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Energy evaluation of biochar obtained from the pyrolysis of pine pellets

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Abstract The wood pellets are mainly used in heating environments, commercial and residential, as well as fuel for production of thermal and electric energy in industrial plants. Furthermore, the heterogeneity and variable moisture content, combined with the high cost of transport, are limiting challenges that must be overcome with new technologies and new products. In this context, torrefaction and pyrolysis are attractive alternatives for increasing energy density and decreasing the moisture content of the samples, based on thermochemical conversion in a non-oxidizing atmosphere. Samples were produced to perform the energetic characterization of biochar from pine pellet using different heating rates 5–30 °C min^{-1}, different residence temperatures 200, 280 and 570 °C and different residence time (1 and 0.5 h). The high heating value (HHV) of each variable was measured and allowed to observe that the heating rate did not influence of a significant way the results, in other words, a 5 % variation between the lowest and highest heating rate. Notwithstanding, the HHV was expressive compared to the pellet in nature, when it has been found an energetic gain over 80 %. In general, the biochar from pine pellets obtained by torrefaction or pyrolysis has appropriated characteristics compared to pellets in nature, showing a greater amount of energy per unit, high stability, reduced moisture content and reduced ash content. The kinetic of combustion to biochar in oxygen-rich atmosphere showed the dependence between the activation energy and conversion degree, with a continuous decrease in the activation energy, characteristic of complex processes comprised by initial reversible reaction followed by an irreversible one.

Keywords Energetic characterization · Torrefaction · Pyrolysis · Pine pellets · Biochar · Non-isothermal kinetic

Introduction

Burning wood pellets is mainly used for warm-up environments (commercial and residential environments), but it can also be used as fuel for generating electricity in industrial plants, or even in power plants. The versatility and availability of biomass, combined with its characteristic of renewable energy and do not contribute to global warming, and in addition its cost is an average 25–50 % less than fossil heating fuels, are strong arguments to enhance its use worldwide [1–5]. Moreover, the heterogeneity, low energy density, and variable humidity, combined with the high cost of transport, are limited challenges that must be overcome with new technologies and new products [6–9]. In this context, torrefaction and pyrolysis are attractive alternatives for increasing energy density and decreasing the moisture content of the samples, based on thermochemical conversion in a non-oxidizing atmosphere (a procedure that contributes to the generation of an additional product of appreciable economic value). These advantages make interesting the use of pyrolyzed biomass for energy purposes, requiring, however, a proper characterization. Thus, the aim of this work was to

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produce and characterize biochar from pine pellet for further use of it as fuel. It has shown the caloric value, moisture content, density and immediate analysis of the most important properties of wood for use as fuel. Thus, the present study produced biochar of the pine pellet and determined the properties of the same following the above recommendation [10–12].

Materials and methods

The biomass used in the study is constituted by residues from furniture industry composed solely of *Araucaria angustifolia* [13], also known as Paraná pine, Brazilian pine or candelabra tree, shaped like pellets (pine pellets). The pellets of the wood of *Araucaria angustifolia* contain 58.3 % cellulose and 28.5 % lignin with long fibers [14] and were obtained by the BrBiomassa Company, Paraná State, Brazil. The development process of biochar made in this work consisted of subjecting the sample to a slow pyrolysis (since it presents the highest yields in solids) in a muffle furnace under a nitrogen atmosphere (flow of 1 L min^{-1}). Following several temperature settings of 200, 280 and 570 °C and residence time of one hour and a half hours, in addition to varying the heating rate from 5 to 30 °C min^{-1} [15].

Particle density

The bulk density is the mass of the sample per volume occupied by the particle (solid and internal pore volume). The particle density of the biochar was found by determining the mass of the sample in a calculated volume using a caliper [16].

Bulk density

The bulk density is the mass of sample in a specific volume [17]. In this study, it was used a regular container (prism) with a capacity of around 0.2 m^3. The bulk density was calculated by Eq. 1:

$$D_{\mathrm{gran}} = m_{\mathrm{biochar}} / V_{\mathrm{recip}} \tag{1}$$

where D_{gran} is the bulk density of coal in kg m^{-3}; m_{biochar} is the biochar mass in kg; V_{recip} is the container volume in m^3.

Heating values

The heating value or calorific value of a wood sample is defined as the amount of energy in the form of heat released by the combustion of a unit mass or volume, hence MJ kg^{-1} for solids [18]. The higher heating value (HHV) is one in which combustion takes place at constant volume and in which the water formed during combustion is condensed, and the heat which derived from this condensation recovered [18]. The lower heating value (LHV) is the energy available per unit mass of fuel after deducting losses from evaporation of water. The HHV of biochar was determined by bomb calorimeter, model *IKAC*2000, according to ASTM E7 [19], using the mass of 0.5 g in triplicate. The LHV was obtained by Eq. 2 [20]:

$$\mathrm{LHV} = \mathrm{HHV} - 51.14 \times H_{\mathrm{T}} \tag{2}$$

where LHV is the lower heating value in MJ kg^{-1}; HHV is the higher heating value in MJ kg^{-1}, and H_{T} is the hydrogen content in %.

Moisture and ash

Moisture and ash contents were determined by gravimetric technique, according to ASTM D-3173 [21], ASTM D-3174 [22]. The samples were heated at 105 °C until constant mass. In a subsequent experiment, the same sample was used for the determination of ash content, raising the temperature to 775 °C maintaining per one hour.

Thermal stability and kinetic evaluation

The thermal stability of the biochar and pellet samples was determined by a thermal gravimetric analysis performed in an apparatus *SDT* − 2960 from TA Instruments. For these analyses, it was used around 3.5 mg of sample, in alumina pan, under an atmosphere of nitrogen and air (gas flow of 100 mL min^{-1}). The heating rate was of 10–30 °C min^{-1}, from ambient temperature (±25 °C) to 850 °C.

For kinetics study, the conditions applied for biochars were 5, 10, 20, 25 and 30 °C min^{-1} heating rates under dynamic air atmosphere to simulate the combustion condition. Previously to kinetic experiments, several flow rates of air were tested, and the flow of 100 mL min^{-1} was chosen as the most suitable for not providing oscillations in the signals of TG curves. Preliminary tests indicated that the sample mass of 3.5 mg was suitable for kinetic study, as it did not provide any dependence of mass for the profiles observed in thermogravimetric curves [23, 24]. All assays were performed in inert α-alumina sample holder and previously to the experiments, the equipment was calibrated for baseline, mass, and temperature in the proper experimental conditions.

Activation energy: local linear integral isoconversional method

The activation energy for combustion of biochars samples was obtained employing the isoconversional integral method based on interactive theorem for integral average value, analogous to the method of Wanjun and Donghua [25], where the kinetics of the reactions of decomposition of organic matter can be initially described by the differential, Eq. 3, given by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\mathrm{e}^{-\mathrm{E/RT}} f(\alpha) \tag{3}$$

Assuming that the parameters E_α, A_α and the local heating rate β_α are constants in $[\alpha - \Delta\alpha, \alpha + \Delta\alpha]$, from Eq. 3, we can obtain that:

$$\Delta g(\alpha) = \int_{\alpha-\Delta\alpha}^{\alpha+\Delta\alpha} \frac{1}{f(\alpha)}\mathrm{d}\alpha = \frac{A_\alpha}{\beta_\alpha}\int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha+\Delta\alpha}} \mathrm{e}^{-\frac{\mathrm{E}_\alpha}{\mathrm{RT}}}\mathrm{d}T \tag{4}$$

where $\Delta g(\alpha) = g(\alpha + \Delta\alpha) - g(\alpha - \Delta\alpha)$ and $g'(\alpha) = 1/f(\alpha)$. The function g is known as the integral reaction kinetic model. By applying the mean value theorem to the integral in Eq. 4, obtains

$$\Delta g(\alpha) = \frac{A_\alpha}{\beta_\alpha}(T_{\alpha+\Delta\alpha} - T_{\alpha-\Delta\alpha})\mathrm{e}^{-\frac{\mathrm{E}_\alpha}{\mathrm{RT}}} \tag{5}$$

for some τ_α in $[T_{\alpha+\Delta\alpha} - T_{\alpha-\Delta\alpha}]$. Rearranging Eq. 5 and applying logarithm lead to

$$\ln\left[\frac{\beta_\alpha}{\Delta T_\alpha(1+\gamma)}\right] = B_\alpha - \frac{E_\alpha}{RT_\alpha} \tag{6}$$

where γ and B_α are defined as:

$$\gamma = \frac{E_\alpha}{RT_\alpha^2}(\tau_\alpha - T_\alpha) + \left(\frac{E_\alpha^2 - 2E_\alpha RT_\alpha}{R^2T_\alpha^4}\right)(\tau_\alpha - T_\alpha)^2 \tag{7}$$

$$B_\alpha = \ln\left[\frac{A_\alpha}{\Delta g(\alpha)}\right] \tag{8}$$

For a given conversion and a series of $n \geq 3$ non-isothermal experiments carried out at different heating rates $\beta_{\alpha,\mathrm{i}}$, $i = 1, 2, \ldots, n$, Eq. 6 can be used to develop a local linear integral isoconversional method. The procedure begins by considering the plotting $\ln[\frac{\beta_{\alpha,\mathrm{i}}}{\Delta T_{\alpha,\mathrm{i}}(1+\gamma_\mathrm{i})}]$ versus $\frac{1}{RT_{\alpha,\mathrm{i}}}$ for $\gamma_\mathrm{i} = 0$, $i = 1, 2, \ldots, n$. Estimates of the E_α and B_α are obtained, respectively, from the slope and linear coefficient of the line; introducing those estimates in Eq. 7, values of γ_i are calculated and a new estimates of parameters are obtained. The steps are repeated up to the convergence of the sequences of estimates.

Results and discussion

Gravimetric yield of biochar

The temperature is presented as the key process variable. Several experiments were performed to identify the influence of final pyrolysis temperature, for a given plant species on the yields of charcoal, liquid and gas. Data show that the behavior of the coal, when the pyrolysis temperature increases, is losing its volatiles, which will enhance its liquid and gas phases. Although the charcoal yield decreases with increasing temperature, there is a significant improvement in fixed carbon content, this indication of quality input [26]. Another notable impairment is observed when yields are compared to coal and liquids in different heating. Several studies show that it is possible to increase the recovery of liquid products significantly by increasing the heating rate [27–29].When the heating is conducted at a low heating rate, the temperature takes to reach a particular value, where a higher rate of thermal decomposition of biomass components occurs, there are a reduced speed and output and the newly formed components of the system. To remain in the system under high temperature, the newly formed components suffer further decomposition reactions (secondary reactions), mainly being converted into compounds of lower molecular mass in most of the atmospheres, such as CO_2, CO, and H_2O and as residue the biochar [30, 31]. According to Tables 1 and 2, there was a lower yield of biochar in the higher temperatures of residence and higher heating rates, corroborating the results found in the literature. Thus, the reactions of secondary thermal decomposition contribute to increasing the yield of biochar in the decrease of heating rate, Table 1. However, in this work it has not been possible to observe an increase in yield with increasing residence time. This phenomenon can be explained by the fact that the system used in the pyrolysis not be closed, allowing the removal of volatile as they were being produced. Cellulose, hemicellulose, and lignin are the major constituents of the biomass taken into account the studies of pyrolysis as a means of biomass energy utilization. Despite the importance of these three constituents in the process, the difficulty of implementation and the inaccuracy of the methods of quantification of these components, coupled with the complexity of the reactions of thermal decomposition biomass, makes it standard in many of these works not quantify the biomass studied [30]. For this reason, in this study the content of cellulose, hemicellulose and lignin were not quantified in the pellet used in the study of Pine. The lack

Table 1 Gravimetric yield of biochar as function of heating rate for a pyrolysis temperature at 570 °C

β/°C min^{-1}	Yield/%
30	19.8
25	20.0
20	20.3
15	21.1
10	21.4
5	22.4

Table 2 Gravimetric yield of biochar as function of temperature and residence time for a heating rate of 10 °C min^{-1}

t_r/min	T/°C	Yield/%
30	200	27.4
60	200	26.2
30	280	24.2
60	280	23.9
30	570	21.4
60	570	21.4

of this information does not result in the main problems in interpreting the results from the thermal decomposition, and these components tend to occur in characteristic temperatures, independent of biomass studied. Hemicellulose is the least stable of the three components of the biomass, and its thermal decomposition takes place in the range of 150–350 °C and a maximum rate of about 270 °C. Cellulose has a similar chemical composition to the hemicellulose, but due to its crystalline arrangement, is more resistant to thermal decomposition, which occurs in the range of 275–400 °C, with a maximum around 350 °C. The lignin thermal decomposition occurs at 250–500 °C, but without any temperature range in which the decomposition rate is more intense [32]. With such information, it can be inferred that the income which occurred on heating to 280 °C (yield above 25 %) is close to the average lignin content (25.18 %) plus some remaining holocellulose residue, while the yield of coal pyrolysis at 570 °C (yield below 25 %) is close to the lignin content. This comparison is consistent with the knowledge that the lignin component whose content is at best correlates with the biomass yield of biochar while cellulose and hemicellulose are the main responsible ones for the production of bio-oil and non-condensable gas [33].

Thermal gravimetric analysis

The thermal decomposition resistance of the biochar samples was also tested, and all of them exhibited high thermal stability compared to the pellet in nature, especially to the biochar produced at 570 °C of temperature residence. Figures 1 and 2 present TG curves, in nitrogen and air atmosphere, respectively, for several biochar samples. Figure 3 shows the biochar prepared at 570 °C and time residence of one hour submitted at several heating rates. In the initial stage of heating, the samples was noted an event, commonly associated with loss of water or volatiles present in the samples. Patterns of decomposition of biochar were not similar to the pellet. As a consequence of previous thermal treatment, the biochar has a lower mass loss in the first event of thermal decomposition (Figs. 1, 2), characteristic region of the hemicellulose decomposition. It was observed that, under a nitrogen atmosphere, the biochar only had a small decomposition above temperatures which were produced.

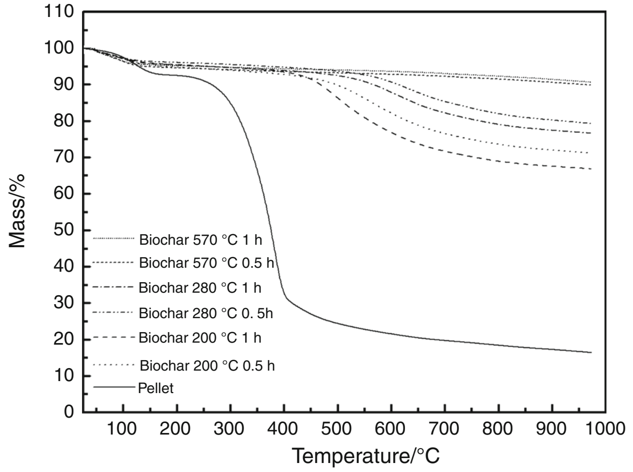

Fig. 1 TG curves (biochar and pine pellet) under nitrogen atmosphere and heating rate of 30 °C min^{-1}

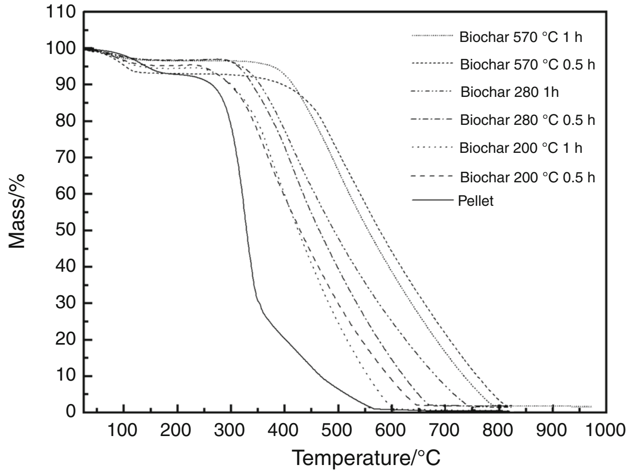

Fig. 2 TG curves (biochar and pine pellet), in air atmosphere and a heating rate of 30 °C min^{-1}

The mass loss in the first event of decomposition, under an atmosphere of air, calculated on the mass of the sample without the moisture content, was 71 % for the pellet, although this value also included the mass loss from the decomposition of other wood components. For biochar, this mass loss varied from 35 to 44 %, suggesting that this reduction in mass loss is linked to the loss of hemicellulose due to thermal treatment in its production. The second thermal event has had its maximum at 470 °C in the pellet and at 475, 580 and 630 °C in the biochar 200, 280 and 570 °C, respectively, and resulted in reduction of 13, 45, 55, and 41 % of dry weight, respectively. The highest temperature to biochar is due to the partial transformation

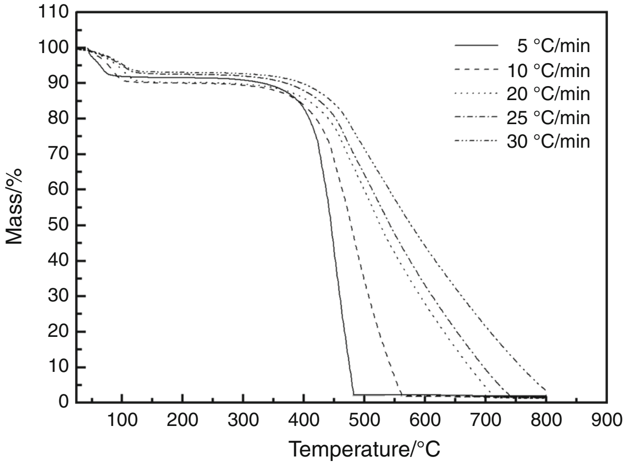

Fig. 3 Curves in an air atmosphere and heating rate of 30 °C min^{-1} for samples of biochar produced at 570 °C of temperature residence, different heating rates and 1 h of residence time

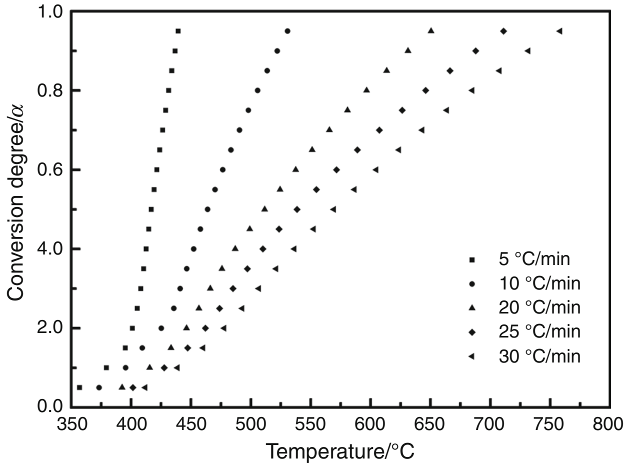

Fig. 4 Conversion degree versus temperature for samples of biochar produced at 570 °C of temperature residence, 1 h of residence time and different heating rates

undergone by cellulose with thermal pretreatment, with consequently increasing its temperature resistance [47]. The highest mass loss of these biochar associated with this second event must have occurred because of its enrichment in cellulose, caused by the previous decomposition of hemicellulose. The third event of mass loss reinforces this hypothesis, with identical pattern thermal decomposition among biochar, which culminated in the loss of additional mass of 13, 4 and 11 % for biochar 200, 280 and 570 °C, respectively, with heating up to 850 °C.

Kinetic behavior and activation energy

Conversion degree (α), versus temperature curves obtained for combustion of biochar obtained at 570 °C and residence time of 1 h in different heating conditions are presented in Fig. 4. The similar behavior can be observed for Biochars 570 °C 0.5 h and 280 °C 1 h. The biochar obtained at 200 °C 0.5 and 1 h as well as one in 280 °C 0.5 hours presented dependence with heating rate, preventing the kinetic evaluation by isoconversional non-isothermal experiments.

Table 3 shows the calculated activation energy, (E), according to the conversion degree of the samples, from 0.05 (5 %) to 0.95 (95 %). The correlations between the calculated values of activation energy and the conversion degree of samples are also presented in Fig. 5, in which can be observed a profile of $\alpha - T$ dependence. This kind of dependence, decreasing $E - \alpha$, is a characteristic of complex processes comprised of initial reversible reaction followed by an irreversible one [34], which reflect the expected behavior of a coal combustion process. There are several values for activation energy of mineral coal or biochar found in literature [35] using different methods such as differential isoconversional [36–40], model-fitting [41–45] and model-free isoconversional one [38, 40, 46]; however, the decrease in activation energy with respect to the degree of conversion is emphasized in a few articles.

Table 3 Activation energy (E_α) obtained for the combustion process of biochar

α	280 1 h kJ mol^{-1}	STD	Biochar 570 0.5 h kJ mol^{-1}	STD	570 1 h kJ mol^{-1}	STD
0.05	108	12	134	15	116	7
0.1	81	2	122	10	114	10
0.15	72	2	126	11	108	12
0.20	68	3	116	10	99	9
0.25	64	2	104	8	90	9
0.30	60	0.6	94	6	81	7
0.35	55	0.1	84	5	74	6
0.40	50	0.3	76	5	67	5
0.45	45	0.3	70	4	62	4
0.50	42	0.4	64	4	57	3
0.55	39	0.5	59	3	53	3
0.60	36	0.6	54	3	49	2
0.65	34	0.6	51	3	46	2
0.70	32	0.7	48	2	43	2
0.75	30	0.8	45	2	41	1
0.80	29	0.9	42	2	39	1
0.85	27	1	40	2	37	1
0.90	26	1	38	2	35	1
0.95	25	4	36	2	33	1

Particle density

The particle density is one of the parameters used to explain the resistance of a given carbonized material, in

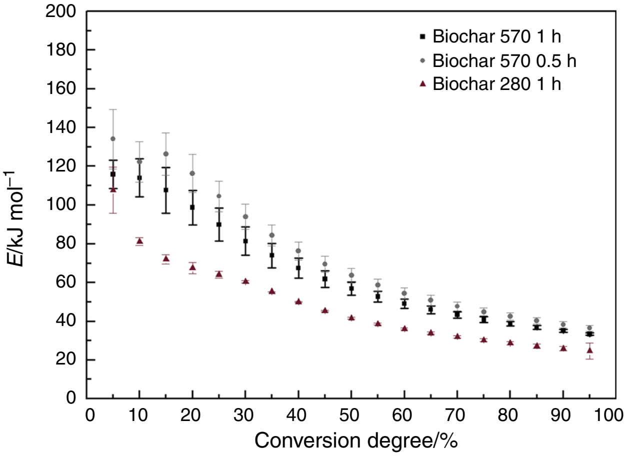

Fig. 5 Relation between the activation energy (*E*) and the conversion degree (α) for Biochar

Table 4 Particle density of biochar and pellet

t_r/min	*T*/°C	Particle density/g cm^{-3}
	Pellet	1.3640
30	200	0.5830
60	200	0.5774
30	280	0.4971
60	280	0.4839
30	570	0.8900
60	570	0.8951

addition to the degradation of wood components and morphological structure thereof. It is a property that depends on the nature of the raw material (precursor material) and also in the manufacturing process of coal. The particle density values are shown in Table 4. The biochar prepared in this work shows significant variation in particle density for temperature residence. It was hoped to increase the particle density with an increase in temperature of residence due to loss of volatile compounds from wood and mainly as a concomitant increase in the structural organization of biochar about the pellet. However, it was observed that the particle density decreased to 280 °C residence temperature. The reason for this phenomenon may be linked to the large formation of small pores in the structure of biochar at this temperature. As for biochar at 570 °C, there is the formation of large pores and cracks, with significant loss of the initial compounds pyrolyzed sample, which provides a higher particle density. Regarding the length of residence, it was not possible to clearly distinguish any pattern of behavior with increasing residence time.

Table 5 Higher heating value of biochars produced at 570 and 200 °C of temperature residence at different heating rate

T/°C	*β*/°C min^{-1}	HHV/kJ g^{-1}
Biochar 570	30	31.306
Biochar 570	15	31.720
Biochar 570	5	31.993
Biochar 200	30	29.899
Biochar 200	15	30.037
Biochar 200	5	30.112

Table 6 Higher and lower heating values of the pellet and biochars

Sample	HHV/kJ g^{-1}	*H*/%	LHV/kJ g^{-1}
Pellet	18.484	6.59	18.128
Biochar 570 1 h	31.747	3.00	31.585
Biochar 570 0.5 h	31.662	3.05	31.500
Biochar 280 1 h	32.253	5.21	31.969
Biochar 280 0.5 h	33.054	5.26	32.770
Biochar 200 1 h	29.735	6.10	29.384
Biochar 200 0.5 h	30.219	6.50	29.868

Heating value

It has been described in the literature [48, 49] that the heating value of char from the biomass pyrolyzed generally increases with the treatment temperature. Itmeasured the heating value of the biochar produced at 570 and 200 °C temperature residence at different heating rates (Table 5), and it was observed that, in our experiments, the heating rate did not influence significantly the results, with a variation of 5 % between the lowest and highest heating rate. However, the temperature of residence had a greater influence on the heating value, and it observed a 10 % variation between the variables (Table 5). The data of the heating value of biochar (higher and lower) are shown in Table 6.

The heating value significantly increased as there was an increase in residence temperature of 280 °C, which won approximately 10 % in energy when compared to other variants of biochar and 80 % more when comparing with the pellet. This energy gain might be due to secondary reactions occurring in the sample during the pyrolysis, for example, as a result of structural changes (or steric) or exposure of aromatic compounds. After this temperature residence, the heating value back to decrease, as observed for biochar produced at 570 °C. This decline in heating value is associated with total decomposition of hemicellulose and cellulose and partial decomposition of lignin, which are materials with high energy capacity. However, the calorific value has an asymptotic behavior concerning residence time; thus, prolonging the residence time indiscriminately to improve the characteristics of the final product does not provide favorable results.

Moisture and ash

The moisture content expressed as a percentage about the original mass affects the adsorptive capacity of biochar. For the adsorption of organic molecules, the efficiency decreases as the moisture content increases, and it is because certain pores that would be available for adsorption are filled with water molecules. The moisture of biochar occurs by absorbing water from the atmosphere in samples, due to the certain hygroscopicity of biochar. By comparing the residence times, it observed an increase of water in biochar with increasing residence time (Table 7). This result may be associated with an increased pore size of the biochar, mainly in one produced at 570 °C, and also as a consequence of the additional loss of mass about the other biochar. The highest moisture in the pellet is associated with the hydrophilic character of cellulose and hemicellulose, which had already suffered some degradation in biochar produced at 200 °C. Furthermore, tests were conducted to demonstrate the moisture resistance of biochar and can be observed that they were unchanged when immersed in water for several hours, which shows the hydrophobic character of the samples. Low ash content was observed, and this feature is necessary due to the low residue generated after power generation (Table 7). It is observed that both results were consistent with the thermal gravimetric method, which showed low moisture content and ash.

Bulk density

The bulk density is imperative to quantify volumes of products with irregular shapes because it provides information that may be useful for logistics and transportation since it considers the voids between a particle and supply of real volume data for transport. Furthermore, it is used to calculate the energy density. It has been shown that the density increases with decreasing particle size. It is due to the voids between the particles be smaller. In this way, the greater of bulk density, greater the mass that can be transported or stored in a container fixed volume thereby minimizing transport and storage costs [50, 51]. The bulk density provides the degree of compaction of one material about another (Table 8). As an example, the pellet is 1.397 times more compressed than biochar produced at 570 °C (540.9/387.1 = 1.397). Therefore, an immediate analysis suggests that the pellet would be advantageous as compressed fuel; however these two materials do not carry the same heating value per unit volume. So, it is necessary to analyze the heating value of each of them for comparison of proportion.

Table 7 Moisture and ash of biochars

Sample	Moisture/%	Ash/%
Biochar 570 1 h	1.80	1.80
Biochar 570 0.5 h	1.24	1.71
Biochar 280 1 h	1.76	1.54
Biochar 280 0.5 h	0.94	1.55
Biochar 200 1 h	1.62	1.27
Biochar 200 0.5 h	0.93	1.25

Table 8 Bulk density of pellet and biochars

Sample	ρ bulk kg m^{-3}
Pellet	540.9
Biochar 570	387.1
Biochar 280	355.0
Biochar 200	349.0

Energy density

The energy density was obtained by multiplying the bulk density and LHV (Table 9). The energy density increased when the residence temperature was increased (minimum increase of around 4 % and maximum around 25 %) but was little changed about the variation of residence time. From this test, it can be concluded that there is a greater amount of energy per unit volume, in particular to biochar produced at 570 °C.

Evaluation of costs and prices

The briquettes expenses in a factory, in Brazil, with an annual capacity of 1,200 tons were around 45 US$/t in 2004, whereas the sales price ranged from 61 to 75 US$/t [52]. The factory cost for torrefaction of briquettes would

Table 9 Energy density of the pellet and biochar

Sample	LHV/kJ g^{-1}	ρ granel/g cm^{-3}	ρ energy/g cm^{-3}
Pellet	18.128	0.5409	9.805
Biochar 570 1 h	31.585	0.3871	12.226
Biochar 570 0.5 h	31.500	0.3870	12.193
Biochar 280 1 h	31.969	0.3550	11.348
Biochar 280 0.5 h	32.770	0.3548	11.633
Biochar 200 1 h	29.384	0.3490	10.255
Biochar 200 0.5 h	29.868	0.3487	10.424

Table 10 Economic competitiveness indicators between biochar at 570 °C and raw pellet

Sample	Sale value/ US$/t	PCS/ GJ/t	PCI/ GJ/t	Value HHV/ US$/GJ	Value LHV/ US$/GJ
Pellet biochar	163	18.5	18.0	8.81	9.06
Of pellet	233	32.0	31.0	7.28	7.52

be approximately 65 US$/t, i.e., 31 % higher. In this way, the value of sale would be from 88 to 108 US$/t. From the Markup method, it may estimate the price at which biochar pellet would sell at the current sales value. The current price of the pellet is 163 US$/t (pellet from BrBiomassa industry), and using the previous correlations, it follows that the current value of the pellet production is 121 US$/t. Thus, the minimum cost of production of biochar would be approximately 172 US$/t and the market price of about 233 US$/t. These values can vary depending on the U.S. dollar monetary worth in the producer country.

Comparison between the sales value (FOB) of the pellet and biochar

In a modern vision, pellet prices are quoted for its energy capacity, whose sale value would be 4 US$/GJ [53].

Based on the aforementioned and results from Table 10. It has 21 % more GJ buying biochar than a pellet. Biochar being more economically advantageous has no vulnerability to moisture compared to raw pellet. The hygroscopic condition causes rapid decompression of the pellet in sawdust. The most economically viable product for transportation and storage is biochar because it has 13 % more power for the same volume of the pellet.

Conclusions

In general, the heating treatment of pellets confers superior characteristics to biochar compared to pellet in nature, showing a greater amount of energy per unit volume, reduced moisture content, and reduced ash. It represents a more significant generation of energy per volume of product per unit mass, a reduction in the space required for storage and transportation of this fuel, and an improvement in the storage and transport of biochar. The optimum conditions were observed in biochar produced at 570 °C temperature residence, with an increase of 25 % in energy density, 30 % reduction in bulk density and a 67 % reduction in moisture content, all about pellet in nature. This fact indicates that this treatment can be a vehicle to enable the use of biomass residues, mainly in the form of pellets heat-treated. The kinetic evaluation shows the dependence of activation energy and conversion degree characteristic of complex processes comprised of initial reversible reaction followed by an irreversible one. It also observed a continuous decrease in the activation energy with the increase of conversion degree as expected to this kind of material.

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