Comparative Study of Two Softwood Species Industrially Modified by Thermowood® and Thermo-Vacuum Process

Mohamed Jebrane,[a] Michael Pockrandt,[b] Ignazia Cuccui,[c] Ottaviano Allegretti,[c] Ernesto Uetimane Jr.,[d] and Nasko Terziev [a,*]

Scots pine and Norway spruce, the most used commercial wood species in Europe, were thermally treated under industrial conditions by steam (Thermowood®) and vacuum (Termovuoto). Matched boards were treated, and the alterations in chemistry, color, mass loss, mechanical properties, and durability were compared. In treatments at identical temperature and duration, Thermowood® and the thermo-vacuum process caused similar mass loss in both wood species. The thermal treatments showed minor effects on the released acetic acid during the thermal degradation of polysaccharides. The equilibrium moisture content correlated well with the mass loss and confirmed indirectly the similarity of the two processes. The chemical composition and durability of the two groups of treated wood were similar. In conclusion, Thermowood® and thermo-vacuum treatments according to Termovuoto technology both produce similar final products with regard to chemical composition, physical-mechanical properties, and durability, with some differences in the appearance.

Keywords: Mass loss; Mechanical properties; Norway spruce; Scots pine; Physical properties; Thermally modified wood

*Contact information: a: Department of Forest Products, Swedish University of Agricultural Sciences, Box7008, 750 07 Uppsala, Sweden; b: Faculty of Wood Science and Technology, University of Applied Sciences, Eberswalde, Germany; c: CNR- IVALSA, Timber and Trees Institute, Laboratory of wood drying, San Michele all'Adige, Italy; d: Faculty of Agronomy and Forest Engineering, Eduardo Mondlane University, Maputo, Mozambique; *Corresponding author: nasko.terziev@slu.se*

INTRODUCTION

While there are appreciated features of wood materials, there are also a number of disadvantages. These detrimental aspects have been investigated with the aim of improving the dimensional stability and extending the service life of the material. Timber can be modified by various new and already established methods. In this context, several new methods have been considered to make sustainable bio-products that comply with governmental regulations banning the use of toxic chemicals (Boonstra 2008).

Thermal treatment is a method to modify wood, improve decay resistance, and improve dimensional stability of the material when the wooden material is heated in the absence of oxygen, *i.e.*, subjected to mild pyrolysis. Stamm and Hansen (1937) described decreased shrinkage, equilibrium moisture content, and swelling in wood exposed to heat treatment, but the first attempt to introduce heat-treated timber to the market (Stamm *et al.* 1946) was unsuccessful. Nevertheless, further studies concerning thermal modification were carried out by Kollmann and Schneider (1963) and Hillis (1984).

Thermal modification of wood affects predominantly hemicelluloses; the process of thermal degradation of these compounds begins at 120 °C, and its intensity is

proportional to the temperature ascent and duration (Kollmann and Fengel 1965). During the modification, acetic acid is released by the hydrolysis of hemicelluloses. Acetic acid plays a role in the depolymerisation of cellulose and thus, increases its crystallinity. Thermal modification of wood causes additional transformation of lignin and extractives (Boonstra *et al.* 2007; Windeisen *et al.* 2009). Thermal treatments of wood decrease the number of hydroxyl groups responsible for bonding water molecules. Because the hemicelluloses content is significantly decreased, the moisture adsorption of the material decreases accordingly, which improves the dimensional stability and resistance to microbiological degradation (Mazela *et al.* 2004; Peters *et al.* 2009; Mohareb *et al.* 2012).

Thermal modification comprises several industrial processes applied for altering the wood properties by temperatures higher than 160 °C. The features of thermally modified wood are well documented in the literature, *e.g.*, a comprehensive literature review by Esteves and Pereira (2009) on the chemical, physical-mechanical and durability aspects of the modified wood.

The difference between the industrial thermal modification (TM) processes is the medium in which the wood is treated, *e.g.*, steam, water, nitrogen, or oil. The on-going research in the area is concentrated on finding the optimal treatment conditions that improve physical properties and durability but retain the wood strength. Several modification processes, which can be generally distinguished by the used process parameters (temperature and time) and the heat-transferring medium (oil, steam, and nitrogen), have been developed. Examples are Bois Perdure and Rectification (both in France), Plato (Netherlands), oil heat treatment (OHT, Germany) and Westwood (USA). The most commonly used process is TM. Originally called Thermowood® and developed by VTT (Technical Research Centre of Finland), 179,507 m^3 of timber were treated by TM in 2016 (ITWA 2016).

Termovuoto, is a patented thermal modification of wood in which oxygen is substituted by a partial vacuum and heating is provided by forced convection. There is a scarcity of data and information on thermo-vacuum modification processes for wood (Giordano 1986; Hill 2006). The physical-mechanical properties of some hardwood timbers treated under vacuum and high temperature were reported recently by Wetzig *et al.* (2012).

This study compared selected chemical properties, physical-mechanical properties, and durability of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.) wood modified in industrial conditions by steam according to Thermowood® technology (TW) and under vacuum by the Termovuoto process (TV). The comparison determined the features of modified wood and revealed differences caused by the applied processes. The choice of the wood species reflects the most commercially used and thermally modified timbers in Europe.

EXPERIMENTAL

Sample Origin, Sawing and Thermal Modification

Five trees of Scots pine (*Pinus sylvestris* L.) and Norway spruce (*Picea abies* Karst.) were selected and cut from an area near Uppsala (52 km Southeast direction), Sweden. The trees were sampled according to ISO standard 3129 (1975) and according to the least diameter at breast height (DBH) over bark for harvesting. Each tree was cut to three logs that were sawn to 50-mm-thick radial planks, which were packed in plastic and

stored at -20 °C. The planks were later sawn into boards (28 × 120 × 3100 mm) while avoiding juvenile wood, knots, and other visible defects. The boards were stored and dried at room temperature for 2 months.

Twelve boards were chosen for the present experiment and cut into three sub-samples (28 × 120 × 1000 mm); the first two sub-samples were treated by TW and TV methods while the third sub-sample served as the untreated control. In this way, the natural variability between the sub-samples was minimized. Wood density at room temperature was determined according to ISO standard 3131 (1975). Prior to the thermal treatments, a 10-mm thick slice was cut from each sub-sample and the initial moisture content (MC) calculated. All boards subjected to thermal treatment were weighed. In order to ensure comparability between the two treatments, both TW and TV thermal modification consisted of *a)* initial drying to achieve very low MC prior to the real thermal treatment; *b)* heating phase from 100 °C and up to the target temperature set value with an approximate increase of 10 °C per h; *c)* thermal modification phase at constant temperature (212 °C) and a defined duration (3 h); and *d)* cooling phase to slow down the wood temperature to 50 °C.

Thermal modification according to TW technology was carried out in an industrial treatment chamber at a company accredited to perform this method. Twelve samples were set in the chamber, dried to approximately 0% MC, and then thermally treated at 212 °C for 3 h. After the treatment, the boards were left to cool to 50 °C inside the chamber.

TV modification of the 12 adjacent boards was conducted as described by Allegretti *et al.* (2012). Initially, vacuum drying at 100 °C and vacuum pressure of 25 ± 2.5 kPa, (corresponding to water boiling temperature of 65 °C) were applied to the boards to dry them to 0% MC. The drying process was carried out in the same cylinder where the thermo-vacuum treatment would take place later. The rate of temperature variation during wood heating and cooling was not controlled in the two treatments.

Chemical Analyses

Extractive content

Five slices were cut from treated and untreated boards and milled to pass a 40-mesh screen. The milled wood was homogenized, and 5 g was taken for extraction. Each sample was extracted in a Soxhlet apparatus with a mixture of toluene/ethanol (2/1; v/v) for 6 h and with water for an additional 6 h and then dried at 103 °C for 24 h.

Lignin, monosaccharides, and acetyl content

Treated and untreated pine and spruce wood samples were analyzed for acid soluble (ASL) lignins, acid insoluble lignins (AIL), monosaccharides, and acetyl content (AC) according to Sluiter *et al.* (2011). ASL was determined using a Hitachi U-2910 spectrophotometer (Tokyo, Japan) with an absorptivity of 110 L g^{-1} cm^{-1} at wavelength of 205 nm. The monomeric carbohydrates were determined using a Chromaster high-performance chromatography (HPLC; Tokyo, Japan) system equipped with an evaporative light scattering detector (ELSD-90), and a Metacarb 87P column (300 × 6.5 mm; Santa Clara, CA, USA) with a guard column (Metacarb 87P 50 × 4.6 mm). The ELSD-90 was operated at 50 °C, 2.5 bars and N_2 was used as nebulizing gas. The sugars were eluted using ultra-pure water as mobile phase at a constant flow rate of 0.5 mL min^{-1} and column temperature of 85 °C. The acetyl content (AC) was determined using a diode array detector (DAD) operated at 210 nm, and a Metacarb 87H column with a guard column (MetaCarb

87H 50 × 4.6 mm). The mobile phase was 0.005 mol L^{-1} H_2SO_4 solution (pH 2.1), with a flow rate of 0.6 mL min^{-1} at 30 °C.

Mass Loss and Colour Evaluation

After the thermal modifications, all boards were weighed to calculate mass loss (ML) (Table 2). Five boards for each species and treatment were randomly selected; the color measurements were carried out on board areas without defects. Five measurements were recorded for each board and compared to the five measurements on the adjacent board but treated with the other thermal method. A Konica Minolta CM-2500d surface reflectance spectrophotometer (Tokyo, Japan) was used to determine the color change on the surface of the boards of pine and spruce. Three-dimensional L^*, a^*, and b^* color space was employed for color evaluation. L^* specifies the lightness in a range from black (0) to white (100), a^* is red-green share, and b^* is blue-yellow share. Both a^* and b^* are positive/negative co-ordinates defining the hue and intensity of the color. Color change (ΔE^*) was calculated according to Eq. 1,

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

where ΔL^*, Δa^*, and Δb^* represent the changes of lightness (L^*) and chromatic parameters (a^* and b^*) between the measurements on the boards treated by TW and TV process. The color of the untreated boards was not considered in the comparison.

Mechanical Properties

Samples were cut according to the requirements of the standards below, and mechanical tests were performed after conditioning. The untreated control samples were kept at 30 °C and 40% RH, while the treated specimens were kept at 25 °C and 85% RH. The two climates ensured similar MC of the treated and untreated samples (Table 2). The mechanical tests were carried out by a universal testing machine (Shimadzu AG-X 50 KN, Kyoto, Japan). The measurement accuracy was ± 0.01 mm for position, ± 0.1% for speed, and ± 0.5% for loading. Pine and spruce samples were prepared according to the methods and general requirements for mechanical tests as recommended by ISO 3129 (1975). The following properties were measured: modulus of elasticity (MOE, ISO 3349 1975); modulus of rupture (MOR, ISO 3133 1975); static hardness perpendicular and parallel to grain (ISO 3350 1975); compression stress perpendicular to grain (ISO 3132 1975); compression stress parallel to grain (ISO 3787 1976); and ultimate shearing strength parallel to grain (ISO 3347 1976).

Durability Test with Basidiomycetes

Assessment of wood durability after the thermal modification was performed according to the European standard EN 350-1 (1994) through a laboratory test method involving white and brown rot fungi (EN 113 2004). Untreated and treated blocks (15 × 25 × 50 mm along the grain) were used. Beech blocks were included in the test to serve as reference for natural durability determination of the studied species. Decay fungi used were *Coniophora puteana* BAM Ebw. 15, *Gloeophyllum trabeum* BAM Ebw. 109, *Postia placenta* FPRL 280, and *Trametes versicolor* CTB 863A. Prior to the test, the treated samples were leached in water according to standard EN 84 (1989). The ratio of ML of test samples to the ML of the reference samples was expressed as durability class (EN 350-1 1994).

RESULTS AND DISCUSSION

Chemical Analyses

The extractive, lignin, and monosaccharide content of pine and spruce wood treated under either vacuum or steam were determined and compared with the untreated samples (Table 1). Both treatments increased the extractive content because of the thermal degradation of wood components. The extractives content increase was more pronounced after the TW process for pine because the degradation products were retained in the wood; they were partly extracted by vacuum during the TV process. However, the extractive content after the TW process for spruce was slightly less than the amount measured after the TV process. The ASL and AIL contents were increased after thermal treatment. The increase in AIL content was higher for pine and spruce after the TW process than after the TV process. However, the amount of ASL increased more after the TV process for spruce wood; in pine the two processes engendered similar increases (0.3%). The hemicellulose monomers, particularly xylose and arabinose, noticeable decreased after TM for both wood species and processes, while glucose content increased slightly after the treatments. The decrease in hemicellulose monomers was more pronounced after the TW process than the TV process for both wood species. Candelier *et al.* (2013a) reported similar results when beech wood (*Fagus sylvatica*) was thermally modified under two treatment conditions (nitrogen and vacuum).

Table 1. Chemical Constituents (%) of Untreated and Thermally Modified Pine and Spruce Boards

	Pine			Spruce		
	UN	TW	TV	UN	TW	TV
Extractives	3.8	7.8	6.4	2.2	5.9	7.0
Total Lignins	26.6	32.5	31.2	27.8	31.0	29.8
AIL	25.9	31.5	30.2	27.2	29.8	28.5
ASL	0.7	1.0	1.0	0.6	1.2	1.3
Monosaccharides						
Glucose	40.6	44.9	43.1	43.0	45.5	46.3
Xylose	4.1	2.5	2.6	3.6	2.0	2.6
Galactose	2.0	1.3	1.6	1.7	1.1	1.3
Arabinose	1.5	0.2	0.3	0.8	0.1	0.3
Mannose	16.7	12.9	13.7	17.4	12.2	14.4
Acetyl Content	2.6	2.3	2.4	2.9	2.6	2.8
UN, untreated, TW, Thermowood treated, and TV, Thermo-vacuum treated						

A key factor influencing the thermal degradation of polysaccharides is the presence of acetyl groups that are thermally labile and lead to the formation of acetic acid, thereby causing acid-catalyzed degradation of the polysaccharides. Thus, the degree of hemicellulose degradation during the thermal modification of wood is proportional to the decrease of AC. In order to evaluate the effect of vacuum in removing the produced acetic acid and other volatiles during TV and thereby limiting the degradation of polysaccharides, the residual AC in both wood species before and after the thermal modifications was determined. Since the residual AC was determined on extracted samples, its values were

low, but still a noticeable decrease between the untreated and TM pine and spruce was observed. Another explanation is the fact that hemicelluloses of softwoods have lower AC compared to hardwoods. The thermal degradation of softwoods at the defined temperature and duration is expected to be less compared to hardwoods. The observed decrease in hemicellulose monomers after thermal treatments could be attributed to the combination effect of acid-catalyzed and free-radical intermediates (Fengel and Wegener 1989). The free-radical intermediates are bigger molecules than acetic acid molecules, and thus are difficult to remove by vacuum. As a result, the TV resulted in similar mass loss as TM.

Mass Loss

Density and ML of the treated timbers are shown in Table 2. The obtained data have been processed statistically by *t*-test comparisons between the groups and $\alpha = 0.01$ level of significance has been applied for the presentation of the differences.

Table 2. Density, Moisture Content (MC), and Mass Loss (ML) of Thermally Modified Pine and Spruce Boards

Specimens and Treatments	Density (kg m^{-3})	MC Before Treatment (%)	ML After Treatment (%)	MC Prior to Mechanical Tests (%)	
				Conditioned at 30 °C, 40% RH	Conditioned at 25 °C, 85% RH
Pine UN	409 (27)*	11.7 (1.2)	−	8.1 (0.6)	−
Spruce UN	402 (47)	14.2 (1.0)	−	8.0 (0.5)	−
Pine TW		−	9.3 (2.0)		7.9 (0.5)
Pine TV		−	9.0 (1.9)		8.8 (0.9)
Spruce TW		−	7.1 (1.2)		8.1 (0.8)
Spruce TV		−	7.5 (0.6)		9.7 (0.8)

***** Standard deviation within parentheses
UN, untreated, TW, Thermowood treated, and TV, Thermo-vacuum treated

The MC of the untreated and treated material was equalized prior to the mechanical testing. The untreated pine and spruce samples achieved a MC of 8%. The treated samples deviated with less than 1% compared to the untreated ones. Only thermo-vacuum treated spruce was conditioned to 9.7% MC, *i.e.* larger deviation. The way of sample conditioning before the mechanical tests is of importance, since it allows for excluding or significantly decreasing the effect of the MC on the mechanical properties of wood.

The measured ML illustrated no statistical differences between the two thermal processes (Table 2). The differences between measured ML of pine (9.3 and 9.0%) and spruce (7.1 and 7.5%) were not statistically significant. The TW process did not cause higher mass loss than the thermo-vacuum process for the studied wood species. The result does not support earlier reports (Allegretti *et al.* 2012; Candelier *et al.* 2013a, b) showing that a significant amount of thermal degradation products, *e.g.*, acetic acid, are evacuated out of the material by vacuum and thus, limited hemicellulose destruction occurs. Pine wood demonstrated higher ML than spruce, which is explained by natural variations in carbohydrate and extractive content between the species.

Gas permeability was found to be larger in Eastern white pine than in red spruce, due to differences in the anatomical structure and the level of resins and other extractives (Rice and D'Onofrio 1996). Thus, the effect of vacuuming away the acetic acid during the course of thermal modification is expected to be easier in pine than in spruce wood. In contrast, hot water and steam treatments drastically decrease permeability in beech wood (Taghiyari *et al.* 2011). The decrease in permeability in hardwoods can be caused by

deposition of extractives on vessel perforations and cell walls, blocking fluid transfer through the porous media. However, pine and spruce in this study demonstrated similar mass loss after the TW and TV processes (Table 2), which did not prove the effect of vacuum on the content of acetic acid.

The results in Table 1 showed that the AC decreased slightly in both wood species after the treatment by either the TW or TV processes. The difference in AC between both thermal processes was small, and thus it was not appropriate to correlate its decrease to the decrease of hemicelluloses and, respectively, mass loss. Although previous studies (Candelier *et al.* 2013a,b) claimed that the formed acetic acid and other volatiles during TV are progressively removed and thereby limiting the degradation of polysaccharides, the above-mentioned hypothesis could not be confirmed in the present study.

Colour Changes

The results of the color comparison are shown in Table 3. The untreated wood color is not shown, analyzed, or discussed here because it is very distinguishable from that of the thermally treated wood.

Table 3. Color Characteristics and Changes after Thermowood (TW) and Thermo-Vacuum (TV) Processes

Wood Species and Treatments	*L**	*a**	*b**	Δ*E**
Pine TW	45.9 (1.4)^	12.6 (0.5)	25.2 (1.1)	3.0 (1.3)
Pine TV	47.8 (1.7)	12.1 (0.6)	25.1 (1.1)	
Spruce TW	47.4 (2.3)	12.3 (0.7)	23.6 (0.9)	5.7 (2.1)
Spruce TV	52.6 (2.0)	11.5 (0.6)	24.9 (1.1)	
^ Standard deviation within parentheses				

TW treated wood was darker than that treated by thermo-vacuum for spruce, as shown by the lower L^* value. The color change ΔE^* was larger for spruce than for pine treated wood. The value of difference for spruce color ($\Delta E^* = 5.7$) was large enough to be identified visually since color changes where $\Delta E^* > 3$ are visible for the naked human eye (Hon and Minemura 2001). The difference for pine was exactly 3 units, *i.e.*, the difference might be difficult to be distinguished visually. The color coordinates a^* and b^* were similar if not identical for the two treatment processes and wood species.

The color difference originates from the brightness L^* which was higher for both species after TV treatment, *i.e.* wood treated by TV was brighter than that treated by the TW process. Color is used for property prediction of thermally modified wood; *e.g.* Gonzalez-Pena and Hale (2009) found ΔE^* to be the best predictor to describe the reduction of several mechanical properties of thermally treated beech, Scots pine, and spruce woods. Contrary to the above, Johansson and Moren (2006) designed a model for prediction of thermally modified wood strength based on its color and found weak color-to-strength relationship. Brischke *et al.* (2007) found strong correlation between the lightness decrease L^* and the decrease of mass caused by the thermal treatments of spruce, Scots pine, and beech. Somewhat darker color of TW treated samples in the present study together with similar ML between the treatments indicate probably insignificant structural changes that cannot affect wood mechanical properties and durability significantly.

Mechanical Properties

Mechanical performance was tested on triples (control and two treated samples) for best comparability. As the equilibrium moisture content (EMC) of control and treated samples was achieved separately prior to mechanical testing (Table 2), the best comparability, excluding the effect of moisture, was guaranteed. A difference in 1% MC leads to a 3 to 4% difference in the mechanical properties (Rowell 1996), *i.e.*, the applied approximation did not influence significantly the results and conclusions of the study.

The measured mechanical features of the untreated and treated wood are presented in Table 4. The comparison between the untreated and treated samples did not differ from other similar investigations dedicated to the thermal modification of wood (Esteves and Pereira 2009). MOE did not change while MOR, share, compression strength, and hardness perpendicular to grain decreased significantly after thermal modification by both processes. Hardness parallel to grain was unchanged for pine but decreased for spruce wood treated by TW.

Table 4. Selected Mechanical Properties (N mm^{-2}) of Untreated and Treated Samples

Measured Properties	Wood Species and Treatments					
	Pine UN	Pine TW	Pine TV	Spruce UN	Spruce TW	Spruce TV
MOE	10133^{A} (1652)*****	9821^{A} (1814)	10279^{A} (1305)	11303^{A} (2419)	10546^{A} (2077)	10360^{A} (1766)
MOR	85.1^{A} (9.2)	62.8^{B} (12.3)	73.0^{C} (10.7)	85.9^{A} (18.5)	64.5^{B} (14.8)	65.1^{B} (10.6)
Hardness Perpendicular	15.0^{A} (1.0)	12.3^{B} (1.9)	12.9^{B} (1.9)	14.1^{A} (2.1)	10.9^{B} (1.8)	10.3^{B} (2.1)
Hardness Parallel	39.0^{A} (5.0)	41.4^{A} (5.0)	41.1^{A} (5.3)	38.1^{A} (5.2)	35.2^{B} (4.0)	39.8^{A} (5.3)
Compression Perpendicular	6.3^{A} (1.1)	4.8^{B} (1.2)	5.1^{B} (1.2)	5.5^{A} (1.3)	3.3^{B} (0.6)	3.4^{B} (0.6)
Compression Parallel	48.7^{A} (6.7)	42.0^{B} (5.5)	43.5^{B} (4.5)	50.1^{A} (8.2)	41.5^{B} (8.3)	40.0^{B} (6.6)
Share Parallel	7.9^{A} (0.7)	6.5^{B} (1.0)	6.6^{B} (1.1)	7.7^{A} (1.2)	5.6^{B} (0.9)	5.5^{B} (1.2)

***** Each value represents a mean of 60 replicates. Standard deviation within parentheses UN, untreated, TW, Thermowood treated, and TV, Thermo-vacuum treated. Within the measured properties and wood species, means with the same letter are not significantly different at the 0.05 level, according to the Tukey test

When the two treatment methods were compared, only two features differed significantly, namely MOR of pine wood and hardness parallel to grain of spruce (Table 4). Both values were larger for wood treated by TV than TW. It is difficult to interpret and explain these results because it is presumed that the mass loss governs the physical-mechanical properties of wood as well as its durability. The ML in this study was similar after both treatment processes and thus, there is no reasonable explanation why these two particular mechanical features deviated from the general trend.

Mechanical properties of thermally modified wood are the most studied wood features that correlate with the intensity of the treatment temperature, duration, and chemical alterations (Boonstra *et al.* 2007; Li Shi *et al.* 2007; Windeisen *et al.* 2009.

Table 5. Mass Loss (ML) of Control and Treated Samples Exposed to Basidiomycete Fungi in a Standard EN 113 (2004)

Wood Species and Treatments	ML Caused by Treatment	ML (%) After Fungal Exposure and Calculated Durability Classes (DC)				
		Trametes versicolor	*Postia placenta*	*Gloeophyllum trabeum*	*Coniophora puteana*	DC
Pine UN (virulence)	−	20.6 (2.8)[a]	35.0 (3.1)	32.3 (2.8)	32.7 (3.5)	3-4[b]
Spruce UN (virulence)	−	19.2 (2.1)	37.2 (3.8)	29.0 (3.2)	35.4 (4.3)	4[b]
Pine UN	−	18.7 (1.6)	48.0 (1.8)	27.8 (2.7)	40.5 (5.4)	
Pine TW	9.3 (2.0)	1.9 (0.2)	25.6 (2.2)	3.5 (0.7)	3.0 (1.4)	1/3/2/1[c]
Pine UN	−	18.0 (2.1)	48.4 (2.5)	33.3 (1.9)	38.9 (5.7)	
Pine TV	9.0 (1.9)	2.1 (0.3)	35.6 (6.1)	9.8 (3.6)	6.8 (6.7)	1/4/2/2
Spruce UN	−	19.0 (1.7)	49.7 (4.8)	34.5 (4.1)	35.8 (5.2)	
Spruce TW	7.1 (1.2)	4.3 (0.9)	21.3 (6.2)	6.1 (2.1)	7.4 (5.3)	2/3/2/2
Spruce UN	−	18.8 (1.6)	49.4 (2.4)	32.0 (3.3)	43.0 (4.4)	
Spruce TV	7.5 (0.6)	5.5 (1.5)	28.5 (4.4)	7.0 (2.1)	10.9 (2.1)	2/3/2/2

[a] Each value represents a mean of 5 replicates. Standard deviation within parentheses
[b] Natural durability class according to standard EN 350-2
[c] Calculated durability classes for the test fungi in order of appearance
UN, untreated, TW, Thermowood treated, and TV, Thermo-vacuum treated

The results of the study do not support previous findings indicating lower thermal degradation of wood treated under vacuum comparatively to those treated under nitrogen (Candelier *et al.* 2013a). However, Candelier *et al.* (2013a) studied beech, which is a porous, permeable hardwood species, which might explain the difference. TV resulted in lower degradation of pine and spruce hemicelluloses (1.6 and 3.2% more hemicelluloses left after TV than after TW, Table 1), but the above differences are probably not enough to provoke statistically significant differences in most of the measured mechanical properties after the two processes.

Wood Durability

The results of the standard durability test are shown in Table 5. Pine and spruce were classified as moderately to slightly durable wood species (DC 3-4, EN 350-2 1994). The brown rot fungus, *P. placenta*, was the most destructive among the test fungi, causing on average 48.0 to 49.7% ML on untreated pine and spruce samples (Table 5). Both thermal modification processes decreased significantly the ML caused by the test fungi; *P. placenta* was still the most aggressive fungus in the test. Pine wood treated by the TW process demonstrated lower ML caused by the test fungi than that caused after TV treatment. For instance, 25.6, 3.5, and 3.0% average mass loss caused by *P. placenta*, *G. trabeum*, and *C. puteana* after the TW process can be compared to 35.6, 9.8, and 6.8% caused by the same fungi on the TV treated wood. In order to exemplify the effect of treatments, DC are calculated for the test fungi and shown in Table 5. With *P. placenta* as the most severe case, pine durability was altered from natural moderately-slightly-durable status to DC 3 (moderately durable) after TW but was unchanged (DC 4, slightly durable) after TV treatment. Apparently, the similar ML of *ca.* 9% (Table 2) caused by the test processes ensures similar durability of the treated wood.

Both TW and TV treatments improved the durability of spruce wood from DC 4 to DC 3 (*i.e.*, moderately durable). *P. placenta* was the most destructive among the test fungi causing 21.3 and 28.5% ML on samples treated by TW and TV (Table 5). The trend of higher ML on TV treated spruce was observed for all test fungi. Although there was significant difference in the ML of spruce caused by the test fungi on the TW and TV treated samples, it did not lead to a difference in the improved DC, *i.e.*, both treatments increased spruce wood durability to DC 3.

The effect of thermal modifications on the wood durability confirmed previous findings on the chemical changes, mass loss under the process, and improved durability against basidiomycete fungi (Mohareb *et al.* 2012). Differences in untreated and treated wood durability between pine and spruce are explained by differences in the chemical composition (Table 1) and initial extractive content.

The effect of TM on wood durability did not vary between pine and spruce. Higher gas permeability of pine did not demonstrate any advantage (*e.g.*, lower ML) when the TV process was applied. TV modification shifts the wood durability to an upper class than the initial natural durability (Gao *et al.* 2016), which is also confirmed in the present study. Even with the higher ML of samples treated by the TV method, the overall conclusion was that the TW and TV processes did not differ significantly regarding their effect on wood's durability which is improved to un upper DC for both pine and spruce.

CONCLUSIONS

1. Thermowood® and thermo-vacuum Termovuoto treatments of two test wood species Scots pine and Norway spruce led to similar final products. Performed at identical temperature and duration, the Thermowood® and thermo-vacuum processes caused similar mass loss of both wood species.
2. Chemical analyses showed that both processes resulted in a decrease in hemicelluloses monomers content in both wood species, while no significant effect on the acetyl content was observed, suggesting a combination effect of acid and free radical intermediates-catalysed degradation mechanisms.
3. Although demonstrating similar mass loss, thermo-vacuum treated wood had lighter color than wood treated by Thermowood® technology.
4. EMC correlated well with the mass loss and confirm indirectly the similarity of the two processes.
5. The mechanical and durability tests confirmed the basic role of the mass loss caused by the thermal modification as an indicator of the woods' physical and mechanical properties and durability. In general, the measured mechanical properties and durability of the wood treated by the two treatments were similar.
6. Thermowood® and thermo-vacuum treatment according to Termovuoto technology produced similar final products in terms of chemical properties, physical-mechanical properties, and durability, with some difference in the appearance (color).

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REFERENCES CITED

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), 3656-3669. DOI: 10.15376/biores.7.3.3659-3669

Boonstra, M. J., Van Acker, J., Tjeerdsma, B. F., and Kegel, E. F. (2007). "Strength properties of thermally modified softwoods and its relation to polymeric structural wood constituents," *Ann. Forest Sci.* 64(7), 679-690. DOI: 10.1051/forest:2007048

Boonstra, M. (2008). *A Two-stage Thermal Modification of Wood*, Ph.D. Dissertation, Henry Poincaré University, Nancy, France.

Brischke, C., Welzbacher, C. R., Brandt, K., and Rapp, A. O. (2007). "Quality control of thermally modified timber: Interrelationship between heat treatment intensities and CIE L*a*b* color data on homogenized wood samples," *Holzforschung* 61(1), 19-22. DOI: 10.1515/HF.2007.004

Candelier, K., Dumarçay, S., Pétrissans, A., Gérardin, P., and Pétrissans, M. (2013a). "Comparison of mechanical properties of heat treated beech wood cured under nitrogen or vacuum," *Polym. Degrad. Stabil.* 98, 1762-1765. DOI: 10.1016/j.polymdegradstab.2013.05.026

Candelier, K., Dumarçay, S., Pétrissans, A., Desharnais, L., Gérardin, P., and Pétrissans, M. (2013b). "Comparison of chemical composition and decay durability of heat treated wood cured under different inert atmospheres: Nitrogen or vacuum," *Polym. Degrad. Stabil.* 98, 677-681. DOI: 10.1016/j.polymdegradstab.2012.10.022

Esteves, B. M., and Pereira, H. M. (2009). "Wood modification by heat treatment: A review," *BioResources* 4(1), 370-404. DOI: 10.15376/biores.1.1.1-2

EN 113 (2004). "Wood preservatives. Test method for determining the protective effectiveness against wood destroying basidiomycetes. Determination of the toxic values," European Committee for Standardization, Brussels, Belgium.

EN 84 (1989). "Wood preservatives: Accelerated ageing of treated wood prior to biological testing: Leaching procedure," European Committee for Standardization, Brussels, Belgium.

EN 350-1 (1994). "Durability of wood and wood-based products – Natural durability of solid wood. Part 1: Guide to the principles of testing and classification of the natural durability of wood," European Committee for Standardization, Brussels, Belgium.

EN 350-2 (1994). "Durability of wood and wood-based products – Natural durability of solid wood. Part 2: Guide to natural durability and treatability of selected wood species of importance in Europe," European Committee for Standardization, Brussels, Belgium.

Fengel, D., and Wegener, G. (1989). *Wood: Chemistry, Ultrastructure, Reactions*, Walter De Gruyter, Berlin, Germany.

Gao, J., Kim, J. S., Terziev, N., and Daniel, G. (2016). "Decay resistance of softwoods and hardwoods thermally modified by the Termovouto type thermo-vacuum process to brown rot and white rot fungi," *Holzforschung* 70(9), 877-884. DOI: 10.1515/hf-2015-0244

Giordano, G. (1986). *Tecnologia del Legno*, UTET, Torino, Italy. ISBN 8802036233.

Gonzalez-Pena, M. M., and Hale, M. D. C. (2009). "Colour in thermally modified wood of beech, Norway spruce and Scots pine. Part 2: Property predictions from colour changes," *Holzforschung* 63(4), 394-401. DOI: 10.1515/HF.2009.077

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

Hillis, W. (1984). "High temperature and chemical effects on wood stability. Part 1. General considerations," *Wood Sci. Technol.* 18, 281-293.

Hon, D. N. S., and Minemura N. (2001). "Color and discoloration," in: *Wood and Cellulosic Chemistry*, D. N. S. Hon, and N. Shiraishi (eds.), Marcel Dekker, New York, pp. 385-442.

International ThermoWood® Association (ITWA) (2016). *ThermoWood®: Production Statistics 2016*, Helsinki, Finland, (https://asiakas.kotisivukone.com/files/en.thermowood.palvelee.fi/uutiset/Productionstatistics2016.pdf).

ISO 3129 (1975). "Wood – Sampling methods and general requirements for physical and mechanical tests," International Organization for Standardization, Geneva, Switzerland.

ISO 3131 (1975). "Wood – Determination of density for physical and mechanical tests," International Organization for Standardization, Geneva, Switzerland.

ISO 3132 (1975). "Wood – Testing in compression perpendicular to grain," International Organization for Standardization, Geneva, Switzerland.
ISO 3133 (1975). "Wood – Determination of ultimate strength in static bending," International Organization for Standardization, Geneva, Switzerland.
ISO 3347 (1976). "Wood – Determination of ultimate shear stress parallel to grain," International Organization for Standardization, Geneva, Switzerland.
ISO 3349 (1975). "Wood – Determination of modulus of elasticity in static bending," International Organization for Standardization, Geneva, Switzerland.
ISO 3350 (1975). "Wood – Determination of static hardness," International Organization for Standardization, Geneva, Switzerland.
ISO 3787 (1976). "Wood – Test method – Determination of ultimate stress in compression parallel to grain," International Organization for Standardization, Geneva, Switzerland.
Johansson, D., and Moren, T. (2006). "The potential of colour measurement for strength prediction of thermally treated wood," *Eur. J. Wood & Wood Prod.* 64(2), 104-110.
Kollmann, F., and Schneider, A. (1963). "On the sorption behaviour of heat stabilized wood," *Holz als Roh- und Werkst* 21(3), 77-85.
Kollmann, F., and Fengel, D. (1965). "Changes in the chemical composition of wood by thermal treatment," *Holz als Roh- und Werkst* 23(12), 461-468.
Li Shi, J., Kocaefe, D., and Zhang, J. (2007). "Mechanical behavior of Québec wood species heat-treated using ThermoWood process," *Holz als Roh- und Werkst* 65(4), 255-259. DOI: 10.1007/s00107-007-0173-9
Mazela, B., Zakrzewski, R., Grzeskowiak, W., Cofta, G., and Bartkowiak, M. (2004). "Preliminary research on the biological resistance of thermally modified wood," in: *Abstracts of the First European Conference on Wood Modification*, Ghent, Belgium.
Mohareb, A., Sirmah, P., Pétrissans, M., and Gérardin, P. (2012). "Effect of heat treatment intensity on wood chemical composition and decay durability of *Pinus patula*," *Eur. J. Wood & Wood Prod.* 70(4), 519-524. DOI: 10.1007/s00107-011-0582-7
Peters, J., Pfriem, A., Horbens, M., Fischer, S., and Wagenführ, A. (2009). "Emissions from thermally modified beech wood, their reduction by solvent extraction and fungicidal effect of the organic solvent extracts," *Wood Materials Science and Engineering* 4(1-2), 61-66. DOI: 10.1080/17480270903340562
Rice, R. W., and D'Onofrio, M. (1996). "Longitudinal gas permeability measurements from Eastern white pine, red spruce, and balsam fir," *Wood Fiber Sci.* 28(3), 301-308.
Rowell, R. M. (1996). "Physical and mechanical properties of chemically modified wood," in: *Chemical Modification of Lignocellulosic Materials*, D. S. Hon (ed.) CRC Press, Boca Raton, FL, USA, pp. 295-310.
Sluiter, A., Hames, B., Ruisz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2011). *Determination of Carbohydrates and Lignin in Biomass* (NREL/TP 510-42618, National Renewable Energy Laboratory, Golden, CO, USA.
Stamm, A., and Hansen, L. (1937). "Minimizing wood shrinkage and swelling: Effect of heating in various gases," *Ind. Eng. Chem.* 29(7), 831-833.
Stamm, A., Burr, H., and Kline, A. (1946). "Stayb-wood – A heat stabilized wood," *Ind. Eng. Chem.* 38(6), 630-634.
Taghiyari, H. R., Talaei, A., and Karimi, A. (2011). "A correlation between the gas and liquid permeabilities of beech wood heat-treated in hot water and steam mediums," *Maderas. Ciencia y tecnología* 13(3), 329-336.

Wetzig, M., Sieverts, T., Bergemann, H., and Niemz, P. (2012). "Mechanische und physikalische Eigenschaften von mit dem Vakuumpress – Trocknungsverfahren thermisch behandeltem," *Holz. Bauphysik* 34, 1-10.

Windeisen, E., Bächle, H., Zimmer, B., and Wegener, G. (2009). "Relations between chemical changes and mechanical properties of thermally treated wood," *Holzforschung* 63(6), 773-778. DOI: 10.1515/HF.2009.084

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