, Germany. DOI: 10.1002/pol.1985.130231112.

Hailwood, A. J., and Horrobin, S. (1946). "Absorption of water by polymers analysis in terms of a simple model," *Trans. Faraday Soc.* 42, 84-102. DOI: 10.1039/TF946420B084

Hill, C. A. S. (2008). "The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents: A reappraisal," *Holzforschung* 62, 423-428. DOI: 10.1515/HF.2008.078

Hill, C. A. S., Norton, A. J., and Newman, G. (2010). "The water vapour sorption properties of Sitka spruce determined using a dynamic vapour sorption apparatus," *Wood Sci. Technol.* 44, 497-514. DOI: 10.1007/s00226-010-0305-y

Hill, C. A. S., Keating, B., Jalaludin, Z., and Mahrdt, E. (2012a). "A rheological description of the water vapour sorption kinetics behaviour of wood invoking a model using a canonical assembly of Kelvin-Voigt elements and a possible link with sorption hysteresis," *Holzforschung* 66(1), 35-47. DOI: 10.1515/HF.2011.115

Hill, C.A.S., Ramsay, J., Keating, B., Laine, K., Rautkari, L., Hughes, M., and Constant, B. (2012b) "The water vapour sorption properties of thermally modified and densified wood," *J. Mat. Sci.* 47, 3191-3197. DOI: 10.1007/s10853-011-6154-8

Himmel, S., and Mai, C. (2015). "Effects of acetylation and formalization on the dynamic water vapor sorption behavior of wood," *Holzforschung* 69, 633-643. DOI: 10.1515/hf-2014-0161

Himmel, S., and Mai, C. (2016). “Water vapor sorption of wood modified by acetylation and formalisation - Analysed by a sorption kinetics model and thermodynamic considerations,” *Holzforschung* 70(3), 203-213. DOI: 10.1515/hf-2015-0015

Hosseinpourpia, R., Adamopoulos, S., and Mai, C. (2016). “Dynamic vapour sorption of wood and holocellulose modified with thermosetting resins,” *Wood Sci. Technol.* 50, 165-178. DOI: 10.1007/s00226-015-0765-1

Hosseinpourpia, R., and Mai, C. (2016). “Mode of action of brown rot decay resistance of thermally modified wood: resistance to Fenton’s reagent,” *Holzforschung* 70,691-697. DOI: 10.1515/hf-2015-0141

Hosseinpourpia, R., Adamopoulos, S., Holstein, N., and Mai, C. (2017). “Dynamic vapour sorption and water-related properties of thermally modified Scots pine (*Pinus sylvestris* L.) wood pre-treated with proton acid,” *Polym. Degrad. Stabil.* 138, 161-168. DOI: 10.1016/j.polymdegradstab.2017.03.009

Jalaludin, Z., Hill, C. A. S., Xie, Y., Samsi, H. W., Husain, H., Awang, K., and Curling, S. F. (2010). “Analysis of the water vapour sorption isotherms of thermally modified acacia and sesendok,” *Wood Mater. Sci. Eng.* 5, 194-203. DOI: 10.1080/17480272.2010.503940

Jämsä, S., and Viitaniemi, P. (2001). “Heat treatment of wood – Better durability without chemicals,” in: *Proceedings of Special Seminar*, Antibes, France. pp. 19-24.

Kamden, D. P., Pizzi, A., Guyonnet, R., and Jermannaud, A. (1999). *Durability of Heat-treated Wood* (Doc. No. IRG/WP 99-40145), International Research Group on Wood Preservation, Rosenheim, Germany.

Kamden, D. P., Pizzi, A., and Triboulot, M. C. (2000). “Heat-treated timber: potentially toxic byproducts presence and extent of cell wall degradation,” *Holz Roh. Werkst.* 58, 253-257. DOI: 10.1007/s001070050420

Kasemsiri, P., Hiziroglu, S., and Rimdusit, S. (2012). “Characterization of heat treated eastern redcedar (*Juniperus virginiana* L.),” *J. Mater. Process. Tech.* 212, 1324-1330. DOI: 10.1016/j.jmatprotec.2011.12.019

Kim, G. -H., Yun, K. -E., and Kim, J. -J. (1998). “Effect of heat treatment on the decay resistance and bending properties of radiata pine sapwood,” *Mater. Org*. 32(2), 101-108.

Lu, Y., and Pignatello, J. (2002) “Demonstration of the conditioning effect in soil organic matter in support of a pore deformation mechanism for sorption hysteresis,” *Environ. Sci. Technol.* 36, 4553-4561. DOI: 10.1021/es020554x

Malmquist, L., and Söderström, O. (1996). “Sorption equilibrium in relation to the spatial distribution of molecules - Application to sorption of water by wood,” *Holzforschung* 50, 437-448. DOI: 10.1515/hfsg.1996.50.5.437

Mahnert, K. -C., Adamopoulos, S., Koch, G., and Militz, H. (2013). “Topochemistry of heat-treated and N-methylol melamine-modified wood of koto (*Pterygota macrocarpa* K. Schum.) and limba (*Terminalia superba* Engl. et. Diels),” *Holzforschung* 67(2), 137-146. DOI: 10.1515/hf-2012-0017

Mburu, F., Dumarcay, S., Bocquet, J. F., Petrissans, M., and Gerardin, P. (2008). “Effect of chemical modifications caused by heat treatment on mechanical properties of Grevillea robusta wood,” *Polym. Degrad. Stabil.* 93, 401-405. DOI: 10.1016/j.polymdegradstab.2007.11.017

Militz, H., and Altgen, M. (2014). “Processes and properties of thermally modified wood manufactured in Europe,” *Deterioration and Protection of Sustainable Biomaterials, ACS Sym. Ser.* 1158, 269-285. DOI: 10.1021/bk-2008-0982.ch022

Mohr, P. J., Taylor, B. N., and Newell, D. B. (2008). "CODATA recommended values of the fundamental physical constants: 2006," *Rev. Mod. Phys.* 80, 633-730.

Olsson, A. M., and Salmén, L. (2004). "The softening behavior of hemicelluloses related to moisture," *ACS Sym. Ser*. 864, 184-197. DOI: 10.1021/bk-2004-0864.ch013

Rowell, R. M., Ibach, E. R., McSweeny, J., and Nilsson, T. (2009). "Understanding decay resistance, dimensional stability and strength changes in heat treated and acetylated wood," in: *Proceedings of the 4th European Conference on Wood Modification*, , Stockholm, Sweden, pp. 489-502. DOI: 10.1080/17480270903261339

Siau, J. F. (1995). *Wood: Influence of Moisture on Physical Properties*, Department of Wood Science and Forest Products, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA.

Simpson, W. (1980). "Sorption theories applied to wood," *Wood Fiber* 12, 183-195.

Skaar, C. (1988). *Wood Water Relationship*, Springer, Berlin.

Stamm, A. J. (1959). "Dimensional stabilisation of wood by thermal reactions and formaldehyde cross-linking," *TAPPI* 42, 39-44.

Stevens, M., and Parameswaran, N. (1981a). *Microscopical Analysis of Formaldehyde-acid Modified Wood* (Doc. No. IRG/WP 3182), International Research Group on Wood Preservation, Sarajevo, Yugoslavia.

Stevens, M., and Parameswaran, N. (1981b). "Effects of formaldehyde-acid catalyzed-reactions on wood ultrastructure," *Wood. Sci. Technol.* 15, 287-300. DOI: 10.1007/BF00350946

Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Holz Roh. Werkst.* 56, 149-153. DOI: 10.1007/s001070050287

Tjeerdsma, B. F., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *Holz Roh. Werkst.* 63, 102-111. DOI: 10.1007/s00107-004-0532-8

Van den Berg, C. (1984). "Description of water activity of foods for engineering purposes by means of the GAB model of sorption," *Engineering and Foods* 1, 311-321.

Vrentas, J. S., and Vrentas, C. M. (1991). "Sorption in glassy polymers," *Macromolecules* 24, 2404-2412. DOI: 10.1021/ma00009a043

Weiland, J. J., Guyonnet, R., and Gibert, R. (1998). "Analyse de la pyrolyseménagée du bois par un couplage TG-DSC-IRTF," *J. Therm. Analysis.* 51, 265-274. DOI: 10.1007/BF02719028

Wikberg, H., and Liisa, M.S. (2004). "Characterisation of thermally modified hard- and softwoods by 13C CPMAS NMR," *Carbohyd. Poly.* 58, 461-466. DOI: 10.1016/j.carbpol.2004.08.008

Xiao, Z., Xie, Y., Militz, H., and Mai, C. (2010). "Effect of glutaraldehyde on water related properties of solid wood," *Holzforschung* 64, 483-488. DOI: 10.1515/hf.2010.087

Xie, Y., Hill, C. A. S., Xiao, Z., Mai, C., and Militz, H. (2011). "Dynamic water vapour sorption properties of wood treated with glutaraldehyde," *Wood Sci. Technol.* 45, 49-61. DOI: 10.1007/s00226-010-0311-0

Xing, D., and Li, J. (2014). "Effects of heat treatment on thermal decomposition and combustion performance of Larix spp. wood," *BioResources* 9(3), 4274-4287.

Yan, L., and Morrell, J. J. (2014). "Effects of thermal modification on physical and mechanical properties of Douglas-fir heartwood. *BioResources* 9(4), 7152-7161.

Yasuda, R., Minato, K., and Norimoto, M. (1994). "Chemical modification of wood by non-formaldehyde cross-linking reagents," *Wood Sci. Technol.* 28, 209-218. DOI: 10.1007/BF00193329

Yasuda, R., Minato, K., and Norimoto, M. (1995). "Moisture adsorption thermodynamics of chemically modified wood," *Holzforschung* 49, 548-554. DOI: 10.1515/hfsg.1995.49.6.548

Zaihan, J., Hill, C. A. S., Curling, S., Hashim, W. S., and Hamdan, H. (2009). "Moisture adsorption isotherms of *Acacia mangium* and *Endospermum malaccense* using dynamic vapour sorption," *J. Trop. For. Sci.* 21, 277-285.

Article submitted: June 30, 2017; Peer review completed: September 30, 2017; Revised version received and accepted: November 12 2017; Published: November 20, 2017.
DOI: 10.15376/biores.13.1.331-345