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Energy Reports 6 (2020) 738–743
www.elsevier.com/locate/egyr

6th International Conference on Energy and Environment Research, ICEER 2019, 22–25 July, University of Aveiro, Portugal

Oxidative pyrolysis of *Guadua angustifolia* Kunth

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Received 29 July 2019; accepted 17 September 2019
Available online 30 September 2019

Abstract

This is a study of the behavior of the species of bamboo *Guadua angustifolia* Kunth during oxidative pyrolysis. Thus, thermogravimetric analysis of *G. angustifolia* combustion in an oxygen flow rate of 50 cm^3/min and at a heating rate of 10 ^oC/min was carried out. Moreover, the combustion profile was compared with the pyrolysis profile of *G. angustifolia* in nitrogen, using the same flow rate and the same heating rate. For this type of bamboo, devolatilization during combustion (oxidative pyrolysis) is boosted by the heterogeneous oxidation of the pyrolyzable fraction of this material. Therefore, the emission of volatiles is highly accelerated. This fact may be due to both the use of an oxygen flow and the inorganic composition of *G. angustifolia*, which contains high concentrations of potassium. This potassium may act as a catalyst that weakens organic matter bonds by an oxygen transfer mechanism. This behavior is not observed for all types of biomass. Therefore, it is likely that inorganic matter of biomass plays an important role in the way its oxidation occurs, which has a significant influence on the choice of the most suitable process for its valorization.

Peer-review under responsibility of the scientific committee of the 6th International Conference on Energy and Environment Research, ICEER, 2019.

Keywords: *Guadua angustifolia* Kunth; Thermogravimetric analysis; Oxidative pyrolysis; Inert pyrolysis; Potassium

1. Introduction

Colombia is the Latin America country with the second greatest level of bamboo diversity. It has 24 endemic species of this large woody grass that includes *Guadua angustifolia* Kunth [1]. *G. angustifolia* covers an area of 51 500 ha of which almost 90% is wild and the rest has been cultivated [2]. Nowadays, bamboo has attracted major international interest, which is why Colombia may intensify its production in order to increase exportation. The great interest that it has awakened is related to the fact that *G. angustifolia* has ideal physico-chemical characteristics for its use in the construction, furniture, paper, textile, food and chemical industries and handicrafts [3,4]. Additionally, it is a type of biomass with rapid growth and great adaptability to different terrains and it is a crop which needs little maintenance. *G. angustifolia* has also a regenerative mechanism of self-propagation that guarantees its supply

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https://doi.org/10.1016/j.egyr.2019.09.057

Peer-review under responsibility of the scientific committee of the 6th International Conference on Energy and Environment Research, ICEER, 2019.

[3]. Thus, its cultivation may constitute a natural and efficient system for fixing large amounts of CO_2. However, an uncontrolled spread of *G. angustifolia* may have a negative impact on bio-diversity and, consequently, on the environment, one reason why an adequate balance should be sought.

Another less studied application of *G. angustifolia* is as an energy source [5] or as a source for obtaining valuable liquid or solid fractions [6,7]. In order to take advantage of its energy potential, *G. angustifolia* can be treated using thermochemical processes (combustion, pyrolysis and gasification). Thus, this natural resource may be converted into a value energy source for isolated rural communities in Colombia. Both pyrolysis and combustion are included among the stages of gasification, which is why knowledge of these processes is important in order to optimize the whole process. Accordingly, the aim of this paper is to deepen knowledge of the behavior of *G. angustifolia* during oxidative pyrolysis in comparison with its inert pyrolysis and the influence of its chemical composition on this behavior.

2. Materials and methods

The material used in this research is bamboo of the species *Guadua angustifolia* Kunth from the coffee region of Colombia. The samples of *G. angustifolia* culm were crushed and sieved to a size lower than 800 μm. The proximate analysis was carried out according to the standards for solid biofuels UNE-EN ISO 18134-3, UNE-EN 18123, UNE-EN ISO 18122, for moisture, volatile matter and ash, respectively. Carbon, hydrogen, nitrogen and sulphur were analyzed with a Macro Elementar Vario. Its lignocellulosic composition was determined according to the standard TAPPI T222 om-15, while major (Al, Ca, Fe, Mg, P, K, Si, Na, Ti) and minor (As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, Zn) element concentrations were determined according to the standards UNE-EN ISO 16967 and UNE-EN ISO 16968, respectively. Higher heating value was determined using an analytical balance Mettler Toledo model AB 204SNR 111660708 and a calorimeter IKA C 2000 Basic S1. Thermogravimetric analyses (TGs) were carried out with a Mettler-Toledo TGA/SDTA851e, using both nitrogen and oxygen flow rates of 50 cm^3/min. For both profiles (pyrolysis and combustion), the samples were heated from the ambient temperature to 800 °C at a heating rate of 10 °C/min. TG runs were repeated two times and the maximum standard deviation of the weight loss curves was lower than 0.5%.

3. Results and discussion

3.1. Characterization of G. angustifolia

Table 1 shows the proximate and ultimate analysis, higher heating value (HHV) and lignocellulosic composition of *Guadua angustifolia* Kunth and its comparison with other species of bamboo. The bamboos shown in Table 1 came from Mexico (*Guadua amplexifolia* and five species of *Bambusa* and *Dendrocalamus*) [7,8], Japan and China (*Phyllostachys*) [9], Southeast Asian rainforest (*Bambusa Tulda*) [10] and Taiwan (*Dendrocalamus latiflorus* Munro) [11]. Table 1 shows that the differences among the species of bamboos are not significant. Proximate analysis of *G. angustifolia* is intermediate among the types of bamboos indicated in Table 1. With regard to the ultimate analysis, the concentration of sulphur is higher in both species of bamboo of the genus *Guadua*, whilst the species *Bambusa Tulda* has the highest concentration of nitrogen (Table 1). Sulphur concentration in *Guadua* is higher than the mean value for herbaceous and agricultural biomass and natural biomass, being 0.14 wt% (db) and 0.19 wt% (db) respectively [12]. Differing from the rest of the species of Table 1, *Guadua angustifolia* Kunth has higher concentrations of lignin than hemicellulose. This result agrees with that obtained by Salas-Enríquez et al. [7]. In comparison with the mean values for natural biomass (43.3 wt% daf of cellulose, 31.8 wt% daf of hemicellulose and 24.9 wt% daf of lignin) [13], bamboo has higher concentrations of cellulose and lignin.

Table 2 shows the concentrations of major and minor elements in *G. angustifolia*. As can be seen in Table 2, the concentration of K is very high in comparison with the rest of elements. This is typical of fast growing plants, such as grasses, and a significant part of it is probably contained in water-soluble salts [13]. The water soluble salts are normally highly mobile and reactive and have low decomposition and melting temperatures during thermal processes [13]. Moreover, these inorganic compounds may have a catalytic effect on pyrolysis and combustion [13]. This has to be taken into account for choosing the best way of valorizing this type of biomass.

Table 1. Characterization of bamboo *Guadua angustifolia* Kunth and comparison with other species. Contents of cellulose, hemicellulose and lignin are expressed on dry ash-free basis and normalized to 100.0%.

Analysis	*Guadua angustifolia* Kunth	*Guadua amplexifolia*[c]	*Phyllostachys*[d]	*Bambusa Tulda*[e]	*Dendrocalamus latiflorus* Munro[f]	*Bambusa* and *Dendrocalamus*[g]
Moisture [wt%, ad]	7.8[b]	8.1			3.6	
Proximate analysis [wt%,db]						
Volatile matter	75.8[b]	86.8	80.0–83.7	80.0	69.5	75.9–79.1
Ash	3.8[b]	2.2	0.5–1.3	4.5	4.1	3.3–5.2
Fixed carbon[a]	20.4[b]	10.9	15.9–18.8	15.2	26.4	17.5–19.3
HHV [MJ/kg, db]						
	19.1[b]	n.a.	19.1–19.6	18.4	17.1	18.2–18.5
Ultimate analysis [wt%,db]						
C	47.9[b]	42.7	50.9–52.3	47.9	n.a.	45.9–47.0
H	6.7[b]	6.1	4.5–5.4	6.5	n.a.	5.8–6.1
N	0.5[b]	0.8	0.2–0.6	2.8	n.a.	0.12–0.15
S	0.7[b]	0.8	0.03–0.05	n.a.	n.a.	0.05
O[a]	40.4[b]	47.4	41.1–42.9	38.3	n.a.	43.1–43.8
Structural components [wt%,daf]						
Cellulose	52.6	50.1	44.2–47.7	n.a.	57.8	n.a.
Hemicellulose	19.7	27.5	26.7–28.6	n.a.	23.8	n.a.
Lignin	27.6	22.4	25.4–27.3	n.a.	18.4	n.a.
Extractives	7.3	n.a.	3.5–4.7	n.a.	n.a.	n.a.

n.a. not available
[a]By difference.
[b]Folgueras et al. [6].
[c]Salas-Enríquez et al. [7].
[d]Scurlock et al. [9].
[e]Dutta et al. [10].
[f]Lu and Chen [11].
[g]Salovaara et al. [8].

Table 2. Concentrations of major and minor elements of bamboo *Guadua angustifolia* Kunth.

Major elements	[ppm, ad]	Minor elements	[ppm, ad]
Al	18.1	As	<1.0
Ba	5.26	Mn	2.72
Ca	25.1	Cd	<0.5
Fe	16.4	Cu	3.13
Mg	46.2	Cr	<1.0
K	5229	Ni	<1.0
Si	234	Pb	<1.0
Na	584	Cu	<1.0
Ti	<1.0	Mo	<1.0
P	164	Sb	<1.0
		V	<1.0
		Zn	11.7

3.2. Thermogravimetric analysis of G. angustifolia

Fig. 1 shows the comparison of the derivative thermogravimetric curves (DTGs) and differential thermal analysis (DTA) of the pyrolysis and combustion of *G. angustifolia*. Moreover, in Table 3, the mass losses for several intervals of these processes are indicated. In both processes, from 25 °C to 209 °C, the mass loss (8.1 wt%) is mainly due to the vaporization of moisture in the sample (7.8 wt%, ad). For pyrolysis and combustion, the temperatures for

Table 3. *G. angustifolia* mass loss during pyrolysis and combustion for several temperature ranges.

Temperature range [°C]	Mass loss [wt.%]
Pyrolysis	
25–209	8.1
209–330	36.3
330–600	30.6
600–800	2.3
Combustion	
25–209	8.3
209–285	37.5
285–315	29.0
315–333	18.1
333–800	3.4

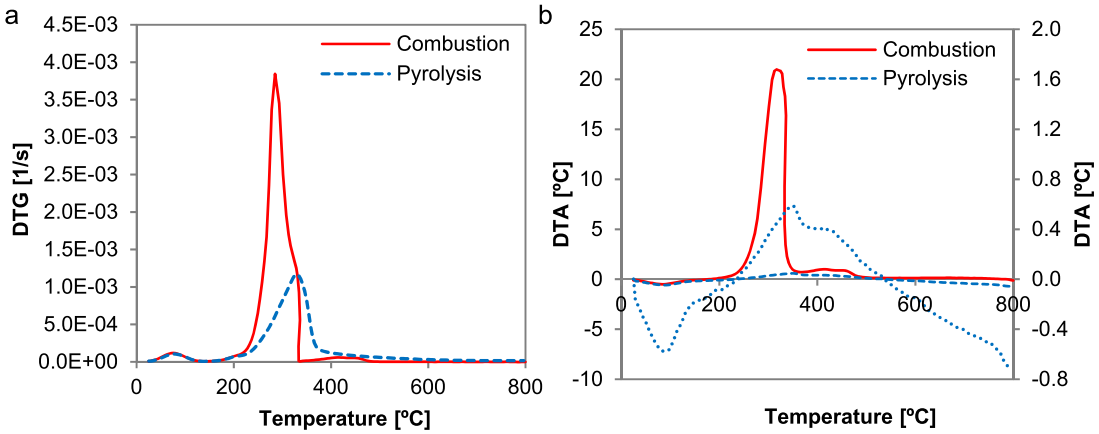

Fig. 1. (a) DTG and (b) DTA curves of pyrolysis and combustion of *G. angustifolia*.

which maximum mass loss rate occur are 330 °C and 285 °C, respectively. During the pyrolysis of *G. angustifolia* between 209 °C and 330 °C, there is a loss of volatile matter (36.3 wt%) approximately equal to that of the interval 209–285 °C of combustion (37.5 wt%). This mass loss is due to the total decomposition of hemicellulose, partial of cellulose and slight decomposition of lignin, whose intervals of decomposition during pyrolysis at 10 °C/min are 220 °C–315 °C, 315 °C – 400 °C and 160 °C – 900 °C, respectively [14]. Therefore, the devolatilization process of combustion is accelerated with respect to that of pyrolysis. During combustion, the maximum mass loss rate is 3.84 10^{-3} s^{-1}, whilst during pyrolysis it is 1.17 10^{-3} s^{-1} (Fig. 1a). In the range of temperatures 285–315 °C of the combustion process (from the maximum of the peak to the beginning of the shoulder), the mass loss is 29.0 wt%, very similar to that of the interval 330–600 °C of *G. angustifolia* pyrolysis. For this interval, the mass loss can be attributed to partial decomposition of cellulose and lignin. Again, this devolatilization occurs at a higher rate during combustion than during pyrolysis. Thus, from 209 °C to 315 °C of *G. angustifolia* combustion, oxidative pyrolysis occurs, the total mass lost being 66.5 wt%, which roughly corresponds to the volatile matter of the sample (69.9 wt%, ad). During combustion, from the beginning of the shoulder (315 °C) to 333 °C, the mass loss is 18.1 wt%, which is approximately equal to the fixed carbon (18.8 wt%, ad). Thus, *G. angustifolia* combustion can be divided into four main stages, each dominated by the following processes: (1) moisture removal from 25 °C to 209 °C; (2) oxidative pyrolysis (devolatilization + volatile combustion) from 209 °C to 315 °C; (3) char combustion from 315 °C to 333 °C and (4) inorganic matter transformation from 333 °C to 800 °C.

Fig. 1b shows the DTA of the combustion and pyrolysis of *G. angustifolia*. The dotted line of Fig. 1b corresponds to pyrolysis, its vertical axis being the one on the right side. DTA pyrolysis of *G. angustifolia* is also plotted with the scale of the left vertical side (dashed line) in order to be compared with *G. angustifolia* combustion. DTA of

combustion shows two clear exothermic stages, the first one from 200 °C to 340 °C (highly exothermic) and the second one from 340 °C to 500 °C. DTA of *G. angustifolia* pyrolysis shows an endothermic peak from 25 °C to 237 °C (mainly moisture and volatile extractives removal), an exothermic peak from 237 °C to 533 °C (mainly hemicellulose and cellulose decomposition) and an endothermic stage from 533 °C to 800 °C (probably the last stage of lignin degradation and other secondary reactions that causes char). For bamboo pyrolysis at a heating rate of 10 °C/min, Oyedun et al. [15] found an exothermic peak in the range 350 °C – 450 °C. The exothermic peak found during bamboo pyrolysis is probably due to the heterogeneous secondary reactions of the volatiles, which also cause the formation of char [16].

According to Senneca et al. [17], there are several pathways for solid fuel combustion, the extreme ones being: (a) devolatilization (pyrolysis) and volatile combustion followed by char combustion, which occur as sequential steps; and (b) heterogeneous oxidation of fixed carbon and volatile matter. The pathway undergone by the solid fuel depends on the characteristics of the fuel and the operational conditions (particle size, temperature and oxygen partial pressure) [17]. Fig. 1 shows that in an oxidizing atmosphere, devolatilization is highly accelerated in comparison with an inert atmosphere. There is one peak that ends at a lower temperature than that corresponding to inert pyrolysis, and which has in addition a shoulder related to char combustion. In the combustion profile of forest pinewood waste, Amutio et al. [18] found not only that the main peak ends at lower temperatures but also a second peak at higher temperatures. Lu and Chen [11] also obtained similar results in the DTG of a type of bamboo (*Dendrocalamus latiflorus* Munro). In the DTG of this research, the second peak was converted into a shoulder due probably to the fact that a much higher oxygen concentration (100%) was used. According to Senneca et al. [17], DTG profile (Fig. 1) would indicate that the pathway for *G. angustifolia* combustion is intermediate between the two extreme ones (a) and (b). Thus, during oxidative pyrolysis, not only the emission and diffusion of volatiles is produced, but also the heterogeneous oxidation of the pyrolyzable fraction. This heterogeneous oxidation may be enhanced by the high concentrations of potassium in *G. angustifolia*. Shen and Qinlei [19] reported that alkalis (including potassium salts) weaken the intermolecular interaction of the polymeric chains by an oxygen transfer mechanism. Therefore, the activation energy of the pyrolysis decreases, volatile concentration increases and, consequently, ignition (the beginning of stable combustion) occurs earlier [19]. Thus, the high K concentration of *G. angustifolia* may affect its combustion substantially. During oxidative pyrolysis, for all types of biomass, heterogeneous oxidation of the pyrolyzable fraction not always occurs [17]. The behavior of *G. angustifolia* during oxidative pyrolysis may be an advantage for its gasification in a downdraft gasifier. Salovaara et al. [8] found that, in general, Bamboo seems to be a satisfying feedstock for downdraft gasifiers. However, not all the five species studied showed the same characteristics, *Bambusa oldhamii* Munro and *Dendrocalamus strictus* being the best ones [8].

4. Conclusion

The combustion profile of the bamboo species *Guadua angustifolia* Kunth obtained by thermogravimetric analysis with an oxygen flow rate of 50 cm/m^3 and at a heating rate of 10 °C/min shows that devolatilization + volatile combustion stage and char combustion occurs mainly in the ranges 209 °C – 315 °C and 315 °C–333 °C, respectively. The devolatilization of *G. angustifolia* during its oxidative pyrolysis is highly accelerated with respect to that during inert pyrolysis. The devolatilization interval during pyrolysis in nitrogen with the same flow rate and heating rate was 209 °C – 370 °C. The maximum mass loss rate during combustion (3.84 10^{-3} s^{-1}) was much higher than during pyrolysis (1.17 10^{-3} s^{-1}). This fact is related to the use of a flow of oxygen and, probably, also to the high content of potassium of *G. angustifolia*, since it acts as a catalyst promoting the heterogeneous oxidation of the pyrolyzable fraction at lower temperature. Thus, in spite of the fact that biomass has low ash yield, its inorganic composition has a significant influence on its behavior during its thermal processing.

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