EFFECT OF TORREFACTION TEMPERATURE ON PROPERTIES OF PATULA PINE

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ABSTRACT

The objective of this work was to study the effect of torrefaction temperature on properties of patula pine *(Pinus patula)* wood that could be of interest for further thermochemical processing. Torrefaction temperature was varied from 200 to 300 °C for 30 minutes using a batch spoon type reactor. Raw and torrefied materials were characterized for proximate and ultimate analyses, thermogravimetry, and pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). Results showed that torrefied pine has greater higher heating value and chemical exergy due to the reduction of O/C and H/C ratios. Compared with raw biomass, the material torrefied at 200 and 250 °C did not present significant changes in chemical composition and thermal behavior. Conversely, material torrefied at 300 °C did show important changes in both chemical composition and thermal behavior. Py-GC/MS results suggested that the main constituents of biomass, i.e., hemicellulose, cellulose and lignin, suffer a progressive thermal degradation with increase in torrefaction temperature.

Keywords: Biomass, Chemical-energy properties, *Pinus patula*, pyrolysis, thermal degradation, thermochemical processes.

1. INTRODUCTION

Historically, wood has been a ubiquitous resource for manufacturing tools, ships, weapons, musical instruments, or for house-building, until less than a century ago. Wood has been at the same time a key fuel used worldwide. For instance, the fuel used for locomotion in the US during the 1850s was entirely

35   wood (Schurr and Netschert 1960) and currently there are several regions that still use abundant

36   amounts of wood as fuel, for example, for cooking (Iiyama et al. 2014). However, since approximately

37   the midst of the 19th century to the beginning of the 20th century, wood fuel has been progressively

38   substituted by fossil fuels in several countries. Despite this reduction of wood as fuel in some regions,

39   other structural and non-structural wood uses are unavoidable and global wood-derived products

40   utilization has been increasing. According to FAOSTAT, the decade from 2002 to 2012 showed an

41   impressive increase of the consumption of wood composites (e.g., by almost 200% in the case of

42   medium density fiberboard – MDF) and other wood-based products, accompanied by a slight decrease

43   in sawn-wood utilization (by approximately 5%) (FAOSAT 2014). This information evidences that an

44   important component of the global wood market is constituted by wood-composites, especially MDF

45   and particleboard.

46   Deforestation, growing wood demand, and environmental restrictions could affect future wood

47   availability, as observed in tropical countries since 2009 (International Tropical Timber Organization

48   (ITTO) 2012). Fast growing timber species and materials that today in several places are considered

49   "residues" are alternatives to timber. In Colombia, fast growing wood species such as patula pine (*Pinus*

50   *Patula*) present enormous energy prospective due to the existence of land potentially usable for

51   dedicated energy trees. The country has approximately 17 million hectares of land suitable for

52   reforestation (Pérez and Osorio 2014). Currently, these lands are poorly used as pastureland or they are

53   simply abandoned due to limited fertility. Thus, part of these lands have been seen as an opportunity for

54   planting trees for both commercial use and bioenergy production (Pérez and Osorio 2014). There are

55   evidences showing that lands not adequate for agricultural use offer potential for planting trees (Phalan

56   2009), without negatively impacting agricultural or pasture lands. Additionally, Colombia already

57   possesses large plantations of this wood species (approximately 55% of the forest planted area) (Ospina

58   et al. 2011). Small diameter pine trees and the corresponding cropping residues are expected to serve as

59   an important raw material for producing biofuels, bioenergy, and other bio-products (Quaak et al. 1999).

60   For an optimum use of fast growing wood species, pretreatment operations aiming at improving

61   some wood properties are required. The use of forest biomass for energy, chemicals, or biofuels,

62   requires pretreatment operations to increase energy content, reduce moisture, and increase bulk density

63   (Pelaez-Samaniego et al. 2013). Difficulty on hauling and processing lignocellulosic biomass in an

64   economical way is greatly limited by these critical properties. One of the recognized strategies for

65   improving these properties is torrefaction. Torrefaction is a mild thermochemical process conducted in

66 oxygen-free environments at temperatures ranging from 200 to 300 °C (Bridgeman et al. 2010, Chen

67 and Kuo 2010, Ibrahim et al. 2013, Phanphanich and Mani 2011, Xue et al. 2014). In this range of

68 temperatures, in addition to moisture and volatiles release, degradation of hemicelluloses occurs, while

69 cellulose is subjected to dehydration and both cellulose and lignin are subjected to partial

70 depolymerization (da Silva Grassmann et al. 2016, Pelaez-Samaniego et al. 2013).

71   Several works have extensively discussed about the advantages of torrefied wood. Arias et al. (2008)

72 studied the effect of temperature and residence time on the grindability of Eucaliptus as well as its

73 reactivity with air, using thermogravimetry. As expected, volatiles decreased when temperature

74 increased and the energy content (i.e., its higher heating value) and C content augmented. O content

75 decreased when time or torrefaction temperature increased, due to the formation of CO_2 and the

76 degradation of hemicelluloses. Grindability depended on the conditions of the process: the more severe

77 the conditions of the process, the better the degree of grindability. Repellin et al. (2010) studied the

78 effect of torrefaction of two types of biomass (spruce and beech) on power consumption during the

79 grinding operation. It was observed that power consumption decreased as a consequence of the thermal

80 treatment. Similar findings have been reported by Bridgeman et al. (2010).

81   The process of torrefaction alters the physical properties of biomass, reducing its bulk density and its

82 fibrous tenacious nature (da Silva Grassmann et al. 2016). This could allow increased rates of co-milling

83 and co-firing in coal fired power stations, which in turn would enable reduction of the amount of coal

84 used and an increase in the use of renewable fuels, without the need for additional infrastructure.

85 Phanphanich et al. (2011) y Chen et al. (2011) investigated the pulverization behavior of two torrefied

86 energy crops, namely: willow and Miscanthus. Results showed that the untreated fuels and materials

87 torrefied at low temperatures had very poor grindability behavior. However, more severe torrefaction

88 conditions caused the fuels to exhibit similar pulverization properties as coals. Medic et al. (2012) have

89 investigated the solid, liquid, and gas products of the torrefaction of corn stover with moisture content of

90 3, 22, and 41%. The temperature was varied from 200 to 300 °C and the residence time from 10 to 30

91 min. As in other types of materials (Pelaez-Samaniego et al. 2014), the yield of solids decreased when

92 the temperature of the process increased. This has been attributed to the degradation of hemicelluloses

93 and probably part of cellulose (Medic et al. 2012). Peláez-Samaniego et al. (2014) investigated the

94 influence of torrefaction conditions on amount, composition, molecular weight, and pattern of

95 deposition of lignin liquid intermediates (LLI). The authors mentioned that it is possible to control the

96 conditions of the torrefaction process to increase or decrease the amount of lignin liquid intermediates

97 on wood fibers surface, which could be of interest for pellets production and wood composites

98 manufacture. Another option is using torrefied wood for fast pyrolysis, as reported by Yang et al.

99 (2014). These authors conducted torrefaction of switchgrass at 230 and 270 °C prior to pyrolysis.

100 Results showed that torrefaction promotes increase of anhydrosugars and phenols in pyrolysis bio-oil.

101 Similar results have been obtained by Zheng et al. (2015), who studied the effect of wet and dry

102 torrefaction on chemical structure and pyrolysis behavior of corncob.

103 The mentioned works show that torrefaction, in addition to modifying critical properties of

104 lignocellulosic biomass, can serve as a strategy to pretreat this material for further thermochemical

105 operations. Therefore, information on the torrefaction process and the effects of softwood, such as

106 abundant patula pine in the Colombian highlands, will help to plan the use of low quality pine (e.g.,

107 small diameter trees) and softwood cropping residues. The objective of this study is to evaluate the

108 effect of torrefaction temperature on some properties of patula pine that are expected to impact further

109 processing as a fuel, as a raw material for thermochemical downstream operations, or for the production

110 of wood pellets.

111

112 2. MATERIALS AND METHODS

113 *2.1. Materials*

114 The material used for torrefaction was patula pine, obtained from a commercial plantation located

115 nearby Medellín, Colombia. The selection of this wood species took into account the potential that it

116 offers as an abundant lignocellulosic material in Colombian highlands. Small diameter logs were

117 debarked before a chipping process. The wood sample was chipped using a BANDIT 95XP chipper,

118 then located on the floor (trying to keep a uniform thickness layer of chips) and dried at room conditions

119 during two weeks. Then, a representative amount of chips (approximately 2 kg) was collected and

120 ground, using a laboratory knife table mill, equipped with a 40-mesh sieve. The ground material was

121 then dried for 24 h at 105 °C prior torrefaction and prior to characterization of raw material properties.

122 *2.2. Methods*

123 Torrefaction of the patula pine (PPat) sample was carried out in a Lindberg Blue tube furnace (spoon

124 reactor, capacity of approximately 3 g of biomass per batch). The reactor is described in detail by Wang

125 et al. (2014). Three levels of temperature were selected for torrefaction: 200, 250, and 300 °C, and 30

126 minutes of residence time, following previous works (Pelaez-Samaniego et al. 2014, Phanphanich and

127 Mani 2011). The samples were coded as Raw (untreated material), and PPat200, PPat250, and PPat300,

128   for the materials torrefied at 200, 250, and 300 °C, respectively. The torrefaction process was conducted

129   in duplicates and, due to close yields, the averages of the results are reported.

130   *2.3.*   **Ultimate and proximate analyses**

131   Elemental composition (CHNS) was determined using a LECO® TruSpec CHN instrument,

132   coupled with a LECO® 628S module (Pelaez-Samaniego et al. 2014). For CHN, approximately 0.13 g

133   of oven dry material were fed in the combustion chamber of the Truspec CHN module. The S content

134   was determined by using approximately 0.1 g of dried material, which was burned in the 628S module.

135   Details about the whole process can be found at (Pelaez-Samaniego et al. 2014). In all cases, the test was

136   replicated twice to verify results. Results of ash content were used to correct the results of elemental

137   composition of each material.

138   Ash content was determined following ASTM D1102-84 (reapproved 2007) for raw pine and using a

139   correction factor (i.e., mass yield) for torrefied material. Volatiles content was determined using

140   thermogravimetry (TGA), as suggested by previous works (García et al. 2013; Pelaez-Samaniego et al.

141   2014). Prior to TGA analysis, the torrefied materials were ground using the knife-mill already described.

142   Again, particles used for the test passed through a 40 mesh sieve. For the test, a TGA equipment

143   (TGA/SDTA851e, Mettler Toledo) was used. The heating rate was 10 °C/min and the temperature

144   varied from room conditions to 600 °C. Approximately 7 mg of material was employed in each case and

145   tests were conducted in duplicate to verify results.

146   *2.4.*   **Heating value and chemical exergy**

147   The higher heating value (HHV) and chemical exergy (e^{ch}) of the initial material and torrefied

148   material was calculated using correlations that take into account the ultimate analysis (C, H, N, O and S)

149   in dry basis, following to Friedl et al. (2005) and Kotas (1995), respectively (Eqs. 1, 2, and 3). Equation

150   1 shows the calculus of HHV, while equations 2 and 3 show the estimation of e^{ch}.

$$HHV_{bms}(kJ/kg) = 3.55 \cdot C^2 - 232 \cdot C - 2230 \cdot H + 51.2 \cdot C \cdot H + 131 \cdot N + 20600 \quad (1)$$

$$e^{ch}(kJ/kg) = HHV_{bms} \cdot \lambda_{bms} + 9417 \cdot S \quad (2)$$

$$\lambda_{bms} = \frac{1.0438 + 0.1882 \cdot H/C - 0.2509 \cdot (1 + 0.7256 \cdot H/C) + 0.0383 \cdot N/C}{1 - 0.3035 \cdot O/C} \quad (3)$$

151   Where λ_{bms} is a dimensionless coefficient that relates the heating value and the chemical exergy of a

152   solid fuel (Kotas 1995), and C, H, N are the elemental composition (in wt.%).

153   *2.5.*   **Mass and energy yield**

154 Mass and energy yield are important parameters used in torrefaction process as indicators of the mass

155 degradation and energy content changes due to the thermal pretreatment (Bridgeman et al., 2010). These

156 parameters are calculated according to Eqs. (4) and (5).

$$Mass \quad yield = \frac{m_{bms,torr}}{m_{bms}} \qquad (4)$$

$$Energy \quad yield = \frac{m_{bms,torr} \cdot HHV_{bms,torr}}{m_{bms} \cdot HHV_{bms}} \qquad (5)$$

157

158 Where m_{bms} and $m_{bms,torr}$ are the masses and HHV_{bms} and $HHV_{bms,torr}$ are the higher heating values of

159 the raw and torrefied material, respectively. The energy yield is a measure of the energy content of the

160 torrefied biomass after the torrefaction process was carried out (Chen and Kuo 2010, Phanphanich and

161 Mani 2011, Prins et al. 2006a).

162 *2.6.* **Py-GC/MS**

163 Characterization of the untreated and torrefied materials was also carried out using pyrolysis gas

164 chromatography/mass spectrometry (Py-GC/MS). Py-GC/MS was performed using a GC/MS system

165 (6890N Network GC System with a 5975B inert XL MSD, from Agilent Technologies) coupled with a

166 CDS pyro-probe 5000 series (CDS Analytical, Inc). The tests were conducted in duplicate at 500 °C for

167 1 min, using ~0.5–0.8 mg of material. Compounds that showed the highest intensity in the pyrolysis

168 chromatograms were identified considering retention time, mass spectra, and comparison with database

169 of the NIST/EPA/NIH Mass Spectral Library V. 2.0d (Fair Com Corp). The areas of peaks were then

170 divided by the mass of the corresponding material for normalization of areas.

171 **3. RESULTS AND DISCUSSION**

172 *3.1.* **Mass and energy yield**

173 Table 1 shows the mass and energy yields of raw and torrefied pine at different temperature

174 conditions. As expected, the mass yield of torrefied wood decreased when torrefaction temperature

175 increased. The mass yield for PPat200 and PPat250 was not reduced significantly compared with

176 PPat300 where the mass loss increased drastically. The mass loss during torrefaction results from the

177 drying process and the thermal degradation of low thermally stable wood constituents (Chen and Kuo

178 2010, Hill et al. 2013, Phanphanich and Mani 2011).

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Table 1. Mass and energy yield of torrefied samples.

Sample	Mass yield (%)	Energy yield (%)
PPat 200	98.46	99.37
PPat 250	93.94	97.45
PPat 300	67.75	78.51

183

184   The energy yield for the torrefied patula pine decreases as the temperature of the torrefaction process

185   increases as shown in Table 1. The mass loss increases from 1.54 to 32.25% and the heating value gain

186   varies from 0.63 to 21.49%, depending on the temperature of torrefaction. However, the HHV of

187   torrefied woods augments (Table 2), which is associated with the modification in their elemental

188   compositions (e.g. ultimate analysis) during torrefaction process as described in the next section.

189   *3.2.*   **Proximate and ultimate analysis**

190   Table 2 shows the proximate and ultimate analyses, higher heating values, and chemical exergies of

191   the raw and torrefied materials. A slight effect on the proximate analysis was observed in material

192   torrefied up to 250 °C, while a significant change occurs in material torrefied at 300 °C. At higher

193   torrefaction temperature, volatile matter decreases while fixed carbon and ash contents increase. Similar

194   results were reported by Pelaez-Samaniego et al. (2014) for ponderosa pine wood species. It is also

195   observed that the carbon content gradually increases while oxygen content decreases as the torrefaction

196   temperature is augmented. The hydrogen and nitrogen contents remain approximately constant at all

197   levels of torrefaction temperature; this trend is attributed to the low mass concentration of these

198   components in wood biomass. The chemical exergy of a fuel is a measure of the maximum potential that

199   can be obtained as useful work (Kotas 1995). Thereby, the increase of exergy (as torrefaction

200   temperature increases) leads to higher availability of useful work using torrefied biomass as feedstock

201   for power plants or downstream thermochemical processes.

202   Figure 1 presents a Van Krevelen diagram, showing the decomposition progression of patula pine

203   during torrefaction. The H/C and O/C atomic ratios decrease as torrefaction temperature increases. This

204   is due to the release of volatile matter, constituted by non-condensable CO, CO_2 and condensable gases

205   such as H_2O, CH_3OH, $HCOOH$ and CH_3COOH. Volatiles have high H/C and O/C ratios, implying a

206   reduction in the H/C and O/C atomic ratios of the remaining solid after torrefaction process (Deng et al.

207   2009, Nocquet et al. 2014, Prins et al. 2006b). Materials with higher heating value and low moisture

208   content can benefit thermochemical processes such as combustion and gasification as the reaction

209   temperatures in those processes can be increased (Pérez et al. 2012, Torres-Fuchslocher and Varas-

210   Concha 2015). Other authors have reported results on the changes in biomass composition (at different

211 torrefaction conditions) that are consistent with the findings of this study (Bridgeman et al. 2010, da

212 Silva Grassmann et al. 2016).

213

214 **Table 2.** Proximate and ultimate analysis of raw and torrefied samples.

| Sample	Raw	PPat200	PPat250	PPat300
Proximate analysis (wt. %, dry basis)				
Volatile matter (VM)	81.12	79.53	80.82	70.65
Fixed carbon [a] (FC)	18.62	20.20	18.90	28.97
Ash	0.26	0.26	0.28	0.38
Ultimate analysis (wt. %, dry basis)				
C	49.95	50.33	51.46	56.24
H	5.94	5.80	5.70	5.56
N	0.14	0.13	0.15	0.15
O [a]	43.97	43.74	42.69	38.05
HHV_{db} (MJ/kg)	19.84	19.96	20.40	22.46
e^{ch} (MJ/kg)	21.45	21.47	21.60	22.37

[a] Calculated by difference

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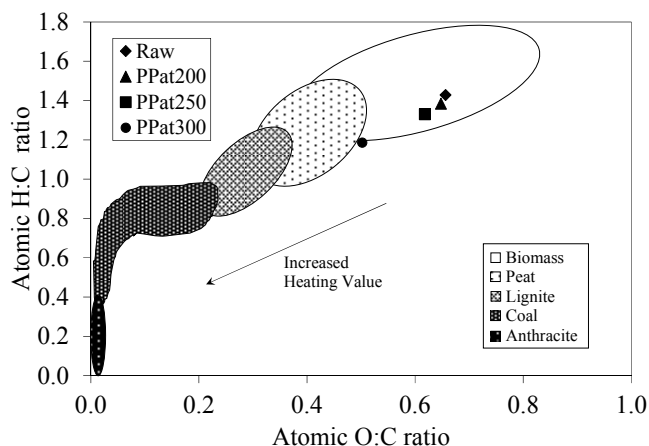
216
217 **Figure 1.** Van Krevelen diagram of raw and torrefied biomass.

218
219 *3.3.* **DTG results**

220 Figure 2 shows the TG and DTG curves of the raw and torrefied PPat to evaluate the effect of

221 torrefaction process. The curves for torrefied material (PPat200, PPat250 and PPat300) have been

222 multiplied for the mass yield reported in Table 1 in order to obtain the same basis (raw) for comparison

223 purposes, following the process of Pelaez-Samaniego et al. (2014). TG curves (Figure 2a) shows that

224 thermal stability slightly increases as torrefaction temperature increases; which is due to lower amount

225 of volatile matter in torrefied biomass (see Table 2). It is evident that material torrefied at higher

226 temperature (300 °C) shows better thermal stability than the other tested materials (its degradation starts

227 at approximately 320 °C).


2a) TG curves   2b) DTG curves
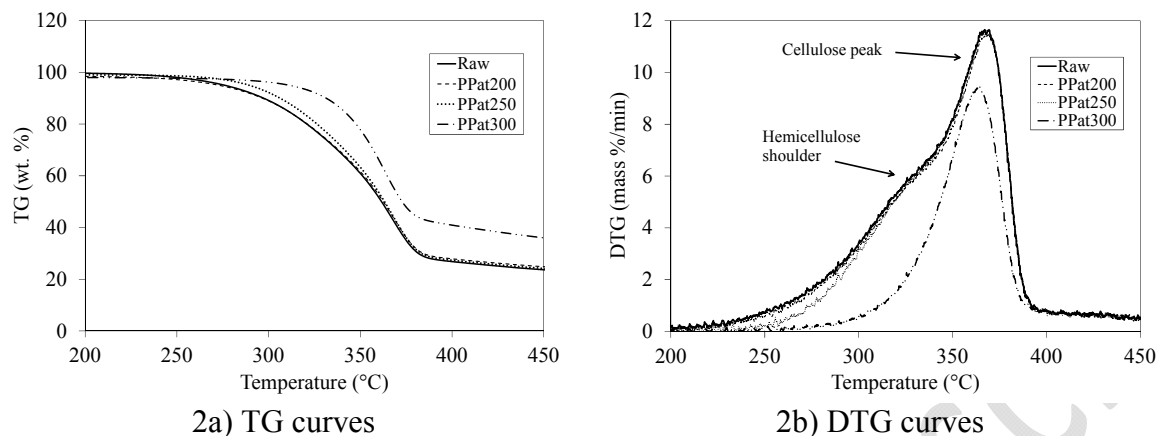
228 **Figure 2.** DTG curves of raw and torrefied samples at different temperatures.

229

230 Figure 2b shows the DTG curves. It can be seen that there is not significant change in biomass

231 torrefied up to 250 °C. Raw pine, PPat200 and PPat250 exhibit a shoulder, which can be related with the

232 presence of hemicelluloses. Absence of this shoulder in the TG curve of material torrefied at 300 °C

233 could be explained in part by the partial removal of hemicelluloses during torrefaction at this

234 temperature. The large peak at around 370 °C, in all cases, can be related with the degradation of

235 cellulose (Chen and Kuo 2010, Park et al. 2013, Pelaez-Samaniego et al. 2014). The thermal stability of

236 the samples is consistent with the proximate and ultimate analyses in Table 2, where no major changes

237 were observed on chemical composition of the raw material ant the samples of material torrefied at 200

238 and 250 °C. Additionally, the peak corresponding to cellulose degradation was affected during

239 torrefaction but its position (365 °C) did not change visibly. This behavior might indicate that the

240 structural characteristics of cellulose fraction of patula pine was preserved after torrefaction process

241 (Park et al. 2013).

242 *3.4.* **Py-GC/MS**

243 Since the results of DTG and the proximate and ultimate analyses (Table 2) suggest that the PPat200

244 and PPat250 samples show quite similar composition and thermal stability, we used an additional

245 technique, Py-GC/MS to indirectly determine if, in fact, the composition of the materials has changed as

246 a result of torrefaction. Py-GC/MS allowed the determination of the main products of the pyrolysis of

247 the raw and torrefied materials. Figure 3 and Table 3 show the compounds resulting from the pyrolysis

248 of each material. These compounds were classified as acids, ketones, furans, nitrogen-containing

249 compound, sugars and phenols according to their chemical functional groups (Zhang et al. 2015).
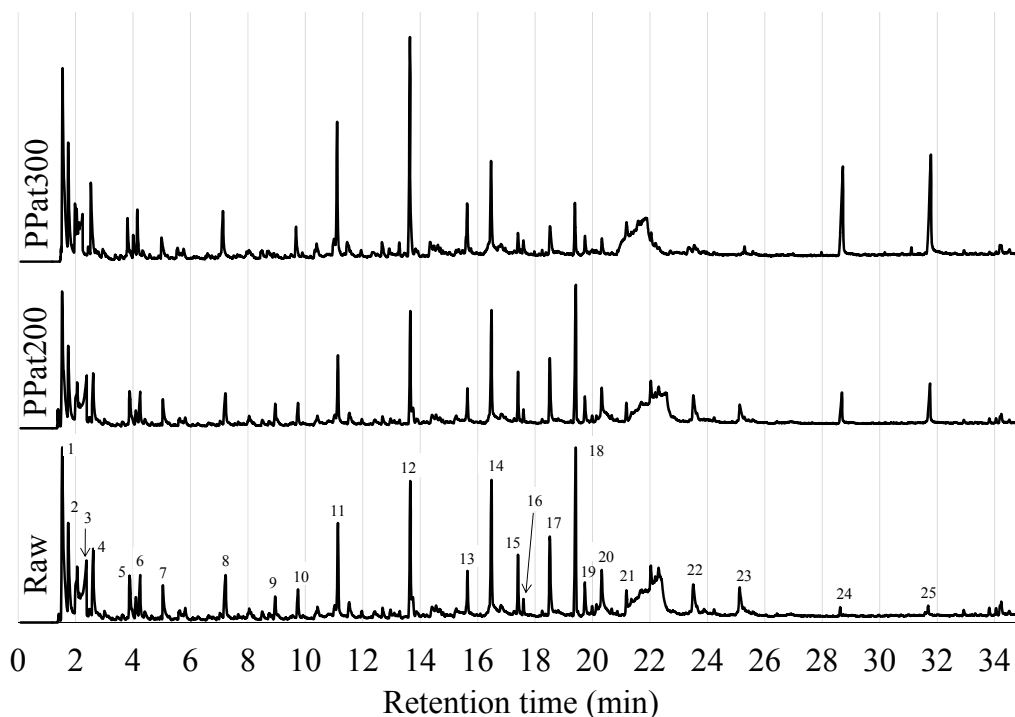
250
251 **Figure 3.** Chromatograms of the raw and torrefied materials.
252

253 **Table 3.** Identification of the main compounds found in the Py-GC/MS chromatograms and their
254 area/mass ratio.

RT	m/z	Formula	Compound	Area/mass		
				Raw	PPat200	PPat300
Acids						
2.43	43	$C_2H_4O_2$	Acetic acid	155406	131242	49585
28.68	73	$C_{16}H_{32}O_2$	n-Hexadecanoic acid	74136	74136	179492
31.75	43	$C_{18}H_{36}O_2$	Octadecanoic acid	94661	94661	217106
Total				324202	300038	446183
Ketones						
2.66	43	$C_3H_6O_2$	2-Propanone, 1-hydroxy-	91240	84480	93957
7.33	98	$C_5H_6O_2$	2-Cyclopenten-1-one, 2-hydroxy-	66704	60897	70513
9.76	112	$C_6H_8O_2$	1,2-Cyclopentanedione, 3-methyl-	45474	36005	47639
3.89	43	$C_4H_8O_3$	1,2-Ethanediol, monoacetate	60789	46165	46409
Total				264207	227547	258518
Furans						
5.05	96	$C_5H_4O_2$	Furfural	43340	44411	43733
Total				43340	44411	43733

Esters

1.8	43	$C_5H_8O_2$	1-Propen-2-ol, acetate	130609	102551	129055
4.25	43	$C_4H_6O_3$	Propanoic acid, 2-oxo-, methyl ester	54736	42607	59207
Total				185346	145158	188262

Nitrogen-containing compounds

8.95	114	$C_8H_{17}NO$	Oxazolidine, 2,2-diethyl-3-methyl-	29923	28720	0
Total				29923	28720	0

Sugars

21.33	60	$C_6H_{10}O_5$	Levoglucosan	823508	814179	706676
Total				823508	814179	706676

Phenols

11.28	109	$C_7H_8O_2$	Phenol, 2-methoxy-	104292	79954	141905
13.6	123	$C_8H_{10}O_2$	Phenol, 2-methoxy-4-methyl-	135393	111258	252044
15.65	137	$C_9H_{12}O_2$	Phenol, 4-ethyl-2-methoxy-	45189	37766	68296
16.47	135	$C_9H_{10}O_2$	2-Methoxy-4-vinylphenol	158860	131233	136737
17.4	164	$C_{10}H_{12}O_2$	Eugenol	65973	54450	37899
17.65	137	$C_{10}H_{14}O_2$	Phenol, 2-methoxy-4-propyl-	24619	18469	26438
18.53	152	$C_8H_8O_3$	Vanillin	119131	98610	71676
19.55	164	$C_{10}H_{12}O_2$	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	184856	156604	67096
19.73	137	$C_{10}H_{14}O_2$	Phenol, 2-methoxy-4-propyl-	56392	44965	34565
20.31	151	$C_9H_{10}O_3$	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	75392	71623	35945
23.53	137	$C_9H_{10}O_4$	Vanillacetic Acid	99430	87774	0
25.12	178	$C_{10}H_{10}O_3$	4-Hydroxy-2-methoxycinnamaldehyde	79658	61321	0
Total				1149185	954027	872601

Others

1.57	44	CO_2	Carbon Dioxide	314536	248343	335355
Total				314536	248343	335355

255

256   Acetic acid, levoglucosan and phenols are the most abundant compounds and the main

257 decomposition products from the pyrolysis of hemicellulose, cellulose and lignin, respectively (Klinger

258 et al. 2015; Pelaez-Samaniego et al. 2014; Yang et al. 2014; Zhang et al. 2015). Figure 4 shows the

259 abundance of acetic acid, levoglucosan and phenols for raw and torrefied pine. It can be seen that the

260 abundance of the three compounds decreases with torrefaction temperature. According to Zheng et al.

261 (2015), the reduction in the acetic acid may be due to the elimination reaction of acetyl groups in

262 hemicellulose structure. The thermal degradation of cellulose and some thermally unstable lignin

263 compounds results in the decrease on the abundances of levoglucosan and phenols, respectively. This

264 behavior is accentuated with the increase of the torrefaction temperature. The progressive reduction in

265 the abundance of levoglucosan and phenols suggests that: a) cellulose is subjected to different degrees of

266 degradation, mainly to the decomposition of the amorphous fraction, and b) the thermal degradation of

267 lignin occurs in a wide temperature range (Pétrissans et al. 2014, Chen and Kuo 2010, Wang et al.

268 2014).

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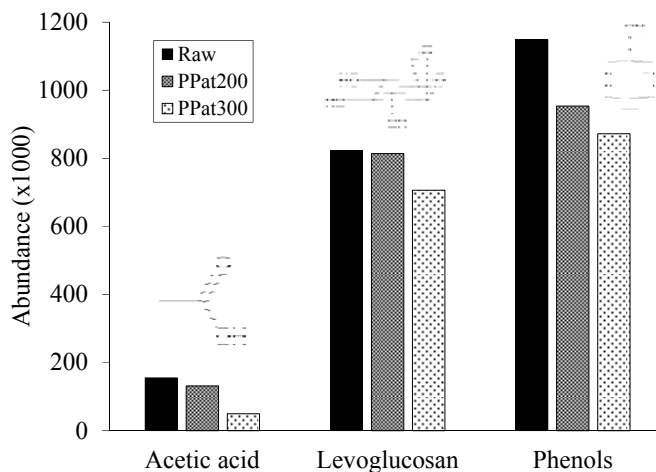
270
271 **Figure 4.** Effect of torrefaction on abundance of acetic acid, levoglucosan and phenols (PyGC/MS).

272

273 The upgrading process of wood biomass via torrefaction leads to a feedstock with lower moisture

274 content and reduced amount of light weight volatiles and hemicellulose in its structure. It is also

275 expected that the torrefied biomass subjected to thermochemical processes such as fast pyrolysis will

276 produce high quality products (e.g., pyrolysis bio-oil) than the corresponding untreated material. This

277 improvement in bio-oil quality is because the bio-oil from a torrefied material is not plenty of water and

278 light weight compounds since these were released during the torrefaction process (Yang et al. 2014,

279 Zheng et al. 2015).

280 **4. CONCLUSIONS**

281 Torrefaction of patula pine promotes mass loss ranging from 1.5 to 32.2 wt. %, depending on the

282 temperature of the process. This is due to the drying process and thermal decomposition of low-

283 molecular weight components of wood biomass. For PPat300, the higher heating value and chemical

284 exergy increase up to 13.2% and 4.29% respectively, which is due to the reduction of O/C and H/C

285 ratios. The found trends in molar ratios are due the H content reduction and/or by C increment with

286 torrefaction temperature. The mass loss prevails more than the increment of heating value of torrefied

287 biomass. Therefore, the energy content tends to diminish with torrefaction temperature. Pretreated

288 biomasses at 200 and 250 °C do not present major changes in chemical composition and thermal

289 behavior. In material torrefied at 300 ºC, the volatile matter decreases by 13% while fixed carbon and

290 ash contents increase by 55.6% and 41.6%, respectively. The use of torrefied wood as feedstock for

291 thermochemical processing (e.g., fast pyrolysis and gasification) and production of pellets offers an

292 important strategy for improving the quality of both the product. In the case of Colombia, torrefaction is

293 a promising strategy for integration of technologies that allow a complete use of patula pine. Due to the

294 potential of patula pine, this study could positively impact planning and management of this important

295 wood source in the country.

296 **ACKNOWLEDGEMENTS**

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