



COB-2021- 1194 PYROLYSIS OF MACAUBA FRUIT TO OBTAIN FLAVORED CHARCOAL: "GOURMET CHARCOAL"

Emilly Caroline Costa Silva¹

Fabio Cordeiro de Lisboa²

University of Brasília (UnB) - St. Leste Projeção A - Gama Leste, Brasília, Brazil

¹emilly_caroline2@hotmail.com; ²fabiolisboa@unb.br

Abstract

Macauba is known for its high production of bio-oil, and the use of this raw material has become interesting for the development of fuels and for the food industry. The objectives of this work are identifying the substances that attribute aromas to smoke and study the thermal degradation of macauba fruit, analyzing the gases produced during the thermal degradation through TG-FTIR. The methodologies that are applied to reach the objectives are composed of: measuring of calorific value, immediate analysis of the charcoal, lignocellulosic analysis and TG-FTIR of coal samples to identify the degradation regions. Three degradation ranges were observed: biomass drying, hemicellulose degradation and cellulose degradation which started at temperatures 54.45°C, 283.11°C and 352.56°C. The spectra emitted during the thermal degradation were analyzed and the gases compounds in each region identified. It was observed which region contained the presence of aromatic amines - for roast it was at 283.11°C. The results obtained were confirmed by the meat tasting performed with macauba charcoal, showing that the fruit influenced positively both the taste and the texture of the final result.

Keywords: Charcoal, Smoking, slow pyrolysis, Macauba

1. INTRODUCTION

The macauba (*Acrocomia aculeata*) is a palm tree native to tropical forests widely dispersed in Brazil and in some neighboring countries such as Colombia, Bolivia and Paraguay. Known for its high level of oil yield per hectare, the use of raw material macauba has become an important alternative for the production of biodiesel and cultivation for rural populations that depend on forest products for subsistence. As reported by Lorenzi and Negrelle (2006), macauba is being used not only for the production of biodiesel but also for the production of edible oils, and human consumption to combat malnutrition (Prates-Valério et al.) (Prates-Valério, Celayeta, & Cren, 2019). The oil extracted from the Macauba kernel is rich in short- and medium-chain saturated and unsaturated fatty acids, the most abundant of which are lauric and oleic acids; the oil thus has a relatively high melting point and high oxidative stability (Coimbra and Jorge) (Coimbra & Jorge, 2012). The oil also contains bioactive compounds such as carotenoids and tocopherols (Schex et al.) (Schex et al., 2018; Teixeira et al., 2019).

Several applications for Macauba kernel oil (MKO) are presented by (Magalhães et al.) for processing various foods with a substantial contribution to human consumption, taking advantage of the beneficial characteristics of substances contained in MKOs for human health. In order to keep these oils, present in an auxiliary component for cooking, it was tested to obtain charcoal, whose carbonization process was controlled to keep these oils present in its structure, in order to release them during burning.

According to Wild et al. (2011) roasting is characterized by low heating rates, which keeps MKOs inside the roasted fruits and at the same time extends the life cycle of the fruit in the form of a charcoal. Named gourmet charcoal, this type of charcoal is used in cooking with the purpose of smoking and roasting foods, associating the beneficial characteristics of vegetable oil with the high calorific power of the solid parts of the fruit (Froehlich and Moura, 2017).

The objective of this work was to produce charcoal from the whole fruit of macauba, preserving it as substances that confer aromas and to promote the smoking of foods.

2. METHODOLOGY

To identify the desired culinary substances for charcoal combined with the good combustible properties of the processed fruit, the following analyzes were performed:

2.1 Sample preparation

The samples used in this work were obtained from Embrapa Cerrados (CPAC), from plantations located at 15°35'57.0"S 47°42'38.0"W. For the analysis of the calorific value and for immediate analysis, the samples were completely crushed with a sledgehammer, a hammer mill and a knife crusher located at the Forestry Products Laboratory (LPF). For lignocellulosic and thermogravimetric analysis as well as for slow pyrolysis, the crusher used is located in the laboratory of Faculty of Gama (FGA). Sample preparations were carried out in accordance with the Brazilian Association of Technical Standards - NBR 14660 (NBR, 2004).

The following figures show the process of separating the sample parts Figure 1(a), Figure 1(b), Figure 1(c).



(a) Broken shell.

(b) Broken pulp.

(c) Broken Fruit.

Figure 1. Sample preparation. Source: The author, 2017

To dry the sample, the macaubas were weighed on an analytical scale and placed in a metal container at room temperature, and then placed in an oven at 105°C for 24 hours. Afterwards, the samples were immediately placed in a desiccator for cooling for at least 30 minutes before final weighing. The difference in mass was due to the loss of water from the sample, and was considered the moisture content for this study.

2.2 Lignocellulosic and thermogravimetric analysis

The lignocellulosic analysis was performed according to Morais et al. (2011), used by Embrapa for lignocellulosic analysis. Through this procedure, it was possible to determine the percentage, by mass, of the lignocellulosic fractions (moisture, ash, extractives, lignin, hemicellulose and cellulose) of macauba, helping to optimize its use.

According to Ferreira et al. (2012), thermal analysis is a set of techniques capable of measuring the physical or chemical properties of a given substance as a function of temperature or time.

The method used for thermogravimetric analysis was the use of an SQD Q600 TA analyzer, which provides an instantaneous measurement of the mass change (TGA) of a sample at a ramp of 10°C per minute with a threshold of 1000°C.

The thermal analyzer used has a dual horizontal beam design with automatic beam growth compensation, and can analyze two TGA samples simultaneously. The FTIR analysis of the gases that are released during thermogravimetry was performed using a TGA / FTIR THERMOSCIENTIFIC TGA / FTIR equipment coupled to a Nicolet IS10 spectrophotometer. This equipment allowed the gases resulting from the thermogravimetric analysis to be guided by a heated transfer line to a flow cell at the TGA-IR interface, where the infrared spectra were collected. The gas cell is nickel plated, is 100 mm long and has an internal volume of 23 mL with KBr windows, capable of withstanding temperatures of up to 325°C. The transfer line is made of stainless steel coated glass and is directly connected to the TGA furnace tube, providing a fully inert gas passageway to the gas cell.

The TGA analysis was performed with 10 mg of powdered macauba sample, using a platinum crucible and a 10°C/min ramp with a 1000°C plateau under N₂ flow at 60 ml/min. The THERMO SCIENTIFIC interface between TGA / FTIR was configured at 200°C in the cell and 190°C in the line.

3. RESULTS AND DISCUSSION

3.1 Biomass Characterization

According to Arantes et al. (2008), the proximate analysis is applied to assess its quality for energy purposes. Data from eucalyptus wood and babassu endocarp, taken from the literature, were inserted to serve as a comparison parameter in relation to data obtained from macauba. Table 1 shows the results obtained from the proximate analysis of the fixed carbon yield and the higher calorific value for charcoal and macauba endocarp and the comparison with different biomasses.

Table 1. Average results of immediate analysis, fixed carbon yield and higher calorific power for Macauba

	Macauba in Natura¹	Macauba endocarp¹	Eucalyptus wood²	Babassu endocarp²
Higher Calorific Power (MJ/KJ)	23.12	23.44	17.00	17.00
Fixed Carbon (% _(p/p))	74.61	60.48	69.24	61.04
Volatile Content (% _(p/p))	23.20	38.03	30.17	34.59
Ash Content (% _(p/p))	5.40	1.48	0.58	4.37
Moisture Content (% _(p/p))	29.85	9.32	34.00	12.6

¹Source: The author, 2017; ² Source: Adapted from SILVA *et al.* (1986).

It is observed that the macauba volatile contents are close to those normally obtained for most plant biomasses. It is important to emphasize that the percentage of volatile material is very significant, especially for ignition and in the stages of biomass combustion. However, it is possible to see that there were significant differences in some compared parameters, showing the differences between macauba and other biomasses.

As for the physical properties, it is observed that macauba stands out for major values of higher heating value (HHV), the high value of HHV in both the endocarp and in natura macauba are probably due to the high concentration of fixed carbon and the high contents of lignin are discussed in the sequel, another factor that contributes to the high HHV is the oil residues of the pulp. Both the fixed carbon and the heat power of macauba fruits are close to or superior to several other agricultural and wood residues used for energy production, demonstrating macauba's potential for energy generation (Paula *et al.*, 2011).

3.2 Chemical Composition

The data presented in Table 2 are an adaptation of the results obtained from the lignocellulosic analysis of the macauba endocarp with the compilation of data from two other biomasses for comparison purposes, as described above. With the help of the literature, it was possible to confirm the results found in the laboratory. As said by (SILVA *et al.*, 1986) the high percentages of lignin and extractives are impressive, especially when we talk about macauba, as these are factors of great influence on charcoal production. The low moisture content of the macauba endocarp found in this analysis, when compared to the previous ones, is justified due to the non-hygroscopic characteristic of the endocarp.

Table 2. Data from lignocellulosic analysis of macauba endocarp

	Macauba endocarp	Eucalyptus wood	Babassu endocarp
Lignin (% _(p/p))	32.76	24.60*	27.90*
Ashes (% _(p/p))	1.14	0.23*	1.94*
Extractives (% _(p/p))	14.50	6.40*	7.80*
Holocellulose (% _(p/p))	39.56	69.00*	64.30*
Alpha cellulose (% _(p/p))	20.98	-	-
Moisture (% _(p/p))	2.41	34.00*	12.60*

The values shown in the table above are the averages of three determinations.

* Comparative values taken from the literature (SILVA *et al.*, 1986). Source: The author, 2017.

3.3 Thermal Degradation Analysis - TG-FTIR

The analysis presented in Figure 2 of TG and DTG were carried out with the objective of identifying the temperatures and regions related to the degradation of hemicellulose and cellulose.

The TG/DTG curves indicate three ranges of thermal degradation, which are highlighted in Figure 2. According to Pereira *et al.* (2013) the first range is attributed to drying of biomass and the other two are related to the degradation of hemicellulose and cellulose, it is necessary to emphasize that each one degrades in its own way and in different

temperature ranges. It was not possible to detect the specific range of lignin degradation, in line with Yang *et al.* (2007) as it occurs over a wide temperature range.

In agreement with Lisboa (2016) the first degradation region, which involves the drying of biomass, occurred between room temperature and about 100°C. The second region, where hemicellulose degrades, occurred at around 283°C. The third region, where cellulose degrades, was found to be in the range of 325°C and 375°C. For the total thermal degradation of the material, it is necessary to use temperatures above the temperatures of the highest degradation peak, and thus the cellulose, lignin and hemicellulose can be completely degraded.

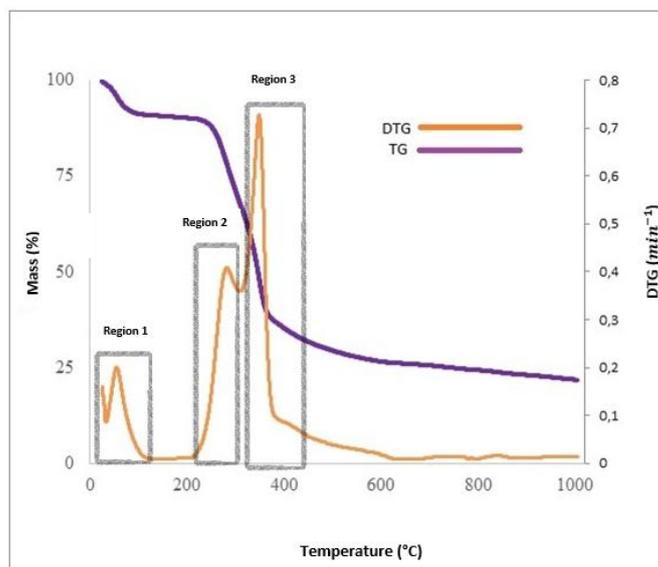


Figure 2. TG and DTG graphs of macauba endocarp with demarcated regions. Source: The author, 2019.

After identifying the degradation regions, an analysis of the spectra of gases emitted during thermal degradation was carried out in relation to transmittance and temperature. The gases that were emitted during the experiment were shown in Table 3, which shows a brief summary of the compounds found as a function of wave number, data were taken from interpretations of the spectra contained in the literature (Yang *et al.*; Silverstein *et al.*; Lisboa *et al.*).

Table 3. Correspondence between wave number and compounds contained in the gas.

Number of waves (cm ⁻¹)	Compounds	Number of waves (cm ⁻¹)	Compounds
400 - 700	Aliphatic C-C	1640 - 1667	Alkanes
866	C-H	1540 - 1870	Ketones, aldehydes, carboxylic acids, carboxylic esters, amines, etc.
950 - 1058	R-OH	1880-2000	Amine salts
1000-1100	Furans	2000 - 2250	CO
1280 - 1360	Aquillas	2250-2500	CO ₂
1365-1600	Propanol	2860-3000	CH ₄ , CH _x
1610- 1650	Aromatics	3500- 3750	H ₂ O

Source: Table Adapted by (Lisboa, 2016); (Silverstein and Bassler, 1962)

Figure 3 shows the spectra emitted during the thermal degradation of the macauba fruit endocarp. The blue color spectrum occurred at the thermal degradation temperature 54.45°C, the red color at 283.11°C in region 2 and the black color at the temperature 352.56°C in region 3.

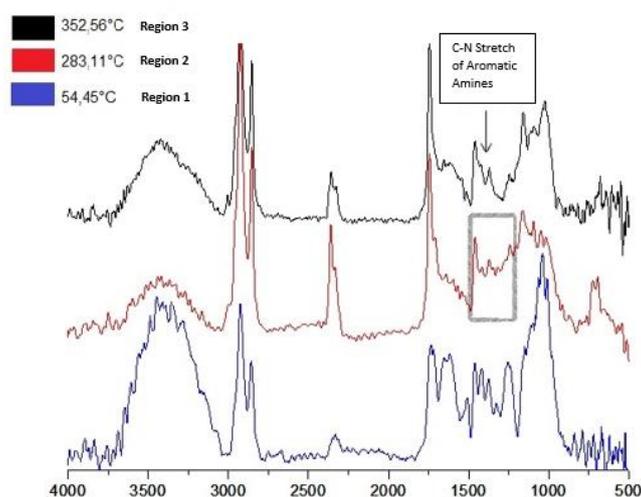


Figure 3. Infrared spectra of emission gases during thermal degradation of macauba endocarp. Source: author, 2019.

The macauba gases have different compounds in each region. Region 1 presented evidence of water emission, CO₂ and carboxylic acids. Region 2, in addition of showing emission of gases from the anterior region, also showed evidence of CO and aliphatic compounds characterized by CC and CH bonds, aromatic amines were also found, the latter is a very important compound for the purpose of this work. Finally, the third region showed strong CO emission and ketones, carboxylic acid aldehydes, carboxylic esters, in addition to a greater number of aliphatic compounds. After the results presented above, it was identified that the spectrum of region 2, as shown in Figure 3, emits aromatic amines, which are responsible for a set of desirable characteristics in food smoking, especially in meat smoking, flavor improvement and an increase in the microbiological stability of meat are some of them. Table 4 shows the data for the region of absorption that aromatic amines can be found in the infrared spectrum of gases.

Table 4. C-N Stretch of Aromatic Amines

Aromatic Amines	Absorption region (cm ⁻¹)
Primary	1340 - 1250
Secondary	1350 - 1280
Tertiary	1360-1310

Source: Adapted Table (Silverstein and Bassler, 1962).

3.4 Pyrolysis Yield

Pyrolysis is the high temperature decomposition of biomass. The volatile particles end up going through a process of reduction and release of hydrocarbon gases. The parameters used in the first test were a ramp at 2°C per minute, in a super long plateau of 430°C for 18 hours. Pyrolysis is controlled by a computer program, which analyzes the temperature curve and sample yield. The result obtained for the pyrolysis yield was 30.3% - initial mass 387.3g and final mass of charcoal was 118.3g.

3.5 Roasting

The ramp used to carry out the roasting was about 283°C for approximately two hours, this temperature was chosen after the results obtained from TG/DTG and FTIR, where the temperature at which the aromatic amines are emitted was identified.

The roasting process carried out to obtain the coal generated some heating curves that were obtained by each of the three thermocouples present in the reactor, thermocouple A located on the bed surface, thermocouple B located 20 cm from the lid and thermocouple C at 10 cm from the lid.

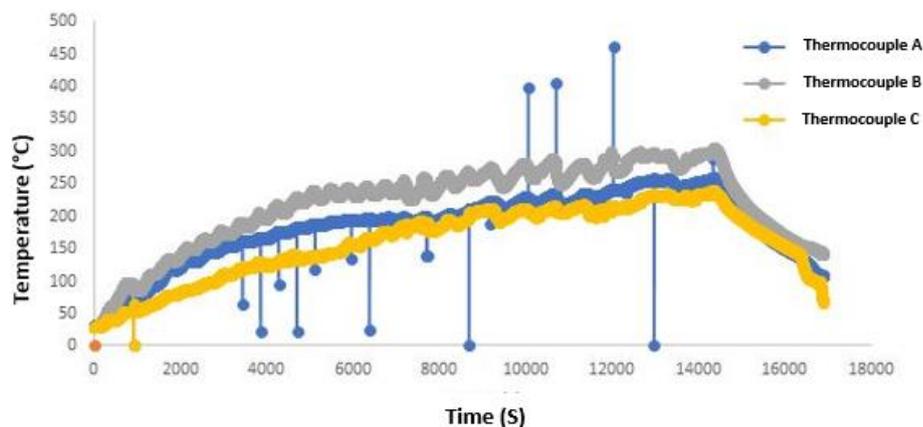


Figure 4 Heating curves. Source: The author, 2019.

The differences in the temperature curves obtained in Figure 4 were due to the heterogeneity of the roasting steps due to the different bed heights. The curves had a characteristic of increasing temperature, which were determined according to the phase of sensitive heat gain, and constant temperature situations, which resulted from the latent heat gain and the roasting stage. The peaks identified in the graph occurred because the thermocouple was not inside the material. At the end of the graph it is also possible to identify the cooling process taking place.

3.6 Organoleptic Test

The last step for evaluating the charcoal was the organoleptic test, which consisted on having an actual barbecue with the macauba that was roasted at the identified temperature. The test was carried out as follows: four students and a professor from Faculty of Gama were chosen to try the meats that were roasted using two different processes. Some pieces of meat were roasted with macauba charcoal while other pieces were roasted on an electric grill. The meats were served in 4 rounds and the participants evaluated flavor, appearance, tenderness, juiciness and aroma without information on which process the meat they tasted belonged to. In the breaks of each round, the participants had to drink sparkling water so that the taste of the previous round did not influence the next round.

By carrying out the organoleptic test it was possible to prove that the meat made with macauba charcoal had the desired flavor and characteristics. The responses obtained were quite positive, and some participants highlighted evident differences between the flavor and texture of the meat offered, such as darker meat and stronger smell, some participants also identified a more bitter taste. The identified bitter taste and strong smell can be justified by the characteristic properties of the biomass. However, the participants approved the flavor and reported that the meat was succulent and had a pleasant color and appearance.

4. CONCLUSION

From the results presented throughout this work, it is concluded that there is technological and culinary feasibility in the use of macauba for the production of new charcoals called gourmet charcoal. Since the beginning of the analysis, macauba presented encouraging results, the characterization of the biomass and its chemical composition already presented great potential for the production of charcoal.

With the preliminary analysis carried out using TG-FTIR, it was possible to identify the degradation temperature that macauba charcoal emits gases desirable for the smoking process. The thermal degradation test showed results from three different areas of degradation: the first related to the drying of the material, the second showed the degradation of hemicellulose and the third the degradation of cellulose. The analysis of the infrared spectrum showed that during the degradation of hemicellulose, biomass emits a compound called aromatic amines, which are responsible for a set of desirable characteristics in food smoking, especially in meat smoking, improving flavor and increasing stability meat microbiology are some of them.

The pyrolysis and roasting processes also obtained satisfactory results, biomass showed potential in the analysis carried out with pyrolysis yield and the final product obtained through roasting was capable of generating a value-added product. Finally, the organoleptic test was the last step carried out to prove the results obtained previously, and it showed by tasting the meat made with macauba charcoal that this fruit positively influences the final result not only in terms of flavor but also in texture and in the consistency of the food. This proves that macauba charcoal can be used for both energy and culinary purposes.

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Emilly Silva, Fabio Lisboa
Pyrolysis of macauba fruit to obtain flavored charcoal: "Gourmet Charcoal"

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