



HAL
open science

Evaluation of heat treated wood swelling by differential scanning calorimetry in relation with chemical composition

Vincent Repellin, René Guyonnet

► **To cite this version:**

Vincent Repellin, René Guyonnet. Evaluation of heat treated wood swelling by differential scanning calorimetry in relation with chemical composition. *Holzforschung*, 2005, 59(1), pp.28-34. 10.1515/HF.2004.131 . hal-00123858

HAL Id: hal-00123858

<https://hal.science/hal-00123858>

Submitted on 11 Jan 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Evaluation of heat treated wood swelling by differential scanning calorimetry in relation with chemical composition.

Vincent REPELLIN*¹, repellin@emse.fr, tel : +33(0) 4 77 42 02 74

René GUYONNET¹, guyonnet@emse.fr, tel : +33(0) 4 77 42 00 30

¹Département PCMM
Centre SPIN
Ecole des Mines de Saint Etienne (ENSM-SE)
158, Cours Fauriel
F-42 023 SAINT ETIENNE
FRNACE

Keywords : differential scanning calorimetry ; fiber saturation point ; heat treatment ; swelling ; wood.

DOI 10.1515/HF.2004.131

Abstract

Retification® is a heat treatment which decreases the swelling of wood and increases its resistance to fungal attack. In this study, differential scanning calorimetry (DSC) was applied in order to determine the fiber saturation point (FSP) of natural and retified® wood. FSP values were used to determine the total swelling of natural and heat-treated wood. The DSC method was compared to the volumetric shrinkage approach. The influence of the heat treatment temperature and duration on the swelling of wood was investigated. Relationships between chemical changes and the reduction of swelling were analysed thoroughly.

The equivalence of the DSC method and the volumetric shrinkage method is shown. FSP in association with anhydrous density is a good indicator for the evaluation of the overall swelling of heat-treated wood. Reduction of wood swelling with increasing temperature and duration of thermal treatment is often attributed to hemicelluloses destruction. This study shows that the reduction of beech wood swelling can not only be attributed to the disappearing of adsorption sites that goes with the hemicelluloses destruction. It is suggested that other phenomena such as structural modifications and chemical changes of lignin also play an important part.

Introduction

Heat treatments of wood become widely used for wood protection against fungal attack, and for reduction of wood swelling (Kamden et al. 2002; Mouras et al. 2002; Niemz and Bekhta 2003). Retification® is a mild pyrolysis of wood that takes place under nitrogen atmosphere (Guyonnet and Bourgois 1986). Oxidation phenomena and cellulose hydrolyse due to the presence of oxygen and water steam are then reduced. Coloration and chemical modifications take place in the mass of wood, and allow further machining of the material (Bourgois et al. 1991). Moreover, retification® avoids the use of chemical compounds that may cause pollutions. The industrial development of this type of heat treatment requires rapid methods for the control of end use properties. This study focussed on the swelling of heat-treated wood.

Wood cell wall is thought to be a composite material made of cellulose microfibrils embedded in a water reactive matrix of hemicelluloses and lignin. The ability of the matrix to adsorb water is thus of critical importance in the swelling of wood (Barber 1968; Cave 1972). It is known that heat treatments reduce wood hygroscopicity by modifying this water reactive matrix (Obataya et al. 2000; Obataya and Tomita 2002) in different ways.

In order to quantify the overall swelling, the fiber saturation point (FSP) was used. The FSP of wood may be defined as the moisture content (MC) at which cell walls are saturated with water and cell cavities are free of liquid water. At the FSP all the adsorption sites of water are busy. Any increase in MC above the FSP results in negligible dimensional increase in the material, whereas any decrease in MC below the FSP leads to a shrinkage of the material. As a consequence, the FSP is traditionally measured by the volumetric shrinkage method. This method requires slow drying, and takes much time to meet the needs of industry.

Nevertheless, the state of water in wood can be quantitatively and qualitatively measured by other methods. For instance ^1H MNR was used (Labbé et al. 2002) to determine the water state and distribution in maritime pine wood. A somewhat more simple method, using

differential scanning calorimetry (DSC), can be employed to determine the state of water and the FSP of various cellulosic materials (Nakamura et al. 1981; Kabeya 1993). The FSP of green wood has already been successfully measured by DSC (Simpson and Barton 1991). In this study, FSP of heat-treated wood was determined by DSC.

The FSP values measured by DSC were compared to FSP values measured by volumetric shrinkage. The relevance of the FSP as an indicator of the total swelling of wood was then evaluated. The influence of the heat treatment temperature and duration on the swelling reduction of wood was examined in relation with changes of chemical composition.

Materials and Methods

Heat treatments and samples

Nine batches of common beech (*fagus sylvatica*), and four batches of maritime pine (*pinus pinaster*) were carried out in a pilot kiln. The corresponding values of the parameters (duration and temperature) are mentioned in Table 1. Each batch consisted in 16 boards of size 25x85x850 mm. Before treatment, the boards had been equilibrated in a climatic chamber at 20°C and 65% relative humidity during three months.

One board was randomly chosen among each treated batch. In this board, a 2 cm edge square cross section beam was cut across the natural directions of wood. In each beam 10 cubes and a thin lamella of thickness inferior to 1 mm were cut. The cubes were used for volumetric shrinkage measurement of FSP. Each thin lamella was cut again in parallelepipedic samples, that were used for FSP measurements by DSC. Their dry weight ranged from 2 mg to 5 mg. A part of the retified® wood of each batch was ground and sieved for the determination of the chemical composition of natural and heat-treated beech wood.

FSP measurement by Volumetric shrinkage

The cubic samples were immersed in water until constant weight and volume were reached. Then, they were slowly dried. Their weight and length along the three directions were measured. In this way, the volumetric swellings of the cubes versus their moisture content were plotted (Fig. 1). The FSP was then given by the intersection of the two straight lines obtained by a linear regression of the four first points and the four end points of these curves.

FSP measurement by Differential Scanning Calorimetry

Water in wood:

The state of water in cellulosic materials was accurately studied by DSC (Nelson 1977; Nakamura et al. 1981; Kabeya 1993). In wood as well as in cellulosic materials, water can be present under three main distinct states: free water, non-freezing bound water and freezing bound water. Free water is held in the wood large pores at a liquid state. On the DSC curves, free water presents a melting endothermic peak at a temperature equivalent to pure water (0°C). Non-freezing bound water consists of water molecules adsorbed on the cell wall and presents no melting peak. The quantity of non-freezing bound water present in wood corresponds to the FSP. Freezing bound water is mainly located in small pores and its physical properties are affected by the vicinity of the cell walls. The endothermic ‘melting’ peak of freezing bound water can be observed at temperatures inferior to 0°C, according to the Gibbs-Thompson relationship.

DSC device and calibration

The device was a SETARAM 131 DSC. Samples were sealed in hermetic stainless steel crucibles. A cooling system using liquid nitrogen allowed to reach temperatures inferior to 0°C. Heat flow and Temperature have been calibrated with three standards: mercury, deionised water and gallium. Afterwards, experimental conditions were set as follows: increase in temperature from –40°C to +40°C, with a heating rate of 2°Cmin⁻¹. A preliminary study verified the linearity domain of melting enthalpy of pure deionised water droplets weighed from 0.8 mg to 11.0 mg.

Method for FSP measurements

The “direct method” of Simpson and Barton (Simpson and Barton 1991) was applied to natural and retified® beech wood and maritime pine wood. At first, the samples were oven dried at 103°C and weighed in their anhydrous state (m_0). Then they were immersed in deionised water for 48 hours. The water saturated samples were weighed (m_s). Integration of the endothermic peak of free water gave its total heat of melting (ΔH_{obs} , in J). Free water is assumed to behave like pure water, its melting enthalpy (Δh_f) is taken equal to 334 Jg⁻¹. It is then possible to calculate the mass of non freezing bound water and the FSP, in percent, thanks to equation (1):

$$FSP = \frac{100}{m_0} \left(m_s - m_0 - \frac{\Delta H_{obs}}{\Delta h_f} \right) \quad (1).$$

Mercury Porosimetry

A mercury porosimetry test was carried out using a Micromeritics Autopore IV. The sample was a 0.156 g cube of natural beech wood, cut across wood natural directions. A penetrometer for solid sample analysis was used. It had a bulb volume of 5 cm³ and a stem volume of 0.392 cm³. The pressure was increased from 0.0037 MPa to 185.7661 MPa.

Chemical analysis of heat-treated beech wood

Extractives, lignin, and carbohydrates contents of natural and heat-treated beech wood were determined.

Extractives content was determined according to ASTM method D 1107-96. The initial sample is made of 2 g of wood ground and sieved between 212 μm and 560 μm . These samples were extracted in a soxhlet with a mix of ethanol and toluene. The weight lost during extraction gives the extractives content. The resulting extractive free wood was used to determine the Klason's lignin content according to the ASTM method D 1106-96. This method consists in an acid hydrolysis. The extractive free wood powder is firstly mixed with a 72% sulphuric acid solution. Secondly, water is added. And finally, this solution is filtered. The mass of the solid fraction gives the amount of Klason's lignin in the extractive free wood. The filtrate is kept for further analysis because it contains the soluble fraction of lignin and different simple sugars resulting from the wood polysaccharides hydrolysis. Soluble fraction of lignin is determined in a semi quantitative way by UV spectroscopy (Singleton and Rossi 1965; Alberto et al. 2001). The amount of soluble lignin is given in mg catechine equivalent per g of extractive free anhydrous wood. The amount of sugar resulting from the hydrolysis of wood polysaccharides is measured by high pressure liquid chromatography (HPLC). Glucose, xylose, mannose, cellobiose and glucuronic acid were identified. Their amount in the filtrate (for example the filtrate xylose content) was quantitatively determined in weight percent of extractive free anhydrous wood.

Results and discussion

Shape of the DSC melting peak of water in wood saturated samples.

The DSC curves of pure water had a unique and simply shaped endothermic peak. An endothermic peak matching to the melting of free water was also present for water saturated wood samples. This peak presented a shoulder almost for all specimens (Fig. 2) as it had already been noticed by Simpson and Barton (Simpson and Barton 1991). It is assumed here that this shoulder is due to freezing bound water located in wood pores. Thanks to the Gibbs-Thompson's law equation (2) it is possible to calculate the decrease of the water melting temperature present in pores:

$$\Delta T = T_0 - T = (T_0 + 273) \left(1 - \exp \left\{ - \frac{V_m \sigma_{ls}}{r \Delta h_f} \right\} \right) \quad (2)$$

where T_0 is the melting temperature of pure water in Celsius degrees. T is the melting temperature of water held in pores of diameter $2r$. V_m is the molar volume of frozen water

($19.6 \text{ m}^3 \text{ mol}^{-1}$). The value of the liquid/solid surface tension (σ_{ls}) is chosen equal to 20.4 mNm^{-1} which corresponds to the case of water melting in porous silica media (cited by Maloney and Paulapuro 1998).

On a DSC curve, the melting temperature is represented by the onset temperature. Since the shoulder is located at the end left of the peak of free water (to the low temperatures), the onset temperature measured on water saturated wood samples corresponds to the melting temperature of freezing bound water. Consequently, the difference in onset temperatures between pure water and water in saturated wood samples should be linked to the size of the pores containing the freezing bound water. From the experimental point of view the difference in average onset temperatures of pure water and free water in beech wood is 0.06°C .

The porometry test showed three populations of pore diameters around $20 \text{ }\mu\text{m}$, $0.44 \text{ }\mu\text{m}$ and $0.015 \text{ }\mu\text{m}$ (Fig. 3). The corresponding temperature shifts were calculated according to the Gibbs-Thompson's law: $0.9 \cdot 10^{-3}^\circ\text{C}$, 0.04°C and 1.18°C respectively. As regards the first population ($20 \text{ }\mu\text{m}$), the temperature shift is too little to be detected. As the difference in average onset temperatures of pure water and water in wood is of 0.06°C , the second population (pore diameter around $0.44 \text{ }\mu\text{m}$ and temperature shift of 0.04°C) can match to the shoulder of Fig. 2. Moreover, pores of diameter inferior to $9 \text{ }\mu\text{m}$ are attributed to fibres lumen (Trenard 1980). Thus the shoulder can match to freezing bound water present in fiber lumen. The third pore population ($0.015 \text{ }\mu\text{m}$) should result in a temperature shift of about 1.2°C . However, no corresponding peak was visible on the DSC curves. On the porometry curves obtained by Trenard in 1980, one can notice that this population is present on 10 mm thick samples and not on $240 \text{ }\mu\text{m}$ thick samples (thickness inferior to the fibre length). It is suggested that the distribution around $0.015 \text{ }\mu\text{m}$ visible on Fig. 3 is linked to the sampling and does not correspond to an existing pore population. That would explain why no peak is visible at the corresponding temperature on the DSC curves.

Effect of the thermal treatment on wood swelling and precisions about FSP

Obataya showed that dry heat treatments result in reversible and irreversible effect on wood

hygroscopicity (Obataya et al. 2002). Both reversible and irreversible effects may affect wood swelling. It is thus necessary to indicate which effect the FSP accounts for.

Reversible effects are due to softening and relaxation of the cell wall matrix at high temperature. This phenomenon induces the tightening of the matrix structure during cooling.

The mobility of the polymer chains is then reduced. At low relative humidity, the tightened structure prevents water adsorption. However, if the heat-treated material is moistened at high relative humidity, polymer chains recover their mobility, and water adsorption occurs again.

Irreversible effects are due to the chemical modifications of the material. The sample preparation for DSC as well as for volumetric shrinkage measurement requires water saturation. By this way reversible effects are cancelled. Consequently, the FSP measurement accounts only for the irreversible effects induced by heat treatment.

Comparison of the two methods for FSP measurement and evaluation of overall swelling

Thanks to a suitable choice of parameters, a large range of FSP values could be reached: from 15% to 33%. Fig. 4 shows the linear regression between the FSP measured by volumetric shrinkage and the FSP measured by DSC. The reliability of the DSC method is demonstrated by a slope equal to 1.03 and a correlation coefficient equal to 0.93.

Swelling of wood (G in %) is defined by equation (3):

$$G = 100 \times \frac{V_s - V_0}{V_0} \quad (3)$$

where V_0 is the anhydrous volume, and V_s the water saturated volume of the specimen.

Experimental swelling was measured on the cubic samples. By assuming that the swelling of wood corresponds to the adsorbed water a calculated swelling (G_c) can be assessed by equation (4) (Skaar 1988):

$$G_c = d_{\text{anh}} \text{FSP} \quad (4).$$

Where d_{anh} is the apparent anhydrous density of wood. This relation does not take into account the pore size variations during drying that was studied in 1962 by Boutelje (Boutelje 1962). On Fig. 5, the linear regression between G and G_c exhibits a slope of 0.94 and a correlation coefficient of 0.92. The FSP associated with anhydrous density can be thus used as a good indicator for the evaluation of wood swelling.

Influence of temperature and duration on the FSP.

Table 2 shows the FSP values measured by DSC on natural and heat treated wood. An increase in retification® temperature leads to a decrease in FSP of common beech and Maritime pine. An increase in retification® duration for beech wood also leads to a decrease in wood FSP. The effect of a long time exposure at low retification® temperatures seems to be equivalent to short times at high temperature. The same average swelling reduction level could be reached with treatments E, I and J that correspond respectively to 5 min at 260°C, 180 min at 220°C and 600 min at 200°C. This observation is consistent with the idea that the reduction of wood hygroscopicity follows an Arrhenius relation as a function of the time – temperature combination, as mentioned by Skaar (Skaar 1988).

Reduction of FSP in relation to chemical composition of beech wood.

Tables 2 and 3 present the chemical composition of natural and heat treated beech wood. In this part, it is proposed to analyse the relationship between reduction of FSP and wood chemical changes due to thermal treatment.

Variations of extractives content with retification® parameters.

Extractives content increases with increasing temperature and length of treatment. However, we assume in the following discussion, that extractives content has negligible influence on the FSP value. Consequently, FSP decrease by heat treatment is discussed in function of the chemical composition of extractive free anhydrous wood.

Variation of lignin content with retification® parameters.

The soluble fraction of lignin is almost stable whatever parameter values (Table 2). The amount of Klason's lignin increases with increasing temperatures. At 220°C, the quantity of lignin increases significantly for treatments longer than 60 min. At 200°C, it decreases for treatments of 60 min and 180 min length, and increases again with a 600 min treatment. More precisely, the Klason's lignin content of treatments B and J (5 min at 200°C and 600 min at 200°C respectively) are very close ($24.3\pm 0.1\%$ and $24.6\pm 0.2\%$ respectively). In the same time the FSP is seriously lowered ($30.6\%\pm 2.2\%$ and $15.3\%\pm 1.8\%$ respectively). This observation shows that lignin content has a minor influence on the FSP.

Variations of polysaccharides content with retification® parameters

Two types of sugar polymers are present in hardwood: hemicellulose (glucuronoxylans, glucomannans) and cellulose (Sjöström 1993). During acid hydrolysis, these molecules are depolymerised into simple sugar dissolved in the filtrate. Consequently, cellobiose and glucose content in the filtrate match to the cellulose proportion in wood, as well as glucuronic acid and xylose filtrate content match to glucuronoxylane proportion in wood, and mannose filtrate content matches to mannanes proportion in wood.

The main variation (Table 3) regarding polysaccharides is a decrease of the xylose content in the filtrate with increasing temperatures and durations of retification®. Glucuronic acid presents the same tendency. This observation shows that glucuronoxylan proportion in heat treated beech wood is lower than in natural beech wood. Hemicelluloses are the most thermally sensitive constituents of wood. They are the first components to be destroyed, as it is reported by numerous authors (Beall and Eickner 1970; DeGroot et al.1988; Avat 1993; Weilland 2000). Mannose content is low and almost stable whatever the parameter values. Glucose and Cellobiose content increase slightly and monotonously with increasing parameter values. Cellulose is resistant in the temperature range of retification®. Consequently, its

proportion in extractive free anhydrous wood should increase proportionally to the decrease of the other constituents.

Relationship between polysaccharides content and FSP

Both glucuronoxylan content and FSP decrease. It is often assumed that the destruction of hemicelluloses goes together with a vanishing of water adsorption sites (mainly hydroxyl groups) that induces a reduction of wood swelling. In order to verify if hemicelluloses destruction is the only reason for the FSP reduction, we propose to calculate a FSP value related only to the polysaccharides content of natural and retified® wood. The filtrate xylose content (FXC in %) and the filtrate glucose content (FGC in %) stand for the proportion of glucuronoxylane and cellulose in wood. We assume that they allow to calculate the FSP, thanks to equation (5):

$$FSP = M_{wa} n_{xy} \frac{(FXC)}{M_{xy}} + M_{wa} n_{gl} \frac{(FGC)}{M_{gl}} + C \quad (5).$$

Where n_{xy} , (resp. n_{gl}), is the number of water molecules that can be adsorbed by a xylose (resp. glucose) unit of glucuronoxylane (resp. cellulose). M_{wa} , (resp. M_{xy} , M_{gl}), is the molar mass of water (resp. xylose, glucose). FXC and FGC values are issued from experimental data (Table 3), they are given in weight percent of extractive free anhydrous wood. The term C accounts for the contribution to the FSP of the other constituents. C is chosen constant because the calculated FSP is chosen to be only related to wood polysaccharides content.

Equation (5) should be understood as follow. For 100g of free extractive anhydrous wood,

one have (FXC)g of xylose unit in the filtrate, i.e. $\left(\frac{FXC}{M_{xy}}\right)$ mol of xylose unit. It is thus

possible to adsorb $n_{xy} \left(\frac{FXC}{M_{xy}}\right)$ moles of water molecule, i.e. $M_{wa} n_{xy} \left(\frac{FXC}{M_{xy}}\right)$ g of water per

100 g of extractive free anhydrous wood.

Values of n_{xy} and n_{gl} are issued from literature (Nakamura et al. 1981; Kabeya 1993). It was shown that 4 molecules of water can adsorb on one xylose unit of larch xylan and that 2 water molecules can adsorb on one glucose unit of wood cellulose of crystallinity 44%.

Once the FSP value is calculated thanks to FXC and FGC, it is possible to compare the experimental and calculated reduction of FSP for each treatment. We define FSP variations from natural to retified® wood by:

$$\Delta FSP = FSP(\text{natural wood}) - FSP(\text{heat treated wood}) \quad (6).$$

Assuming that hemicelluloses destruction is the only reason for the FSP reduction, the calculated ΔFSP should be equal to the experimental ΔFSP . Fig. 6 compares experimental and calculated ΔFSP values. The first observation is that experimental and calculated ΔFSP show the same tendency in spite of a rather large scattering. It is consequently expected that the FSP value depends on the hemicellulose content. Nevertheless the slope of the linear regression is 3.3, which means that the experimental variations of the FPS are to 3.3 times higher than the expected calculated variations. We admit that the number of water molecules that can adsorb on cellulose and glucuronoxyane in natural and retified® beech wood is close to the values found by Kabeya and Nakamura. As a consequence the decrease of wood swelling can not be explained simply in terms glucuronoxyane destruction. Some other reasons for the reduction of wood swelling have to be found.

Modifications of the lignin carbohydrate complex by heat treatments

It has been shown that some cross linking and condensation phenomena take place in lignin during retification® (Weiland 2000). As a consequence, the ability of lignin to adsorb water may be decreased. Though the lignin content does not vary significantly (treatments B, F, H, J), it is not excluded that chemical modifications of lignin induce significant decrease in the FSP. In addition, lignin is closely linked to the other constituents, and forms the lignin carbohydrate complex (LCC). Working on milled wood lignin, Obataya (Obataya et al. 2002)

suggested that the modification of lignin and of the LCC during the heat treatment is mainly responsible for the irreversible reduction of wood hygroscopicity.

In this study, Klason's lignin from natural and heat treated wood (treatment E) were equilibrated at 70% relative humidity and 20°C after drying at room temperature. The MCs were low due to the drastic procedure used for the extraction of Klason's lignin destroying the LCC. Lignin from natural wood presented a MC of 7.05% and lignin from treated wood had a MC of 3.72%. Reduction of lignin hygroscopicity during heat treatment should thus take part in the reduction of wood swelling.

Moreover, lignin and hemicelluloses are closely linked to each other in cell wall. The lignin and hemicellulosic matrix of wood cell wall is generally thought to be isotropic and amorphous. Some authors however (Vincent 1999; Yan and Zhu 2003) report that hemicelluloses are regularly distributed in the cell wall structure: hemicelluloses are located in a lattice between the cellulose fibrils. The remove of hemicelluloses should thus modify this particular structure, and the ability of the wood cell wall to adsorb water. It would explain why in our study the FSP is so dependent on the FXC. Thus, structural modifications due to hemicelluloses destruction could be also involved in the reduction of wood swelling by heat treatment.

Conclusion

This study deals with the use of DSC for evaluation of the swelling of heat-treated wood. The method is based on the measurement of the FSP. The correlation of the DSC method with the volumetric shrinkage method is shown with linear regression. Moreover, the FSP associated with anhydrous density is a good indicator for the evaluation of the overall swelling of heat-treated wood. This study shows that the reduction of wood swelling of beech wood can not be explained only in terms of the disappearing of hemicelluloses adsorption sites that goes with the hemicelluloses destruction. It is suggested that other phenomena such as structural modifications and chemical changes of lignin also play an important part.

- Alberto, M.M., Mougel, E., Zoulalian, A. (2001) Influence des extractibles d'essences du Mozambique sur l'hydratation du ciment. Les cahiers scientifiques du bois. 2:1-14
- ASTM Standard (1998) 04.10. D1106-96. Standard test method for acid insoluble lignin in wood.
- ASTM Standard (1998) 04.10. D1107-96. Standard test method for ethanol toluene solubility of wood.
- Avat, F. Contribution à l'étude des traitements thermiques du bois jusqu'à 300°C : transformations chimiques et caractérisations physico-chimiques. Ph-D Thesis, Ecole des Mines de Saint Etienne, Saint Etienne (France), 1993.
- Barber, N.F. (1968) A theoretical model of shrinking wood. *Holzforshung*. 22(4):97-103.
- Beall, F.C., Eickner, H.W. (1970) Thermal degradation of wood components, a review of the literature. USDA forest service research paper, FPL 130.
- Bourgois, J., Janin, J., Guyonnet, R. (1991) La mesure de la couleur : une méthode d'étude et d'optimisation des transformations chimiques du bois thermolysé. *Holzforshung*. 45(5):377-382.
- Boutelje, J. (1962) On shrinkage and change in microscopic void volume during drying as calculated from measurements on microtome cross section of Swedish pine (*pinus sylvestry L.*). *Swensk papperstidning*. 6:209-215.
- Cave, I.D. (1972) A theory of the shrinkage of wood. *Wood science and technology*. 6:284-292.
- DeGroot, W.F., Pan, W.P., Rahman, D., Richards, G.N., (1988) First chemical events in pyrolysis of wood. *Journal of analytical and applied pyrolysis*. 13:221-231.
- Guyonnet, R., and Bourgois, J. (1986). Patent Fr. 86 14138.
- Kabeya, H. (1993) Effect of grinding on bound water in cellulosic materials. *Mokuzai gakkaiishi*. 39(11):1291-1297.
- Kamden, D.P., Pizzi, A., Jermaud, A. (2002) Durability of heat-treated wood. *Holz als roh- und werstoff*, 60(1):1-6.
- Labbé, N., De Jéso, B., Lartigue, J.C., Daudé, G., Pétraud, M., Ratier, M. (2002) Moisture content and extractive materials in maritime pine wood by low Field ¹H MNR. *Holzforshung*. 56:25-31.
- Maloney, C., Paulapuro, H. (1998) Hydration and Swelling of pulp fibers measured with differential scanning calorimetry. *Nordic pulp and paper reaserch journal*. 13(1),31-36.
- Mouras, S., Girard, P., Rousset, P., Permadi, P., Dirol, D., Labat, G. (2002) Propriétés physiques de bois peu durables soumis à un traitement de pyrolyse ménagée. *Ann. for. sci*. 59:317-326.
- Nakamura, K., Hatakeyama, T., Hatakeyama, H. (1981) Studies on Bound Water of Cellulose by differential scanning calitymetry. *Textile research journal*. 72(9):607-613.
- Nelson, R.A. (1977) The determination of moisture transition in cellulosic materials using differential scanning calorimetry. *Journal of applied polymers science*. 21:645-654.
- Niemz, P., Bekhta, P. (2003) Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. *Holzforshung*. 57(5):539-546.
- Obataya, E., Tanaka, F., Norimoto, M., Tomita, B. (2000) Hygroscopicity of heat-treated wood I - effects of after treatments on the hygroscopicity of heat-treated wood. *Mokuzai gakkaiishi*. 46(2):77-87.
- Obataya, E., Tomita, B. (2002). Hygroscopicity of heat-treated wood II - reversible reductions in the hygroscopicity of wood due to heating. *Mokuzai gakkaiishi*. 48(4):288-295.
- Obataya, E., Higashihara, T., Tomita, B. (2002) Hygroscopicity of heat-treated wood III - effect of steaming on the hygroscopicity of wood. *Mokuzai gakkaiishi*, 48(5):348-355.

- Singleton, V.L., Rossi, J. A. (1965) Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagent. American journal of enology and viticulture. 16:144-158.
- Simpson, L.A., Barton, A.F.M. (1991) Determination of the fibre saturation point in whole wood using DSC. Wood science and technology. 25:301-308.
- Sjöström, E. Wood chemistry, fundamentals and applications. Academic press. San diego. 1993. 51-70.
- Skaar, C. Wood–water relations. Springer-verlag. Berlin. 1988. p.129, p. 172.
- Trenard, Y. (1980) Comparaison et interprétation de courbes obtenues par porosimétrie mercure sur diverses essences de bois. Holzforshung. 34:139-146.
- Vincent, J.F.V. (1999) From cellulose to cell. Journal of experimental biology, 202(23):3263-3268.
- Weiland, J.J. Etude physico-chimique du traitement thermique du bois. Optimisation de paramètres du procédé de réification®. Ph-D Thesis, Ecole des Mines de Saint Etienne, Saint Etienne (France), 2000
- Yan, L., Zhu, Q. (1999) Direct observation of the main cell wall components of straw by AFM. Nordic pulp and paper research journal. 14 (2):129-139.

Vincent REPELLIN (corresponding author)
Département PCMM
Centre SPIN
Ecole des Mines de Saint Etienne
158, Cours Fauriel
F-42 023 SAINT ETIENNE
France

René GUYONNET
Département PCMM
Centre SPIN
Ecole des Mines de Saint Etienne
158, Cours Fauriel
F-42 023 SAINT ETIENNE
France

Fig. 1. Measurement of the FSP by the volumetric shrinkage method ; the FSP is the abscissa value of the intersection of the two straight lines.

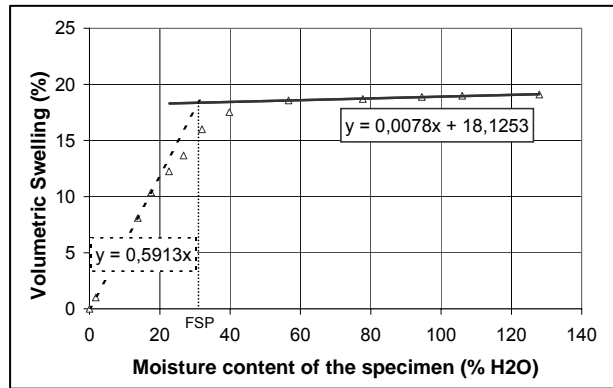


Fig. 2. DSC melting peaks of pure deionised water and free water present in saturated wood samples. The peak of free water presents a shoulder.

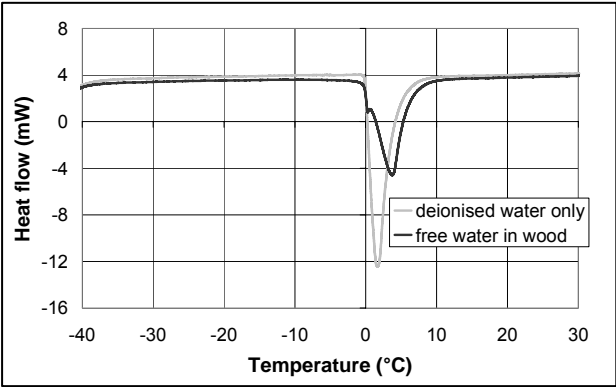


Fig. 3. Pore size repartition of natural beech wood (carried out with mercury porosimetry), on a sample of 5 mm thickness in the longitudinal direction. Three populations of pore size ranging approximately around 20 μm , 0.44 μm and 0.015 μm are visible.

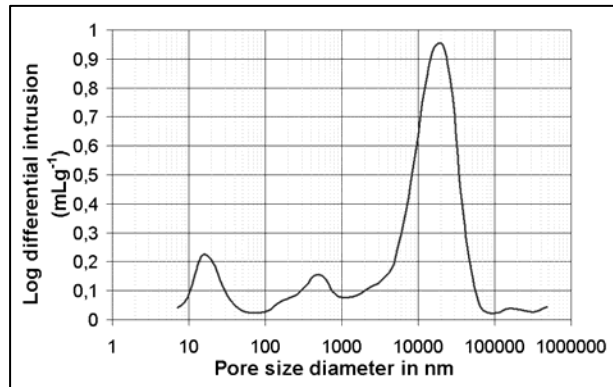


Fig. 4. Comparison of two different methods for the measurement of the FSP of heat-treated beech (●) and pine wood (Δ).

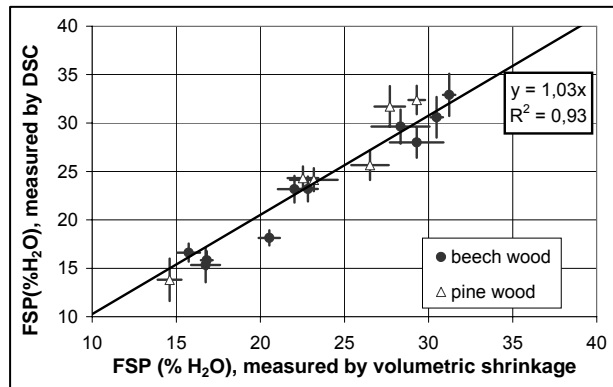


Fig. 5. Comparison of experimental swelling and swelling calculated from FSP and anhydrous density (for heat-treated beech and pine wood).

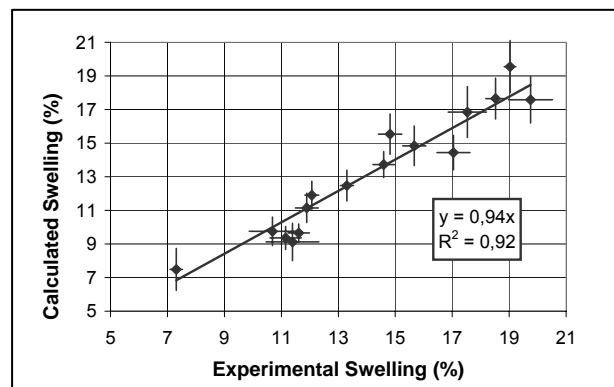


Fig. 6. Comparison of the experimental and calculated variations of the fibre saturation point due to heat treatment (Δ FSP). The calculated Δ FSP is a value that takes into account only the FSP variations due to the changes of polysaccharides proportion in extractive free anhydrous wood. It is calculated in function of FXC and FGC. The experimental Δ FSP is issued from the experimental results. According to the linear regression, experimental Δ FSP are 3.3 times higher than the calculated Δ FSP.

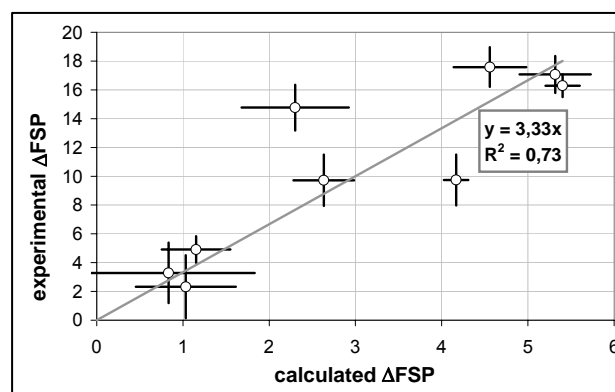


Table 1. Parameters of the heat treatments of retification® (time and temperature).

Treatment number	species	Temperature (°C)	Time (min)
A	Common beech	Untreated	Untreated
B	Common beech	200	5
C	Common beech	220	5
D	Common beech	240	5
E	Common beech	260	5
F	Common beech	200	60
G	Common beech	220	60
H	Common beech	200	180
I	Common beech	220	180
J	Common beech	200	600
K	Maritime Pine	Untreated	Untreated
L	Maritime Pine	180	5
M	Maritime Pine	230	5
N	Maritime Pine	240	5
O	Maritime Pine	260	5

Table 2. FSP in %H₂O and chemical composition of natural and heat-treated wood:

Extractive content in % of anhydrous wood (ASTM D1107-96), klason's lignin content in % of extracted anhydrous wood (ASTM D1106-96), and soluble fraction of lignin in mg equivalent catechine per g of extracted anhydrous wood (U.V. spectroscopy). The values presented are averages on four samples and the standard deviations are presented in brackets.

Treatment	FSP (%)	Extractive content (% of anhydrous wood)	Klason's Lignin content (% of extractive free anhydrous wood)	Soluble fraction of lignins (mg catechine equivalent per g of extractive free anhydrous wood)
A	32.9 (2.2)	0.7 (0.2)	24.3 (0.1)	13.5 (2.7)
B	30.6 (2.1)	1.1 (0.2)	24.3 (0.6)	11.3 (0.8)
C	28.0 (1.6)	2.8 (0.1)	23.8 (0.4)	11.5 (1.3)
D	18.1 (0.8)	4.1 (0.3)	26.5 (0.5)	7.9 (0.3)
E	16.6 (0.9)	5.0 (0.5)	35.4 (1.8)	9.1 (0.5)
F	29.6 (1.8)	1.5 (0.1)	19.9 (0.1)	12.2 (1.5)
G	23.2 (1.3)	4.2 (0.2)	26.6 (0.3)	14.8 (2.4)
H	22.0 (1.0)	3.3 (0.2)	20.3 (0.1)	12.7 (1.6)
I	15.8 (0.9)	5.0 (0.3)	29.7 (0.2)	12.2 (1.0)
J	15.3 (1.8)	4.1 (0.2)	24.6 (0.2)	9.9 (0.1)
K	31.7 (2.1)	-	-	-
L	32.4 (1.5)	-	-	-
M	24.1 (1.2)	-	-	-
N	24.3 (1.2)	-	-	-
O	13.8 (2.2)	-	-	-

Table 3. Chemical composition of natural and heat-treated beech wood: carbohydrates and glucuronic acid content in weight percent of extractive free anhydrous wood (measured by HPLC).

Treatment	Glucose (FGC) in (weight % of extractive free anhydrous wood)	Cellobiose in (weight % of extractive free anhydrous wood)	Xylose (FXC) in (weight % of extractive free anhydrous wood)	Glucuronic acid in (weight % of extractive free anhydrous wood)	Mannose in (weight % of extractive free anhydrous wood)
A	33.4 (0.8)	2.3 (0.3)	20.6 (0.9)	12.1 (1.7)	3.3 (0.6)
B	34.3 (1.3)	2.3 (0.4)	18.0 (1.6)	10.9 (2.2)	3.8 (0.7)
C	35.1 (1.0)	2.7 (0.4)	17.4 (0.9)	9.4 (2.1)	3.5 (0.6)
D	38.8 (0.6)	3.4 (0.2)	13.5 (0.2)	8.9 (1.4)	3.4 (0.5)
E	39.7 (1.1)	4.5 (0.8)	6.7 (0.5)	3.9 (2.1)	3.8 (0.3)
F	34.1 (0.4)	3.5 (0.2)	18.5 (0.1)	11.3 (0.5)	4.8 (0.6)
G	34.6 (0.7)	3.9 (0.3)	14.6 (0.6)	10.0 (1.1)	6.5 (3.8)
H	35.0 (0.5)	4.7 (0.3)	11.2 (0.7)	7.9 (0.6)	4.7 (1.0)
I	38.8 (1.4)	4.4 (0.1)	7.2 (0.2)	10.1 (0.3)	3.1 (0.6)
J	35.8 (0.7)	4.4 (0.1)	10.1 (0.4)	4.8 (1.3)	4.2 (0.4)

Fig. 1. Measurement of the FSP by the volumetric shrinkage method ; the FSP is the abscissa value of the intersection of the two straight lines.

Fig. 2. DSC melting peaks of pure deionised water and free water present in saturated wood samples. The peak of free water presents a shoulder.

Fig. 3. Pore size repartition of natural beech wood (carried out with mercury porosimetry), on a sample of 5 mm thickness in the longitudinal direction. Three populations of pore size ranging approximately around 20 μm , 0.44 μm and 0.015 μm are visible.

Fig. 4. Comparison of two different methods for the measurement of the FSP of heat-treated beech (\bullet) and pine wood (Δ).

Fig. 5. Comparison of experimental swelling and swelling calculated from FSP and anhydrous density (for heat-treated beech and pine wood).

Fig. 6. Comparison of the experimental and calculated variations of the fibre saturation point due to heat treatment (ΔFSP). The calculated ΔFSP is a value that takes into account only the FSP variations due to the changes of polysaccharides proportion in extractive free anhydrous wood. It is calculated in function of FXC and FGC. The experimental ΔFSP is issued from the experimental results. According to the linear regression, experimental ΔFSP are 3.3 times higher than the calculated ΔFSP .

Table 1. Parameters of the heat treatments of retification® (time and temperature).

Table 2. Table 2. FSP in %H₂O and chemical composition of natural and heat-treated wood: Extractive content in % of anhydrous wood (ASTM D1107-96), Klason's lignin content in % of extracted anhydrous wood (ASTM D1106-96), and soluble fraction of lignin in mg equivalent cathechine per g of extracted anhydrous wood (U.V. spectroscopy). The values presented are averages on four samples and the standard deviations are presented in brackets.

Table 3. Chemical composition of natural and heat-treated beech wood: carbohydrates and glucuronic acid content in weight percent of extracted anhydrous wood (HPLC).

List of corrections on **reg. no. 099/04**:

- 1- p.2, line 3 parallelepipedic instead of “parallel epipedic”
- 2- p.2 table 1 : could you please center the letters in column “treatment number”?
- 3- p.5 table 2 : idem could you please center the letters in column “treatment”?
- 4- p.5 table 3 column 4 , line9, 7.2 (0.2) instead of “7.2 (02.)”
- 5- p.6 number of equation (6) on the same line that the equation if possible.
- 6- p.6 found in literature (Nakamura et al. 1981; Kabeya 1993) instead of “found by Kabeya and Nakamura ((■■■authors: citation? ■■■))”
- 7- p.7 references:
Bourgois, J., Janin, G., Guyonnet, R. (1991) The color measurement : A fast method to study and to optimize the chemical transformations undergone in the thermally treated wood. Holzforshung. 45(5):377-382.
Instead of
“Bourgois, J., Janin, J., Guyonnet, R. (1991) La mesure de la couleur : une méthode d’étude et d’optimisation des transformations chimiques du bois thermolysé. Holzforshung. 45(5):377-382. ((■■■authors: provide English title ■■■))”
- 8- p.7 references
Trenard, Y. (1980) Comparison and interpretation of mercury porosimeter curves obtained on some wood species. Holzforshung. 34:139-146.
Instead of
“Trenard, Y. (1980) Comparaison et interprétation de courbes obtenues par porosimétrie mercure sur diverses essences de bois. Holzforshung. 34:139-146. ((■■■authors: provide English title ■■■))”
- 9- p.7 references
Yan, L., Zhu, Q. (2003) Direct observation of the main cell wall components of straw by AFM. Nordic pulp and paper research journal. 14 (2):129-139.
Instead of
“Yan, L., Zhu, Q. (1999) Direct observation of the main cell wall components of straw by AFM. Nordic pulp and paper research journal. 14 (2):129-139. ((■■■authors: check date, 2003 cited in text ■■■))”