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**UTILIZATION OF TEMPERATURE KINETICS AS A METHOD TO
PREDICT TREATMENT INTENSITY AND CORRESPONDING
TREATED WOOD QUALITY: DURABILITY AND MECHANICAL
PROPERTIES OF THERMALLY MODIFIED WOOD**

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ABSTRACT

Wood heat treatment is an attractive alternative to improve decay resistance of wood species with low natural durability. However, this improvement of durability is realized at the expense of the mechanical resistance. Decay resistance and mechanical properties are strongly correlated to thermal degradation of wood cells wall components. Mass loss resulting from this degradation is a good indicator of treatment intensity and final treated wood properties. However, the introduction of a fast and accurate system for measuring this mass loss on an industrial scale is very difficult. Nowadays, many studies are conducted on the determination of control parameters which could be correlated with the treatment conditions and final heat treated wood quality such as decay resistance. The aim of this study is to investigate the relations between kinetics of

27 temperature used during thermal treatment process representing heat treatment intensity, mass
28 losses due to thermal degradation and conferred properties to heat treated wood. It might appear
29 that relative area of treatment temperature curves is a good indicator of treatment intensity. Heat
30 treatment with different treatment conditions (temperature-time) have been performed under
31 vacuum, on four wood species (one hardwood and three softwoods) in order to obtain thermal
32 degradation mass losses of 8, 10 and 12%. For each experiment, relative areas corresponding to
33 temperature kinetics, mass loss, decay resistance and mechanical properties have been
34 determined. Results highlight the statement that the temperature curves' area constitutes a good
35 indicator in the prediction of needed treatment intensity, to obtain required wood durability and
36 mechanical properties such as bending resistance and Brinell hardness.

37
38 **Keywords:** control quality, decay resistance, heat treatment, mass losses, mechanical properties,
39 temperature kinetics.

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INTRODUCTION

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43 Wood heat treatment by mild pyrolysis is used to improve wood properties such as its decay
44 resistance and dimensional stability (Rowell *et al.* 2009, Poncsak *et al.* 2010). These improved
45 properties result from the wood cell polymers' chemical modifications occurring during treatment
46 (Esteves *et al.* 2013), which confer the new wood properties (Tjeerdma and Militz 2005).
47 Previous studies have shown that the wood thermal degradation mass loss is a good indicator for
48 the treatment intensity directly related to the temperature and the duration of the heat treatment
49 (Welzbacher *et al.* 2007, Pétrissans *et al.* 2014). Elemental wood composition has been reported

50 as a good marker of treatment intensity and consequently of the mass loss level, allowing further
51 prediction of the heat treated wood decay resistance (Nguila *et al.* 2009). According to previous
52 experiments, mass losses between 10 and 14% are generally required to reach a weight loss
53 against fungal attacks lower than 3%. The decay resistance of the treated wood matches to a full
54 durability (Chaouch *et al.* 2010), according to the European Standard EN 113/A1 (2004). In
55 parallel with improvement of wood durability, mechanical properties were generally significantly
56 weakened (Bengtsson *et al.* 2002). The wood properties' modifications are directly correlated to
57 the treatment intensity (Chaouch *et al.* 2010, Gunduz *et al.* 2009). Nowadays, the main concern is
58 the difficulty to produce in an industrial scale heat treated wood with constant and controlled
59 final wood product quality (durability, dimensional stability, color). Most of thermal treatment
60 processes are performed by convection and don't record the wood mass loss during the process
61 (Abibois 2012). Moreover, heat transfer by convection may give rise to an unsatisfactory
62 treatment homogeneity on the set of treated samples (Pétrissans *et al.* 2007). So, it's necessary to
63 elaborate some parameters to estimate the mass loss, resulting from treatment intensity, the new
64 properties of heat treated wood, and which could be easily used for industrial process. In this
65 study, heat treatment was performed by conduction to obtain a better thermal homogeneity.
66 Wood mass loss was recorded during the thermal degradation. Curing was carried out under
67 vacuum. The global treatment duration by comparison with a process using a nitrogen
68 atmosphere (Candelier *et al.* (a) 2013) is reduced, because re-condensation and thermal
69 reticulation of wood degradation products are avoided.

70 The aim of this study is to investigate the relations between the heat treatment intensity and the
71 thermal degradation kinetics, mass losses and the final properties conferred to the heat treated
72 wood. The relative area of treatment temperature curves is proposed as an indicator of heat

73 treatment. This area represents the amount of the heat absorbed by the treated wood samples.
74 Heat treatments with various intensities (temperature-time) have been performed on four wood
75 species in order to obtain thermal degradation mass losses of 8, 10 and 12%. For each treatment,
76 relative areas, masse losses, decay resistance and mechanical properties have been determined
77 and correlated.

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MATERIAL AND METHODS

80 Wood sample and heat treatment protocol

81 Each heat treatment was carried out simultaneously on two wood boards of 250 x 25 x 110 mm³
82 (L x R x T). Four wood species have been studied, one hardwood; Zeen oak (*Quercus*
83 *canariensis*) and three softwoods; Aleppo pine (*Pinus halepensis*), Radiata pine (*Pinus radiata*),
84 Maritime pine (*Pinus pinaster*). Thermal treatment was performed in a 0.25 cubic meter
85 laboratory autoclave by conduction between two electric heated metallic plates equipped to
86 record dynamic mass loss and temperature (SEIR, Charmes France). Each board was initially
87 dried at 103 °C for 48 h and placed in the oven. The oven was then closed and placed under
88 vacuum (200 mbar). The plate temperature was slowly increased by 0.3 °C.min⁻¹ from ambient to
89 the drying temperature (103 °C) until complete stabilization of the boards' mass. After this
90 period, the plate's temperature was increased by 0.3 °C.min⁻¹ from 103 °C to 170 °C and the
91 temperature maintained for 2 h. The temperature was then increased by 0.2 °C.min⁻¹ from 170 °C
92 to 220 °C to perform wood thermal modification to different mass losses of 8, 10 and 12%
93 (Figure 1). The heating system was then stopped and wood samples cooled down to room
94 temperature under an oxygen free atmosphere.

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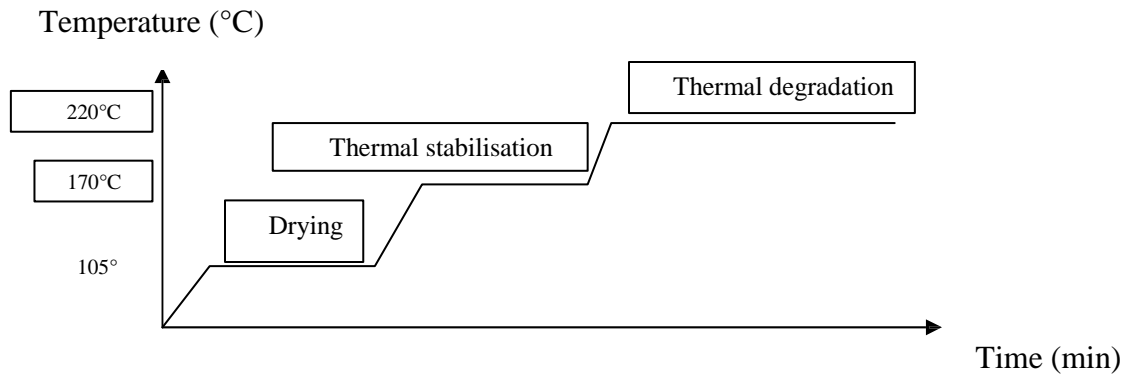
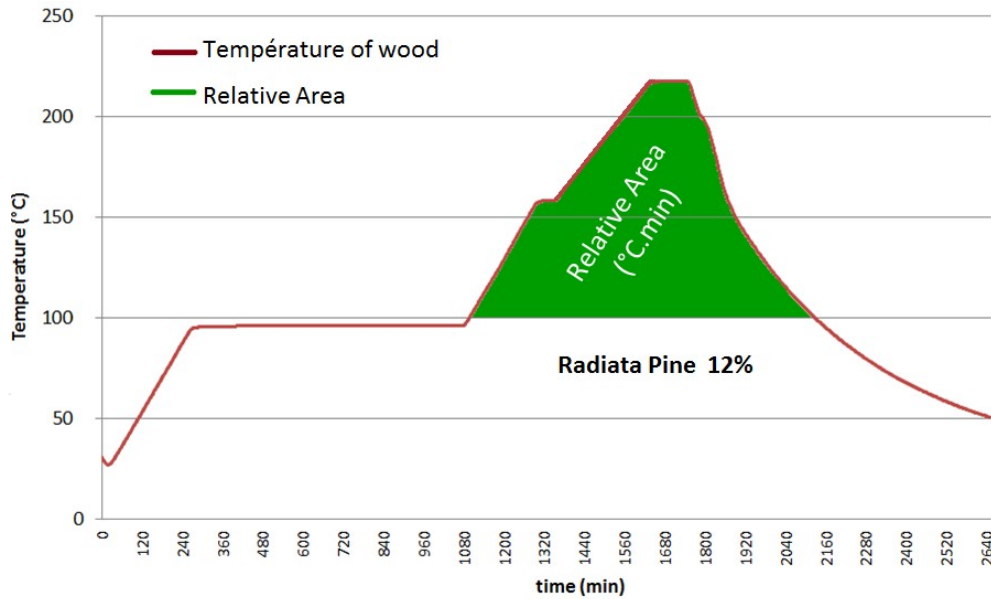


Fig.1. Temperature evolution to achieve thermal treatment.

112 **Relative area determination**

113 The heat treatment device allows dynamic recording of wood temperature and wood mass loss
114 curves. Relative area was calculated between the end of the drying step at 105°C (m_0) and the
115 process of cooling down to 105°C (Figure 2).

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Fig.2. Relative area from temperature kinetic representing radiata pine heat treatment to obtain a mass loss of 12%.

121 The relative area was calculated during the effective thermal modification step for each heat
122 treatment and each wood species. The temperature curves are obtained by averaging both
123 simultaneously treated wood boards. The relative area represents the quantity of the effective heat
124 power exchanged during the treatment process leading to a required wood mass loss. Relative
125 area takes into account on one hand the capacitive thermal power transferred by conduction in the
126 oven, and on the other hand to the reaction enthalpy due to the exothermic character of the
127 thermodegradation reactions.

128 **Decay resistance**

129 Blocks of 25 x 10 x 5 mm³ in longitudinal, radial and tangential directions were cut from heat
130 treated and untreated wood and dried at 103 °C for 48 h (m₁). Petri dishes (90 mm diameter) were
131 filled with sterile culture medium prepared by mixing 30 g malt and 40 g agar in one L of
132 distilled water, inoculated with the different fungi and incubated at 22 °C and 70% relative
133 humidity to allow full colonization of the surface by the mycelium. The decay resistance was
134 tested on four different fungies: *Coriolus versicolor* (CV), *Gloeophyllum trabeum* (GT),
135 *Coniophora puteana* (CP) and *Poria placenta* (PP). Three blocks (2 treated and one untreated as
136 control) were placed in each Petri dish and incubated during 16 weeks to evaluate the effect of
137 thermal modification. Each experiment was triplicated. After this period, mycelia were removed
138 and the blocks were dried at 103 °C and weighed (m₂) to determine the weight loss caused by the
139 fungal attack.

$$140 \quad \text{WL (\%)} = 100 \times \frac{m_1 - m_2}{m_1} \quad [1]$$

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142 **Mechanical properties**

143 In order to assess the effect of heat-treatment parameters on the mechanical properties, three
144 point bending (MOE, MOR) and Brinell hardness were carried out for untreated and heat treated
145 samples, results are compared. An INSTRON 4467 Universal Mechanical Test Machine was
146 used for the measurements. Samples were conditioned in a room with 65% RH and 22 °C during
147 the time necessary to stabilize the samples weights.

148 Three point static bending tests were carried out according to the EN 408 (2003). The sample size
149 was 200 x 10 mm x 10 mm³ (L x R x T). The moving head speed and the span length were 1.8
150 mm.s⁻¹ and 160 mm, respectively. The load deformation data obtained were analyzed to
151 determine the modulus of elasticity (MOE) and the modulus of rupture (MOR). Tests were
152 replicated twenty times for each treatment condition, 10 samples were used for each heat treated
153 boards.

154 Brinell hardness tests were performed according to the EN 408 (2003) standard. The force was
155 applied by a sphere with a diameter of 10 mm. This force is applied in three steps. It was slowly
156 increased by 0.2 kN.s⁻¹ during 15 s. After this period, a force of 3 kN was maintained for 25 s and
157 finally the applied force was decreased. Brinell hardness tests were replicated twenty times (10
158 tests for each wood boards). Every test was separated by at least 30 mm from the edge of the
159 boards and 25 mm between each test. Accuracy of the measurement of the ball penetration depth
160 was 0.01 mm and the applied force's one was 0.005 kN.

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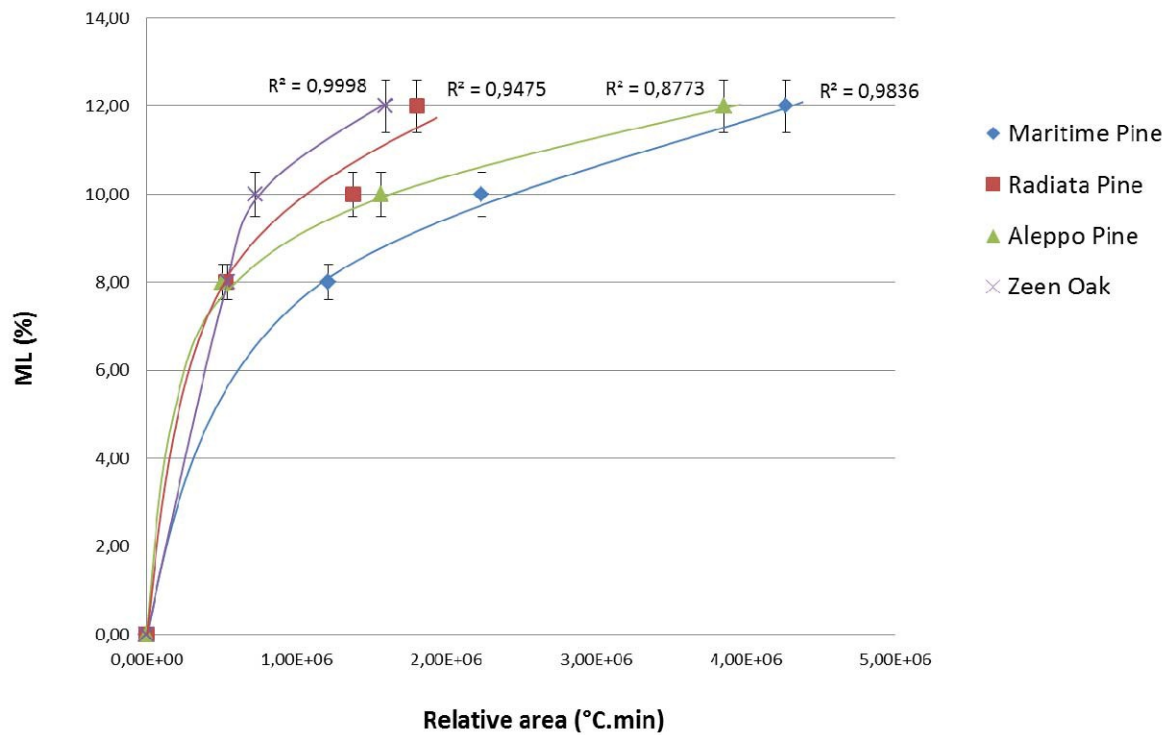
RESULTS AND DISCUSSION

163 **Relative area and treatment intensity**

164 Figure 3 gives the relations between the relative area and wood samples mass losses issued from
165 the thermal degradation obtained for a given treatment intensity. For all wood species, heat

166 treatment was performed at 220°C. The difference between treatment intensities is determined by
 167 process duration. Treatment time will then determine the wood mass loss. Relative areas are
 168 representative to the treatment intensity. For a given mass loss, the relative area is determined as
 169 shown on Figure 2. The relative area corresponding to the kinetics of Zeen oak wood thermal
 170 degradation was found less important compared to the three others softwood species. These
 171 results are in agreement with previous studies (Candelier *et al.* 2011) that have showed the higher
 172 sensitivity to thermal degradation of hardwood than softwood. The thermal susceptibility
 173 differences between hardwood and softwood species are more pronounced for mass loss higher
 174 than 8%. Similar result have been found by Chaouch *et al.* (2010) in a study of the correlation
 175 between mass loss and treatment intensity (time and temperature) during the heat treatment of
 176 several wood species such as silver fir, pine, beech, poplar and ash.

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Fig.3. Correlation between Relative Area and Mass losses due to thermal degradation of different wood species.

182 The main difference concerns the thermal degradation kinetics, which is directly influenced by
183 the treatment temperature (Candelier *et al.* 2011) and the quantity of acetic acid liberated during
184 the heat treatment (Stamm 1956). The acetic acid production strongly depends on the wood
185 species nature: hardwoods lead to higher amounts of acid compared to softwoods. This may be
186 related to the nature of hemicelluloses initially present in hardwood and softwood species
187 (Sjöström 1981, Fengel and Wegener 1989).

188 The observed in these work relations between the process heat energy characterized by the
189 relative area and the occurring wood mass loss show a good agreement with a previous study
190 based on a thermal-gravimetric device coupled with DSC analysis system (Candelier *et al.* (b)
191 2013).

192 **Prediction of decay resistance**

193 Durability of untreated and heat wood were investigated with various brown rot and white rot
194 fungi. Similar results are obtained for each fungus: *Coriolus versicolor* (CV), *Gloeophyllum*
195 *trabeum* (GT), *Coniophora puteana* (CP) and *Poria placenta* (PP). Higher weight loss was
196 caused by *Poria placenta*, results are presented on the Figure 4. After a 16 weeks fungal
197 exposure, all heat treated samples show an improved decay durability revealed by the measured
198 reduced weight losses, while untreated samples were strongly degraded. Softwood species'
199 weight losses are greater than 22% according to the used fungal species. Zeen oak wood exhibits
200 a higher natural durability, however thermal treatment improves further its decay resistance.

201 According to the determination coefficients (R^2) values comprised between 0.95 and 0.99, the
202 relative area seems to be a good parameter to predict final durability of the studied wood species.
203 Moreover, whatever is the studied wood species, when a mass loss of 12 % is reached, the decay
204 resistance is improved to confer a durability class 3. Similar results have been found by Chaouch

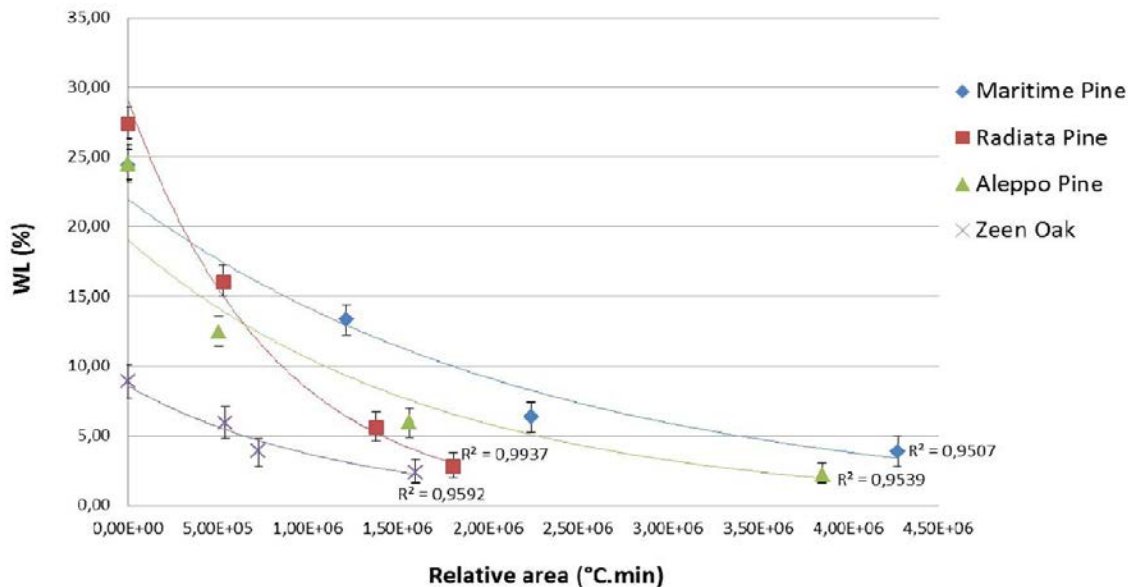


Fig.4. Prediction of Weight Losses due to *Poria placenta* exposure by determination of Relative Area, for different wood species.

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211 *et al.* (2010) indicating that treatment intensity represented by mass loss comprised between 10
212 and 12 % improves significantly the decay resistance of several hardwood and softwood species.

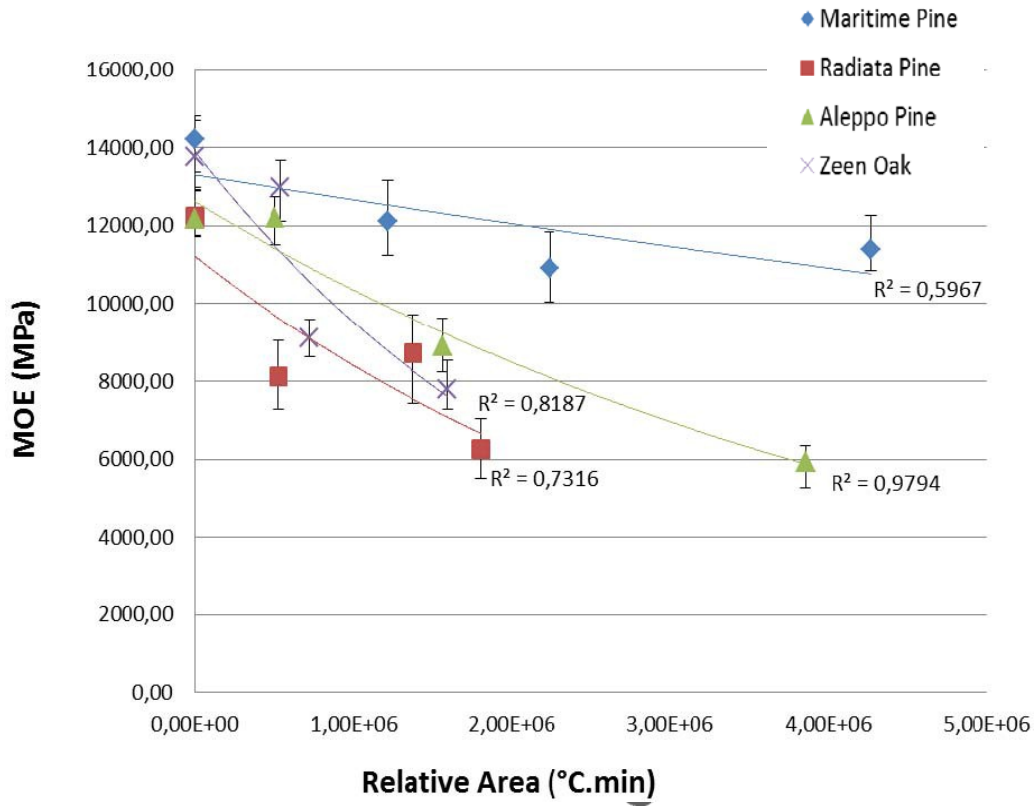
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214 Evaluation of mechanical properties

215 Whatever is the wood species nature, mechanical properties are modified by the thermal
216 treatment. Results indicate that, modulus of elasticity (MOE) is less affected after heat treatment
217 comparatively to the modulus of rupture (MOR), while Brinell hardness is only slightly affected.
218 Similar results have been found by (Yildiz *et al.* 2006). Moreover, the decrease of these three
219 mechanical properties seems to be correlated to the relative areas introducing the treatment
220 intensity (Figures 5-7).

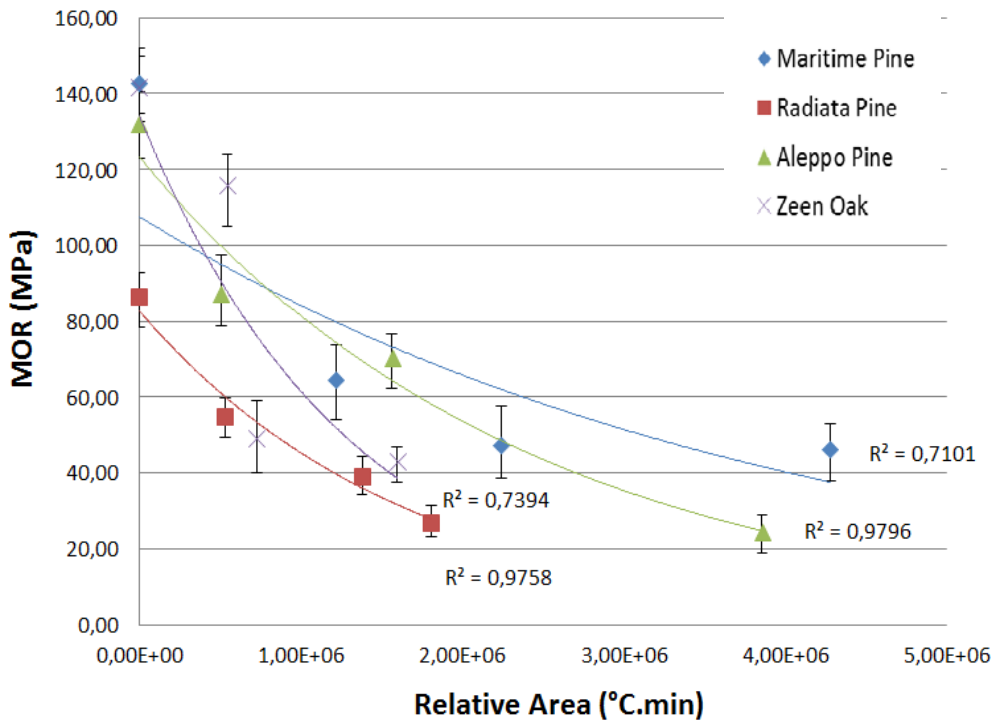
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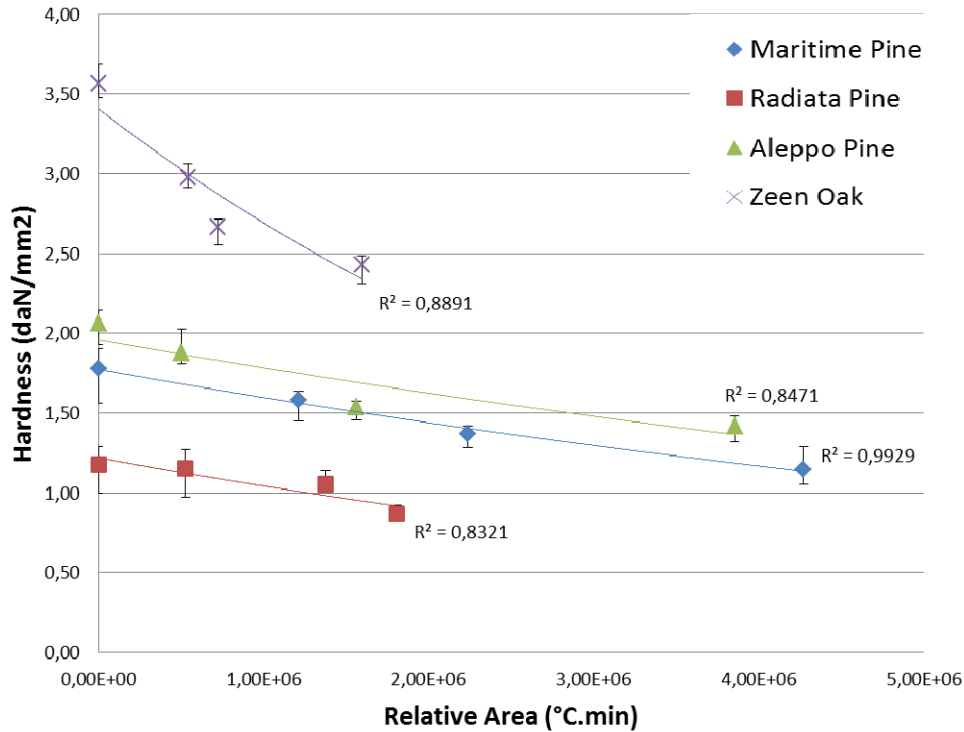
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Fig.5. Determination of bending MOE by Relative Area values, for different wood species.



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Fig.6. Determination of bending MOR by Relative Area values, for different wood species.



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233 **Fig.7. Determination of Brinell Hardness by Relative Area values, for different wood species.**
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235 Previous studies have indicated that MOE and MOR in Bending strength decrease as a function
236 of the increased treatment severity (Mburu *et al.* 2008). In addition, the influence of heat
237 treatment on different strength properties is not proportional (Boonstra *et al.* 2007). These
238 mechanical modifications depend on the wood species nature (Arnold 2010) but also on the
239 natural defects, such as knots, resin pockets. Wood strength properties appeared to be affected by
240 the heat treatment (Boonstra *et al.* 2007). These observations may explain the scatter of results
241 and consequently the lower value of the determination coefficients ($0.60 < R^2 < 0.98$, Figures 5-
242 6).

243 Concerning Brinell hardness properties, Hardness decreases as a function of the increased
244 treatment intensity (Unsal *et al.* 2003) and the influence of the wood nature on this hardness

245 weakening is more pronounced (Figure 7). Results indicate that treatment severity causes higher
246 hardness degradation on the zeen oak than the other softwood species. Indeed, although zeen oak
247 wood had the highest hardness value for control samples, its hardness reduction was also larger
248 than for any other species considered in this work. Similar results have been found through
249 previous studies (Priadia and Hiziroglu 2013). They found also that, in the oak wood, hardness
250 is more degraded by the heat treatment intensity than in other wood species as mindi, mahogany
251 and pine woods. Extreme porous structure along with high extractive amount of oak would be
252 considered for such findings. Additionally, SEM microscopic analyses (Priadia and
253 Hiziroglu 2013) have shown that in the heat treated oak wood there are more cracks and
254 distorted parts than in the heat treated pine. That observation can explain the higher oak wood
255 hardness sensibility to thermal degradation compared to other species. Further studies on the
256 relative areas could provide additional information for industrial applications giving
257 recommendation about the heat treatment cycle consumptions, necessary for treat thermally a
258 considered wood species to obtain desired quality of the final material.

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CONCLUSION

261 Relative area representative to heat treatment intensity seems to be a good indicator to predict
262 wood mass loss due to the thermal degradation. This parameter can be used also to estimate the
263 final product quality. Indeed, relative area appears to be a good means to predict the durability
264 improvement after a thermal modification of wood using a conduction process. In spite of less
265 important correlation coefficients, mechanical properties seem to be related to the relative areas.
266 Heat treated woods presents lower MOR and MOE in bending and lower Brinell hardness
267 comparatively to control wood samples. Between the three investigated mechanical properties,

268 MOR was the most sensitive property to the heat treatment conditions. However, reduction of
269 these properties seems to be correlated with the relative area. Finally, the utilization of the
270 relative area, as indicator of decay resistance and mechanical properties of heat treated wood,
271 could be investigated for other industrial wood thermal modification processes such as
272 Thermowood®. While similar correlations as these found in our study could be transposed to
273 other industrial convection processes. The relative area could be a means to control and predict
274 heat-treated wood quality.

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