Chapter 4

Fractional Distillation of Bio-Oil Produced by Pyrolysis of Açaí (*Euterpe oleracea*) Seeds

Douglas Alberto Rocha de Castro,
Haroldo Jorge da Silva Ribeiro,
Caio Campos Ferreira, Márcio de Andrade Cordeiro,
Lauro Henrique Hamoy Guerreiro,
Anderson M. Pereira, W. G. dos Santos,
Marcelo Costa Santos, Fernanda B. de Carvalho,
Jose Otavio Carrera Silva Junior, R. Lopes e Oliveira,
Sergio Duvoisin, Luiz Eduardo Pizarro Borges and
Nélio Teixeira Machado

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Abstract

In this work, the seeds of açaí (*Euterpe oleracea*, Mart), a rich lignin-cellulose residue, has been submitted to pyrolysis to produce a bio-oil-like fossil fuels. The pyrolysis carried out in a reactor of 143 L, 450°C, and 1.0 atm. The morphology of Açaí seeds *in nature* and after pyrolysis is characterized by SEM, EDX, and XRD. The experiments show that bio-oil, gas, and coke yields were 4.38, 30.56, and 35.67% (wt.), respectively. The bio-oil characterized by AOCS, ASTM, and ABNT/NBR methods for density, kinematic viscosity, and acid value. The bio-oil density, viscosity, and acid value were 1.0468 g/cm^3, 68.34 mm^2/s, and 70.26 KOH/g, respectively. The chemical composition and chemical functions of bio-oil are determined by GC-MS and FT-IR. The GC-MS identified in bio-oil 21.52% (wt.) hydrocarbons and 78.48% (wt.) oxygenates (4.06% esters, 8.52% carboxylic acids, 3.53% ketones, 35.16% phenols, 20.52% cresols, 5.75% furans, and 0.91% (wt.) aldehydes), making it possible to apply fractional distillation to obtain fossil fuel-like fractions rich in hydrocarbons. The distillation of bio-oil is carried out in a laboratory-scale column, according to the boiling temperature of fossil fuels. The distillation of bio-oil yielded fossil fuel-like fractions (gasoline, kerosene, and light diesel) of 4.70, 28.21, and 22.35% (wt.), respectively.

Keywords: açaí, seeds, pyrolysis, bio-oil, distillation, biofuels

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1. Introduction

During the processing of açaí juice from açaí (*Euterpe oleracea*, Mart) seeds *in nature*, a native palm of natural occurrence in the Amazon region, belonging to the family Arecaceae and compassing approximately 200 genera and about 2600 species, distributed predominantly in tropical and subtropical areas [1], a by-product is produced and/or discharged, the açaí seeds, posing a huge environmental problem of solid waste management in Belém metropolitan region, as well as in the municipalities around the city of Belém-Pará-Brazil.

The State of Pará is the largest national producer of açaí with 1,012,740 ton/year of fruits [2], being the production due to extractive 198,149 tons/year of fruits in the crop year 2014 [3], representing 55.4% (wt.) of the national production of extractive açaí in the crop year 2014, and the production due to agricultural systems using a planted area of 154,500 hectare, was 814,590 tons in the year 2014. Of the total 1,012,740 tons/year of fruits, 8,405,742 tons/year is a residue (açaí seeds) representing approximately 83% (wt.).

The metropolitan region of Belém-Pará-Brazil, capital the State of Pará, has approximately 10,000 stores of açaí commercialization, producing an average of 200 kg açaí seeds/day per store, thus producing around 2000 tons residue/day [4]. In 2015, there was a growth of 27.35% (wt.) in production, 10.86% (wt.) in planted area and 14.88% (wt.) on the specific production yield, compared to 2014 [2]. The seed of açaí is an oil-fiber seed, and according to the literature, constituted by a small solid endosperm attached to a tegument, rich in cellulose with approximately 53.20% (wt.), hemicelluloses 12.26% (wt.), lignin 22.30% (wt.), as well as 3.50% lipids (wt.) [5–9].

In a scenery, the modern industrial society focuses on minimization of global warming and CO_2 emission, as well as energy efficient supply systems and less consumption of fossil-based fuels. To achieve this, the use of renewable energy resources is essential [10]. In this context, processes that minimize the industrial and agro-industrial residues either by reusing or recycling them result in energetic and environmental benefits to the global society. In addition, recycling industrial and agro-industrial residues enables to use raw materials of low cost, making it possible to increase the economic viability of biofuels' production [11].

Among the most important renewable energy sources, this biomass is considered as an important one, since it could be a suitable alternative for conventional fossil fuels [12]. In addition, biomass energy producing systems may be implemented not only close to industrial and agro-industrial production systems, but also in any location where vegetable species can be grown and/or domestic animals are reared [12]. The systematic use of biomass makes it possible to reduce global warming compared to fossil fuel energy systems, as all the vegetable species use and store CO_2 for the photosynthesis process [13]. CO_2 stored in the plant is released when the plant material is burned and/or decays [12, 13]. Thus, by replanting the crops, the new growing vegetable species can use the CO_2 produced by burning vegetable species, as in the carbonization processes (e.g., pyrolysis), and hence contributing to close the carbon dioxide cycle, as reported in the literature by Kelli et al. [14].

The residual açaí seeds, an oil-fiber seed rich lignin-cellulose material, whose centesimal composition reported in the literature is constituted of lipids between 1.65 and 3.56% (wt.), total fibers between 29.69 and 62.75% (wt.), hemicellulose between 9.01 and 14.19% (wt.), cellulose

between 39.83 and 40.29% (wt.), lignin between 4.00 and 8.93% (wt.), ash between 0.15 and 1.68% (wt.), moisture between 10.15 and 39.39% (wt.), protein between 5.02 and 7.85% (wt.), 0.83% (wt.) fixed carbon, and 7.82% (wt.) volatile matter approximately [5–9]. A process that makes it possible for the use of açaí seeds, an oil-fiber seed rich lignin-cellulose-based material, of low quality for producing liquid and gaseous fuels is pyrolysis [15, 16].

In the last years, several process schemes have been proposed to remove oxygenate compounds from biomass-derived bio-oils, including molecular distillation to separate water and carboxylic acids from pyrolysis bio-oils [17–19], fractional distillation to isolate chemicals and improve the quality of bio-oil [20–25], liquid-liquid extraction using organic solvents and water to recover oxygenate compounds of bio-oils [26, 27]. Non-conventional separation methods using aqueous salt solutions for phase separation of bio-oils have been also applied [28]. Recently, the bio-oil obtained by pyrolysis of açaí seeds in nature have been upgraded by fractional distillation, as described in detail as follows [15, 16]. Guerreiro et al. [15, 16] investigated the influence of column height by fractional distillation of bio-oil obtained by pyrolysis of açaí seeds at 350°C in pilot scale using Vigreux columns of 10 and 30 cm. The yields of gasoline were 6.60 and 7.12% (wt.), while that of kerosene were 11.05 and 12.64 (wt.), respectively, for columns of 10 and 30 cm, showing no significant variation. The acid value of gasoline-like fraction using Vigreux column of 10 and 30 cm were 17.08 and 16.79 mg KOH/g, respectively, while that of kerosene were 62.34 and 59.35 mg KOH/g, respectively, showing no significant variation. In addition, the kinematic viscosity of gasoline-like fraction using columns of 10 and 30 cm were 1.58 and 1.45 mm^2/s, respectively, while that of kerosene were 4.04 and 3.10 mm^2/s, a variation between 8.23 and 23.27% showing that kinematic viscosity is more sensitive to the influence of column height, decreasing with column height.

In this work, the pyrolysis of Açaí seeds (*Euterpe oleracea*, Mart) has been systematically investigated in pilot scale at 450°C 1.0 atmosphere to produce a bio-oil, a pyrolysis reaction liquid product, been submitted to fraction distillation carried out in a laboratory-scale column (Vigreux Column) according to the boiling temperature range of fossil fuels to study the feasibility of producing fossil fuels like fractions (gasoline, kerosene, and diesel), as well as the morphology of solid phase products (coke), of açaí seeds (*Euterpe oleracea*, Mart) pyrolysis process at 450°C.

2. Materials and methods

2.1. Materials

The seeds of Açaí (*Euterpe oleracea*, Mart) obtained in a small Store of Açaí Commercialization, located in the District of Guamã, Belém-Pará-Brazil. **Figure 1** shows the anatomy of aça ́ı fruits (cross section): (1) Embryo, (2) Endocarp, (3) Scar, (4) Pulp, (5) Pericarp + Tegument, and (6) Mesocarp.

2.2. Pre-treatment of açaí (*Euterpe oleracea*, Mart) seeds

The seeds of Açaí (*Euterpe oleracea*, Mart) are submitted to drying at 105°C using a pilot oven with air recirculation (SOC, FABBE, Ltd, Brazil, Model: 170) for a period of 24 h. Afterward,

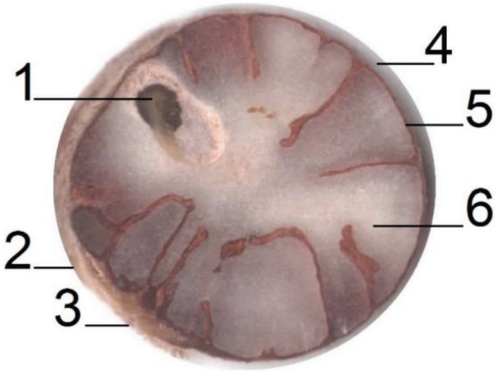

Figure 1. Anatomy of Açaí (*Euterpe oleracea*, Mart) fruit *in nature* (cross section): (1) embryo, (2) endocarp, (3) scar, (4) pulp, (5) pericarp + tegument, and (6) mesocarp.

the dried seeds are grinded using a laboratory knife cutting mill (TRAPP, Brazil, Model: TRF 600). Then, the dried and grinded açaí seeds are sieved using an 18 Mesh sieve to remove the excess fiber material.

2.2.1. Centesimal and elemental characterization of açaí (Euterpe oleracea, Mart) seeds

The centesimal and elemental characterizations of açaí (*Euterpe oleracea*, Mart) seeds are performed for moisture (AOAC 935.29), volatile matter (ASTM D 3175-07), ash (ASTM D 3174-04), fixed carbon (ASTM D6316-09), lipids (AOAC 963.15), proteins (AOAC 991.20), fibers according to the official methods reported in the literature [29], and insoluble lignin according to the method of Klason described elsewhere [30].

2.3. Fractional distillation of bio-oil

2.3.1. Distillation: experimental apparatus and procedures

The fractional distillation of bio-oil is performed by using an experimental apparatus, as described in the literature [31]. The distillation apparatus, illustrated in **Figure 2**, has an electrical heating blanket of 480 W (Fisaton, Model: 202E, Class: 300), which is thermostatically controlled, a 500 ml round bottom, and two neck flasks with outer joints. The side joint is used to insert a long-thin thermocouple of a digital thermometer, and the center joint is connected to a distillation column (Vigreux) of 30 cm. The center top-outer joint is connected to the bottom inner joint of a Liebig glass-borosilicate condenser. The Liebig glass-borosilicate condenser is connected to a 250 ml glass separator funnel by the top-outer joint. A thermocouple connected to the top-outer joint 24/40 of the distillation column makes it possible to measure the vapor temperature at the top of the borosilicate-glass distillation columns (Vigreux). A cryostat bath provides cold water at 15°C to the Liebig glass-borosilicate condenser. The 500-ml round-bottom borosilicate-glass flask and the distillation column are insulated with glass wool and aluminum foil sheet to avoid heat losses, respectively. The mass of distillation

Figure 2. Vigreux borosilicate-glass distillation column of 500 ml, electrical heating mantel, cryostat bath, Liebig condenser, and separating funnel.

fractions (gasoline, kerosene, and light diesel-like fuels) is recorded and weighed. The distillation fractions are submitted to the pre-treatment of decantation to separate the aqueous and organic phases.

2.4. Physicochemical analysis of bio-oil and distillation fractions and chemical composition of bio-oil

2.4.1. Physicochemical analysis of bio-oil and distillation fractions

Bio-oil and the distillation fractions are obtained according to the boiling temperature range of fossil fuels (gasoline, kerosene, and diesel) physicochemical characterized for acid value (AOCS Cd 3d-63), density (ASTM D4052) at 25°C, kinematic viscosity (ASTM D445/D446), and refractive index (AOCS Cc 7-25), as described in the literature [31]. The qualitative analyses of chemical functions present in the bio-oil are performed by FT-IR spectroscopy, according to the literature [31].

2.4.2. GC-MS of bio-oil

The separation and identification of all the compounds present in bio-oil are performed by GC-MS, using a gas chromatograph (Agilent Technologies, USA, Model: GC-7890B) coupled to MS-5977A Mass Spectrometer, a SLBTM-5 ms (30 m × 0.25 mm × 0.25 mm) fused silica capillary column. The temperature conditions used in the GC-MS were: injector temperature: 250°C; split: 1:50, detector temperature: 230°C and quadrupole: 150°C; injection volume: 1.0 mL; oven: 60°C/1 min; 3°C/min; 200°C/2 min; 20°C/min; 230°C/10 min. The intensity,

retention time, and compound identification were recorded for each peak analyzed according to the NIST (Standard Reference Database 1A, V14) mass spectra library, which is part of the software. The identification is made based on the similarity of the peak mass spectrum obtained with the spectra within the library database, included in the software. The contents of all identified oxygenates and hydrocarbons present in each sample were separated and the chemical composition of each experiment was estimated.

2.5. Morphology of solid phase products of açaí seeds (*Euterpe oleracea*, Mart)

The characterization of solid phase products (coke) obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale, was performed by scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) according the equipment's and procedures described in detail elsewhere [31, 32].

3. Results and discussions

3.1. Centesimal and elemental characterization of açaí (*Euterpe oleracea*) seeds

Table 1 shows the centesimal and elemental characterization of açaí (*Euterpe oleracea*) seeds *in nature*. The experimental results obtained for moisture, proteins, and cellulose are according to those reported by Altman [9], while those for lipids, proteins, and fibers are according to those reported by Kabacknik and Roger [8]. In addition, the results for lipids and proteins are according to those reported by Tamiris et al. [7]. The centesimal characterization of açaí (*Euterpe oleracea*) seeds totalizes 98.07% (wt.) in dry basis, showing that summation (moisture, lipids, proteins, fibers, hemicellulose, cellulose, lignin, volatile matter, fixed carbon, and ash) is almost close to 100% (wt.). The summation of centesimal characterization of açaí seeds (moisture, lipids, proteins, fibers, ash, and nitrogen) reported by Tamiris et al. [7] is also close to 100% (wt.). The results for fibers are much higher than those reported by Tamiris et al. [7], who reported 85.69% (wt.) of carbohydrates, and much lower than those reported by Altman [9].

3.2. Process parameters and overall steady state material balances of dried açaí (*Euterpe oleracea*, Mart) seeds pyrolysis

The process conditions and steady state material balances of dried Açaí (*Euterpe oleracea*, Mart) seeds pyrolysis are shown in **Table 2**. The experimental results show that bio-oil, gas, water phase, and coke yields were 4.38, 29.39, and 35.67% (wt.), respectively. The bio-oil yield of 4.39% (wt.) is lower compared to similar data for bio-oil yield obtained by fast pyrolysis of forestry residues at 520°C reported in the literature [33, 34], ranging from 10 to 20% (wt.), and depends on the feedstock composition. The low bio-oil yield is probably due to the high fiber content, as illustrated in **Table 3**. The high yield of water phase is probably due to dehydration reactions along the pyrolysis process, as the initial moisture content is 10.15% (wt.), being the water phase yield of 29.39% (wt.) close to that of 28.0% (wt.), as reported in the literature [34].

Physicochemical analysis	Cordeiro [6]	Tamiris et al. [7]	Kabacknik and Roger [8]	Altman [9]
	Wet Basis	Dry Basis	Wet Basis	Wet Basis
Moisture (%)	10.15	0.79	58.30	13.60
Lipids (%)	0.61	1.98	1.65	3.48
Proteins (%)	6.25	7.85	5.56	5.02
Fibers (%)	29.79	2.1	21.29	62.95
Hemicelluloses (%)	5.5	—	—	14.19
Cellulose (%)	40.29	—	—	39.83
Lignin (%)	4.00	—	—	8.93
Volatile matter (%)	0.5	—	—	—
Fixed carbon (%)	0.83	—	—	—
Ash (%)	0.15	1.68	5.97	1.55
Nitrogen (%)	—	1.26	—	—
Carbohydrate (%)	—	85.69	—	—

Table 1. Centesimal and elemental characterization of Açaí (*Euterpe oleracea*, Mart) seeds *in nature*.

3.3. Physicochemical characterization of bio-oil

Table 3 presents the physicochemical characterization of bio-oil obtained by pyrolysis of dried açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm. The bio-oil density and viscosity were 1.0468 g/cm^3 and 68.34 mm^2/s, respectively. The density and kinematic viscosity are according to similar data reported in the literature [35], where average density of wood bio-oil is 1.2 g/cm^3 and the kinematic viscosity of wood bio-oils at 50°C varies between 40 and 100 mm^2/s. The acid value of bio-oil was 70.26 KOH/g, being the acidity due to the presence of oxygenates compounds, such as carboxylic acids, phenols, cresols, ketones, and aldehydes, as described in **Table 5**, confirming the results reported by Oasmaa et al. [36], who stated that acidity of fast pyrolysis bio-oil is mainly due to volatile carboxylic acids, but not only, as well as other functional groups such as phenols, resin acids, and hydroxy acids [36].

3.4. Mass balances, yields (distillates and raffinate) of fractional distillation, and physicochemical characterization of distillation fractions of bio-oil obtained by pyrolysis of dried açaí (*Euterpe oleracea*, Mart) seeds

Mass balances and yields (distillates and raffinate) of fractional distillation of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm are illustrated in **Table 4**. The distillation of bio-oil yielded fossil fuel-like fractions (gasoline, kerosene, and light diesel) of 4.70, 28.21, and 22.35% (wt.), respectively, totalizing 55.26% (wt.), being according to similar results for distillation of bio-oil reported in the literature [22, 23, 25, 37]. Zheng and Wie [22], investigated the distillation of fast pyrolysis bio-oil at 80°C and 15 mmHg, obtaining a distilled bio-oil yield of 61% (wt.), being the oxygenates' content of distilled bio-oil 9.2% (wt.).

Process parameters	Cracking temperature (°C)
	450
Mass of Açaí (kg)	30
Mass of GLP (kg)	
Cracking time (min)	150
Mechanical stirrer speed (rpm)	0
Initial cracking temperature (°C)	179
Mass of aqueous phase (OLP + H_2O) (kg)	10,133
Mass of Coke (kg)	10,700
Mass of OLP (kg)	1316
Mass of H_2O (kg)	8.816
Mass of gas (kg)	9167
Yield of OLP (kg)	4.39
Yield of coke (kg)	35.67
Yield of H_2O (kg)	29.39
Yield of Gas (kg)	30.56

Table 2. Process parameters and overall steady state material balances of dried Açaí (*Euterpe oleracea*, Mart) seeds pyrolysis at 450°C and 1.0 atm, in pilot scale.

Physicochemical properties	450°C	ANP N° 65
	Bio-oil	
ρ (g/cm^3)	1.0468	0.82–0.85
Acid value (mg KOH/g)	70.26	—
Refractive index (—)	ND	—
ν (cSt)	68.34	2.0–4.5

ANP: Brazilian National Petroleum Agency, resolution N° 65 (specification of diesel S10).

Table 3. Physicochemical characterization of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale.

Zhang et al. [23] investigated the atmospheric distillation of fast pyrolysis bio-oil and reported an accumulated distillate of 51.86% (wt.). The major organic compounds identified in distillate fractions include phenols, guaiacols, furans, and volatile carboxylic acids (acetic acid and propanoic acid) were also observed in raw bio-oil [23]. In addition, Zhang et al. [23] reported that as the distillation temperature reached 240°C, condensation reactions take place, generating water. Elkasabi et al. [25] reported organic yields from distillation of tail-gas reactive pyrolysis (TGRP) bio-oil ranging from 55 to 65% (wt.).

Distillation: vigreux column	OLP	Gas	Raffinate	Distillates (g)					Yield (wt.%)				
	(g)	(g)	(g)	H_2O	G	K	LD	HD	H_2O	G	K	LD	HD
450°C	136.84	0	40.98	20.26	6.43	38.60	30.59	0	14.80	4.70	28.21	22.35	0

G = gasoline, K = kerosene, LD = light diesel, HD = heavy diesel.

Table 4. Mass balances and yields (Distillates and Raffinate) of fractional distillation of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale.

3.4.1. Physicochemical characterization of distillation fractions (gasoline, kerosene, and light diesel-like fractions)

The physicochemical characterization of distillation fractions (gasoline: 80–175°C, kerosene: 175–235°C, and light diesel-like fraction: 235–305°C) of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm is shown in **Table 5**. It can be observed that acidity of distillation fractions (gasoline, kerosene, and light diesel-like) increases with increasing boiling temperature, showing a drastic decrease compared to the acidity of raw bio-oil. This is probably due to the high concentration of higher boiling-point compounds in the distillate fractions, such as p-cresol, o-cresol, guaiacol, phenol, and furans, which increases with the increasing boiling temperature [23]. In addition, the densities and viscosities of kerosene and light diesel-like fractions increase with increasing boiling temperature.

3.5. Qualitative and compositional analyses of bio-oil

3.5.1. Qualitative analyses of chemical functions in bio-oil by FT-IR spectroscopy

Figure 3 illustrates the FT-IR analysis of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale. The identification of absorption bands/peaks done according to previous studies [31, 38, 39]. The spectrum of bio-oil presents a wide band of axial deformation at 3435 cm^{-1}, characteristic of O–H intramolecular hydrogen bond, indicating probably the presence of carboxylic acids. The spectra of bio-oil exhibit intense peaks between 2921 and 2964 cm^{-1} and between 2858 and 2964 cm^{-1}, indicating the presence of aliphatic compounds, associated to methylene (CH_2) and methyl (CH_3) groups. This confirms the presence of hydrocarbons [31, 38]. It has been observed that for bio-oil, an intense axial deformation band, characteristic of carbonyl (C=O) groups, with the peaks at 1742, 1745, and 1747 cm^{-1}, probably associated to a ketone and/or carboxylic acids [31, 38]. The spectra of bio-oil exhibit between 1455 and 1465 cm^{-1}, a characteristic asymmetrical deformation vibration of methylene (CH_2) and methyl (CH_3) groups, indicating the presence of alkanes [31, 38]. The spectrum of bio-oil identified at 1377 cm^{-1}, a band of symmetrical angular deformation of C–H bonds in methyl group (CH_3) [31, 38]. The peaks between 995 and 905 cm^{-1} for bio-oil, are characteristic of an angular deformation outside the plane of C–H bonds, indicating the presence of alkenes [31, 38]. The spectra of bio-oil exhibit bands between 721 and 667 cm^{-1}, peaks characteristic of an angular deformation outside the plane of C–H bonds in methylene (CH_2) group, indicating the presence of olefins [31, 38]. The characteristic peaks of phenols

Physicochemical properties	450° C			ANP N° 65
	G	K	LD	
ρ (g/cm³)	SNA	0.9191	0.9816	**0.82–0.85**
I.A (mg KOH/g)	19.94	61.08	64.78	
I.R (–)	1455	1479	1497	
ν (cSt)	SNA	4.29	9.05	**2.0–4.5**

I.A = acid value, I.R = refractive index, SNA = amount of sample not enough for analysis.

Table 5. Physicochemical characterization of distillation fractions (gasoline: 80–175°C, kerosene: 175–235°C, and light diesel-like fraction: 235–305°C) of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale.

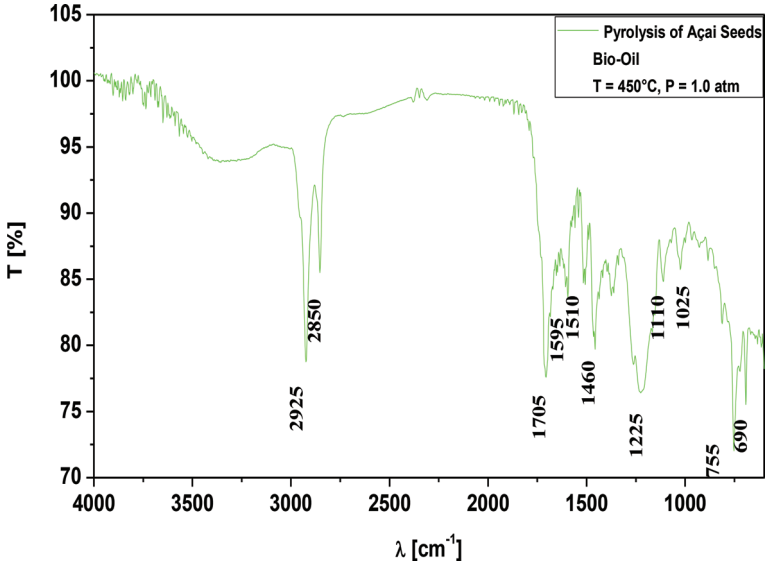

Figure 3. FT-IR of Açaí (*Euterpe oleracea*, Mart) seeds bio-oil after pyrolysis at 450°C and 1.0 atm, in pilot scale.

at 1510 cm^{-1} corresponded to the C=C aromatic ring vibrations [39]. The peaks at 1240 and 1180 cm^{-1} corresponded to the C–C–O asymmetric stretch and C–H in-plane deformations, respectively, while the 990 and 747 cm^{-1} peaks belonged to the C–H out-of-plane vibrations. The frequency due to OH in-plane bonding vibration in phenols, in general, lies in the region 1150–1250 cm^{-1}. The 1500 cm^{-1} vibration is a triplet appearing at 1515 and 1460 cm^{-1}, corresponding probably to the presence of p-cresol and m-cresol, respectively. The OH deformation and C–O stretching vibrations in phenols are close to each other, and therefore they are strongly coupled. They fall above 1100 cm^{-1}and extend up to 1330 cm^{-1}. A broad absorption is observed in this region due to the presence of numerous phenols. The out-of-plane hydrogen vibrations appearing in the region 900–675 cm^{-1} suggest the presence of m-cresol and

p-cresol. The peaks appearing in the range of 1000–1200 cm^{-1} indicate the presence of C–O–C bond, associated with those in a lower range of 650–750 cm^{-1}, from –CH=CH– bonds, showing the presence of furans, coupled with peaks in the 3000–3100 and 1400–1600 cm^{-1}, suggesting the presence of aromatic rings in the form of C–H and C=C stretching, respectively, corresponding to the presence of furans (benzofuran) [39]. The FT-IR analysis of bio-oil identifies the presence of hydrocarbons (alkanes, alkenes, aromatic hydrocarbons, etc.,) and oxygenates (phenols, cresols, carboxylic acids, ketones, furans, etc.).

3.5.2. Compositional analyses of bio-oil by GC-MS

Figure 4 illustrates the chromatogram of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale. The classes of compounds, summation of peak areas, CAS numbers, and retention times of chemical compounds are identified by GC-MS described in **Table 6**. The chemical compounds identified by GC-MS were hydrocarbons (alkanes, alkenes, aromatic hydrocarbons, and cycloalkenes) and oxygenates (esters, phenols, cresols, carboxylic acids, ketones, furans, and aldehydes). The bio-oil is composed

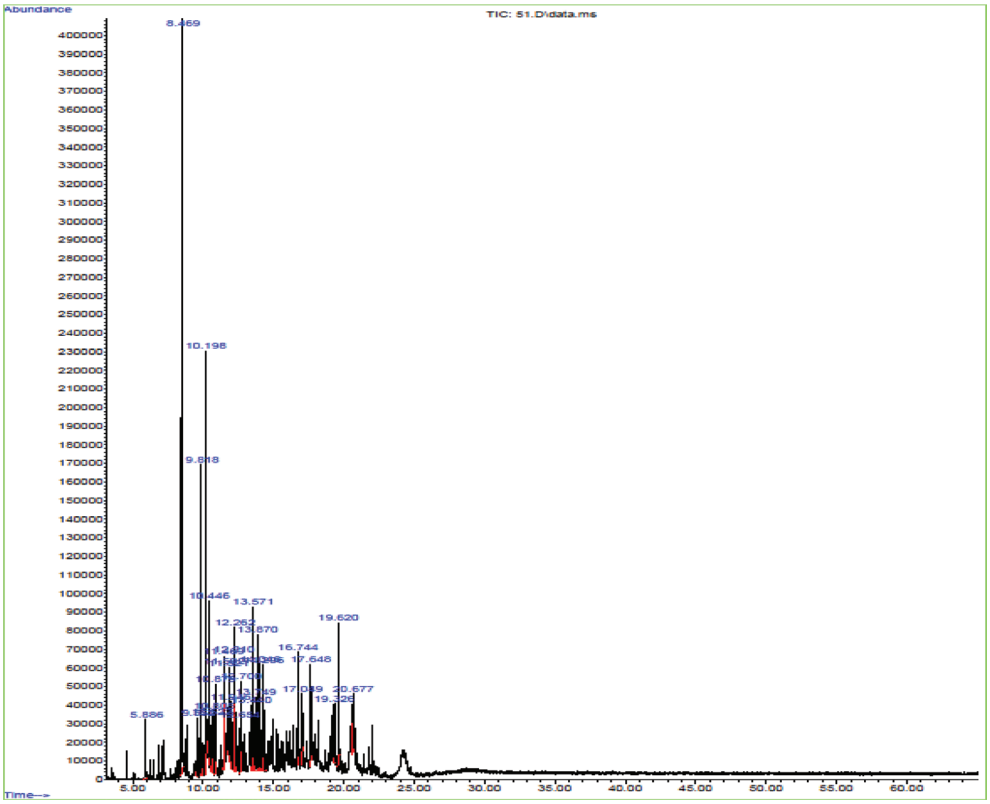

Figure 4. GC-MS of bio-oil obtained by pyrolysis of Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale.

450°C			
Class of compounds: chemical compounds	**RT (min)**	**CAS**	**ω_i% (Area)**
Alkanes			
Undecane	10,622	1120–21–4	1124
Tridecane	13,870	629–50–5	2481
Pentadecane	16,744	629–62–9	2290
Dodecane, 5,8-diethyl	19,326	24.251–86–3	1626
Σ (Area.%) =			**7521**
Alkenes			
6-Tridecene, (Z)-	1626	6508–77–6	2118
Σ (Area.%) =			**2118**
Cycloalkenes			
Megastigma-4,6(E), 8 (Z)-trien	13,440	5298–13–5	1847
Σ (Area.%) =			**1847**
Aromatic hydrocarbons			
Naphthalene	12,262	91–20–3	4399
Naphthalene, 1-methyl	14,046	90–12–0	2390
1H-Indene, 1-ethylidene	14,296	2471–83–2	3249
Σ (Area.%) =			**10,038**
Esters			
Undecanoic acid, 10-methyl-, methyl ester	17,049	5129–56–6	1096
Methyl tetradecanoate	19,620	124–10–7	2969
Σ (Area.%) =			**4065**
Carboxylic acids			
Dodecanoic acid	17,648	334–48–5	4307
Tetradecanoic acid	20,677	544–63–8	4216
Σ (Area.%) =			**8523**
Ketones			
2-Pentanone, 4-hydroxy-4-methyl	5886	123–42–2	1878
2-Cyclopenten-1-one, 2,3-dimethyl	9552	1121–05–7	1655
Σ (Area.%) =			**3533**
Phenols			
Phenol	8469	108–95–2	15,932
Phenol, 2-methoxy	10,446	90–05–1	4583

450°C			
Class of compounds: chemical compounds	**RT (min)**	**CAS**	**ω_i% (Area)**
Phenol, 2,6-dimethyl	10,805	576–26–1	1991
Phenol, 2,4-dimethyl	11,469	105–67–9	2034
Phenol, 2,5-dimethyl	11,502	95–87–4	2215
Phenol, 3,4-dimethyl	11,821	95–65–8	3845
Phenol, 4-ethyl-2-methoxy	13,571	2785–89–9	4567
Σ (Area.%) =			**35,167**
Cresols			
p-Cresol	9818	108–39–4	6331
m-Cresol	10,198	106–44–5	11,054
Cresol	12,210	93–51–3	3141
Σ (Area.%) =			**20,526**
Furans			
Benzofuran, 2-methyl	10,879	4265–26–2	1879
Furan, 2-(2 furanylmethyl)-5-methyl	11,946	13,678–51–8	2089
Benzofuran, 4,7-dimethyl	12,700	28,715–26–6	1783
Σ (Area.%) =			**5751**
Aldehydes			
Cinnamaldehyde, β-methyl-	12,654	1196–67–4	0.910
Σ (Area.%) =			**0.910**

Table 6. Classes of compounds, summation of peak areas, CAS numbers, and retention times of chemical compounds identified by GC-MS of bio-oil obtained by pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale.

by 21.52% (area) hydrocarbons (2.12% alkenes, 7.52% alkanes, 10.04% aromatic hydrocarbons, and 1.85% cycloalkenes), and 78.48% (area) oxygenates (4.06% esters, 8.52% carboxylic acids, 3.53% ketones, 35.16% phenols, 20.52% cresols, 5.75% furans, and 0.91% aldehydes). The presence of carboxylic acids, as well as phenols and cresols, but not only, confers the high acidity of bio-oil, as described in **Table 3**.

The chemical composition of bio-oil is according to similar bio-oil compositions reported in the literature [22, 23, 25, 26, 36, 37], showing the presence of hydrocarbons, phenols, cresols, furans, carboxylic acids, esters, among other classes of chemical compounds. The hydrocarbons identified in bio-oil by GC-MS present carbon chain length between C_{11} and C_{15} with following carbon chain lengths, alkenes C_{13}, alkanes C_{11}–C_{15}, and cycloalkenes C_{13}. The chemical composition of bio-oil indicates the presence of heavy gasoline compounds with C_{11} (C_5–C_{11}), kerosene-like fractions (C_{11}–C_{12}), and light diesel-like fractions (C_{13}–C_{15}), as observed by fractional distillation illustrated in **Table 4**.

3.6. Morphology of solid phase products of açaí seeds (*Euterpe oleracea*, Mart)

3.6.1. SEM analysis of solid phase

The scanning electron microscopies of açaí (*Euterpe oleracea*, Mart) seeds *in nature* and after pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm are shown in **Figures 5** and **6**, respectively. SEM was applied to investigate changes on the vegetal surface structure during the pyrolysis process. By comparison of SEM images of açaí seeds *in nature* and after pyrolysis, it can be observed for açaí seeds *in nature* that an aggregate, amorphous

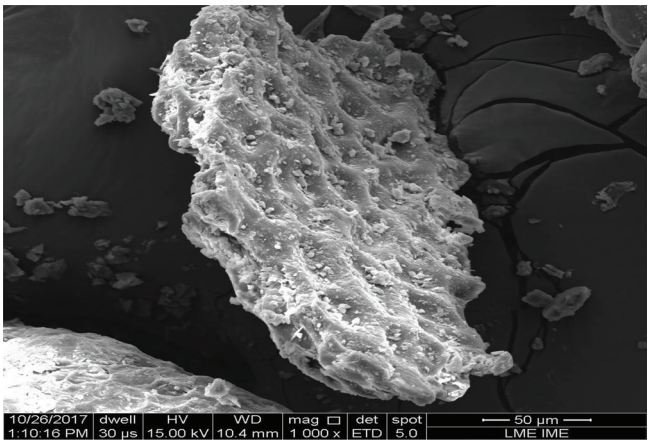

Figure 5. SEM of Açaí (*Euterpe oleracea*, Mart) seeds *in nature*.

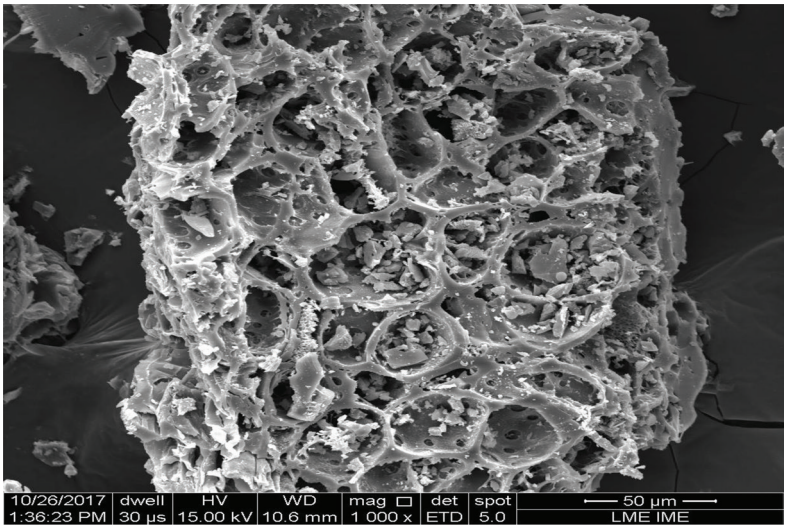

Figure 6. SEM of Açaí (*Euterpe oleracea*, Mart) seeds coke after pyrolysis at 450°C and 1.0 atm, in pilot scale.

and homogeneous structure with irregular shapes dominates, showing the pyrolysis process had a drastic effect on the vegetal morphology, as the vegetal structure differs largely from its original microscopic characteristics, as observed in **Figure 6**, as all the plant cell walls are constituted by cavities. The pyrolysis process produced an aggregate, amorphous solid phase, heterogeneous structure with irregular shapes, being the morphology after pyrolysis completely different compared to the characteristics of original vegetal surface structure. In addition, according to **Table 7**, the carbonization grade is higher, showing that temperature has caused substantial changes on the morphological structure of açaí (*Euterpe oleracea*, Mart) seeds *in nature* by destructing and/or degrading the plant cell walls.

Table 7 illustrates the energy dispersive X-ray spectroscopy of açaí seeds *in nature* and after pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale. The results show that after pyrolysis the carbon content increases, while that of oxygen decreases, compared to those of açaí seeds *in nature*, showing that carbonization grade is higher. Finally, the morphological structure of açaí (*Euterpe oleracea*, Mart) seeds after pyrolysis presents open cavities caused by destruction of the plant cell walls, and may be probably used as a bio-adsorbent.

3.6.2. EDX analysis of solid phase

Table 7 illustrates the energy dispersive X-ray spectroscopy of açaí seeds *in nature* and after pyrolysis of dried Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm by EDX technique. The results show that carbon content increases from 79.28 to 89.98% (wt.), showing a carbonization grad of 13.5%, while that of oxygen decreases from 20.71 to 6.94% (wt.) along with the pyrolysis process. The EDX also identified the presence of K and S in açaí seeds *in nature*.

3.6.3. XRD analysis of solid phase

Figure 7 shows the XRD analysis of solid phase products obtained by pyrolysis of Açaí (*Euterpe oleracea*, Mart) seeds at 450°C and 1.0 atm, in pilot scale. The results confirm the presence of

	450°C			**Açaí seeds**		
Chemical elements	**Mass (wt.%)**	**Atomic mass (wt.%)**	**SD**	**Mass (wt.%)**	**Atomic mass (wt.%)**	**SD**
C	89.98	93.55	4.64	79.28	83.60	4.85
O	6.94	5.41	0.54	20.71	16.39	1.50
Mg	—	—	—	—	—	—
Si	—	—	—	—	—	—
K	2.45	2.45	0.07	—	—	—
S	0.60	0.60	0.04	—	—	—
Al	—	—	—	—	—	—

SD = standard deviation.

Table 7. Percentages in *Atomic Mass* of dried Açaí (*Euterpe oleracea*, Mart) seeds *in nature* and after pyrolysis at 450°C and 1.0 atm by EDX technique.

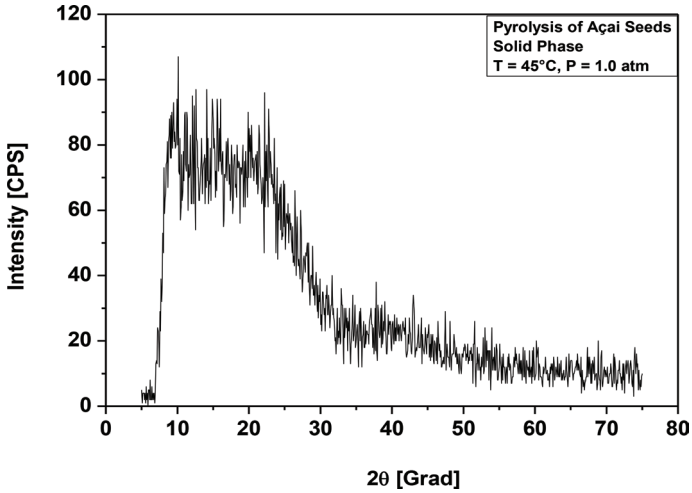

Figure 7. XRD of Açaí (*Euterpe oleracea*, Mart) seeds coke after pyrolysis at 450°C and 1.0 atm, in pilot scale.

three crystalline phases: (1) graphite (C) with a peak of high intensity (100%) on the position 2: 26.52 (ICDD: 00–025-0284); (2) cristobalite (SiO2) with peaks of medium intensity on the positions 2: 15.07 (71.53%) (ICDD: 01-077-1316); (3) quartz (SiO_2) with a peak of high intensity on the position 2: 20.40 (90.30%) (ICDD: 01-089-8940). The pyrolysis favors the formation of mineralogical phase graphite (C). This is according to the results described in Section 3.2.2, whereas a carbonization takes place during the pyrolysis process.

4. Conclusions

The experimental results show that bio-oil, gas, water phase, and coke yields were 4.38, 30.56, 29.39, and 35.67% (wt.), respectively. The bio-oil yield of 4.38% (wt.) is lower compared to similar data for bio-oil yield obtained by fast pyrolysis of forestry residues at 520°C reported in the literature [33, 34], ranging from 10 to 20% (wt.). The bio-oil density and viscosity were 1.0468 g/cm^3 and 68.34 mm^2/s, respectively, being according to similar data reported in the literature [35]. The acid value of bio-oil was 70.26 KOH/g, showing the presence of oxygenates compounds, such as carboxylic acids, phenols, cresols, ketones, and aldehydes, confirming the results reported by Oasmaa et al. [36].

The distillation of bio-oil yielded fossil fuel-like fractions (gasoline, kerosene, and light diesel) of 4.70, 28.21, and 22.35% (wt.), respectively, totalizing 55.26% (wt.), being the results according to similar studies for distillation of bio-oil reported in the literature [22, 23, 25, 37]. The acidity of distillation fractions (gasoline, kerosene, and light diesel-like) increases with increasing boiling temperature, showing a drastic decrease compared to the acidity of raw bio-oil. This i probably due to the high concentration of higher boiling-point compounds in the distillate fractions, such as p-cresol, o-cresol, guaiacol, phenol, and furans [23].

The FT-IR analysis of bio-oil identifies the presence of hydrocarbons (alkanes, alkenes, aromatic hydrocarbons, etc.) and oxygenates (phenols, cresols, carboxylic acids, ketones, furans, etc.). The bio-oil is composed by 21.52% (area) hydrocarbons (2.12% alkenes, 7.52% alkanes, 10.04% aromatic hydrocarbons, and 1.85% cycloalkenes), and 78.48% (area) oxygenates (4.06% esters, 8.52% carboxylic acids, 3.53% ketones, 35.16% phenols, 20.52% cresols, 5.75% furans, and 0.91% aldehydes). The presence of carboxylic acids, as well as phenols and cresols, but not only, confers the high acidity of bio-oil, as described in **Table 3**.

The pyrolysis process produced an aggregate, amorphous solid phase, heterogeneous structure with irregular shapes, being the morphology after pyrolysis completely different compared to the characteristics of original vegetal surface structure. In addition, the temperature has caused substantial changes on the morphological structure of açaí (*Euterpe oleracea*, Mart) seeds *in nature* by destructing and/or degrading the plant cell walls. The results of EDX show that carbon content increases from 79.28 to 89.98% (wt.), showing a carbonization grad of 13.5%, while that of oxygen decreases from 20.71 to 6.94% (wt.) along with the pyrolysis process. The results of EDX confirm the presence of three crystalline phases: (1) graphite (C); (2) cristobalite (SiO_2); (3) quartz (SiO_2), being graphite the peak of high intensity (100%) on the position 2: 26.52 (ICDD: 00-025-0284). The pyrolysis favors the formation of mineralogical phase graphite.

The fractional distillation makes it possible to obtain fossil fuel-like fractions (gasoline, kerosene, and light diesel) rich in hydrocarbons, based on the boiling temperature of hydrocarbons.

Author details

Douglas Alberto Rocha de Castro[1,2,3], Haroldo Jorge da Silva Ribeiro[1,2],
Caio Campos Ferreira[1,2], Márcio de Andrade Cordeiro[1], Lauro Henrique Hamoy Guerreiro[1],
Anderson M. Pereira[1,2,4], W. G. dos Santos[1,2,4], Marcelo Costa Santos[1,2],
Fernanda B. de Carvalho[3], Jose Otavio Carrera Silva Junior[3], R. Lopes e Oliveira[5],
Sergio Duvoisin[5], Luiz Eduardo Pizarro Borges[6] and Nélio Teixeira Machado[1,2]*

*Address all correspondence to: machado@ufpa.br

1 Laboratory of Separation Processes and Applied Thermodynamic (TERM@), Faculty of Chemical Engineering-UFPA, Belém, Pará, Brazil

2 Graduate Program of Natural Resources Engineering-UFPA, Belém, Pará, Brazil

3 Laboratory of Pharmaceutical and Cosmetic Research and Development, Faculty of Pharmacy-UFPA, Belém, Pará, Brazil

4 Faculty of Agricultural Sciences-UFAM, Coroado, Brazil

5 Faculty of Chemical Engineering-UEA, Manaus, Amazonas, Brazil

6 Laboratory of Catalyst Preparation and Catalytic Cracking, Section of Chemical Engineering-IME, Rio de Janeiro, RJ, Brazil

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