ENERGY BIOMASS CARACTERIZATION FOR AMAZON SPECIES

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Abstract. *Biomass has obtained relevance as energy fuel once it can be produced at large scale and also does not contribute for the greenhouse effect. Most of the Amazon region electricity production uses fossil fuel despite in such region exists large quantities of biomass residues coming from forest management and also industrial and agricultural residues such as açaí seed (Euterpe oleracea), castanha-do-pará shell (Brasilian Nuts) (Bertholletia excelsa), angelin pedra (Hymenolobium modestum) and jatobá (Hymenaea courbaril). The prime evaluation to consider the use of Amazon biomass residue as fuel is quantification of their energetic properties through an energetic characterization. Biomass energetic characterization is performed through a series of tests namely the Proximate and Ultimate Analysis, quantification of the High Heat Value and the thermo-gravimetric analysis. This work presents the energy characterization for the above list of species. Proximate Analysis present their content on moisture, volatiles, fixed carbon and ash as well, all performed using the ASTM standards. Proximate Analysis present their content on carbon, hydrogen, nitrogen and oxygen, as mass fraction, with oxygen fraction obtained subtracting the total content of C, H and N from 100. Their high heating value (HHV) is presented, obtained after ASTM standard, together with their low heating value (LHV) calculated from HHV value and the hydrogne fraction obtained from the ultimate analysis. Results for their thermo-gravimetric tests are also showed in the form of energy activation together with their pre-exponential factor (frequency factor), values for the pyrolysis process, both to be applied in the Arrenhius equation and to perform calculations related to the chemical kinetic of the pyrolysis process.*

Keywords: Biomass, Immediate Analysis, Elemental Analysis, High Heating Value, TGA/DTA.

1. INTRODUCTION

The Brazilian energy sector is seeking new alternatives to increase the diversity of its current matrix. Among the alternative energy highlights are the hydroelectricity, wind, solar, and biomass. In the north of Brazil, due to large distances between locations and low electric loads, the grid electric transmission cost turn to be very costly promoting the use fossil fuel thermoelectric generators. On the other hand, the region is a major producer of forest and agriculture residues that can be used for energy purposes.

According to IBGE, in 2006, domestic production of açaí from tree native specimens totaled 101,341 tons. The pulp corresponds 15% of the total weight of the fruit while the core is 85%. Actually the pulp is commercialized while the core, pit, is waste and goes to the municipality garbage. The pit can be used in steam generation, charcoal and organic fertilizer among others (Homa, 2005). Biomass only can be used as fuel if their energetic properties are know in advance. The minimum needed tests are: HHV, proximate analysis, ultimate analysis and thermogravimetric analysis.

In 2004, Vale, et. al., have worked with the objective of characterizing the Bahia coconut *(Cocos nucifera L.)* and its charcoal. The samples were characterized and showed 0,99 g/cm³ for density, 7.433 cal/g for higher heating value and proximate analysis was found in 23,41% volatile mater, 1,5% ash and 63,78% fixed carbon.

Santos *et. al.* (2007) conducted a survey of woody species aiming to analyze physical and chemical properties of forest native species with fast growing with energetically acceptable for use as firewood. He presented results for High Heating Value – HHV 17,02 MJ/kg, 0,67 g/cm³ for bulk density and the results of ultimate analysis were 49,20% de C, 45, 5,73% de H, 0,19% de N e 41% de O.

This work will be characterized *acai (Euterpe oleracea) brazilian nuts (Bertholletia excelsa) angelin pedra (Hymenolobium modestum) and jatoba (Hymenaea courbaril)* due to large amount of wastes of its production and its importance in local economy. The results presented in final will be compared to previous work by Santos *et. al.* (2007).

2. MATERIAL AND METHODS

The equipment used for sample preparation and analysis were: analytical mill (A-11 Basic mod.), pump calorimetric by Ika Werke, analytical balance (mod. AS200) by OHAUS, oven (mod. el-1.4) by Odontobras horizontal furnace (mod. 1100 AAF) by Carbolite, dissector of glass, porcelain crucibles and petri dishes.

2.1. Sample Preparation

The sample preparation was done according to ASTM E 1757-01 for samples with amounts up to 20g. A crusher was used together with mill, screens (20 mesh and 80 mesh), petri dishes for sample storage and balance with accuracy of four digits for gram.

The samples were spread prior to grinding not exceeding the height of 15cm for at least 24 hours to dry. The dry material was placed in the crusher and then sieved. The sieves were placed on the shaker in the following order: top cover, 20 mesh, 80 mesh and background. They were shaken for 15 ± 1 min. At the end of the period, the fraction retained on 20 mesh sieve was discharged, the fraction retained on 80 mesh sieve was taken for proximate analysis (moisture, volatile and fixed carbon) and the "fines" which were at the bottom of the sieve were used for ash analysis.

2.2. Proximate Analysis

This Analysis followed ASTM E 871-82, E 872-82 and E 1755-01.

2.2.1. Moisture Content %:

After sample preparation as specified above, the *Petri* dish was placed with 50 g of sample (a set) in the oven for 30 min. at temperature of 103 ± 1 °C, and then the set (plate-sample) was removed from the oven and placed in desiccators to get in equilibrium with room temperature for weighting. The assembly was then placed back in the oven at 103 ± 1 °C for 16h, weighed and placed back in the oven for another 2 hours and weighted again. The process is repeated until the final weight did not change. The calculation of moisture content in the sample, wet basis, is given by Eq.(1):

$$M = \quad M_i - M_f \quad M_i - M_p \quad x100 \tag{1}$$

Where:
M_i = initial mass of the set, g,
M_f = final mass of the set, g,
M_p = mass of *petri* dish, g,

2.2.2. Volatile Content %:

This procedure is used to determine in a controlled environment, the percentage of gaseous products that will feed the combustion of biomass, except for the moisture that was removed earlier. The covered crucible with the sample and weight approximately 1 g (set) was placed into the furnace at a temperature of 950 ± 20 °C for exactly 7 min. After this time the crucible with the residue of the sample is removed and placed in the desiccator to cool down. When its temperature balances the ambient temperature, it is weighed again and the value is noted. Mass loss calculation was performed by Eq.(**2**):

$$V = \quad M_i - M_f \quad M_i - M_c \quad x100 \tag{2}$$

Where:
M_i = initial mass of the set, g,
M_f = final mass of the set, g,
M_c = mass of crucible and lid, g,

2.2.3. Ash Content %:

The ash content is a rough measurement of mineral content and other inorganic materials in biomass. The sample was dried at 105°C according to standard E 1757 and stored until use. A biomass sample with mass in the range of 0.5 to 1.0g was added into a weighted crucible and this set is the initial mass.

The container with contents was placed in furnace at 575 ± 25 °C for a minimum of 3 hours or until all the carbon is removed. Taking care to avoid sample loss, withdraws crucible and its contents to a desiccators until they reached room temperature, the mass is then weighed and recorded. The heating is repeated for periods of one hour until the dough after cooling varies less than 0.3 mg. The calculation of the percentage of ash in the sample is given by Eq.(**3**):

$$M_{ash} = \quad M_f - M_{cad} \quad M_i - M_{cad} \quad x \ 100 \tag{3}$$

Where:
M_{cz} = ash percent, on the mass a sample dried at 105 º C,
M_i = initial mass of the set, g,
M_f = final mass of the set, g,
M_{cad} = mass of crucible, g.

2.2.4. Fixed Carbon Content %:

The content of fixed carbon is obtained by difference between the full (100%) and the percentage of volatiles and ash, according to Eq.(4)

$$M_{CF} = 100 - M_v + M_{cz} \tag{4}$$

Where:
M_{CF} = fixed carbon percent;
M_v = volatile matter percent;
M_{cz} = ash percent;

2.3. Higher Heating Value (HHV)

The determination of the HHV was performed according to standard ASTM E 711-87. Using a calorimeter bomb Model C2000 Control, the company Ika Werke with average error <0.2% and standard deviation <0.4%. The test was 10min long per sample and was performed in triplicate. The value presented is the average of the values found.
The calorific value was determined burning a weighed sample in a calorimeter bomb in oxygen atmosphere under controlled conditions. The calorific value is calculated with temperature measurements taken before and after combustion.

2.4. Lower Heating Value (LHV)

The LHV was calculated by subtracting the heat of reaction of the amount of energy released during water condensation contained in the product combustion gases dividing by the fuel mass. The Eq.(5) was used to evaluate the LHV as it is described in (Nogueira *et al.*, 2008).

$$LHV = 1 - U * HHV - 9 * h * 1 - U * h_{lv} - U * h_{lv}] \tag{5}$$

Where:
LHV = lower heating value of wet biomass (kJ/kg of wet biomass);
HHV = higer heating value (kJ/kg of dry biomass);
U = moisture content of biomass (mass on wet base);
h = hidrogen content of biomass (mass on dry base);
h_{lv} = enthalpy of vaporization of water (kJ/kg) a 1 atm (2442 kJ/kg).

2.5. Ultimate Analysis

Ultimate analysis was determined by an analyzer (mod. 2400 Series II CHNS / O) with sample weight given in ultra microbalance (mod. AD-6) both from Perkin Elmer located at LACBIO - Laboratory Sector Characterization of Biomass of the School of Mechanical Engineering, UFPa.
The analysis was performed with 1.5 to 3mg of sample, which was oxidized at 975 ºC in a quartz tube in the slightly above the stoichiometric ratio. The complete oxidation is enhanced by through catalyze with agent composed of tungsten oxide and zirconium oxide (EA 6000).The gas stream leaving the combustion area includes carbon dioxide, water, nitrogen oxides and an excess of oxygen. The combustion eluded gases flows through a quartz tube where the copper beads are packed to reduce the excess of oxygen and nitrogen oxide (NO_2) into gaseous nitrogen (N_2) and sulfur oxides (SO_x) into sulfur dioxide (SO_2).The gas mixture is carried by helium pressure for a reactor blend and further transferred to a system of gas chromatography. The elements N, C, H and S are in the state of gas, N_2, CO_2, H_2O and SO_2, are separated by a packed column GC coupled with a thermal conductivity detector. Oxygen content in the sample was solved by difference. The whole process is shown in simplified form in Fig. 1. The gases were used in the process, oxygen for combustion and helium for the drag of the gases generated by combustion.
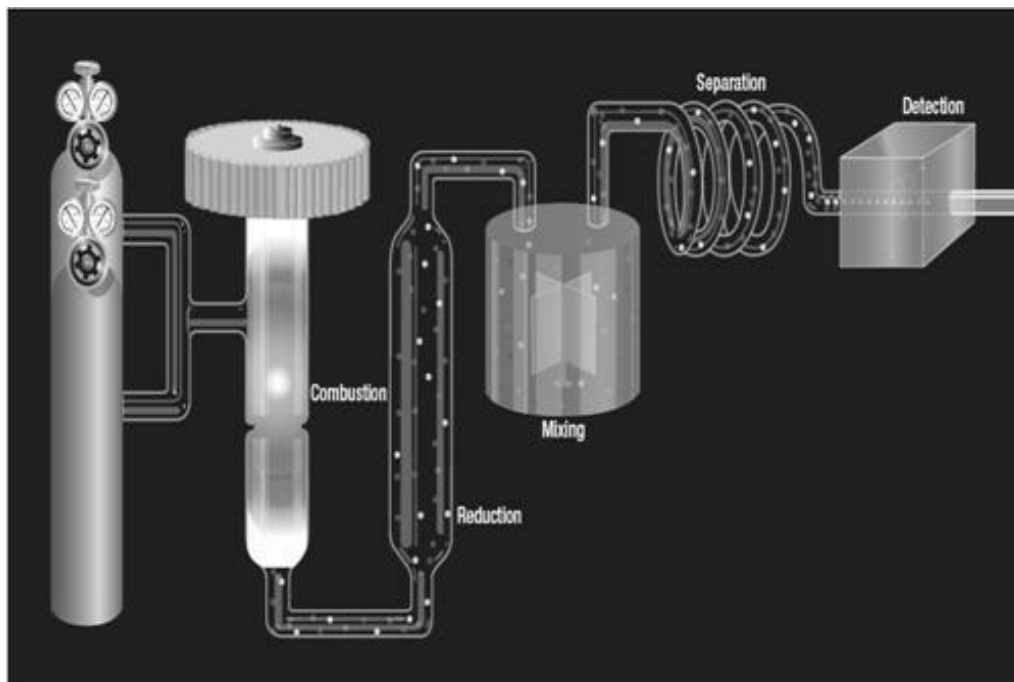
Figure 1 – Simplified operation of the elemental analyzer Perkin Elmer 2400

2.6. Thermogravimetric Analysis

Thermogravimetric experiments were performed at Thermal Analysis sub-laboratory for Geoscience Laboratory, at UFPA with the balance made by Thermal Science PL-STA.

Thermobalances are instruments that allow continuous weighing of a sample as a function of temperature. After weighing the initial thermogravimetric analysis was performed by measuring the mass of the sample at the beginning, which is then placed inside an oven where it was defined the heating rate in K/min. The measurement was performed in nitrogen atmosphere with low flows so that there is no interference in the reading equipment (Ionashiro, 2005).

The thermogravimetric balance generates two types of graph that allows drawing conclusions about the thermal stability of the sample, the composition and stability of intermediate compounds and the residue composition. The first graph shows mass loss as a function of temperature. The second graph shows the gradient of mass loss to temperature as a function of temperature, where the gradient peaks identifies, for each phase,where it stars, ends and the temperature of maximum speed.

2.6.1. Mathematical formulation used for Thermogravimetric Analysis.

The mathematical procedure used to analyze the TG data and obtain the kinetic parameters follows the integral method used by Seye et al. (2000). The reaction rate or conversion rate $d\alpha/dt$ for the thermal decomposition of the solid is described as the product of two functions (Riegel et al, 2008).

$$\frac{d\alpha}{dt} = k \ T \ f \ \alpha \qquad \qquad \textbf{(6)}$$

Where α is the fraction fumed at each instant of time for different temperatures and is defined as:

$$\alpha = \frac{W_o - W_t}{W_o - W_f} \qquad \qquad \textbf{(7)}$$

Where:
W_o = initial mass of the sample (mg);
W_t = mass of sample in any one time (mg);
W_f = final mass of the sample (mg).

According to the Arrhenius relationship, the temperature dependent term, k (T), is given by:

$$k\ T\ = Ae^{-\frac{E_a}{RT}} \tag{8}$$

Where:
A = pre-exponential factor frequency;
E_a = activation energy;
R = universal gas Constant.

Overriding Eq. (8) in Eq. (6), we have:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_a}{RT}} f\ \alpha \tag{9}$$

Replacing the term $\frac{d\alpha}{dt}$ by $\frac{d\alpha}{dT}$ as the heating rate is constant over time. Rearranging, the equation of the variation in the degree of transformation function of temperature.

$$\frac{\frac{d\alpha}{dT}}{f\ \alpha} = Ae^{-\frac{E_a}{RT}} \tag{10}$$

It was assumed that the reaction kinetics follows a 1st order for the treatment of isothermal data, leaving the function in the form below:

$$f\ \alpha\ =\ 1 - \alpha \tag{11}$$

So, inserting Eq. (11) in Eq. (10) this equation becomes:

$$\frac{\frac{d\alpha}{dT}}{1-\alpha} = Ae^{-\frac{E_a}{RT}} \tag{12}$$

Applying then the natural logarithm on both sides of Eq. (12) we have:

$$ln\ \frac{\frac{d\alpha}{dT}}{1-\alpha}\ =\ \boldsymbol{ln}\ A\ -\ \frac{E_a}{RT} \tag{13}$$

Using the experimental values of α and dα/dT, the graph versus 1/T gives a straight line whose slope is equal to-Ea/R and the point where the line touches the ordinate is equal to *ln (A)*.

3. RESULTS AND DISCUSSION

The results of the higher heating value (HHV), low calorific value (LHV), proximate analysis and elemental analysis of biomass are presented below in Table 1.

Table 1 - HHV, LHV, proximate and ultimate analysis carried out LACBIO.

	AÇAÍ	BRASILIAN NUTS	JATOBÁ	ANGELIM PEDRA
HHV (kJ/kg)	19,26	2051	20,35	20,04
LHV (kJ/kg)	17,24	17,18	17,06	16,55
MOISTURE %	9,32	14,48	9,40	10,01
FIXED C. %	19,91	13,55	20,57	16,53
VOLATILES %	78,88	66,68	79,06	82,94
ASH %	1,21	19,77	0,37	0,53
C %	48,45	57,28	50,17	49,15
H %	5,79	5,13	5,77	6,26
N %	0,02	2,61	4,97	3,88
S %	0,79	0,68	0,67	0,86
O* %	44,95	34,30	38,42	39,38
***** **Oxygen obtained by difference**				

TGA curves of four kinds of biomass were obtained with a heating rate of 10 °C/min and presented two major regions of volatilization (macro steps). The first, at lower temperatures, can be attributed to water loss. The second most intense can be attributed to the biomass degradation, whose main components are cellulose, hemicellulose and lignin (Riegel et al, 2008).

Thermogravimetric curves of samples of biomass can be seen below. Figure 2 shows the percentage of weight loss in relation to initial mass. Figure 3 represents the derivative of mass loss and it is observed that the temperature peaks indicate that the reaction occurs with greater intensity. In Fig. 3 can be seen that during the volatilization two peaks for the species acaí and jatobá, identifying and converting the cellulose and hemicellulose, respectively. The ordinate axis has been normalized to facilitate comparison between species and was assigned the temperature range that occurs in the further degradation of biomass.
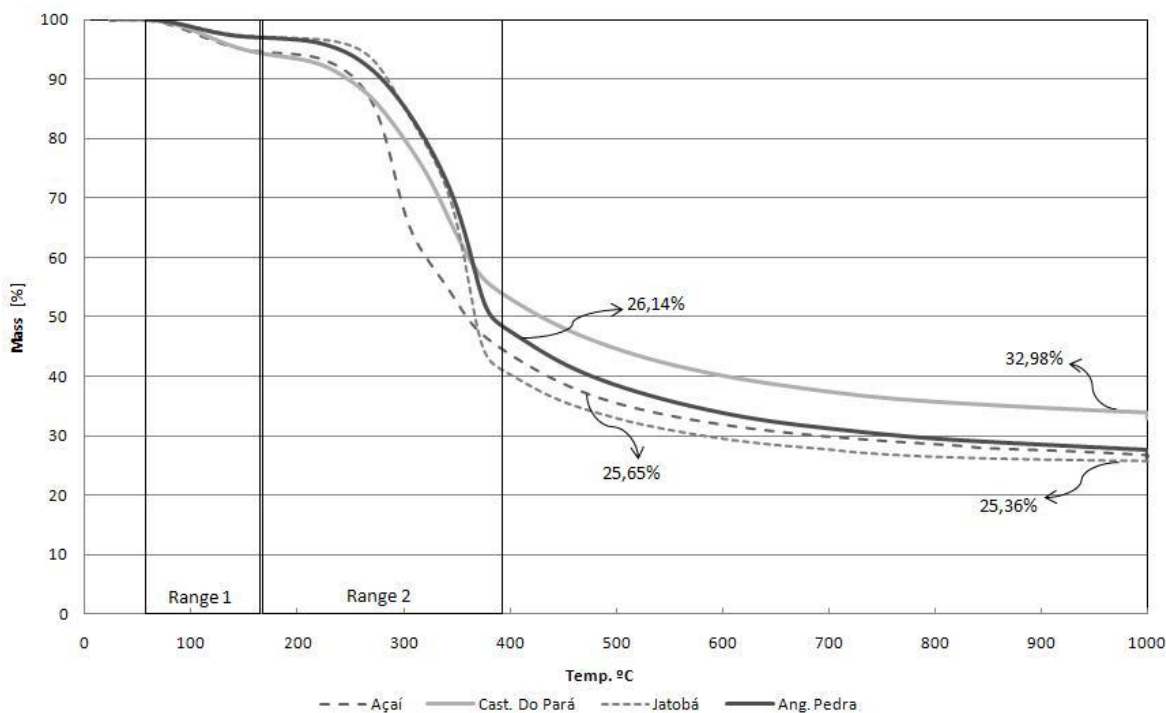

Figure 2 – curve of weight loss with increasing temperature, indicating the final percentage of residue samples.
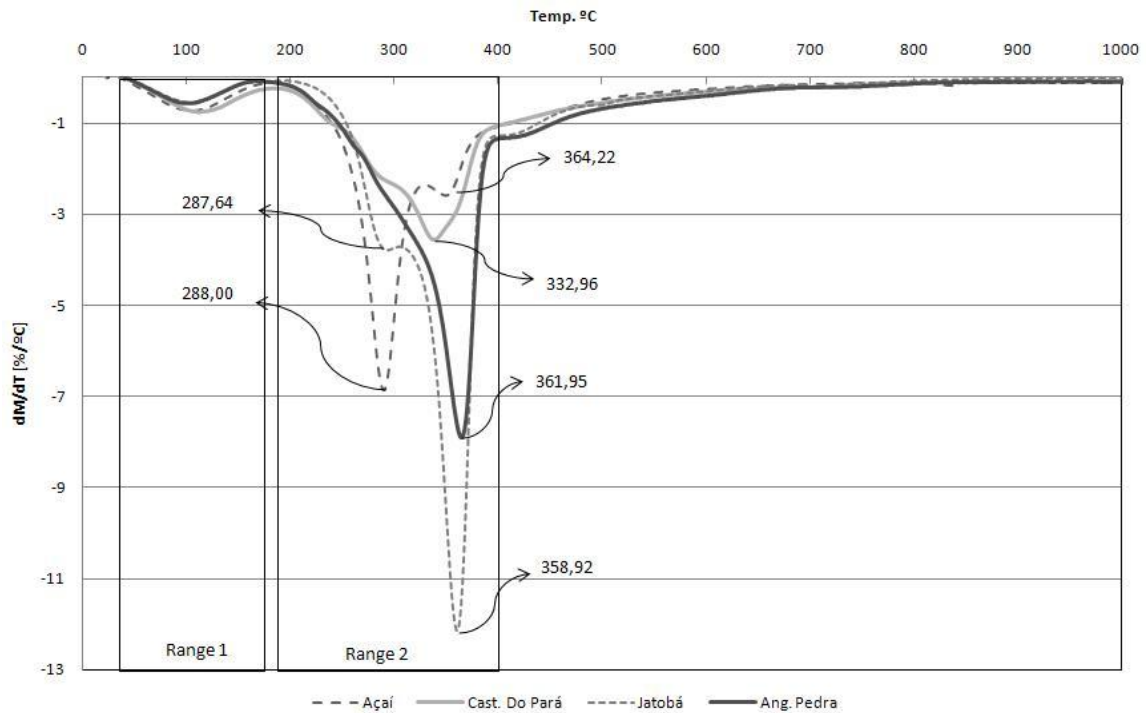
Figure 3 – first derivative of mass loss on temperature showing temperature where the reaction rate is maximum.
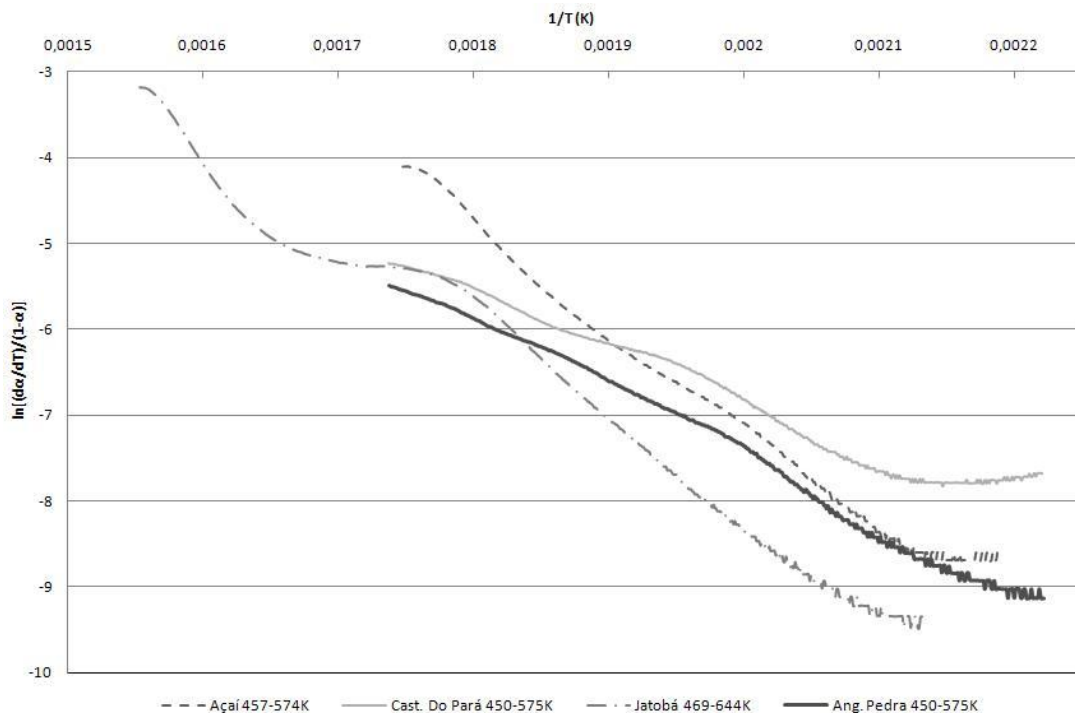

Figure 4 – chart that lists the values of reaction rates and the corresponding temperatures for obtaining the slope of the first temperature range.

The chart that lists the value for reaction rates and its temperature is shown above in Figure 4 for the second temperature range. Through the linear fit of the points presented in Figure 4, the slope was calculated from straight lines resulting from which we obtained the activation energy and frequency factor for each temperature range, according to Eq. (13). Table 2 shows, for the temperature range 2, the equation that describes the curve adjustment, the adjustment factor curve, the activation energy and frequency factor of each species.

Table 2 – Range temp.2, the equation describing the curve, explanatory factor, activation energy and frequency factor.

Species	2° range of temp.	R²	Ea	A
AÇAI	457-574 K	0.9929	93,32	7,39E+05
BRASILIAN NUTS	450-575 K	0.9868	53,41	6,64E+01
JATOBÁ	469-644 K	0.9790	86,29	5,08E+04
ANG. PEDRA	450-575 K	0.9922	64,67	5,28E+02

Table 3 below presents the results (two species) obtained by Santos et. al (2007), which are now posted in the article cited. Similarly we present the results obtained with two species in this study for comparison.

Table 3 – Comparative results of species composition and calorific value goes higher Santos et. al. and the current work.

	Species	Ultimate Analysis					HHV (MJ/kg)
		C	**O***	**H**	**N**	**ASH**	
Santos et. al.	*Ocotea sp* (louro)	48,1	45,58	6,32	0,57	1,1	18,65
	Cassia leiandra Benth (mari-mari)	53,44	41,01	5,46	0,002	0,09	17,46
Current Work	*Bertholletia excelsa* (Brasilian nuts)	57,28	34,30	5,13	2,61	19,77	20,50
	Hymenaea courbaril (jatobá)	50,17	38,42	5,77	4,97	0,37	20,35
* Oxygen determined by difference.							

4. CONCLUSION

By means of dynamic tests, obtained by thermogravimetric analysis (TGA) showed that the profile of mass loss from the pyrolysis process of the species involved a macro step associated with decomposition of cellulose, hemicellulose and lignin in this sequence. Based on the results of this study and the results obtained in the literature we can conclude that:

• Açaí, jatobá and agelim pedra can be used in combustion processes due to its high content of volatile;

• High-carbon and low oxygen in the sample of Brazil nuts in increasing influence of the HHV, as the large amount of ashes make the HHV decrease.

There is the kind Bertholletia excelsa (Brazilian nut), which due to its low activation energy requires less energy used in the process to produce the pyrolysis products and coal.

Finally we can conclude that the species has interesting potential energy by the value of HHV found, 20.50 MJ / kg, compared with the HHV wood of forest origin. For high carbon content found in elemental analysis can confirm the use of biomass for direct burning or coal production through appropriate procedures. It should, however, conduct feasibility studies related to technical and economic productivity, adequacy of equipment and other associated factors.

ACKNOWLEDGEMENTS

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