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2 [221X2013000200010](http://www.scielo.cl/scielo.php?script=sci_arttext&pid=S0718-221X2013000200010)

## 3 4 **Chemical changes of heat treated pine and eucalypt wood monitored** 5 **by FTIR** 6

### 7 **Abstract**

8 A hardwood, *Eucalyptus globulus* Labill., and a softwood *Pinus pinaster* Aiton., were heat treated at  
9 temperatures between 170 and 210°C in an oven and in an autoclave. The samples were pre-extracted with  
10 dichloromethane, ethanol and water and ground prior to Fourier Transform Infrared (FTIR) spectroscopic  
11 analysis.

12 The heat treatment caused significant changes in the chemical composition and structure of wood, in  
13 lignin and polysaccharides. Hemicelluloses were the first to degrade as proved by the initial decrease of the 1730  
14  $\text{cm}^{-1}$  peak due to the breaking of acetyl groups in xylan. Hardwood lignin changed more than softwood lignin,  
15 with a shift of maximum absorption from 1505  $\text{cm}^{-1}$  to approximately 1512  $\text{cm}^{-1}$  due to decrease of methoxyl  
16 groups, loss of syringyl units or breaking of aliphatic side-chains. The macromolecular structure becomes more  
17 condensed and there is a clear increase of non-conjugated (1740  $\text{cm}^{-1}$ ) in relation to conjugated groups (1650  $\text{cm}^{-1}$ ).  
18 However, the changes induced by the thermal treatment are difficult to monitor by FTIR spectroscopy due to  
19 the different chemical reactions occurring simultaneously.

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21  
22 **Keywords:** *Eucalyptus globulus*, FTIR, Heat treatment, *Pinus pinaster*

### 23 24 **Introduction**

25 Heat treatment is one of the processes for modifying the wood with greater  
26 commercial success. There are different treatments: the Thermowood® process, originated in  
27 Finland, uses steam (Viitanen et al. 1994), the Plato® process, developed in the Netherlands,  
28 uses a combination of steam and heated air (Tjeerdsma et al. 1989), the Retiwood® process,  
29 of French origin, uses an inert gas (Dirol and Guyonnet 1993), the OHT® from Germany,  
30 uses hot oil (Sailer et al. 2000) and the Perdure® process, initially developed in France but  
31 later sold to a company from Canada (Kocafe et al. 2008a) uses steam.

32 Heat treatments lower the equilibrium moisture content of wood (Jämsä and  
33 Viitaniemi 2001; Wang and Cooper 2005; Esteves et al. 2007a, b; 2008a), increase its  
34 dimensional stability (Viitaniemi et al. 1997; Yildiz 2002. Wang and Cooper 2005. Esteves et  
35 al. 2007 a, b), and increase its durability (Dirol and Guyonnet 1993. Kamdem et al. 2002) and  
36 its darkness (Mitsui et al. 2001; Bekhta and Niemz 2003; Esteves et al 2008c). The main  
37 disadvantage of these heat processes is the reduction of the wood mechanical strength  
38 properties, such as static and dynamic bending strength (Yildiz 2002; Esteves et al. 2007 b)  
39 and resistance to compression (Unsal and Ayrilmis 2005).

40 There are chemical changes in the the wood during heating. They start by  
41 deacetylation of hemicelluloses followed by depolymerization catalysed by the released acetic

42 acid (Tjeerdsma et al. 1998; Sivonen et al. 2002; Nuopponen et al. 2004). Simultaneously  
43 hemicelluloses undergo dehydration with the decrease of hydroxyl groups (Weiland and  
44 Guyonnet 2003). In accordance with Esteves et al. (2008 b) hemicelluloses are affected first,  
45 followed by cellulose and lignin.

46 FTIR is widely used in quantitative and qualitative analysis of wood because of its  
47 capacity to give information on the presence of functional groups, on composition and on  
48 some specific structural features.

49 The main objective of this paper was to track the chemical changes occurring along  
50 the heat treatment (two different treatments, one with hot air and the other with steam) of a  
51 hardwood (*Eucalyptus globulus*) and a softwood (*Pinus pinaster*) by FTIR.

52

### 53 **Material and methods**

54

55 Two of the most important tree species in Portugal were tested: the hardwood  
56 *Eucalyptus globulus* Labill. and the softwood *Pinus pinaster* Aiton.. The pine samples were  
57 taken from the sapwood of a 40 year old tree from the Portuguese region of Águeda. For the  
58 eucalypt samples only heartwood was used from a tree with approximately 1 m in diameter,  
59 from the same region. The samples were treated in an oven and in an autoclave under several  
60 operating conditions.

61 Cubic samples were prepared, with 40 mm edge, free from knots, resin canals or other  
62 singularities, with faces parallel to radial, tangential and longitudinal directions. The samples  
63 were stabilized during three weeks in a room conditioned at 50% relative humidity and 20°C.  
64 The equilibrium moisture content and the mass of all samples were determined.

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### 67 **Oven heat treatments**

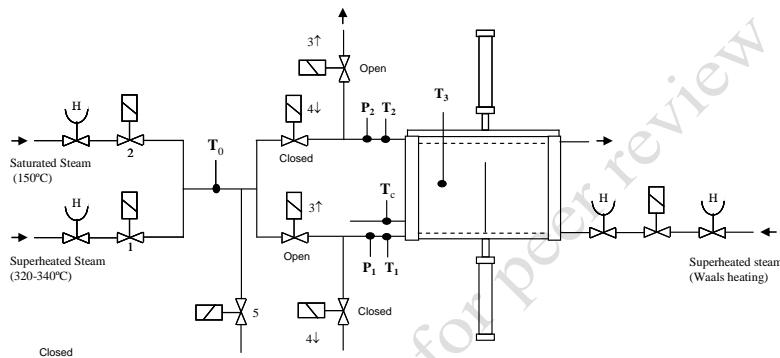
68 The stabilized samples were treated in a Selecta 125 litre oven without forced  
69 convection but with an outlet for gases exhaustion. The trials were conducted in the presence  
70 of air during 2, 6, 12 and 24 h, at 170°C and 180°C. The time to reach the treatment  
71 temperature was one hour. Four samples were used in each test, making up a total of 32  
72 samples for each species. At the end of the heat treatment all samples remained for one hour  
73 in a desiccator and were weighted. The mass loss was determined for each sample in relation  
74 to its initial dry mass in accordance with:

75  $\text{Mass loss (\%)} = (\text{dry mass} - \text{treated mass}) / \text{dry mass} * 100$

76 where the dry mass is the mass of the specimen without treatment, and the treated mass  
77 corresponds to the dry mass of the specimen after heat treatment.

### 78 Autoclave heat treatment

79 The heat treatment in autoclave was carried out in an industrial prototype (Fig. 1),  
80 used for the production of expanded cork agglomerates, installed in an industrial plant of the  
81 Amorim Group located in Silves, Portugal.



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Figure 1. Autoclave used in the heat treatment in the absence of oxygen.

The autoclave (1 m<sup>2</sup> x 0.5 m in height), is divided into two parts by a metal plate placed vertically. The heating was achieved by superheated steam jacket as well as a mixture of superheated and saturated steam (Figure 1) from bottom to top. Since the experiments were made with a free autoclave volume, without any flow resistance, the steam rises vertically through the plate holes but with a preferentially horizontal direction from left to right with some projection against the wall on the right side, rising and moving then to the left.

Tests were performed at normal pressure and temperatures between 190°C and 210°C for 2, 6 and 12 h. It was not possible to test the samples at lower temperatures since the minimum working temperature for the autoclave was 190°C. The heating in the autoclave was done slowly up to 130°C through the sleeve and between 130°C and the working temperature the heating was quick and done with a mixture of saturated and superheated steam introduced inside the autoclave. The temperature of the treatment was maintained through the heating by the autoclave sleeve. The samples were taken from the autoclave after the treatment and placed in a desiccator. The mass loss was determined for each sample in relation to its initial dry mass as mentioned before.

110 For FTIR analysis, samples with approximately the same mass loss were chosen for  
111 both species and treatments. For each treatment, at least three samples were chosen, one with  
112 mass loss less than 1%, another one with mass loss around 3% which is generally considered  
113 the necessary mass loss to obtain a good stability, and a higher mass loss. For eucalypt treated  
114 in the autoclave a sample with mass loss less than 1% could not be obtained because all of the  
115 samples had a higher mass loss due to the treatment.

116

### 117 **FTIR Analysis**

118 Treated and untreated samples were cut into small pieces and then ground separately  
119 in a knife mill Retsch SMI, followed by a Thomas mill. The crushed material was subject to a  
120 screening using a Retsch AS200basic with 40, 60 and 80 mesh sieves. The sieving was  
121 carried out during a period of 20 minutes at a speed of 50 rpm. The sample was separated into  
122 4 fractions (>40, 40-60, 60-80 and <80 mesh). The samples from the 40-60 fraction were then  
123 extracted with dichloromethane, ethanol and water and air dried, according to Tappi Standard  
124 (T 264 om-88). After that 200 mg of air-dried wood were weighted, placed in an oven at 60°C  
125 overnight. The next day the samples were ground in a ball mill (Mixer Mill MM2, Retsch) for  
126 30 min at maximum power and left in a desiccator over phosphorus pentoxide. Heat treated  
127 pine and eucalypt wood samples with similar mass losses were chosen to collect the spectra.  
128 One spectrum was collected for each treatment-time-species combination.

129 The spectra were obtained with 1.50 to 1.55 mg of material with 200 mg of dry KBr  
130 ground in a ball mill (Mixer Mill MM2, Retsch) for 20 s. Disk (13 mm in diameter) were  
131 formed on a 10 tons load hydraulic press. The sample and reference spectra were obtained  
132 with 32 scans in a Bio-Rad FTS spectrometer 165 with a DTGS detector at 4 cm<sup>-1</sup> resolution  
133 for the 500-4000 cm<sup>-1</sup> range. As reference we used the empty sample compartment. The  
134 spectra were analysed with the program OPUS (Bruker), fixing the baseline on 20 points. No  
135 normalization was made since no band stayed unaltered throughout the treatment. To clarify  
136 some results the band height ratio between 1740 and 1650 cm<sup>-1</sup> was determined according to  
137 Faix and Böttcher (1992).

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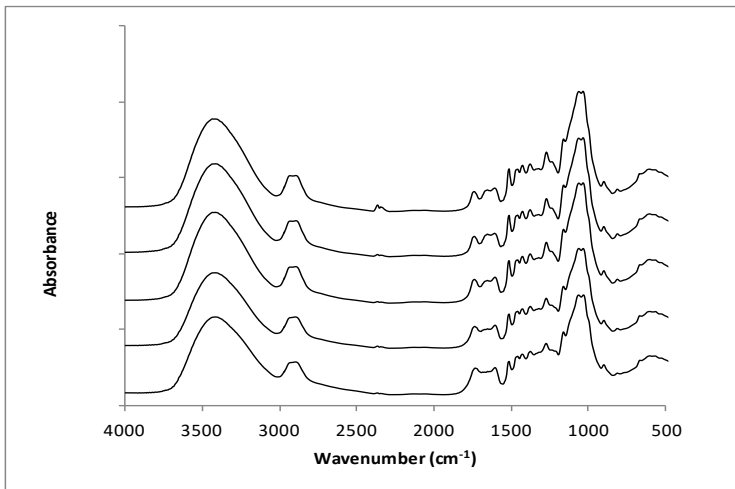
### 139 **Results and Discussion**

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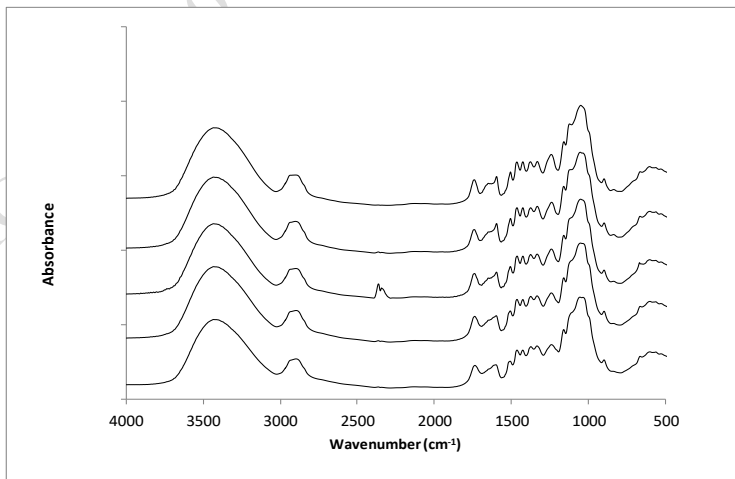
141 Figures 2 and 3 present the FTIR spectra of pine and eucalypt wood without treatment  
142 and after heat treatment in the oven. Eucalypt wood treated at 170°C for 2, 6, 12, and 24 h had

143 mass losses of 0.1%, 1.1%, 2.7% and 3.7%, respectively. While pine wood treated at 180°C  
144 during 2, 6, 12, and 24 h had mass losses of 0.8%, 1.4%, 4.0% and 7.4%, respectively.

145 Figures 4 and 5 present the FTIR spectra of pine and eucalypt wood without treatment  
146 and after treatment in autoclave. Eucalypt wood treated at 190°C during 2 and 12 h had mass  
147 losses of 4.8% and 9.0% respectively. While pine wood treated at 190°C during 2 and 6 h and  
148 at 210°C during 12 h had mass losses of 0.4%, 3.5% and 13.2% respectively. In order to show  
149 more than one spectrum in each figure a shifting in the y axis was made.



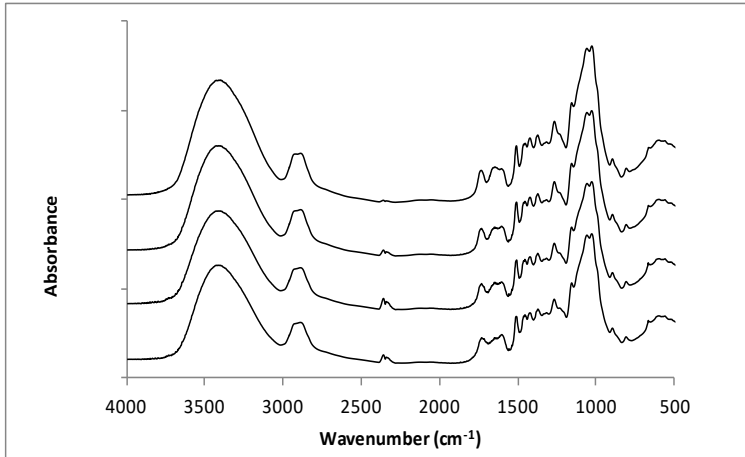
150  
151 **Figure 2.** FTIR spectra of pine wood: from top to bottom without treatment initial and after  
152 treatment in an oven at 180°C for 2 h, 6 h, 12 h and 24 h



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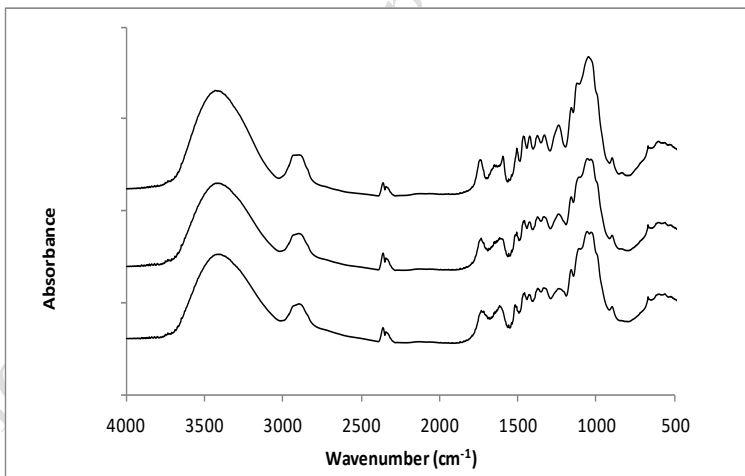
154 **Figure 3.** FTIR spectra of eucalypt wood: from top to bottom without treatment initial and  
155 after treatment in oven at 170°C for 2 h, 6 h, 12 h and 24 h



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157 **Figure 4.** FTIR spectra of pine wood: from top to bottom without treatment initial and  
158 after treatment in autoclave at 190°C for 2 h, 6 h, and at 210°C for 12 h

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161 **Figure 5.** FTIR spectra of eucalyptus wood: from top to bottom without treatment initial and  
162 after treatment in autoclave at 190°C for 2 h and 12 h

163 Table 1 presents the most important bands that are observed in an infrared spectrum of  
164 wood and their assignment to functionality.

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168 **Table 1.** Main bands of infrared spectrum of wood and their assignment to functionality

Wavenumber (cm <sup>-1</sup> )	Functionality	Vibrating type
3400	O-H of alcohols, phenols and acids	O-H stretching <sup>1,2</sup>
2970-2850	CH <sub>2</sub> , CH- and CH <sub>3</sub>	C-H stretching <sup>1,2</sup>
1750-1720	C=O of esters, ketones, aldehydes and acids	C=O stretching, non-conjugated <sup>1,2</sup>
1700-1550	Conjugated C=O and C=C	Conjugated C = O stretching, and C=C stretching <sup>1,2</sup>
1600	Aromatic ring	Benzene ring stretching vibrations <sup>1,2</sup>
1515-1500	Aromatic ring	Benzene ring stretching vibrations <sup>1,2</sup>
1460	CH	C-H deformations <sup>2</sup>
1420	Aromatic ring and CH	Benzene skeletal combined with C-H deformations <sup>1,2</sup>
1240-1330	Lignin S and G units and OH	C-O stretching and bending OH <sup>1,2</sup> antisymmetric stretching vibration of the acetyl ester groups
1140	G- Guaiacyl lignin and C-O	C-H deformations in G lignin and C-O stretching <sup>3</sup>
1128	S- Syringyl lignin and C-O	C-H deformations in S lignin and C-O stretching <sup>1,3</sup>
1025-1035	C-O-C	Deformation <sup>1,2</sup>
897	anti-symmetric out-of-phase stretching in pyranose ring	stretching in pyranose ring <sup>1,2</sup>

169 <sup>1</sup> Rodrigues et al. (1998); <sup>2</sup> Mitchell and Higgins (2002) <sup>3</sup> Faix (1991)

170 The differences between spectra from untreated and heat treated wood were difficult to  
 171 interpret since there are several reactions occurring at the same time. Nevertheless, there were  
 172 changes in the FTIR spectra of wood with the heating treatments even for the mildest  
 173 conditions corresponding to small mass losses, as can be seen in the spectrum of eucalypt  
 174 treated in oven (Figure 3) at 170°C during 2 h, corresponding to 0.1% mass loss. Even though  
 175 there aren't significant changes from untreated wood a small decrease of the 1740 cm<sup>-1</sup> peak

176 was noticeable. With an increase in mass loss all of the wood compounds were affected  
177 leading to several changes in the spectrum.

178 It is a well known fact that chemical changes due to heat treatment start by  
179 deacetylation followed by depolymerization catalysed by the released acetic acid (Tjeerdsma  
180 et al 1998; Sivonen et al 2002; Nuopponen et al 2004). At the same time there is a  
181 carbohydrate dehydration that reduces accessible OH groups (Weiland and Guyonnet 2003)  
182 and leading to the formation of furfural and hydroxymethylfurfural (Tjeerdsma and Militz  
183 2005). Lignin bonds are cleaved, resulting in a higher concentration of phenolic groups  
184 (Kollmann and Fengel 1965). The increased reactivity leads to lignin autocondensation and  
185 condensation reactions with aldehydes.

186 The FTIR spectra of heat-treated pine and eucalypt wood (Figures 2-5) showed a  
187 broadening to lower wavenumbers of the band at 3430 cm<sup>-1</sup> corresponding to the O-H  
188 stretching vibration from alcohols (3600-3300 cm<sup>-1</sup>) and carboxylic acids (3300-2500 cm<sup>-1</sup>),  
189 present either in polysaccharides and lignin. We suggest that this broadening might be due to  
190 the increase in carboxylic acids due to primary OH oxidation and/or hydrolysis of acetyl  
191 groups from hemicelluloses. Moreover the change of O-H stretching frequencies can also be  
192 due to the modification of cellulose crystallinity influenced by dehydration effects (Moharram  
193 and Mahmoud 2008, Spiridon et al. 2011). Even though O-H stretch due to polysaccharides  
194 should decrease, at the same time O-H from phenolic groups in lignin increases since it is a  
195 well known fact that the lignin percentage increases due to carbohydrate degradation (Esteves  
196 et al. 2011).

197 The two bands at 2900-2800 cm<sup>-1</sup> are composed by the overlapping of the stretch  
198 asymmetric vibrations of -CH<sub>2</sub>- (generally around 2935-2915 cm<sup>-1</sup>) and -CH<sub>3</sub> (2970-2950 cm<sup>-</sup>  
199 ) and by the overlapping of stretch symmetric vibrations of -CH<sub>2</sub>- (2865-2845 cm<sup>-1</sup>) and -  
200 CH<sub>3</sub> (2880-2860 cm<sup>-1</sup>). Normally the asymmetric band presents a higher absorptivity. The  
201 apparent shift in frequency for the maximum of CH band is due to structural and relative  
202 composition changes, namely changes at cellulose crystallinity level which influences the C-  
203 H and O-H stretch frequencies (Moharram and Mahmoud 2008, Spiridon et al. 2011), and  
204 changes in the relative importance of lignin methoxyl groups for which the CH<sub>3</sub> stretching  
205 vibrations have lower CH stretching frequencies (Coates, 2000). If the OCH<sub>3</sub> increases by  
206 reduction of the carbohydrates this implies that the contribution of the OCH<sub>3</sub> becomes larger  
207 and the consequence is that we can see that the right shoulder becomes maximum. Although  
208 the asymmetric/symmetric stretch of methylene group (-CH<sub>2</sub>) appears at slightly lower

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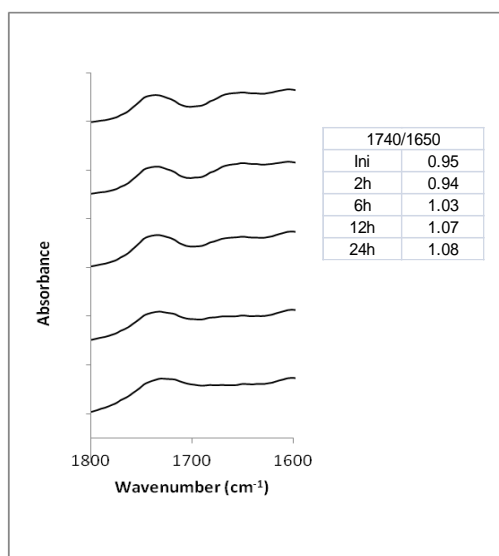
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210 wavelengths this does not necessary mean that there is an increase in methylene groups at the  
211 expense of methyl groups.

212 The C=O linkage exhibits strong absorptions in FTIR spectra between 1750 and 1700  
213  $\text{cm}^{-1}$ , and the precise wavenumber depends of the functional group (carboxylic acid: at about  
214 1725-1700  $\text{cm}^{-1}$ ; ester, ketone: 1725-1705  $\text{cm}^{-1}$ , aldehyde: 1740-1720  $\text{cm}^{-1}$ ) and of its  
215 structural location, with lower wavenumbers for conjugated C=O. According to Mitchell and  
216 Higgins (2002), the band around 1730  $\text{cm}^{-1}$  is almost exclusively due to the carbonyl groups  
217 of acetoxy groups in xylan. In the spectra of eucalypt and pine oven treated wood (Figures 2  
218 and 3) this band decreased initially but for longer treatments the band increased, shifting to  
219 smaller wavenumbers. The decrease at the beginning of the heat treatment (with mass losses  
220 around 1%) might be due to the breaking of acetyl or acetoxy groups in xylan. Similar results  
221 were obtained by Tjeerdsma and Militz (2005) after the first hydrothermal step of the Plato  
222 process and by Kocaefe et al. (2008b) with wood treated by the Perdure process. In the  
223 spectra of wood treated in autoclave (Figures 4 and 5) there was no initial decrease but only  
224 an increase and shifting to about 1730  $\text{cm}^{-1}$ . A possible reason for the absence of the initial  
225 decrease in these spectra is that the smaller mass losses for autoclave heat treated wood are  
226 around 4-5 % and the cleavage of acetyl groups had already occurred, possible around 1-2%  
227 mass loss. At these mass losses (4-5%) the decrease can no longer be seen because another  
228 effect superimposes. The increase and shifting for smaller wavenumbers with increasing  
229 treatment severity may be due to an increase of carbonyl or carboxyl groups in lignin or  
230 carbohydrates by oxidation. This increase was also obtained by Kotilainen et al. (2000) with  
231 *Pinus sylvestris* and *Picea abies* and González-Peña et al. (2009) who attributed this increase  
232 to lignin condensation reactions at the expense of C=C double bonds in conjugated carbonyl  
233 groups in lignin, vibrating at 1654  $\text{cm}^{-1}$ . Tjeerdsma and Militz (2005), who studied the FTIR  
234 spectra of holocellulose and lignin of heat-treated *Fagus sylvatica* and *Pinus sylvestris*,  
235 concluded that the increase of the 1740  $\text{cm}^{-1}$  band was due only to the lignin as there was no  
236 increase in holocellulose. These authors considered this increase to be due to the occurrence  
237 of esterification when the existent acid reacts with the hydroxyl groups of the cell-wall  
238 material. If esterification occurs the band at 1240  $\text{cm}^{-1}$  should also increase due to  
239 antisymmetric stretching vibration of the acetyl ester groups which with our samples doesn't  
240 happen. Nevertheless since this is a composed band the eventual increase could be overlapped  
241 by the decrease of other compound. Li et al. (2002) studied the heat degradation of lignin in  
242 hardwood and softwood and obtained an increase in the peak at 1720  $\text{cm}^{-1}$  with increasing  
243 temperature, which they concluded to be due to the production of C=O bonds in lignin

244 To better understand what happens between 1800 and 1600  $\text{cm}^{-1}$  wavenumber Figure 6  
245 shows this range of Figure 2 in detail (Pine oven treated wood) and presents also the ratio of  
246 the band heights at 1740 and 1650  $\text{cm}^{-1}$ . In this figure an initial decrease followed by an  
247 increase of the 1740  $\text{cm}^{-1}$  band in relation to 1650  $\text{cm}^{-1}$  band can be seen. The maximum of  
248 the 1740  $\text{cm}^{-1}$  band shifts from the initial point around 1738  $\text{cm}^{-1}$  to about 1729  $\text{cm}^{-1}$ .

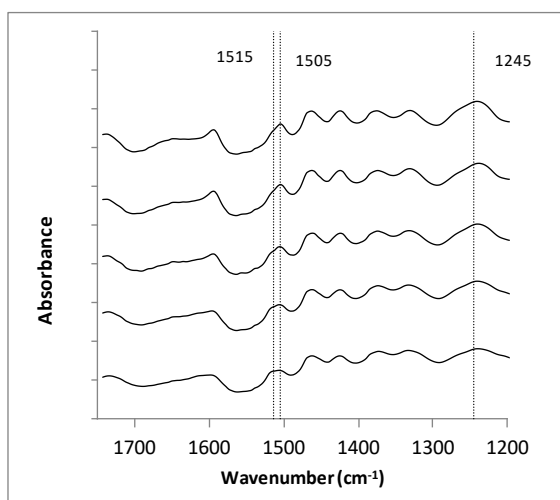


249 **Figure 6.** FTIR spectra of pine wood in the wavenumber range from 1800 to 1600  $\text{cm}^{-1}$ . From top to  
250 bottom: without treatment and after treatment in an oven at 170°C for 2 h, 6 h, 12 h and 24 h and ratio  
251 of band heights at 1740  $\text{cm}^{-1}$  / 1650  $\text{cm}^{-1}$ .  
252

253  
254 The increase of the peak at 1740  $\text{cm}^{-1}$  in relation to 1650  $\text{cm}^{-1}$  means that non-  
255 conjugated C=O groups increased in relation to conjugated groups. Similar results were  
256 described by González-Peña et al. 2009.

257 The band at 1595  $\text{cm}^{-1}$  corresponds to vibrations in the aromatic ring of lignin plus  
258 C=O stretching. The band at 1595  $\text{cm}^{-1}$  broadens to about 1613  $\text{cm}^{-1}$  for eucalypt but not for  
259 pine wood (Figures 2 to 5). This peak broadening suggests that there was an increase of  
260 structural diversity around the aromatic rings, absorbing at a greater range of frequencies. The  
261 height of the band seemed to increase only in the spectrum of eucalypt wood treated in  
262 autoclave (Figure 5). According to Kotilainen et al. (2000) this band increases due to an  
263 increase in the percentage of lignin in treated wood. Li et al. (2002) also obtained an increase  
264 of the peak at 1595  $\text{cm}^{-1}$  in lignin at temperatures between 25°C and 460°C, although no  
265 explanation was given.

266 Aromatic rings exhibit, most of the times, a characteristic band at approximately 1500  
267  $\text{cm}^{-1}$ , corresponding to benzene ring stretching vibrations. This band is very important  
268 because it is at about  $1505 \text{ cm}^{-1}$  for hardwood lignin (Guaiacyl - G and Syringyl - S) and at  
269 about  $1510 \text{ cm}^{-1}$  for softwood lignin (Guaiacyl-G) (Faix 1991). The band at  $1505 \text{ cm}^{-1}$  for  
270 eucalypt wood decreased, shifting to about  $1512 \text{ cm}^{-1}$  (Figure 7). This can be due to the  
271 decrease of the methoxyl groups in lignin which would lead to a lignin more similar to  
272 softwood (G-lignin) or to the loss of S units, since this monomer is generally less condensed  
273 by C-C bonds than guaiacyl monomers and is more prone to be liberated by a thermal  
274 degradation (Faix et al. 1990).



275  
276 **Figure 7.** FTIR spectra of eucalypt wood from top to bottom without treatment and after treatment in  
277 oven at  $170^\circ\text{C}$  for 2 h, 6 h, 12 h and 24 h in the range  $1750\text{-}1200 \text{ cm}^{-1}$

278 The shifting of this band is in agreement to the results presented by Windeisen et al.  
279 (2007) and Kocaefe et al. (2008b), and attributed to the breaking of aliphatic side-chains in  
280 lignin and/or condensation reactions.

281 The band at  $1460 \text{ cm}^{-1}$  corresponds to the asymmetric deformation of C-H bond of  
282 xylan, while the band at  $1420 \text{ cm}^{-1}$  corresponds to the vibration of the aromatic ring of lignin,  
283 but also to the C-H bending in cellulose (Mitchell and Higgins 2002). No consistent variation  
284 was found for the  $1460 \text{ cm}^{-1}$  and  $1420 \text{ cm}^{-1}$  peaks. According to Kotilainen et al. (2000) and  
285 Weiland and Guyonnet (2003) the peaks at  $1460 \text{ cm}^{-1}$  and  $1420 \text{ cm}^{-1}$  increase with heat  
286 treatment. The band at  $1375 \text{ cm}^{-1}$  broadened to smaller wavenumbers but with no consistent  
287 variance. The band at  $1333 \text{ cm}^{-1}$  represents the contributions of all structural components of  
288 wood because it corresponds to C-H bending of polysaccharides which joins the band at  $1327$

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290  $\text{cm}^{-1}$  of S and G lignin condensed units (Faix 1991). There was a clear increase at  $1330 \text{ cm}^{-1}$   
291 corresponding to an increase in lignin condensation. The same was reported by Windeisen et  
292 al. (2007).

293 For eucalypt wood (Figures 3, 5 and 7) the band at  $1245 \text{ cm}^{-1}$ , decreased in height but  
294 broadened which once again confirms the existence of a more condensed structure  
295 (Windeisen et al. 2007; Kocaefe et al. 2008b). According to Kotilainen et al. (2000) this peak  
296 increases, but no explanation was given. The band at  $1140 \text{ cm}^{-1}$  is the result of the sum of the  
297 contribution of C-H deformation in aromatic rings and C-O stretching in primary alcohols.  
298 This band has a shoulder at  $1140 \text{ cm}^{-1}$  in woods with G lignin (Figure 2 and 4) and  $1128 \text{ cm}^{-1}$   
299 in the woods with GS lignin (Figures 3 and 5) (Faix 1991). No consistent variation was found  
300 for this band.

301 The peak at  $897 \text{ cm}^{-1}$ , corresponding to the sugar ring tension, seemed to decrease with  
302 increasing severity of the treatment which is consistent with ring opening (Figures 2 to 5).  
303 Similar results were obtained by Kotilainen et al. (2000) and González-Peña et al. (2009).

304 These results are generally consistent with the chemical changes determined by wet  
305 chemistry for heat treated pine and eucalypt in oven and in autoclave (Esteves et al. 2006;  
306 Esteves et al. 2008b; Esteves et al. 2011). In the beginning of the treatment, hemicelluloses  
307 are the first to degrade, as proved here by the initial decrease of the  $1740 \text{ cm}^{-1}$  peak attributed  
308 to the cleavage of acetyl or acetoxy groups in xylan. The attack on polysaccharides during  
309 heating is clear by the decrease of the peak at  $897 \text{ cm}^{-1}$  corresponding to the pyranose ring  
310 opening. The increase in lignin content that derived from the carbohydrate loss can be seen by  
311 the later increase of the  $1740 \text{ cm}^{-1}$  peak which according to Li et al (2002) is due to the  
312 formation of carbonyl groups in lignin.

313 No significant differences between oven and autoclave treatments were observed. In  
314 the range of the studied thermal treatments and wood mass losses, no influence of air or steam  
315 heating was detected by FTIR analysis. The different chemical reactions occurring at the same  
316 time make the existing differences between spectra very difficult to follow.

317

## 318 **Conclusions**

319

320 The heat treatment caused significant changes in the chemical composition and  
321 structure of wood, by changing polysaccharides and lignin. That can be observed by FTIR  
322 analysis. Hemicelluloses are the first components to degrade due to deacetylation. Hardwood  
323 lignin changes more than softwood lignin, due to demethoxylation, loss of S units or breaking

324 of aliphatic side-chains. The macromolecular lignin structure becomes more condensed with  
325 the presence of non-conjugated/conjugated groups. The changes induced by the thermal  
326 treatment are due to different chemical reactions occurring simultaneously.

327

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331

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