Doctoral Thesis

The effect of hydrothermal treatment on the sorption properties of black locust wood

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Sopron

2002

1. THE AIM OF THE RESEARCH

Wood is a material of biological origin. It is produced by the vascular cambium as a water-filled tissue. The walls of the newly formed wood cells remain saturated with water while there is sap-flow between the roots and the crown. As this flow stops, the cells lose their water content and air gets into the wood-water system. This will take place when we cut a living tree. From that point on the wood begins a „new life”: depending on the conditions of the physical environment, the wood will change its moisture content and with that most of its physical properties.

The importance of the subject of this thesis is emphasised by the area of the black locust forests in Hungary (320 000 ha). These forests will insure raw material supply to industry for several decades. The author of this work hopes that his research will contribute to the improved utilisation of this very valuable raw material.

The effective utilisation of black locust wood is hardly imaginable without steaming. The steaming of black locust wood is a common procedure all over Europe. In addition to the low value traditional products (e.g. tool handles, agricultural implements), black locust wood is also used for high value up-to date products (e.g. window frames, structural components in buildings). The new products and the accompanying new technologies give new tasks and challenges for technical experts and scientists.

Steaming improves both the colour uniformity and the processing of black locust wood. At the same time, steaming causes permanent changes in the wood-water relationships. Presently the sorption characteristics of the steam-treated wood are not well defined.

In my research work, I set the following objectives:

- The EMC of wood is very important for both artificial drying and for the various wood products in service. I designed and conducted experiments to determine the relationship between the EMC of the wood and the relative humidity of the air. In order to this, I measure the sorption isotherms at 23°C.
- In my study, I investigate the differences in the sorption behaviour between sapwood, heartwood and juvenile wood of black locust.
- I demonstrate the effects of steaming on the EMC. I show how steaming of different duration influences the EMC of the three different kinds of wood.
- With several sorption cycles, I determine the magnitude of the hysteresis. Furthermore, I investigate the effects of steaming, tissue structure, and repeated wetting and drying cycles on the hysteresis.
- A further aim of my research work was to show, whether the positive changes in the wood are stable; that is, whether the EMC-decreasing effect of steaming is permanent.
- I wish to emphasise the importance of my investigations on the juvenile wood. Considering the short rotation time of black locust, it is clear that juvenile wood represents a relatively high ratio in the harvested round wood. This part of wood differs in its properties from mature wood. Its presence is an important problem in practice. The utilisation of juvenile wood was hindered by the fact that its sorption properties were not investigated till the present time. MOLNAR and PESZLEN have done outstanding research on the anatomical structure of juvenile wood in black locust.
- A further goal of my work was to apply several sorption models based on different theories. In addition, to show which models are the most applicable to black locust. Finally, to draw appropriate conclusions from the work with respect to steaming practice. On the steaming of black locust wood, MOLNÁR S., TOLVAJ L., NÉMETH K., BÁLINT J., BÉLDI F., HORVÁTH-SZOVÁTI E. have made significant contributions in their previous research.
- My research will answer the important practical question whether the three kinds of wood (i.e. sapwood, mature wood and juvenile wood), and the steamed and un-steamed wood could be dried together in the industry.

2. PRELIMINARIES

Wood is one of our ancient raw materials, therefore one of the most studied substances. The first „publication” came from Theophrastus (372–287 B.C.), who lived in ancient Greece and pointed out the importance of the role of the water in wood.

Regarding sorption phenomenon, a very extensive literature came into being during the last century. To lay the foundations for my work, I examined much of this literature. Among the extensive list of publications on wood-water relationships, only a few were from Hungarian authors. I would like to mention some notable Hungarian researchers who worked on this field: NÉMETH K., NÉMETH J., SITKEI GY., MOLNÁR S., WINKLER A., TOLVAJ L., VARGÁNÉ H. F., TAMÁSINÉ BÁNÓ M., BÉLDI F., BÁLINT J.

Considering the evolution of sorption theories, the model of LANGMUIR (1918) was proposed first, followed by BRUNAUER'S EMMET'S and TELLER'S (BET, 1938) multi-layer sorption model. HAILWOOD and HORROBIN (1946) deduced a solid solution model. Classical thermodynamics served also as a basis for several models, e.g. the model of ANDERSON and MCCARTHY (1963). BARISKA, PIZZI and EATON (1987) built up a so called conformational model, which is based on the shape of the 3D-shape of hemicelluloses and cellulose. The newest theories approach the phenomenon of sorption based on the cluster and fraktal theories (PATHERIA 1988, FAN et al. 1999).

3. METHODS OF THE RESEARCH

3.1. The material, preparation procedures, and number of specimen

The specimens were cut from black locust wood (*Robinia pseudoacacia*). The material was transported as 1 m long logs with 30 annual rings to the Institute of Wood Sciences, at the University of West-Hungary. Then from each round wood a 30 mm board, including the pith, was cut. The boards were separated into two groups: steamed and un-steamed. The steamed material was separated into further three groups: 3, 6, 14 days steamed material. For each treatment, the mature, the sap- and juvenile wood were tested separately. The mature wood and the juvenile wood were separated on the basis of the annual rings.

MOLNAR (1999) suggests to assign the boundary between mature and juvenile wood in black locust at the 9th annual ring, based on average fibre length, The sapwood of black locust contains only the 2-5 external annual rings. As opposed to the mature wood, not all of the vessels are filled with tyloses, and the wood has a light yellow colour. During processing in sawmills, this part of the wood is usually trimmed off from the boards, therefore sapwood has no practical importance. Since the cells of sapwood are also lignified, the differences (if any) in the sorption behaviour of sapwood and heartwood can only be caused by the processes of heartwood formation (i.e. storage of extractives). Therefore, the study of this apparently "unimportant" tissue gives useful information to the science and to the practice.

The number of the specimen (6 in each set) was limited by the capacity of the sorption apparatus. Simultaneously 6 specimen could be tested. In accordance with the time-consuming measurement methods, the relatively low number of replications had to be accepted. In this way, the continuous measurements required 36 months to complete.

The boards were steamed in a laboratory equipment of the Institute of Physics, at 98°C and atmospheric pressure. The steaming schedule was built up according to the schedules used in the industry, and recommended by MOLNAR (1994). As described in his work, for a 30 mm thick board by 95°C temperature, 6 days steaming time was needed. To analyse the effect of steaming more precisely, a shorter (3 days) and a longer (14 days) treatments were also chosen. The steadiness of the temperature ensured a contact thermometer, with an accuracy of ±0,3°C.

Because the measurements were aimed at the EMC, it was essential to stabilise the initial moisture content, that is the sorption history of wood (PERALTA, 1955). In order to do this, the boards were covered in plastic bags and kept below freezing. This is a common procedure for sorption measurements, and ensures a controlled sorption history.

3.2. The devices and methods of measurements

The sorption measurements were conducted in a sorption apparatus, which was provided by Prof BARISKA M. from the Univ. of Stellenbosch. Sorption measurements with such a precision were not available in Hungary yet. The unique feature of this device is, that it works under vacuum. In that way the duration of the measurements could be reduced to $1/10^{th}$.

For each series of treatments, 5 isotherms were measured. The required relative humidity conditions were produced by saturated salt solutions.

The order of the investigations was as follows:

- first desorption,
- first adsorption, } 1. hyteresis loop
- second desorption,
- second adsorption } 2. hysteresis loop
- third desorption.

Each desorption process was followed by drying to constant mass in a vacuum chamber.

The mass of the specimen could be computed from the elongation of the quartz glass springs. The accuracy was ±0,1g. The EMC could be measured with an accuracy from ±0,1%. The vacuum made possible the measurement of the sapwood also, since in the absence of oxygen no fungal attack could affect the simple sugar compounds stored there.

4. THE THESIS OF THE DISSERTATION

1. New results regarding the effect of steaming on the equilibrium moisture content (EMC)

I was the first to determine the sorption isotherms of the sapwood, the mature wood and the juvenile wood of black locust

I determined that steaming decreases the EMC of the sap- and the juvenile wood in the whole relative humidity (RH) range, whereas for mature wood an increase in EMC was found at the higher RH levels.

In environments with a high RH, the EMC of the steamed mature wood is higher, than that of the un-steamed wood. This means lower durability against fungal attack, and lower strength at higher RH-s.

At lower RH-s, the steaming decreases the EMC noticeably. This means, that in low RH environments the strength values of the wood are better. (For example, a sample with 2% lower EMC has an 8–10% higher strength value.)

2 New results concerning the fibre saturation point (FSP)

I was the first to determine the FSP for black locust wood with the Hunter-model. According to my computations, the model describes the sorption isotherms of black locust wood well. The results are supported by the observations, indicating that the EMC-s at 98% RH correspond to the FSP, which was predicted by the model.

3 New results regarding the effect of the tissue structure on the EMC

I pointed out, that in all sorption cycles the sapwood reached the highest EMC-s, followed by the juvenile wood and the mature wood. According to the EMC-differences, I showed that the juvenile wood and the sapwood reached similar values. The tissue structure affected the EMC only above 57% RH. The steaming decreased the EMC-differences. The longer was the duration of the steaming treatment, the lower were the differences. The practical importance of this is that the moisture content distribution of a board – including juvenile wood – can be made more homogenous with steaming. Furthermore, during the drying procedure of juvenile and mature wood, similar values for the intensity of the drying (DP) will be obtained. Therefore, steamed boards will show a more homogenous moisture content distribution after drying.

Sapwood contains the least amount of extractives, therefore the highest EMC could be observed in this type of wood. Regarding the high EMC and low durability of sapwood, the wood products which contain sapwood are expected to have a shorter lifetime. However, the differences in the EMC can be reduced with steaming.

4. New results regarding the effect of the repetition of the sorption cycle on the EMC

With the repeated sorption cycles, I have shown that the EMC decrease does not change under the influence of the changing environmental conditions (i.e. wetting, drying). Following repeated sorption cycles, the EMC-s were lower than in the first cycle. This observation can be explained by the blockage of selected sorption sites.

5. New results regarding the sorption hysteresis

5.1. The effect of steaming on the sorption hysteresis

Regarding the effects of steaming, it was shown, that the treatment decreased the value of the hysteresis significantly. The longer the steaming period, the lower was the hysteresis value. The increase of the hysteresis of mature wood can be explained by the change in the capillary structure, likely caused by collapses and micro-cracks in the cellular structure.

5.2. Effect of the tissue structure on the sorption hysteresis

Regarding tissue structure, I have shown that in the RH range of 7–70% the mature wood has the greatest hysteresis, followed by juvenile wood and sapwood. At RH-s over 81%, the mature wood has the lowest hysteresis value. In the case of steamed materials, the differences over 81% RH were not significant.

5.3. Effect of the repeating the sorption cycle on the hysteresis

For the RH range of 7–57(70)%, I have shown that the repetition of the cycle increased the hysteresis for all the 3 kinds of tissues. Within each type of tissue the steaming increases the differences. At RH=81%, the decrease of the hysteresis value was observed for all test materials. The explanation of this is that the repeated cycles enhanced the plasticity of the material. Consequently the internal stress were partly relaxed.

6. New results deducted from the sorption theories

With several theories, I was the first to determine the coefficients of the sorption isotherms for black locust wood. The following models were used: BET, Dent, HH, Kollmann, Malmquist, Cluster, Hunter, Fraktal, Polányi, Polarisation (Anderson & McCarthy). In the following, I detail the physical explanation of the coefficients, and I draw the conclusions from them.

6.1. Water content in the monomolecular layer, internal surface

Steaming causes a reduction in the water content of the monomolecular layer. A part of the sorption sites are blocked definitely, therefore the internal surface area decreases.

6.2. Poly-molecular water content

I have shown, that according to the Dent theory, steaming increases the poly-molecular water content. The explanation for this phenomenon is the leaching of extractives and the sub-microscopic cracks in the cell wall.

6.3. I have pointed out, that regarding the tissue structure, sapwood contains the most poly-molecular water. This is due to the lower amount of extractives and the higher cell wall porosity**.**

6.4. With my measurements I have shown, that the repetition of the sorption cycles (drying, wetting) alters the moisture content in the wood. The content of the monomolecular bound water increases, which indicates loose wood-wood relations, i.e. lower strength. The last point is also supported by practical observations.

6.5. It is well known, that **steaming decreases the mechanical strength of wood.** According to my measurements and computations, the two mechanical based models – Hunter G_{RT} and Malmquist k_c – produce the same results.

6.6. **I proved the linear relationship between the cohesion factor (kc) and the steaming time.** According to this relationship, the sorption isotherm can be drawn for all 3 kinds of wood with steaming times in the range of 0–14 days only by measuring the EMC at RH=98%.

6.7. I have shown, that the cluster size of the water molecules increases with the steaming time, which represents the decreased affinity of wood to water

6.8. I pointed out, that fractal dimension of the wood decreases with the steaming time, which correlates with the decreased MC. I was the first to determine the fractal dimension of black locust wood, and its value ranges from 2,3197 to 2,5434.

6.9. With the theory of Polanyi, I have shown the interaction between the bound water molecules.

5. POSSIBLE APLICATIONS OF THE SCEINTIFIC RESULTS

In the analyses of my results, I explored the sorption behaviour of the sap-, the mature and the juvenile wood of black locust wood. I compared the various sorption theories and discussed the sorption process from several points of view. I attempted to link the practical and the experimental observations with appropriate theory.

The measured sorption isotherms can serve to establish new drying schedules, and also provide information for prospective equilibrium moisture content values under different end use conditions.

The EMC of the wood under usual climatic conditions can be reduced with steaming, which by the given climatic conditions results in higher mechanical strength and durability against fungi. Under conditions of high RH, the steamed mature wood reaches higher EMC-s, than the un-steamed material. Therefore, for outdoor uses, special attention should be paid to the protection of steamed mature wood.

The steaming decreased the EMC primarily of the sap- and the juvenile wood. The EMC-s of the 3 kinds of wood are drawn closer by steaming. Due to the relatively small dimensions of black locust sawn timber, the wood often contains juvenile wood. Following steaming, this kind of timber will show a more homogenous MC-distribution, which reduces the incidence of drying defects and improves dimension stability.

With the repeated the sorption cycles, the decrease of EMC does not change further.

The sapwood has the highest EMC, therefore (and because of the high amount of simple sugar molecules) this type of wood is less durable against fungi, for that reason the wooden products should not contain sapwood.

Steaming decreased the hysteresis value. In the case of the steamed materials, it is not important whether the wood reached the EMC during ad- or de-sorption.

For the sorption isotherms of black locust wood the most suitable equations are those of the Dent- and the Hunter-models. The last two equations and their co-efficients are the most recommendable for computer-controlled drying chambers.

6. PUBLICATIONS CONNECTED TO THE SUBJECT

Book chapter

1. NÉMETH R 2000: *A faanyagok fizikai tulajdonságai*, Faipari Kézikönyv I. Szerk. Molnár S., Faipari Tudományos Alapítvány, Sopron, 59-73pp.

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2. NÉMETH R., BABIAK M., MOLNÁR S. 2000: Evaluation of the effect of steaming on the wood-water system of Black locust wood by sorption theories. 2nd Workshop of COST Action E15 on „Quality Drying of Hardwood”, Sopron, Hungary

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3. NÉMETH R 1998: Drying of cylindrical wood material Hengeres faanyagok száradása, Faipar, 1998/2, 30-31.o.
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5. NÉMETH R 2001: *A Hunter-modell alkalmazása az akác szorpciós izotermáinak jellemzésére*. Faipar, 2001 – kiadásra elfogadva
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2. NÉMETH R. 2001: *A nyíró rugalmassági modulusz becslése a faanyag szorpciós izotermájából.* Univ. of W-Hungary, Sopron

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1. Technology for HQ products from Black Locust. INCO Copernicus final report, 15+13 pages, Homepage: http://www.dainet.de/bfh/inst4/41. Search engine: Netscape, keyword: Robinia pseudoacacia

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5. Genetically improving of the quality of wood. Univ. of W-Hungary, Institute of Wood sciences
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