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Article

Improving the Antioxidant Activity, Yield and Hydrocarbon Content of Bio-Oil from Açaí Seeds Pyrolysis by Chemical Activation: Effect of Temperature and Molarity

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Abstract: This study explores the impact of temperature and molarity on the pyrolysis of Açaí seeds (*Euterpe Oleraceae*, Mart.) activated with KOH on the yield of bio-oil, hydrocarbon content of bio-oil, antioxidant activity of bio-oil and chemical composition of aqueous phase. The experiments were carried out at 350, 400, and 450 °C and 1.0 atmosphere, with 2.0 M KOH, and at 450 °C and 1.0 atmosphere, with 0.5 M, 1.0 M and 2.0 M KOH, in laboratory scale. The composition of bio-oils and aqueous phase determined by GC-MS, while the acid value, a physical-chemical property of fundamental importance in biofuels, of bio-oils and aqueous phases by AOCS methods. The antioxidant activity of bio-oils determined by the TEAC method. The solid phase (biochar) characterized by X-ray diffraction (XRD). The diffractograms identified the presence of Kalicinite (KHCO₃) in biochar, and those higher temperatures favor the formation peaks of Kalicinite (KHCO₃). The pyrolysis of Açaí seeds activated with KOH show bio-oil yields from 3.19 to 6.79 (wt.%), aqueous phase yields between 20.34 and 25.57 (wt.%), solid phase yields (coke) between 33.40 and 43.37 (wt.%), and gas yields from 31.85 to 34.45 (wt.%). The yield of bio-oil shows a smooth exponential increase with temperature. The acidity of bio-oil varied between 12.3 and 257.6 mgKOH/g, decreasing exponentially with temperature, while that of aqueous phase between 17.9 and 118.9 mgKOH/g, showing and exponential decay behavior with temperature, demonstrating that higher temperatures favor not only the yield of bio-oil but also bio-oils with lower acidity. For the experiments with KOH activation, the GC-MS of bio-oil identified the presence of hydrocarbons (alkanes, alkenes, cycloalkanes, cycloalkenes, and aromatics) and oxygenates (carboxylic acids, phenols, ketones, and esters). The concentration of hydrocarbons varied between 10.19 to 25.71 (area.%), increasing with temperature, while that of oxygenates from 52.69 to 72.15 (area.%), decreasing with temperature. For the experiments with constant temperature, the concentrations of hydrocarbons in bio-oil increase exponentially with molarity, while those of oxygenates decrease exponentially, showing that higher molarities favor the formation of hydrocarbons in bio-oil. The antioxidant activity of bio-oils decreases with increasing temperature, as the content of phenolic compounds

decreases, and decreases with increasing KOH molarity, as higher molarities favors the formation of hydrocarbons. Finally, it can be concluded that chemical activation of Açaí seeds with KOH favors the not only the yield of bio-oil but also the content of hydrocarbons. The study of process variables is of utmost importance in order to clearly assess reaction mechanisms, economic viability and design goals that could be derived from chemically activated biomass pyrolysis processes.

Keywords: açaí seeds; chemical activation; pyrolysis; bio-oil; acidity; antioxidants, hydrocarbons

1. Introduction

Waste management and its final destination presents considerable challenges for the modern society due to population growth and increasing waste generation, causing not only social but also environmental damage, thus becoming a complex problem to be resolved [1-2]. A class of waste to be considered, due to its physicochemical characteristics and huge volume generated, is lignin-cellulosic biomass, particularly those associated to agro-industrial processes [3], such as Açaí (*Euterpe oleracea*, Mart.) seeds.

The Açaí plant (*Euterpe oleracea*, Mart.), is a species of palm that is indigenous to the Amazon region of Brazil [4]. It grows in large numbers in the floodplains of the Amazon estuary [5-6]. The fruits of the Açaí plant have significant economic value for both the agroindustry and for extractive activities conducted by rural communities in the state of Pará in the Brazilian Amazon [7].

When the Açaí pulp and skin are processed with warm water, a thick, purple juice is produced [3, 6]. This process also generates a residue, which consists of the Açaí seeds. These seeds are a valuable biomass residue that contains lignin and cellulose and has the potential to be used for energy and fuel production in both solid and liquid forms [8-12]. During the 2016-2017 crop season, Brazil produced approximately 1200-1274 million tons of Açaí fruits, with the state of Pará being the primary producer (94%). This high level of production results in a significant amount of solid waste [7, 13].

Pyrolysis is a process of thermo-chemical conversion that can transform biomass into energy and fuel by subjecting it to high temperatures in an inert environment [8, 11]. This process produces gaseous byproducts such as CH₄, CO₂, and CO, as well as liquid bio-oil and solid biochar [8, 11]. The nature of the biomass, the type of pyrolysis process (analytical pyrolysis, flash pyrolysis, and vacuum pyrolysis), the type of reactor (drop-tube, fixed bed, and fluidized bed), the operating mode (batch, semi-continuous, continuous), and the process parameters (temperature, catalyst, catalyst-to-biomass ratio, gas flow rate, weight hour space velocity, etc.) all affect the yield and properties of the resulting products [14-16].

Although research has been conducted on the pyrolysis of residual Açaí seeds [8, 11, 17-31], most of these studies have focused on producing activated carbon/bio-adsorbents [8, 17-29]. These studies have used residual Açaí seeds in their natural state [17-19] or activated residual Açaí seeds [8, 20-31] and have involved chemical activation with NaOH [8, 21, 27], KOH [20, 22-31], H₃PO₄ [24, 26], HNO₃ [20, 26], or physical activation with CO₂ [28-29]. However, to date, no systematic study has examined simultaneously the effects of temperature and alkali activation of residual Açaí seeds on the yield, chemical composition, acidity, and antioxidant activity of bio-oil, as well as the chemical composition and acidity of the aqueous phase. Investigating these variables, such as temperature and KOH concentration, is essential to understand the behavior and reaction mechanisms of the process and to design an effective process. Due to the complexity of the topic and the wide range of conditions under which the process (chemical activation followed by pyrolysis) can be carried out, technical data from different biomass pyrolysis feedstocks, reactors, and conditions are of fundamental importance in understanding and optimizing the process.

In addition, temperature is one of the key factors influencing the thermochemical decomposition of biomass compounds during the production of bio-oil by pyrolysis. The bio-oil obtained by pyrolysis of Açaí seeds contains hydrocarbons and a oxygenate fraction rich in phenols [31-32], which are of great interest due to their potential applications as sources of antioxidants, nutraceuticals, and preservatives in the food industry [34]. In the food industry, phenolic compounds are recognized for

their natural antioxidant properties. Phenolic compounds can eliminate free radicals and inhibit oxidation, thus preventing or delaying oxidative processes in food products [35].

In the last years, there has been a great interest in studying the antioxidant capacity/activity of biomass pyrolysis derived bio-oils from different materials including birch wood [33], coffee silverskin [34], red pine [35], Colombian spent coffee grounds [36], tobacco, tomato and coffee ground [37], Japanese red pine [38], grape pomace [39], ship wood [40]. However, until the moment, the influence of pyrolysis temperature on antioxidant capacity of bio-oil has been investigated only in a few studies [34, 37, 39-40]. In addition, no study investigated simultaneously the influence of temperature and chemical activation (molarity) on the antioxidant capacity of pyrolysis bio-oils.

This study aims to investigate the impact of temperature and chemical activation with alkalis on the yield, hydrocarbon content, acidity, and antioxidant activity of bio-oil, as well as the chemical composition and acidity of the aqueous phase. To accomplish this goal, pyrolysis experiments were conducted with residual Açai seeds at 350, 400, and 450 °C, and 1.0 atmosphere. The residual Açai seeds were subjected to chemical activation using aqueous solutions of 0.5 M, 1.0 M, and 2.0 M KOH. These experiments will provide the basis to examine the effects of temperature and alkali activation on the optimization of bio-oil yield and hydrocarbon content in order to gain insights into the potential applications of Açai seed pyrolysis bio-oil.

2. Materials and Methods

2.1. Methodology

The methodology employed for the production of bio-oil from Açai seeds through pyrolysis is presented in Figure 1. This process follows a systematic approach, incorporating various chemical methods and experimental procedures using a fixed bed reactor at a laboratory scale. Initially, Açai seeds are collected from local açai producers, then subjected to drying, milling, and sieving. The resulting powdered biomass is chemically activated with KOH, followed by water washing and drying. The pyrolysis experiments are conducted using a reactor system connected to a condenser and a separating funnel, without the use of a catalyst, while considering the influence of alkali activation. The AOCS method is employed to measure the acidity of the resulting bio-oil. The TEAC method applied to determine the antioxidant capacity of bio-oil. The chemical composition of both the bio-oil and aqueous phase is determined through GC-MS and FT-IR analysis, while the characterization of the biochar is accomplished through XRD techniques.

The applied methodology for producing bio-oil by pyrolysis of Açai seeds is summarized in Figure 1. This process involves a logical sequence of ideas, chemical methods, and procedures to conduct experiments using a fixed bed reactor in laboratory scale. The Açai seeds are initially collected from the sidewalks and streets, dried, milled, and sieved. The powder biomass is then chemically activated with KOH, washed with water and dried. The experiments are carried out in a pyrolysis reactor coupled to a condenser and a separating funnel without a catalyst, and the effect of alkali activation is analyzed. The AOCS and TEAC methods applied to determine the acidity and antioxidant capacity of bio-oil. The chemical composition of bio-oil and aqueous phase are determined using GC-MS and FT-IR, and the biochar is characterized by XRD.

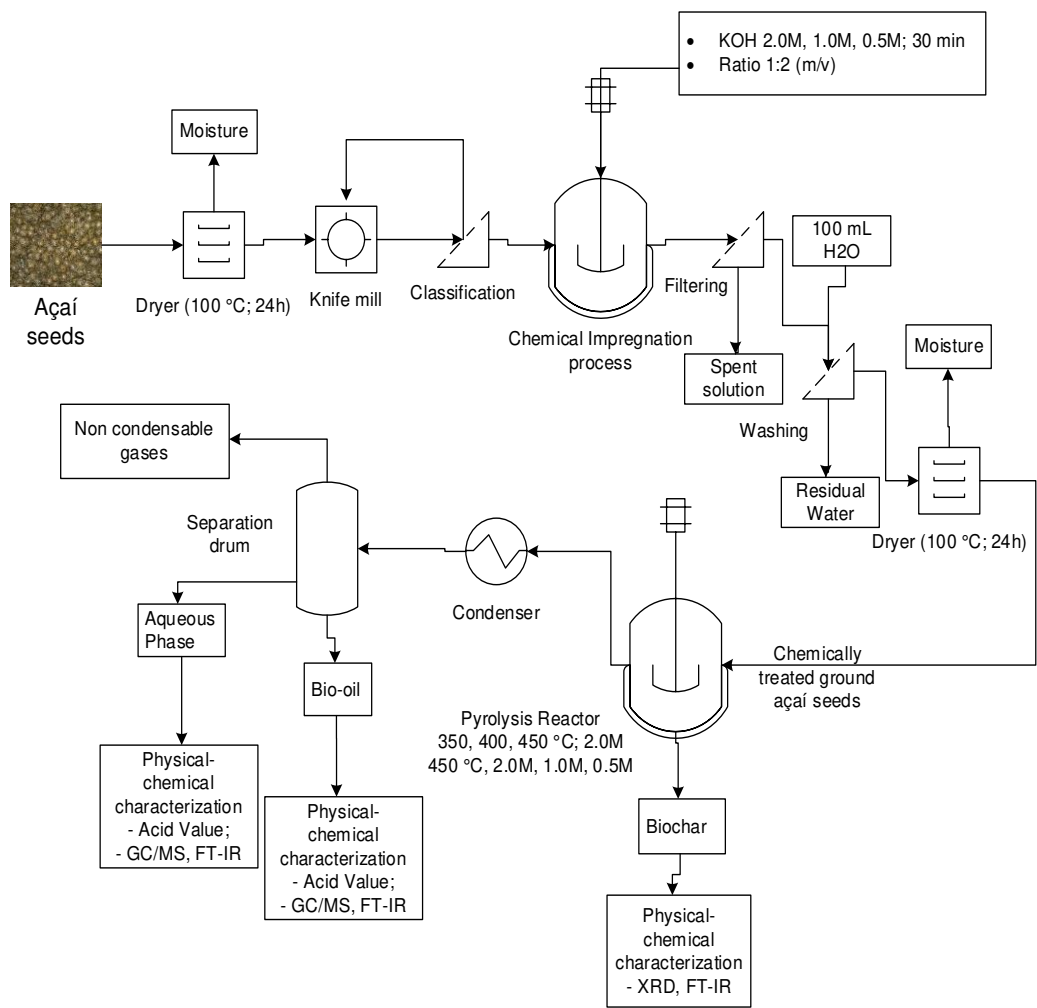


Figure 1. Process flow schema of bio-oil production by pyrolysis of Açai seeds at 350, 400, and 450 °C, 1.0 atm, 2.0 M KOH, and 450 °C, 1.0 atm, 0.5 M, 1.0 M, and 2.0 M KOH, using a fixed bed reactor, in laboratory scale.

2.2. Materials

The Açai seeds (*Euterpe oleracea* Mart.) that were discarded on the sidewalks and streets by a local Açai store in the Jurunas District of Belém-Pará-Brazil, were collected and stored in plastic bags. Figure 2 visually displays the Açai seeds (*Euterpe oleracea* Mart.) that were found scattered on the sidewalks and streets near the Açai store in the Jurunas District of Belém-Pará-Brazil.



Figure 2. Biomass waste in the form of açai seeds in Belém-Pará.

2.3. Pre-treatment of Açai seeds (*Euterpe oleracea*, Mart.)

The Seeds of Açai (*Euterpe oleracea*, Mart.) were submitted to physical pre-treatments of natural and forced drying, grinding, and sieving. The prepared seeds were subjected chemical treatment using solutions of 0.5 M, 1.0 M, and 2.0 M KOH in order to evaluate the effect of KOH concentration in pyrolysis products and yields, and the procedures described in detail in sections 2.3.1 and 2.3.2.

2.3.1. Physical pre-treatment of Açai seeds (*Euterpe oleracea*, Mart.)

The Açai (*Euterpe oleracea*, Mart.) seeds were subjected to drying in an oven controlled by an analog device (DeLeo, Porto Alegre-Brazil, Model: DL-SE) at a temperature of 105°C for a duration of 24 hours. Afterwards, the dried seeds were ground using a laboratory knife cutting mill (TRAPP, Brazil, Model: TRF 600). Then, the dried and grinded Açai seeds were sieved using a set of sieves of 28, 35, 48, 60 Mesh in order to remove the excess fiber material, as well as to decrease the specific particle diameter. The drying, grinding and sieving of Açai seeds is shown in Figure 3.



Figure 3. Açai seeds pre-treatment [Dried Açai seeds (a); Knife cutting mill (b); Mechanical sieve shaker (c); Dried, grinded and sieved Açai seeds (d)].

2.3.2. Chemical activation of Açai seeds (*Euterpe oleracea*, Mart.)

Following the physical pre-treatment outlined in section 2.3.1, the prepared Açai seeds underwent chemical activation using 0.5 M, 1.0 M, and 2.0 M KOH solutions. The procedure involved the following steps: Approximately 60 g of dried, ground, and sieved Açai seeds were gently mixed with 120 mL of 0.5 M, 1.0 M, or 2.0 M KOH solutions (1:2 mass/volume ratio) for 30 minutes in a 250 mL Becker. The impregnation process was conducted at room temperature. The formed suspension was then transferred to a paper filter, washed with 120 mL of distilled water, and left to rest for 24 hours, following a previously described method [31]. Subsequently, it was dried at 100 °C ± 5 °C for 24 hours. Finally, the dried and impregnated seeds were ground using a porcelain pestle and mortar. Figure 4 depicts the chemical activation process of Açai seed fine powders using a 2.0 M KOH solution.



Figure 4. Chemical activation of dried, grinded and sieved Açai seeds with 2.0 M KOH solution [Açai seeds fine powders mixed with 0.5 M, 1.0 M, and 2.0 M KOH solution (a); washing/filtration of Açai pasty cake (b); KOH activated Açai fine powders seeds (c)].

2.4. Centesimal and immediate characterization of Açai seeds

The Açaí seeds (*Euterpe oleracea*, Mart.) were previously characterized for moisture, ash, volatiles, and fixed carbon [9, 11], as well as for lipids, proteins, fibers, cellulose, hemicellulose, and insoluble lignin [41].

2.5. Experimental apparatus and procedures

2.5.1. Experimental apparatus

A diagram in Figure 5 shows a simplified setup of a small borosilicate glass reactor used in the laboratory experiments. The system consists of a cylindrical reactor made of borosilicate glass with a diameter of 3.3 cm and a height of 22.8 cm, with a volume of 195 mL. The reactor is placed inside a cylindrical oven with a ceramic heating system of 800 W, and the temperature is controlled by a digital temperature controller. The temperature inside the reactor is measured with a K-type thermocouple. A Liebig condenser is connected to the exit of the glass reactor using a Y-shaped connection, and the liquid products are collected in a 50 mL borosilicate glass flask. The non-condensable gases are sent to the flare system through an opening in the 90° curve, coupled between the Liebig condenser and the glass separating funnel. Figure 6 shows the laboratory scale pyrolysis reactor used in the experiments.

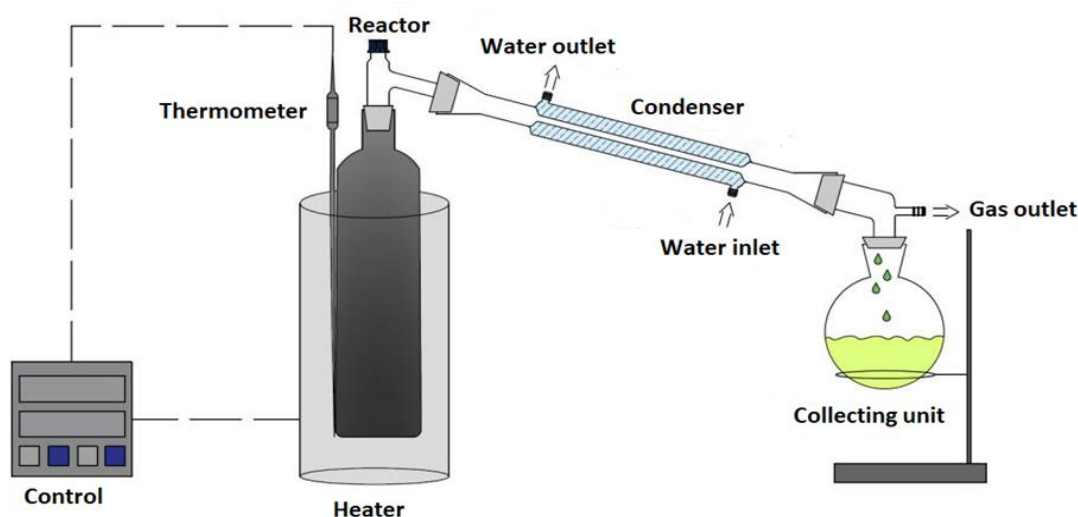


Figure 5. Schematic diagram of a laboratory scale borosilicate glass reactor.



Figure 6. Laboratory scale pyrolysis reactor.

2.5.2. Experimental procedures

By the pyrolysis of chemically activated Açaí seeds, approximately 40.0 g weighed using a semi-analytical balance (Marte Científica e Instrumentação Industrial Ltda, São-Paulo-Brazil, Model: AD330). Then, the chemically activated Açaí seeds placed inside the glass reactor. After connecting the glass reactor to the Liebig condenser, using a Y shaped connection, and the condenser to the separating funnel, the cooling system is turned on and the water temperature was set at 10 °C. Then, the desired heating rate (10 °C/min), and temperature (350, 400, or 450 °C) were set-up. After the desired reactor temperature (set-point temperature) is reached, the reactor set-point temperature is maintained for 30 minutes. The temperature of the reactor was monitored at 10-15 minutes intervals. The weight of the liquid phase (consisting of bio-oil and aqueous phase) and biochar were measured, and the weight of gas was calculated by subtracting the total weight of the liquid and biochar from the total weight of the feedstock. The bio-oil was separated from the aqueous phase through decantation in the separation funnel. The bio-oil was then analyzed for its physical and chemical properties, including acid value.

2.6. Acidity, antioxidant activity and chemical composition

2.6.1. Acidity of liquid fractions

The acid value of the bio-oils and aqueous phases was determined according to the official methods (AOCS Cd 3d-63), as detailed in previous studies [42-45].

2.6.2. Antioxidant activity of bio-oils

The total antioxidant capacity was determined according to the Trolox® equivalent antioxidant capacity (TEAC) method proposed by Miller et al. [46], and modified by Re et al. [47], being adapted for conditions of temperature, proportions of reagents and reaction time. TEAC is a colorimetric technique based on the reaction between ABTS (Sigma A1888) and potassium persulfate ($K_2S_2O_8$), producing the ABTS• (cation radical), a green/blue chromophore, with maximum absorbance at 645, 734 and 815 nm. Addition of antioxidants to the cation radical reduces it again to ABTS. The reaction was measured spectrophotometrically by observing the changes in absorbance measured at 734 nm over a time interval of 05 (five) minutes, using a spectrophotometer (Spectrum, Shanghai, China, Model: SP-2000UV). Thus, the extent of discoloration, defined as an index of inhibition of the ABTS• (cation radical), is measured, being equal to the total antioxidant activity of the sample. The TEAC results were expressed in micromoles per liter ($\mu\text{moles/L}$). Initially, the AC-ABTS standard curve was constructed by successive dilution of standard Trolox solution (2.5 mM), and each point measured in triplicate to compute a mean absorbance value. Afterwards, 2970 μL of ABTS is read, corresponding to initial time (τ_0). Then, 30 μL of sample (bio-oil) is added. The reading of absorbance is carried out after 05 (five) minutes (τ_5).

2.6.3. Chemical composition of bio-oils and aqueous phase

CG-MS was used to determine the chemical composition of bio-oils and aqueous phases, following the procedures described by Castro et. al. [11]. A 1.0 μL sample was injected in split mode into a gas chromatographer (Agilent Technologies, GC-7890B), equipped with a fused silica capillary column (SLBTM-5ms) coupled to a mass spectrometer (Agilent, MS-5977A). The peak intensity, retention times, and identification of compounds were analyzed based on the NIST mass spectra library. Since no internal standard was used, the concentrations were expressed in area.%. The presence of chemical groups was confirmed by Fourier transform infrared spectroscopy (FT-IR) (BRUKER, Ettlingen-Germany, Model: VERTEX 70v) at the Laboratory of vibrational spectroscopy and high pressure (LEVAP-PPGF/UFGA), and the procedures applied to determine the qualitative FT-IR analysis described elsewhere [48-51].

2.7. Characterization of hidrochar

2.7.1. XRD analysis

The crystalline and mineralogical analysis of chemically activated Açaí seeds after pyrolysis was conducted using an X-ray diffraction (XRD) technique. The XRD measurements were carried out using a BRUKER D8 ADVANCE diffractometer with Bragg-Brentano geometry, coupled with a LynxEye detector. The analysis was performed at the Laboratory of X-ray Diffraction (PPGF/UFGA), and the equipment used had the following specifications: a generator with a maximum power of 3 kW, a tube voltage of 40 kV, a tube current of 40 mA, and a Cu X-ray tube with $K\alpha_1$ wavelength of

1.540598 Å. The optical setup of the instrument included fixed divergence, scattering, and receiving slits, with a K β filter of Ni and a graphite monochromator. The soller slit was set to 2.5°, and the divergent slit was 0.6 mm. The goniometer used was a vertical model, allowing a scanning range of 5-110° (2 θ) with a scanning speed of 0.2°/min (2 θ) and an accuracy of $\pm 0.02^\circ$. The XRD data were recorded with an angular step of 0.02° and a scan rate of 0.2°/min at room temperature. The identification of crystalline phases in the chemically activated Açai seeds was performed following established procedures described in the literature [9, 15-16, 31, 52-53].

2.8. Mass balances by pyrolysis of Açai seeds

An overall mass balance was done in order to calculate the quantity of gas formed. Basically, the weight of feed, bio-oil, aqueous phase and coke formed are recorded and a global integral mass balance calculation yields the quantity of gas formed by difference [54-55]. A differential mass balance of the considered system is described by the following equation (1):

$$\frac{dM}{dt} = \dot{M}_i - \dot{M}_o \quad (1)$$

Where \dot{M}_i and \dot{M}_o are the mass flow rates in and out of the control volume, respectively. Multiplication of equation (1) by dt and integrating, yields:

$$\int_{t_i}^{t_f} \frac{dM}{dt} dt = \int_{t_i}^{t_f} \dot{M}_i dt - \int_{t_i}^{t_f} \dot{M}_o dt \quad (2)$$

$$M_{t_f} - M_{t_i} = \int_{t_i}^{t_f} \dot{M}_i dt - \int_{t_i}^{t_f} \dot{M}_o dt \quad (3)$$

Where M_{t_f} is the remaining material in the reactor after pyrolysis i.e. the bio-char formed and M_{t_i} corresponds to the feed weight loaded. Since there is no mass being added to the reactor, $\dot{M}_i = 0$. The mass flowing out of the reactor, \dot{M}_o , is represented by the vapors formed during the pyrolysis process and condensed or not afterwards as bio-oil, aqueous phase and non-condensable gases. Then, equation (2) becomes:

$$M_{char} - M_{feed} = - \left[\int_{t_i}^{t_f} \dot{M}_{bio-oil} dt + \int_{t_i}^{t_f} \dot{M}_{aqueous\ phase} dt + \int_{t_i}^{t_f} \dot{M}_{gas} dt \right] \quad (4)$$

$$M_{feed} - M_{char} = \int_{t_i}^{t_f} \dot{M}_{bio-oil} dt + \int_{t_i}^{t_f} \dot{M}_{aqueous\ phase} dt + \int_{t_i}^{t_f} \dot{M}_{gas} dt \quad (5)$$

Assuming constant behavior of the flow rates of bio-oil, aqueous phase and gas phases, equation (4) yields the final form of mass balance for the pyrolysis process.

$$M_{feed} - M_{char} - M_{bio-oil} - M_{aqueous\ phase} = M_{gas} \quad (6)$$

3. Results

3.1. Characterization of catalyst

3.1.1. XRD analysis

3.1.1.1 Effect of pyrolysis temperature

Figures 7 illustrate the XRD of biochar produced by pyrolysis of Açai seeds at 350 (a), 400 (b), and 450 °C (c), 1.0 atmosphere, activated with 2.0 M KOH, in laboratory scale, respectively. The diffractogram of biochar illustrated in Figure 7 shows the presence of 01 (one) peak (K2) of high intensity on the position 2 θ : 30.0 (100%), and 02 (two) peaks of medium intensity, the first (K1) on the position 2 θ : 24.2 (66.8%) and the second (K3) on the position 2 θ : 40.6 (68.6%), being all the peaks associated to Kalicinite (KHCO₃), the dominant crystalline phase in biochar. The findings from Prakongkep et al. [56], who conducted a study on the chemical properties, elemental analysis, nutrient content, as well as morphological and crystalline characteristics of biochar obtained from the pyrolysis of durian shell at 350 °C on a laboratory scale, align with the results of this study. Prakongkep et al. [56], observed that the dominant crystalline phase identified in the biochar was Kalicinite (KHCO₃).

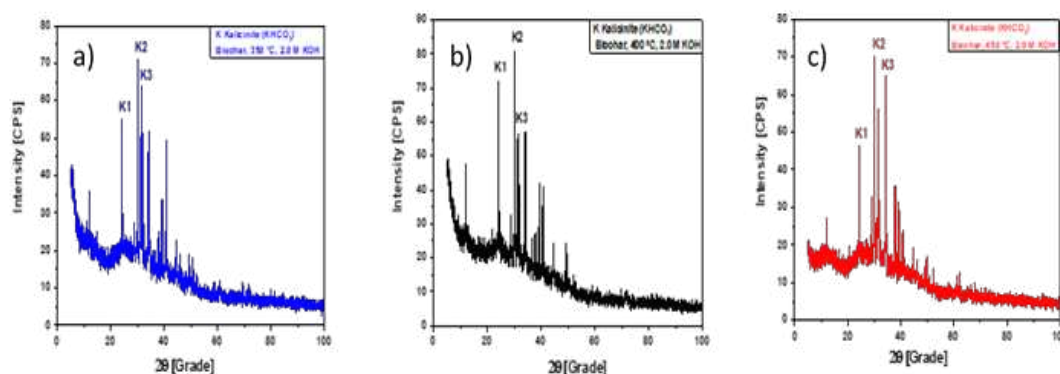


Figure 7. XRD of biochar produced by pyrolysis of Açaí seeds at 350 °C (a), 400 °C (b) and 450 °C (c), 1.0 atmosphere, activated with 2.0 M KOH, in laboratory scale.

The diffractogram of biochar illustrated in Figure 7b shows the presence of 02 (two) peaks of high intensity, the first observed on the position 2θ : 24.1 (81.73%), the second on the position 2θ : 30.0 (100%), and 01 (one) peak of medium intensity on the position 2θ : 31.3 (62.2%), being all the peaks associated to Kalicinite (KHCO_3), the dominant crystalline phase in biochar, as reported by Prakongkep *et al.* [56]. The diffractogram of biochar illustrated in Figure 7c shows the presence of 03 (three) peaks of high intensity, the first observed on the position 2θ : 30.2 (100.0%), the second on the position 2θ : 31.3 (79.9%), and the third on the position 2θ : 34.2 (92.1%), being all the peaks associated to Kalicinite (KHCO_3), the dominant crystalline phase in biochar, as reported by Prakongkep *et al.* [56].

Furthermore, Han Lee and co-workers [57], investigated the XRD patterns of biochar that had been chemically modified using K agents. Despite undergoing thermo-chemical transformations at much higher temperatures (600°C-900°C), they observed similar behavior, which is illustrated by the diffractograms shown in Figures 7. Han Lee *et al.* [57], proposed that XRD patterns change with increasing temperature is due to thermal decomposition of KHCO_3 into other oxides, such as K_2O and K_2CO_3 , producing CO_2 and H_2O . In a study conducted by Díaz-Terán *et al.* [58], the chemical activation of lignocellulosic material using KOH was investigated. XRD analysis of the activated material showed the presence of K_2CO_3 at a position of 2θ : 31.0. It was observed that the intensity of the peak increased with temperature, indicating a temperature-dependent effect on the formation of K_2CO_3 . Similar results were observed in Figure 7. Díaz-Terán *et al.* [58], proposed the possibility of CO_2 formation by reaction of K_2CO_3 with biochar, close to 470 °C, as well as the possibility of formation of K salts that could oxidize and form potassium oxides and even KOH again, so that it is expected that presence of KHCO_3 (Kalicinite) and K_2CO_3 crystalline phases in biochar after pyrolysis of Açaí seeds activated with 2.0 M KOH may show a maximum peak intensity over the diffractogram on the position 2θ .

3.2. Process Analysis

3.2.1. Effect of process temperature

Pyrolysis experiments were conducted on activated Açaí seeds at temperatures of 350, 400, and 450 °C, and a pressure of 1.0 atm, after activation with a 2.0 M KOH solution. These experiments were carried out using a laboratory-scale borosilicate glass reactor. The results showed that the bio-oil yields ranged from 3.19% to 6.79% (wt.), while the aqueous phase yields ranged from 20.34% to 25.57% (wt.). The yields of biochar ranged from 33.40% to 43.37% (wt.), and the gas yields ranged from 31.85% to 34.45% (wt.). These findings are consistent with the bio-oil yields reported by Serrão *et al.* [30], who conducted a study on the pyrolysis of Açaí seeds in a natural setting, and with the yields reported by Castro *et al.* [11], who investigated the pyrolysis of Açaí seeds in pilot, bench, and laboratory scales. The bio-char yields obtained in this study are also in agreement with similar data reported in the literature for the pyrolysis of Açaí seeds, whether in their natural state [17-19] or chemically activated [8, 20-31]. It is important to note that the observed increase in bio-oil yield with increasing temperature is attributed to the temperature range being within the range of maximum

decomposition, where the original material is primarily decomposed into its initial products. These findings are summarized in Table 1, which presents the yields of the different reaction products.

Table 1. Mass Balance and yield of reaction products by pyrolysis of Açai seeds.

Process Parameters	2.0 M KOH		
	350 °C	400 °C	450 °C
Mass of Açai seeds (g)	40.12	40.12	40.06
Cracking time (min)	62	67	72
Solid weight (Coke) (g)	17.40	13.40	16.17
Liquid weight (Bio-oil) (g)	1.28	2.64	2.72
Weight of H ₂ O (g)	8.16	10.26	8.41
Weight of gas (g)	13.28	13.82	12.76
Bio-oil Yield (wt.%)	3.19	6.58	6.79
H ₂ O Yield (wt.%)	20.34	25.57	20.99
Bio-char Yield (wt.%)	43.37	33.40	40.36
Gas Yield (wt.%)	33.10	34.45	31.85
Acidity (mg KOH/g)	257.6	15.0	12.3

Figure 8 illustrates the yields of different reaction products, namely liquids, solids, H₂O, and gas, obtained from the pyrolysis of activated Açai seeds in a laboratory-scale borosilicate glass reactor. The pyrolysis was conducted at temperatures of 350, 400, and 450 °C, pressure of 1.0 atm, and the Açai seeds were activated using a 2.0 M KOH solution. The results demonstrate that the yield of bio-oil increases gradually as the temperature rises, and this trend was well-fitted with a first-order exponential decay model, yielding an r^2 value of 1.00. These findings align with the observations made by Serrão et al. [30], who investigated the pyrolysis of Açai seeds in a natural environment at temperatures of 350, 400, and 450 °C and 1.0 atm on a pilot scale. Their study also reported an increase in bio-oil yield with temperature. Similar studies focusing on biomass pyrolysis have consistently reported an increase in bio-oil yield within the temperature range of 200 to 450 °C [59-70].

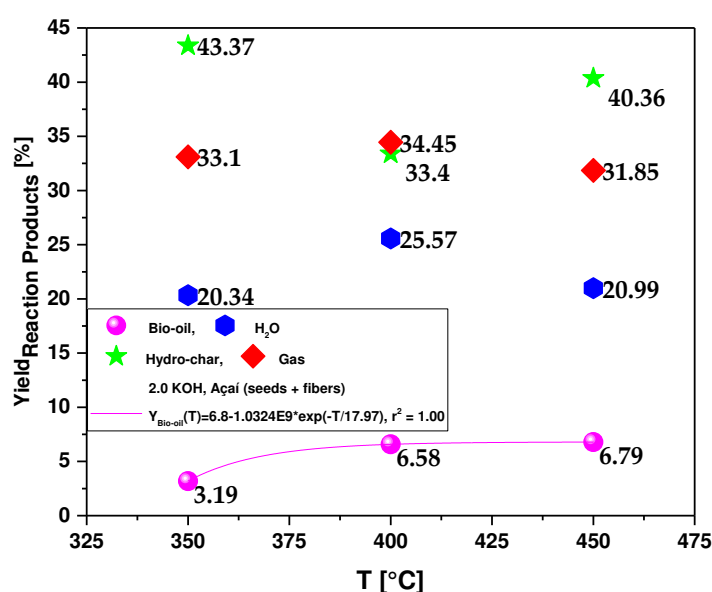


Figure 8. Yield of reaction products (bio-oil, H₂O, biochar, gas) by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart) in the temperature range of 350-450 °C.

The data indicate that pyrolysis at 400 °C generates minimum char and maximum gas and water, suggesting that the pyrolysis mechanism is optimized by the reaction temperature of 400 °C when using chemical activation with KOH. The yield of biochar increases with a higher concentration of KOH, indicating a relationship between the mechanisms of gas and water formation and bio-char formation. Previous research on Açai seed pyrolysis has shown that gas phase yields are associated with bio-char formation [11], and alkaline salts serve as catalysts that affect gas and char reactions.

3.2.1.1. Effect of temperature on the composition of hydrocarbons and oxygenates in bio-oil

Figures 9 and 10 provide visual representations of the impact of process temperature on the composition of bio-oil derived from the pyrolysis of activated Açai seeds (*Euterpe Oleracea*, Mart). The Açai seeds were chemically activated using a 2.0 M KOH solution, and the pyrolysis experiments were conducted at temperatures of 350, 400, and 450 °C, under a pressure of 1.0 atm, on a laboratory scale. The chemical composition of the liquid fraction of bio-oil was categorized into two main groups: hydrocarbons and oxygenates. Hydrocarbons encompass acyclic saturated/unsaturated hydrocarbons (alkanes + alkenes) as well as heterocyclic hydrocarbons (cycloalkanes + cycloalkenes + aromatics). On the other hand, oxygenates consist of phenols, ketones, and esters. This categorization allows for an assessment of the suitability of the designed process in producing chemical compounds that can serve as effective fuels. It is worth noting that oxygenates, due to their acidic nature, often do not burn efficiently, leading to the accumulation of residues in engines [11]. Therefore, the distinction between hydrocarbons and oxygenates serves as a valuable means of evaluating and comparing different thermochemical conversion processes for their potential fuel applications.

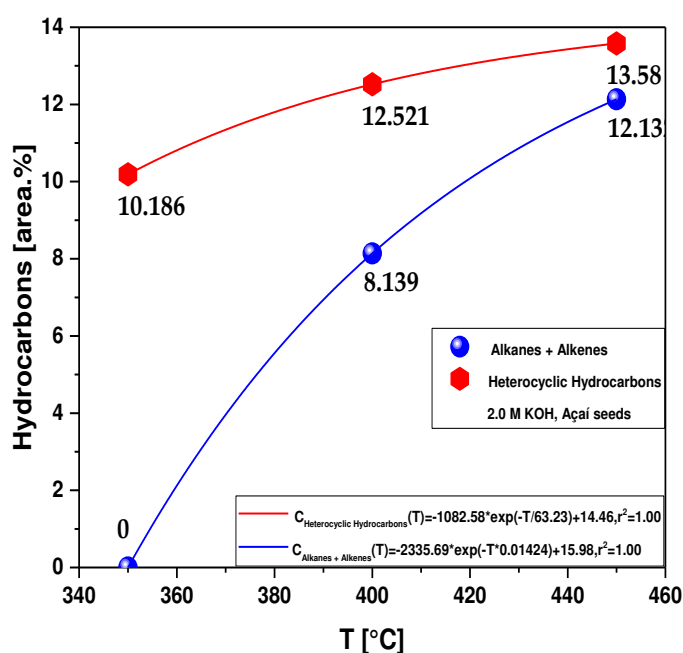


Figure 9. Concentration of acyclic saturated/unsaturated hydrocarbons (alkanes + alkenes) and heterocyclic hydrocarbons (cycloalkanes + cycloalkenes + aromatics) in bio-oil by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), in the temperature range of 350-450 °C.

Supplementary Tables S1-S3 present the chemical functions, CAS numbers, sum of peak areas, and retention times of all molecules identified by GC-MS in the bio-oil obtained from the pyrolysis of activated Açai seeds (*Euterpe Oleracea*, Mart) with 2.0 M KOH solution at laboratory scale, using 350, 400, and 450 °C and 1.0 atmosphere. The concentration of acyclic saturated/unsaturated hydrocarbons and heterocyclic hydrocarbons increases with temperature, particularly for the concentration of acyclic saturated/unsaturated hydrocarbons, as depicted in Figure 9.

The concentrations of both acyclic saturated/unsaturated hydrocarbons and heterocyclic hydrocarbons in the bio-oil obtained from the pyrolysis of activated Açaí seeds were observed to rise as the process temperature increased. These results were effectively modeled using a first-order exponential growth model, with an r^2 value of 1.00 for both categories. These findings align with the research conducted by de Sousa *et al.* [32], who investigated the influence of process temperature on the concentration of hydrocarbons and oxygenates in bio-oil derived from Açaí seeds using a pilot-scale pyrolysis setup. Their study, which examined temperatures of 350, 400, and 450 °C under a pressure of 1.0 atm, demonstrated that the concentration of hydrocarbons increased while the concentration of oxygenates decreased with rising temperature. Additionally, it was observed that the concentrations of alkanes, alkenes, and aromatics in the bio-oil increased with temperature, suggesting that higher pyrolysis temperatures promote the formation of hydrocarbons [32].

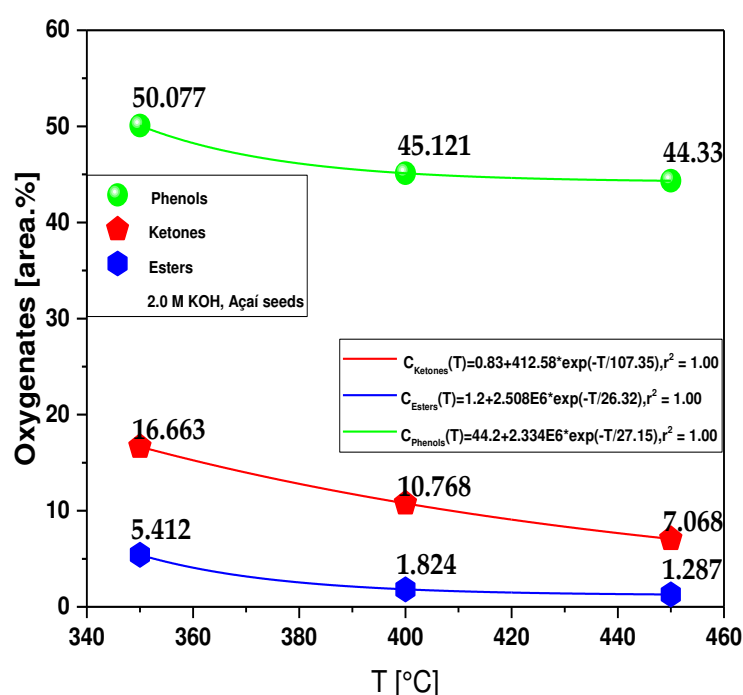


Figure 10. Concentration of oxygenates (phenols, ketones, and esters) in bio-oil by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart), in the temperature range of 350-450 °C.

Figure 10 illustrates the concentration of oxygenates in bio-oil. The concentrations of phenols, esters, and ketones decrease with increasing pyrolysis temperature, showing a smooth exponential decay behavior, as shown in Figure 10. The results are according to those reported by de Sousa *et al.* [32]. The concentration of oxygenates in bio-oil were correlated with a first order exponential decay model, exhibiting in all the cases root-mean-square error (r^2) of 1.00. According to de Sousa *et al.* [32], the concentration of cresols, phenols, and ketones decrease with increasing pyrolysis temperature because of deoxygenation reactions converting phenols, esters and ketones into hydrocarbons, carbon monoxide, carbon dioxide and water (decarboxylation and decarbonylation). Mechanism of deoxygenation is not well understood but it seems that reaction rate of deoxygenation is influenced positively by reaction temperature. Studies show that adipic acid (dicarboxylic acid) can be converted to cyclopentanone via deoxygenation reactions and at higher temperatures a considerable amount of cyclo-pentene is formed [15,16].

Figure 11 depicts the acid value, which represents the acidity, of the bio-oils obtained from the pyrolysis of activated Açaí seeds. The results reveal a notable reduction in bio-oil acidity as the pyrolysis temperature increases, following a sharp exponential decay trend. The acid value of the bio-oil ranged from 257.6 to 12.3 mgKOH/g and exhibited a strong correlation with a first-order

exponential decay model, demonstrating an r^2 value of 1.00. These findings are in line with the observations presented in Figure 10, suggesting that higher concentrations of oxygenates in the bio-oil contribute to elevated levels of acidity.

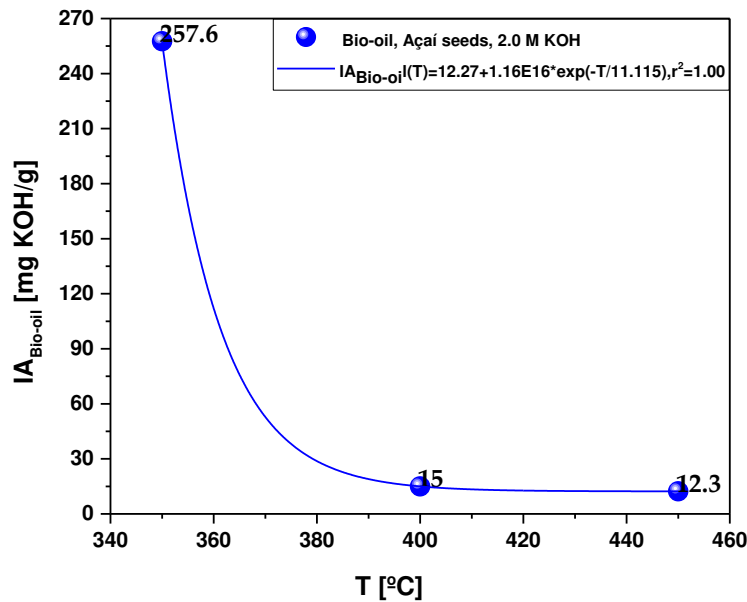


Figure 11. Acidity of bio-oil obtained by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), in the temperature range of 350-450 °C.

3.2.1.2. Effect of temperature on chemical composition of products

Table 2 presents the chemical composition and acidity of the aqueous phase generated from the pyrolysis of Açai seeds, and data depicted graphically in Figure 12. The determination of the chemical components and acidity of the aqueous phase was carried out using GC-MS analysis. Supplementary Tables S4-S6 provide detailed information on the chemical functions, sum of peak areas, CAS numbers, and retention times of all identified molecules.

Table 2. Chemical composition of aqueous phase obtained by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), identified by GC-MS.

Chemical Composition C _i (area.%)	2.0 M KOH		
	350 °C	400 °C	450 °C
Alcohols	2.34	20.74	26.62
Carboxylic Acids	4.05	15.02	9.23
Ketones	52.81	44.38	19.69
Oxygenates	40.80	19.86	44.46
$\sum_{i=1}^n C_i$	100.00	100.00	100.00
Acidity (mg KOH/g)	118.9	26.8	17.9

Similar studies reported in the literature have identified the major oxygenate compounds in the aqueous phase as alcohols, carboxylic acids, and ketones, with remaining oxygen compounds such as phenols, aldehydes, and amines grouped under the category of oxygenates. Zhang et al. [71] found carboxylic acids, ketones, phenols, and furans in the aqueous phase produced by sawdust pyrolysis, while Torri and Fabbri [72] identified carboxylic acids, aldehydes, phenols, furans, sugars, and N-compounds in the aqueous phase produced by corn stalk pyrolysis. Similarly, Zhou et al. [73]

reported the presence of carboxylic acids, aldehydes, phenols, ketones, furans, furfurals, sugars, and amines in the aqueous phase produced by corn stover pyrolysis.

The contribution of alcohols to the acidity of the aqueous phase is generally considered small or negligible due to their weak acidic nature. However, the α -hydrogen atoms of ketones exhibit acidic properties, which contribute to the overall acidity of the aqueous phase. Additionally, carboxylic acids with low carbon chain lengths are known to have a significant impact on the acidity of the aqueous phase. As the concentration of ketones decreases, it is expected that the acidity of the aqueous phase will also diminish. The acidity of the aqueous phase can be correlated with a first-order exponential decay model, indicating a decrease in acidity with increasing pyrolysis temperature.

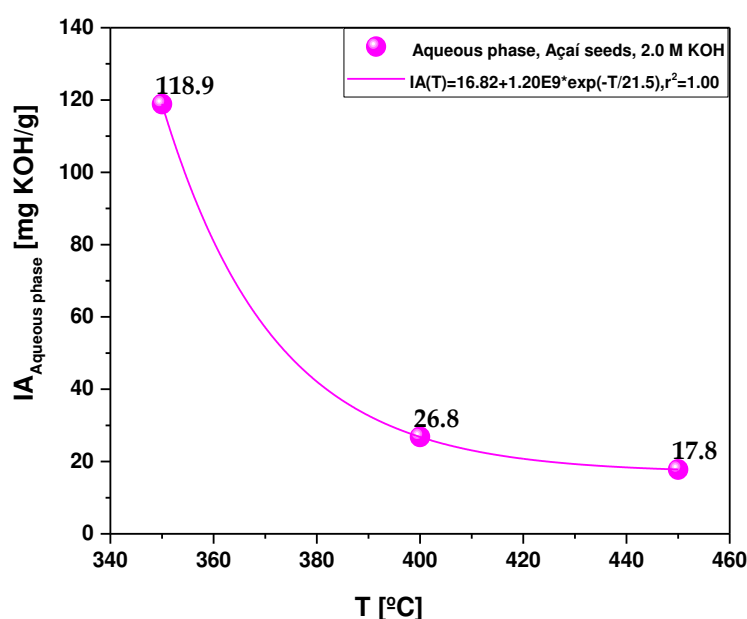


Figure 12. Acidity of aqueous phase obtained by pyrolysis of Açaí seeds.

3.2.1.3. Effect of temperature on the antioxidant activity of bio-oil

Figure 13 demonstrates the effect of pyrolysis temperatures on the total antioxidant capacity of bio-oil produced by the pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart) with 2.0 M KOH solution, 1.0 atmosphere, on a laboratory scale. The effect of temperature on the average antioxidant capacity of pyrolysis bio-oil are shown in Table 3. As previously described, pyrolysis is a complex process involving the thermal degradation of biomass, and reaction conditions, particularly temperature, plays a critical role in determining the chemical composition of the bio-oil [31]. At different pyrolysis temperatures, various intermediate reactions occur, leading to the formation of different chemical compounds within the bio-oil, but also production of a gaseous and a solid phase with different composition and characteristics [9, 30-32]. The results presented in Table 3 indicate that the strong antioxidant activity of the bio-oil at 350°C may be probably associated with its high concentration of oxygenated compounds at this temperature, particularly phenolic compounds, which accounts for 50.077 (area.%) of total oxygenated compounds, as shown in Figure 10. Recently, Valdez et. al. [31], demonstrated that higher pyrolysis temperatures (450°C) of Açaí seeds activated with a 2.0 M KOH solution do not favors the formation of oxygenates in the bio-oil, leading to the formation of hydrocarbons rich bio-oils. On the other hand, lower pyrolysis temperatures (350°C) favor the formation of oxygenates, particularly phenolic compounds, in the Açaí seed bio-oil [31]. In this context, phenolic compounds are strongly associated with high antioxidant activity, as described in the literature [74-76]. The results are according to similar studies reported by del Pozo et. al. [34], who investigated the effect of temperature on the antioxidant capacity of pyrolysis bio-oil of coffee silver skin, and by del Pozo et al. [39], who investigated the effect of temperature on the antioxidant capacity

of pyrolysis bio-oil of grape pomace, showing that higher pyrolysis temperature leads to bio-oils with lower antioxidant capacity.

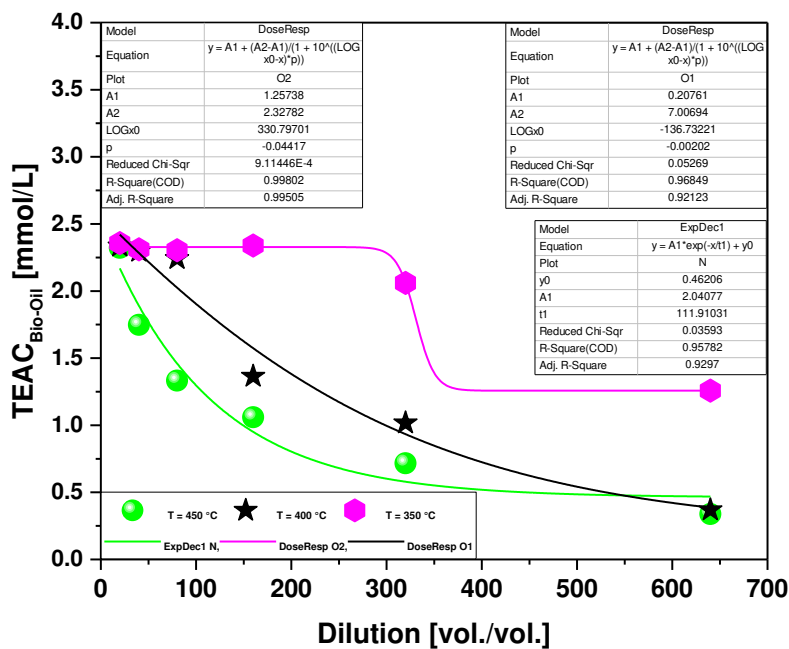


Figure 13. Total antioxidant capacity in the bio-oil produced by the pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart) with 2 M KOH solution, in the temperature range of 350-450 °C.

In general, by thermochemical degradation of biomass, higher temperatures result in the degradation of valuable compounds within the bio-oil, including phenolic com-pounds, while lower temperatures favor not only the formation, but also preserve phenols in bio-oil [31]. Furthermore, bio-oil is the reaction product most abundant in valuable chemical compounds, making it particularly significant for the food, cosmetic and pharmaceutical industries. One of the essential components found in bio-oil are phenolic compounds. These compounds have gained substantial interest due to their potential applications as natural sources of antioxidants, nutraceuticals, and preservatives in the food industry [34, 38].

Phenolic compounds possess strong antioxidant properties, which help in neutralizing harmful free radicals and reducing oxidative stress, that can delay or inhibit the oxidation of DNA, proteins, and lipids [75]. As a result, they can extend the shelf life of food products by inhibiting the oxidation of fats and oils, preventing rancidity, and maintaining the overall quality and freshness of the food [74]. In addition, these compounds may confer health benefits beyond basic nutrition when incorporated into the diet. Nutraceuticals derived from phenolic compounds have been associated with various health-promoting effects, such as anti-inflammatory, anticancer, and cardioprotective properties [74-76]. Therefore, the temperature at which pyrolysis occurs is a critical parameter that influences both the quantity and quality of the produced bio-oil.

Understanding the impact of pyrolysis temperature is essential to maximize desired compounds, such as phenolic compounds and/or hydrocarbons, and ensure that the bio-oil meets specific industrial and application requirements whether in applications such as biofuels or chemical products with high added value in the food, cosmetics and pharmaceutical industries.

Table 03. Antioxidant capacity of bio-oils by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart).

Dilution	TEAC (µM/L) 2.0 M KOH		
	350 °C	400 °C	450 °C
1:20	2.35	2.33	2.32

1:40	2.31	2.29	1.74
1:80	2.30	2.24	1.33
1:160	2.33	1.36	1.05
1:320	2.06	1.01	0.71
1:640	1.25	0.36	0.33

3.2.2. Effect of KOH solution molarity

Table 4 illustrates the process parameters, mass balances, yields of reaction products (bio-oil, biochar, H₂O, and gas), and acidity of bio-oils by pyrolysis of activated Açaí seeds at 450 °C, 1.0 atm, activated with 0.5 M, 1.0 M, and 2.0 M KOH.

Table 4. Mass balance by pyrolysis of activated Açaí seeds at 450 °C, 1.0 atm, activated with 0.5 M, 1.0 M, and 2.0 M KOH.

Process Parameters	450 °C		
	0.5 M	1.0 M	2.0 M
Mass of Açaí seeds (g)	33.285	40.040	40.06
Cracking time (min)	72	72	72
Solid weight (Coke) (g)	9.650	13.080	16.17
Bio-oil weight (g)	3.431	2.720	2.72
H ₂ O weight (g)	12.290	11.99	8.41
Gas weight (g)	7.914	12.25	12.76
Bio-oil Yield(wt.%)	10.31	6.79	6.79
H ₂ O Yield(wt.%)	36.92	29.94	20.99
Bio-char Yield(wt.%)	29.99	32.67	40.36
Gas Yield(wt.%)	23.78	30.59	31.85
Acidity (mg KOH/g)	112.7	103.7	12.3

In laboratory-scale pyrolysis experiments, activated Açaí seeds were subjected to different concentrations of KOH solution (0.5 M, 1.0 M, and 2.0 M) and pyrolyzed at 450 °C and 1.0 atm in a borosilicate glass reactor. The yields of bio-oil, aqueous phase, biochar, and gas were determined and found to range from 6.79% to 10.31%, 20.99% to 36.92%, 29.99% to 40.36%, and 23.78% to 31.85% (wt.), respectively. The bio-oil yields obtained were higher than those reported by Serrão et. al. [30], but similar to those reported by Castro et. al. [11]. The yields of biochar were also consistent with those reported in previous studies of Açaí seed pyrolysis chemically activated with NaOH [8, 21, 27], KOH [20, 22-31], H₃PO₄ [24, 26], and HNO₃ [20, 26]. Chemical activation of biomass with alkalis may enhance the bio-oil yield as reported by Wang et. al. [77], as well as promote cracking of long-chain molecules into smaller gas molecules. This effect is attributed to the presence of alkaline and alkaline earth salts, which act as catalysts for the cracking process. The XRD analysis of the biochar indicated the presence of KOH and its salts, which may have contributed to the observed yields. Figure 14 depicts the data in chart form. The yield of biochar increases linearly with increasing solution molarity, and root-mean-square error (r^2) of 0.99, while that of gas increases exponentially, and a root-mean-square error (r^2) of 1.00, showing that higher molarities favor gas production. The results show that bio-oil yields tend to increase and reach a plateau around 1.0 M, physical-chemical analysis, though, show that acidity is heavily lowered when using 2.0M and higher amounts of water are obtained, indicating that mechanism of basic pre-treatment on biomass pyrolysis further deoxygenates the bio-oil, trapping oxygenates in water and bio-char phases.

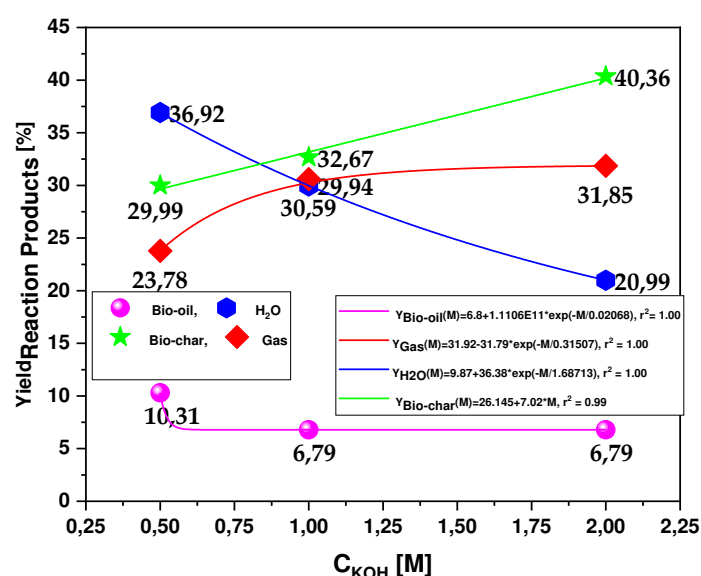


Figure 14. Yield of reaction products (bio-oil, H₂O, biochar, gas) by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH, in laboratory scale.

3.2.2.1. Effect of molarity in chemical composition of bio-oil

Figure 15 demonstrates the effect of different molarities of KOH solution on the concentration of hydrocarbons and oxygenates in the bio-oil produced by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart) at 450 °C, 1.0 atmosphere, in laboratory scale.

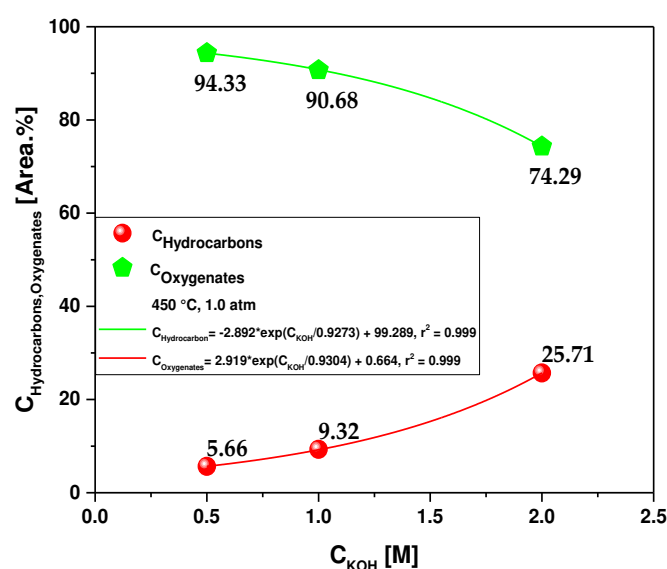


Figure 15. Concentrations of hydrocarbons and oxygenates in bio-oil obtained by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart) at 450 °C, 1.0 atmosphere, using different KOH concentration (0.5-2.0 M).

Supplementary Tables S7-S8 display the chemical functions, sum of peak areas, CAS numbers, and retention times of all the molecules identified in the aqueous phase by GC-MS during the pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), activated with 0.5 M and 1.0 M KOH solutions, at 450 °C, 1.0 atmosphere, in laboratory scale. The concentrations of hydrocarbons, including alkanes, alkenes, aromatics, and cyclic hydrocarbons, increase with molarity and follow a first-order exponential growth model, while those of oxygenates, including alcohols, amine, carboxylic acids,

phenols, ketones, furans, and others, decrease with molarity and follow a first-order exponential decay model. The results are consistent with those of de Castro [78], who studied the pyrolysis of Açaí seeds at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M NaOH, in pilot scale, respectively, and observed that higher NaOH solution molarities favored the formation of hydrocarbons. Both the hydrocarbons and oxygenates concentrations were found to have a high correlation, as evidenced by their root-mean-square error (r^2) values of 0.999.

Figure 16 demonstrates the acid value (acidity) of bio-oils obtained from the pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart) that were activated with 2.0 M KOH solution at 450 °C and 1.0 atmosphere, as well as activated with 0.5 M, 1.0 M, and 2.0 M KOH solutions in laboratory scale. The data indicates that the acidity of the bio-oil decreases as the molarity of the KOH solution increases, following a sharp exponential decay pattern. The acid value of the bio-oil ranged from 113.7 to 12.3 (mgKOH/g) and can be correlated with a first-order exponential decay model, with an r^2 value of 0.999. This finding aligns with the results presented in Figure 14, suggesting that higher concentrations of hydrocarbons in the bio-oil lead to lower acidity.

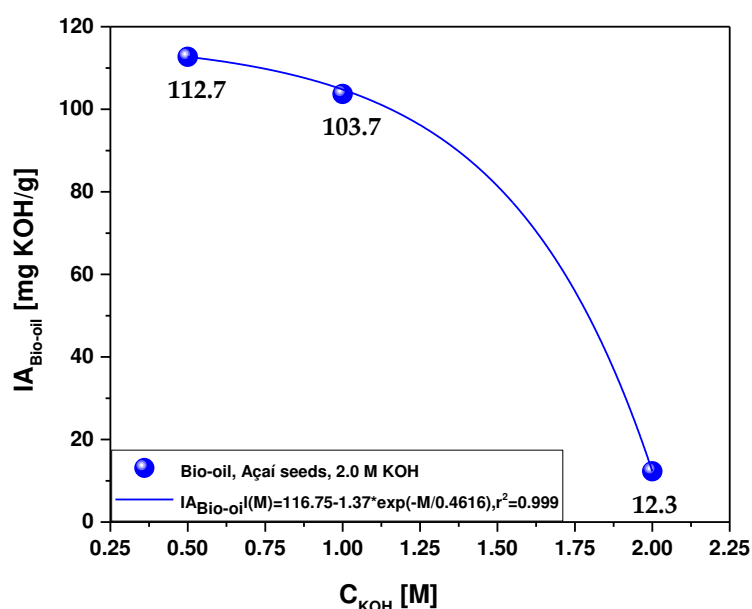


Figure 16. Acidity of bio-oil obtained by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart) at 450 °C, 1.0 atmosphere, using different KOH concentration (0.5-2.0 M).

3.2.2.2. Effect of molarity on antioxidant activity of the bio-oil

Table 5 shows the antioxidant capacity of bio-oils produced by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), with different molarity (0.5-2.0 M KOH solution), at 450 °C, 1.0 atmosphere, on a laboratory scale, and data depicted graphically in Figure 17. Data clearly show that the bio-oil produced by pyrolysis of 0.5 and 1.0 M of KOH solutions of 450°C exhibited higher antioxidant activity compared to the bio-oils produced at 2.0 M of KOH solution. These findings indicate that the high antioxidant activity of the bio-oil from residual açai seeds found at lower molarities of KOH solution (0.5 and 1.0 M) is associated with an increased formation of oxygenated compounds under these conditions, particularly phenolic compounds, which accounts for 94.33 (area.%) of the oxygenated compounds at this molarities, as shown in Figure 15. In this context, our previous study also demonstrated that alkali activation of residual açai seeds during pyrolysis for bio-oil production altered the yield, content of hydrocarbons and oxygenates, acidity, as well as the chemical composition of the bio-oil [31].

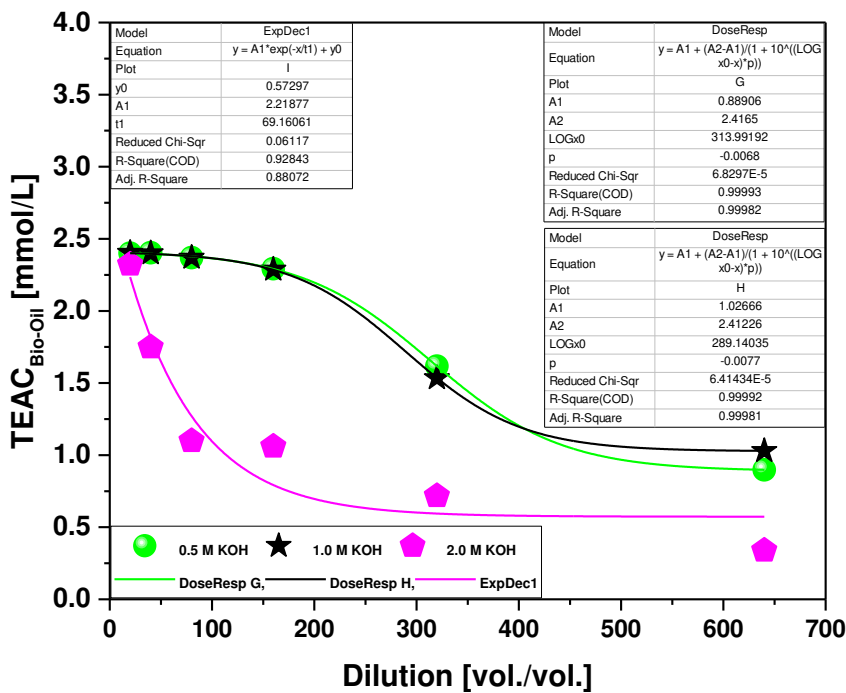


Figure 17. Total antioxidant capacity in the bio-oil produced by the pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart) with different molarity (0.5-2 M KOH solution), at a temperature of 450° C.

Table 05. Antioxidant capacity of bio-oils by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), with different molarity (0.5-2.0 M KOH solution), at 450° C.

Dilution	TEAC (mmol/L) 450 °C		
	0.5 M KOH	1.0 M KOH	2.0 M KOH
1:20	2.40	2.40	2.32
1:40	2.40	2.40	1.74
1:80	2.37	2.37	1.33
1:160	2.29	2.29	1.05
1:320	1.62	1.53	0.71
1:640	0.90	1.03	0.33

4. Conclusions

The X-ray diffraction (XRD) analysis of biochar derived from the pyrolysis of activated Açai seeds treated with 2.0 M KOH solution at 350, 400, and 450 °C and 1.0 atm in a laboratory scale indicates that Kalicinite (KHCO3) is the dominant crystalline phase present. The yield of bio-oil increases smoothly as the pyrolysis temperature rises, and this increase can be correlated with a first-order exponential decay model. The concentration of hydrocarbons, particularly acyclic saturated/unsaturated hydrocarbons and heterocyclic hydrocarbons, in the bio-oil also increases with temperature, while the concentration of oxygenates (such as cresols, phenols, and ketones) decreases. This suggests that higher pyrolysis temperatures promote the formation of hydrocarbons while suppressing the formation of oxygenates. The significant reduction in oxygenate concentration leads to a sharp decrease in bio-oil acidity from 257.6 to 12.3 (mgKOH/g) as the temperature increases. The aqueous phase generated during the pyrolysis of activated Açai seeds contains carboxylic acids, ketones, alcohols, phenols, and other compounds. The acidity of the aqueous phase decreases sharply

with temperature, mainly due to the decreased concentration of ketones. The yields of biochar increase linearly with higher molarities of the KOH solution, while the yields of gas and solid phase (biochar) increase exponentially and linearly, respectively, with increasing molarity. Higher molarities of the KOH solution favors the production of gas and bio-char. At 450 °C and 1.0 atm, the concentration of hydrocarbons in the bio-oil increases exponentially with the molarity of the KOH solution, while the concentration of oxygenates decreases exponentially. Moreover, the acidity of the bio-oil decreases sharply with increasing molarity, exhibiting a sharp exponential decay behavior. These findings are consistent with similar studies reported in the literature [71-73].

Supplementary Materials: The following are available. Table S1: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350 °C, 1.0 atmosphere, in laboratory scale. Table S2: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 400 °C, 1.0 atmosphere, in laboratory scale. Table S3: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 450 °C, 1.0 atmosphere, in laboratory scale. Table S4: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in aqueous phase by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350 °C, 1.0 atmosphere, in laboratory scale. Table S5: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in aqueous phase by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 400 °C, 1.0 atmosphere, in laboratory scale. Table S6: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in aqueous phase by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 450 °C, 1.0 atmosphere, in laboratory scale. Table S7: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 0.5 M KOH solution, at 450 °C, 1.0 atmosphere, in laboratory scale. Table S8: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 1.0 M KOH solution, at 450 °C, 1.0 atmosphere, in laboratory scale.

Author Contributions: The individual contributions of all the co-authors are provided as follows: F.P.V. contributed with formal analysis and writing original draft preparation, investigation and methodology, K.C.A.B. contributed with investigation and methodology, F.P.d.C.A. contributed with investigation and methodology, L.P.B. contributed with formal analysis, investigation and methodology, S.P.A.d.P. contributed with investigation and methodology, M.C.S. contributed with chemical analysis and methodology, W.P.F. contributed with physicochemical analysis and methodology, R.M.P.S. contributed with chemical analysis and methodology, N.M.M. contributed with resources and chemical analysis, D.A.R.d.C. contributed with investigation and methodology, S.D.J. contributed with resources and chemical analysis, A.R.Q.G. contributed with investigation and methodology, V.R.C.S. contributed with chemical analysis and methodology, M.C.M. contributed with investigation, methodology, data curation and writing original draft preparation and N.T.M. contributed with supervision, conceptualization, and data curation. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Andrezza de Melo Barbosa, Viviane Siqueira Magalhães Rebelo, Lucieta Guerreiro Martorano, Virginia Mansanares Giacon. Caracterização de partículas de açaí visando seu potencial uso na construção civil. revista Matéria, v.24, n.3, 2019, ISSN 1517-7076 artigo e-12435

2. Felipe Fernando da Costa Tavares, Marcos Danilo Costa de Almeida, João Antonio Pessoa da Silva, Ludmila Leite Araújo, Nilo Sérgio Medeiros Cardozo and Ruth Marlene Campomanes Santana. Thermal treatment of açaí (*Euterpe oleracea*) fiber for composite reinforcement. *Polímeros*, 30(1), e2020003, 2020, <https://doi.org/10.1590/0104-1428.09819>
3. D.R. Pompeu, E.M. Silva, H. Rogez. Optimisation of the solvent extraction of phenolic antioxidants from fruits of *Euterpe oleracea* using Response Surface Methodology. *Bioresource Technology* 100 (2009) 6076–6082, <https://doi.org/10.1016/j.biortech.2009.03.083>
4. Marcelo Morita Lindolfo, Gilson Sérgio Bastos de Matos, Wendel Valter da Silveira Pereira, Antonio Rodrigues Fernandes. Productivity and nutrition of fertigated açaí palms according to boron fertilization. *Rev. Bras. Frutic., Jaboticabal*, 2020, v. 42, n. 2: (e-601)
5. Michael Heinrich, Tasleem Dhanji, Ivan Casselman. Açaí (*Euterpe oleracea* Mart.) – A phytochemical and phar-macological assessment of the species' health claims. *Phytochemistry Letters* 4 (2011) 10–21
6. Sara Sabbe, Wim Verbeke, Rosires Deliza, Virginia Matta, Patrick Van Damme. Effect of a health claim and personal characteristics on consumer acceptance of fruit juices with different concentrations of açaí (*Euterpe oleracea* Mart.). *Appetite* 53 (2009) 84–92
7. DAVID DEL POZO-INSFRAN, SUSAN S. PERCIVAL, AND STEPHEN T. TALCOTT. Açaí (*Euterpe oleracea* Mart.) Polyphenolics in Their Glycoside and Aglycone Forms Induce Apoptosis of HL-60 Leukemia Cells. *J. Agric. Food Chem.* 2006, 54, 1222–1229
8. D. A. R. de Castro; H. J. da Silva Ribeiro; C. C. Ferreira; L. H. H. Guerreiro; M. de Andrade Cordeiro; A. M. Pereira; W. G. dos Santos; F. B. de Carvalho; J. O. C. Silva Jr.; R. Lopes e Oliveira; M. C. Santos; S. Duvoisin Jr; L. E. P. Borges; N. T. Machado. Fractional Distillation of Bio-Oil Produced by Pyrolysis of Açaí (*Euterpe oleracea*) Seeds. Fractionation, Editor Hassan Al-Haj Ibrahim: Fractionation, Intechopen ISBN: 978-1-78984-965-3, DOI: 10.5772/intechopen.79546
9. Lauro Henrique Hamoy Guerreiro, Ana Cláudia Fonseca Baia, Fernanda Paula da Costa Assunção, Gabriel de Oliveira Rodrigues, Rafael Lopes e Oliveira, Sergio Duvoisin Junior, Anderson Mathias Pereira, Erika Milene Pinto de Sousa, Nélío Teixeira Machado, Douglas Alberto Rocha de Castro and Marcelo Costa Santos. Investigation of the Adsorption Process of Biochar Açaí (*Euterpea olerácea* Mart.) Seeds Produced by Pyrolysis. *Energies* 2022, 15, 6234. <https://doi.org/10.3390/en15176234>
10. Bufalino, L.; Guimaraes, A.A.; de Silva, B.M.; de Souza, R.L.F.; de Melo, I.C.N.A.; de Oliveira, D.N.P.S.; Trugilho, P.F. Local variability of yield and physical properties of açaí waste and improvement of its energetic attributes by separation of lignocellulosic fibers and seeds. *J. Renew. Sustain. Energy* 2018, 10, 053102
11. Douglas Alberto Rocha de Castro, Haroldo Jorge da Silva Ribeiro, Lauro Henrique Hamoy Guerreiro, Lucas Pinto Bernar, Sami Jonatan Bremer, Marcelo Costa Santo, Hélio da Silva Almeida, Sergio Duvoisin, Jr., Luiz Eduardo Pizarro Borges and Nélío Teixeira Machado. Production of Fuel-Like Fractions by Fractional Distillation of Bio-Oil from Açaí (*Euterpe oleracea* Mart.) Seeds Pyrolysis. *Energies* 2021, 14, 3713. <https://doi.org/10.3390/en14133713>
12. Conceição de Maria Sales da Silva, Douglas Alberto Rocha de Castro, Marcelo Costa Santos, Hélio da Silva Almeida, Maja Schultze, Ulf Lüder, Thomas Hoffmann and Nélío Teixeira Machado. Process Analysis of Main Organic Compounds Dissolved in Aqueous Phase by Hydrothermal Processing of Açaí (*Euterpe oleraceae*, Mart.) Seeds: Influence of Process Temperature, Biomass-to-Water Ratio, and Production Scales. *Energies* 2021, 14, 5608. <https://doi.org/10.3390/en14185608>
13. Anna Cristina Pinheiro de Lima, Dandara Leal Ribeiro Bastos, Mariella Alzamora Camarena, Elba Pinto Silva Bom, Magali Christe Cammarota, Ricardo Sposina Sobral Teixeira, Melissa Limoeiro Estrada Gutarra. Physicochemical characterization of residual biomass (seed and fiber) from açaí (*Euterpe oleracea*) processing and assessment of the potential for energy production and bioproducts. *Biomass Conv. Bioref.* (2021) 11:925–935
14. Fassinou Wagnon Ferdinand, Laurent Van de Steene, Koua Kamenan Blaise, Toure Siaka. Prediction of pyrolysis oils higher heating value with gas chromatography–mass spectrometry. *Fuel* 96 (2012) 141–145
15. Bernar, L.P.; Ferreira, C.C.; Costa, A.F.d.F.; Ribeiro, H.J.d.S.; dos Santos, W.G.; Pereira, L.M.; Pereira, A.M.; Moraes, N.L.; Assunção, F.P.d.C.; Mota, S.A.P.d.; et al. Catalytic Upgrading of Residual Fat Pyrolysis Vapors over Activated Carbon Pellets into Hydrocarbons-like Fuels in a Two-Stage Reactor: Analysis of Hydrocarbons Composition and Physical-Chemistry Properties. *Energies* 2022, 15, 4587. <https://doi.org/10.3390/en15134587>
16. Ferreira, C.C.; Bernar, L.P.; de Freitas Costa, A.F.; da Silva Ribeiro, H.J.; Santos, M.C.; Moraes, N.L.; Costa, Y.S.; Baia, A.C.F.; Mendonça, N.M.; da Mota, S.A.P.; et al. Improving Fuel Properties and Hydrocarbon Content from Residual Fat Pyrolysis Vapors over Activated Red Mud Pellets in Two-Stage Reactor: Optimization of Reaction Time and Catalyst Content. *Energies* 2022, 15, 5595. <https://doi.org/10.3390/en15155595>
17. M.K. Sato, H.V. de Lima, A.N. Costa, S. Rodrigues, A.J.S. Pedroso, C.M.B. de Freitas Maia. Biochar from Acai agroindustry waste: study of pyrolysis conditions. *Waste Manag.*, 96 (2019), pp. 158-167

18. Michel Keisuke Sato, Herdjanía Veras de Lima, Aline Noronha Costa, Sueli Rodrigues, Sacha J. Mooney, Michèle Clarke, Augusto José Silva Pedroso, Claudia Maria Branco de Freitas Maia. Biochar as a sustainable alternative to ac, aí waste disposal in Amazon, Brazil. *Process Safety and Environmental Protection* 139 (2020) 36–46
19. Leandro Rodriguez Ortiz, Erick Torres, Daniela Zalazar, Huili Zhang, Rosa Rodriguez, German Mazza. Influence of pyrolysis temperature and bio-waste composition on biochar characteristics. *Renewable Energy* 155 (2020) 837e847
20. Leandro S. Queiroz, Luiz K.C. de Souza, Kelly Taise C. Thomaz, Erika Tallyta Leite Lima, Geraldo N. da Rocha Filho, Luis Adriano S. do Nascimento, Luiza H. de Oliveira Pires, Kelson do Carmo Freitas Faial, Carlos E.F. da Costa. Activated carbon obtained from amazonian biomass tailings (acai seed): Modification, characterization, and use for removal of metal ions from water. *Journal of Environmental Management* 270 (2020) 110868
21. T.S. Pessôa, L.E. de Lima Ferreira, M.P. da Silva, L.M. Pereira Neto, B.F. do Nascimento, T.J.M. Fraga, E.F. Jaguaribe, J.V. Cavalcanti, M.A. da Motta Sobrinho. Açai waste benefiting by gasification process and its employment in the treatment of synthetic and raw textile wastewater. *J. Clean. Prod.*, 240 (2019), p. 118047
22. Danilo Gualberto Zavarize. Insights on preparation and characteristics of KOH-doped carbons derived from an abundant agroindustrial waste in Brazil: Amazon açai berry seeds. *Bioresource Technology Reports* 13 (2021) 100611
23. De Souza, L.K.C., Gonçalves, A.A.S., Queiroz, L.S., Chaar, J.S., da Rocha Filho, G.N., da Costa, C.E.F., 2020a. Utilization of acai stone biomass for the sustainable production of nanoporous carbon for CO₂ capture. *SM&T*, e00168. <https://doi.org/10.1016/j.susmat.2020.e00168>
24. De Souza, T.N.V., Vieira, M.G.A., da Silva, M.G.C., Brasil, D. do S.B., de Carvalho, S.M.L., 2019. H₃PO₄-activated carbons produced from açai stones and Brazil nut shells: removal of basic blue 26 dye from aqueous solutions by adsorption. *Environmental Science and Pollution Research*, <https://doi.org/10.1007/s11356-019-04215-0>
25. Araujo, R.O., Chaar, J. da S., Queiroz, L.S., da Rocha Filho, G.N., da Costa, C.E.F., da Silva, G.C.T., Landers, R., Costa, M.J.F., Gonçalves, A.A.S., de Souza, L.K.C., 2019. Low temperature sulfonation of acai stone biomass derived carbons as acid catalysts for esterification reactions. *Energy Convers. Manag.* 196, 821–830. <https://doi.org/10.1016/j.enconman.2019.06.059>
26. De Souza, T.N.V., de Carvalho, S.M.L., Vieira, M.G.A., da Silva, M.G.C., Brasil, D. do S.B., 2018. Adsorption of basic dyes onto activated carbon: experimental and theoretical investigation of chemical reactivity of basic dyes using DFT-based descriptors. *Appl.Surf. Sci.* 448, 662–670. <https://doi.org/10.1016/j.apsusc.2018.04.087>
27. Do Nascimento, B.F., de Araujo, C.M.B., do Nascimento, A.C., da Silva, F.L.H., de Melo, D.J.N., Jaguaribe, E.F., Lima Cavalcanti, J.V.F., da Motta Sobrinho, M.A., 2020. Detoxification of sisal bagasse hydrolysate using activated carbon produced from the gasification of açai waste. *J. Hazard. Mater.* 124494 <https://doi.org/10.1016/j.jhazmat.2020.124494>
28. Ribeiro, L.A. de S., Thim, G.P., Alvarez-Mendez, M.O., dos Reis Coutinho, A., de Moraes, N.P., Rodrigues, L.A., 2018. Preparation, characterization, and application of low-cost açai seed-based activated carbon for phenol adsorption. *Int. J. Environ. Res.* 12, 755–764. <https://doi.org/10.1007/s41742-018-0128-5>
29. De Souza, L.K.C., Martins, J.C., Oliveira, D.P., Ferreira, C.S., Gonçalves, A.A.S., Araujo, R.O., da Silva Chaar, J., Costa, M.J.F., Sampaio, D.V., Passos, R.R., Pocrifka, L.A., 2020b. Hierarchical porous carbon derived from acai seed bio-waste for supercapacitor electrode materials. *J. Mater. Sci. Mater. Electron.* 31, 12148–12157. <https://doi.org/10.1007/s10854-020-03761-5>
30. Alisson Caio Magalhães Serrão, Conceição Maria Sales Silva, Fernanda Paula da Costa Assunção, Haroldo Jorge da Silva Ribeiro, Marcelo Costa Santos, Hélio da Silva Almeida, Sergio Duvoisin Jr., Luiz Eduardo Pizarro Borges, Douglas Alberto Rocha de Castro, Nélío Teixeira Machado. Process analysis of pyrolysis of Açai (*Euterpe Oleracea*, Mart) seeds: Influence of temperature on the yield of reaction products and physico-chemical properties of Bio-Oil. *Brazilian Journal of Development*, Curitiba, v.7, n.2, p.18200-18220feb. 2021, <http://doi.org/10.34117/bjdv7n2-453>
31. Daniel Valdez, G.; Valois, F.P.; Bremer, S.J.; Bezerra, K.C.A.; Hamoy Guerreiro, L.H.; Santos, M.C.; Bernar, L.P.; Feio, W.P.; Moreira, L.G.S.; Mendonça, N.M.; et al. Improving the Bio-Oil Quality of Residual Biomass Pyrolysis by Chemical Activation: Effect of Alkalis and Acid Pre-Treatment. *Energies* 2023, 16, 3162. <https://doi.org/10.3390/en16073162>
32. Jordy Lima de Sousa, Lauro Henrique Hamoy Guerreiro, Lucas Pinto Bernar, Haroldo Jorge da Silva Ribeiro, Rafael Lopes e Oliveira, Marcelo Costa Santos, Hélio da Silva Almeida, Sergio Duvoisin Jr., Luiz Eduardo Pizarro Borges, Douglas Alberto Rocha de Castro, Nélío Teixeira Machado. Chemical Analysis of Bio-Oil Produced by Pyrolysis of Açai (*Euterpe Oleracea*, Mart) Seeds. *Brazilian Journal of Development*, Curitiba, v.7, n.2, p. 15549-15565feb. 2021, <http://doi.org/10.34117/bjdv7n2-261>
33. Sriraam R. Chandrasekaran, Dheeptha Murali, Karen A. Marley, Richard A. Larson, Kenneth M. Doll, Bryan R. Moser, John Scott, and Brajendra K. Sharma. Antioxidants from Slow Pyrolysis Bio-Oil of Birch

- Wood: Application for Biodiesel and Biobased Lubricants. ACS Sustainable Chemistry & Engineering 2016 4 (3), 1414-1421, <http://doi.org/10.1021/acssuschemeng.5b01302>
34. Del Pozo C, Bartrolí J, Alíer S, Puy N, Fàbregas E. Production of antioxidants and other value-added compounds from coffee silver skin via pyrolysis under a biorefinery approach. Waste Manag. 2020 May 15;109:19-27. <http://doi.org/10.1016/j.wasman.2020.04.044>
 35. Patra JK, Kim SH, Hwang H, Choi JW, Baek KH. Volatile compounds and antioxidant capacity of the bio-oil obtained by pyrolysis of Japanese red pine (pinus densiflora siebold and zucc.). Molecules. 2015 Mar 2;20(3):3986-4006. <http://doi.org/10.3390/molecules20033986>
 36. Dionisio Malagón-Romero, Andres C. Torres-Velasquez, Lizeth K. Tinoco Navarro & Juan P. Arrubla-Vélez (2023). Pyrolysis of Colombian spent coffee grounds (SCGs), characterization of bio-oil, and study of its antioxidant properties. International Journal of Sustainable Energy, 42:1, 811-829, DOI: 10.1080/14786451.2023.2235025
 37. Hossain, M.M., Scott, I.M., Berruti, F. et al. Application of Novel Pyrolysis Reactor Technology to Concentrate Bio-oil Components with Antioxidant Activity from Tobacco, Tomato and Coffee Ground Biomass. Waste Biomass Valor 9, 1607–1617 (2018). <https://doi.org/10.1007/s12649-017-9943-8>
 38. Patra, J.K.; Kim, S.H.; Hwang, H.; Choi, J.W.; Baek, K.-H. Volatile Compounds and Antioxidant Capacity of the Bio-Oil Obtained by Pyrolysis of Japanese Red Pine (Pinus Densiflora Siebold and Zucc.). Molecules 2015, 20, 3986-4006. <https://doi.org/10.3390/molecules20033986>
 39. Cristina del Pozo, Jordi Bartrolí, Santi Alíer, Neus Puy, Esteve Fàbregas. Production, identification, and quantification of antioxidants from torrefaction and pyrolysis of grape pomace. Fuel Processing Technology 211 (2021) 106602, <https://doi.org/10.1016/j.fuproc.2020.106602>
 40. Aihui Chen; Xifeng Liu; Haibin Zhang; Hao Wu; Dong Xu; Bo Li; Chenxi Zhao. Influence of pyrolysis temperature on bio-oil produced from hazelnut shells: Physico-chemical properties and antioxidant activity of wood vinegar and tar fraction featured. Journal of Renewable and Sustainable Energy 13, 043102 (2021), <https://doi.org/10.1063/5.0051944>
 41. de Andrade Cordeiro, M.; de Almeida, O.; de Castro, D.A.R.; da Silva Ribeiro, H.J.; Machado, N.T. Produção de Etanol através da Hidrólise Enzimática do Caroço de Açaí (Euterpe oleracea, Mart.). Rev. Bras. Energ. Renov. 2019, 8, 122–152
 42. H. da Silva Almeida, O.A. Corrêa, J.G. Eid, H.J. Ribeiro, D.A.R. de Castro, M.S. Pereira, L.M. Pereira, A. de Andrade Mâncio, M.C. Santos, J.A. da Silva Souza, Luiz E.P. Borges, N.M. Mendonça, N.T. Machado. Production of biofuels by thermal catalytic cracking of scum from grease traps in pilot scale. Journal of Analytical and Applied Pyrolysis 118 (2016) 20–33
 43. H. da Silva Almeida, O.A. Corrêa, J.G. Eid, H.J. Ribeiro, D.A.R. de Castro, M.S. Pereira, L.M. Pereira, A. de Andrade Mâncio, M.C. Santos, S.A.P. da Mota, J.A. da Silva Souza, Luiz E.P. Borges, N.M. Mendonça, N.T. Machado. Performance of thermochemical conversion of fat, oils, and grease into kerosene-like hydrocarbons in different production scales. Journal of Analytical and Applied Pyrolysis 120 (2016) 126–143
 44. H. da Silva Almeida, O.A. Corrêa, C.C. Ferreira, H.J. Ribeiro, D.A.R. de Castro, M.S. Pereira, A. de Andrade Mâncio, M.C. Santos, S.A.P. da Mota, J.A. da Silva Souza, Luiz E.P. Borges, N.M. Mendonça, N.T. Machado. Diesel-like hydrocarbon fuels by catalytic cracking of fat, oils, and grease (FOG) from grease traps. Journal of the Energy Institute 90 (2017) 337-354
 45. S.A.P. da Mota, A.A. Mancio, D.E.L. Lhamas, D.H. de Abreu, M.S. da Silva, W.G. dos Santos, D.A.R. de Castro, R.M. de Oliveira, M.E. Araújo, Luiz E.P. Borges, N.T. Machado. Production of green diesel by thermal catalytic cracking of crude palm oil (Elaeis guineensis Jacq) in a pilot plant. Journal of Analytical and Applied Pyrolysis 110 (2014) 1–11
 46. Miller, N.; Rice-Evans, C.; Davies, M.; Gopinathan, V.; Milner, A. A novel method for measuring antioxidant capacity and its application to monitoring the antioxidant status in premature neonates. Clin Sci. 1993, 84: 407-412.
 47. Re, R.; Pellegrini, R.; Proteggente, A.; Pannala, A.; Yang, M.; Rice-Evans, C. Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Rad Biol Med. 1999, 26:1231-1237.
 48. A.A. Mancio, S.A.P. da Mota, C.C. Ferreira, T.U.S. Carvalho, O.S. Neto, J.R. Zamian, M.E. Araújo, L.E.P. Borges, N.T. Machado. Separation and characterization of biofuels in the jet fuel and diesel fuel ranges by fractional distillation of organic liquid products. Fuel 215 (2018) 212–225
 49. A.A. Mâncio, K.M.B. da Costa, C.C. Ferreira, M.C. Santos, D.E.L. Lhamas, S.A.P. da Mota, R.A.C. Leão, R.O.M.A. de Souza, M.E. Araújo, L.E.P. Borges, N.T. Machado. Process analysis of physicochemical properties and chemical composition of organic liquid products obtained by thermochemical conversion of palm oil. Journal of Analytical and Applied Pyrolysis 123 (2017) 284–295
 50. M.C. Santos, R.M. Lourenço, D.H. de Abreu, A.M. Pereira, D.A.R. de Castro, M.S. Pereira, H.S. Almeida, A.A. Mâncio, D.E.L. Lhamas, S.A.P. da Mota, J.A. da Silva Souza, S.D. Júnior, M.E. Araújo, L.E.P. Borges, N.T. Machado. Gasoline-like hydrocarbons by catalytic cracking of soap phase residue of neutralization

- process of palm oil (*Elaeis guineensis* Jacq). Journal of the Taiwan Institute of Chemical Engineers 71 (2017) 106–119
51. C.C. Ferreira, E.C. Costa, D.A.R. de Castro, M.S. Pereira, A.A. Mâncio, M.C. Santos, D.E.L. Lhamas, S.A.P. da Mota, A.C. Leão, S. Duvoisin, M.E. Araújo, Luiz E.P. Borges, N.T. Machado. Deacidification of organic liquid products by fractional distillation in laboratory and pilot scales. Journal of Analytical and Applied Pyrolysis, 127 (2017) 468-489, <https://doi.org/10.1016/j.jaap.2017.06.016>
 52. Costa, M.E.G.; da Costa Assunção, F.P.; Teribele, T.; Pereira, L.M.; de Castro, D.A.R.; Santo, M.C.; da Costa, C.E.F.; Shultze, M.; Hofmann, T.; Machado, N.T. Characterization of Bio-Adsorbents Produced by Hydrothermal Carbonization of Corn Stover: Application on the Adsorption of Acetic Acid from Aqueous Solutions. Energies 2021, 14, 8154. <https://doi.org/10.3390/en14238154>
 53. Teribele, T.; Costa, M.E.G.; Sales da Silva, C.d.M.; Pereira, L.M.; Bernar, L.P.; de Castro, D.A.R.; da Costa Assunção, F.P.; Santos, M.C.; de Sousa Brandão, I.W.; Fonseca, C.J.N.; et al. Hydrothermal Carbonization of Corn Stover: Structural Evolution of Hydro-Char and Degradation Kinetics. Energies 2023, 16, 3217. <https://doi.org/10.3390/en16073217>
 54. de Freitas Costa, A.F.; Ferreira, C.C.; da Paz, S.P.A.; Santos, M.C.; Moreira, L.G.S.; Mendonça, N.M.; da Costa Assunção, F.P.; de Freitas, A.C.G.d.A.; Costa, R.M.R.; de Sousa Brandão, I.W.; et al. Catalytic Upgrading of Plastic Waste of Electric and Electronic Equipment (WEEE) Pyrolysis Vapors over Si–Al Ash Pellets in a Two-Stage Reactor. Energies 2023, 16, 541. <https://doi.org/10.3390/en16010541>
 55. Assunção, F.P.d.C.; Pereira, D.O.; Silva, J.C.C.d.; Ferreira, J.F.H.; Bezerra, K.C.A.; Bernar, L.P.; Ferreira, C.C.; Costa, A.F.d.F.; Pereira, L.M.; Paz, S.P.A.d.; et al. A Systematic Approach to Thermochemical Treatment of Municipal Household Solid Waste into Valuable Products: Analysis of Routes, Gravimetric Analysis, Pre-Treatment of Solid Mixtures, Thermochemical Processes, and Characterization of Bio-Oils and Bio-Adsorbents. Energies 2022, 15, 7971. <https://doi.org/10.3390/en15217971>
 56. Nattaporn Prakongep, Robert J. Gilkes and Wanpen Wiriyaakitnatekul. Agronomic benefits of durian shell biochar. J. Met. Mater. Miner. 24(1)2014, <https://doi.org/10.14456/jmmm.2014.2>
 57. Jeong Han Lee, Young Lok Cha, Yong-Mook Kang, and Kwang Chul Roh. Study on the reaction mechanism of the potassium bicarbonate alkali activation process in black liquor. APL Mater. 10, 101105 (2022); <https://doi.org/10.1063/5.0104772>
 58. J. Díaz-Terán, D.M. Nevskaja, J.L.G. Fierro, A.J. López-Peinado, A. Jerez. Study of chemical activation process of a lignocellulosic material with KOH by XPS and XRD. Microporous and Mesoporous Materials, 60 (2003) 173-181, [https://doi.org/10.1016/S1387-1811\(03\)00338-X](https://doi.org/10.1016/S1387-1811(03)00338-X)
 59. Piyali Das, Anuradda Ganesh. Bio-oil from pyrolysis of cashew nutshell—a near fuel. Biomass and Bioenergy, Volume 25, Issue 1, July 2003, 113-117
 60. M. Asadullah; M. A. Rahman; M. M. Ali; M. S. Rahman; M. A. Motin; M. B. Sultan; M. R. Alam. Production of bio-oil from fixed bed pyrolysis of bagasse. Fuel Volume 86, Issue 16, November 2007, 2514-2520
 61. Zheng Ji-lu. Bio-oil from fast pyrolysis of rice husk: Yields and related properties and improvement of the pyrolysis system. J. Anal. Appl. Pyrolysis 80 (2007) 30–35
 62. Mohamad Azri Sukiran, Chow Mee Chin, Nor Kartini Abu Bakar. Bio-oils from Pyrolysis of Oil Palm Empty Fruit Bunches. American Journal of Applied Sciences 6 (5): 869-875, 2009
 63. Seon-Jin Kim, Su-Hwa Jung, Joo-Sik Kim. Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. Bioresource Technology, Volume 101, Issue 23, December 2010, 9294-930
 64. Gaurav Kumar, Achyut K. Panda, R. K. Singh. Optimization of process for the production of bio-oil from eucalyptus wood. J Fuel Chem Technol, 2010, 38(2), 162-167
 65. Hyeon Su Heo, Hyun Ju Park, Jong-In Dong, Sung Hoon Park, Seungdo Kim, Dong Jin Suh, Young-Woong Suh; Seung-Soo Kim, Young-Kwon Park. Fast pyrolysis of rice husk under different reaction conditions. Journal of Industrial and Engineering Chemistry, Volume 16, Issue 1, 25 January 2010, 27-31
 66. John V. Ortega, Andrew M. Renahan, Matthew W. Liberatore, Andrew M. Herring. Physical and chemical characteristics of aging pyrolysis oils produced from hardwood and softwood feedstocks. Journal of Analytical and Applied Pyrolysis, Volume 91, Issue 1, May 2011, 190-198
 67. Rajeev Sharma, Pratik N. Sheth. Thermo-Chemical Conversion of Jatropha Deoiled Cake: Pyrolysis vs. Gasification. International Journal of Chemical Engineering and Applications, Vol. 6, No. 5, October 2015
 68. Chaturong Paenpong; Adisak Pattiya. Effect of pyrolysis and moving-bed granular filter temperatures on the yield and properties of bio-oil from fast pyrolysis of biomass. Journal of Analytical and Applied Pyrolysis, Volume 119, May 2016, 40-51
 69. Rahul Garg, Neeru Anand, Dinesh Kumar. Pyrolysis of babool seeds (*Acacia nilotica*) in a fixed bed reactor and bio-oil characterization. Renewable Energy, Volume 96, Part A, October 2016, 167-171
 70. Anil Kumar Varma; Prasenjit Mondal. Pyrolysis of sugarcane bagasse in semi batch reactor: Effects of process parameters on product yields and characterization of products. Industrial Crops and Products 95 (2017) 704–717

71. Suping Zhang, Yongjie Yan, Tingchen Li, Zhengwei Ren. Upgrading of liquid fuel from the pyrolysis of biomass. *Bioresource Technology*, 96 (2005) 545-550, <https://doi.org/10.1016/j.biortech.2004.06.015>
72. Cristian Torri, Daniele Fabbri. Biochar enables anaerobic digestion of aqueous phase from intermediate pyrolysis of biomass. *Bioresource Technology*, 172 (2014) 335-341, <https://doi.org/10.1016/j.biortech.2014.09.021>
73. Haoqin Zhou, Robert C. Brown, Zhiyou Wen. Anaerobic digestion of aqueous phase from pyrolysis of biomass: Reducing toxicity and improving microbial tolerance. *Bioresource Technology*, 292 (2019) 121976, <https://doi.org/10.1016/j.biortech.2019.121976>
74. Albuquerque BR, Heleno SA, Oliveira MBPP, Barros L, Ferreira ICFR. Phenolic compounds: current industrial applications, limitations and future challenges. *Food Funct.* 2021 Jan 7;12(1):14-29. <http://doi.org/10.1039/d0fo02324h>
75. Espíndola KMM, Ferreira RG, Narvaez LEM, Silva Rosario ACR, da Silva AHM, Silva AGB, Vieira APO, Monteiro MC. Chemical and Pharmacological Aspects of Caffeic Acid and Its Activity in Hepatocarcinoma. *Front Oncol.* 2019 Jun 21;9:541. <http://doi.org/10.3389/fonc.2019.00541>
76. C. Caleja, A. Ribeiro, M. F. Barreiro and I. C. F. R. Ferreira, Phenolic compounds as nutraceuticals or functional food ingredients, *Curr. Pharm. Des.*, 2017, 23, 2787.
77. Xinde Wang, Shuai Leng, Jiaqi Bai, Hu Zhou, Xing Zhong, Guilin Zhuang and Jianguo Wang. Role of pretreatment with acid and base on the distribution of the products obtained via lignocellulosic biomass pyrolysis. *RSC Adv.*, 2015, 5, 24984–24989
78. Douglas Alberto Rocha de Castro. Tese de Doutorado: ESTUDO DO PROCESSO DE PIRÓLISE DE SEMENTES DE AÇAÍ (Eutero olerace Mart.) PARA PRODUÇÃO DE BIOCOMBUSTÍVEIS. PRODERNA/ITEC, UFPA, 2019. <https://proderna.propesp.ufpa.br/index.php/br/teses-e-dissertacoes/teses/273-2019>

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