COB-2021-XXXX Energetic characterization of lignocellulosic biomass: macauba (*Acrocomia aculeata* (Jacq.) Lodd. Ex Mart)

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Abstract. *The consequences of GHG emissions go through the increase in the average global surface temperature, changes in natural systems, rising sea levels, and losses in biodiversity. Thus, biomass presents itself as an alternative energy source to the use of current fossil fuels. Macauba is a brazilian native palm tree with a high yield of coconuts that have many applications as biofuels. The high-density coconut endocarp has great potential as solid biofuel both in raw and charcoal conditions. The present study compares the energy parameters of macauba coconut endocarp charcoal in two cultivation treatments: irrigation and fertilization, from two locations: Federal District (DF) and Sao Paulo (SP). The energy parameters were structure composition analysis, thermogravimetric analysis, gross calorific value and proximate analysis. The results for GCV of fruits provided by Embrapa did not vary with the values in the literature, being 21.0413 MJ / kg for fruits CI / DF and 20.9409 CI / SP. CA / DF endocarps showed 20.8996 MJ / kg and mean CA / SP of 20.8657 MJ / kg. The TGA Analysis showed a degradation temperature of cellulose, hemicellulose and lignin at 390ºC, which is higher than cupuaçu bark and tucumã, for example. Holocellulose and lignin, together, represented 80,35% of the total energy content of macauba, and with GCV value as 20.86 MJ/kg it can represent the total energy potential of this biomass.*

Keywords: *biomass, gross calorific value, pyrolysis, proximate analysis, thermogravimetry.*

1. INTRODUCTION

The increase in global temperature is intrinsically linked to global economic development and high energy demands (Irfan *et al.*, 2020). According to IEA (2021b), a quarter of the production of greenhouse gas emissions (GHG) comes from energy sector activities, which have generated profound consequences on global ecosystems and temperature. Given that the current global energy demand tends to increase by 4.6% by the year 2021 and that the main source of energy in the world is fossil-based - about 79% -, the viability of other low-carbon sources should be assessed as an alternative (Irfan *et al.*, 2020; IEA, 2021a; Chapman *et al.*, 2018).

The energy transition then presents itself as an action for a change of the sector aiming at its sustainability (Chapman *et al.*, 2018). This movement produces a series of global discussions and initiatives aimed at changes in regulatory frameworks, creation of public policies that subsidize new energy sources (IEA, 2021b). According to Murdock *et al.* (2019), the global installed energy capacity had the participation of a third of renewable sources. This fact is due to the growth in the use of Distributed Energy Resources (EPE, 2018). Solar and wind sources, despite their advantages in terms of low capital cost and high power quality, are intermittent (de Souza *et al.*, 2021). Thus, studies aimed at the characterization of biomass are presented as a safe alternative with great potential (Irfan *et al.*, 2020). Besides being an abundant resource, the use of biomass can be seen as a socio-economic tool and waste reuse (Kwoczynski and Čmelík, 2021).

In 2006, with the institution of the National Agroenergy Plan (2006), some oilseeds began to be the object of research studies in order to increase their productivity. The macauba, therefore, would be one of these oilseeds (Bhering, 2009). The macauba (*Acrocomia aculeata* (Jacq.) Lodd. Ex. Mart.) (fig. 1) is an oilseed species that extends from the North to the South of the country, with greater occurrence in the Midwest region (Aquino *et al.*, 2008). It can also be found in extensions from Mexico to Argentina. The palm has a spike that can reach a height of 15 meters and 40 cm in diameter (Rettore and Martins, 1983).

Figure 1. Macauba.

The use of this palm has always been extractive and does not occur in regions of extreme climate, prone to frost and aridity (Morcote-Rios and Bernal, 2001; Filho *et al.*, 2012; Carvalho *et al.*, 2011). The high productivity of oil from the fruits, around 5000 kg per ha per year, can be even higher than that of palm, if the pulp and kernel oils are taken into consideration (Lora *et al.*, 2008). The productivity values can be even higher if considered the area of occurrence of the Cerrado biome in the country, which comprises 23% of the entire territory (Nunes *et al.*, 2015).The fruit of the macauba has a spherical configuration and can have a diameter of up to 5 cm (Venancio, 2016). The epicarp is the outer part (shell), the mesocarp the pulp. The densest part is the endocarp and it surrounds the almond (Ciconini, 2012).

Thus, the present study proposes to characterize the macauba fruit in order to assess its energy potential from the values obtained in the proximate analysis, thermogravimetry, structural components and analysis of gross calorific value. Also, to evaluate if there are significant differences in gross calorific value of samples with different soil treatments - with irrigation and with fertilization.

1.1 ENERGY AND BIOMASS CHARACTERIZATION

Biomass can be characterized as woody plants, non-woody plants and agricultural residues (Lora *et al.*, 2008). And its energy is obtained through physical, chemical and biological conversion processes, whose products can be solid, liquid or gaseous (Haykırı-Açma, 2003). According to Nimmanterdwong *et al.* (2021), more than 180 billion tons of lignocellulosic biomass is produced annually as crop residue. This means that there is great potential for bioenergy from this biomass.

Macauba, because it is a lignocellulosic material - whose main structure is cellulose, hemicellulose, and lignin - is classified as non-woody biomass of forest origin (Ferreira, 2019). Knowing this, it is necessary that this biomass is characterized using established methodologies in order to know about its structure and thermal properties (Lora *et al.*, 2008; Nimmanterdwong *et al.*, 2021).

Proximate analysis (fixed carbon, volatile matter, moisture and ash contents) is a methodology that can be related to different conversion types. Conversion processes involving combustion and energy production demand information about the biomass that these first analysis can provide (Nikoo and Mahinpey, 2008; Li and Suzuki, 2010; Lan *et al.*, 2018).

Structural components (cellulose, hemicellulose and lignin) would be targeted for thermal and biochemical processes (Gurram *et al.*, 2016; Alzate and Toro, 2006). According to Santos *et al.* (2020), the structure of lignocellulosic biomass has about 45% cellulose, 25% hemicellulose, and 26% lignin, which can be considered natural polymers. In addition, among the routes for converting this biomass into bioenergy, the thermochemical - combustion, gasification, pyrolysis - is the fastest (Ong *et al.*, 2019).

The thermogravimetric analysis (TGA) is set to evaluate the degradation of the sample as a function of increasing temperature. Biomass structures behave differently given their thermal instabilities (Nimmanterdwong *et al.*, 2021). Gross calorific value (GCV), as well as other experimental methods to energetically characterize biomass, is used to assess the energy stored in coal (Chelgani, 2019).

2. METHODOLOGY

The methodology followed the steps presented in figure 2. For the analyses, macauba fruits from two different origins were used: fruits collected from palm trees at the Ulysses Guimarães Convention Center, SDC - Brasília, DF, 70655-775 and fruits provided by Embrapa Cerrados, BR-020, km 18, s/n - Planaltina, Brasília - DF, 73310-970 (their palms were grown from different soil treatments - with and without irrigation and with and without fertilization). After selection and removal of the peel (epicarp), the macauba fruits were prepared for their respective analyses. It is important to know that for Proximate and TGA analyses the whole fruit harvested in Ulysses Guimarães were used - as charcoal after pyrolysis

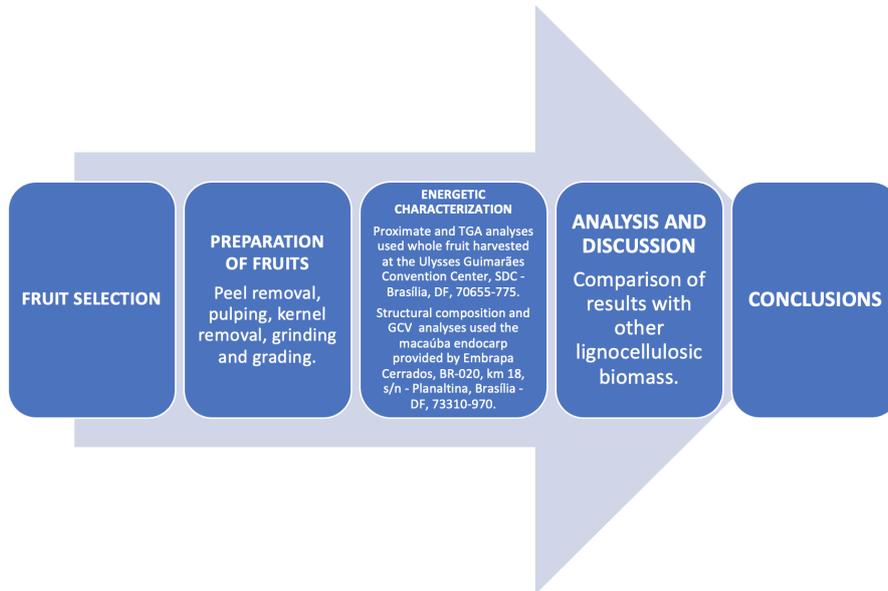for Proximate and raw for TGA analysis. Structural composition and GCV used raw endocarps from Embrapa Cerrados.

Figure 2. Methodology outline.

The proximate analysis was according to NBR 8112/86 (ABNT, 1986) [1] and conducted in the Forest Products Laboratory of the Brazilian Forest Service (LPF/SFB). Charcoal samples were obtained by slow pyrolysis with the following protocol: 2°C.min-[1] heating ramp up to 430°C and 420 min plateau. The pyrolysis reactor consisted of electrical heating with PID controllers and computer monitoring, at the LPF/SFB 3.
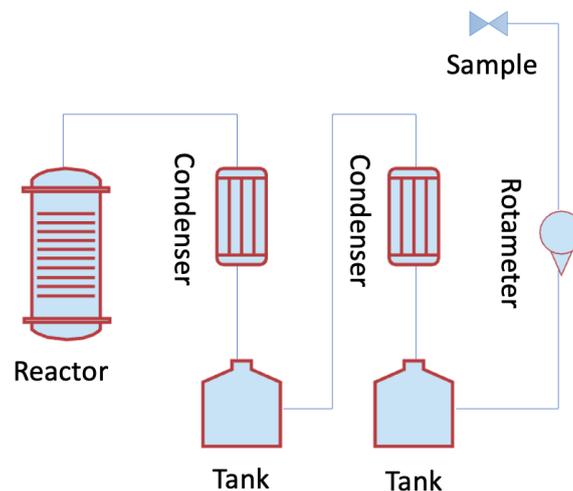

Figure 3. Schematic diagram of the retort SLFI.

Thermogravimetric analysis was carried out in the laboratory of Biomass Technologies at the University of Brasilia - Faculdade do Gama and followed initially set parameters - heating ramp at 10°C /min with 1000 °C plateau, N2 drag fuel at 60 ml/min with SDT Q600 equipment from TA Instruments.

Structural composition followed the Embrapa System methods described by Morais *et al.* (2011).

The GCV of samples was obtained in accordance with NBR 8633/1984 (ABNT, 1984) [1] at the LPF/SFB. The endocarp samples were ground, screened with steel mesh sieves, and pellet-pressed with 12,5 MPa at room temperature. Pellets were dried at 103°C +- 2°C temperature in a forced air circulation oven, then burned in a Parr 6400 isoperibol calorimeter for GCV determination.

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[1]The analyses were carried out while NBR 8112 and 8633 were still in force. Currently, the analyses for biofuels are ISO 18122 - Solid biofuels - Determination of ash content and ISO 18123 - Solid biofuels - Content of voltile matter.

3. RESULTS AND DISCUSSION

3.1 PROXIMATE ANALYSIS

Table 1 presents the values for the proximate analysis of macauba charcoal. A comparative analysis with Guilhen *et al.* (2019), using heating parameters of 450°C, shows close values for fixed carbon (FC) (68.78%), ash content (AC) (2.40%), volatile matter (VM) (28.81%) and gravimetric yield (GY) (38.88%).

Comparing the results of VM with other lignocellulosic biomasses, such as tucumã, guarana seed and cupuaçu fruit shells in table 1, it is seen that macaúba may have a low performance for low temperature ignition. The FC of macauba presents higher biochar energy storage, representing good use for energy generation (Santos *et al.*, 2020). AC represents remaining minerals after organic matter components are degraded by high temperatures and can cause damage on equipment (Guilhen *et al.*, 2019). However, according to Ahmad *et al.* (2017), levels of moisture must be less than 10% for energy conversion purposes.

Table 1. Proximate analysis comparative of lignocellulosic biomasses.

Biomasses	GY%	MC%	VM%	AC%	FC%
Macaúba	30,54	3,88	23,18	5,44	74,61
Tucumã	30,00	7,62	78,64	1,45	19,91
Guaraná seed	-	-	78,34	5,59	16,06
Cupuaçu	-	-	42,28	2,19	55,53

Fonte: Author (2021), Baroni *et al.* (2016), Lopes *et al.* (2018), Albis *et al.* (2014), Lisboa (2016).

3.2 THERMOGRAVIMETRY (TGA)

The TG and DTG curves in figure 4 show the main points where there is degradation of the material with increasing temperature. These points indicate the temperatures where there is loss of moisture and structural components (hemicellulose, cellulose and lignin) (Santos *et al.*, 2020). In the figure, it is possible to see two points of degradation. The first occurs at ambient T_1 to $T_{end\ set\ 1}$ at 90°C, with a peak at $T_{on\ set\ 1}$ at 45°C and which is characterized as moisture loss (Vieira *et al.*, 2021). The second peak, with maximum degradation, at 350°C, and $T_{on\ set\ 2}$ at 260°C and $T_{end\ set\ 2}$ at 390°C. The last peak represents the degradation of hemicellulose and cellulose. Lignin degradation starts around 200ºC. There may also be a loss of extractives at this peak. Vieira *et al.* (2021) presents similar degradation curves for macauba endocarp. Comparing the maximum degradation values of Lisboa (2016) for cupuaçu bark at 288.9ºC and tucumã at 328.7ºC, and relating them to the values of fixed carbon of the samples, the degradation values of macaúba will be higher given the presence in higher percentage of this.
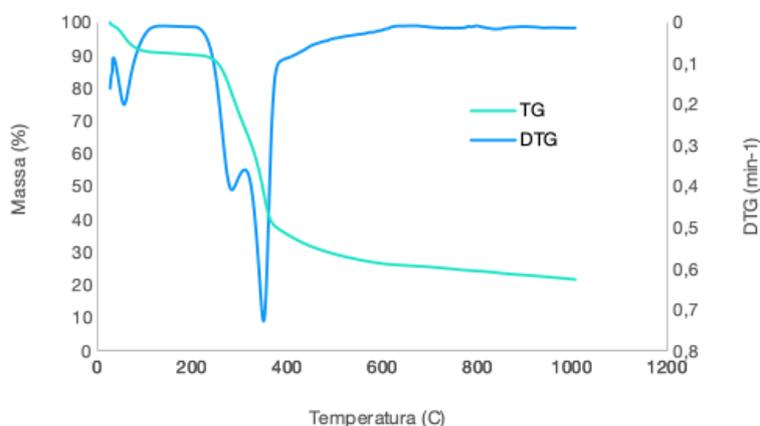

Figure 4. TG and DTG curves from macaúba endocarp TGA analysis.

Also, the curves of TG e DTG looks similar to other lignocellulosic biomasses, such as guaraná seeds residue and pal kernel shell (Santos *et al.*, 2020). Thermodecomposition temperatures are shown in table 2.

Table 2. Main temperatures of macauba endocarp decomposition.

Peaks	Temperatures [ºC]
T_1	40
$T_{on\ set\ 1}$	45
$T_{end\ set\ 1}$	90
$T_{on\ set\ 2}$	260
$T_{end\ set\ 2}$	390
T_{peak}	350

Source: Author (2021).

3.3 STRUCTURAL COMPOSITION

The insoluble lignin for macauba presented by Melo *et al.* (2015) in table 3 were 40.47% and 32.75% from the present study. Lisboa (2016) also presented lignin values for macauba of 36.6% and 1,54% for ash content. Comparing these values with babassu endocarp, 27.90% and its fixed carbon at 15.16%, a correlation between the amount of carbon and lignin in the biomasses is noted, since the fixed carbon value of macauba is higher (Lisboa, 2016; Teixeira, 2002). The endocarp of the macaúba has a non-hygroscopic characteristic. It can absorbs moisture with little intensity compared to other biomasses.

Table 3. Structural composition analysis of macaúba endocarp.

Biomass	Moisture%	Ash%	Extractives%	Lignin%	Holocellulose%
Macauba endocarp	2,40	1,13	14,49	32,75	47,60

Source: Author (2021).

Santos *et al.* (2020) presents a structural composition analysis of açai seeds. The values for this biomass are 2.2% for extractives, 40% for holocellulose and 41.2% for lignin. However, extractives help in the process of biomass ignition in combustion systems, which makes macauba perform better (Demirbas, 2017).

3.4 GROSS CALORIFIC VALUE (GCV)

Gross calorific value were first measured for samples with irrigation in duplicate as in table 4. Samples of all accessions, from DF and SP, were submitted to the analysis and, at the end, the average of the results was obtained.

Table 4. Gross calorific value of samples with irrigation from DF and SP.

With irrigation samples		
DF	1 [MJ/kg]	2 [MJ/kg]
329	21,02	21,06
321	21,07	21,03
333	21,02	21,03
327	21,06	20,99
Average		21,04
SP	1 [MJ/kg]	2 [MJ/kg]
335	20,97	21,95
323	21,92	21,90
325	21,88	21,86
331	21,04	20,97
Average		20,94
With fertilization samples		
	1 [MJ/kg]	2 [MJ/kg]
DF	20,94	20,89
Average		20,92
SP	20,89	21,03
Average		20,86

Source: Author (2021).

The values were close and consistent with the literature, 20.98MJ/kg for macaúba endocarp (Evaristo *et al.*, 2016).

Taking into consideration that macauba endocarp is a residual biomasse, it is possible to compare it's data with other similar biomasses. Lisboa (2016) analysed the epicarp of *Theobroma grandiflorum* (cupuaçu) and the endocarps of *Astrocaryum aculeatum* (tucumã) and *Acrocomia aculeata* (macauba) also. The results still showed macauba as the best option for direct combustion alternative.

Table 5. Comparative between GCV values of other residual biomasses.

Biomasses	GCV [MJ/kg]
Macauba endocarp	24,26
Tucuma endocarp	21,32
Cupuaçu epicarp	19,27

Fonte:Lisboa (2016).

Another observation is that according to Tahir *et al.* (2019), biomass for energy purposes should have GCV between 15 to 19 MJ/kg.

4. CONCLUSIONS

It is important to know that energy crisis can and probably will happen. The high oil prices during the 1970s due to the two oil shocks led to the adoption of energy solutions that would make it possible to substitute and reduce the use of fossil energy resources. These growing difficulties in the exploitation of fossil energy sources make the search for other alternative energy sources and the development of other technologies urgent.

The energy characterization of macaúba presented relevant data for its use in energy conversion systems. Taking into account that holocellulose and lignin together present the total energy contained in biomass, together with the GCV values, we have that the macaúba has 80.35% and 20.86 MJ/kg of energy potential. In the structural composition analysis, a higher content of extractives was observed compared to the açaí seeds.

The GCV of macauba palm endocarps submitted to different soil treatments showed no significant difference, but instigates further analysis to evaluate the impact of different treatments.

Future analyses propose an experimental design, which could be of the factorial type, with appropriate statistical analyses to evaluate the impact of crop and location factors on the energy variables.

5. AKNOWLEDGEMENTS

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