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CONTRIBUTION OF THERMAL DEGRADATION PRODUCTS TO THE HYDROXYL ACCESSIBLITY AND HYGROSCOPICITY OF THERMALLY MODIFIED WOOD

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Abstract: *The moisture exclusion efficiency of thermally modified wood is usually attributed to both reversible and irreversible effects. The purpose of this study was to find whether hydroxyl accessibility contributes to the reversible effects of thermal modification on the hygroscopicity of wood. First, untreated and modified Norway spruce wood specimens were successively extracted with acetone/ethanol (2:1 v/v), hot water, and N, N-dimethylformamide (DMF). Then, the hygroscopic characteristics (i.e., fiber saturation point (FSP), equilibrium moisture content (EMC), moisture sorption isotherms) and hydroxyl accessibility were measured. The hydroxyl accessibility (mmol hydroxyls/g wood) was accurately determined by the deuterium exchange technique. We found that the cell wall bulking caused by the thermal degradation products has no significant impact on the hydroxyl accessibility, but it reduces the hygroscopic nature.*

Key words: *hydroxyl accessibility, hygroscopicity, thermal degradation products, thermally modified wood.*

1. Introduction

Wood is a complex polymeric material with a highly hygroscopic nature which is usually attributed to the cell wall components containing hydroxyl (OH) groups, in particular hemicelluloses. However, not all of the hydroxyl groups are accessible to the water vapor molecules. The hygroscopicity of wood is

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responsible for many of the challenges of using wood as an engineering material. Reduction in the hygroscopicity is possible through modification of the chemical structure of the wood components, for example by using more hydrophobic chemical groups replacing the OH-groups.

Thermal modification of wood is well known as a commercial environmental friendly method to reduce its hygroscopicity and to obtain a more dimensionally stable material by reducing the moisture sorption. It is believed that the heat treatment of wood degrades the cell wall components and reduces its accessible hydroxyl groups, and the effect is more pronounced by increasing the exposure duration and temperature. Consequently, the reduced hygroscopicity of thermally modified wood is often related to its lower accessible hydroxyl groups [2], [9]. However, a poor correlation between the equilibrium moisture content (EMC) and the accessibility of hydroxyl groups in thermally modified wood was reported, and it was concluded that there has to be an additional mechanism to control the EMC in addition to hydroxyl group accessibility [16]. Hemicelluloses may be changed to less hygroscopic substances like furfural polymers because of heat treatment of wood at very high temperatures of over 200°C [10]. In addition to the degradation of hemicelluloses, increase in cellulose crystallinity, the cell wall bulking and cross linking in lignin caused by thermal modification were also suggested as other possible reasons for reducing the hygroscopic behavior of the modified wood [2], [6], [17].

Recent research results showed that the moisture exclusion efficiency and the anti-swelling efficiency of thermally modified wood are due to both reversible and irreversible effects [3], [11], [17]. The efficiencies are mainly due to irreversible chemical changes of the cell wall components and degradation of hemicelluloses. However, the reversible changes in the hygroscopicity may also be due to the presence of thermal degradation products, which reduce the wood porosity by occupying the nanopores of the cell walls [5], [11], [17]. Both cell wall bulking and the annealing effects on the hygroscopicity of thermally modified wood are fully disappeared by water soaking and leaching out the degradation products [14], [17].

Wood extractives (terpenes, fats, phenols, fatty acids, tannins, etc.) are nonstructural compounds of low molecular weight that can be removed from the wood with neutral, organic solvents or water. Although extractives usually comprise only a few percent of wood (2-10%), they may have an important influence on its properties. Most extractives, such as resin acids disappear from the wood with heat treatment [13], but new compounds are formed due to the degradation of the cell wall components [6]. Therefore, complex polyaromatic substances originating from the degradation products of carbohydrates can be extracted with acetone from the heat-treated wood [10]. Lignin also becomes partly acetone soluble after heat treatment of wood at 180 °C or higher [13]. It was reported that the removal of extractives increases EMC, the fiber saturation point (FSP), and the

dimensional changes of wood [8], but the question that arises is if the cell wall bulking caused by thermal degradation products reduces the moisture sorption of the modified wood by shielding the cell walls and reducing the hydroxyl accessibility.

2. Objective

The main purpose of this study was to find whether hydroxyl accessibility contributes to the reversible effects of thermal modification on the hygroscopicity of wood.

3. Material, Method, Equipment

3.1. Sample Preparation and Thermal Modification

Norway spruce (*Picea abies* L.) boards with nominal thickness of 20mm were air dried to about 30% MC. Thermal modification was performed inside a ThermoWood kiln, similar to the Thermo-S process developed by VTT in Finland [19]. For the high temperature drying phase, the kiln temperature was first raised to a level of about 100 °C. Then, the temperature was gradually increased to 140 °C. After drying, the temperature was increased to 180 °C. The time of thermal modification at the target temperature was 3 hours. Finally, cooling and conditioning were applied for 24h. The final moisture content of the boards was about 7%.

3.2. Removal of Extractives and Thermal Degradation Products

1mm thick samples dried in a vacuum oven (0 mbar, 65°C) for 24h were first extracted with acetone/ethanol (2:1 v/v) into a flask at room temperature. The flasks containing the samples and the solvent were gently shaken to ensure complete wetting of the samples. The solvent was replaced with a fresh one 3 times over a period of 7 days. Then, the extracted samples were immersed into glass vials containing distillate water and were kept inside an oven at 65 °C for 7 days. Finally, they were soaked in N, N-dimethylformamide (DMF) using stoppered Erlenmeyer flasks. The solvent was agitated by a magnetic stirrer at room temperature for 3 days.

3.3. Determination of Hydroxyl Accessibility

The hydroxyl accessibility (mmol hydroxyls/g wood) of control and thermally modified Norway spruce was measured before and after the extraction. The accessibility was accurately determined by the deuterium exchange technique using advanced Dynamic Vapor Sorption equipment, DVS-ET1. This equipment is able to measure mass changes of 1µg under controlled conditions of temperature and vapor pressure. First, 6-8mg of each sample were sliced with a razor blade and dried in the apparatus at 60 °C for 6h to obtain the initial dry mass. Then, deuteration of dried sample was carried out with deuterium oxide (D_2O, 99.9 atom % D, Sigma-Aldrich) vapor at 95% RH for 10h. Finally, the

deuterated sample was dried at 60°C for 6h to determine the final dry mass. The accessibility was then calculated by equation (1):

$$HA(mmol\,hydroxyls\,per\,gram\,wood) = \frac{(M_f - M_i}{(1.00616178 \cdot M_i)}. \quad (1)$$

where:

HA is hydroxyl accessibility; M_f – final dry mass (dry mass of deuterated sample); $_i$ – initial dry mass (dry mass of undeuterated sample).

3.4. Measuring Hygroscopic Properties

The fiber saturation point (FSP) was measured by thermoanalytical technique using differential scanning calorimetry (DSC, model, Q 2000). Wood blocks with dimensions of 5 (L) × 10 (R) × 1 (T) mm were cut by razor blade and dried in a vacuum oven (0 mbar, 60°C) for 24h. The dried specimens were first put in a glass vessel, and initial vacuum of 0 mbar was applied for 30 minutes. Then, distillated water was injected into the vessel by using a syringe and the specimens remained submerged at atmospheric pressure for at least 24h. The saturated specimens were cut to fit into the hermetic aluminum DSC pans and weighted using a balance with a precision of 0.01 mg. The samples were first frozen at -20°C and then melted by a continuous heating-up method from -20°C to 20°C with a heating rate of 2^0C/min and a nitrogen flow of 50ml/min. The temperature of -20°C was held for 5min. The sequence was applied twice per sample. After the DSC measurements, several small holes were made through the lids of the pans by means of syringe and the samples were dried in the vacuum oven at 65°C for 24h to determine their moisture content. Finally, enthalpy of melting for each sample was measured and FSP was calculated by equation (2):

$$FSP(\%) = [M_{total} - M_{dry-(\frac{\Delta H \cdot M_{total}}{H_f})}] / M_{dry}. \quad (2)$$

where:

M_{total} and M_{dry} are the green and dry mass of wood sample [g]; $M_{total} - M_{dry}$ is mass of water (free water plus bound water) in wood; ΔH – enthalpy of melting the frozen free water in the cell lumens [J/g]; H_f – enthalpy of water (333.7J/g).

Five replicates were used for each treatment and a water-only DSC sample was also used for each treatment as a reference.

Automated determination of moisture adsorption isotherm of specimens was also carried out using the dynamic vapor sorption (DVS) method. Each test run was initiated by drying 6-8mg of wood specimens at 60°C for 6h and then the

adsorption cycles started at 0% RH and increased up to 95% RH in steps of 10% RH at the constant temperature of 25°C. The acquisition of mass change data was carried out every 10s. The oven-dried specimens were also conditioned at 20°C and relative humidity (RH) of 65% to measure the EMC.

4. Results and Discussion

4.1. Hydroxyl Accessibility

The dry mass increase of the specimens due to the deuterium exchange completed within 5-10h was less than 1%, and ranged from 0.7 to 0.9%. The hydroxyl (-OH) accessibility of untreated Norway spruce ranged from 7.72 to 8.95 mmol.g^{-1}, indicating that within-species variability in the hydroxyl accessibility can be large. The removal of the extractives had no significant effect on the OH accessibility either for untreated wood, or for the thermally modified wood (Figure 1). The modified wood had less accessible hydroxyl groups than the untreated wood (untreated wood: 8.1 mmol. g^{-1}; modified wood: 7.1 mmol.g^{-1}), which is in agreement with previous studies [16]. Degradation of hemicelluloses through thermal modification may be the main reason contributing to the reduction in the accessible hydroxyl groups.

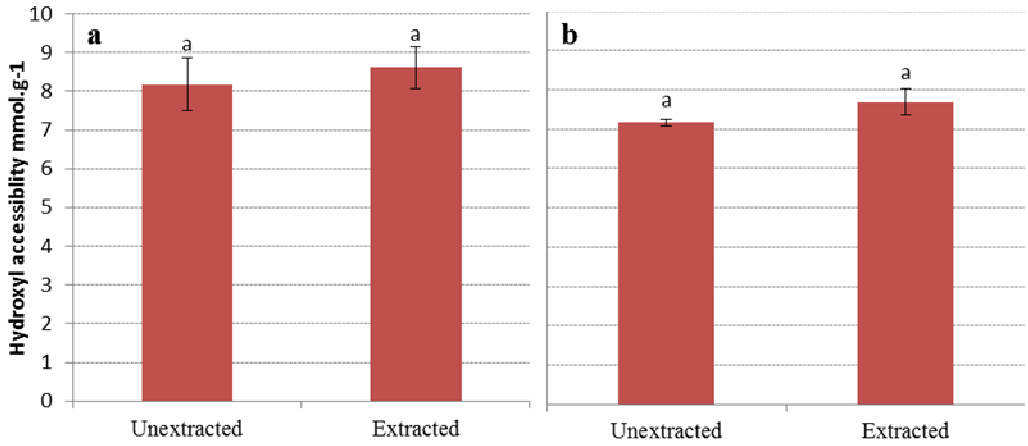

Fig. 1. *Effect of extractives removal on the hydroxyl accessibility of Norway spruce (a) untreated wood; (b) thermally modified wood*

4.2. Sorption Isotherm

The removal of the extractive materials had no influence on the shape of the sorption isotherms. For untreated wood, the isotherms of extracted and unextracted wood coincided along the whole range of RH (from zero to 95%), whereas the extraction lowered the sorption isotherm of thermally modified wood (Figure 2). In the case of modified wood, a greater difference between the isotherms of the extracted and unextracted wood was observed at higher RH, and the difference was at a maximum 2.1% at RH of 95%. The different

behaviour of thermally modified wood can be due to the removal of thermal degradation products in addition to the wood extractives themselves. As expected, the thermally modified wood showed a remarkable reduction in EMC compared with the untreated wood along the whole range of RH, which is in agreement with the literature [16]. The isotherm of untreated wood at RH more than 80% increased more sharply compared to that of thermally modified wood.

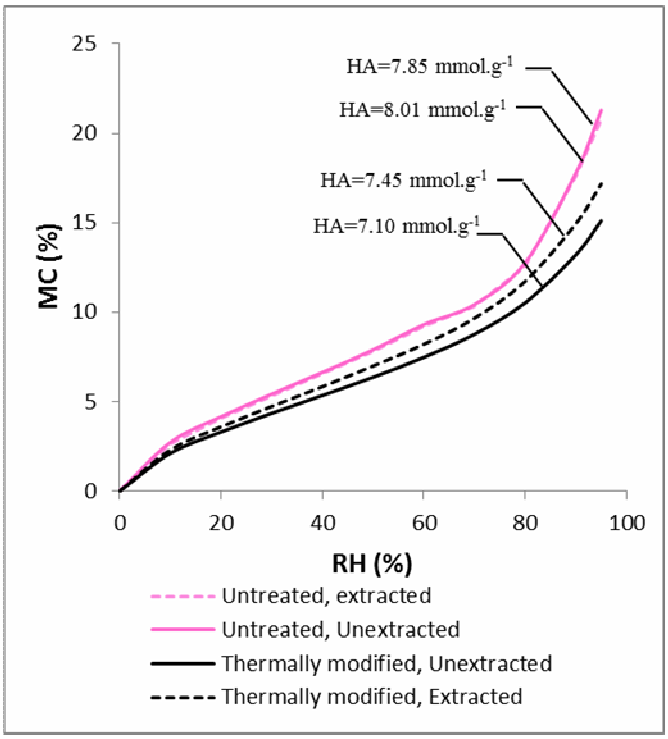

Fig. 2. *Effect of extractives removal on the moisture sorption isotherm of untreated and thermally modified Norway spruce with their corresponding hydroxyl accessibility (HA)*

4.3. Hydroxyl Accessibility vs. Sorption Isotherm

Although the sorption isotherm of thermally modified wood increased by increasing the hydroxyl accessibility, no changes occurred in that of untreated wood (Figure 2). Leaching of thermal degradation products of modified wood through the extraction procedure may explain the observed differences. The reduced OH accessibility was reported to be in agreement with reduced EMC in brown rot wood [7]. However, it was previously indicated that the role of the accessibility of wood hydroxyl groups in relation to controlling the moisture content exclusively is disputed [16]. Although the accessibility of wood hydroxyl groups plays an important role in the moisture sorption, additional mechanisms such as degradation of

hemicelluloses, increase in cellulose crystallinity, and cross linking in lignin may contribute to the hygroscopic behavior of thermally modified wood [6]. Our results also showed that the cell wall bulking caused by thermal degradation products could be another reason for observing the lower hygroscopicity.

4.4. EMC & FSP

Although it is believed that extractives lower the EMC of wood [15], [19], our results showed that the removal of extractives does not always cause an increase in the EMC (Figure 3). No significant change occurred in the EMC of Norway spruce as a result of extractives removal. In contrast to EMC, the FSP was significantly affected by the extractives removal (Figure 4), and the FSP of wood specimens was significantly increased after the removal of extractives.

The FSP of thermally modified wood reduced more significantly than the FSP of unmodified wood, which may confirm the role of thermal degradation products in the maximum water holding capacity of the modified wood. After extractives removal, the FSP of control and thermally modified Norway spruce increased by 40.4 and 57.1%, respectively. Increase in the FSP of wood either after hot water extraction or after organic solvent extraction was also found in some previous studies [4], [8]. The measured FSP of Norway spruce was close to its accepted range. Our results showed that the DSC method does not always yield a high value of FSP, and the result may be dependent on wood species. In contrast to our results, a higher value of 40-42% was reported for the FSP of Norway spruce measured by pressure plate technique [18].

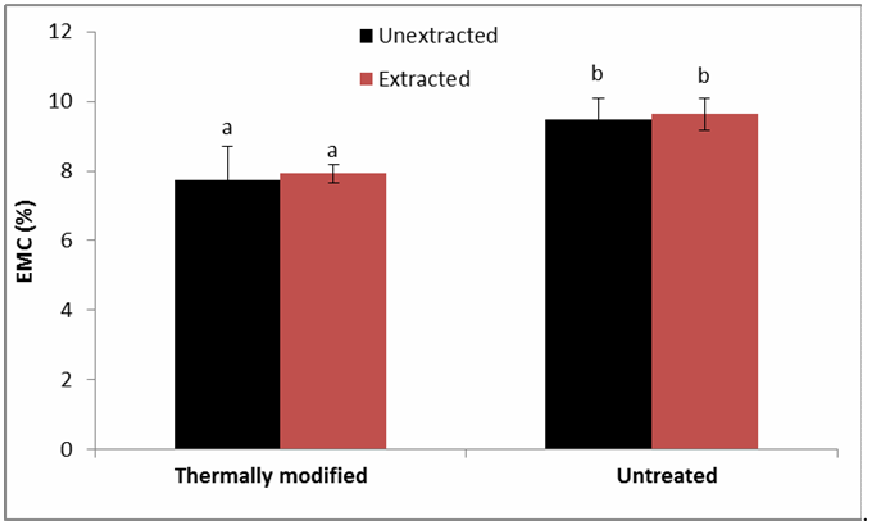

Fig. 3. *EMC of untreated and thermally modified wood before and after extractives removal*

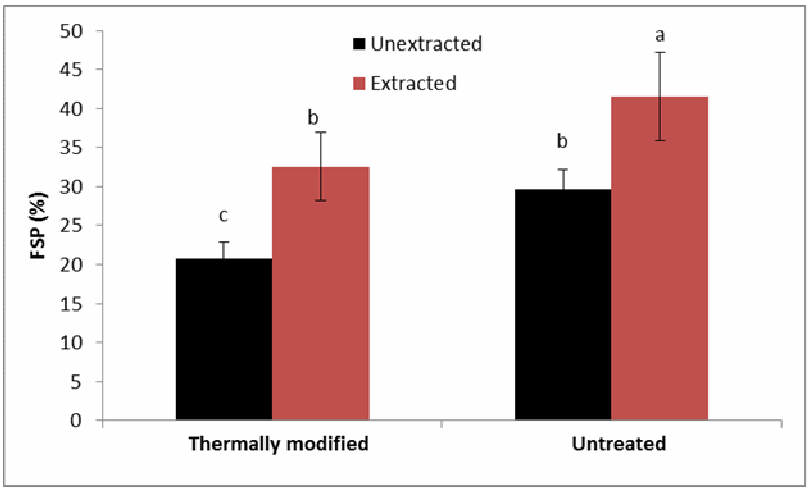

Fig. 4. *FSP of untreated and thermally modified wood before and after extractives removal*

5. Conclusions

In this study, we examined the role of extractives in controlling the OH accessibility and hygroscopicity of untreated and thermally modified Norway spruce. The removal of extractives had no significant effect on the OH accessibility, whereas the hygroscopicity was reduced. Thus, it can be concluded that the role of OH accessibility in the reversible effects of cell wall bulking caused by the thermal degradation products can be neglected. We found that thermal degradation products significantly contribute to the maximum water holding capacity of the modified wood. The extraction increased the sorption isotherm of thermally modified wood and the increase was more pronounced at higher RH. The results of this study also confirm that the removal of Norway spruce extractives before chemical modification cannot be efficient to access more OH groups. However, research on the contribution of each type of extractives to the OH accessibility of extractive-rich woods is recommended in future works.

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