Characterization of Torrefied Biomass of Five Reforestation Species (*Cupressus lusitanica*, *Dipteryx panamensis*, *Gmelina arborea*, *Tectona grandis*, and *Vochysia ferruginea*) in Costa Rica

Johanna Gaitán-Alvarez,[a] Róger Moya,[a,]* Ana Rodríguez-Zúñiga,[a] and
Allen Puente-Urbina [b]

Torrefaction can increase the energy yield of biomass for better utilization in bioenergy, but chemical changes occur during the pretreatment process. Wood residues of *Cupressus lusitanica*, *Dipteryx panamensis*, *Gmelina arborea*, *Tectona grandis*, and *Vochysia ferruginea* were torrefied for three different time periods (8, 10, and 12 min) and three different temperatures (200, 225, and 250 °C). The mass loss, net calorific value, ash, volatiles, lignin, cellulose, extractives, and infrared spectra were evaluated. The results showed that the mass loss in torrefied biomass varied between 10% and 70%, ash content varied between 0.19 and 7.00%, and volatiles content varied between 63 and 85%. Net calorific value values varied between 17 and 23 MJ/kg, increasing with the increased torrefaction temperature. Cellulose varied between 49.85 and 67.57%. Lignin varied between 27.33 and 41.09%. The extractives varied between 3.70 and 16.86%. The change in the ratio of intensity (RI) for the bands identified using FTIR analyses showed that large changes occurred in hemicellulose components. The multivariate analysis showed that lignin, ash, extractives in hot water, volatiles, and mass loss were the variables that contributed most. The analysis of all these variables showed that torrefaction at 250 °C for 12 min presented the greatest biomass degradation. Torrefaction at 200 °C and 225 °C for 8, 10, and 12 min was optimal for thermal treatment of the biomass of these woody species.

Keywords: Biomass; Torrefaction; Thermal stability; Costa Rica

*Contact information: a: Escuela de Ingeniería Forestal, Instituto Tecnológico de Costa Rica, P. O. Box 159-7050 Cartago, Costa Rica; b: Instituto Tecnológico de Costa Rica, Centro de Investigación y de Servicios Químicos y Microbiológicos (CEQIATEC), Escuela de Química, Apartado 159-7050, Cartago, Costa Rica; *Corresponding author: rmoya@itcr.ac.cr*

INTRODUCTION

Accelerated population growth in recent years has generated increased demand for energy at a global level; another 48% increase in this demand is expected in the year 2040 (Fournel *et al.* 2015). However, one of the major environmental phenomena that the global society is facing is climate change due to increased carbon dioxide (CO_2), methane, and nitrous oxide emissions (Chen *et al.* 2015a). In response, sustainable energy technologies based on renewable raw materials are being developed (Bach and Skreiberg 2016).

Biomass is an attractive renewable source of heat-produced energy (Roy and Corscadden 2012). Its major advantage is that the raw material is widely available; it produces low CO_2 emissions, which maintains the natural carbon cycle (Puig-Arnavat *et al.* 2016). However, biomass presents some disadvantages as a source of energy, including disperse distribution, which makes collection difficult; irregular dimensions; low calorific value; high moisture content; hygroscopic nature, which hinders efficient and low-cost material transportation; handling difficulties; storage; and product conversion (Puig-Arnavat *et al.* 2016). Compared with other agricultural crops, lignocellulosic biomass has greater capability to generate renewable energy (Bahng *et al.* 2009; Gokcol *et al.* 2009).

The tropical climate of Costa Rica allows the development of various agricultural and forestry crops. However, generation of lignocellulosic residues poses a major problem (Coto 2013). The use of these wastes is limited, as it represents costs in handling and disposal, in addition to restrictions and even environmental and industrial risks to the sector, such as generation of untreated leachates, greenhouse gas emissions, and fire risks (Chacón 2012). *Cupressus lusitanica*, *Dipteryx panamensis*, *Gmelina arborea*, *Tectona grandis*, and *Vochysia ferruginea* are important woods in the forest sector because of their quality and adaptation in various ecosystems (Petit and Montagnini 2004). They produce great amounts of residues from exploitation and industrialization (Serrano-Montero and Moya-Roque 2011). These residues can be used as energy sources (Tenorio *et al.* 2014; Aragón-Garita *et al.* 2016). However, scarce studies exist that show the energy potential or the possibility to increase this potential by means of chemical or thermal treatments (Tenorio and Moya 2012; Moya *et al.* 2017).

The thermal treatment of biomass can increase its energy potential (Medic *et al.* 2012). Torrefaction increases the energy density of biomass and its resistance to moisture (Wang *et al.* 2011; Peng *et al.* 2013; Chen *et al.* 2015a). In the torrefaction process, the biomass is taken to temperatures between 200 and 300 °C for minutes or hours, usually under atmospheric pressure and in the presence of an inert atmosphere (Chen *et al.* 2014b). Some benefits of the pre-treatment process are high calorific value, atomic decrease of O/C and H/C bonds, less moisture content, greater hydrophobicity, and improved grinding capacity (Chew and Doshi 2011; Ciolkosz and Wallace 2011; van der Stelt *et al.* 2011).

Biomass composition has great importance because it influences both the torrefaction process as well as properties of the resulting fuels, including their efficiency and emission levels (Janvijitsakul and Kuprianov 2008). Some of the most important components are lignin, cellulose, and hemicellulose (Bridgewater 2004; Gosselink *et al.* 2004; Brebu and Vasile 2010). Other minor components are extractives and ash content. Their quantification, together with the influence of calorific value, are very important to understand and optimize the thermal process intended (Chen *et al*. 2017ab). In this regard, standard methods have been widely used to determine composition. However, other techniques (*e.g.*, Fourier transform infrared spectroscopy (FTIR)) have been used recently to gain a better understanding of the chemical modification of lignocellulosic biomass (Xu *et al.* 2013).

Given the constant generation of residues from the wood industry and the possibility to apply torrefaction to these types of biomass (Gaitán-Álvarez and Moya 2016), the present study aimed to establish the energy change (*i.e.*, considering calorific value, volatile content, and ash content), chemical change (*i.e.*, contents of lignin, cellulose, and extractives), and the infrared spectrum of the biomass from 5 woody plantation species. These species were subjected to 3 torrefaction temperatures (200, 225, and 250 °C) and 3 treatment times (8, 10, and 12 min). The goal of this study is to improve the treatment of biomass to obtain renewable viable raw material for the generation of clean energy.

EXPERIMENTAL

Provenance and Characteristics of the Material

Woody sawdust of *C. lusitanica*, *D. panamensis*, *G. arborea*, *T. grandis*, and *V. ferruginea* from fast growth plantations in different sites in Costa Rica were used. The age of the plantations ranged between 8 and 14 years. The details of provenance of the material are available in Moya *et al.* (2017), Gaitán-Álvarez *et al.* (2017), and Gaitán-Álvarez and Moya (2016). Sawdust from all species was collected directly from the sawing process, conditioned to 12% moisture content, and then sieved. After sieving, sawdust particles were used in a proportion of 70% of 450 to 1000 μm and 30% of 200 to 425 μm.

Torrefaction Process

Theree replicates with approximately 500 g of sawdust from each species were applied the torrefaction conditions, which are detailed: 200 °C for 8 min (200-8); 200 °C for 10 min (200-10); 200 °C for 12 min (200-12); 225 °C for 8 min (225-8); 225 °C for 10 min (200-10); 225 °C for 12 min (200-12); 250 °C for 8 min (250-8); 250 °C for 10 min (250-10); and 250 °C for 12 min (250-12). Previous research (Gaitán-Álvarez *et al.* 2017) showed that these five species present the highest percentage of hemicellulose. As can be observed in torrefaction, the hemicellulose is the component presenting the least thermal stability. Consequently, it was necessary to reduce the time and the temperature of the torrefaction to avoid an excessive degradation of the biomass, this specifically for tropical species.

A modified Thermolyne Furnace 48000 (Thermolyne Barnstead, Iowa, USA) was used for each torrefaction process. This furnace was sealed to prevent airflow but was provided with a manual system that was allowed to equilibrate its internal pressure to the external atmospheric pressure. Every 4 to 5 min, hot internal gases were freed, allowing the development of a torrefaction process in an environment with limited oxygen content (Gaitán-Álvarez and Moya 2016). The weight was measured before and after torrefaction process each replicate, and the weight loss was calculated after torrefaction (W_{loss}). After three replicates was grouped in one sample.

Determination of Energy Properties and Chemical Properties

Biomass energy and chemical properties were reported as net calorific value, chemical composition (contents of lignin, cellulose, ash, and volatiles), and extractives in different solvents (hot water, cold water, and ethanol-toluene solution). The net calorific value (NCV) was determined in the absence of water (0% moisture content) using the 6725 Semimicro Calorimeter model Parr (Parr Instrument Company, Illinois, USA), in accordance with the ASTM D5865-04 (2003) standard. To determine the ash content, 5 randomly selected 2 g samples were tested according to ASTM D1102-84 (2013). For the percent volatiles, 3 samples of 3 g each were tested according to ASTM D1762-84 (2013). Lignin, cellulose, ash, volatiles, extractives content were determined. The method used for quantification of lignin was TAPPI T222 om-02 (2002) and for cellulose determination the procedure followed was TAPPI T17 wd-70 (2002). Three samples in triplicate were used for each type of chemical determination. Extractives were determined in hot water (HW) and cold water (CW) in accordance with the ASTM D1110-84 (2003), and in an ethanol-toluene solution according to ASTM D1107-96 (2003). Three tests were performed for each extractive.

FTIR Measurements

For this analysis, 3 samples of torrefied woody biomass were measured for each treatment and species type. FTIR measurements were performed using a Thermo Scientific Nicolet 380 FTIR spectrometer (Wisconsin, USA) with a Smart iTR Attenuated Total Reflectance (ATR) sampling accessory. All the spectra were obtained using 32 scans and a resolution of 1 cm^{-1}, with a background correction before each measurement. The FTIR spectra obtained were processed with Thermo Scientific Omnic software. The main vibrations where the greatest changes in the wood occurred (Calienno *et al.* 2015; Li *et al.* 2015) are identified in Table 1 in Tenorio *et al.* (2016). The height of each peak was recorded and standardized using the band intensity at 1031 cm^{-1} (I_{1031}), given its stability in all study conditions. The intensity ratio between the different peaks in the range of 800 to 1800 cm^{-1} was calculated with Eq. 1.

$$Ratio\ of\ intensity\ \left(\frac{I_n}{I_{1031}}\right) = \left(\frac{Intensity\ of\ peaks\ between\ 1800\ to\ 800\ cm^{-1}}{Intensity\ of\ 1031\ cm^{-1}}\right) \quad (1)$$

Data Analysis

A descriptive analysis (*i.e.*, mean, standard deviation, maximum and minimum values) of the variables was carried out. In addition, it was verified whether they met the assumptions of normality and homoscedasticity of variance. The existence of significant statistical differences between means was verified by analysis of variance (ANOVA, $P \leq 0.05$), and finally, the Tukey test was applied to compare these differences using the InfoStat program (National University of Cordoba, Cordoba, Argentina).

RESULTS AND DISSCUSION

Mass Loss

As expected, W_{loss} increased with the torrefaction temperature, which ranged between 10% and 70% according to species, temperature, or torrefaction time (Fig. 1). Biomass presenting the lowest W_{loss} was treated at 200 °C in periods of 8, 10, and 12 min in the five species studied (Fig. 1). Conversely, the highest values of W_{loss} appeared when the torrefaction was applied at 250 °C and times of 8, 10, and 12 min (Fig. 1). For biomass torrefied at 250-12, the highest W_{loss} occurred in all species (Fig. 1). In all species, torrefaction temperatures of 200 °C and 225 °C rendered an average W_{loss} of 10%, whereas at 250 °C, the W_{loss} was above 20%.

Considering torrefaction times, torrefaction at 200 °C presented a relatively constant W_{loss} in all species. At 225 °C, an increase in W_{loss} was presented with 12 min, especially with *C. lusitanica* (Fig. 1a), *D. panamensis* (Fig. 1b), *G. arborea* (Fig. 1c), and *V. ferruginea* (Fig. 1e), while W_{loss} was similar with 8- and 10-min torrefaction periods in all species. Lastly, torrefaction at 250 °C showed a relatively constant increase in W_{loss} with increasing torrefaction time in *C. lusitanica, G. arborea*, *T. grandis,* and *V. ferruginea* (Fig. 1a, 2c-e), while in *D. panamensis*, torrefaction at 250 °C for 8 and 10 min showed similar values of W_{loss}, which increased after 12 min (Fig. 1b).

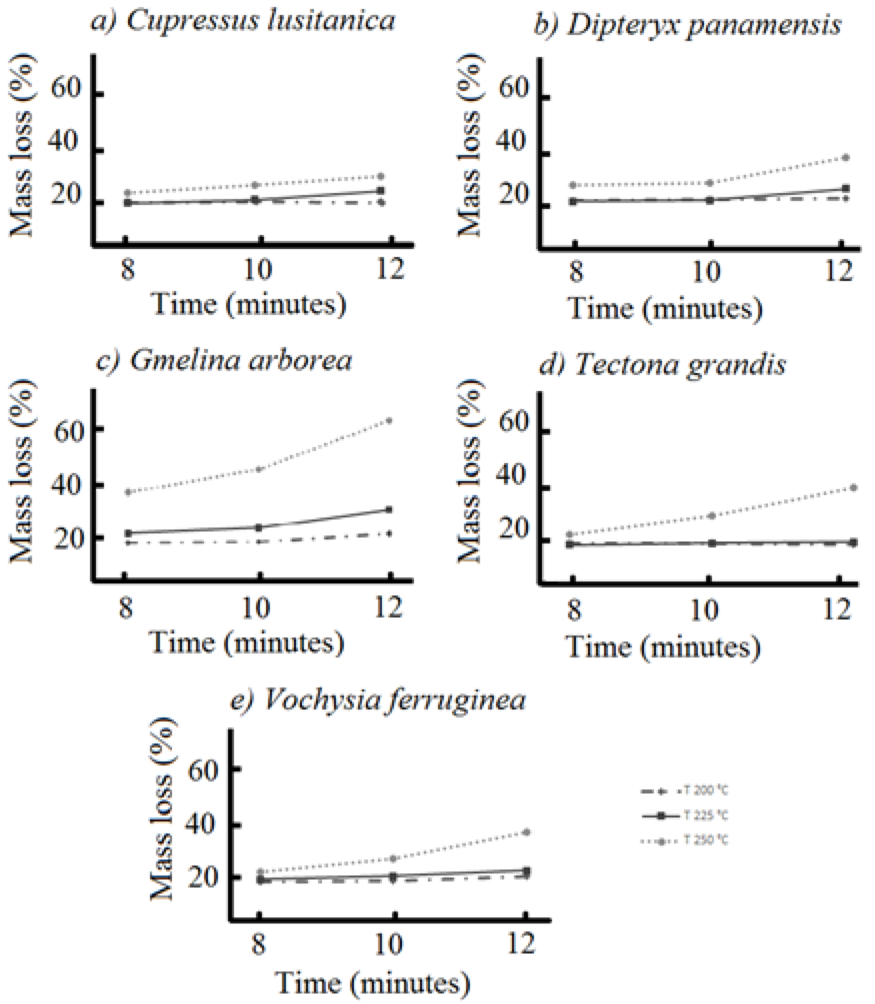

Fig. 1. Weight loss in biomass torrefaction at different temperatures and times of five types of biomass from woody tropical species

W_{loss} of biomass found after torrefaction ranged between 10% and 50% (Fig. 1), which is acceptable; to ensure the economy of the process, mass loss should not surpass 50% (Wannapeera *et al.* 2011). These percentages agree with Chen *et al.* (2011) study, which reported W_{loss} below 50% with torrefaction at 250 °C or less, while at higher temperatures, above 50% mass loss was observed, concluding that such torrefaction conditions are unsuitable. A similar situation was observed in biomass torrefaction for other species such as *Ficus benjamina*, where torrefaction at temperatures above 250 °C cause W_{loss} to be above 50% (Chen and Kuo 2010).

As expected, there was W_{loss} associated with the thermal treatments of the biomasses of all of the species studied (Fig. 1), due to a reduction in mass because of the events that happen when each biomass is treated under the torrefaction conditions. At relative low temperatures (*i.e.*, before the torrefaction temperature), the biomass releases mainly moisture. Then, there is a decrease in mass associated with the release of volatiles as well as decomposition of some components of the material, mainly hemicelluloses, in events greatly influenced by temperature and time of torrefaction (Almeida *et al.* 2010; Wannapeera *et al.* 2011). This explains the higher degree of decomposition and greater W_{loss} with increasing torrefaction time in this study (Fig. 1).

Once the temperature exceeds 225 °C, cellulose and lignin, the main components of woody biomasses start to degrade (Rousset *et al.* 2011; Wannapeera *et al.* 2011; Sabil *et al.* 2013; Tenorio *et al.* 2016). This degradation above 225 °C explains the higher W_{loss} in relation to temperatures of 200 °C and 225 °C (Fig. 1)

Each one of the species studied showed different values of W_{loss} for the various torrefaction temperatures and times (Fig. 1), and different volatilization with temperature, according to the characteristics of each species, which can be explained by the presence of extractives and the anatomical composition of the biomass (Gaitán-Alvarez *et al.* 2017; Moya *et al.* 2017). Each biomass presents different W_{loss} (Wannapeera *et al.* 2011; Moya *et al.* 2017), and each species features unique chemical and structural composition (Pazos and Sotelo 1999; Schroeder 2007), resulting in a distinctive behaviour of each species.

Energy Properties

Table 1 presents the results of ash and volatile contents obtained in the various biomass types torrefied. In general, ash content of different samples did not present statistically significant differences for low torrefaction temperatures but increased for 250 °C. The ash content ranged between 0.19% and 7.00%, with *C. lusitanica* being the one that presented lower ash content at torrefaction temperatures below 225 °C. However, this species, together with *G. arborea* and *V. guatemalensis*, at 250-10 and 250-12 torrefaction conditions presented the highest ash contents. In torrefied biomass of *D. panamensis*, the ash content decreased with respect to un-torrefied biomass, while thermal treatments under 200-12, 225-8, 250-12, and 250-12 conditions did not present statistical differences among them. In *G. arborea* and *V. ferruginea*, the thermal treatments 250-10 and 250-12 resulted in ash contents that were statistically higher relative to the rest of the torrefaction temperatures and un-torrefied biomass.

The volatile percentage in torrefied biomass ranged from 68.8% and 84.9% (Table 1). In general, in biomass torrefied at 200 °C and 225 °C the percentage of volatiles increased with respect to the control, while in biomass torrefied at 250 °C, the percentage of volatiles decreased. In biomass from *C. lusitanica*, torrefaction increased the volatile percentage at 200 °C, 225 °C up to 250 °C with 8 min duration, with no statistical differences among them, whereas under 250-10 and 250-12 torrefaction conditions, volatiles decreased relative to the rest of thermal treatment temperatures. In biomass from *D. panamensis*, no increase was observed in the volatile percentage up to the 225-8 torrefaction condition. Then, with torrefaction under 225-10 and 225-12 conditions, the percentage of volatiles increased, to decrease with torrefaction under 250-10 and 250-12 conditions (Table 1).

For biomass from *G. arborea*, torrefaction increased volatiles at temperatures of 200 °C at the various times and 225-10. Subsequently, torrefaction at 250 °C and the various times and 225-12 decreased volatiles. In the case of *T. grandis*, volatiles increased with torrefaction at 200 °C and all times, 225-8 and 250-8, decreasing though at 225-12 and 250-12 treatments. In *V. ferruginea*, biomass torrefaction increased volatiles up to 225-8, after which the percentage of volatiles tended to decrease.

The net calorific value of torrefied biomass at the various times and temperatures evaluated varied between 17 MJ/kg and 23 MJ/kg. Torrefaction increased the NCV especially at 225 °C and 250 °C. As for *C. lusitanica*, no statistical differences were observed among the torrefaction temperatures and times (Fig. 2a). However, the calorific value increased with respect to un-torrefied material (Fig. 2a). Regarding *D. panamensis*, a slight increase of calorific value with torrefaction temperature and time was observed;

however, it was statistically different in biomass torrefied at 225 °C and 250 °C and 12 min (Fig. 2b). Similarly, the net calorific value was higher in torrefied compared to un-torrefied material.

Torrefaction at 200 °C and un-torrefied material showed the lowest values of calorific value in *G. arborea*, which increased with torrefaction at 225 °C and 250 °C for all treatment times; however, biomass of *G. arborea* under 250-12 conditions was the only treatment that showed significant differences, obtaining the highest value (Fig. 2c). No significant differences were observed among torrefaction temperatures and times in *T. grandis*, and calorific values ranged from 18 MJ/kg and 20 MJ/kg. These values were higher than the values reported for un-torrefied material (Fig. 2d). In *V. ferruginea* no statistical differences were observed between biomass torrefaction at the various temperatures and times, with calorific values within the range of 18 MJ/kg and 20 MJ/kg, and the lowest values belonging to un-torrefied material (Fig. 2e). However, the increase in NCV should be considered with caution. Although there is an increase in energy density, there is a loss of mass during torrefaction, so a balance must be made between the increase with NCV and W_{loss}. In the present research, it was found that there are light torrefaction increases in NCV with W_{loss} acceptable. This indicates that those conditions are appropriate to have a balance between increased energy density and W_{loss}.

The ash content varied from one species to the other, in un-torrefied as in torrefied biomass (Table 1). This behaviour is normal according to other studies that report that the ash content varied among species, tree age, section of the tree, type of soil, and climate (Moya *et al.* 2015; Tenorio *et al.* 2016). In general, ash content tends to increase with the severity of the torrefaction (Bridgeman *et al.* 2008; Couhert *et al.* 2009; Yan *et al.* 2009; Rousset *et al.* 2012). Some of the treatments did not show differences that were statistically significant for ash content in different species. However, for the torrefaction at 250 °C, the ash content increased for all species. This situation is unfavourable for the material, as high ash contents are attributed to high percentages of minerals present in the wood and a decrease in the energy yield of the biomass (Demeyer *et al.* 2001; Tenorio and Moya 2013; Casal *et al.* 2010).

The ash content increase with torrefaction temperature at 250 °C has been observed in other studies that show that at temperatures above 250 °C ash contents begins to increase (Chen *et al.* 2014a, 2015b). This is due to the mass loss in the material and the permanence of the non-volatile minerals, which produces greater biomass-ash ratio. In relation to the ranges obtained, the amount of ash varied from 0.08 to 1.81% in torrefaction at 200 °C and 225 °C (Table 1), which is within the range of variation reported by Casal *et al.* (2010), of 0.5% to 2.0%. However, biomass of *C. lusitanica*, *G. arborea*, and *V. ferruginea* in the thermal treatments 250-10 and 250-12 (Table 1) showed higher values than those of the study carried out by Casal *et al.* (2010).

The content of volatiles in torrefied woody biomass is linked to the amount of water, as well as condensable and non-condensable gases such as acetic acid, formic acid, methanol, carbon dioxide, and carbon monoxide (Granados *et al.* 2016). The percentage of volatiles in biomass varies between 48% and 86% (Vassilev *et al.* 2010). The percentages obtained in the present study (Table 1) are within that range and are therefore acceptable. An additional important aspect to mention is that the content of volatiles was reduced in torrefaction at 250 °C. This situation can be explained by the fact that at this temperature an amount of volatiles from decomposition of hemicellulose, cellulose, and lignin has already occurred; therefore the volatile percentage of the material is low (Demirbas 2004). This is also reflected in the behavior of the material according to the time of exposure to torrefaction, since the volatile content decreases with increasing time of exposure (Table 1). This is because the more exposure time to torrefaction, the greater the degradation of the biomass components, such as cellulose, due to degraded carbohydrate fraction during the thermal treatment (Park *et al.* 2013; Matali *et al.* 2016), which are directly affected by time.

An important aspect of torrefaction is the increase of the calorific value (Keipi *et al.* 2014). According to estimations, in un-torrefied biomass the calorific value ranges between 19 and 21 MJ/kg (Fig. 2), and between 21 and 23 MJ/kg after torrefaction (Keipi *et al.* 2014), which means an increase of approximately 10%. This increase of calorific value after torrefaction (Fig. 2) is due mainly to removal of moisture and volatiles, decomposition of hemicellulose and the structural rupture of lignin chains (Bergman *et al.* 2005; Matali *et al.* 2016). The ranges of calorific values in the different species and different torrefaction temperatures (Fig. 2) are between 19 and 23 MJ/kg. Each of the species studied showed a different behavior (Fig. 2). *G. arborea* and *T. grandis* (Fig. 2 c-d) were the species that presented higher values of calorific value, since each species has a particular behavior with respect to torrefaction.

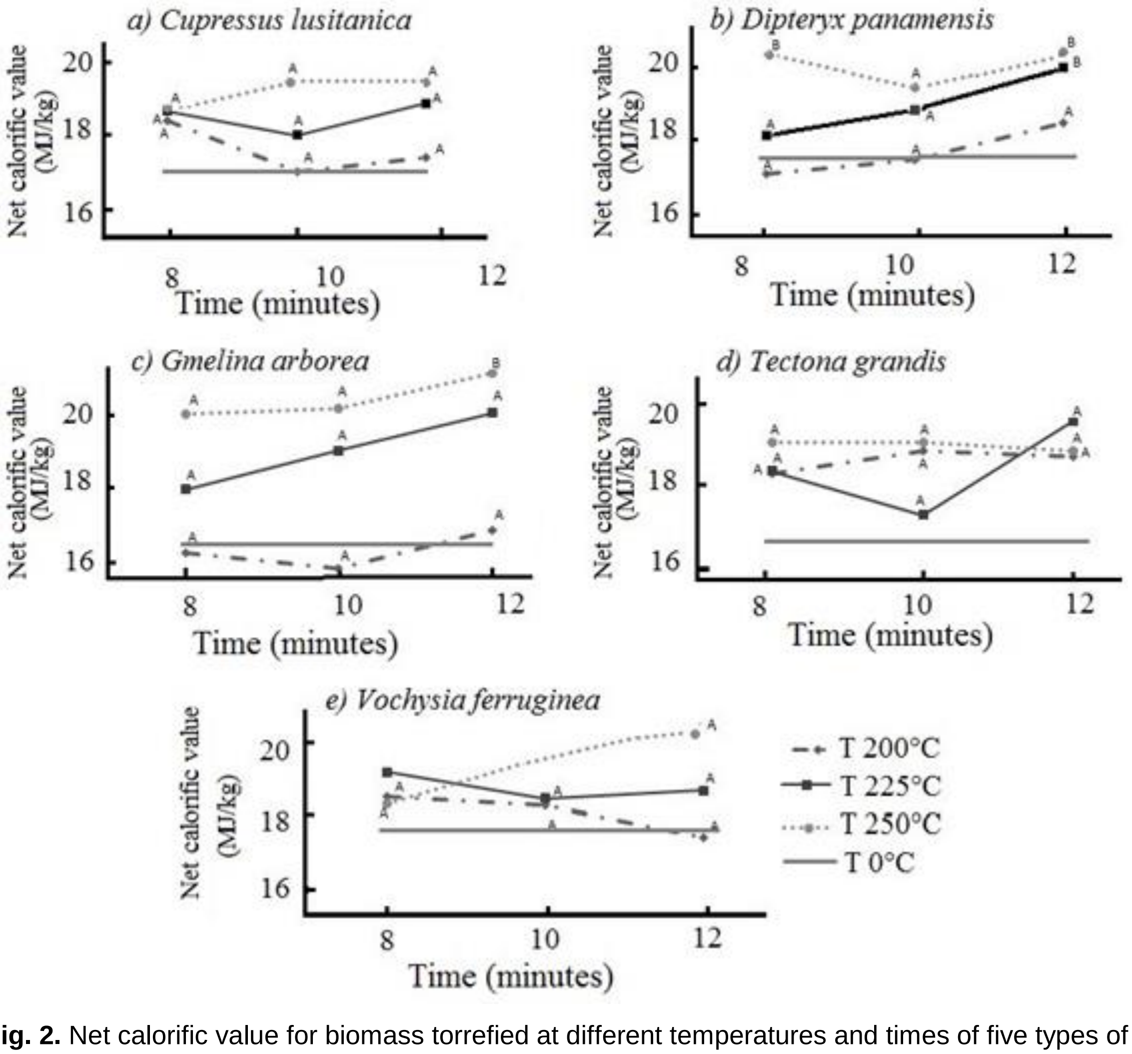

Fig. 2. Net calorific value for biomass torrefied at different temperatures and times of five types of biomass from woody tropical species

Table 1. Percentage of Ashes and Volatiles for Biomass Torrefied at Various Temperatures and Times for Five Types of Biomass from Woody Tropical Species

Temperature (°C)	Time (min)	*Cupressus lusitanica*		*Dipteryx panamensis*		*Gmelina arborea*		*Tectona grandis*		*Vochysia ferruginea*	
		Ash (%)	Volatile (%)	Ash (%)	Volatile (%)	Ash (%)	Volatile (%)	Ash (%)	Volatile (%)	Ash (%)	Volatile (%)
Without torrefaction		0.19^{A} (9.85)	80.45^{A} (1.54)	1.83^{A} (89.67)	82.37^{A} (0.70)	1.00^{A} (3.26)	80.51^{A} (0.71)	2.78^{A} (2.49)	81.75^{A} (0.23)	0.99^{A} (1.50)	80.36^{A} (0.83)
200	8	0.08^{A} (8.25)	85.17^{B} (0.21)	0.24^{B} (15.24)	82.03^{A} (0.63)	0.72^{A} (14.24)	87.47^{B} (0.69)	0.66^{B} (14.97)	85.10^{B} (0.29)	1.49^{A} (17.66)	83.72^{B} (0.71)
	10	0.12^{A} (22.46)	85.36^{B} (0.75)	0.25^{C} (13.47)	82.82^{A} (0.32)	0.77^{A} (2.08)	83.83^{C} (1.83)	0.55^{B} (2.27)	85.95^{B} (0.41)	1.12^{A} (16.95)	83.02^{B} (0.15)
	12	0.09^{A} (3.34)	85.08^{B} (0.37)	1.52^{A} (17.31)	82.87^{A} (0.28)	0.72^{A} (2.47)	85.90^{C} (0.88)	0.60^{B} (4.70)	85.70^{B} (0.30)	1.31^{A} (15.70)	84.59^{B} (0.57)
225	8	0.08^{A} (2.97)	84.64^{B} (0.70)	1.54^{A} (17.25)	83.74^{A} (0.31)	0.60^{A} (11.02)	86.43^{C} (0.67)	0.55^{B} (1.50)	85.18^{B} (0.39)	1.30^{A} (4.73)	83.67^{B} (0.47)
	10	0.22^{A} (19.45)	84.22^{B} (0.45)	0.23^{BC} (6.97)	85.84^{B} (0.31)	1.05^{A} (7.27)	85.04^{C} (0.49)	0.60^{B} (22.42)	83.86^{C} (0.31)	1.52^{A} (20.83)	83.08^{B} (0.81)
	12	0.33^{A} (13.80)	83.32^{B} (0.33)	0.16^{BC} (16.80)	84.94^{B} (0.77)	1.81^{A} (2.37)	68.77^{D} (0.58)	1.81^{B} (2.37)	68.77^{C} (0.58)	1.30^{A} (11.23)	81.36^{A} (2.89)
250	8	0.26^{A} (20.92)	82.63^{B} (1.01)	0.24^{BC} (19.09)	80.99^{A} (0.77)	1.36^{A} (2.79)	72.63^{E} (0.48)	0.66^{B} (0.74)	84.12^{C} (0.40)	1.30^{A} (21.64)	82.57^{A} (0.66)
	10	4.84^{B} (22.65)	79.93^{C} (0.48)	0.33^{A} (8.16)	78.94^{C} (0.37)	3.42^{B} (7.22)	63.41^{F} (1.49)	0.81^{B} (11.18)	81.14^{A} (0.85)	4.82^{B} (23.94)	79.94^{A} (0.37)
	12	7.00^{C} (9.88)	75.35^{D} (1.13)	0.72^{A} (9.86)	79.77^{C} (2.58)	5.59^{C} (16.83)	67.62 (1.68)^{G}	1.05^{C} (2.97)	76.91^{D} (0.53)	7.00^{C} (9.25)	75.35^{C} (0.43)

* Letters next to the number represent statistical significance level at 95% between the torrefaction conditions for the same species; numbers within parentheses represent coefficients of variation

Each species will present different thermal degradation and because this degradation is related to calorific value (Matali *et al.* 2016; Moya *et al.* 2017), then the differences between them are presented. There is an increase in the calorific value with torrefaction at 200 °C, 225 °C, and 250 °C during 12 min, as the material has been exposed longer to thermal degradation. Previous studies have shown that the calorific value tends to increase with increasing torrefaction temperature and time. However, at torrefaction temperatures of 250 °C or higher, the mass loss is greater, for which reason this treatment is considered unsuitable for biomass (Chen *et al.* 2011).

Chemical Properties

Quantification of the percentage of cellulose of *C. lusitanica* showed that this value ranged from 54.7% to 64.7% (Table 2). In addition, biomass of this species torrefied under the tested conditions, only torrefaction conditions of 200-12 and 225-10 caused a decrease in the amount of cellulose. In the case of *D. panamensis,* torrefaction increases the cellulose content when the biomass is torrefied at 250 °C at different times. For *G. arborea*, the percentage of cellulose increased only when the biomass was torrefied under the 250-10 treatment. For *T. grandis*, 250-12 was the only torrefaction process that presented an increase of cellulose. For the biomass of *V. ferruginea,* the torrefaction conditions under 225-10, 225-12, and 250-10 significantly increased cellulose (Table 2).

As for lignin percentage, *C. lusitanica* showed values between 27.3% and 41.1%; the lowest value was under torrefaction conditions of 225-10 and the highest for biomass torrefied under conditions of 250-12 (Table 2). Biomass torrefaction of *D. panamensis* statistically increased lignin content at 250 °C and 8, 10, and 12 min. For *G. arborea,* torrefaction at low temperatures decreased lignin percentage up to 225-8 conditions; then, lignin content increased in biomass torrefied under 250-10 conditions, to decrease in biomass under 250-12 conditions. In the case of *T. grandis*, lignin contents increased with torrefaction, the highest value obtained under 250-12 conditions. Biomass of *V. ferruginea* showed increase of lignin percentage with increasing temperature and torrefaction time.

Table 3 presents the percentages of extractives in biomass in ethanol-toluene, cold water, and hot water. For *C. lusitanica*, *G. arborea*, and *T. grandis*, torrefaction increased extractives content in ethanol-toluene in all temperature and time conditions. In biomass of *D. panamensis*, torrefaction decreased the extractives content. Extractives in ethanol-toluene decreased in biomass of *V. ferruginea*, the lowest values obtained with torrefaction conditions of 200-8, 200-12, 225-10, and 250-12.

Cold-water soluble extractives increased with torrefaction in biomass of *C. lusitanica*, decreased in *D. panamensis* and decreased in *G. arborea* with torrefaction conditions of 200-8 and 225-12, 225-10, and 225-12. In *T. grandis*, torrefaction decreased the content of water-soluble extractives under conditions 225-12, 250-10, and 250-12. Torrefaction decreased extractives in cold water in biomass of *V. ferruginea*, showing no significant differences among the various types of biomass torrefied (Table 3).

The percentage of hot-water soluble extractives in *C. lusitanica* showed no statistical evidence of difference between the different torrefaction conditions and the control. In *D. panamensis* the content of hot-soluble extractives decreased with torrefaction, with 250-10 and 250-12 conditions presenting the lowest percentages. In *G. arborea*, exposure of the biomass to torrefaction increased the percentage of extractives, as in biomass of *T. grandis*, where torrefaction increased the content of hot-water soluble extractives, with 200-8 and

225-8 the conditions under which the highest values were obtained. Torrefaction decreased the content of hot-water soluble extractives in biomass of *V. ferruginea*, the lowest values being those at 200 °C in all time conditions and 225-10 (Table 3).

Studies on un-torrefied biomass indicate that there are differences in the contents of cellulose and lignin between broad-leaved and conifer species (Pereira *et al.* 2003). *C. lusitanica* is a conifer; therefore, its contents of cellulose and lignin differ from those of the other species that are hardwoods (Table 2). Torrefaction of biomass of *C. lusitanica* made evident such differences in the contents of cellulose and lignin (Table 2). These changes are related to the behavior of biomass with respect to torrefaction.

The present work carried out light torrefaction (Chen *et al.* 2015a) in which cellulose and lignin were slightly degraded (Rousset *et al.* 2011). The decomposition behavior of the biomass before light torrefaction occurs primarily in the extensive degradation of hemicellulose and release of volatiles, followed by the intermediate consumption of cellulose and lastly a slight effect of lignin, which is the most difficult component to degrade thermally (Chen *et al.* 2015a). Some studies indicate that the main components of the biomass begin to degrade in a greater percentage when reaching a temperature range between 250 °C and 300 °C (Chen *et al.* 2015a). Thus, this study shows (Table 2) that torrefaction at 250 °C presented an increase in contents of lignin and cellulose directly related to the degradation of hemicellulose, which is the component most affected by light torrefaction. As the hemicellulose content decreases, the proportion of cellulose and lignin in the material increases.

The extractives content is associated with the chemical nature of the biomass (Pereira *et al.* 2003). The extractives in ethanol-toluene are generally considered as polymer structures in wood, such as waxes, fats, resins, and oils, in addition to some tannins (ASTM D1107-96 2003), indicating that torrefaction increases the amount that can be extracted of these components in the biomass for the species of *C. lusitanica*, *G. arborea*, and *T. grandis* (Table 3). In the case of extractives in cold water, torrefaction increased the percentages in *C. lusitanica*, *G. arborea*, and *T. grandis* (Table 3). Therefore, torrefaction of biomass produces greater amount of tannins, gums, sugars, or dyes in biomass that can be extracted in this solvent (ASTM D1110-84 2003). The extractives in hot water decreased after torrefaction in *C. lusitanica*, *D. panamensis*, and *V. ferruginea* (Table 3), resulting in less availability of tannins, gums, sugars, dyes, or starches (ASTM D1110-84 2003). On the contrary, in *G. arborea* and *T. grandis* the content of extractives in hot water increased, evidencing the availability of the components mentioned above.

The content of extractives found in the species studied is attributed to the nature of tropical species, which contain high percentages of these components (Tenorio and Moya 2013; Moya *et al.* 2017; Tenorio *et al.* 2016). Each of the five species studied showed different percentages (Table 3). The percentages of extractives affect the decomposition temperatures of hemicellulose and cellulose, as the higher the percentage of extractives, the lower the temperature required to decompose these components (Moya *et al.* 2017; Shebani *et al.* 2008). Thus, the increase of extractives in torrefaction at 250 °C (Table 3) makes the material more susceptible to thermal degradation, for which reason this is not a suitable torrefaction temperature for the biomass studied.

Table 2. Percentage of Cellulose and Lignin for Biomass Torrefied at Various Temperatures and Times for Five Types of Biomass from Woody Tropical Species

Temperature (°C)	Time (min)	*Cupressus lusitanica*		*Dipteryx panamensis*		*Gmelina arborea*		*Tectona Grandis*		*Vochysia ferruginea*	
		Cellulose (%)	Lignin (%)	Cellulose (%)	Lignin (%)	Cellulose (%)	Lignin (%)	Cellulose (%)	Lignin (%)	Cellulose (%)	Lignin (%)
Without torrefaction		64,71^{A} (2.04)	31.39^{A} (0.77)	49.85^{A} (2.09)	20.26^{A} (4.49)	55.59^{A} (0.78)	23.98^{A} (5.65)	54.40^{A} (7.39)	22.10^{A} (6.36)	50.94^{A} (1.70)	12.63^{A} (12.82)
200	8	59.21^{A} (10.28)	29.92^{A} (0.95)	54.61^{A} (2.65)	24.44^{A} (6.31)	62.47^{A} (10.22)	18.36^{B} (3.33)	49.76^{A} (1.40)	34.88^{B} (1.97)	49.90^{A} (3.11)	13.76^{A} (13.23)
	10	55.79^{A} (2.47)	30.70^{A} (0.79)	50.11^{A} (5.25)	22.35^{A} (1.49)	52.31^{A} (6.77)	21.24^{B} (1.86)	55.84^{A} (3.27)	34.51^{B} (0.85)	49.40^{A} (2.69)	17.63^{B} (0.94)
	12	54.72^{B} (4.40)	29.62^{A} (1.86)	53.52^{A} (1.73)	22.31^{A} (12.95)	54.30^{A} (3.23)	22.65^{B} (7.50)	58.02 ^{A} (0.83)	34.33^{B} (2.98)	52.32^{A} (1.92)	21.58^{C} (1.33)
225	8	59.03^{A} (10.45)	28.95^{A} (3.10)	55.24^{A} (7.38)	26.07^{A} (30.85)	59.40^{A} (6.11)	21.84^{B} (6.23)	60.54^{A} (7.06)	33.34^{B} (6.22)	51.45^{A} (1.48)	22.08^{C} (3.83)
	10	54.08^{B} (2.25)	27.33^{B} (1.08)	47.83^{A} (3.23)	23.97^{A} (1.88)	56.10^{A} (4.42)	27. 01^{C} (4.08)	58.91^{A} (8.46)	29.28^{C} (1.95)	66.00^{B} (11.44)	18.71^{C} (2.84)
	12	57.69^{A} (2.06)	32.30^{A} (5.62)	47.58^{A} (5.04)	26.26^{A} (7.24)	56.10^{A} (1.37)	25.88^{C} (2.33)	56.10^{A} (1.37)	28.18^{C} (3.07)	65.82^{C} (9.28)	19.98^{C} (5.12)
250	8	56.91^{A} (2.97)	34.45^{A} (3.77)	59.28^{B} (1.80)	31.40^{B} (5.27)	57.65^{A} (3.48)	27.34^{C} (2.18)	56.42^{A} (5.17)	29.53^{C} (0.79)	52.58^{A} (0.20)	20.31^{C} (1.65)
	10	63.91^{A} (4.03)	35.09^{C} (4.77)	59.69^{B} (5.92)	31.77^{B} (2.71)	67.57^{B} (1.93)	37.72^{D} (1.27)	57.93^{A} (14.03)	33.81^{B} (0.86)	66.00 ^{B} (11.44)	22.96^{C} (3.13)
	12	63.22^{A} (2.77)	41.09^{D} (5.27)	65.37^{B} (0.23)	35.06^{B} (16.22)	51.21^{A} (2.12)	25.32^{C} (4.41)	68.71^{B} (1.99)	45.52^{D} (1.95)	63.22^{A} (13.18)	41.09^{D} (0.82)

* Letters next to the number represent statistical significance level at 95% between the torrefaction conditions for the same species, numbers within parentheses indicate coefficients of variation

Table 3. Percentage of Extractives in Ethanol-Toluene, Cold and Hot Water for Biomass Torrefied at Various Temperatures and Times for Five Types of Biomass from Woody Tropical Species

Temperature (°C)	Time (min)	*Cupressus lusitanica*			*Dipteryx panamensis*			*Gmelina arborea*			*Tectona grandis*			*Vochysia ferruginea*		
		E-to	Cold water	Hot water	E-to	Cold water	Hot water	E-to	Cold water	Hot water	E-to	Cold water	Hot water	E-to	Cold water	Hot water
Without torrefaction		2.21^{A} (45.27)	4.29^{A} (25.03)	8.01^{A} (16.99)	11.20^{A} (3.64)	11.87^{A} (37.24)	11.38^{D} (20.38)	0.82^{A} (42.68)	9.04^{A} (1.49)	7.81^{A} (0.97)	1.18^{A} (0.00)	8.51^{A} (5.09)	7.22^{A} (1.26)	15.20^{A} (1.50)	16.86^{A} (2.72)	17.88^{A} (2.14)
200	8	10.24^{B} (3.71)	8.54^{B} (4.78)	7.75^{A} (2.23)	9.89^{A} (1.92)	3.70^{B} (12.33)	9.38^{C} (7.09)	10.14^{B} (1.97)	6.39^{B} (4.14)	10.77^{B} (1.91)	8.31^{B} (3.71)	9.05^{A} (6.76)	11.01^{B} (1.92)	10.42^{B} (0.66)	11.59^{B} (9.28)	9.41^{B} (0.67)
	10	9.83 ^{B} (13.10)	7.76^{C} (0.75)	7.01^{A} (2.10)	8.93^{B} (2.66)	7.61 ^{C} (0.45)	8.42 ^{B} (3.35)	9.89 ^{B} (1.09)	9.50^{A} (1.02)	10.65^{B} (2.40)	9.21^{B} (0.69)	8.46^{A} (2.63)	10.80^{B} (2.70)	11.77^{A} (1.69)	10.48^{B} (3.81)	9.74^{B} (2.96)
	12	10.52^{B} (2.38)	7.94^{C} (2.56)	8.17^{A} (4.11)	6.24^{C} (7.83)	7.61^{BC} (2.65)	9.25^{C} (1.32)	7.23^{C} (5.31)	7.87^{A} (0.86)	11.11^{B} (1.85)	9.09^{B} (8.99)	8.25^{A} (5.23)	10.72^{B} (1.73)	10.90^{B} (0.99)	10.32^{B} (4.14)	9.91^{B} (2.22)
225	8	10.70^{B} (1.80)	7.45^{C} (6.19)	8.05^{A} (3.46)	6.98^{C} (4.30)	7.37^{A} (2.24)	10.97^{C} (2.35)	8.79^{BC} (22.81)	7.44^{A} (4.72)	9.94^{C} (0.77)	9.08^{B} (1.37)	8.78^{A} (2.85)	11.31^{B} (4.56)	12.86^{A} (28.51)	10.48^{B} (2.87)	10.02^{B} (1.88)
	10	9.31^{B} (17.95)	7.17^{C} (1.96)	7.78^{A} (2.27)	6.52^{C} (6.19)	6.61^{D} (10.37)	10.39^{C} (2.36)	7.37^{C} (4.34)	7.80^{A} (18.20)	9.81^{C} (4.36)	8.14^{B} (6.31)	6.71^{A} (7.03)	10.24^{B} (0.81)	10.80^{B} (6.28)	11.37^{B} (10.58)	9.88^{B} (2.11)
	12	8.51^{B} (15.29)	7.01^{C} (3.78)	7.94^{A} (6.84)	8.76^{D} (8.11)	6.89^{D} (3.89)	9.72^{C} (1.86)	8.94^{BC} (8.78)	5.56^{B} (3.16)	9.11^{C} (1.31)	8.94^{B} (8.78)	5.56^{B} (3.16)	9.11^{B} (1.31)	12.19^{A} (20.40)	9.91^{B} (0.78)	15.37^{C} (0.84)
250	8	7.88^{B} (2.14)	6.95^{C} (3.48)	8.94^{A} (3.70)	8.60^{D} (15.95)	5.39^{E} (9.15)	6.22^{A} (1.15)	9.92^{B} (1.61)	7.96^{A} (7.68)	10.25^{B} (2.86)	9.80^{C} (1.98)	6.80^{A} (3.67)	9.85^{B} (1.21)	11.53^{A} (6.90)	11.12^{B} (4.98)	14.46^{C} (5.22)
	10	7.73^{B} (10.38)	6.92^{C} (6.14)	8.21^{A} (3.67)	10.14^{A} (7.60)	5.81^{E} (4.15)	5.77^{A} (9.22)	11.41^{B} (1.43)	6.72^{B} (5.23)	8.33^{A} (4.93)	9.55^{C} (1.03)	6.22^{B} (3.72)	8.81^{B} (7.05)	11.02^{A} (2.95)	10.64^{B} (3.71)	15.05^{C} (1.56)
	12	6.33^{B} (10.94)	5.99^{C} (4.38)	7.45^{A} (6.55)	8.37^{D} (3.05)	4.43^{E} (10.35)	5.01^{A} (2.09)	10.96^{B} (3.70)	6.95^{B} (14.33)	9.71^{C} (8.50)	9.31^{C} (3.51)	7. 77^{A} (14.20)	8.82^{B} (11.79)	6.33^{B} (7.61)	5.99^{B} (11.33)	7.45^{D} (5.00)

* Letters next to the number represent statistical significance level at 95% between the torrefaction conditions for the same species; numbers within parentheses indicate coefficients of variation; E-to: ethanol-toluene solution

FTIR Analyses

Figure 4 shows the change in the ratio of intensity (RI) for the bands identified using FTIR analyses. Twelve bands were identified as the most representative of the spectra: 895 cm^{-1}, 1051 cm^{-1}, 1109 cm^{-1}, 1155 cm^{-1}, 1236 cm^{-1}, 1320 cm^{-1}, 1370 cm^{-1}, 1420 cm^{-1}, 1458 cm^{-1}, 1509 cm^{-1}, 1592 cm^{-1}, and 1732 cm^{-1}. The RI showing most variation were those at 1109 cm^{-1}, 1155 cm^{-1}, 1236 cm^{-1}, 1420 cm^{-1}, and 1458 cm^{-1} for all of the species evaluated in the study, indicating thus a change in the structure of hemicellulose, cellulose, and lignin. As for *C. lusitanica* (Fig. 3a), the bands presenting most change in the RI were 1155 cm^{-1}, which represent the structure of hemicellulose and cellulose and 1236 cm^{-1}, 1320 cm^{-1}, and 1420 cm^{-1}, which are related to lignin; variations could be observed in biomass torrefied under 250-10 conditions in the structure of hemicellulose, cellulose, and lignin. As for *D. panamensis* (Fig. 3b), the signal presenting the highest variation was 1155 cm^{-1}, associated to the structures of hemicellulose and cellulose. The rest of the signals show that RI increases in biomass torrefied at 250 °C and the three times evaluated. In the case of *G. arborea* (Fig. 3c), the IR output showing most variation was observed in the intensity of 1109 cm^{-1}, which represents bonds found in polysaccharides and lignin, as well as in the intensities 1155 cm^{-1} and 1458 cm^{-1} associated to cellulose and hemicellulose and in 1236 cm^{-1} and 1420 cm^{-1}, associated to lignin. Biomass torrefied at 250 °C and the three times showed the highest values of RI. In biomass of *T. grandis* (Fig. 3d), the most affected RI were 1236 cm^{-1} and 1320 cm^{-1}, both associated to lignin. In the remaining bands, an increase occurs in RI with respect to increasing torrefaction temperature and times (Fig. 3d). As for *V. ferruginea* (Fig. 3e), the strongest RI variation was observed in the band 1155 cm^{-1}, associated to bonds of the structures of hemicellulose and cellulose, while increase in RI was observed in torrefaction under 250 °C and the three times (Fig. 3e).

FTIR spectroscopy analyses can indicate relative changes in the functional groups and chemical structure of the biomass (Chen *et al.* 2006; Sharma *et al.* 2004). In the present study, the bands presented clear variations in the five species studied (Fig. 3), indicating that the torrefaction of the biomass causes structural changes in the components of the material. The most susceptible component to changes in the temperature ranges studied (*i.e.* 200 to 250 °C) is hemicellulose, due to the early decomposition of these carbohydrates (Garrote *et al.* 2001). The bands 1732 cm^{-1} (O-acetyl-4-O-methylglucurono-xylan) and 1592 cm^{-1} (C=O bonds in carboxyl groups of glucuronic acid in xylan units and C-O bonds of aromatics in lignin) (Åkerholm and Salmén, 2001), associated with hemicellulose structure but also with lignin, showed alterations with an increase in the RI in torrefied biomass (Fig. 4a). These variations indicate modification in the hemicellulose and lignin structures caused by the equatorial alignment of hydrogen in the C_2 atom in the glucomannan residues (Stevanic and Salmén 2009).

In the present study, the band with the greatest variation was 1740 cm^{-1} (Fig. 3 a-e), which corresponds to a carbonyl group (Pandey and Theagarajan 1997; Faix 1992). Its variation in torrefaction can be attributed to degradation of ester groups in hemicellulose, which is caused by deacetylation during the thermal treatment (Carrasco and Roy 1992). The variations in the bands of 1700 cm^{-1} and 1600 cm^{-1} (Fig. 3) correspond to vibrations of C=O and C=C bonds, which come from ketones, aldehydes, esters, carboxyl groups, and aromatic structures (Chen *et al.* 2006). The increase in intensity in the biomass torrefied at 250 °C indicate the carbohydrate degradation and the relative increase of lignin, which intensify the absorption of C=O (1700 cm^{-1}). The increase in the bands of 1592 cm^{-1} and 1509 cm^{-1} can be associated to the structure of aromatic vibrations and to the ring of coniferyl alcohol with C-O bonds. This indicates that the torrefied biomass increases the aromatic fraction, or otherwise, that in the torrefied biomass there are larger condensed coniferyl alcohol units (Faix 1992) present in most lignin (Table 2).

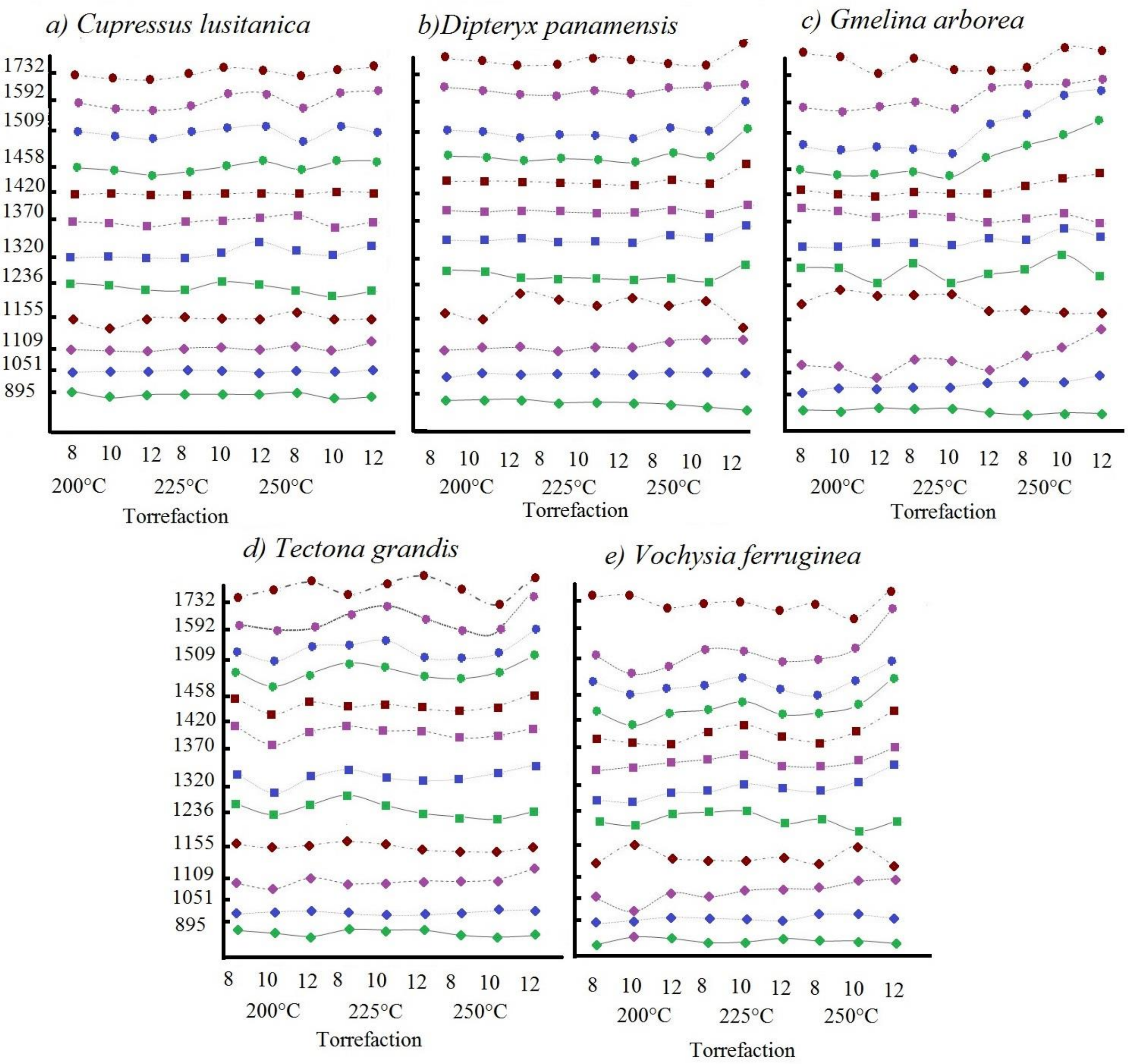

Fig. 3. Change in ratio of intensity (I_n/I_{1031}) for the bands of biomass torrefied at different temperatures and times of five types of biomass from woody tropical species

The increase in the intensities of the bands of 1030 cm^{-1} and 1060 cm^{-1}, corresponding to C-O-C and C-OH aliphatic in alcohol, associated with cellulose (Chen *et al.* 2006; Sharma *et al.* 2004), confirms again higher lignin exposure in torrefied biomass (Table 2). In other bands related to this component of the biomass (1055, 1155, 1370, and 1458 cm^{-1}), there was less variation in the torrefied biomass of *T. grandis* (Fig. 3d), indicating little variation of the cellulose. This confirms the results of the evaluation of the amount of cellulose in *T. grandis* biomass, which showed few differences between temperature and time treatments (Table 2). The variations in cellulose-related bands 1030 cm^{-1} and 1060 cm^{-1} are due to the structural changes occurring in cellulose and the formation of other components such as aliphatic alcohols (Li *et al.* 2015). Finally, the variation in the band of 1320 cm^{-1} is related to vibrations of C-O bonds (Faix 1992), which cause a decrease in the crystallinity of some celluloses (Li *et al.* 2015). This effect occurs by dehydration of carbohydrates during torrefaction (Lionetto *et al.* 2012) and the fragmentation of cellulose crystals during thermochemical degradation (Hill *et al.* 2013).

Multivariate Analysis

The effect of each variable in the present study can be represented by a multivariate component analysis, which was performed for each species (Fig. 4a-e). This analysis showed that the first two components represent approximately 75% of the total variation of the evaluated variables, where 60% is explained by component 1 and 15% by component 2 (Table 4). In the case of *C. lusitanica*, the variables that most influence component 1 are lignin content, percentage of ash, extractives in hot water, volatile content, and mass loss. As for *D. panamensis*, the most representative variables in component 1 are lignin content, extractives in hot water and mass loss. In *G. arborea* the volatile content is the most representative. In the case of *T. grandis*, ash and volatile content variables and the mass loss are the most representative in component 1. The most representative variables of the behavior of torrefied biomass of *V. ferruginea* were the contents of ash and volatiles, the calorific value and the mass loss.

The remaining 15% of the representation is given by component 2, which in *C. lusitanica* is represented by extractives in hot water. In *D. panamensis* this percentage is given by the extractives in ethanol-toluene. In the case of *G. arborea*, the most representative variable for component 2 was cellulose content, while extractives in hot water represented *T. grandis*. For *V. ferruginea* extractives in ethanol-toluene provide this percentage of representation.

By plotting the auto vectors for components 1 and 2 for each species (Fig. 4 a-e) it was possible to identify three different groups of the biomass torrefaction temperatures and times. A first group of biomasses torrefied under 200-8, 200-10, 200-12, 225-8, and 225-10 conditions. A second group was observed in biomass torrefied under 225-12, 250-8, and 250-10 conditions. Finally, the third group was formed by the biomass torrefied under 250-12 condition, which had a completely different behavior to all other torrefied biomasses, completely isolated from the other temperatures and torrefaction times (Fig. 4 a-e).

The multivariate analysis related to all the variables studied (Table 4) make it recognizable that the variables most correlated and that better explain the behaviour of the biomass before torrefaction, are the chemical properties of the material, such as lignin content, extractives in hot water, and mass loss, in the case of component 1. The reasons for this correlation are that torrefaction causes thermal degradation of the material, as evidenced in the FTIR analyses (Fig. 3), and in the behaviour of the chemical properties of the material. The second component of the multivariate analysis shows the effect of the extractives in the torrefaction (Table 4), for their impregnation into the structure of the biomass make it show different behaviours with respect to thermal degradation during torrefaction.

The multivariate analysis shows that when graphing both factors, clear clusters become evident (Fig. 4), where torrefaction at 200 °C and 225 °C for up to 10 min obtained similar behaviour between them. After torrefaction under 225-12 conditions, another group was observed with the material torrefied under 225-12, 250-8, and 250-10 conditions, which caused drastic changes in the composition of the biomass, with high degradation of the material, evidenced by W_{loss} (Fig. 1) and increased cellulose and lignin content (Table 2). The last group consists of the torrefaction under 250-12 condition, which is considered severe condition for the biomass, since in all the variables high degradation of its basic components was evident, with W_{loss} close to 50% (Fig. 1), giving inadequate material as a result.

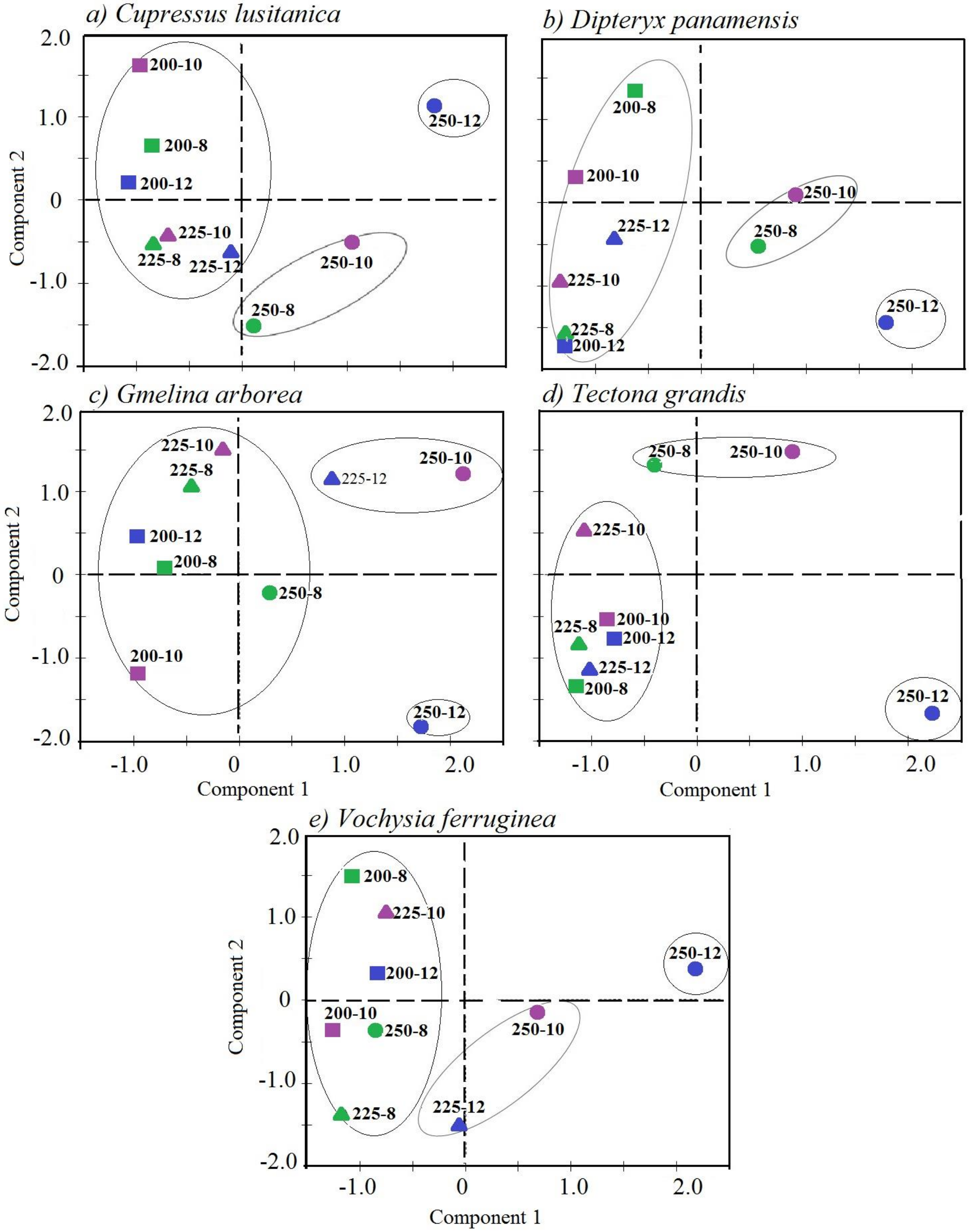

Fig. 4. Relationship between the auto vectors of components 1 and 2 of the multivariate analysis by means of principal components of biomass torrefied at different temperatures and times of five types of biomass from woody tropical species

Table 4. Matrix of Correlations of the Multivariate Analysis for All Variables Evaluated of Biomass Torrefied at Various Temperatures and Times for Five Types of Biomass from Woody Tropical Species

Variable	*Cupressus lusitanica*		*Dipteryx panamensis*		*Gmelina arborea*		*Tectona grandis*		*Vochysia ferruginea*	
	C1	**C2**	**C1**	**C2**	**C1**	**C2**	**C1**	**C2**	**C1**	**C2**
Cellulose	0.81**	-	0.87**	-	-	-	-	-	-	-
Lignin	0.93**	-	0.95**	-	-	-	-	-	0.84**	-
Hot water extractive	-	-	-0.93**	-	-0.86**	-	-	-	-	-
E-to extractive	-0.94**	-	-	0.81**	-	-	-	-	-	-
Ash	0.94**	-	-	0.71**	0.86**	-	0.92**	-	-	-
Volatiles	-0.98**	-	-0.84**	-	-0.94**	-	-	-	-	-
Calorific value	-	-	-	-	-	-	-	-	-	-
Cold water extractive	-	-	-	-	-	-	-	-	-	-
Mass loss	-	-	0.92**	-	-	-	0.99**	-	-	-
Percentage of variance	71.3	13.7	62.7	17.0	59.4	14.7	60.7	14.4	58.6	15.1
Cumulative variance	71.3	85.0	62.7	79.6	59.4	74.0	60.7	75.1	58.6	73.7

* C1: correlations of component 1; C2: correlations of component 2

CONCLUSIONS

1. The best torrefaction temperatures and times for *C. lusitanica*, *D. panamensis*, *G. arborea*, *T. grandis*, and *V. ferruginea* are 200 °C during 8, 10, and 12 min, and 225 °C during 8 and 10 min, according to chemical properties analysis and thermal stability degradation, as evidenced in the FTIR analyses. It is under these conditions that optimum thermochemical degradation of the biomass is obtained for using it as a source of energy, without affecting significantly the chemical composition of the material.
2. The species that present more thermal stability were *C. lusitanica* and *D. panamensis*, under the torrefaction conditions previously mentioned. Following, *T. grandis* and *V. ferruginea* obtained less thermal stability but acceptable behaviour, though with light torrefaction at 200 °C during 8, 10, and 12 min and at 225 °C during 8 min. Lastly, *G. arborea* was the species showing less thermal stability. In this last case, light torrefaction at 200 °C during 8, 10, and 12 min is advised.

ACKNOWLEDGMENTS

The authors thank the Vicerrectoría de Investigación y Extensión of the Instituto Tecnológico de Costa Rica and CONARE for their financial support.

REFERENCES CITED

Åkerholm, M., and Salmén, L. (2001). “Interactions between wood polymers studied by dynamic FT-IR spectroscopy,” *Polymer* 42(3), 963-969. DOI: 10.1016/S0032-3861(00)00434-1

Almeida, G., Brito, J. O., and Perré, P. (2010). “Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: The potential of mass loss as a synthetic indicator,” *Bioresource Technology* 101(24), 9778-9784. DOI: 10.1016/j.biortech.2010.07.026

Aragón-Garita, S., Moya, R., Bond, B., Valaert, J., and Filho, M. T. (2016). “Production and quality analysis of pellets manufactured from five potential energy crops in the Northern Region of Costa Rica,” *Biomass and Bioenergy* 87, 84-95. DOI: 10.1016/j.biombioe.2016.02.006

ASTM D5865-04 (2003). “Standard test method for gross calorific value of coal and coke,” American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1107-96 (2003). “Standard test method for ethanol-toluene solubility of wood,” American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1110-84 (2003). “Standard test method for water solubility of wood,” American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1102-84 (2013). “Standard test method for ash in wood,” American Society for Testing and Materials, West Conshohocken, PA.

ASTM D1762-84 (2013). “Standard test method for chemical analysis of wood charcoal,” American Society for Testing and Materials, West Conshohocken, PA.

Bach, Q.-V., and Skreiberg, Ø. (2016). “Upgrading biomass fuels via wet torrefaction: A review and comparison with dry torrefaction,” *Renewable and Sustainable Energy Reviews* 54, 665-677. DOI: 10.1016/j.rser.2015.10.014

Bahng, M.-K., Mukarakate, C., Robichaud, D. J., and Nimlos, M. R. (2009). “Current technologies for analysis of biomass thermochemical processing: A review,” *Analytica Chimica Acta* 651(2), 117-138. DOI: 10.1016/j.aca.2009.08.016

Bergman, P. C. A., Boersma, A. R., Zwart, R. W. R., and Kiel, J. H. A. (2005). “Torrefaction for biomass co-firing in existing coal-fired power stations,” (Report No. ECN-C-05-013), Energy Research Centre of the Netherlands, Petten, Netherlands.

Brebu, M., and Vasile, C. (2010). “Thermal degradation of lignin—A review,” *Cellulose Chemistry and Technology* 44(9), 353-363. ISSN: 2457-9459

Bridgewater, A. V. (2004). “Biomass fast pyrolysis,” *Thermal Science* 8(2), 21-49. DOI: 10.2298/tsci0402021b

Bridgeman, T. G., Jones, J. M., Shield, I., and Williams, P. T. (2008). “Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties,” *Fuel* 87(6), 844-856. DOI: 10.1016/j.fuel.2007.05.041

Calienno, L., Pelosi, C., Picchio, R., Agresti, G., Santamaria, U., Balletti, F., and Monaco, A. L. (2015). “Light-induced color changes and chemical modification of treated and untreated chestnut wood surface. *Studies in Conservation* 60(2), 131-139.

Carrasco, F., and Roy, C. (1992). “Kinetic study of dilute-acid prehydrolysis of xylan-containing biomass,” *Wood Science and Technology* 26(3), 189-208. DOI: 10.1007/bf00224292

Casal, M. D., Gil, M. V., Pevida, C., Rubiera, F., and Pis, J. J. (2010). “Influence of storage time on the quality and combustion behaviour of pine woodchips,” *Energy* 35(7), 3066-3071. DOI: 10.1016/j.energy.2010.03.048

Chacón, L. (2012). *Estudio: Diagnóstico de las existencias de los residuos forestales en la región Huetar Norte de Costa Rica* [*Diagnosis of forest waste stocks in the North Huetar region of Costa Rica*] San Jose, Costa Rica. Informe Final: Fondo Nacional de Financiamiento Forestal. Minaet, Costa Rica.

Chen, D., Zheng, Z., Fu, K., Zeng, Z., Wang, J., and Lu, M. (2015a). "Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products," *Fuel* 159, 27-32. DOI: 10.1016/j.fuel.2015.06.078

Chen, D., Zhou, J., and Zhang, Q. (2014a). "Effects of torrefaction on the pyrolysis behavior and bio-oil properties of rice husk by using TG-FTIR and Py-GC/MS," *Energy & Fuels* 28(9), 5857-5863. DOI: 10.1021/ef501189p

Chen, D., Zhou, J. Zhang, Q., Zhu, X., and Lu, Q. (2014b). "Upgrading of rice husk by torrefaction and its influence on the fuel properties," *BioResources* 9, 5893-5905. DOI: 10.15376/biores.9.4.5893-5905.

Chen, D., Cen, K., Jing, X., Gao, J., Li, C., and Ma, Z. (2017) An approach for upgrading biomass and pyrolysis product quality using a combination of aqueous phase bio-oil washing and torrefaction pretreatment. *Bioresource Technology*, 233, 150-158. DOI: 10.1016/j.biortech.2017.02.120.

Chen, W.-H., and Kuo, P.-C. (2010). "A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry," *Energy* 35(6), 2580-2586. DOI: 10.1016/j.energy.2010.02.054

Chen, W.-H., Hsu, H.-C., Lu, K.-M., Lee, W.-J., and Lin, T.-C. (2011). "Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass," *Energy* 36(5), 3012-3021. DOI: 10.1016/j.energy.2011.02.045

Chen, W.-H., Peng, J., and Bi, X. T. (2015b). "A state-of-the-art review of biomass torrefaction, densification and applications," *Renewable and Sustainable Energy Reviews* 44, 847-866. DOI: 10.1016/j.rser.2014.12.039

Chen, D., Mei, J., Li, H., Li, Y., Lu, M., Ma, T., and Ma, Z. (2017a). Combined pretreatment with torrefaction and washing using torrefaction liquid products to yield upgraded biomass and pyrolysis products. *Bioresource Technology* 228, 62-68. DOI: 10.1016/j.biortech.2016.12.088.

Cheng, C.-H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H. (2006). "Oxidation of black carbon by biotic and abiotic processes," *Organic Geochemistry* 37(11), 1477-1488. DOI: 10.1016/j.orggeochem.2006.06.022

Chew, J. J., and Doshi, V. (2011). "Recent advances in biomass pretreatment–Torrefaction fundamentals and technology," *Renewable and Sustainable Energy Reviews* 15(8), 4212-4222. DOI: 10.1016/j.rser.2011.09.017

Ciolkosz, D., and Wallace, R. (2011). "A review of torrefaction for bioenergy feedstock production," *Biofuels, Bioproducts and Biorefining* 5(3), 317-329. DOI: 10.1002/bbb.275

Coto, O. (2013). *Evaluación de la generación de residuos agrícolas orgánicos (RAO) en Costa Rica e identificación de Sector Prioritario*. [*Evaluation of the generation of organic agricultural residues (RAO) in Costa Rica and identification of priority sector*] San José, Costa Rica.

Couhert, C., Salvador, S., and Commandré, J.-M. (2009). "Impact of torrefaction on syngas production from wood," *Fuel* 88(11), 2286-2290. DOI: 10.1016/j.fuel.2009.05.003

Demeyer, A., Voundi Nkana, J. C., and Verloo, M. G. (2001). "Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview," *Bioresource Technology* 77(3), 287-295. DOI: 10.1016/s0960-8524(00)00043-2

Demirbas, A. (2004). "Combustion characteristics of different biomass fuels," *Progress in Energy and Combustion Science* 30(2), 219-230. DOI: 10.1016/j.pecs.2003.10.004

Faix, O. (1992). "Fourier transform infrared spectroscopy," in: *Methods in Lignin Chemistry*, S. Y. Lin and C. W. Dence (eds.), Springer-Verlag Berlin, Germany, pp. 83-109.

Fournel, S., Palacios, J. H., Morissette, R., Villeneuve, J., Godbout, S., Heitz, M., and Savoie, P. (2015). "Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops," *Applied Energy* 141, 247-259. DOI: 10.1016/j.apenergy.2014.12.022

Gaitán-Álvarez, J., and Moya, R. (2016). "Characteristics and properties of pellet fabricated with torrefaccioned biomass of *Gmelina arborea* and *Dipterix panamensis* at different time," *Revista Chapingo: Serie Ciencias Forestales y Ambiente* 22(3), 325-337. DOI: 10.5154/r.rchscfa.2015.09.044

Gaitan-Alvarez, J., Moya, R., Puente-Urbina, A., Rodriguez-Zuñiga, A. (2017). "Physical and compression properties of pellets manufactured with the biomass of five woody tropical species of Costa Rica torrefied at different temperatures and times," *Energies* 10, 1205. DOI: 10.3390/en10081205

Garrote, G., Domínguez, H., and Parajó, J. C. (2001). "Study on the deacetylation of hemicelluloses during the hydrothermal processing of *Eucalyptus* wood," *Holz als Roh-und Werkstoff* 59(1), 53-59. DOI: 10.1007/s001070050473

Gokcol, C., Dursun, B., Alboyaci, B., and Sunan, E. (2009). "Importance of biomass energy as alternative to other sources in Turkey," *Energy Policy* 37(2), 424-431. DOI: 10.1016/j.enpol.2008.09.057

Gosselink, R. J. A., de Jong, E., Guran, B., and Abächerli, A. (2004). "Co-ordination network for lignin—Standardisation, production and applications adapted to market requirements (EUROLIGNIN)," *Industrial Crops and Products* 20(2), 121-129. DOI: 10.1016/j.indcrop.2004.04.015

Granados, D. A., Chejne, F., and Basu, P. (2016). "A two dimensional model for torrefaction of large biomass particles," *Journal of Analytical and Applied Pyrolysis* 120, DOI: 10.1016/j.jaap.2016.02.016

Hill, S. J., Grigsby, W. J., and Hall, P. W. (2013). "Chemical and cellulose crystallite changes in *Pinus radiata* during torrefaction," *Biomass and Bioenergy* 56, 92-98. DOI: 10.1016/j.biombioe.2013.04.025

Janvijitsakul, K., and Kuprianov, V. I. (2008). "Similarity and modeling of axial CO and NO concentration profiles in a fluidized-bed combustor (co-)firing biomass fuels," *Fuel* 87(8-9), 1574-1584. DOI: 10.1016/j.fuel.2007.09.006

Keipi, T., Tolvanen, H., Kokko, L., and Raiko, R. (2014). The effect of torrefaction on the chlorine content and heating value of eight woody biomass samples. *Biomass and Bioenergy* (66), 232-239.

Li, M.-Y., Cheng, S.-C., Li, D., Wang, S.-N., Huang, A.-M., and Sun, S.-Q. (2015). "Structural characterization of steam-heat treated *Tectona grandis* wood analyzed by FT-IR and 2D-IR correlation spectroscopy," *Chinese Chemical Letters* 26(2), 221-225. DOI: 10.1016/j.cclet.2014.11.024

Lionetto, F., Del Sole, R., Cannoletta, D., Vasapollo, G., and Maffezzoli, A. (2012). "Monitoring wood degradation during weathering by cellulose crystallinity," *Materials* 5(10), 1910-1922. DOI: 10.3390/ma5101910

Matali, S., Rahman, N. A., Idris, S. S., Yaacob, N., and Alias, A. B. (2016). "Lignocellulosic biomass solid fuel properties enhancement via torrefaction," *Procedia Engineering* 148, 671-678. DOI: 10.1016/j.proeng.2016.06.550

Medic, D., Darr, M., Shah, A., Potter, B., and Zimmerman, J. (2012). "Effects of torrefaction process parameters on biomass feedstock upgrading," *Fuel* 91(1), 147-154. DOI: 10.1016/j.fuel.2011.07.019

Moya, R., Salas, C., Berrocal, A., and Valverde, J. C. (2015). "Evaluation of chemical compositions, air-dry, preservation and workability of eight fastgrowing plantation species in Costa Rica," *Madera y Bosques* 21, 31-47. DOI: 10.21829/myb.2015.210424

Moya, R., Rodríguez-Zúñiga, A., and Puente-Urbina, A. (2017). "Thermogravimetric and devolatilisation analysis for five plantation species: Effect of extractives, ash compositions, chemical compositions and energy parameters," *Thermochimica Acta* 647, 36-46. DOI: 10.1016/j.tca.2016.11.014

Pandey, K. K., and Theagarajan, K. S. (1997). "Analysis of wood surfaces and ground wood by diffuse reflectance (DRIFT) and photoacoustic (PAS) Fourier transform infrared spectroscopic techniques," *Holz als Roh-und Werkstoff* 55(6), 383-390. DOI: 10.1007/s001070050251

Park, J., Meng, J., Lim, K. H., Rojas, O. J., and Park, S. (2013). "Transformation of lignocellulosic biomass during torrefaction," *Journal of Analytical and Applied Pyrolysis* 100, 199-206. DOI: 10.1016/j.jaap.2012.12.024

Pazos, G. B., and Sotelo, R. D. (1999). "Importancia de la lignina en las contracciones de la madera: Revisión bibliográfica," *Madera y Bosques* 5(1), 13-26. ISSN: 1405-0471

Peng, J. H., Bi, X. T., Sokhansanj, S., and Lim, C. J. (2013). "Torrefaction and densification of different species of softwood residues," *Fuel* 111, 411-421. DOI: 10.1016/j.fuel.2013.04.048

Pereira, H., Graça, J., and Rodrigues, J. C. (2003). "Wood chemistry in relation to quality," in: *Wood Quality and its Biological Basis*, J. R. Barnett and G. Jeronimidis (eds.), Blackwell Publishing, Oxford, UK, pp. 53-87.

Petit, B., and Montagnini, F. (2004). "Growth equations and rotation ages of ten native tree species in mixed and pure plantations in the humid neotropics," *Forest Ecology and Management* 199(2), 243-257. DOI: 10.1016/j.foreco.2004.05.039

Puig-Arnavat, M., Shang, L., Sárossy, Z., Ahrenfeldt, J., and Henriksen, U. B. (2016). "From a single pellet press to a bench scale pellet mill—Pelletizing six different biomass feedstocks," *Fuel Processing Technology* 142, 27-33. DOI: 10.1016/j.fuproc.2015.09.022

Rousset, P., Aguiar, C., Labbé, N., and Commandré, J. M. (2011). "Enhancing the combustible properties of bamboo by torrefaction," *Bioresource Technology* 102(17), 8225-8231. DOI: 10.1016/j.biortech.2011.05.093

Rousset, P., Macedo, L., Commandré, J.-M., and Moreira, A. (2012). "Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product," *Journal of Analytical and Applied Pyrolysis* 96, 86-91. DOI: 10.1016/j.jaap.2012.03.009

Roy, M. M., and Corscadden, K. W. (2012). "An experimental study of combustion and emissions of biomass briquettes in a domestic wood stove," *Applied Energy* 99, 206-212. DOI: 10.1016/j.apenergy.2012.05.003

Sabil, K. M., Aziz, M. A., Lal, B., and Uemura, Y. (2013). "Synthetic indicator on the severity of torrefaction of oil palm biomass residues through mass loss measurement," *Applied Energy* 111, 821-826. DOI: 10.1016/j.apenergy.2013.05.067

Schroeder, H. A. (2007). "Shrinking and swelling differences between hardwoods and softwoods," *Wood and Fiber Science* 4(1), 20-25. ISSN: 0735-6161

Serrano-Montero, J. R., and Moya-Roque, R. (2011). "Procesamiento, uso y mercado de la madera en Costa Rica: Aspectos históricos y análisis crítico," [Costa Rican sawmill processing, use and market: historical aspects and critical analysis] *Revista Forestal Mesoamericana Kurú* 8(21), 1-12. ISSN: 2215-2504

Sharma, R. K., Wooten, J. B., Baliga, V. L., Lin, X., Chan, W. G., and Hajaligol, M. R. (2004). "Characterization of chars from pyrolysis of lignin," *Fuel* 83(11), 1469-1482. DOI: 10.1016/j.fuel.2003.11.015

Shebani, A. N., van Reenen, A. J., and Meincken, M. (2008). "The effect of wood extractives on the thermal stability of different wood species," *Thermochimica Acta* 471(1), 43-50. DOI: 10.1016/j.tca.2008.02.020

Stevanic, J. S., and Salmén, L. (2009). "Orientation of the wood polymers in the cell wall of spruce wood fibres," *Holzforschung* 63(5), 497-503. DOI: 10.1515/hf.2009.094

TAPPI T222 om-02 (2002). "Acid-insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.

TAPPI T17 wd-70 (2002). "Cellulose in wood," TAPPI Press, Atlanta, GA.

Tenorio, C., and Moya, R. (2012). "Evaluation of different approaches for the drying of lignocellulose residues," *BioResources* 7(3), 3500-3514. DOI: 10.15376/biores.7.3.3500-3514

Tenorio, C., Moya, R., Salas, C., and Berrocal, A. (2016). "Evaluation of wood properties from six native species of forest plantations in Costa Rica," *Bosque* 37(1), 71-84. DOI: 10.4067/s0717-92002016000100008

Tenorio, C., Moya, R., Tomazello-Filho, M., and Valaert, J. (2014). "Quality of pellets made from agricultural and forestry crops in Costa Rican tropical climates," *BioResources* 10(1), 482-498. DOI: 10.15376/biores.10.1.482-498

Tenorio, C., and Moya, R. (2013). "Thermogravimetric characteristics, its relation with extractives and chemical properties and combustion characteristics of ten fast-growth species in Costa Rica," *Thermochimica Acta* 563, 12-21. DOI: 10.1016/j.tca.2013.04.005

van der Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., and Ptasinski, K. J. (2011). "Biomass upgrading by torrefaction for the production of biofuels: A review," *Biomass and Bioenergy* 35(9), 3748-3762. DOI: 10.1016/j.biombioe.2011.06.023

Vassilev, S. V., Baxter, D., Andersen, L. K., and Vassileva, C. G. (2010). "An overview of the chemical composition of biomass," *Fuel* 89(5), 913-933. DOI: 10.1016/j.fuel.2009.10.022

Wang, G., Luo, Y., Deng, J., Kuang, J., and Zhang, Y. (2011). "Pretreatment of biomass by torrefaction," *Chinese Science Bulletin* 56(14), 1442-1448. DOI: 10.1007/s11434-010-4143-y

Wannapeera, J., Fungtammasan, B., and Worasuwannarak, N. (2011). "Effects of temperature and holding time during torrefaction on the pyrolysis behaviors of woody biomass," *Journal of Analytical and Applied Pyrolysis* 92(1), 99-105. DOI: 10.1016/j.jaap.2011.04.010

Xu, F., Yu, J., Tesso, T., Dowell, F., and Wang, D. (2013). "Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A mini-review," *Applied Energy* 104, 801-809. DOI: 10.1016/j.apenergy.2012.12.019

Yan, W., Acharjee, T. C., Coronella, C. J., and Vásquez, V. R. (2009). "Thermal pretreatment of lignocellulosic biomass," *Environmental Progress & Sustainable Energy* 28(3), 435-440. DOI: 10.1002/ep.10385

Article submitted: May 31, 2017; Peer review completed: August 4, 2017; Revised version received and accepted: August 16, 2017; Published: August 30, 2017.
DOI: 10.15376/biores.12.4.7566-7589