Alteration of the Pore Structure of Spruce and Maple due to Thermal Treatment

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ABSTRACT

The pore structure and the change of these as a result of thermal treatment in untreated and thermally modified spruce (*Picea abies* (L.) Karst.) and maple (*Acer pseudoplatanus* L.) was investigated. Tests were carried out by helium pycnometry and mercury intrusion porosimetry. Conditioning of the specimens was at 22 °C, and at 4 different relative humidities. It was noted, that thermal treatment changes the apparent density, pore structure, and pore size distribution. Measurements by the mercury intrusion porosimetry indicated that the influence of various environmental conditions (humidity, temperature) on the porosity and pore size distribution is small.

INTRODUCTION

Its well known that thermal modification of wood is a procedure to improve the properties in terms of better dimensional stability, and increased decay resistance (Hill 2006). This is a result of a complex change of chemical, physical, mechanical, and structural characteristics (Tjeerdsma *et al.* 2002, Boonstra and Tjeerdsma 2006). The pore structure of wood affects sorption, diffusion and transport of moisture. It's to be expected that thermal treatment influence these properties, which are dependent on the specific surface, porosity, and pore size distribution. This feature is closely related again to the above-mentioned properties concerning sorption and transport of moisture, thermal insulation, filtering properties, and wettability. The objective of this study was to gain further insights into structural changes caused by thermal treatment. The focus was on pore volume analysis by helium pycnometry and mercury intrusion porosimetry. However, one should be aware from the very beginning on the limitations of mercury intrusion porosimetry, which is not suited for the analysis for fine pores within the cell wall.

MATERIALS AND METHODS

The pore structure of spruce (*Picea abies* (L.) Karst.) and maple (*Acer pseudoplatanus* L.) was examined in untreated and thermally modified samples at different equilibrium wood moisture. Conditioning of the specimens: at 22 °C, and at relative humidities of 33, 43, 53, and 75%). Each test series consisted of four pairs of twin samples of modified and unmodified wood collected from the same 5 annual rings. The heat treatment was performed in a single stage dry process at 180 °C and at 200 °C for 4 h in a commercial plant at Mitteramskogler GmbH in Gaflenz (Austria). In this process, the exhaust volatile gases and remaining oxygen are removed from the reaction chamber and burnt off externally.

Tests were carried out by helium pycnometry and mercury intrusion porosimetry. Helium pycnometry was performed in accordance with DIN 51913 with a pycnometer AccuPyc 1330 (Micromeritics) and mercury intrusion porosimetry according to ISO 15901-1 by a porosimeter Pascal 140 and Pascal 240 (Porotec). The same samples were used first for the pycnometry measurement and then the mercury intrusion porosimetry measurement. The full experimental details are given elsewhere (Pfriem *et al.* 2009).

RESULTS AND DISCUSSION

The results (medians) from the measurements with helium pycnometry are shown in Table 1. The porosity of maple increases as a function of treatment temperature, where spruce did not show such clarity. The apparent density of specimens treated at 180 °C was lower than the untreated wood. Thermal treatment at 200 °C, on the other hand, led to higher apparent densities. This trend is more evident in the case of spruce. As expected, the apparent density of maple is higher than that of spruce. This result is confirmed by measurements with mercury intrusion porosimetry.

Table 1: Porosity and apparent density of untreated and thermally modified maple and spruce as measured by helium pycnometry

	Maple			**Spruce**		
	Untreated	180 °C	200 °C	Untreated	180 °C	200 °C
Porosity [%]	59	61	64	64	62	63
App. density [g cm^{-3}]	1.51	1.49	1.52	1.43	1.34	1.50

Wood with lower lignin content generally has a higher apparent density. Coniferous wood contains more lignin than hardwood and lignin has the lowest specific density (1.30 g cm^{-3}) compared to cellulose (1.54 g cm^{-3}) and hemicelluloses (1.53 g cm^{-3}) (Pfriem *et al.* 2009). The reduced apparent density of thermally treated wood at 180 °C is caused by the degradation of the thermally sensitive hemicelluloses, which also increases the percentage of lignin. The increased apparent density after thermal treatment at 200 °C could be interpreted that also lignin is degraded (Windeisen *et al.* 2007). The measurements with mercury intrusion porosimetry revealed no significant influence of the humidity on the porosity and pore size distribution respectively. There was no evidence that the pore structure changes with increasing moisture content (MC). The vacuum generated before introducing the mercury lowers the boiling point of the water and thereby enhances evaporation of water even at low temperatures. This leads to lower MC and promote shrinkage. This effect impedes the measurement concerning the influence of MC. This is the reason why the evaluation of the results was only done regarding the degree of thermal treatment. A comparison of the average pore diameters determined by mercury intrusion porosimetry (pore diameter of 50% of total cumulative volume, according ISO 15901-1) is shown in Figure 1 as Box Plots displaying five-point summaries (median, the two quartiles and the two extreme values). A trend of an increasing average pore diameter with a higher degree of thermal treatment can be observed for maple and spruce, but in the latter case the effect is more pronounced. The scattering of the measured values is higher for spruce. The increase of porosity and average pore diameter of maple as a function of temperature is mainly due to hemicelluloses degradation. The subsequent OH group elimination leads to the improved dimensional stability. Due to the decreasing swelling ability the pore diameters and the porosity is increasing.

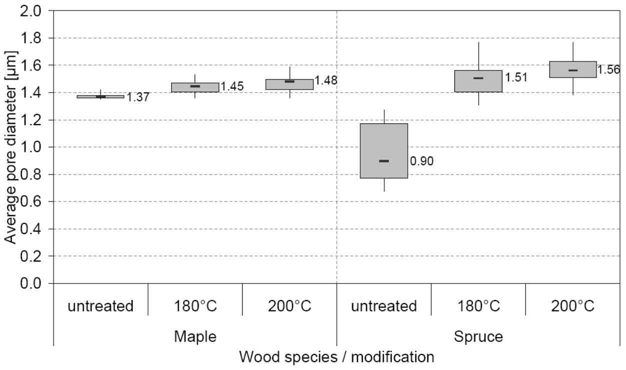

Figure 1: Influence of thermal treatment on the average pore diameter of maple and spruce measures by mercury intrusion porosimetry

The total volume of pores vs. pore diameter (pore size distribution) for untreated and thermally treated spruce is presented in Figure 2. With the intensity of thermal treatment a shift to larger pores can be observed: from 0.25 µm (untreated wood) to 2 µm (treated wood). Beginning with a pore sizes lower than 0.1 µm in the case of untreated spruce, the values decrease asymptotically to values around 0.01 µm. Thermally treated spruce (with a pore size maximum around 2 µm) have – as a results of the compression of the cell-wall – only low amount of pores with diameter lower than 0.5 µm.

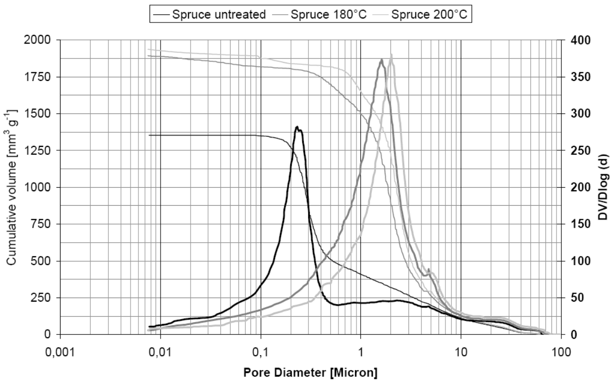

Figure 2: Intruded volume and differential pore volume vs. pore diameter for untreated and thermally modified spruce

The brittleness of the pit membranes of the bordered pits and of the cell wall of the tracheids – containing a lot of pectin, hemicelluloses, and celluloses (Bauch and Berndt 1973) – are particularly vulnerable towards thermal stress. Accordingly, pit membranes are partly responsible for the reduction of the pore size under the given thermal and measurement conditions. As the sample dimensions parallel to the fibre (6 mm) were larger than the tracheids only a fraction of the cell lumina were halved. These cut through tracheids were easily filled with mercury even at low pressures. The unaffected tracheids on the other hand were only accessible at much higher pressures via the pits. This is the so-called „bottle neck effect“, (Schneider and Wagner 1974). Because mercury enters the untreated sample mainly via the cut tracheids the measured values are too low. On the other hand, due to the brittleness of the pit membrane caused by thermal treatment the mercury can pass more easily into the tracheids by the destroyed membranes even at lower pressures. Hence, the measured average pore diameter of the thermally treated samples is increased. This effect must also be taken into consideration for maple as a complex hardwood with its libriform fibres. The difference is, however, that all vessels are connected in vertical direction via apertures at their ends.

CONCLUSIONS

Thermal treatment leads to the change of the apparent density, porosity, and the average pore diameters. Mercury intrusion porosimetry compresses the cell wall cavities with small diameters. The influence of humidity on the porosity and pore size distribution could not be detected by methods applied. Further investigations to develop the sample geometry and modify the measurements are currently in progress.

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