Thermo-vacuum Modification of some European Softwood and Hardwood Species Treated at Different Conditions

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Three softwood species, spruce (*Picea abies* Karst.), fir (*Abies alba* Mill.), and larch (*Larix decidua* Mill.), and five hardwood species, oak (*Quercus petraea* Liebl.), ash (*Fraxinus excelsior* L.), beech (*Fagus sylvatica* L.), cherry (*Prunus avium* L.), and black locust (*Robinia pseudoacacia* L.) were treated at high temperatures under vacuum conditions with Termovuoto® technology. All of the wood species were treated at different temperatures (from 160 to 220°C), different times (from 45 minutes to 5 hours), and under different pressure conditions (160, 210, and 330 mbar). The treated material was characterized in terms of mass loss, color changes, and equilibrium moisture content. Results showed dissimilar behavior of various wood species and their different sensitivities to treatment schedules. Consequently, the series of tests performed allowed a detailed characterization of the Termovuoto® process and its effect on product quality.

Keywords: Ash; Beech; Black locust; Cherry; Color modification; Fir; Larch; Mass loss; Oak; Physical properties; Spruce; Thermally modified wood; Thermo-vacuum method

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INTRODUCTION

Termovuoto® is a new technology for the thermal modification of wood in which oxygen inside the reactor is substituted by partial vacuum, and heating is provided by forced convection. The Termovuoto® system has been designed to combine an efficient vacuum drying process with a thermal treatment process. According to Hill's classification, it is a dry process in an open system (Hill 2006). These conditions ensure high energy efficiency, less corrosion and rust problems, and a lower rate of wood mass loss. The latter might be explained by the fact that the vacuum pump continuously removes from the reactor all volatile compounds that would have contributed to accelerated degradation of polysaccharides in the wood cell wall (Hill 2006).

An earlier description of the process of thermal modification under vacuum for spruce and fir was illustrated in Allegretti *et al*. (2012). The main results for such species were an improvement of durability and a not significant variation of bending strength and elasticity.

This paper describes experiments on thermo-vacuum treatment of some European hardwood and softwood species under various treatment conditions. The species were selected on the basis of their commercial interest in the European market as modified solid wood products with improved performances. In this specific study the interest of the thermal modification focused on the improved durability for the species with low natural durability *i.e.* spruce, fir, ash, and beech, and for outdoor end-uses and the improvement of dimensional stability and color of larch, oak, cherry, and black locust. Some of the species, such as oak and black locust are also known as refractory species; they are difficult to dry and treat because of their tendency to collapse and to develop internal checks.

The objective was to compare the behavior of the selected wood species that were treated with thermo-vacuum and to explore the influence of the process parameters, *i.e.* temperature, duration, and pressure.

A low sampling number and fast characterization tests (*i.e.* mass loss, color, and EMC) were adopted in this early stage of the study. For this reason, the results are not conclusive but they are preparatory towards a next step of tests for the optimization of the process and the full characterization of the treated wood.

EXPERIMENTAL

Materials

Sawn timber of the softwood used for the tests were obtained from the Val di Fiemme forest (average altitude of 1757 m above sea level), Trentino region, Italy. Sawn timber of the hardwood were from different parts of Europe. Nominal normal density (kg m^{-3}) of the treated species was: spruce and fir: 380 to 440; larch: 650; ash: 750, beech: 730; black locust: 750; cherry: 620; oak: 820.

Six sawn boards (32 mm × 150 mm × 1000 mm, initial moisture content around 20%) of each species were randomly disposed in a stack, and they were treated together. In order to minimize the wood variability, all of the wood properties were measured and compared by matched samples cut from the same board 2 m long, which was initially sawn into two parts, *i.e.* a treated and untreated control piece. Three boards for each treatment and for each wood species were sampled from different parts of the stack for the characterization tests.

The Plant

The thermo-vacuum plant used for the test was a semi-industrial prototype with an internal diameter of 1.7 m. It was initially a conventional vacuum kiln that was re-built to function at temperatures up to 250°C. The cylinder walls were heated by diathermic oil circulating between double layers of steel. Under vacuum, heat from the hot walls was convectionally transferred to wood by means of two high efficiency fans (diameter 500 mm) with external motors and a mechanical vacuum-proof and temperature-resistant transmission. The fan speed was proportional to the internal air pressure, ranging from 635 r min^{-1} at atmospheric pressure to a maximum speed of 1930 r min^{-1} at vacuum pressure of 200 mbar. A water ring type pump equipped with a heat exchanger provided the vacuum. An oil-air heat exchanger unit assisted the cooling procedure. The temperature of the oil, air, and wood core was measured by means of thermocouples. All of the process parameters were controlled and recorded by a computer.

The Treatments

The thermo-vacuum treatments were applied to boards dried to 0% moisture content (MC). The drying process from the initial MC was carried out at low temperatures and vacuum conditions in the same cylinder where the thermo-vacuum treatment took place later. The final drying step was carried out at 100°C and a pressure not exceeding 250 mbar, thus corresponding to a water boiling temperature of 65°C. Each board was weighed during a short time interval between the end of drying (at MC = 0%) and the beginning of the thermo-vacuum treatment.

Each thermo-vacuum treatment consisted of:

- a heating phase from 100°C and up to the air temperature set value;
- a thermal treatment phase at a constant air temperature and a defined duration;
- a cooling phase to decrease the wood temperature to 100°C.

The rate of temperature variation during heating and cooling was controlled and kept constant in all of the treatments. Due to the significant heating mass of the system, an oil-air heat exchanger unit assisted the cooling procedure. The parameters used for process control and as nominal values to characterize the treatment as well as for data processing were as follows:

- ***T*** (°C) – average air temperature during the treatment. The tested temperatures were in the range of 160 to 220°C.
- ***t*** (hours) – treatment duration at a given constant air temperature. The duration was measured from the moment when ***T*** became constant until the beginning of the cooling phase. The treatment duration varied between 0.75 and 5 h.
- ***p*** (mbar) – average vacuum pressure (the on-off control of the vacuum pump was set at Δp = 50 mbar). The pressure was kept constant during the entire treatment. Three pressures, namely 160, 210, and 330 mbar corresponding to water boiling temperatures between 53 and 73°C and a theoretical concentration of oxygen between 2 to 7% were tested.

A total of nine thermo-vacuum treatments with various parameter combinations were performed. The process parameters were changed in order to evaluate the effect of temperature, time, and pressure, as reported in Table 1.

Table 1. Parameters of the Performed Treatments*

Treat.n.	***1***	***2***	***3***	***4***	***5***	***6***	***7***	***8***	***9***
***T* [°C]**	*160*	*180*				*190*		*200*	*220*
***t* [h]**	*3*	*0.75*	*1.5*	*3*	*5*	*3*		*3*	*3*
***p* [mbar]**	*210*	*210*	*210*	*210*	*210*	*160*	*330*	*210*	*210*

* In treatments n. 5 and 6 black locust and cherry were absent, respectively.
The pressure is indicated by average values.

The Characterization Tests

After each thermo-vacuum treatment, three sawn boards of each species, selected from a different location of the stack, were chosen for the physical characterization of the material. The physical characteristics investigated are described below:

Mass loss

The mass loss (ML) of the wood is related to its thermal degradation and it is considered to be the main indicator of the treatment intensity. Mass loss is the ratio of the percent between the weight of the board prior to the thermo-vacuum treatment (but after drying when the MC = 0%) and the weight immediately after it. Three boards were measured for each treatment.

Equilibrium moisture content

The equilibrium moisture content (EMC) was measured according to the standards ISO 3130 (1975) on 10 samples of each species. The samples were conditioned in a climatic chamber at a temperature of 20°C and 65% of relative humidity (RH). The number of samples was determined according to the standard ISO 3129 (1975).

Color

Color was measured by using a spectrophotometer (MicroFlash 200D) over an 18 mm diameter spot with a standard light source, D65, at an observation angle of 10°. The color measurements were performed on the same points on planed wood surfaces before and after the heat treatment. A number of 30 measurements were collected for each species. Color coordinates referred to the three dimensional CIE $L^*a^*b^*$ color space, where L^* indicates the lightness in a range from black (0) to white (100), and a^* and b^* define the position in the green-red and blue-yellow axis, respectively. The total color change, ΔE^*, was calculated with the equation reported below (Eq. 1).

$$\Delta E^* = (\Delta L^*2 + \Delta a^*2 + \Delta b^*2)^{1/2} \qquad (1)$$

Statistical tests on color data (t-test and ANCOVA) were effectuated in order to evaluate the effect of the process parameters (***T, t,*** and ***p***) on the wood color. The effect of treatment temperature and time on ΔE^* (response variable) were investigated through ANCOVA, in which the explanatory variables were both continuous (temperature and time) and categorical (wood species). For the analysis, hardwoods were separated from softwoods, and the effects of temperature and time were analyzed separately. Statistical analysis was performed using *R-software*.

RESULTS AND DISCUSSION

Mass Loss as Function of Temperature, Time, and Pressure

Mass loss, ML, caused by the thermo-vacuum treatments is plotted to the treatment parameters ***T*** (at constant ***t*** = 3 hours and ***p*** = 210 mbar), ***t*** (at constant ***T*** = 180° C and ***p*** = 210 mbar), and ***p*** (at constant ***t*** = 3 hours and ***T*** = 190° C), and is shown in Fig. 1.

ML plotted versus ***T*** (Fig. 1a) showed an exponential growth trend. As already stated in the literature (Esteves *et al.* 2007), softwood exhibited ML lower than hardwood due to the different fraction of hemicelluloses. Differences between softwoods and hardwoods were significant at temperatures higher than 180°C. At 220 °C, the ML of softwoods varied between 5.7% and 7.5%, while for hardwoods the ML varied between 9.4% (beech) and 15% (black locust). Figure 1a clearly shows that black locust was the species affected by the highest ML. Hemicelluloses of this species were probably less thermally stable and, as a consequence, they were more sensitive to thermal degradation, as was observed by Sandak *et al*. (2012) using FT-NIR.

ML *vs*. ***t*** (Fig. 1b) demonstrated an asymptotic trend. Such trends were similar to those reported by other authors, *e.g.* Esteves and Pereira (2009) and Kim *et al.* (1998). Nevertheless, the effect of time seemed to be less pronounced during thermo-vacuum treatment; an asymptotic ML value was reached within a few hours. Fir, spruce, cherry, and beech had the lowest ML, which varied between 0.5% and 1.5% for 0.75 and 5 hours, respectively. Oak and ash had an average ML of 1% for 0.75 h and 2.3% for 5 hours. Black locust behaved similarly to ash and oak for t = 0.75 h (ML=1%), but then the ML increased significantly, and it reached a value of 4% for the longest treatment. For short treatments (0.75 and 1.5 h), larch presented the highest ML value (2% and 3%, respectively) and for 5 h it reached 3.5% of ML. The extreme behavior of larch was probably due to the loss of resin. Similar results of ML were observed on spruce by Alén *et al*. (2002) and on spruce and beech by Welzbacher *et al.* (2010) in steam and in air conditions, respectively. Higher values of ML were found for beech heartwood by Todorović *et al*. (2012), who reported a ML variable between 5% and 17% for wood treated from 170 to 210°C for 4 h in air conditions.

One of the advantages of a thermal treatment under vacuum conditions is the enhancement of volatile release at the first stages of biomass devolatilization (between 130 and 220 ºC), as has been demonstrated by Amutio *et al*. (2011). Results showed that ML increased when vacuum decreased (Fig. 1c). This was an expected result because the pressure influenced the oxygen concentration. However, according to Amutio *et al*. (2012), mass loss (ML) is increased by vacuum rather than oxygen concentration since at these low temperatures oxygen does not play an important role. The treatment performed at a higher pressure (330 mbar) produced a higher ML value in the case of black locust, larch, and oak (Fig. 1c). Data were not enough to allow statistical analysis for the investigation of the pressure effect on ML.

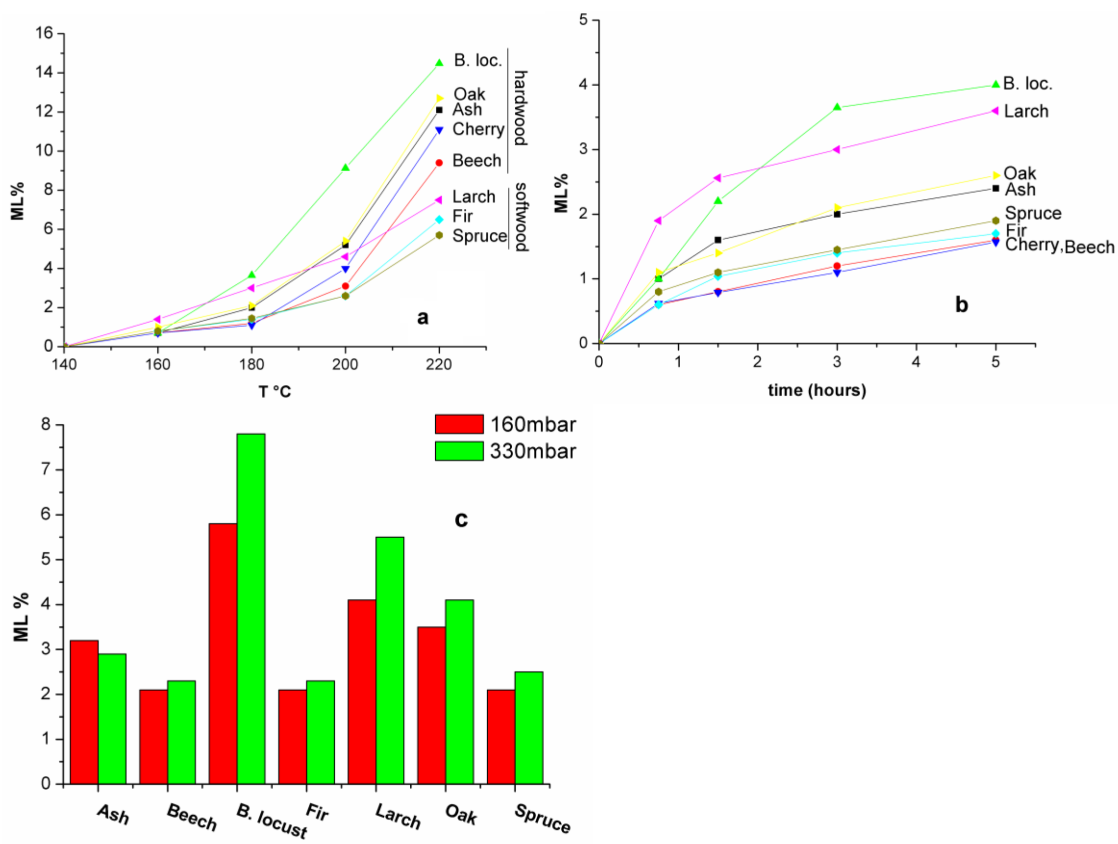

Fig. 1. a: Mass loss *vs*. treatment temperature (t=3 h and p= 210 mbar); b: ML *vs.* time (T=180°C; p=210 mbar); c: ML *vs*. pressure (T=190 °C; t=3 h)

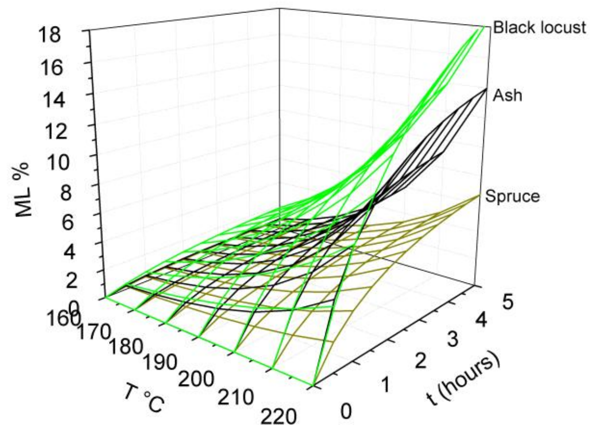

Fig. 2. Three-dimensional rendering of mass loss vs. ***T*** and ***t*** at constant ***p***

The three-dimensional analytical function, shown in Fig. 2, represents a combination of a hyperbola and an exponential function, which is proposed to calculate ML from ***T*** and ***t*** (at constant ***p*** = 210 ±15 mbar) as follows:

$$ML(\mathbf{T}, \mathbf{t}) = (a*exp(\mathbf{T}/k)+b)*t/(c+\mathbf{t}) \quad (2)$$

The values of constants of the equation 2 are reported in Table 2.

Table 2. Constants of Equation 2 for Different Species (P level < 0.05)

	Black locust	*Oak*	*Ash*	*Beech*	*Cherry*	*Spruce*	*Fir*	*Larch*
a	0.1470	0.0023	0.0024	0.0001	0.0003	0.0059	0.0010	0.4666
b	-5.04	-0.38	-0.53	0.29	-0.04	-0.21	0.14	-3.33
c	3.29	2.07	1.51	2.85	2.68	1.85	2.13	0.93
k	39.97	24.03	24.53	18.12	19.38	29.89	23.61	66.04

EMC

The treated wood had a lower EMC compared to wood that was not treated. The EMC variation depended on the treatment temperature, time, and species (Table 3).

Table 3. EMC for the Eight Species Treated at Different Conditions

	NT*	160 °C		180 °C					200 °C		220 °C	
		3 h		0.75 h	1.5 h	3 h		5 h	3 h		3 h	
	EMC	EMC	var%	EMC	EMC	EMC	var%	EMC	EMC	var%	EMC	var%
fir	12.5	10.8	13.3	10.9	11.0	10.6	14.9	10.6	9.5	23.9	7.6	38.9
larch	10.5	10.7	1.9	9.8	8.3	9.3	11.6	8.4	8.0	24.0	7.4	29.1
spruce	12.4	11.6	6.3	11.3	11.3	10.6	14.2	10.7	9.7	22.1	7.8	37.0
black l.	10.0	8	19.7	9.2	6.4	n.a.	n.a.	6.2	6.2	36.9	6.3	36.4
ash	11.5	10.4	9.3	10.5	10.0	9.3	18.8	9.3	7.9	30.8	6.6	42.4
beech	12.0	11.3	5.6	11.0	10.8	9.9	17.7	9.9	8.3	30.4	7.1	40.7
cherry	11.1	10.2	7.1	9.7	9.6	8.8	20.0	9.0	6.9	37.2	6.2	43.8
oak	11.0	10.7	2	10.5	10.0	9.0	17.7	8.9	7.2	34.4	6.6	39.6

* NT = not treated samples

Usually softwoods were characterized by lower EMC variations compared to hardwoods. At 160°C, the EMC reduction was variable among the species considered. For this temperature, larch and oak did not show any significant change in EMC (2%), while black locust had a very high EMC reduction (19.7%). At 220°C, the variation was more uniform among the species with an average value of 40%, except for larch which had a lower value (30%).

Very low values of EMC were reported by Schnabel *et al.* (2007) for beech (5.6 to 3.6%) and ash (5.6 to 4.3%), but the comparison with the present data was difficult because the author did not specify the treatment conditions.

When plotted as a function of ML, the EMC shows an exponential trend (Fig. 3). All of the species showed a similar trend except larch which, as previously observed, has a ML variation significantly affected by resin loss.

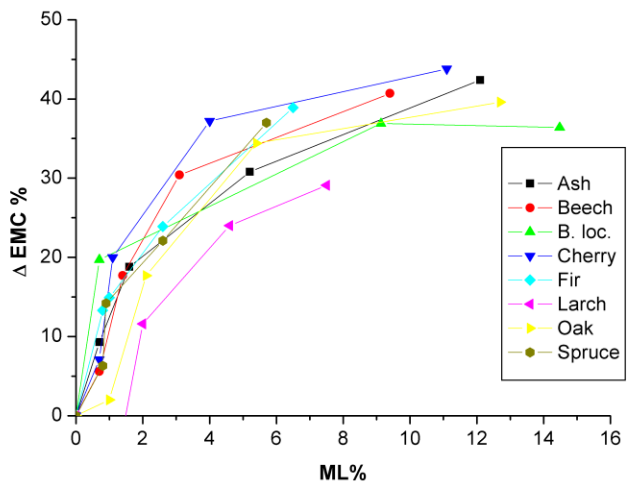

Fig. 3. Equilibrium Moisture Content (EMC) variation vs. mass loss (ML)

Color

The color of the wood changed according to the treatment temperature, time, and pressure. Results of the analysis of variance showed that, in general, temperature, time, and species have a significant effect on the ΔE^* value, except for the variable "species", which does not have an effect in the case of softwoods treated at different times (*p value* = 0.87 with a *P level* of significance < 0.05).

Sahin *et al.* (2010) reported higher values of ΔE^* for oak at low temperatures (ΔE^*=15.7 at 120 °C and 2 h), and they obtained a ΔE^* of 40 for treatment at 180°C for 10 h in air conditions. Color data about beech and cherry were also reported by Aydemir *et al.* (2010) for wood treated in air conditions, who found, in general, lower values of ΔE^* for the same processing temperature and time. In the case of spruce and fir, data were similar to that reported by Gonzales-Peña and Hale (2009) for wood treated in nitrogen medium.

Considering the effect of pressure on ΔE^*, the results of the *t-test* demonstrated that all softwoods and oak are characterized by a significant difference between the average ΔE^* values. For these species, higher pressure (330 mbar) produced a darker color. In the case of the other hardwoods, no significant difference has been reported.

When plotted *vs.* ML (Fig. 4), the ΔE^* of different species has a similar trend and behaved in a similar way.

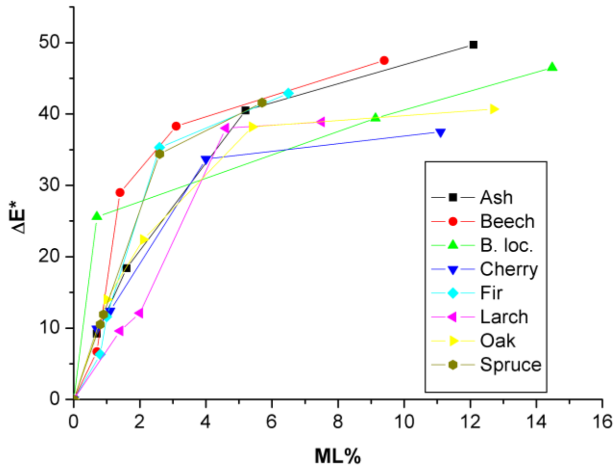

Fig. 4. ΔE* vs.ML%

A representation of the color hues, induced in wood by the different treatment conditions, is reported in Fig. 5.

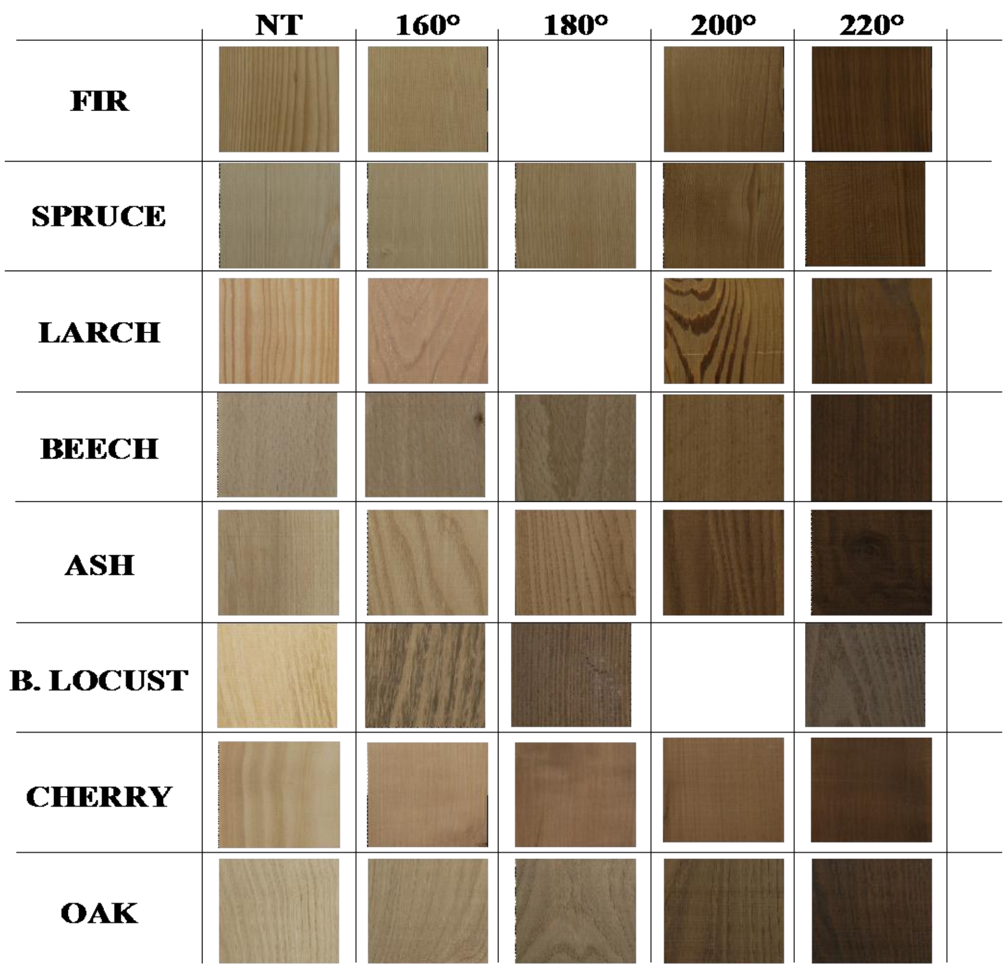

Fig. 5. Colors palette

CONCLUSIONS

1. Each species showed a distinctive curve of mass loss variation. In general, ML was higher for hardwoods compared to softwoods. Among all of the species, black locust showed higher variations in terms of mass loss even at low treatment conditions (160°C for 3 h). The behavior of this species during the treatment was significantly different from the other species. In particular, it was observed that the treatment of this species at a temperature higher than 160°C was difficult because of the occurrence of internal checks. Moreover, a high ML of larch was probably due to loss of resin.
2. Change of color and EMC for each species had a similar trend when plotted *vs*. ML.
3. The boards demonstrated, in general, good quality with no internal tension, no deformations, and very few end- or- pith checks after the thermo-vacuum treatments. Internal checks were observed in black locust treated wood at temperatures higher than 160°C, and in oak when treated at temperatures higher than 180°C. Since such internal checks, that are normally caused to internal stress due to MC gradients during drying, were not observed at the end of the drying and before the thermal treatment, some questions about the mechanism of their formation is still open, and such phenomenon needs more investigation. One hypothesis could be that they are generated by internal stress due to a volume reduction accompanying the mass reduction.
4. Generally, the comparison of data reported in this work with results found in literature for other technologies was a difficult task because the treatment conditions (*T*, *t*), the species tested usually differ.
5. Further tests including mechanical and durability are in progress and the results will allow a complete picture of such species treated with the Termovuoto® system, a promising technology which demonstrated some advantageous peculiarities compared to other systems:
   - an efficient vacuum drying and thermal modification in the same machine, with consequent good quality of the treated wood and reduction of energy and time requirement;
   - an easier and cheaper management of the volatile wastes produced during the treatment which are removed by the vacuum pump and condensed in recycling water;
   - a total absence of odor normally characterizing many other TM wood products. This is due to the action of the vacuum pump which removes volatile products during the process.

ACKNOWLEDGMENTS

The authors would like to acknowledge the WDE-Maspell company (*www.wde-maspell.it*) for technical support.

REFERENCES CITED

Alén, R., Kotilainen, R., and Zaman, A. (2002).” Thermochemical behaviour of Norway spruce (*Picea abies*) at 180-225 °C,” *Wood Sci. Technol*. 36, 163-171.

Allegretti, O., Brunetti, M., Cuccui, I., Ferrari, S., Nocetti, M., and Terziev, N. (2012), “Thermo-vacuum modification of spruce (*Picea abies* Karst.) and fir (*Abies alba* Mill.) wood,” *BioResources* 7(3), 3659-3669.

Amutio, M., Lopez, G., Aguado, R., Artetxe, M., Bilbao, J., and Olazar, M. (2011). “Effect of vacuum on lignocellulosic biomass flash pyrolysis in a conical spouted bed reactor,” *Energy Fuels* 25(9), 3950-3960.

Amutio, M., Lopez, G., Aguado, R., Artetxe, M., Bilbao, J., and Olazar, M. (2012). “Kinetic study of lignocellulosic biomass oxidative pyrolysis,” *Fuel* 95, 305-311.

Aydemir, D., Gunduz, G., and Ozden, S. (2010). “The influence of thermal treatment on color response of wood materials,” *Color Research and Application* 37(2), 148-153.

Esteves, B. M., Marques, A. V., Domingos, I., and Pereira, H. M. (2007b). “Influence of steam heating on the properties of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood,” *Wood Sci. Technol*. 41, 193-207.

Esteves, B. M., and Pereira, H. M. (2009). “Wood modification by heat treatment: A review,” *BioResources* 4(1), 370-404.

Gonzales-Peña, G., and Hale, M. (2009). “Colour in thermally modified wood of beech, Norway spruce and Scots pine. Part 1: Colour evolution and colour changes,” *Holzforschung* 63, 385-393.

Hill, C. (2006). *Wood Modification-Chemical, Thermal and Other Processes*, Wiley Series in Renewable Resources, John Wiley & Sons, Ltd.

ISO 3129 (1975). “Bois – Méthodes d’échantillonnage et conditions générales pour les essais physiques et mécaniques”.

ISO 3130 (1975). “Wood – Determination of moisture content for physical and mechanical tests”.

Kim, G., Yun, K., and Kim, J. (1998). “Effect of heat treatment on the decay resistance and the bending properties of radiata pine softwood,” *Material und Organismen* 32(2), 101-108.

Sahin, H. T., Arslan, M. B., Korkut, S., and Sahin., C. (2010). “Colour changes of heat-treated woods of red-bud maple, European hop hornbeam and oak,” *Color Research and Application* 36(6), 462-466.

Schnabel, T., Zimmer, B., Petutschnigg A. J., and Schönberger, S. (2007). “An approach to classify thermally modified hardwoods by color,” *Forest Prod. J.* 57(9), 105-110.

Sandak, A., Sandak, J., Allegretti, O., Ferrari, S., Cuccui, I., and Pauliny, D. (2012). “Evaluation of thermally treated soft and hardwoods with FT-NIR,” In: *Proc. 6th European Conf. on Wood Modification*, September 16-18, 2012, Ljubljana, Slovenia.

Todorović, N., Popović, Z., Milić, G., and Popadić, R. (2012). “Estimation of heat-treated beechwood properties by colour change,” *BioResources* 7(1), 799-815.

Welzbacher, C. R., Meyer, L., and Brischke, C. (2010). “Prediction of flooring-relevant properties based on colour values of thermally modified timber (TMT),” In: *Proc. 5th European Conf. on Wood Modification*, September 20-21 2010 Riga, Latvia.

Article submitted: October 22, 2012; Peer review completed: January 4, 2013; Revised version accepted: January 11, 2013; Published: January 16, 2013.