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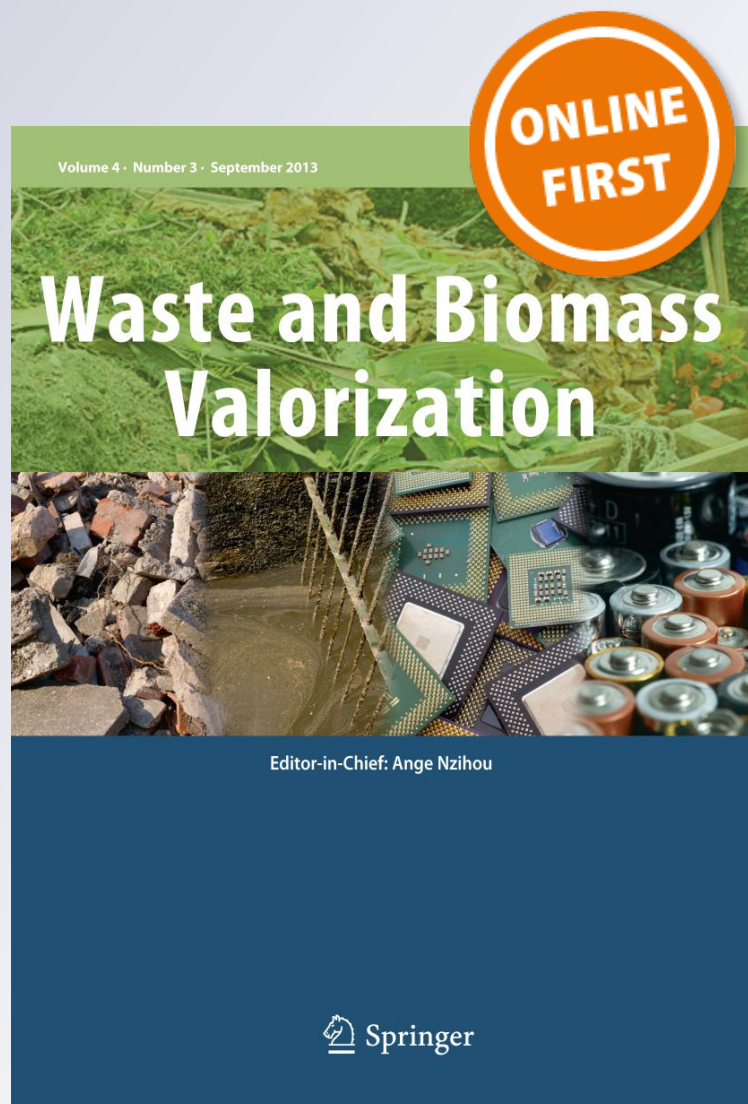
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# Torrefaction of Fast-Growing Colombian Wood Species

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## Abstract

The aim of this paper is to report fuel properties and torrefaction behavior of woody biomass from the Colombian highlands. Four wood species (*Eucalyptus grandis*, *Pinus Maximinoi*, *Pinus patula*, and *Gmelina arborea*) were selected due to their potential for expansion as bioenergy crops. Torrefaction of these feedstocks for the production of pellets for both domestic and international markets is a promising way to take advantage of these resources. Herein we report the impact of torrefaction temperature (between 200 and 300 °C) on the proximate and ultimate composition, heating value, thermal stability, and volatile products of the resulting solids. Although, all samples studied have similar volatile contents (70 wt%), heating value (~18.7 MJ/kg), and ash content (<1 wt%), their thermal behavior during torrefaction is different. Our results confirm that the fuel properties of the materials studied have been improved by torrefaction. Py/GC-MS studies of torrefied materials suggest that the torrefaction conditions studied do not affect the structure of cellulose and lignin fractions; thus, the yield and composition of volatile products was not dramatically affected by the torrefaction conditions. The resulting materials could be good feedstocks for centralized pyrolysis based bio-refineries.

**Keywords** Fast growing wood species · Torrefaction · Thermochemical processing · Pyrolysis products

## Introduction

Colombia heavily depends on fossil fuels as primary energy sources. Approximately 80% of the primary energy consumed in the country is derived from oil, natural gas, and coal [1]. Although Colombia is currently self-sufficient in energy sources, at current consumption rates our known oil reserves will only last for 6.5 years. Our natural gas resources will only last for 13 years [2, 3]. It is expected that the natural gas self-sufficiency could end in 2019 [2, 3]. This could have a dramatic impact on our power generation, transport and in our general standard of living [2]. The production of bio-fuels from the thermochemical conversion

(e.g. pyrolysis) of our abundant renewable lignocellulosic resources is a viable alternative to mitigate the effects of our declining oil resources.

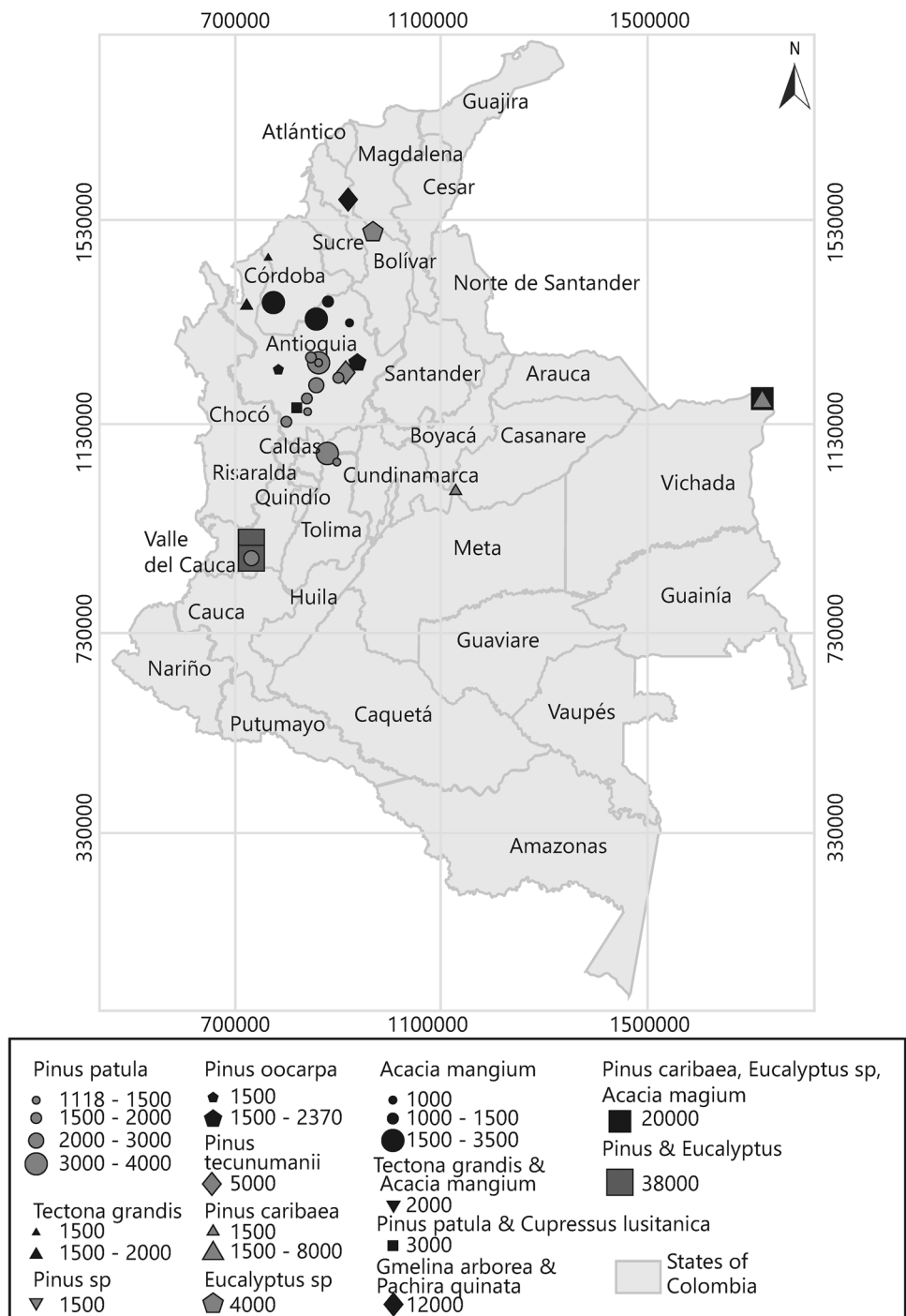
Currently, Colombia has approximately 600,000 ha planted with different fast-growing wood species such as pine and eucalyptus. Figure 1 shows the location of areas across the country planted with fast growing wood species. Pine species are the plantations with the highest occurrence, accounting for approximately 55% of the total [4]. Eucalyptus and other wood species such as *Acacia mangium*, *Tectona grandis*, and *Gmelina arborea* are the second most abundant group of planted wood species, covering approximately 42% of the planted area in the country. A third group includes native wood species such as *Cordia alliodora*, *Tabebuia rosea* and *Alnus acuminata* (3% of the total planted area) [5]. From this information, it is evident that pine species is an important resource that offers options for bioenergy and bioproducts production.

Pine plantations in Colombia are expected to continue growing in the near future. According to the National Plan of Forest Development for the period 2000–2015, Colombia has approximately 20 Mha of land that could be used for planting dedicated fast-growing trees [6, 7], without affecting land potentially suitable for agriculture or cattle

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**Fig. 1** Location of commercial forest cores planted in Colombia, based on a minimum planted area of 1000 ha. The size and color of each circle are related with planted area and wood species, respectively



raising. The places presented in Fig. 1 (circles with different dimensions) show the location of lands with at least 1000 ha of surface area already planted with wood for commercial purposes [5]. These areas have been referred to as “forest cores”. It is important to note that almost all wood plantations are in the highlands or in the coastal region (especially at the north of the country), and that the Amazonian region (South–East of the country) is not

under consideration for planting fast growing wood species. This way, deforestation of virgin forests is avoided.

For wood supply as biofuel, it is necessary to verify properties such as heating value, low moisture and ash contents, or higher reactivity under thermochemical processes [8]. In order to process these materials in large bio-refineries it will be necessary to create suitable supply chains. Biomass torrefaction followed by pelletization is considered one of the most promising approaches to densify and commoditize

lignocellulosic materials [9, 10]. Torrefaction of wood improves grindability index, durability, heating value and decrease oxygen content [11–13]. The commoditized materials obtained after torrefaction and pelletization can then be transported to a centralized bio-refinery for further conversion into fuel and chemicals (e.g. via fast pyrolysis). For an adequate use of these materials, studies comparing fuel properties, chemical composition, or their behavior under pretreatment conditions (e.g., via torrefaction) and thermal processing are required.

There are very few studies on the behavior of Colombian species during torrefaction. The objective of this paper is twofold: (1) to characterize and determine fuel properties of fast growing woody biomass species that are available on the Colombian highlands, and (2) to study the impact of torrefaction on proximate and ultimate analyses, heating value, thermal stability, and pyrolysis products of four selected materials (*E. grandis*, *P. Maximinoi*, *P. patula*, and *G. arborea*). A systematic characterization of these lignocellulosic resources is the first step towards a sustainable use of energy crops and wood residues in Colombia.

## Materials and Methods

### Selection of Forest Species and Preparation of Samples

The selection of wood species was based on a work previously conducted by Del Valle et al. [5], in which forest cores (Fig. 1) were defined considering identifiable, measurable and consistent silvicultural attributes. The species with higher planted area, higher yield or higher mean annual increment (MAI, m<sup>3</sup>/ha/year), and lower harvest time (years) are more suitable for bioenergy projects because biomass supply is ensured. The forest species with the highest energy potential in Colombia, hence studied in this work, are *E. grandis*—EGra (planted area of 46,115 ha, yield of 25 m<sup>3</sup>/ha/year, and expected growing time of 7 years), *G. arborea*, herein referred to as GARb (4972 ha, 23 m<sup>3</sup>/ha/year, 7 years), *P. patula*—PPat (38,495 ha, 20 m<sup>3</sup>/ha/year, 13 years) and *P. maximinoi*—PMax (59,811 ha, 20 m<sup>3</sup>/ha/year, 13 years) [5].

Four pieces of round wood of each wood species (without removing the bark), with dimensions ~ 150 mm diameter and length ~ 1.2 m, were randomly taken from piles of fresh wood logs in the Department of Forestry Sciences of National University from Colombia—Medellin. No effort was made to intentionally separate specific parts of each material. The logs were debarked and chipped using a Bandit 95XP chipper. Then, the chips were dried at room conditions for 1 week and sieved using sieves with dimensions 6–13 mm. Chips used for the tests were those that passed through the 13 mm diameter hole screen and were retained

by the 6 mm hole screen. The wood chips were afterward ground following the procedure described elsewhere [14]. The bulk density of the separated chips of each wood species was estimated by the ratio between mass and volume occupied by the biomass in a specific container vessel with known geometry following the procedure described by Lenis et al. [15].

### Ultimate and Proximate Analyses

Moisture content was determined following ASTM E871–82 (2013) using approximately 2 g of each material, in triplicate. The materials were dried for 24 h at 103 ± 2 °C. Ash content was determined following ASTM D1102-84 (reapproved 2007). Further chemical characterization of ashes of the raw materials was carried out following ASTM D3682-01-06(07) standard.

Volatiles content was determined using thermogravimetry (TGA). For the test, a simultaneous differential scanning calorimetry-TGA equipment (TGA/SDTA851e, Mettler Toledo) was used, following ASTM E1131-08 in inert atmosphere (Nitrogen, flow rate of 100 ml/min) in the temperature range of 35–600 °C at a heating rate of 10 °C/min [16, 17]. Approximately 7 mg of each material was employed in the tests, in duplicates to verify results. DTG curves obtained from TGA were used to investigate the thermal degradation of hemicellulose and cellulose (see Sect. [Thermogravimetric analysis](#)).

Elemental composition (CHN) was determined using a LECO® TruSpec CHN instrument, following the procedure described in a previous study [16]. Briefly, approximately 0.13 g of oven dried material were fed in the combustion chamber of the Truspec CHN module for combustion at 950 °C, using ultra-high purity oxygen (99.993% purity). These tests were also conducted in duplicates to verify results. For S (sulfur) analysis, a LECO® 628S module was used. Approximately 0.1 g of dried material was fed into the 628S module after preparation following the procedure outlined in the Organic Application Note for Sulfur in Biomass and Biofuel (<http://www.leco.com>) and using LECO 528-203 crucibles. Results of ash content were used to correct the results of the elemental composition of each material. The results of elemental composition tests were used for computing the higher heating values (HHV in kJ/kg) employing the correlation of Friedl et al. [18].

### Wood Torrefaction Process

Torrefaction of the four materials was carried out in a single zone electric Lindberg Blue tube furnace (spoon reactor, capacity of approximately 3 g of biomass per batch). The process tube was metallic, with internal diameter of 25.4 mm. The carrier gas used for torrefaction was nitrogen,

with a volumetric flow of 150 ml/min. Prior to conducting the tests, the materials were ground (with particle size as used for TGA) and dried for 24 h at approximately 100 °C. Three levels of temperature were selected for torrefaction: 200, 250, and 300 °C, for 30 min, as reported in previous works [9, 16]. The tests were conducted in duplicate and the mean of the results are reported. Torrefied materials were used for determining elemental composition following a process similar to that used for the raw materials.

Mass and energy yields of the torrefaction process were computed and used as indicators of the mass degradation and energy content changes due to the torrefaction process [19]. These parameters were calculated as per Eqs. (1) and (2), respectively. In these equations,  $m_{bms}$  and  $m_{bms,torr}$  are the masses in grams of untreated and torrefied wood, respectively, while  $HHV_{bms}$  and  $HHV_{bms,torr}$  are the higher heating values (kJ/kg) of each raw and the corresponding torrefied material, respectively.

$$\text{Mass yield} = \frac{m_{bms,torr}}{m_{bms}} \quad (1)$$

$$\text{Energy yield} = \frac{m_{bms,torr} \times HHV_{bms,torr}}{m_{bms} \times HHV_{bms}} \quad (2)$$

### Py-GC/MS Studies

Pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) studies were conducted intending to determine the


effect of torrefaction on the pyrolysis products of the four materials tested. Results could be of interest for future studies involving the production of biofuels via fast pyrolysis and enhancing yields of targeted pyrolysis products via pretreatment operations, in which torrefaction is of interest [20]. Py-GC/MS was performed using a GC/MS system (6890N Network GC System with a 5975B inert XL MSD, from Agilent Technologies) coupled with a CDS pyro-probe 5000 series (CDS Analytical, Inc), as described in elsewhere [16, 21]. The tests were conducted in duplicate, at 500 °C for 1 min, using approximately 0.5 mg of each raw material and the corresponding materials torrefied at 200 and 300 °C. Weighting of samples was conducted using the TGA/SDTA 851e Mettler Toledo equipment described previously. Compounds that showed the highest intensity in the pyrolysis chromatograms were identified considering retention time, mass spectra, and comparison with database of the NIST/EPA/NIH Mass Spectral Library V. 2.0d (Fair Com Corp). The areas of peaks were then divided by the mass of the corresponding sample for normalization of areas [16].

## Results and Discussion

### Raw Biomass Properties

Table 1 shows the properties of the four raw materials. It is seen that volatile matter is approximately the same for all materials, except for *E. grandis*, which shows lower volatile

**Table 1** Results of the proximate and ultimate analyses tests of the four samples

Property	<i>Pinus maximinoi</i>	<i>Pinus patula</i>	<i>Eucalyptus grandis</i>	<i>Gmelina arborea</i>
				
Proximate analysis (wt% d.b.)				
Volatile matter	74.33	72.57	67.35	72.00
Fixed carbon	25.45	27.17	32.34	27.24
Ash	0.22	0.26	0.31	0.77
Ultimate analysis (wt% d.b.)				
C	54.45	55.01	53.31	52.73
H	7.04	7.21	6.74	6.96
O	37.79	36.72	39.26	39.12
N	0.52	0.81	0.39	0.47
S	0	0.01	0.02	0.02
Other properties				
Moisture (wt% w.b.)	8.07	9.36	8.54	10.08
Bulk density of wood chips <sup>a</sup> (kg/m <sup>3</sup> )	175.60	164.09	281.30	151.52
LHV <sub>d.b.</sub> (kJ/kg)	18,990	18,948	18,489	18,582

<sup>a</sup>(w.b.) wet basis (as obtained after drying at room conditions)

matter compared with the other samples. Thus, *E. grandis* also shows the highest fixed carbon among the samples. High volatiles content benefits biomass reactivity because the devolatilization reaction rate increases, and thus thermochemical processes such as combustion and gasification are favored [22], as it is of interest in Colombia. The ash content is approximately similar in *P. maximinoi*, *P. patula*, and *E. grandis*, but higher in *G. arborea*. Results of elemental composition show approximately similar C, H, and O content. Higher O content promotes higher chemical reactivity of biomass in thermochemical processing operations such as gasification [23], due to the oxygenated condition of biomass. Therefore, if the O content increases, the biomass needs a lower amount of oxidative agent to achieve a specific equivalence fuel-oxygen ratio [24]. N content is relatively high in *P. patula*. As expected, the S content is negligible or none, which is beneficial for thermochemical processing operations. The elemental composition is in the range of values for other wood samples reported by Williams et al. [25].

Table 1 also shows the bulk density of the four samples. *Eucalyptus grandis* presents the highest bulk density (by up to 46%) among the tested samples. It is also seen that the LHV is approximately similar for all samples (close to 19 MJ/kg). The raw wood samples have approximately similar volatile matter (70 wt%), and ash content (< 1 wt%).

Table 2 shows the chemical composition of the ashes of the four samples. Literature shows that the composition of ash could be useful to predict the behavior of biomass during gasification and combustion related with the fouling and melting points of ashes [26, 27]. The concentration of the compounds identified in the ashes follows a trend in which

Ca is the most abundant, while Al contents is the least. The identified trend of compounds in each sample is as follows:

PPat: CaO > K<sub>2</sub>O > MgO > SiO<sub>2</sub> > P<sub>2</sub>O<sub>5</sub> > Fe<sub>2</sub>O<sub>3</sub> > Al<sub>2</sub>O<sub>3</sub>

PMax: CaO > MgO > K<sub>2</sub>O > SiO<sub>2</sub> > P<sub>2</sub>O<sub>5</sub> > Al<sub>2</sub>O<sub>3</sub> > Fe<sub>2</sub>O<sub>3</sub>

EGra: MgO > CaO > K<sub>2</sub>O > Fe<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub> > P<sub>2</sub>O<sub>5</sub> > Al<sub>2</sub>O<sub>3</sub>

GArb: CaO > SiO<sub>2</sub> > MgO > K<sub>2</sub>O > Al<sub>2</sub>O<sub>3</sub> > Fe<sub>2</sub>O<sub>3</sub> > P<sub>2</sub>O<sub>5</sub>

The concentration of Fe<sub>2</sub>O<sub>3</sub> in mineral matter is higher for *E. grandis* with regard to the other three samples analyzed in this work (Table 2). This variation is attributed to tissue type, and across harvest time and environments [8], these forest crop parameters were not controlled in this study. Table 2 also shows that the alkali index in the materials varies between 0.02 and 0.09, suggesting that the materials tested present a low tendency to fouling, which can occur if the alkali index is higher than 0.17 [26]. Lower amounts of alkali metals such as K and Na, on the other hand, minimize ash related problems during thermochemical processes (specifically gasification and combustion) due to the higher melting point of ashes that lead to avoid sintering/agglomeration [26, 27]. Moreover, the alkali metals alter the pyrolysis process affecting the product properties [28] (see Sect. [Product distribution from Py-GC/MS analysis](#)).

The base-to-acid ratio estimates the potential of ash melting [29]. As shown in Table 2, this parameter varies between 2.3 and 6.5 for all samples. Since base-to-acid ratio is higher than 0.3, it is expected that the mineral matter of wood species under thermochemical processes

**Table 2** Chemical composition of the ashes of the four raw materials

Compound/property	<i>Pinus maximinoi</i>	<i>Pinus patula</i>	<i>Eucalyptus grandis</i>	<i>Gmelina arborea</i>
Mineral composition (% ash)				
SiO <sub>2</sub>	14.76	10.57	14.09	23.91
CaO	40.27	51.29	18.56	31.84
K <sub>2</sub> O	16.62	13.09	17.00	14.43
P <sub>2</sub> O <sub>5</sub>	4.14	3.50	5.50	0.39
Al <sub>2</sub> O <sub>3</sub>	3.58	1.93	3.02	6.17
MgO	16.02	16.38	21.53	15.72
Fe <sub>2</sub> O <sub>3</sub>	1.41	2.26	15.88	0.71
SO <sub>3</sub>	0.01	0.00	0.01	0.02
Na <sub>2</sub> O	3.06	0.66	3.93	6.73
TiO <sub>2</sub>	0.14	0.32	0.47	0.09
Alkali index <sup>a</sup> (kg K <sub>2</sub> O and Na <sub>2</sub> O/GJ)	0.02	0.02	0.04	0.09
Ratio base-to-acid <sup>b</sup>	4.19	6.53	4.37	2.30

<sup>a</sup>Parameter calculated according to Jenkins et al. [26]

<sup>b</sup>Parameter calculated according to Salour et al. [29]

(gasification or combustion) will present a low trend to melt [27, 29].

### Effect of Torrefaction on Biomass Properties

#### Mass and Energy Yields of Torrefaction Process

The mass yield for the wood species decreases in different proportions when torrefaction temperature increases, as shown in Fig. 2a. For torrefaction at 200 °C, the mass yields for all species are practically the same (~98%) implying that only a small degradation of biomass constituents occurs at these temperatures. The mass lost during torrefaction at 250 °C varies between 4.9% for PMax and 9.2% for EGra. After water evaporation (if moisture is present in the samples), the thermal degradation of hemicelluloses is the first event during torrefaction process. In torrefaction at 300 °C, the mass losses increase to up to 43.9% for Garb and 30.4% for EGra. This behavior is associated mostly with the partial thermal degradation of the constituents of lignocellulosic biomass, especially hemicellulose and, in less proportion, cellulose and lignin [12, 30]. Cellulose suffers a progressive thermal degradation starting with the amorphous fraction [17], whereas lignin thermal degradation occurs in a wide temperature range (e.g. 250–500 °C) [12, 31].

Figure 2a, b show the mass and energy yield, respectively, for the four species at different torrefaction conditions. Since the heating value of hemicellulose is lower than that of cellulose and lignin [32], lower energy losses are expected for these materials. In Fig. 2b it is also seen that the energy yields for torrefaction at temperature of 200 °C is approximately the same for all the materials tested. The wood sample with higher energy content after torrefaction at 300 °C is *E. grandis*. Lu et al. [33] conducted torrefaction of eucalyptus, under nitrogen environment, from 250 to 350 °C for 1 h and obtained similar trends. At 300 °C, the mass and

energy yields reported by the authors for eucalyptus were 57.9 and 75.4%, respectively. These yields are lower than those obtained in this work, probably because longer torrefaction times favor hemicellulose and cellulose thermal degradation.

#### Proximate and Ultimate Analyses

As presented in Table 1, PMax is the species with the highest volatile matter content, which is around 10% higher than EGra (the species with the lower VM content). Figure 3 shows the volatile matter (VM)/fixed carbon (FC) ratio for all species after torrefaction. There are no visible differences in VM/FC ratios in materials torrefied at temperatures up to 250 °C. However, for torrefaction temperature of 300 °C, the four wood species released a considerable amount of volatile matter, which is more visible in the case of GArb. The trend

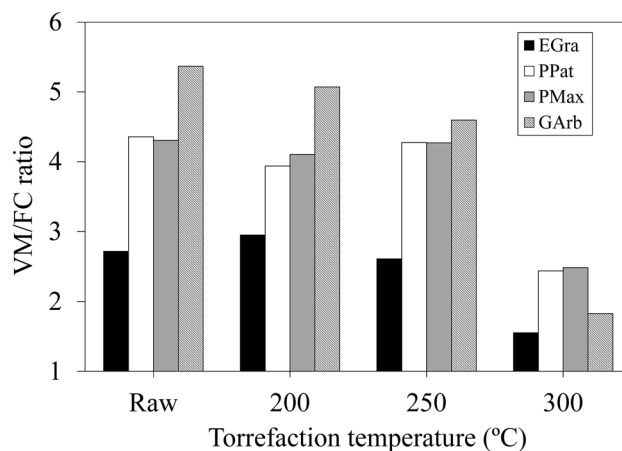


Fig. 3 VM/FC ratio for all species at different torrefaction temperatures

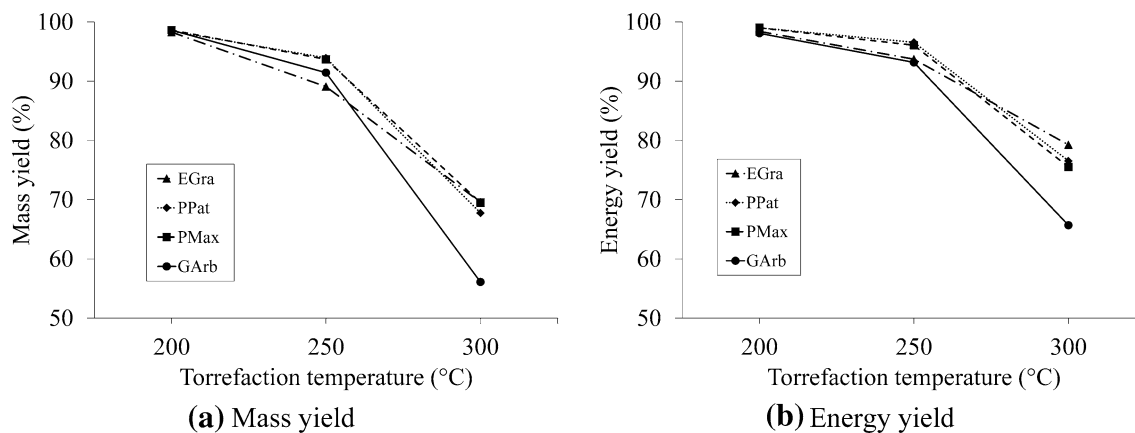
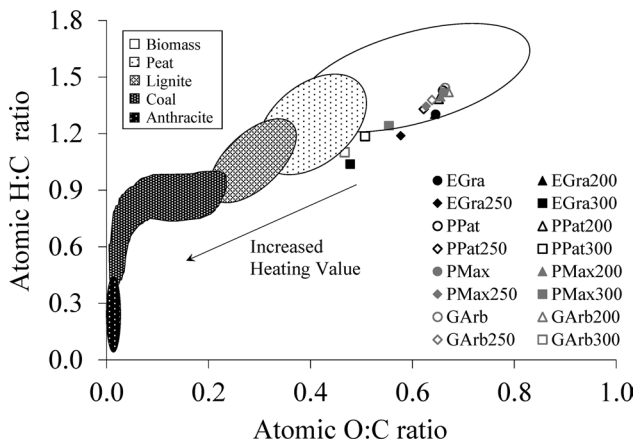


Fig. 2 Mass and energy yields for all species at different torrefaction temperatures





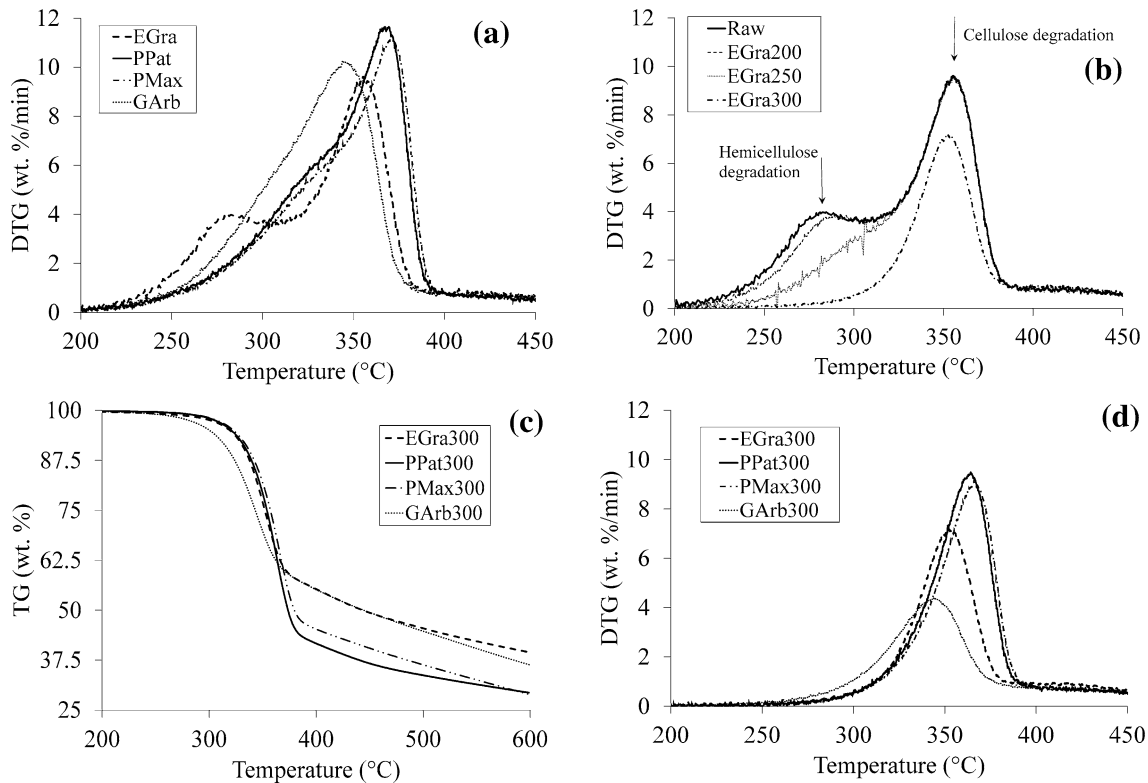
**Fig. 4** Van Krevelen diagram for raw and torrefied materials at different temperatures for 30 min

seen for proximate analysis is consistent with the mass yield discussed previously.

Figure 4 presents a Van Krevelen diagram, showing the decomposition progression of the four biomasses during the torrefaction process. It is seen that the H:C and the O:C atomic ratios decrease as torrefaction temperature increases due to the release of volatile matter. Volatiles released during torrefaction possess high H:C and O:C ratios, suggesting

a reduction of H and O in the remaining solids [34–36]. The main non-condensable volatile products formed during torrefaction are CO<sub>2</sub> and CO due to decarboxylation and cracking reactions [37, 38]; whereas, in the condensable volatile products, the water and the acetic acid are the major compounds. Water is released as a result of moisture evaporation and dehydration reactions, while acetic acid results from hemicellulose degradation [37]. Other authors have reported similar results on the changes of biomass composition at different torrefaction conditions [9, 39–44].

As expected, reduction of the O:C ratio enhances the heating values of the torrefied materials [45]. If the higher heating value is the selection criterion to use a biomass species as feedstock for fuel, *Gmelina* and *Eucalyptus* torrefied at 300 °C are the species that could be selected. Despite that *Eucalyptus* has lower heating value than *Gmelina*, for both torrefied at 300 °C, the *Eucalyptus* sample has a higher energy yield during torrefaction. This result suggests that, from an energy content point of view, this material is the best choice among the four wood species if torrefaction is conducted as a pre-treatment method when the material is intended, for instance, for fuel pellets production. Higher heating values improve the global efficiency of thermochemical processes such as gasification and combustion [24, 46–48].



**Fig. 5** TG and DTG results of the four raw materials and the corresponding torrefied materials. **a** DTG for all raw species, **b** DTG for raw and torrefied eucalyptus, **c** TG for all species torrefied at 300 °C, **d** DTG for all species torrefied at 300 °C

## Thermogravimetric Analysis

Figure 5 shows the TGA and DTG behavior of the raw and the torrefied materials. The curves for torrefied materials have been multiplied by their corresponding mass yield (Fig. 2a) in order to obtain a standard basis (raw biomass) for comparison purposes, following the procedure proposed by Pelaez-Samaniego et al. [16]. Figure 5a shows the DTG curves for raw species. The DTG curves suggest that both hemicellulose and cellulose structures are different for each species [12, 49]. Therefore, the degradation rate for each species will be different leading to different mass losses (mass yield) for materials at the same torrefaction conditions (see Fig. 2a).

Figure 5b shows the effect of torrefaction temperature on the thermal decomposition behavior of EGra. GARb and pine species presented similar behavior in function of process temperature (data not shown). *Eucalyptus* torrefied samples at 200 and 250 °C and raw materials present a similar behavior under thermal conditions due to the low changes in composition obtained in the proximate analysis (Fig. 3). Additionally, at the most severe torrefaction condition (i.e., 300 °C), DTG curve only shows a large peak with lower intensity than the raw and torrefied materials up to 250 °C. A complete degradation of hemicellulose and a partial degradation of a fraction of cellulose occur at this torrefaction temperature [12, 16, 49]. Figure 5c, d show the TG and DTG curves for all species torrefied at 300 °C, respectively. At this torrefaction condition, the thermal stability is quite

**Table 3** Identification of the main compounds found in the Py-GC/MS chromatograms

Peak number	Retention time (RT)	<i>m/z</i>	Compound	Name
1	1.57	44	CO <sub>2</sub>	Carbon dioxide
2	1.8	43	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	1-Propen-2-ol, acetate
3	2.43	43	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Acetic acid
4	2.66	43	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	2-Propanone, 1-hydroxy-
5	3.89	43	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	1,2-Ethandiol, monoacetate
6	4.25	43	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	Propanoic acid, 2-oxo-, methyl ester
7	5.05	96	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	Furfural
8	7.33	98	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	2-Cyclopenten-1-one, 2-hydroxy-
9	8.04	28	C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>	Succinic acid, cyclic hydrazide
10	8.95	114	C <sub>8</sub> H <sub>17</sub> NO	Oxazolidine, 2,2-diethyl-3-methyl-
11	9.76	112	C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>	1,2-Cyclopentanedione, 3-methyl-
12	11.28	109	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	Phenol, 2-methoxy-
13	13.6	123	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	Phenol, 2-methoxy-4-methyl-
14	15.65	137	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	Phenol, 4-ethyl-2-methoxy-
15	16.47	135	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	2-Methoxy-4-vinylphenol
16	17.4	164	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	Eugenol
17	17.65	137	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	Phenol, 2-methoxy-4-propyl-
18	18.53	152	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	Vanillin
19	19.55	164	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-
20	19.73	137	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	Phenol, 2-methoxy-4-propyl-
21	20.31	151	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
22	21.33	43, 60	C <sub>6</sub> H <sub>10</sub> O <sub>5</sub>	Levoglucosan
23	21.76	167	C <sub>10</sub> H <sub>14</sub> O <sub>3</sub>	5-tert-Butylpyrogallol
24	21.79	165	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	3',5'-Dimethoxyacetophenone
25	22.47	194	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
26	23.53	137	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	Vanillic acid
27	24.12	194	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
28	25.12	178	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	4-Hydroxy-2-methoxycinnamaldehyde
29	25.75	167	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	Desaspidino
30	28.68	73	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	n-Hexadecanoic acid
31	29.27	208	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	3,5-Dimethoxy-4-hydroxycinnamaldehyde
32	31.75	43	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	Octadecanoic acid

The peak numbers correspond to those used to identify peaks in the chromatograms

similar for the pine species and EGra. GARb is the most reactive wood species since its degradation starts at 260 °C approximately; this material was the most affected by torrefaction in terms of mass loss (Fig. 2). The higher reactivity of GARb is also shown in the Fig. 5a, where the maximum devolatilization rate is reached at lower temperatures than the other pine species and Eucalyptus. The DTG curves of species torrefied at 300 °C (Fig. 5d) suggest that the four materials torrefied at this temperature are mainly composed by cellulose and lignin due to partial degradation of hemicelluloses (i.e., the characteristic shoulder associated with hemicelluloses degradation is not visible as the materials are torrefied at higher temperatures [50]). Similar results were reported by Chen et al. [51], who torrefied eucalyptus in nitrogen from 250 to 350 °C under a residence time of 1 h. These authors highlighted that the torrefaction process is a suitable pretreatment to upgrade the lignocellulosic biomass properties due to the thermal stability of cellulose and lignin [33].

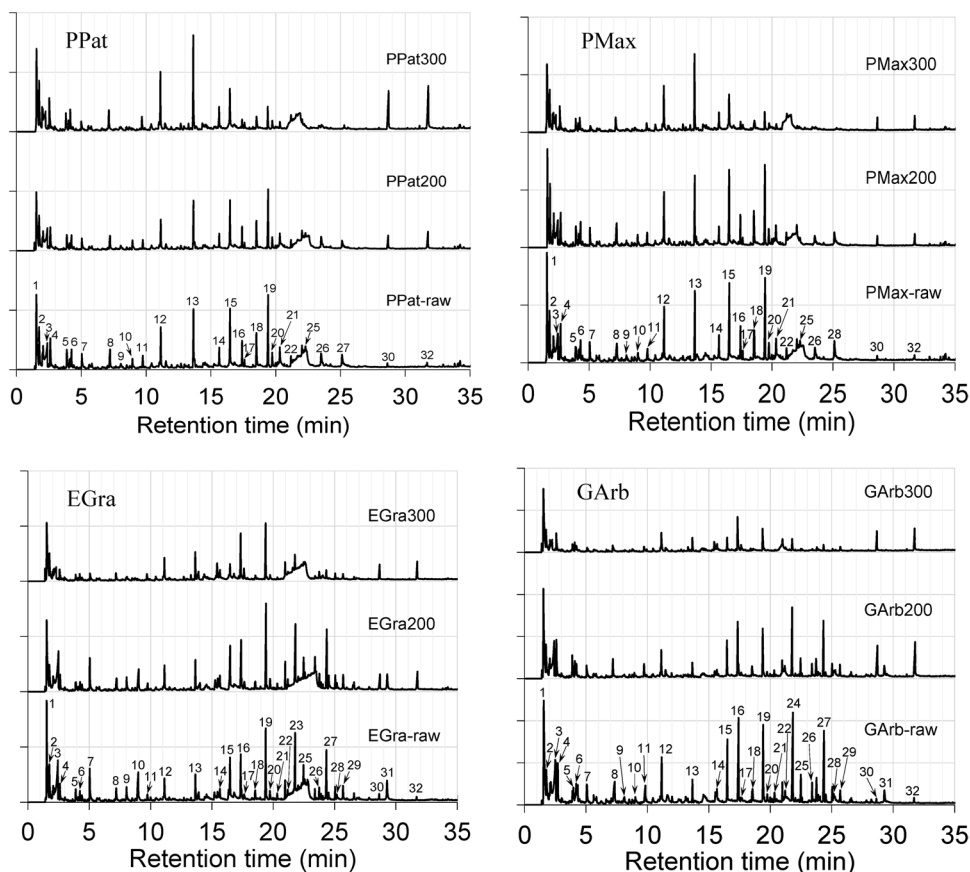
### Product Distribution from Py-GC/MS Analysis

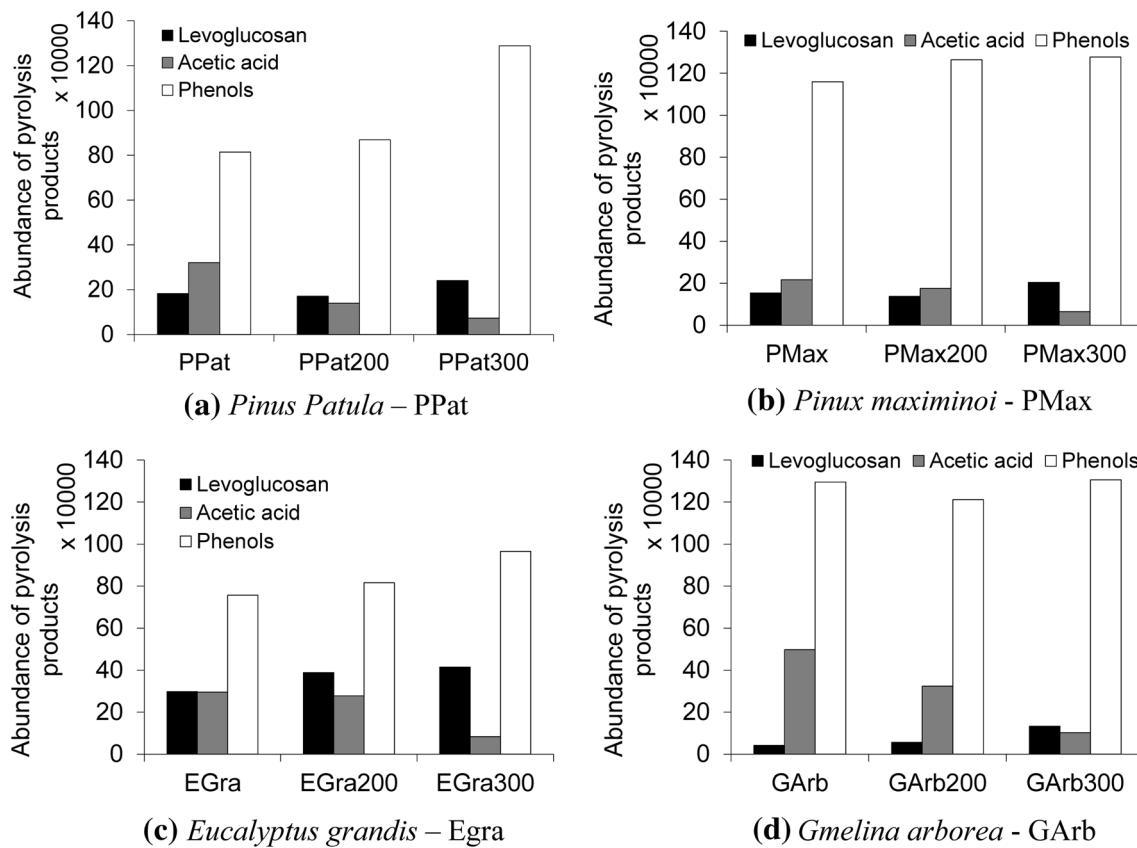
Py-GC/MS was performed to determine the changes on the composition of the four materials as a result of torrefaction. Additionally, this procedure allows to estimate the

main pyrolysis products of the raw and torrefied material. As mentioned in Sect. [Product distribution from Py-GC/MS analysis](#), the Py-GC/MS analysis was carried out for raw and samples torrefied at 200 and 300 °C, due to the similarities found between samples torrefied at 200 and 250 °C. Table 3 shows the main compounds identified for samples, and Fig. 6 shows the chromatograms of the pyrolysis of each material raw and torrefied at 200 and 300 °C.

Figure 7 shows a comparison of the presence of acetic acid, levoglucosan, and phenols in the pyrolysis products of the raw materials and materials torrefied at 200 and 300 °C. Acetic acid (peak number 3, RT of 2.43 min), levoglucosan (peak number 22, RT of 21.33 min), and some phenolic compounds (peak numbers 11–21, at different retention times 9.76, 11.28, 13.6, 15.65, 16.47, 17.4, 17.65, 18.53, 19.55, 19.73, and 20.31 min) are the most abundant compounds identified in the products of the pyrolysis of the raw materials of the four samples and the corresponding torrefied materials. These compounds are associated with the pyrolysis of hemicellulose, cellulose, and lignin, respectively [14, 21, 52–54]. Figure 7 shows the effect of torrefaction temperature on abundance of acetic acid, levoglucosan and phenols of all materials. It is observed that: (1) acetic acid presents a declining trend, which is expected since the presence of hemicelluloses is reduced as the temperature of

**Fig. 6** Typical chromatograms of the four tested materials and their corresponding torrefied samples (identification of compounds is presented in Table 3). Original chromatograms were divided by the mass of the corresponding sample for normalization of peaks





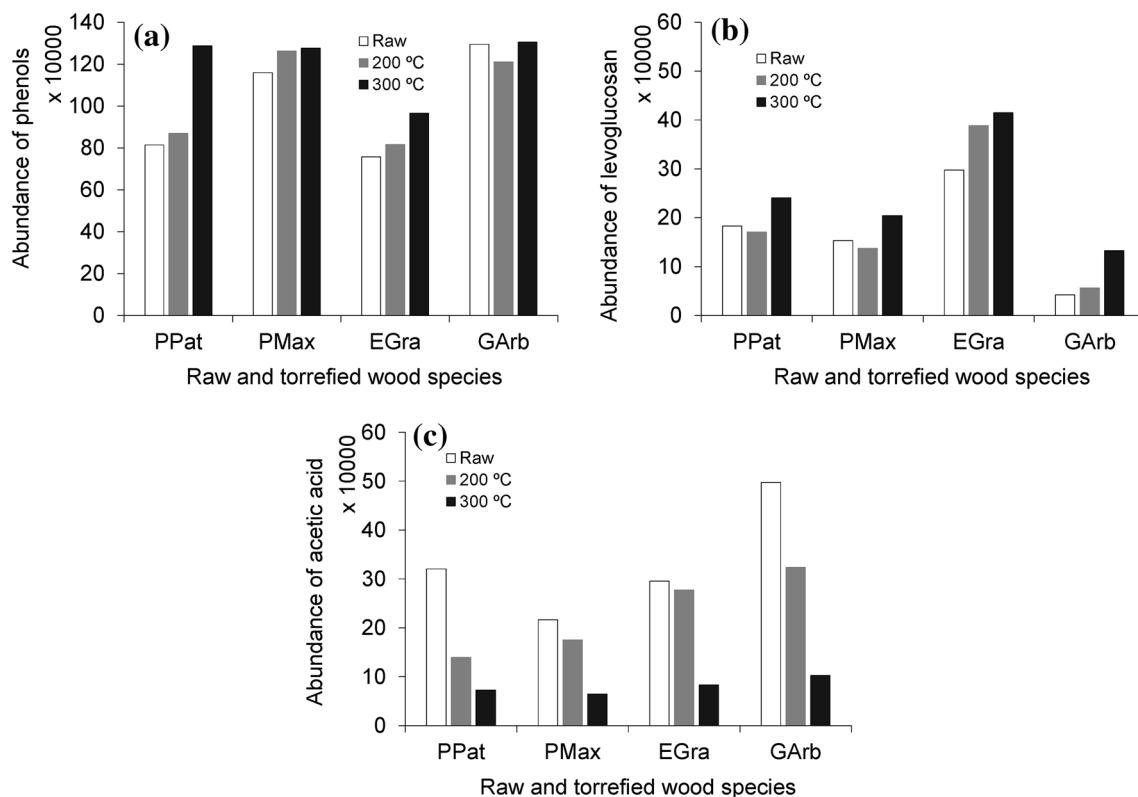
**Fig. 7** Abundance of pyrolysis products in the raw and materials torrefied at 200 and 300 °C (obtained via Py–GC/MS)

torrefaction increases due to the elimination of acetyl groups in hemicellulose structure [28], (2) the presence of phenols show an increasing trend, which is expected as lignin (from which phenols are derived during pyrolysis) in the torrefied material is degraded only in minor proportion compared to hemicellulose, and (3) the products of the pyrolysis of cellulose, i.e., levoglucosan, shows an increasing trend as the torrefaction temperature is increased. This result is also expected since cellulose is relatively more stable than other wood constituent in the range of torrefaction temperatures. The result also suggests that torrefaction is an appropriate thermal pretreatment to increase the yields of levoglucosan in pyrolysis products, which is of interest for further studies intending the production of biofuels using these materials. It is known that levoglucosan, besides cellobiosan (which is not shown in Table 3 due to low yields in our experiments), is one of the targeted pyrolysis products for biofuels production via fast pyrolysis of lignocellulosic biomass [52, 53]. The tendency described above is also shown in Fig. 6 for most compounds. The peak corresponding to acetic acid decreases as the temperature of torrefaction increases. The trend of the intensity of the peaks corresponding to the formation of levoglucosan and phenols shows an increase (although not in all phenolic compounds). As expected, the

peak height of levoglucosan (peak number 22) shows an increasing trend as the temperature of torrefaction increases. These results are in agreement to those reported for torrefaction-fast pyrolysis multistep studies [55, 56].

Figure 8 shows a comparison of the abundance of the pyrolysis products in function of the materials tested. It is seen that EGra shows the lowest presence of phenols in all conditions (i.e., in untreated conditions and after torrefaction at 200 and 300 °C), see Fig. 8a. Additionally, this material presents the highest abundance of levoglucosan (in all conditions of torrefaction and as untreated material) (see Fig. 8b). This can be attributed due to the lower amount of cellulose decomposed for this species [30]. Even though these results are not conclusive, the findings suggest that, among all the materials tested, EGra offers more potential for biofuels production via fast pyrolysis. However, it appears that the two pine species and GARb offer more potential than EGra if the targeted product is, for instance, fuel pellets due to the similar amount of phenols produced, since the lignin of torrefied species (PPat, PMax, and GARb) favors the pelletization of lignocellulosic biomass [16].

GArb produces the highest amount of acetic acid and phenols, and the lowest amount of levoglucosan. The delayed



**Fig. 8** Comparison of the relative presence of the main pyrolysis products in the materials treated at different conditions and the corresponding raw material. **a** Abundance of phenols, **b** abundance of levoglucosan, **c** abundance of acetic acid

formation of levoglucosan can be attributed to the high ash content and its high alkali index in GArb (Table 1). Alkali metals alter the pyrolysis reaction pathway of biomass constituents resulting in the significant changes in the pyrolysis specification and product properties [28].

## Conclusions

Fast growing wood species (*E. grandis*, *P. Maximinoi*, *P. patula*, and *G. arborea*) in Colombian highlands offer enormous potential for energy, biofuels, or bioproducts via thermochemical processing (i.e., gasification, combustion, or pyrolysis). Thermochemical processing has been seen as a promising pathway to take advantage of abundant wood species and woody residues in Colombia. We found that torrefaction is a promising pathway for improving fuel properties of these materials. The samples have approximately similar volatile matter (70 wt%), low heating value (~19 MJ/kg), and ash content (<1 wt%). The mass yield for the wood species decreases in different proportions when torrefaction temperature increases. For torrefaction at 200 °C, the mass yields for all species are practically the same (~98%),

suggesting that only a small degradation of biomass constituents occurs at these temperatures. The mass lost during torrefaction at 250 °C varies between 4.9% for PMax to 9.2% for EGra. Pyrolysis of torrefied samples showed that wood torrefied at 300 °C offers better yields of anhydro-sugars compared to the corresponding raw materials. The abundance of biomass derived from fast growing species can be combined with strategies to modify and improve the properties of woody biomass, thus making the use of these materials possible. Further studies are needed to advance an understanding on the economics and logistics of the process.

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