Cellulose

Comparative Study of Historical Woods from XIX Century by Thermogravimetry coupled with FTIR Spectroscopy
--Manuscript Draft--

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1 **Comparative Study of Historical Woods from XIX Century by Thermogravimetry coupled with FTIR**

2 **Spectroscopy**

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4 Giuseppe Cavallaro[a,b*], Aurelio Agliolo Gallitto[a], Lorenzo Lisuzzo[a], Giuseppe Lazzara[a,b]

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6 [a]*Dipartimento di Fisica e Chimica - Emilio Segrè, Università degli Studi di Palermo, Viale delle Scienze, pad. 17,*

7 *90128 Palermo, Italy. E-mail:giuseppe.cavallaro@unipa.it*

8 [b]*Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, INSTM, Via G. Giusti, 9, I-50121*

9 *Firenze, Italy.*

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Abstract

Thermal and structural properties of historical woods from apparatuses of the Historical Collection of the Physics Instruments of the University of Palermo have been investigated by FTIR spectroscopy coupled with thermogravimetric (TG) analysis. Specifically, the wooden portions of apparatuses from XIX century have been studied. The thermal behavior of the wooden materials has been successfully interpreted on the basis of specific indexes determined by the quantitative analysis of the FTIR spectra. The kinetics of the wood pyrolysis have been investigated by using a non-isothermal approach based on model-free isoconversional procedures, such as Kissinger−Akahira−Sunose (KAS) and Friedman methods. Interestingly, the activation energy of the pyrolysis process reflects both the peculiar composition (related to the specific wooden taxon) and the conservation state of the historical woods. The thermogravimetric parameters have been correlated to the lignin index of the woods by proper experimental equations, which can be considered as a novel protocol to estimate the preservation conditions of historical woods from different taxon.

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Introduction

65   Within the Cultural Heritage issues, the preservation of wooden artworks represents a challenging issue for

66   restorators and scientists because of the acidic deterioration of lignin and lignocellulosic polysaccharides (Bugg et al.

67   2011; Dedic et al. 2013; Rasmussen et al. 2017). Recent studies proved that the efficient protection of the wooden

68   structures can be achieved by the consolidation with resins (Cavallaro et al. 2017; Moise et al. 2019), sustainable

69   polymers (Walsh et al. 2017), organosilicon compounds (Broda et al. 2019) and alkaline nanoparticles, such as

70   calcium/magnesium hydroxides (Giorgi et al. 2005; Poggi et al. 2014) and nanotubes filled with antiacid compounds

71   (Cavallaro et al. 2018). Prior to their preservation, the wooden artworks should be properly characterized in order to

72   determine the structural and compositional features of the woods. In this regards, an extensive investigation of the

73   wooden materials can be achieved by using several diagnostics techniques, such as Nuclear Magnetic Resonance

74   (NMR) spectroscopy (Bardet et al. 2002; Žlahtič Zupanc et al. 2019; Iwamoto et al. 2019), X-ray diffraction analysis

75   (XRD) (Carrillo-Varela et al. 2018), Fourier Transform Infrared (FTIR) spectroscopy (Popescu et al. 2007; Emmanuel

76   et al. 2015; Broda and Popescu 2019), Scanning Electron Microscopy (SEM) (Guo et al. 2006; Borysiak 2013; Lin et

77   al. 2018), Atomic Force Microscopy (AFM,) (Notley and Wågberg 2005; Casdorff et al. 2017) and thermal analyses

78   (Cavallaro et al. 2011a; Sebio-Puñal et al. 2012; Blanco et al. 2017; Girometta et al. 2017).

79   FTIR spectroscopy is a suitable and quick method to determine the molecular groups of the wood. Consequently,

80   the analysis of FTIR spectra can provide the effect of the weathering agents on the deterioration of the wood

81   component molecules (cellulose, hemicelluloses and lignin) (Emmanuel et al. 2015). In addition, the crystallinity

82   degree of the cellulose in the wooden materials can be estimated by specific indexes (total crystalline index and later

83   order index) obtained from the quantitative analysis of FTIR data (Carrillo et al. 2018).

84   Among the thermal analysis techniques, thermogravimetry (TG) revealed as an efficient tool for the characterization

85   of wooden samples. It was demonstrated (Janković 2014) that the analysis of TG curves endows to investigate the

86   decomposition processes of the major wooden components. Accordingly, thermogravimetry represents an indirect

87   method for the determination of the wood composition. Wooden samples from different *Eucalyptus* species exhibited

88   distinctive thermal decomposition processes for cellulose (Carrillo-Varela et al. 2018). Furthermore, the maximum

89   water content (MWC) of archaeological woods can be easily obtained by the thermogravimetric investigations

90   (Cavallaro et al. 2011a). The consolidation efficiencies of colophony (Cavallaro et al. 2017) and polyethylene glycols

91   (Cavallaro et al. 2018) towards wooden materials of historical value were estimated by studying the thermal

92   decomposition of treated woods through thermogravimetry.

93   The kinetics of the pyrolysis process of wood biomass samples can be studied by thermogravimetric measurements

94   using both isothermal (Janković 2014) and non-isothermal (Barneto et al. 2011; Mohomane et al. 2017) approaches.

95   Thermogravimetric kinetic studies evidenced the variable degradation state of archaeological and sound woods from

96   different taxa (*Pinus pinaster and Fagus sylvatica L*) on the basis of their activation energies to the pyrolysis process

97   (Cavallaro et al. 2011a). Kinetic analysis of thermogravimetric data allowed to discriminate softwood from hardwood

98   species according to peculiar variations of the activation energy values (Janković 2014).

99   Non-isothermal investigations are based on isoconversional procedures, which are model-free methods that provide

100   the activation energy without any assumptions on the reaction mechanism (Budrugeac et al. 2004; Rotaru 2016, 2017).

101   Based on the mathematical analysis of TG data, the isoconversional procedures are classified in integral and differential

102   methods (Vyazovkin et al. 2014; Budrugeac 2018).

103   Here, we investigated the structural and thermal characteristics of historical woods from apparatuses of the

104   Historical Collection of the Physics Instruments of the University of Palermo, which collects physics instruments of

105   mechanics, acoustic, calorimetry, electromagnetism and optics, dating from the XIX (Agliolo Gallitto et al. 2018), on

106   exhibit at the Department of Physics and Chemistry - Emilio Segrè, in the historical building of via Archirafi 36. In this

107   study, we explored the conservation state of acoustic apparatuses by studying the physico-chemical properties of their

108   wooden parts. Specifically, the samples were characterized through FTIR spectroscopy and thermogravimetry allowing

109   to obtain a complete description of the compositional, structural and thermal features of historical woods. The FTIR

110   and thermogravimetric results were correlated to the specific wood taxon as well as to the preservation conditions of

111   the historical apparatuses. According to the mathematical analysis of TG and FTIR data, this work opens a novel route

112   for the development of suitable protocols to study the conservation state of historical woods with their structural and

113   thermal characteristics.

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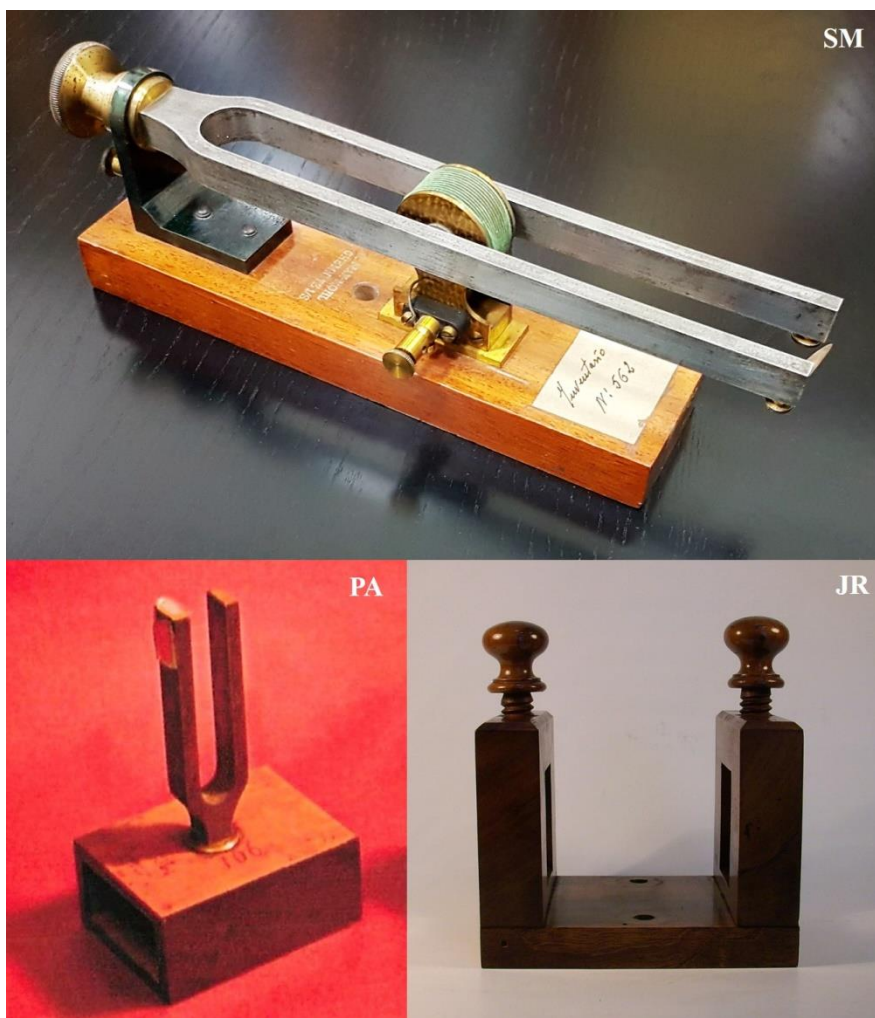115 **Experimental**

116

117 **Materials**

118 Three wooden samples were obtained from apparatuses of the Historical Collection of the Physics Instruments of
119 University of Palermo. In particular, one sample has been extracted from the wooden base of a chronograph tuning
120 forks with electromagnetic drive, one from the wooden resonance box of a tuning forks and one from the support for
121 tuning forks, as summarized in Table 1. As reported in Table 1, the samples differ in the age and in the wood taxon. All
122 the apparatuses (presented in Fig. 1) were manufactured in the XIX century (Agliolo Gallitto et al. 2017). In order to
123 avoid their structural deterioration, the historical wooden items are light protected and kept under controlled
124 environmental conditions. Specifically, relative humidity and temperature are set at ca. 60% and ca. 20 °C,
125 respectively.

126

127 **Table 1.** List of the historical wooden samples

Symbol	Wood taxon	Physics apparatus	Manufacturer	Year
SM	*Swietenia mahagoni*	Chronograph tuning forks with electromagnetic drive	Max Kohl, Germany	1906
PA	*Picea abies*	Tuning forks on resonance box (sound frequency of 768 Hz)	Rudolph Koenig, France	1868
JR	*Juglans regia*	Support for tuning forks	Rudolph Koenig, France	1864

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Fig. 1. Photos of the physics apparatuses from the Historical Collection of the Physics Instruments at University of Palermo.

Methods

Thermogravimetry

Thermogravimetry (TG) experiments were carried out through a Q5000 IR apparatus (TA Instruments) under inert atmosphere. To this purpose, nitrogen flows of 25 and 10 cm^3 min^{-1} were used for the sample and the balance, respectively. The experiments were carried out by heating the sample (ca. 5 mg) from room temperature up to 600 °C. The heating rate (β) was systematically changed in order to investigate the kinetics of the non-isothermal degradation of the wooden historical materials through isoconversional methods. Specifically, five different heating rates (5, 10, 15, 20 and 25 °C min^{-1}) were selected. As reported elsewhere (Blanco et al. 2014), the temperature calibration was conducted by using the Curie temperatures of proper standards (nickel, cobalt, and their alloys).

6

145   Fourier transform infrared (FTIR) spectroscopy

146   Fourier transform infrared (FTIR) measurements were performed at room temperature through a Frontier FTIR

147   spectrometer (PerkinElmer). The spectra were recorded in the range between 450 and 4000 cm^{-1}, while the spectral

148   resolution was set at 2 cm^{-1}. The experiments were conducted on KBr pellets with a low content (< 2 wt%) of milled
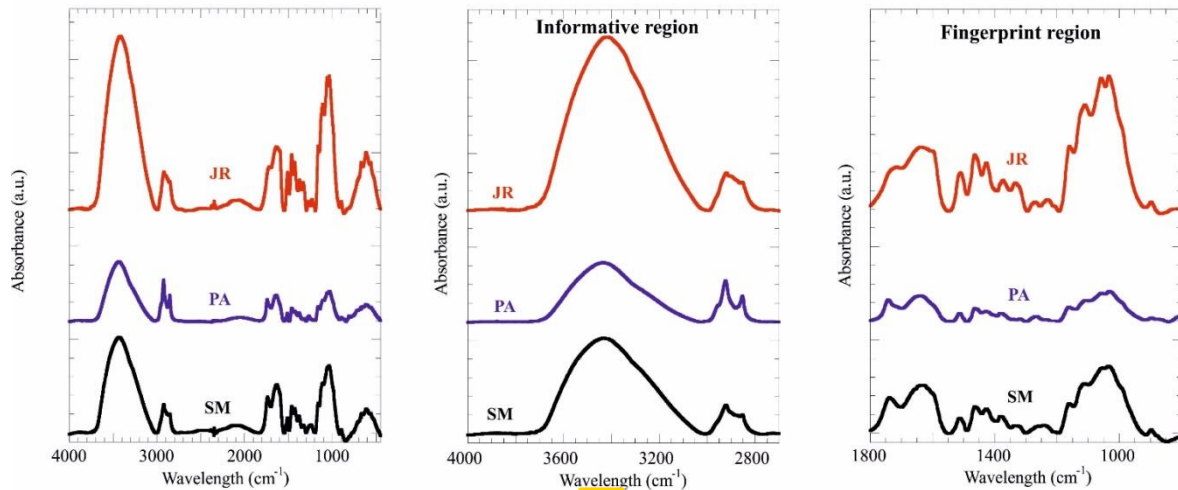
149   wooden sample.

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Results and discussion

153

154 **FTIR spectroscopy**

155 The analysis of FTIR spectra (Fig. 2) provided interesting insights on the composition and conservation state of the
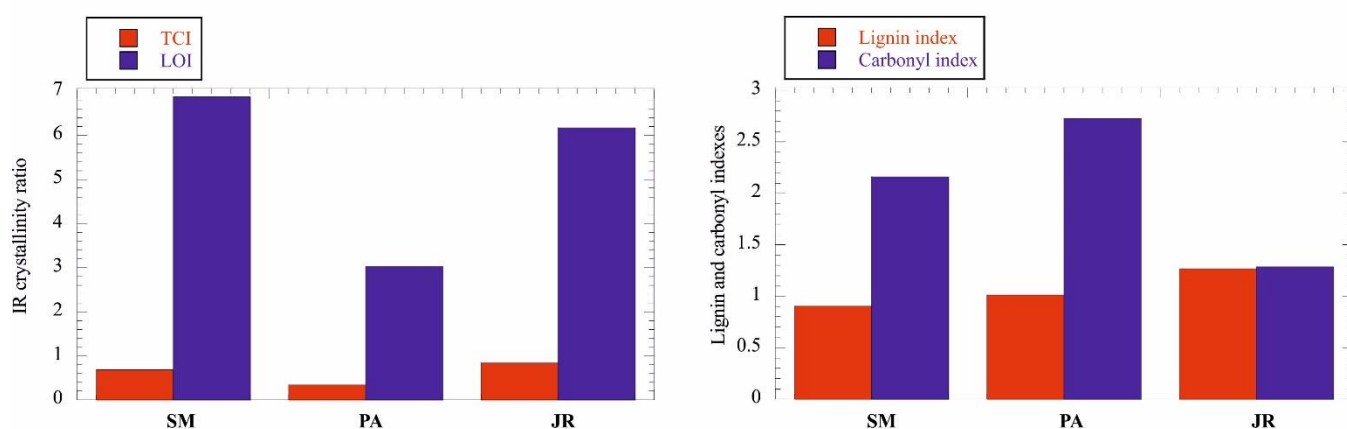
156 investigated wooden samples.

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158

159 **Fig. 2.** FTIR spectra for the investigated wood samples.

160

161   As reported for Eucalyptus species (Carrillo-Varela et al. 2018), FTIR spectra of wooden materials are characterized

162 by two regions on dependence of the wavelength range. As shown in Fig. 2, all the samples present a significant broad

163 peak (centered at ca. 3400 cm^{-1}) in the "informative" region, which refers to the wavelength range between 4000 and

164 2700 cm^{-1}. This peak can be attributed to OH stretching vibration (Fengel 1992; Kondo 1997). Consequently, this

165 signal can be related to the degree of hydrogen bonding between hydroxyl groups in wood components (cellulose,

166 hemicellulose, lignin and water) (Církva et al. 2004; Popescu et al. 2011). Within the "informative" region, we detected

167 a band at ca. 2900 cm^{1}, which is due to asymmetric and symmetric CH stretching (Collier et al. 1997; Schwanninger et

168 al. 2004). Generally, the absorption intensity at 2900 cm^{-1} is used as internal standard for determination of the cellulose

169 structural degree in wooden samples (Poletto et al. 2014; Odabas et al. 2016).

170 Within the wavelength range between 1800 and 800 cm^{-1} ("fingerprint" region), we focused on the following signals

171 characteristic of wood (Carrillo-Varela et al. 2018): 1) C=O stretching vibrations of carboxyl and acetyl groups in

172 hemicellulose (peak centered at 1740 cm^{-1}) 2) C=C stretching of the aromatic ring in lignin (band at 1510 cm^{-1}); 3) CH$_2$

173 bending of cellulose (band at 1430 cm^{-1}); 4) CH bending in cellulose and hemicellulose (band at 1372 cm^{-1}); 5) C-H

174 vibrational mode in cellulose (peak centered at 897 cm^{-1}). The quantitative analysis of the mentioned FTIR signals

175 allowed us to determine specific indexes related to both the cellulose crystallinity and the composition of the wooden

8

samples. Regarding the cellulose crystallinity, we estimated the total crystalline index (TCI) by the ratio between the absorption intensities at 1372 and 2900 cm^{-1}. In addition, we calculated the lateral order index (LOI) by ratio between the bands at 1429 and 897 cm^{-1}. Fig. 3 compares the FTIR crystallinity indexes for the investigated wood samples. We detected that PA presents the lowest TCI and LOI values with respect to those of the other woods (SM and JR), which possess similar cellulose crystallinity. Based on these results, we can state that cellulose in PA exhibits the largest degree of disorder (Carrillo et al. 2004; Poletto et al. 2012).

Fig. 3. Relative crystallinity (TCI and LOI) and lignin/carbonyl indexes determined from the FTIR spectra analysis of the investigated wood samples.

Regarding the wood composition, we determined the lignin and carbonyl indexes as

Lignin index (L.I.) = $(I_{1510\,cm^{-1}})/(I_{1372\,cm^{-1}})$ (1)

Carbonyl index (C.I.) = $(I_{1740\,cm^{-1}})/(I_{1372\,cm^{-1}})$ (2)

It should be noted that both indexes can be used to evaluate the conservation state of historical and archaeological woods (Gupta et al. 2015; Cavallaro et al. 2018). As evidenced by Fig. 3, the investigated wood samples possess different L.I. and C.I. values. We observed that C.I. and L.I. follow the trends PA > SM > JR and JR > PA > SM, respectively. These results highlight that the lignin contribution is not correlated with that of C=O groups.

Thermal properties

The thermal properties of the investigated wood samples were investigated by thermogravimetry. Fig. 4 shows the thermogravimetric curves (obtained at $\beta = 10$ °C min^{-1}) of the historical woods.
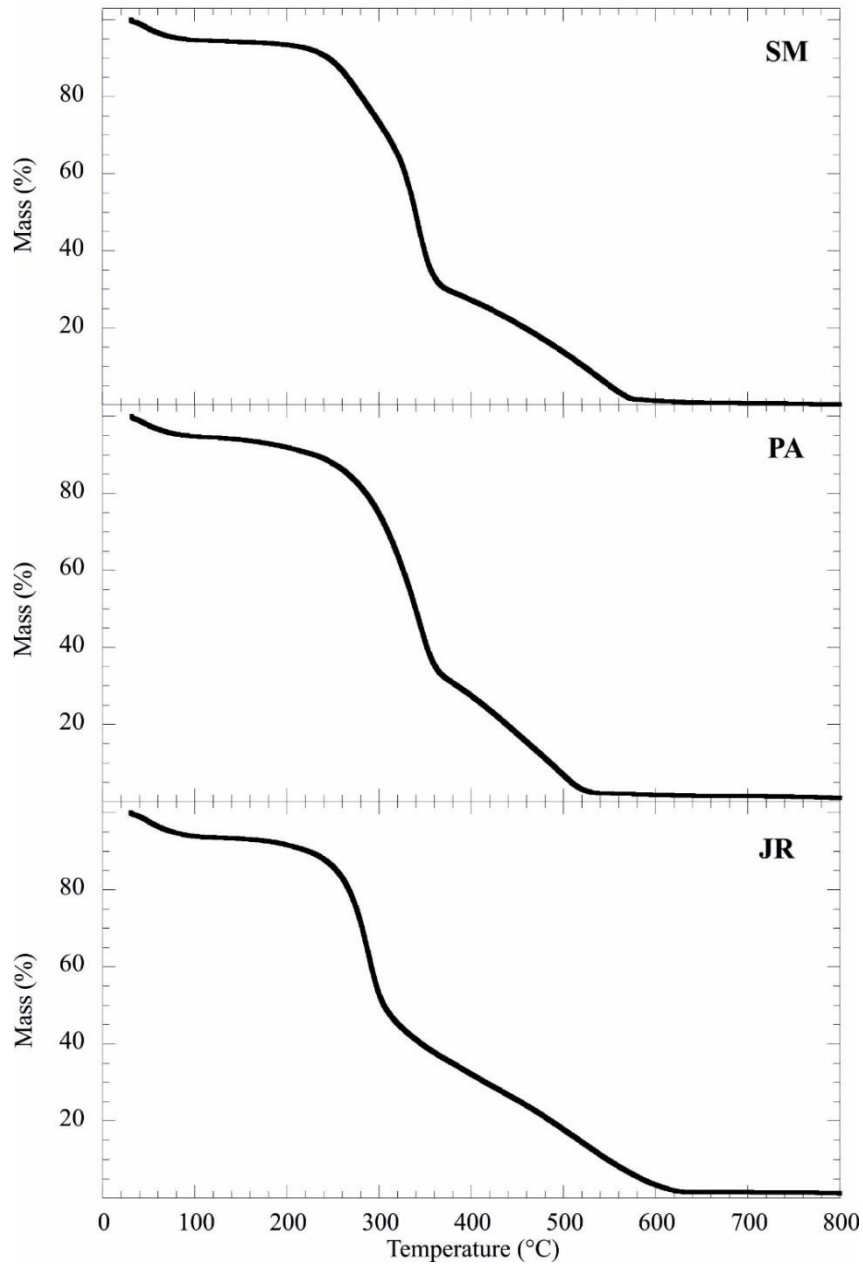
Fig. 4. Thermogravimetric curves of the wood samples.

As a general result, we observed three different mass losses that can be attributed to specific degradation processes of wooden materials. The several mass losses of each wood are collected in Table 2.

Table 2. Mass losses of the historical woods obtained by TG measurements at $\beta = 10$ °C min^{-1}

Wood	ML_{25-150} (wt%)	$ML_{180-380}$ (wt%)	$ML_{380-600}$ (wt%)	$(ML_{180-380})/(ML_{380-600})$	DTG peak (°C)
SM	5.65 ± 0.06	64.6 ± 0.7	28.1 ± 0.3	0.435 ± 0.009	342 ± 3
PA	5.93 ± 0.06	62.0 ± 0.7	28.9 ± 0.3	0.46 ± 0.01	341 ± 3
JR	6.67 ± 0.07	57.6 ± 0.6	31.5 ± 0.3	0.54 ± 0.01	288 ± 3

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208 The first degradation step takes place within the temperature range between 25 and 150 °C as a consequence of the

209 expulsion of the water molecules physically adsorbed into the wood structure. Accordingly, the mass loss at 25-150 °C

210 (ML_{25-150}) is correlated to the moisture content of the sample (Lisuzzo et al. 2019). As evidenced by Table 2, the largest

211 ML_{25-150} was detected for JR, which is the wood with the strongest hygroscopic degree.

212 As expected for the pyrolysis of lignocellulosic materials (Barneto et al. 2011), the historical woods mostly degraded

213 within the temperature interval between 180 and 600 °C (Fig. 3). In particular, we observed two separated mass losses

214 (at 180-380 and 380-600 °C) highlighting that the wood pyrolysis represents a multistep degradation mechanism.

215 Accordingly to literature (Cao et al. 2010; Barneto et al. 2011), the mass losses at 180-380 °C ($ML_{180-380}$) and 380-600

216 °C ($ML_{380-600}$) can be associated to the pyrolysis processes of the wood components, which are hemicellulose, cellulose

217 and lignin. Specifically, the depolymerization of hemicellulose and the cleavage of the glycosidic linkage of cellulose

218 occur between 180 and 380 °C, while lignin degrades in a wider temperature range (from 250 to 600 °C) (Kim et al.

219 2006). On this basis, the ($ML_{180-380}$)/($ML_{380-600}$) ratio could be correlated to the specific composition of the historical

220 wood. As shown in Table 2, the largest ($ML_{180-300}$)/($ML_{380-600}$) ratio was estimated for JR, while SM exhibited the

221 lowest value. These results are consistent with the lignin index data determined through FTIR spectroscopy. The

222 interpretation of the differential thermogravimetric (DTG) curves (Fig. 5) provided a more accurate description of the

223 wood pyrolysis.
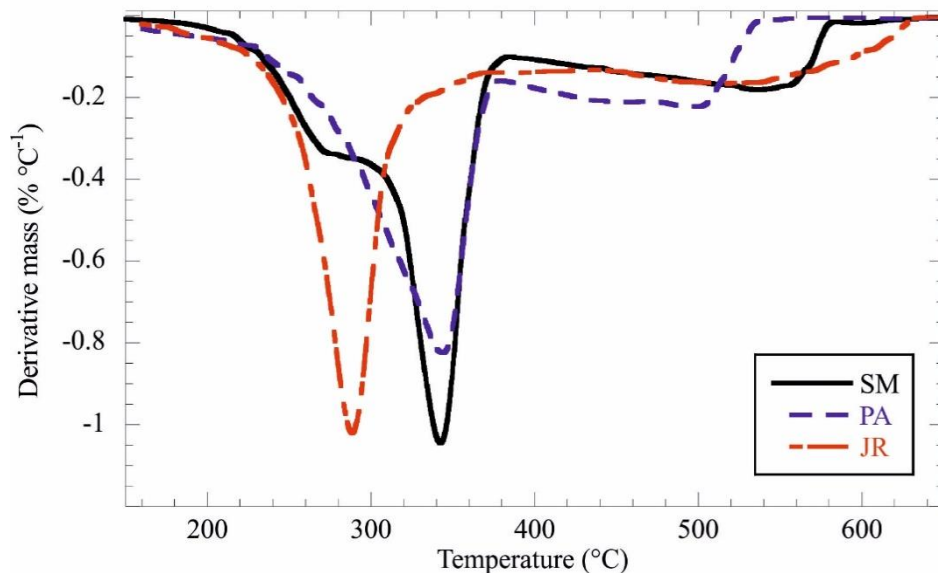
225 **Fig. 5.** Differential thermogravimetric curves of the wood samples.

227 Within the first degradation step, all the samples evidenced a DTG peak that can be attributed to the cellulose

228 degradation. Compared to the other woods, a relevant reduction (ca. 60 °C) of the DTG peak temperature was observed

229 for JR. Namely, cellulose in JR exhibited the lowest thermal stability. In addition to the main peak, the DTG curve of

11

230 SM showed a shoulder at lower temperature (ca. 275 °C), which is due to the hemicellulose degradation. Similar

231 thermal behavior was observed in sapwood of *Pinus* canariensis, which was extensively used in the traditional Canarian

232 architecture (González-Díaz and Alonso-López 2017). Finally, all DTG curves exhibited a broad tail at higher

233 temperature (within the second degradation step) as a consequence of the lignin thermal decomposition.

234

235 **Kinetics of wood pyrolysis**

236 We investigated the kinetic aspects of the wood pyrolysis process by a non-isothermal thermogravimetric study based

237 on model free isoconversional methods, which include both integral and differential procedures (Vyazovkin et al. 2014;

238 Trache et al. 2017). To this purpose, thermogravimetric experiments at five different heating rates were conducted. The

239 data analyses were limited to the temperature interval between 180 and 380 °C, where the pyrolysis of all the wood

240 components occurs. Among the integral isoconversional procedures, the Kissinger−Akahira−Sunose (KAS) method

241 was selected. Literature reports that the KAS method is suitable to investigate the wood pyrolysis (Slopiecka et al.

242 2012; Azizi et al. 2017), the combustion reaction of low-rank coal char (Hu et al. 2018) and the thermal decomposition

243 of natural polymers (Makaremi et al. 2017; Bertolino et al. 2018). The KAS method can be expressed as

244

245 $\ln(\beta/T^2) = \ln(AR/E_a g(\alpha)) - E_a/RT$ (3)

246

247 where A and R are the pre-exponential factor and gas constant, respectively, while $g(\alpha)$ represents the integral

248 conversion function. According to equation 3, we can determine the activation energy (E_a) at each conversion degree

249 (α) by the slope of the ln (β/T^2) vs 1/T plot.

250 Fig. 6 shows the dependence of E_a on α for the pyrolysis of the investigated historical woods.
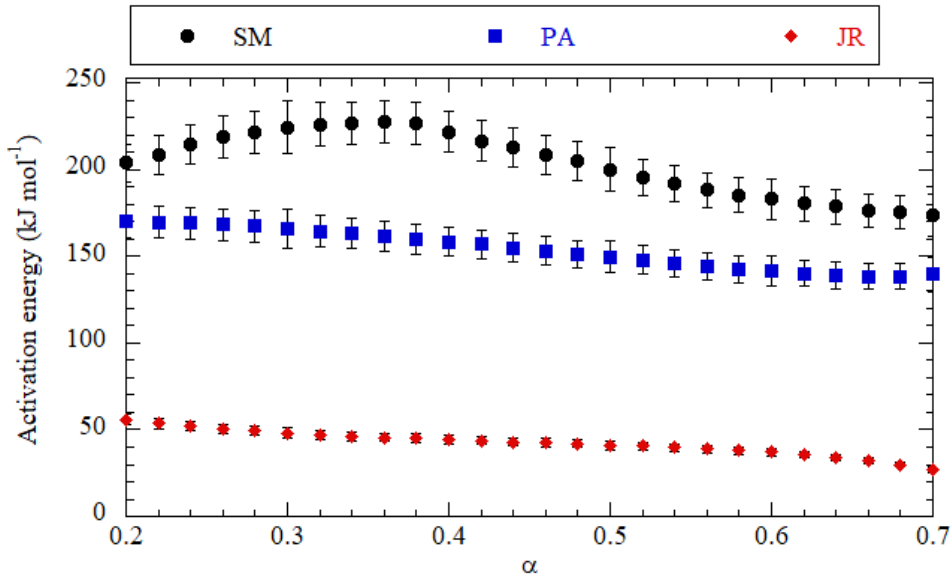
Fig. 6. KAS activation energy as a function of the conversion degree for the wood samples.

We observed that E_a is not significantly influenced by α (ranging between 0.2 and 0.7) for JR and PA, while a small peak (at $\alpha = 0.35$) was detected for SM. The latter might be related to the presence of hemicellulose evidenced by the shoulder in the DTG curve of SM wooden sample (Fig. 5). Interestingly, the historical woods exhibited different E_a values, which reflect variable kinetic properties in the pyrolysis of the wood components. We calculated that the average E_a values are 203, 156 and 43 kJ mol^{-1} for SM, PA and JR, respectively. On this basis, we can state that JR possesses the lowest energetic barrier to the pyrolysis. These results agree with the DTG peak data (Table 2), which revealed that JR is the worst wood in terms of thermal stability under inert atmosphere. According to the TG data, we can assert that JR is the most sensitive wood to the decay and structural deterioration. Therefore, JR needs more accurate protocols for its preservation.

In addition to the KAS method, kinetic studies were carried out using the differential Friedman approach, which was successfully employed for the investigation of the pyrolysis processes in pinewood (Mishra et al. 2015), beechwood and flax shives (Abdelouahed et al. 2017). Furthermore, the Friedman method revealed as a suitable model free procedure for the kinetic analysis of the thermal decomposition of modified cellulose, such as methylcellulose (Bertolino et al. 2016) and hydroxypropylcellulose (Cavallaro et al. 2011b). The Friedman method is expressed by the following equation

$$\ln(\beta \cdot da/dT) = \ln(A \cdot f(\alpha)) - E_a/RT \qquad (4)$$

13

272 where f(α) is a function of the conversion degree that is related to the reaction mechanism. Based on the equation 4, the

273 specific slope of the $\ln(\beta \cdot da/dT)$ vs $1/T$ function provides E_a at variable α. The E_a vs α trends obtained by the

274 Friedman equation are presented in Fig. 7.
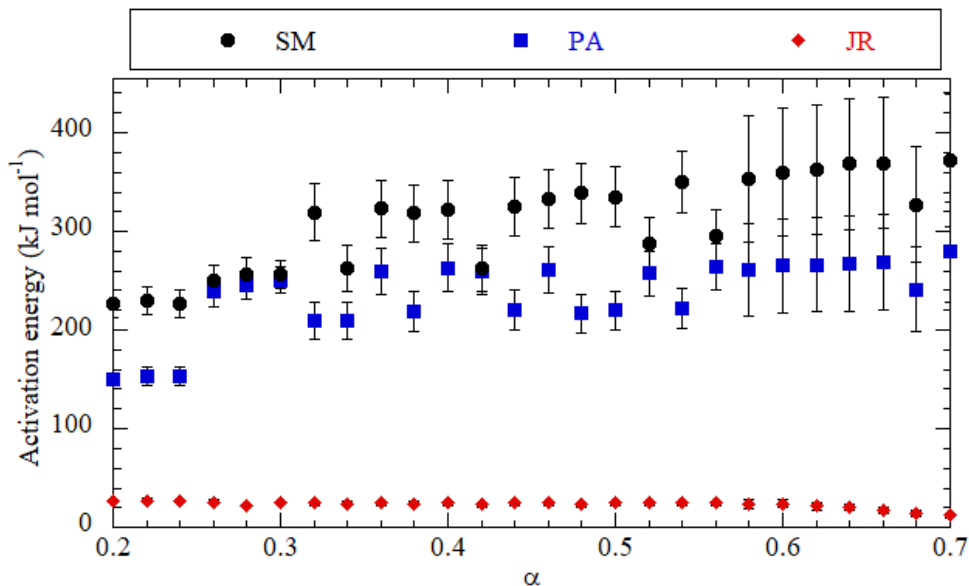
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276 **Fig. 7.** Friedman activation energy as a function of the conversion degree for the wood samples.

277

278 Compared to the KAS method, we observed a higher level of fluctuations as well as larger errors on the E_a values

279 indicating that the Friedman procedure provided less accurate results on the kinetics of pyrolysis of the historical

280 woods. However, it should be noted that the Friedman analysis confirmed that JR is characterized by much lower E_a

281 values with respect to those of SM and PA.

282

283 **Correlation between thermal properties and FTIR spectroscopy**

284 As evidenced in the previous paragraphs, the thermogravimetric results can be properly interpreted on the basis of the

285 wood composition obtained by the FTIR spectroscopy analysis. In this regards, Fig. 8 shows the influence of the lignin

286 index on the thermogravimetric parameters, such as $(ML_{380-600})/(ML_{180-380})$ ratio and the average activation energy

287 calculated through the KAS method.

288 As concerns the $(ML_{380-600})/(ML_{180-380})$ ratio, we observed a linear increase with the lignin index (Fig. 8a) confirming

289 that the thermal degradation of the cellulosic components occurs at 180-380 °C, while lignin mostly decomposes in the

290 temperature interval between 380 and 600 °C. Based on the linear fitting, we determined the following relation

291

292 $(ML_{380-600})/(ML_{180-380}) = (0.158 \pm 0.006) + (0.306 \pm 0.005) \cdot L.I.$ (5)

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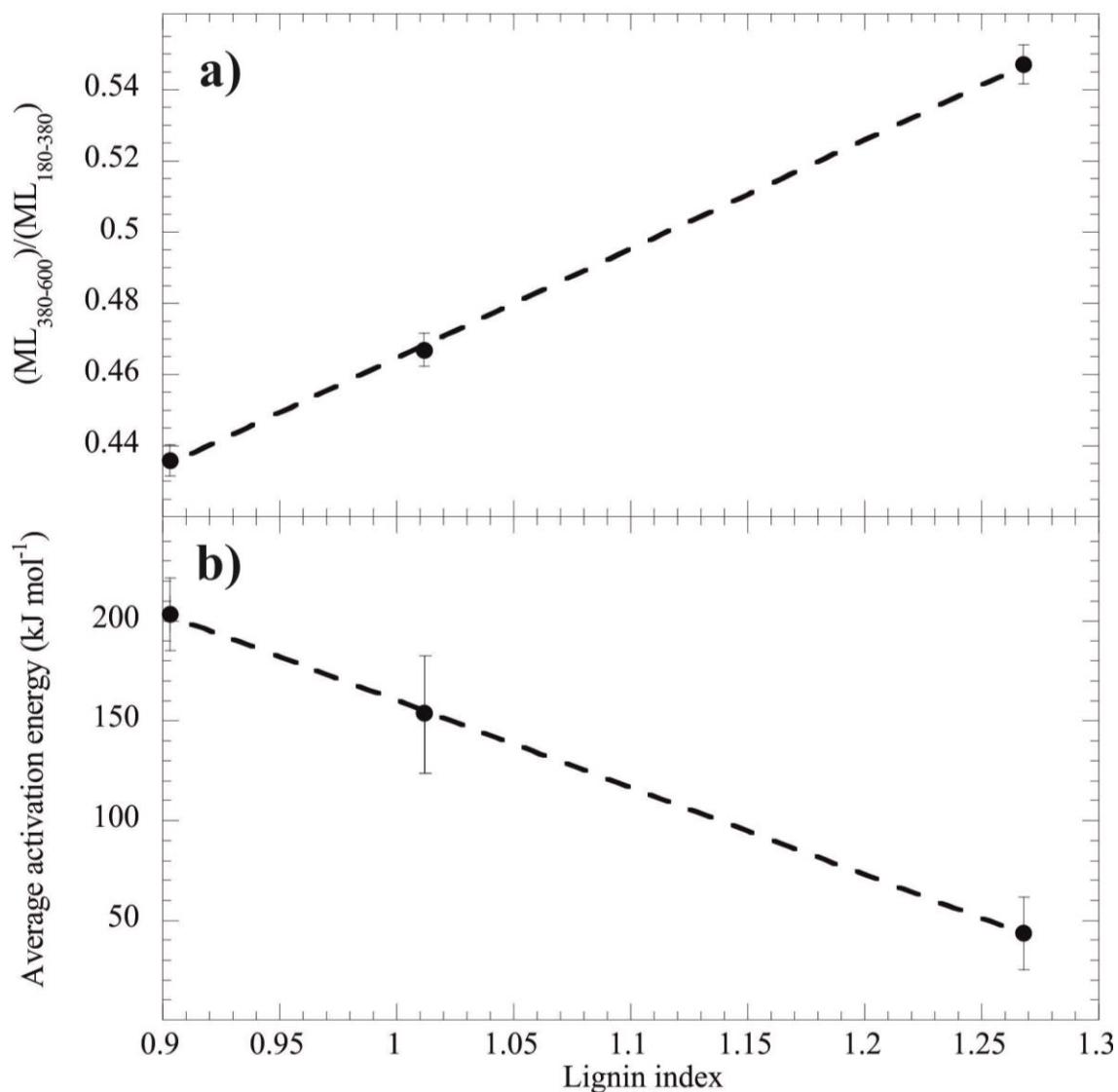
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296 **Fig. 8.** Dependence of the $(ML_{380\text{-}600})/(ML_{180\text{-}380})$ ratio (a) and KAS average activation energy (b) on the lignin index of

297 the wood samples. The dashed lines represent the linear fitting according to equations 5 and 6.

298

299 According to equation 5, the lignin composition in the wooden samples might be indirectly estimated by

300 thermogravimetric experiments. As highlighted by Fig. 8b, the average activation energy for the wood pyrolysis shows

301 a decreasing linear trend with the lignin index. The linear regression of the E_a vs L.I. trend (Fig. 8b) allowed us to

302 determine the following equation

303

304 $E_a = (596 \pm 7) - (436 \pm 6) \cdot L.I.$ (6)

305 According to equation 6, we could predict the kinetics of the pyrolysis for wooden materials by considering their

306 specific lignin index determined through FTIR spectroscopy.

307 It should be noted that equations 5,6 cannot be used as a general protocol for the thermal and structural characterization

308 of wooden materials. Nevertheless, the obtained functions demonstrated that thermogravimetric results can be

309 univocally interpreted by the analysis of the FTIR spectra of the woods. This consideration is remarkable being that the

310 investigated woods were employed in the manufacturing of physical apparatuses from XIX century. Therefore, the

311 combination of TGA and FTIR spectroscopy analyses might be useful to investigate the conservation state of wooden

312 artworks.

313

314 **Conclusions**

315 Historical woods from XIX century were characterized by thermogravimetry and FTIR spectroscopy. In detail, the

316 investigated samples refer to wood portions of apparatuses of the Historical Collection of the Physics Instruments at the

317 University of Palermo. In addition, the woods belong to different taxa (*Swietenia mahagoni*, *Picea abies* and *Juglans*

318 *regia*), which were extensively used for the fabrication of physics instruments during XIX century.

319 According to their different taxon, the woods exhibited variable lignin and carbonyl indexes as well peculiar cellulose

320 crystallinity degree. In this regards, we detected that cellulose in *Picea abies* possesses the highest degree of disorder.

321 As concerns the thermal properties, we investigated the wood pyrolysis by performing thermogravimetric

322 measurements under inert atmosphere. The analysis of both thermogravimetric and differential thermogravimetric

323 curves evidenced that the historical woods present different thermal stability depending on their structural and

324 compositional characteristics. Compared to the other woods, we observed that *Juglans regia* exhibits a strong reduction

325 (ca. 60 °C) of the cellulose degradation temperature. This result was supported by the non-isothermal

326 thermogravimetric studies, which evidenced that the activation energy of the wood pyrolysis for *Juglans regia* is ca. 4-

327 5 times lower than those of the other wooden samples. On this basis, we can state that *Juglans regia* is the most

328 sensitive wood to the structural deterioration. The thermal properties of the historical woods were correlated to the

329 specific indexes estimated from FTIR spectra. Interestingly, we observed that the activation energy of the pyrolysis

330 process linearly decreases with the lignin index of the wood.

331 In conclusion, this work evidenced that the combination of FTIR spectroscopy and thermogravimetic analysis can

332 provide a robust protocol to predict the conservation state of historical woods with variable structural and thermal

333 characteristics.

334

335 **Acknowledgment**

338　　　　　　　　　　　　　　　　　　**References**

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Figs. captions

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520   **Fig. 1.** Photos of the physics apparatuses from the Historical Collection of the Physics Instruments at University of

521   Palermo.

522   **Fig. 2.** FTIR spectra for the investigated wood samples.

523   **Fig. 3.** Relative crystallinity (TCI and LOI) and lignin/carbonyl indexes determined from the FTIR spectra analysis of

524   the investigated wood samples.

525   **Fig. 4.** Thermogravimetric curves of the wood samples.

526   **Fig. 5.** Differential thermogravimetric curves of the wood samples.

527   **Fig. 6.** KAS activation energy as a function of the conversion degree for the wood samples.
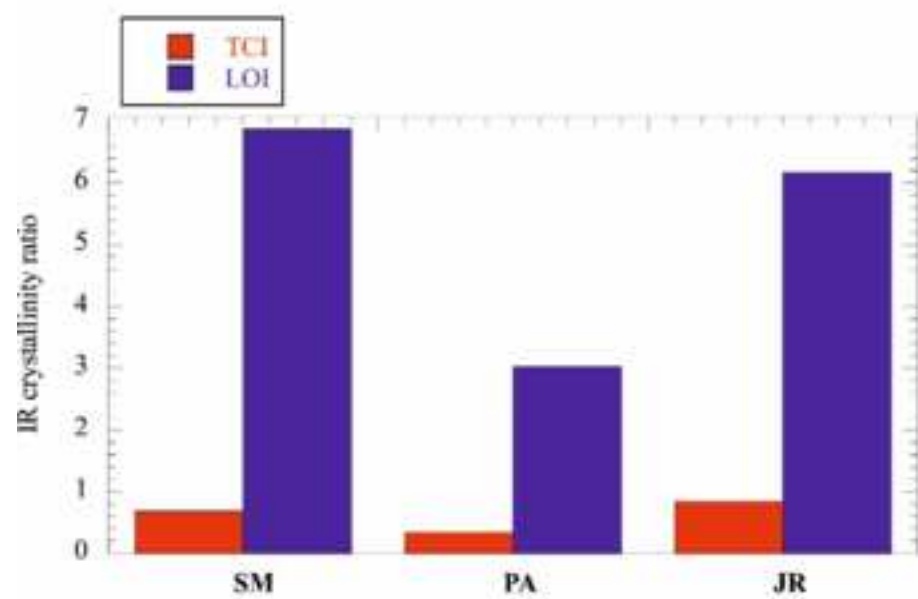
528   **Fig. 7.** Friedman activation energy as a function of the conversion degree for the wood samples.
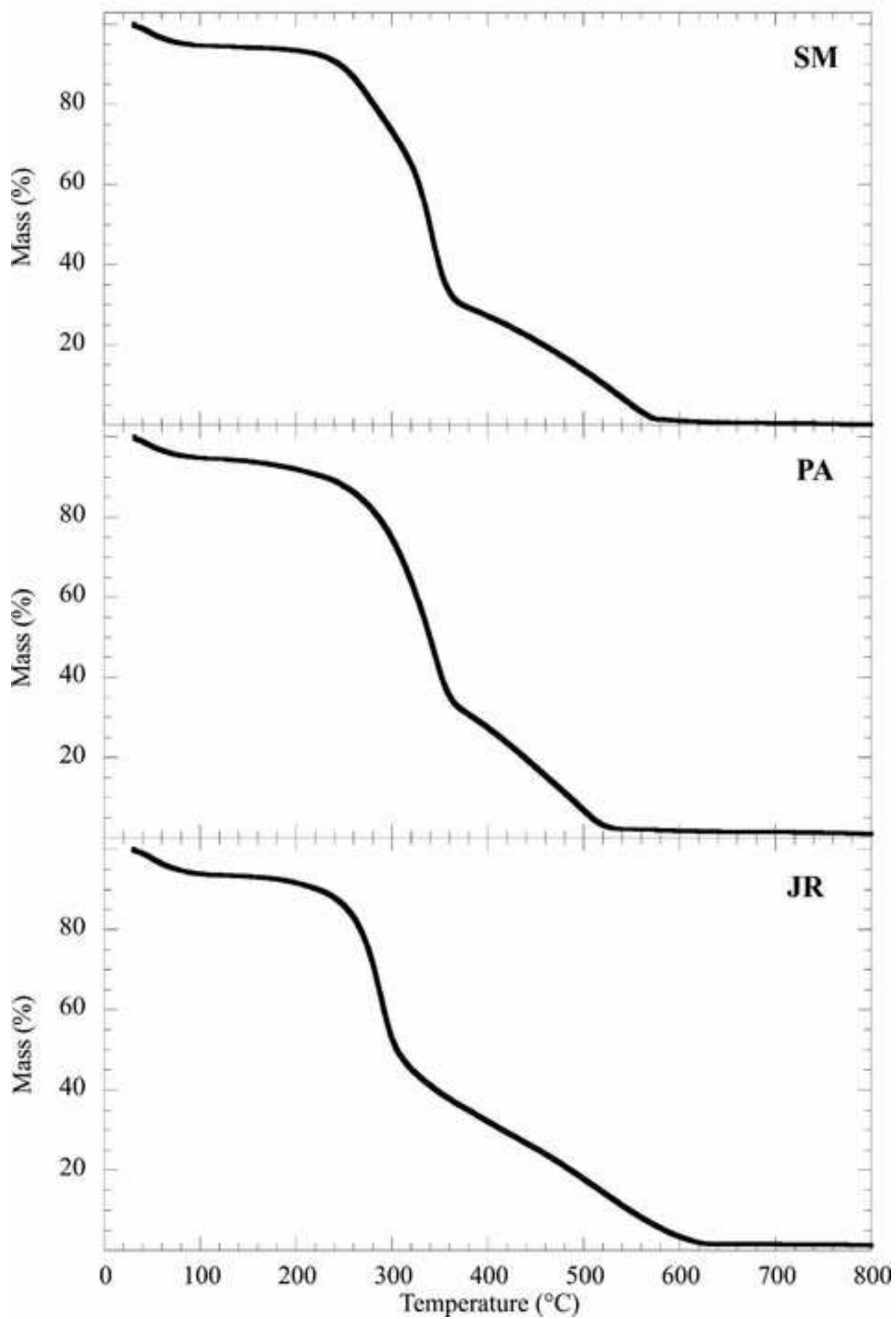
529   **Fig. 8.** Dependence of the (ML380-600)/(ML180-380) ratio (a) and KAS average activation energy (b) on the lignin

530   index of the wood samples. The dashed lines represent the linear fitting according to equations 5 and 6.
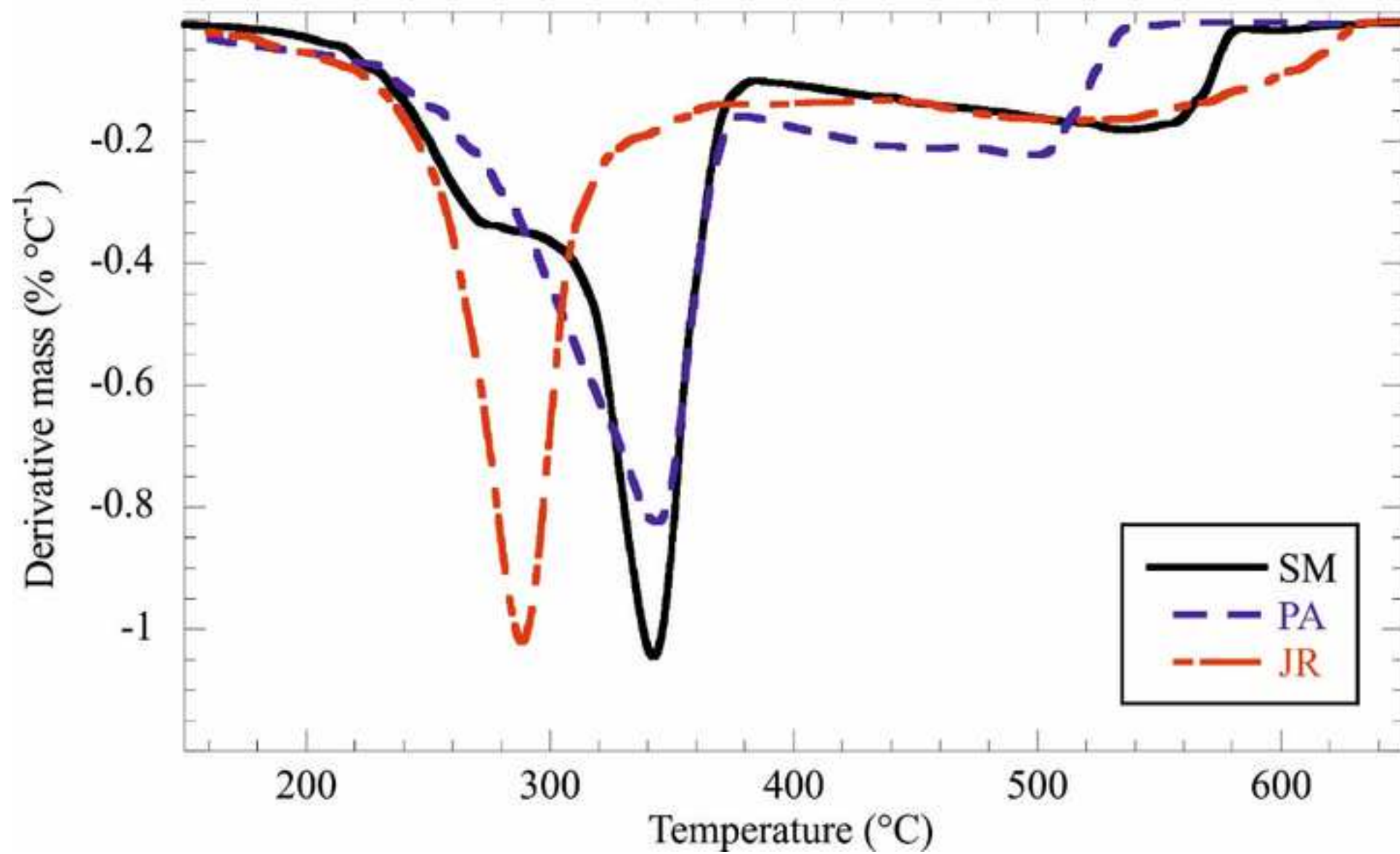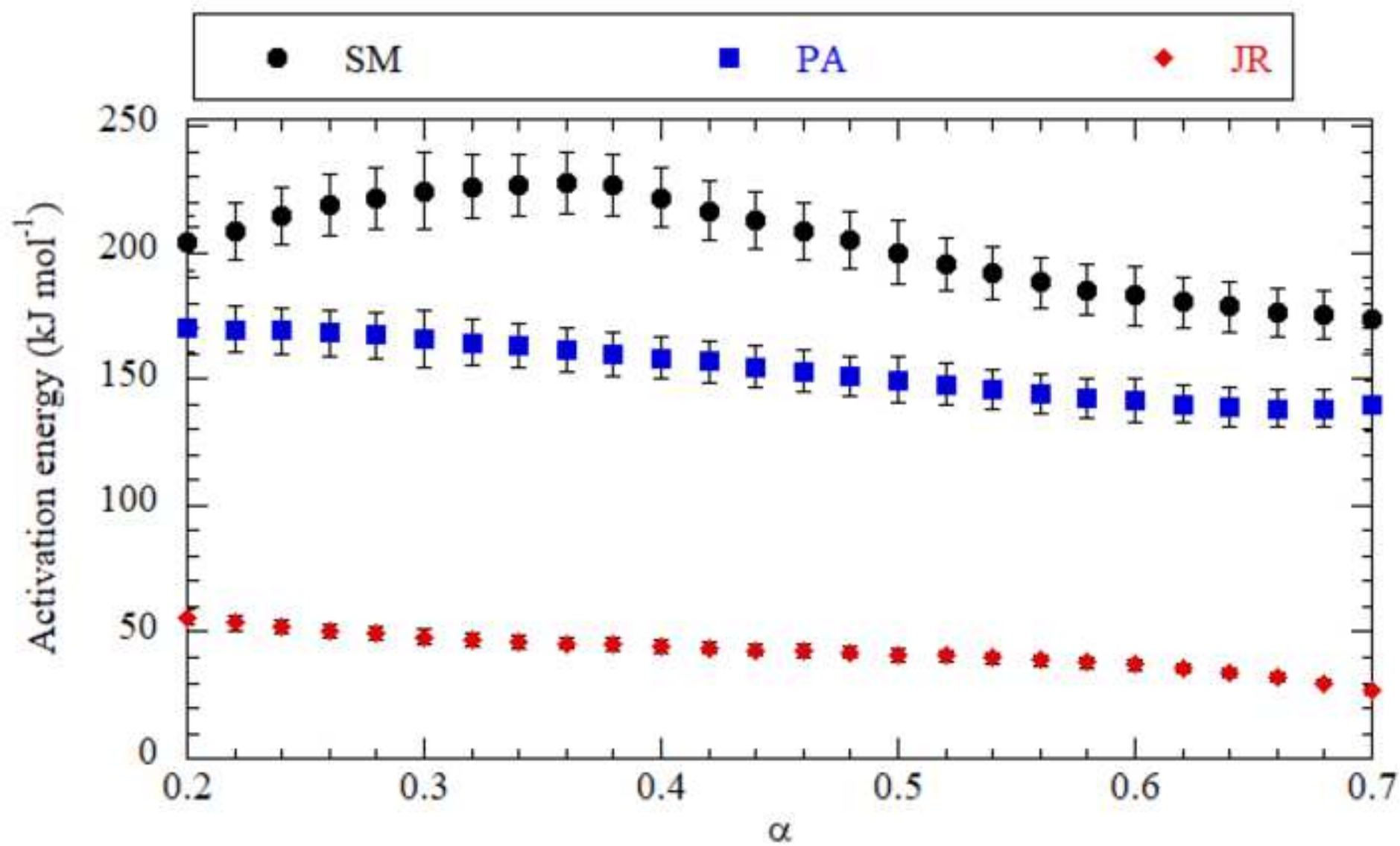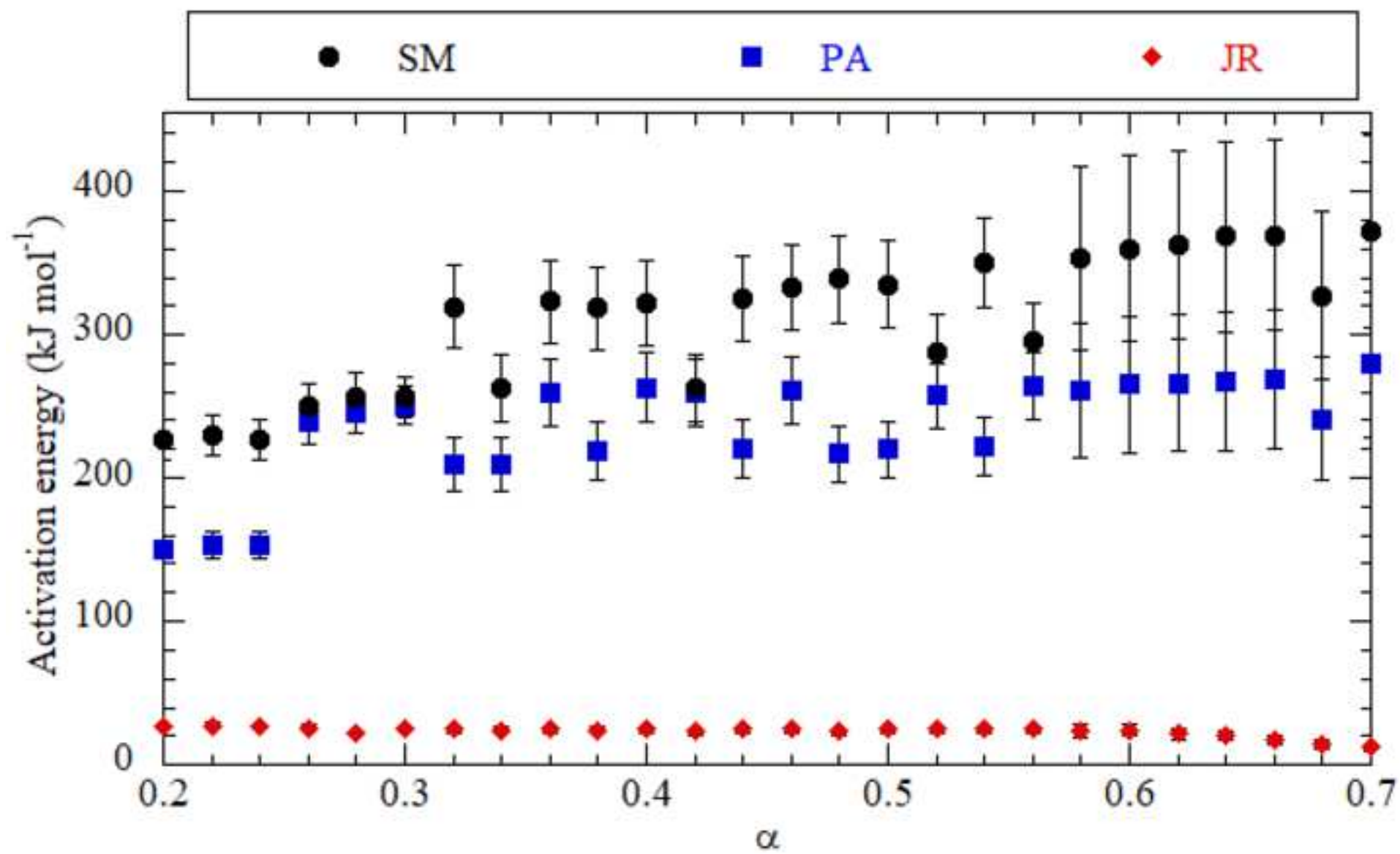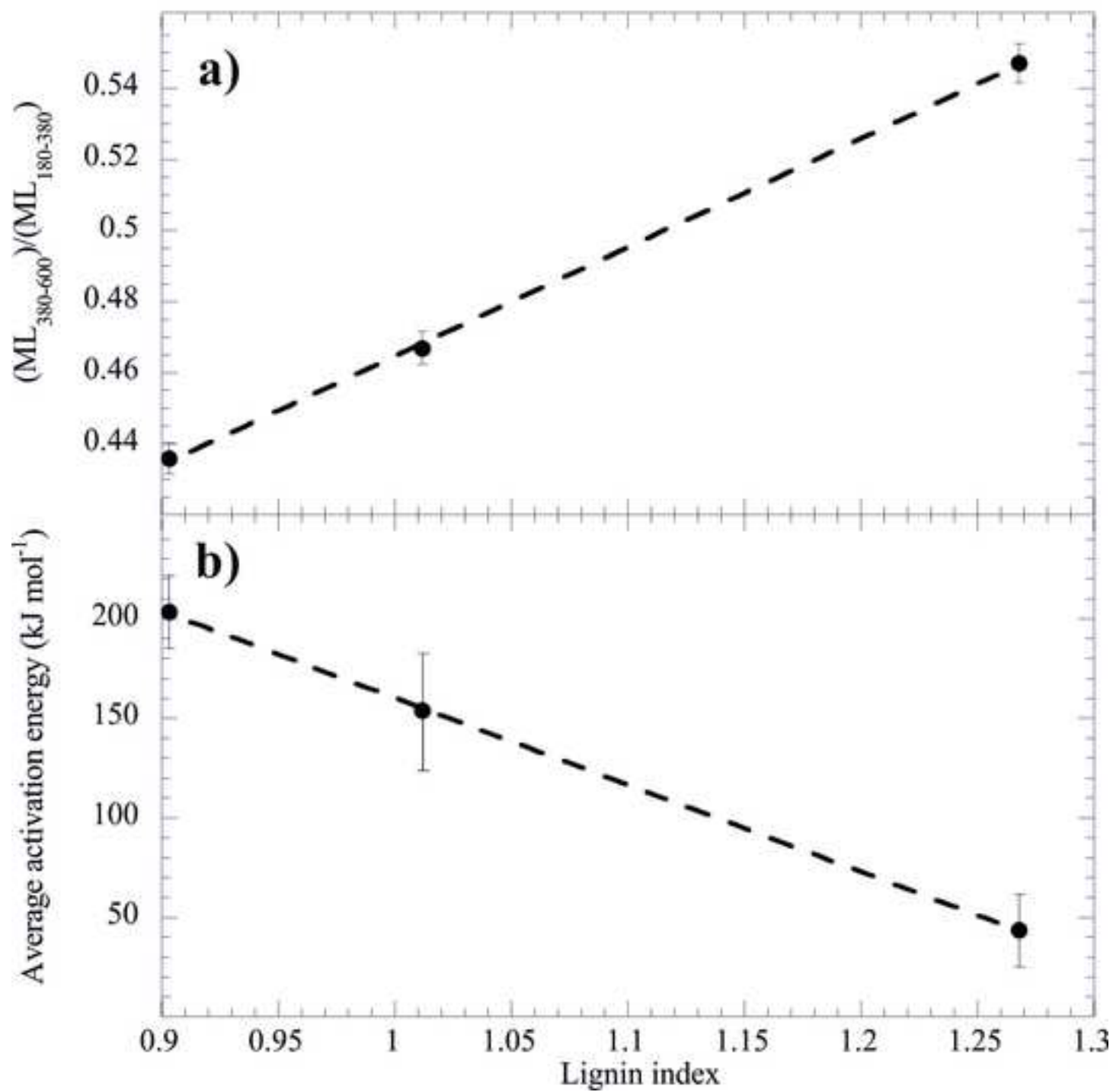
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Table 1. List of the historical wooden samples

Symbol	Wood taxon	Physics apparatus	Manufacturer	Year
SM	*Swietenia mahagoni*	Chronograph tuning forks with electromagnetic drive	Max Kohl, Germany	1906
PA	*Picea abies*	Tuning forks on resonance box (sound frequency of 768 Hz)	Rudolph Koenig, France	1868
JR	*Juglans regia*	Support for tuning forks	Rudolph Koenig, France	1864

Table 2. Mass losses of the historical woods obtained by TG measurements at $\beta = 10$ °C min^{-1}

Wood	ML_{25-150} (wt%)	$ML_{180-380}$ (wt%)	$ML_{380-600}$ (wt%)	$(ML_{180-380})/(ML_{380-600})$	DTG peak (°C)
SM	5.65 ± 0.06	64.6 ± 0.7	28.1 ± 0.3	0.435 ± 0.009	342 ± 3
PA	5.93 ± 0.06	62.0 ± 0.7	28.9 ± 0.3	0.46 ± 0.01	341 ± 3
JR	6.67 ± 0.07	57.6 ± 0.6	31.5 ± 0.3	0.54 ± 0.01	288 ± 3