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REVIEW PAPER

Control of wood thermal treatment and its effects on decay resistance: a review

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Abstract

• *Key message* **An efficient use of thermal treatment of wood requires a depth understanding of the chemical modifications induced. This is a prerequisite to avoid problems of process control, and to provide high quality treated wood with accurately assessed properties to the market. Properties and structural anatomy of thermally modified woods are slightly different than un-processed woods from a same wood species. So it is necessary to create or adapt new analytical methods to control their quality.**

• *Context* Heat treatment as a wood modification process is based on chemical degradation of wood polymer by heat transfer. It improves mainly the resistance of wood to decay and provides dimensional stability. These improvements, which come at the expense of a weakening of mechanical properties, have been extensively studied. Since a decade, researches focused mainly on the understanding of wood thermal degradation, on modelling, on quality prediction and quality control.

• *Aims* We aimed at reviewing the recent advances about (i) the analytical methods used to control thermal treatment; (ii) the effects on wood decay resistance and (iii) the advantages and drawbacks of a potential industrial use of wood heating.

• *Methods* We carried out a literature review of the main industrial methods used to evaluate the conferred wood properties, by thermal treatment. We used papers and reports published between 1970 and 2015, identified in the web of science data base..

• *Results* Approximately 100 papers mostly published after 2000 were retrieved. They concentrated on: (i) wood mass loss due to thermal degradation determination, (ii) spectroscopic analyses of wood properties, (iii) colour measurements, (iv) chemical composition, (v) non-destructive mechanical assessments and (vi) use of industrial data.

• *Conclusions* One of most interesting property of heat-treated wood remains its decay resistance. Durability test with modified wood in laboratory are expensive and time-consuming. This review displays data from different analytical methods,

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such as spectroscopy, thermogravimetry, chemical analyses or mechanical tests that have the potential to be valuable indicators to assess the durability of heat treated wood at industrial scale. However, each method has its limits and drawbacks, such as the required investment for the equipment, reliability and accuracy of the results and ease of use at industrial scale.

Keywords Heat treatment · Mass loss · Durability · Mechanical resistance · Prediction methods · Quality assessment

1 Historical overview

The use of heat treatments to modify the properties of the wood is not recent. Heat-treated wood raised significant research in various countries, for some decades. The first study has been conducted in 1920 Tiemann (1920) on high temperature wood drying process. Results issued from this work have shown that such a process allows mainly to decrease the Equilibrium Moisture Content (EMC) and consequently the wood swelling. In Stamm and Hansen (1937) confirmed these results finding that equilibrium moisture, swelling and shrinkage of wood decreased with heating in several gaseous atmospheres. Then, Stamm *et al*. (1946) reported a heat treatment to improve wood dimensional stability and resistance to wood-destroying fungi without densification process. None of these modified wood products had much success on the industrial market, probably due to the availability of other high quality timber at the time. Nevertheless, heat treatment was not completely forgotten and several studies were presented later by Seborg et al. (1953), Kollman and Schneider (1963), Kollman and Fengel (1965), Burmester (1973, 1975), Rusche (1973a, 1973b). Shortly after, thermal degradation process had been oriented to produce recoverable energy from lignocellulosic biomasses (Ecoles des Mines de Paris et de Saint Etienne, 1976–77). This material was considered as an energetic resource in between coal and firewood. Thermal Modified Wood (TWM) was studied again as material only since the 80s. After a study involving gas and liquid released during wood thermal degradation, advantageous properties such as wood dimensional stability and decay resistance ameliorations were highlighted (Gieleber 1983; Hillis 1984). The energetic way was then forgotten in favor of the production of a new modified wooden material. More recently there has been a revival interest in heat treatment processes. According to Boonstra (2008) this restored interest is due, to the deforestation of especially sub-tropical forests, the declining production of durable timber, the increasing demand for sustainable building materials and to the increased introduction of governmental restrictive regulations reducing the use of toxic chemicals.

Since the 2000s, studies have been conducted around the world: Netherlands (Boonstra *et al*. 1996; Tjeerdsma *et al*. 1998; Militz 2002), Germany (Rapp 2001) and Finland (Kotilainen et al. 2000, Sivonen et al. 2002, Hietala *et al*. 2002, Nuopponen *et al*. 2004), leading to set up various industrial processes. All of these industrial processes use sawn timbers and treatment temperatures between 160 °C and 260 °C, but they differ in terms of process conditions, such as the presence of a shield gas (nitrogen, steam), humid or dry-environment, conduction or convection heat transfer, use of oils, vacuum or reintroduction of combustion gases (Militz 2002).

2 Introduction

Wood modification process has become an attractive way to protect wood material against Moisture Content (MC) variations (Pétrissans *et al*. 2013) and Basidiomycetes attacks. Heat treatment consists in a wood torrefaction at temperatures ranging from 180 °C to 250 °C, performed in a very poor oxygen atmosphere to avoid wood combustion. The environmental impact of this process is low, heat is introduced in the treatment system and smokes issued from wood thermal degradation can be retrieved, condensed and purified (Pétrissans *et al*. 2007). At its end of life cycle, heat-treated wood can be recycled without detrimental impact to the environment to the contrary of chemically treated wood impregnated with biocidal active ingredients (CRIQ 2003). This environmental acceptable treatment improves wood decay resistance (Tjeerdsma *et al*. 2000) and dimensional stability (Korkut *et al*. 2012), decreases wood Equilibrium Moisture Content (EMC) (Hill 2006) and induces a darker coloration of wood (Chen *et al*. 2012), without additional chemical products. Therefore, heat treatment allows to use low durability local timber whose natural durability is low by making them resistant towards decay for a end-use in use class 2 and 3 (use class 4 being excluded due to the occurrence of soft rots) (EN 335 2013) and with high economic value (Allegretti *et al*. 2012 ; Kamdem et al. 2002). These upgraded properties conferred to the wood are the result of chemical modifications of wood cell wall polymers occurring during treatment (Tjeerdsma and Militz 2005; Yildiz *et al*. 2006; Inari et *al*. 2007). However, these durability enhancements have an adverse effect on wood mechanical properties (Gunduz *et al*. 2009; Andersons *et al*. 2012; Dilik and Hiziroglu 2012). Although the surface hardness of the heat treated wood is improved, its other mechanical properties, such as bending and compression strengths, stiffness and shear strength, are considerably weakened according to thermal process conditions and treatment intensities (Kocaefe *et al*. 2008; Candelier *et al*. 2013d; Hannouz *et al*. 2015).

During this last decade several ameliorations on thermal treatment of wood have led to the development of several treatment processes to the European market. The main differences between them lie in the nature of the inert atmosphere and the curing conditions used during the heat treatment: gases (fumes, nitrogen), steam pressure, oil, and recently vacuum (Surini *et al.* 2012; Allegretti *et al.* 2012). Earlier works have shown that thermal degradation of wood depends on heat treatment intensity which is directly related to treatment temperature and duration, conditioning thus the final properties of heat treated wood (Rep *et al.* 2004; Welzbacher *et al.* 2007). However, even if different studies have been conducted on the effect of treatment intensity (time and temperature) on properties conferred to the material, much less has been reported on the effect of inert atmosphere during the process. Indeed, it is obvious that this parameter impacts directly thermal degradation reactions and consequently the final properties of the material (Candelier *et al.* 2013a). Thermal degradation reaction mechanisms are different depending on wood specie, treatment intensity and process conditions (Militz 2002; Candelier *et al.* 2011a). However, some chemical reaction mechanisms occurred during wood thermal degradation still remains unknown according to the modification process used.

Hakkou *et al.* (2006) and Chaouch *et al.* (2013) studies, mainly achieved at laboratory scale, have proven good correlations between mass loss issued from wood thermal degradation (ML%), treatment intensity (time and temperature) and weight loss (WL%) of heat treated wood due to fungal decay (Hakkou et al. 2005; Chaouch *et al.* 2013). Because of dehydration reaction occurring during thermal treatment, wood carbon content increases along with treatment intensity whereas oxygen content decreases (Nguila *et al.* 2009). Elemental wood composition has been reported as a good marker of treatment intensity and, consequently, of mass losses issued from the different degradation reactions allowing further prediction of heat treated wood rot resistance (Šušteršic *et al.* 2010; Chaouch *et al.* 2010). However, several authors raised the question of the reliability of heat treated wood durability laboratory tests. According to Junga and Militz (2005), thermal modified wood material is different than untreated wood and it is necessary to adapt different testing methods to evaluate the final durability of this new material. They particularly showed that the EN 113 (1996), usually use as decay resistance test for chemically treated wood, needed some amendments to evaluate the resistance of modified wood towards Basidiomycetes, such as a prolonged test exposure. Kamden *et al.* (2002) had stated the same conclusions, as they imparted the biological resistance of the heat treated material to its low equilibrium moisture content during a decay test (i.e. the moisture content of the heat treated material is not enough for fungal growth).

Thus, durability tests on modified wood should be carried out over a longer exposure time (i.e. longer than 16 weeks of exposure) so as to overcome a poor estimation of the durability of the new material. These laboratory wood decay resistance tests are destructive, time and money consuming and derivative methods to predict the durability of heat-treated materials are crucially needed. Due to differences of chemical compositions and anatomical structures between untreated and heat treated woods, it is necessary to use other quality characterization methods for modified woods than unprocessed woods.

In addition, most industrial thermal treatment processes use convection heat transfer (Militz 2002) which induces sometimes heterogeneous treatment temperature propagation within the oven (between the periphery and the center of the stack of wooden plates) and lead to the heterogeneity in treatment efficiency (Pétrissans *et al.* 2007). The wood material variability, wood species and the importance of its initial properties (anatomy, chemical composition, moisture content, etc.) increase these up scaling problems (Willems 2013a; Hamada et al. 2013). Thus, it is common that treatment is not completely effective on several stack boards, in a same batch. Moreover, phenomena of cracking or delamination on the final product can be observed, causing then material and economical losses (Pétrissans *et al.* 2007). There is a substantial need to understand deeply chemical modifications occurring into the timber during the different heat treatment processes, in order to avoid problems of process control and to insure that the quality of treated timber is properly evaluated with a view to putting this modified timber on the market under a chain of custody.

3 Wood mass loss (ML %) due to its thermal degradation

Mass loss of wood due to its thermal degradation is one of the most important features in heat treatment and it is commonly referred to as an indication of its quality of treatment. Candelier *et al.* (2013b), Tenorio and Moya (2013) studied mass loss (ML%) along with heat treatment and concluded that thermal degradation kinetic of wood depends on wood species and process conditions such as drying step, heating medium and treatment intensity (couple temperature - duration).

Most of the collected data from literature are difficult to compare because different treatment processes, wood species and their respective initial moisture contents, as well as treatment intensities were used.

Firstly, several authors have shown that wood species and their respective chemical compositions are directly correlated to thermal degradation reaction kinetic. Chaouch (2011) compared the mass losses between hardwood and softwood species, during heat treatment performed by conduction under nitrogen atmosphere. Figure 1 shows that kinetic of

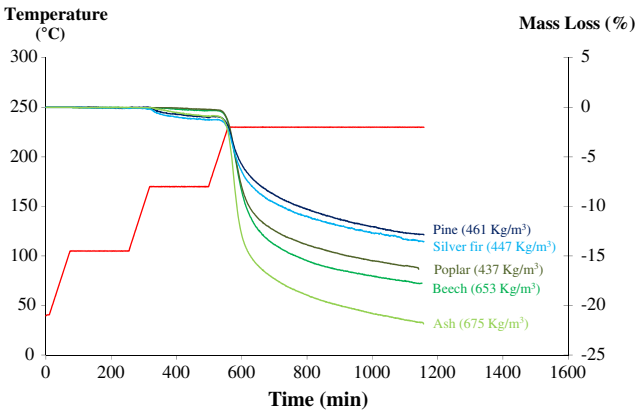

Fig. 1 Time course of mass loss (in % of initial values) of wood from different species [Pine (*Pinus sylvestris* L.), Silver fir (*Abies pectinate* Lam.), Poplar (*Populus nigra* L.), Beech (*Fagus sylvatica* L.) and Ash (*Fraxinus excelsior* L.)] treated with a step wise increasing temperature up to 230 °C (in red). Initial wood density (kg dry mass per m3) is indicated for each species. The mass loss started at 160 °C but was particularly important at 230 °C. From Chaouch 2011, with permission

degradation for similar curing condition (230 °C) are strongly influenced by the nature of wood species. Hardwoods [beech (*Fagus sylvatica L.*), poplar (*Populus nigra L.*) and ash (*Fraxinus excelsior* L.)] have been shown to be more sensitive to thermal degradation than softwoods [pine (*Pinus sylvestris L.*) and silver fir (*Abies pectinate* Lam.)] as demonstrated by the higher mass losses recorded for a same treatment duration. Even if wood density cannot be totally excluded to justify these differences, wood species of lower densities being generally more resistant to thermal treatment than those of higher density. Wood chemical observed differences (Boonstra and Tjeerdsma 2006a). Hemicellulose composition of hardwoods can corroborate their higher susceptibility. Softwoods contain mainly arabinoglucoronoxylan and galactoglucomannan, while hardwoods contain a lower amount of glucomannan and mainly glucoroxylan. These hardwood xylan units are strongly acetylated, comparatively to softwood hemicelluloses (Fengel and Wegener 1989; Sjöström 1981). Moreover, an important amount of acetic acid is released during deacetylation of hemicellulose which catalyses depolymerisation of the less ordered carbohydrates as hemicelluloses and amorphous cellulose (Prinks *et al.* 2006). These differences were attributed to the differences of reactivity of the acetoxy and methoxy groups present as side chains in xylose units in the xylan containing hemicelluloses fraction.

Esteves *et al.* (2007) reported also a higher mass loss for eucalypt wood *(Eucalyptus globulus* Labill.*)* (hardwood) than for pine (*Pinus pinaster* L.*)* (softwood) under the same treatment conditions. Results have been confirmed by the identification of volatiles products formed during wood thermal degradation. With TD-GC-MS analyses, Candelier *et al.* (2011a) have shown that the high amount of acetic acid generated during thermal degradation of strongly acetylated glucoroxylan of hardwoods is associated to the formation of numerous degradation products resulting from lignin as well as hemicelluloses acid catalyzed degradations, such as furfural, hydroxymethylfurfural, guiaicol and vanillin. The quantities of these different components during thermal treatment are also linked to treatment intensity (Pétrissans *et al.* 2014). For a given temperature, the quantity of each degradation product increases progressively as the treatment duration increases (Candelier *et al.* 2013c). Zanuncio *et al.* (2014), using eucalyptus treated between 140 and 230 °C during 3 hours, found that mass loss varied from 0.33 % (140 °C) to 0.63 % (170 °C), to 2.73 % (200 °C) and to 10.73 % (230 °C). Olarescu *et al.* (2014) studied the mass loss of lime wood (*Tilia cordata* Mill.) treated at 180 and 200 °C, combined with four treatment durations; 1, 2, 3 and 4 hours and showed that mass loss of heat treated wood increases according to temperature and treatment duration (Table 1).

Even if the strong influence of treatment temperature on the treatment intensity has been mentioned by several authors (Burmester 1970; Mazela *et al.* 2004; Boonstra *et al.* 2006b; Paul *et al.* 2006), according to the exponential kinetic of wood thermal degradation, the treatment duration has also an impact on treatment intensity as well as on mass loss kinetic (Bourgeois *et al.* 1989). Chaouch *et al.* (2010) found strong relations between mass loss (ML %) and time of poplar (*Populus nigra L.*) thermal treatment, for several temperatures and treatment durations (Fig. 2).

Several studies have shown the influence of process atmosphere used on wood thermal degradation kinetic. Mazela *et al.* (2003) compared mass losses with heat treatment in air and in a water vapor atmosphere, using *Pinus sylvestris* L. at 160 °C, 190 °C and 220 °C during 6 and 24 hours. They verified that mass losses in the presence of air and of water vapor for 6 hours were very similar, but with 24 hours treatment the mass losses in air were higher, especially at 190 °C and 220 °C. Candelier *et al.* (2013c) found also differences of mass loss kinetic reaction of beech (*Fagus sylvatica* L.) heat treated wood between nitrogen and vacuum process, for

Table 1 Mass loss (ML, in % of initial values) of heat-treated lime (*Tilia cordata* Mill.) wood according to treatment intensity. Mass Loss of heat treated wood increases according to temperature and treatment duration. From Olarescu et al. (2014), with permission

Heat treatment conditions	Mass Loss ML (in % of initial values)
180 °C / 1 h	1,3 ± 0,2
180 °C / 2 h	1,7 ± 0,1
180 °C / 3 h	2,1 ± 0,2
180 °C / 4 h	2,4 ± 0,3
200 °C / 1 h	4,3 ± 1,1
200 °C / 2 h	5,0 ± 0,4
200 °C / 3 h	6,7 ± 0,4
200 °C / 4 h	9,3 ± 0,7

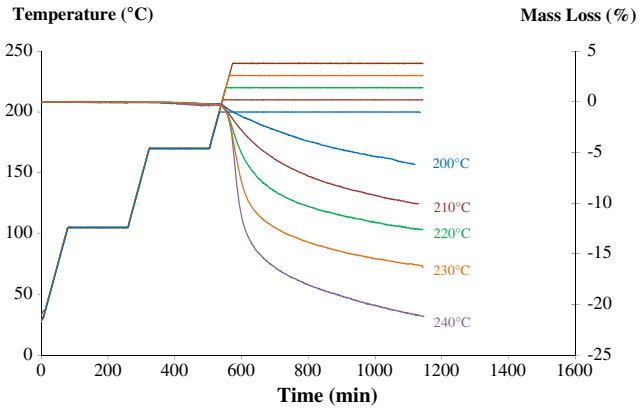

Fig. 2 Time course of mass loss (in % of initial values) of wood from Poplar (*Populus nigra* L.) treated with a step wise increasing temperature up to different treatment temperatures from 200 °C to 240 °C. The mass loss kinetic was impacted by the treatment temperature level. From Chaouch (2011), with permission

similar treatment intensity level. It appeared that vacuum utilization allows reducing the necessary drying time to stabilize wood mass (anhydrous) before thermal modification step limiting the overall treatment duration. Moreover heat treated wood under vacuum seemed to be less degraded than those treated under nitrogen. This difference may be easily explained by the effect of vacuum. Under vacuum, all volatile degradation products like acetic acid or furfural are removed progressively as soon as they are formed limiting the degradation of wood polysaccharides and the re-condensation of degradation products through thermal reticulation and crosslinking reactions (Candelier *et al.* 2013c). The influence of vacuum is also supported by the weakening of mechanical properties occurring during wood thermal modification (Candelier *et al.* 2014).

4 Durability prediction by mass loss (ML %) determination

Several authors reported an increased resistance to decay for different wood species and several types of rots. The important degradation of hemicelluloses due to thermal treatment, which are generally considered as an important nutritive source as well as a prime key in the hygroscopic wood behavior for the development of wood rotting fungi, and modification of lignin network are also be involved to explain the ineffectiveness of fungal enzymatic attacks. These heat treated wood modifications are represented by mass loss (ML). Various authors compared the weight loss (WL) caused by fungal attack to the decrease in mass of wood by heat treatment (ML). For instance, Welzbacher et *al.* (2008) made a comparison between WL caused by *Poria placenta* (*Poria placenta Coocke sensu* J. Erikson (PP) *[Fries, FPRL 280])* and ML, with heat treatment of Norway spruce (*Picea abies* Karst.) performed in temperature range from 180 °C to 240 °C and for durations comprised between 0,25 and 40 hours.

Figure 3 shows also that the impact of treatment temperature on ML was stronger than the impact of treatment time: for the same decrease in mass, higher temperatures led to lower WL by fungal decay (*Poria placenta Coocke sensu J. Erikson (PP)* [Fries, FPRL 280]) compared with lower temperatures. This concurs with results from Paul *et al.* (2006) and Mazela *et al.* (2004), who reported on limited improvement of resistance to fungal decay for heat treatment temperatures below 200 °C. Indeed, two pieces of thermally modified wood may show the same ML due to heat treatment, but have completely different properties such as decay resistance, swelling shrinkage (Welzbacher *et al.* 2007) and mechanical properties (Candelier et al. 2011b).

Others studies verified WL-ML relationships with other type of processes, wood species and treatment intensity (230 °C). Chaouch *et al.* (2010) studied heat treatment (under nitrogen atmosphere) on five European wood species [beech (*Fagus sylvatica* L.), poplar (*Populus nigra* L.), ash (*Fraxinus excelsior* L.), pine (*Pinus sylvestris* L.) and silver fir (*Abies pectinate* Lam.)] and proved a strong correlation between ML (5, 10 and 15 %) and WL due to *Coniophora puteana* Karsten (CP) [Schumacher ex Fries, Bam Ebw. 15] (Fig. 4), *Poria placenta Coocke sensu* J. *Erikson* (PP) [Fries, FPRL 280], *Coriolus versicolor* Quélet (CV) [Linnaeus, CTB 863 A] and *Gloeophyllum trabeum* Murill (GT) [Persoon ex Fries, BAM Ebw. 109].

In another study conducted by Elaieb *et al.* (2015), 3 Tunisian softwood [Aleppo pine (*Pinus halepensis* Mill), Maritime Pine (*Pinus pinaster* Aiton) and Radiata pine (*Pinus insignis* D. Don)] and 1 Hardwood [Zeen oack (*Quercus canariensis* Willd)] species have been heat treated,

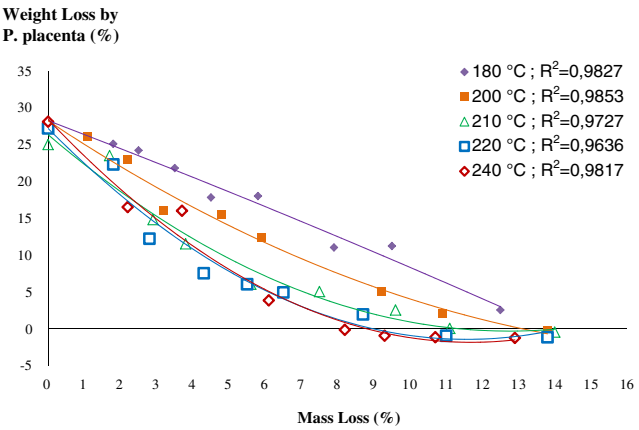

Fig. 3 Correlation between weight loss (WL %) by *Poria placenta* (*Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280]) and decrease in mass (ML %) for heat treatments on Norway spruce (*Picea abies* Karst.) performed with different treatment intensities. Treatment temperature (°C) is indicated for each process. For the same decrease in mass (ML %), higher temperatures led to lower WL. From Welzbacher et al. (2008), with permission

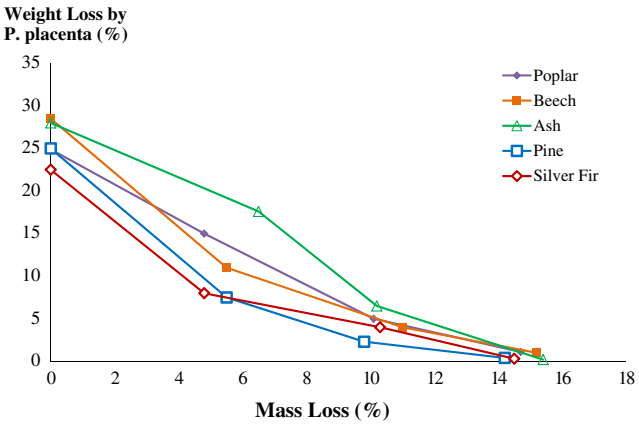

Fig. 4 Correlation between weight loss (WL %) caused by *Coniophora puteana* (*Coniophora puteana* Karsten (CP) [Schumacher ex Fries, Bam Ebw. 15]) and Mass Loss due to wood thermal degradation (ML %) for heat treatment on different European wood species [Pine (*Pinus sylvestris* L.), Silver fir (*Abies pectinate* Lam.), Poplar (*Populus nigra* L.), Beech (*Fagus sylvatica* L.) and Ash (*Fraxinus excelsior* L.)] performed at 230 °C. ML was correlated with WL, for each wood species. From Chaouch et al. (2011), with permission

under vacuum process, at 230 °C during the required treatment duration to obtain wood Mass Loss (ML) of 8, 10 and 12 %. Strong correlations between ML and WL (due to *Poria placenta Coocke sensu J. Erikson* (PP) [Fries, FPRL 280]) have also been proven through this work. In most studies, an average mass loss (ML) of 12 % confers to heat treated wood a durability class 3 according to the specifications of EN 350–1 (1994) standard (Welzbacher and Rapp 2002; Kamdem *et al.* 2002; Chaouch *et al.* 2010; Elaieb *et al.* 2015). In conclusion, treatment intensity which is characterized by ML has been demonstrated to be strongly correlated to each heat treated wood decay resistance. However, the introduction of a fast and accurate system for measuring this mass loss on an industrial scale is very difficult. Studies are currently conducted on the determination of others control parameters which could be also correlated with the treatment conditions and final heat treated wood quality such as decay resistance like spectroscopy analyses (Sandak *et al.* 2015; Popescu and Popescu 2013a), colour measurements (Kačíková *et al.* 2013), chemical composition determinations (Chaouch 2011), non-destructive mechanical tests (Hannouz *et al.* 2012), and industrial recording data (Candelier *et al.* 2015)

5 Durability prediction by spectroscopic analyses

Electron Spin Resonance (ESR) spectroscopy is a technical method based on the measurement of microwave resonance absorbance in the presence of an applied magnetics field. This microwave absorbance, recorded as its first derivative, is the ESR signal, which increases proportionally with the number of unpaired electrons present in the respective sample (Senesi and Senesi 2005). For thermally modified wood, an increase of the ESR signal intensity can be measured due to the formation of free radicals during the process (Viitaniemi *et al.* 2001). Therefore, ESR-spectroscopy is regarded as a potential method for the quality control of thermally modified wood (Viitaniemi *et al.* 2001; Willems *et al.* 2010). Recent investigations on ESR-Spectroscopy were done by Altgen *et al.* (2012), applied to several thermal modified wood species [ash (*Fraxinus excelsior* L.), beech (*Fagus sylvatica* L.) and spruce (*Picea abies* Mill.)] under different treatment intensities on laboratory as well as on industrial scale. Figure 5 shows correlations between ESR-relative intensities (ESR intensity sample / ESR intensity reference) and decay resistance (WL) (*Gloeophyllum trabeum* Murill (GT) [Persoon ex Fries, BAM Ebw. 109] and *Trametes versicolor* (L.) Lloyd [1920].

NIR-Spectroscopy method has been also investigated to predict wood thermal degradation intensity. Esteves and Pereira (2008) have found good correlations between predicted values issued from NIR analysis model and experimental values with mass loss (ML), MOE (Modulus of

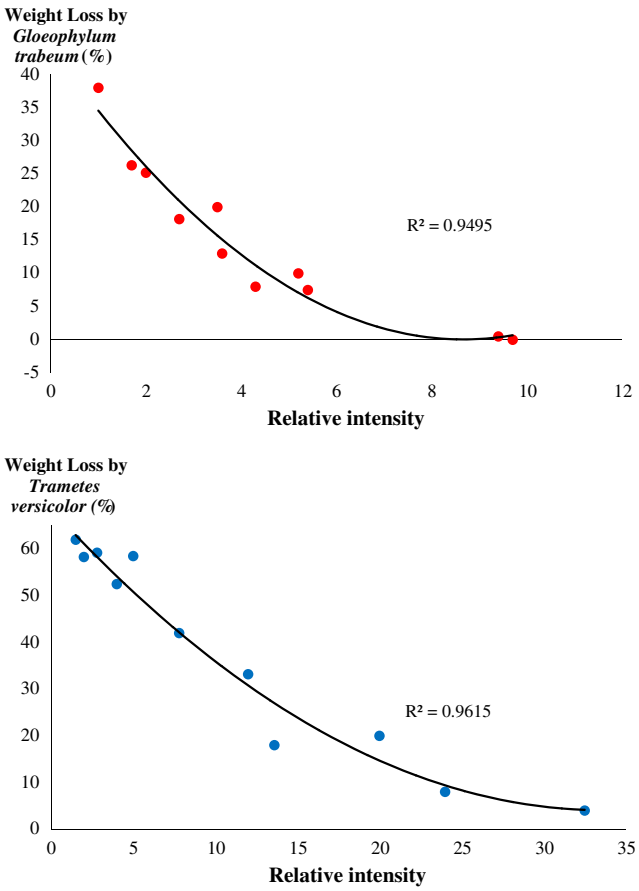

Fig. 5 Correlation between Weight Loss (WL %) by *Gloeophyllum trabeum* (*Gloeophyllum trabeum* Murill [Persoon ex Fries, BAM Ebw. 109]) and *Trametes versicolor* (*Trametes versicolor* (L.) Lloyd [1920] and ESR- relative intensity. For the both fungal attacks, ESR- relative intensity was correlated with WL. From Altgen et al. (2012), with permission

elasticity) and MOR (Modulus of Rupture) in bending strength, equilibrium moisture content of wood and colour variation according to treatment intensities (170-210 °C; 2-24 h) and wood species (*Pinus pinaster* L. and *Eucalyptus globulus* Labill.). NIR-Spectroscopy showed a good potential to be used for heat treated wood quality checking (Bächle *et al.* 2012), but no study has yet been conducted to compare directly heat treated durability with results issued to this spectrum analysis methods. However, NIR-Spectroscopy (NIRS) as a rapid and non-destructive technique was successfully used for the final physical product properties quality control. Sandak *et al.* (2015) have recently shown that the NIRS analysis allows to evaluate the ML and EMC, with errors 0.9 % and 0.36 % respectively and with coefficients of determination higher than 0.94. Therefore, both important parameters characterizing quality of Thermal Modified Wood (TMW) in vacuum conditions (EMC and ML) were predicted with high accuracy. Near Infrared Spectroscopy could be also used for decay resistance prediction and for optimization of the treatment procedure at the industrial scale and/or for on-line process control (Sandak *et al.* 2015). Indeed, Popescu and Popescu (2013a), 2013b) showed that the lime (*Tilia cordata* Mill.) wood samples treated at 140 °C and about 10 % relative humidity for a period up to 504 hours, investigated by NIRS - second derivative - principal component analysis and 2D correlation analysis, indicates transformations in the chemical composition and structural changes induced by the degradation of wood components. The modifications and/or degradation of wood components occurring by hydrolysis, oxidation, and decarboxylation reactions could be evaluated by differences in the bands intensities or position from NIR and second derivative spectra.

Fourier Transform mid Infrared Spectroscopy (FT-IR) is another technical approach adapted to fast and non-destructive measurement of organic materials. The important advantages are accuracy, simplicity, and ability of performing very high number of tests without needs of any destruction to the material. Indeed, Li *et al.* (2015) found strong relationships between treatment intensity and main chemical components of stem heat treated teak (*Tectona grandis* L.F.) wood determined by FT-IR spectra and SD-IR (Second Derivative Infrared Spectroscopy) spectra analyses. FT-IR analysis method shows also good potential utilization to estimate heat treated wood durability, relating to heat treated wood chemical changes.

6 Durability prediction by colour measurement

Colour is a very important wood property for the final consumer and, in some cases is the key factor for the selection of a specific wood since for some end uses the aesthetic point of view is often prevailing. The darkening can be an important benefit of the heat treatment giving to the wood an aspect more valuable in some countries. This darker shade which is conferred to the wood by heat treatments is given by the production of colored degradation products from hemicelluloses (Sehistedt-Persson 2003; Sundqvist 2004) and from the extractives components (McDonald *et al.* 1997; Sundqvist and Morén 2002). Patzelt *et al.* (2003) suggested that colour evolution could be also used as a classification method of treated wood, because it has a significant correlation with treatment intensity (Viitaniemi *et al.* 1997; Mitsui et al. 2001, 2003), the mass loss (Bekhta and Niemz 2003; Esteves *et al.* 2008) and also the thermal process used. The classification of heat treated wood colour evolution can be valuable for one treatment methods but it cannot be used to compare the modification level of several modified woods issued from different industrial process. The CIELAB system is the most common method to estimate material colour. This L*a*b* model measures the colour differences according to 3 axis: the *a* axis extends from green (−a) to red (+a), the *b* axis from blue (−b) to yellow (+b), and the brightness (L) increases from black to white. The advantage of this system is that it is similar to human vision and very useful for camera or scanner imaging editing. Several studies have shown parabolic correlations between ΔE [$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$], representing color changes, after heat treatment, with the CIELAB system, and Mass Loss (ML) due wood thermal degradation (Gonzáles Peña and Hale 2008; Tudorović et al. 2012). The wood browning after thermal treatment was also observed by Chen *et al.* (2012), and was caused primarily by changes in the polysaccharides. Bourgois *et al.* (1991) showed that both a decrease in ΔL∗ and an increase in ΔE∗ for wood subjected to heat treatments at 240–310 °C were caused by a decrease in the content of hemicelluloses, especially pentosans. The nature of colour change is complex as all essential wood components including the extractives may contribute to the change. Matsuo *et al.* (2010) have reported that the darker colour of heat-treated wood was attributed to the formation of degradation products from hemicelluloses, changes in extractives, and the formation of oxidation products such as quinones.

The CIELAB colour measurement was also mentioned as a possible approach for determinig treated wood quality by Brischke *et al.* (2007). Chemical, mechanical and colour traits of thermally modified wood showed close relationships, and therefore they can be used for their mutual predictions (Kačíková *et al.* 2013). Welzbacher *et al.* (2007) verified strong relations between color evolution, represented by luminescence change (L*), of Norway spruce (*Picea abies* Karst.) heat treated, treatment intensity and the final wood material decay resistance (Fig. 6). However, Matsuo *et al.* (2010, 2011) have shown that treatment temperature has not a significant impact of heat treated hinoki (*Chamaecyparis obtusa* Endl.) wood colour evolution. These results indicate that it could be

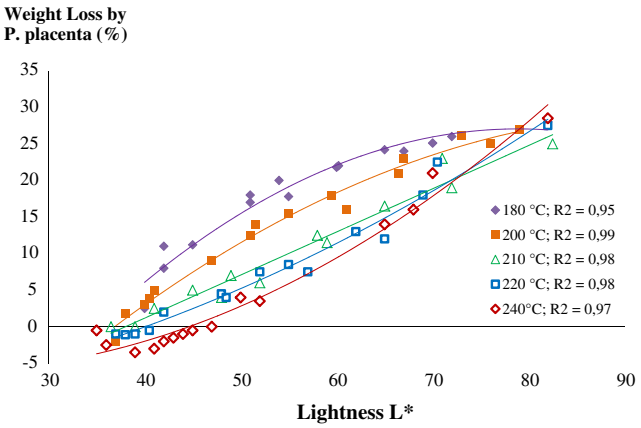

Fig. 6 Correlation between weight loss (WL %) by *Poria placenta* (*Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280] and Lighteness L*, for different heat treatments on Norway spruce (*Picea abies* Karst.). Treatment temperature (°C) is indicated for each process. For each treatment intensity, Lighteness L* from colour measurement was correlated with WL. From Welzbacher et al. (2008), with permission

possible to predict treated wood mofidications and also its decay resistance, without taking into consideration the treatment temperature, for a same process used..

However, Johansson and Moren (2006) believe that colour is not suitable as predictor of heat treated wood quality because colour distribution through the thermally treated boards is not homogeneous. As a matter of fact, Esteves *et al.* (2008) have found that colour of the Pine wood (*Pinus pinaster* L.), heat-treated under steam pressure process at 190 °C during 6 hours, was not uniform because of the increased contrast between earlywood and latewood, and therefore the color of samples depended on the earlywood/latewood ratio from the sample surface. Moreover, in some cases, there was a formation of darker spots at the surface due to the exudation of some resins.

7 Durability prediction by elemental composition (O/C) analysis

Control and measurement of the mass loss of the material during the heat treatment process will allow predicting its finale decay resistance. This mass loss issued from wood thermal degradation is due to an importance rate of dehydration reactions occurring during the heat treatment, caused by degradation of amorphous polysaccharides (Fengel and Wegener 1989; Sivonen *et al.* 2002; Yildiz *et al.* 2006), jointly with the formation of carbonaceous materials within the wood structure leading to a strong decrease of wood Oxygen/Carbon ratio (O/C) (Inari *et al.* 2006, 2007). The behavior of carbon and oxygen contents has been evaluated through determination of wood's elemental composition by Inari *et al.* (2009). Since, several authors have investigated the way of O/C molar ratio (Elaieb *et al.* 2015) and carbon oxidation state (Willems *et al.* 2013b) uses to predict heat treated wood decay resistance. Chaouch (2011) evaluated the correlations between the wood durability improvement of different softwood and hardwood species [beech (*Fagus sylvatica* L.), poplar (*Populus nigra* L.), ash (*Fraxinus excelsior* L.), pine (*Pinus sylvestris* L.) and silver fir (*Abies pectinate* Lam.)] and their respective O/C ratios, on the basis of their ML due to thermal degradation. This author investigated the effect of thermal treatment temperatures (180, 200, 210, 220 and 240 °C) and durations on the conferred durability to different European wood species. For the range of temperatures used, wood chemical composition appeared therefore to be a valuable marker of wood durability due to the strong correlations existing between treatment intensity and decay resistance towards (Coriolus versicolor Quélet (CV) [Linnaeus, CTB 863 A], *Gloeophyllum trabeum* Murill (GT) [Persoon ex Fries, BAM Ebw. 109], *Coniophora puteana* Karsten (CP) [Schumacher ex Fries, Bam Ebw. 15] and *Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280].

Evolution of lignin and holocellulose contents and their respective chemical structures or chemical compositions are directly correlated to Mass Losses (ML) due to thermal degradation reactions, which are also directly correlated to weight losses due to fungal attack (Mohareb *et al.* 2012). Even if mass losses of wood due to its thermal degradation reactions are not always readily available on industrial processes, it seems possible to easily establish calibration curves for given treatment conditions allowing further correlations between elemental composition, treatment intensity and wood decay resistance (Fig. 7). Elaieb *et al.* (2015) found similar results with thermal treatment performed under vacuum on Tunisian wood species (Aleppo pine [*Pinus halepensis* Mill.], Radiata pine [*Pinus radiata* D.Don.], Maritime pine [*Pinus pinaster* Aiton.] at

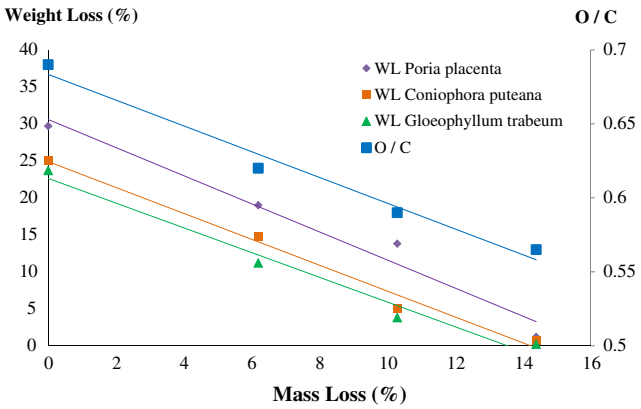

Fig. 7 Correlation between Weight Loss by different rots (WL) (*Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280], *Coniophora puteana* Karsten (CP) [Schumacher ex Fries, Bam Ebw. 15] and *Gloeophyllum trabeum* Murill (GT) [Persoon ex Fries, BAM Ebw. 109]), Mass Loss due to heat treatment (ML) and O/C ratio, from poplar (*Populus nigra* L.) treated under nitrogen at 230 °C. For each fungal attack, ML and O/C ration were correlated to WL. From Chaouch (2011), with permission

230 °C and exposed to *Poria placenta* (*Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280]) attacks.

8 Durability prediction by tests carried out on industrial sites

8.1 Mechanical properties by nondestructive tests

Most of thermal treatment processes are performed by convection and do not record the wood Mass Loss (ML) during the process (Borgeais 2012). Moreover, heat transfer by convection may give rise to unsatisfactory treatment homogeneity on the set of treated samples (Pétrissans *et al.* 2007). So, it is necessary to find and/or select some parameters, which could be easily used for industrial process, to estimate the ML (resulting from treatment intensity) and consequently predict the conferred decay resistance of heat treated wood.

Heat treated wood mechanical resistance, and particularly MOE and MOR in bending, decrease according to the treatment intensity (Kim *et al.* 1998; Bal 2014). Similar results have been reported by Jimenez *et al.* (2009). These authors studied also the decrease of mechanical properties and the improvement of decay resistance towards two fungi species; *Fomes lividus* (Kalchbr. ex Cooke) Sacc. (white rot) and *Lenzites striata* var. striata (Sw.) Fr. (brown rot), during heat treatment performed on Malapapaya (*Polyscias nodosa* (Blume) Seem.) wood under different treatment intensities (180-230 °C, 30–120 min). Comparing the results of these two studies, it appears that MOR in bending destructive tests and WL (%) issue from fungal attacks are correlated (Fig. 8). Even if MOE is constant whatever the process conditions and the conferred durability to the material, good correlations between MOR and WL (%) have been highlighted.

It would therefore seem possible to predict final heat treated wood decay resistance by measuring some mechanical characteristics. However, some authors who have studied the durability prediction by mechanical properties determination have used destructive methods (Welzbacher et al. 2007; Elaieb *et al.* 2015). More recently, Hannouz *et al.* (2012) studied the possibility to use nondestructive mechanical tests, in order to estimate the mass loss and also the decay resistance of modified wood. By measuring MOE and MOR in bending before and after treatment, with BING® system analysis, Hannouz *et al.* (2012) found high correlations between mechanical properties and Mass Loss (ML). They established, mainly, a relation between ML (%) derived/calculated from MOR measured with BING® method and real ML (%) after thermal treatment of ash (*Fraxinus excelsior* L.) wood (Fig. 9). The BING® analysis system is a method of mechanical properties characterization which is based on the study of the vibrations of wood material. It involves determining the linkage between the mechanical properties and the wooden material vibration behavior. The analysis of resonant frequency spectrum allows to obtain the elastic properties (longitudinal-MOE, transverse shear) and inelastic (internal friction associated with each resonant frequency) of any rigid material. The specimen is subjected to longitudinal or transverse vibrations whose recording and analysis lead to the identification of desired material characteristics. Such a nondestructive method could be also a good option to predict the final decay resistance of heat modified wood. However, such correlation does not operate on bending MOE values (Hannouz *et al.* 2012). It could be explained by the low moisture content of heat treated wood. Indeed, BING® method parameters have been determined for wood

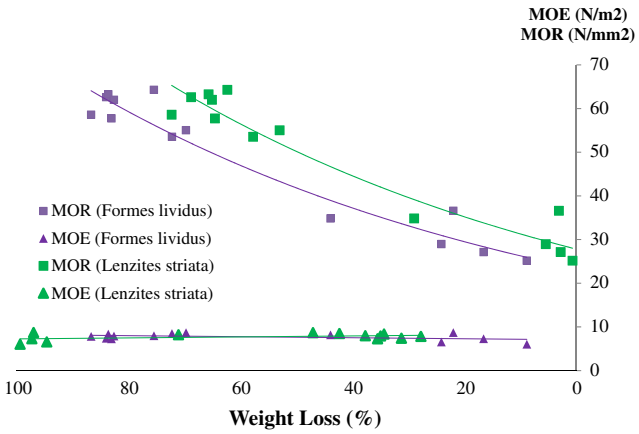

Fig. 8 Correlation between weight loss (WL%) by white and browns rots [*Fomes lividus* (Kalchbr. ex Cooke) Sacc. and *Lenzites striata* var. striata (Sw.) Fr.], MOE and MOR in bending destructive tests, for heat treatments performed on Malapapaya [*Polyscias nodosa* (Blume) Seem] wood. Thermal process conditions used are the following: temperature ranged from 180 to 230 °C, and various durations comprised between 30 and 120 min. Even if MOE is constant, MOR was correlated to WL. From Jimenez et al. (2011), with permission

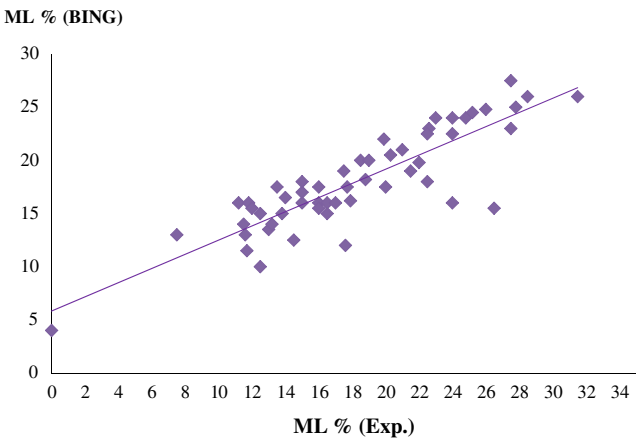

Fig. 9 Correlation between modelling ML (%) and real ML (%) from treated Ash (*Fraxinus excelsior* L.) wood under water steam pressure system. Treatment temperature used was 210 °C and different durations were performed to obtain various ML from 0 to 32 (in% of initial values). Modelling ML (%) and real ML (%) were correlated but we observe a deviation probably due to a lower humidity of modified wood. From Hannouz et al. (2012), with permission

moisture content of approximately 12 %, and it is difficult to obtain such moisture content for thermally modified wood.

8.2 Utilization of wood temperature kinetic

Another approach concerning modified wood decay resistance prediction consists in investigating the wood temperature kinetic during heat treatment (Candelier *et al.* 2015). The relative area, calculated from wood temperature curve, above 100 °C till heating temperature, has been proved to be an indicator of heat treatment intensity. Candelier *et al.* (2015) have shown, that for several wood species (Aleppo pine [*Pinus halepensis* Mill.], Radiata pine [*Pinus radiata* D.Don.], Maritime pine [*Pinus pinaster* Aiton.] and Zeen oak [*Quercus canariensis* Willd.]) and for different process conditions, this relative area seems to be a good indicator to estimate the final product quality and more particularly its durability improvement after a thermal modification (Fig. 10). Even if this study was conducted at a laboratory scale, relative area appears to be an easy and good potential industrial method to estimate the final commercialized products quality. The benefit of this method is to be efficiently achievable at industrial scale through heat treatment device which allow dynamic recording of wood temperature along the process. Even if the utilization of relative area from wood temperature kinetic gives to the producer a global quality estimation of heat treated wood issue from one treatment, this method not allow to obtain a quality control for each treated wood boards.

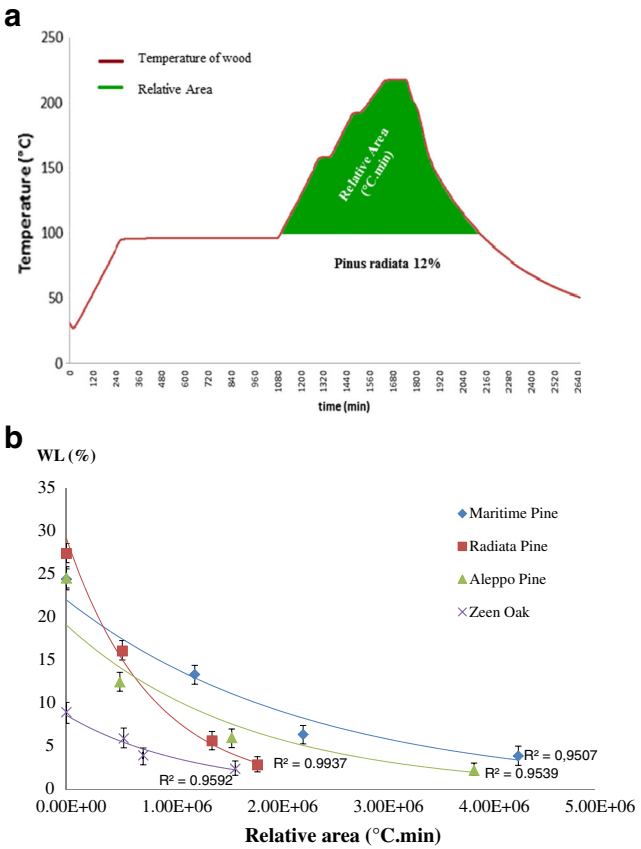

Fig. 10 (**a**) Relative area determination and (**b**) Prediction of Weight Losses due to *Poria placenta* (*Poria placenta* Coocke sensu J. Erikson (PP) [Fries, FPRL 280]) exposure by determination of relative Area, for different wood species (Aleppo pine [*Pinus halepensis* Mill.], Radiata pine [*Pinus radiata* D.Don.], Maritime pine [*Pinus pinaster* Aiton.] and Zeen oak [*Quercus canariensis* Willd.]. For each wood specie, relative area seems to be correlated to WL due to fungal exposure. From Candelier et al. (2015), with permission

9 Conclusion

One of the most efficient indicators of the treatment efficiency is mass loss of wood due to its thermal degradation. However, the introduction of a fast and accurate system for measuring the mass loss and/or elemental composition on an industrial scale is very difficult. Nevertheless, an effective quality control measurement is overriding to estimate heat treated wood quality but also to optimize the process parameter. Colour tests allow to obtain a fast rating of heat treated wood durability, but this sort of measure is not precise and efficient enough taking into account wood variability and treatment heterogeneity. Spectroscopic analyses such as NIR or FT-IR are able to give information on the process extent (by estimating mass loss) and on the properties that are relevant for this wood modification and for the uses of heat treated wood (i.e. EMC, dimensional stability, and decay resistance), by an overall a single spectrum averaged over the solid surface of a heat treated wood sample. Therefore and given that the acquisition of NIR spectrum can be done quickly and easily on the solid surface of the samples using a fiber probe, and that spectral data processing can be done immediately afterwards, this is a methodology with an interesting potential for process and product quality control, once calibration and validation of the models have been made for the processed wood species. More recently, utilization of mechanical test on wood before and after thermal modification process (non-destructive methods, such as BING®) could allow obtaining quickly and easily the acquisition of resonant frequency spectrum to estimate the heat treated wood properties. Although this method is widely and effectively used on industrial scale on native wood, this methodology needs calibration steps in order to be correctly used on modified wood material. Finally, use of relative area indicator issue from wood temperature kinetic is easily achievable at industrial scale through heat treatment device which allow dynamic recording of wood temperature along the process. Even if this indicator gives to the producer a global quality estimation of modified wood issue from one heat treated batch, this method not allow to obtain a quality control for each wood boards from this batch. This last method seems to be more efficient, easier and cheaper to consider it in

industrial site, but it needs to be investigated for different wood thermal modification processes and on an industrial scale.

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