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Article

Effect of temperature and molarity on the bio-oil yield and quality by pyrolysis of Açaí seeds (*Euterpe Oleraceae*, Mart.) activated with KOH

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Abstract: This study explores the impact of temperature and molarity in the pyrolysis of Açaí seeds (*Euterpe Oleraceae*, Mart.) activated with KOH on the yield of bio-oil, hydrocarbon content 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 physico-chemical property of fundamental importance in bio-fuels, of bio-oils and aqueous phases by AOCS methods. The solid phase (biochar) characterized by X-ray diffraction (XRD). The diffractograms identified the presence of Kalicinite ($KHCO_3$) in biochar, and those higher temperatures favor the formation peaks of Kalicinite ($KHCO_3$). 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. 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; Acidity, Liquid 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 agro-industry 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 CH_4, CO_2, 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 some research has been conducted on the pyrolysis of residual Açaí seeds [8, 11, 17-29], the majority 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, 20-29] and have involved chemical activation with NaOH [8, 21, 27], KOH [20, 22-29], H_3PO_4 [24, 26], HNO3 [20, 26], or physical activation with CO_2 [28-29]. However, to date, no systematic study has examined the effects of alkali activation of residual Açaí seeds on the yield, chemical composition, and acidity 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, data from different biomass pyrolysis feedstocks, reactors, and conditions are of great value in understanding and optimizing the process as a whole.

The objective of this study is to examine how temperature and chemical activation with alkalis affect the yield, hydrocarbon content, and acidity of bio-oil, as well as the chemical composition and acidity of the aqueous phase. This will be achieved by conducting pyrolysis on residual Açaí seeds at 350, 400, and 450 °C and 1.0 atmosphere. The residual Açaí seeds will be activated using aqueous solutions of 0.5 M, 1.0 M, and 2.0 M KOH on a laboratory scale.

2. Materials and Methods

2.1. Methodology

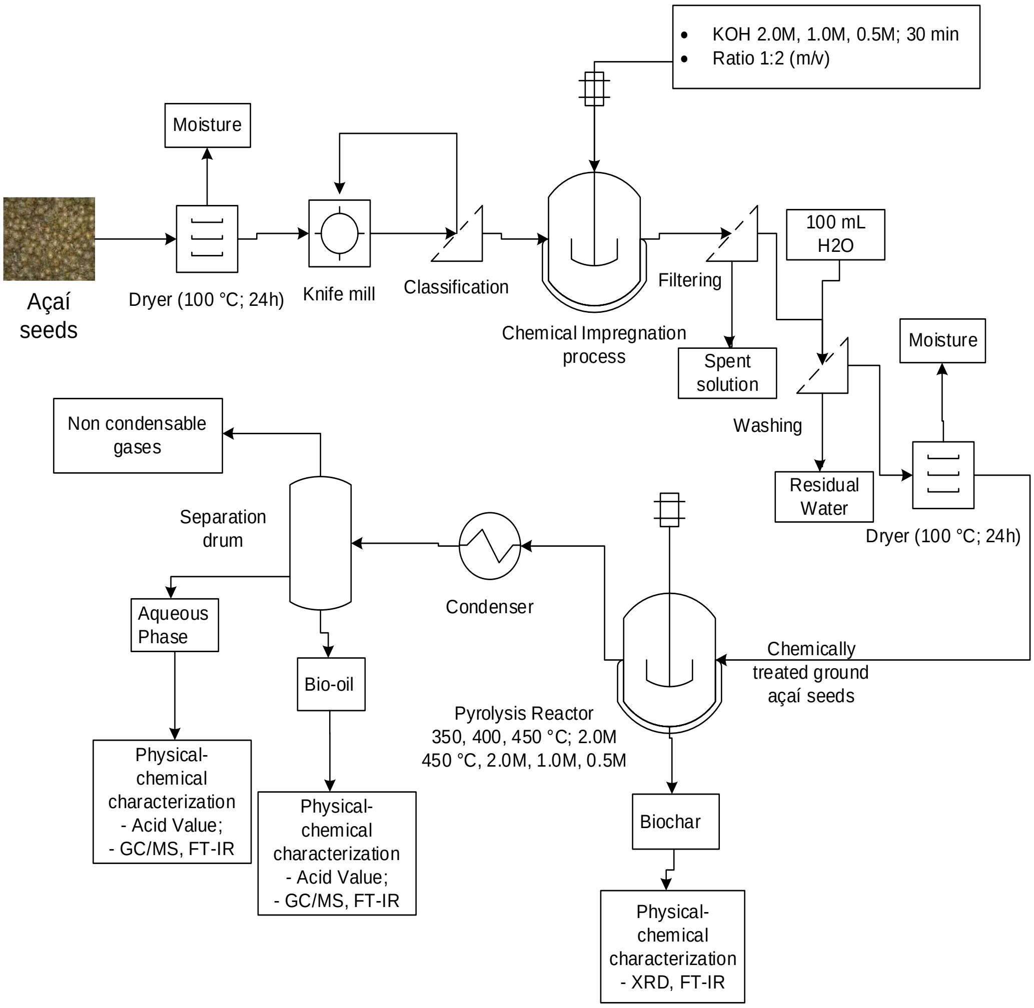

Figure 1. Process flow schema of bio-oil production by pyrolysis of Açaí seeds at 350, 400, and 450 °C, 1.0 atm, 2.0 M KOH, and 450 °C, 1.0 atm, 0.5 M, 1.0 M, and 2.0 M KOH, using a fixed bed reactor, in laboratory scale.

The applied methodology for producing bio-oil by pyrolysis of Açaí 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 Açaí 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 method is used to determine the acidity 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.

2.2. Materials

The seeds of Açaí (*Euterpe oleracea* Mart.), discharged/disposed on the sidewalks and streets by a small store of Açaí commercialization, located in the District of Jurunas, Belém-Pará-Brazil, were collected and stored in plastic bags. Figure 2 shows seeds of Açaí (*Euterpe oleracea,* Mart.) discharged on the sidewalks and streets by a small store of Açaí commercialization, located in District of Jurunas, Belém-Pará-Brazil.

Figure 2. Local biomass waste in the form of açaí seeds in Belém, Pará.

2.3. Pre-treatnent of Açaí seeds (Euterpe oleracea, Mart.)

The Seeds of Açaí (*Euterpe oleracea*, Mart.) were submitted to physical pre-treatments of natural and forced drying, grinding, and sieving. Afterwards, the dried, grinded and sieved seeds were activated chemically 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 Açaí seeds (*Euterpe oleracea*, Mart.)

The Açaí (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 Açaí 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. A charge of Açaí (*Euterpe oleracea*, Mart.) seeds *in nature* weighting approximately 5.0 kg was collected for the pyrolysis experiments. The drying, grinding and sieving of Açaí seeds in shown in Figure 3.

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

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

After the physical pre-treatment described in section 2.3.1, the dried, grinded and sieved Açaí seeds were activated chemically with 0.5 M, 1.0 M, and 2.0 M KOH solutions and the procedures described as follows: Approximately 60 g of dried, ground, and sieved Açaí seeds was mixed manually in a gentle manner with 120 mL of 0.5 M, 1.0 M, and 2.0 M HCl solutions (1:2 mass/volume ratio) for 30 minutes, using a Becker of 250 mL. The impregnation process was carried out in ambient temperature. The addition of 0.5 M, 1.0 M, and 2.0 M KOH solutions into the fine powder of Açaí seeds produced a moisture sludge. Afterwards, the moist sludge was placed into a paper filter and washed with 120 mL distilled water, and the mixture let in rest for 24 hours, as described elsewhere [9]. Then, the retained moist sludge is dried at 100 °C ± 5 °C for 24 hours. Finally, the dried and impregnated seeds were grounded using a porcelain pestle and a mortar. Figure 4 shows the chemical activation of Açaí seeds fine powders with a 2.0 M KOH solution.

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

2.4. Centesimal and immediate characterization of Açaí 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 [30].

2.5. Experimental apparatus and procedures

2.5.1. Experimental apparatus

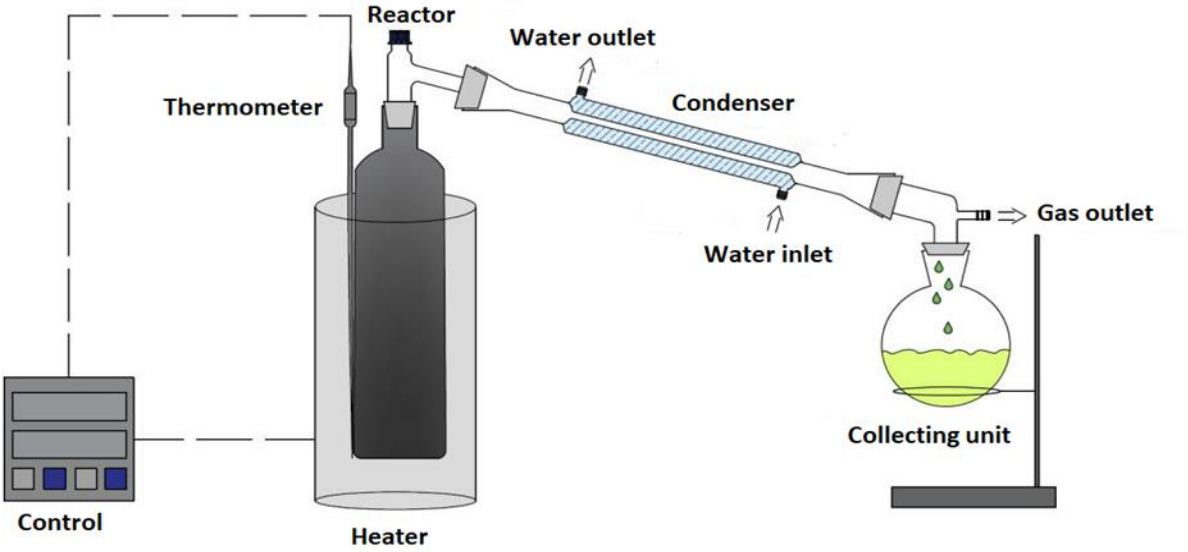

Figure 5. Schematic diagram of a laboratory scale borosilicate glass reactor.

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 actual laboratory scale pyrolysis reactor used in the experiments.

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. Physical-chemistry analysis and chemical composition of bio-oils and aqueous phase

2.6.1. Physical-chemistry analysis of bio-oils and aqueous phase

The bio-oils and aqueous phases were physicochemical analyzed for acid value according to official methods (AOCS Cd 3d-63), as described elsewhere [31-34].

2.6.2. 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.%.

2.6.3. FT-IR analysis

The identification of chemical groups (carbonyl, carboxyl, hydroxyl, phenyl, etc.) preset in bio-oils and aqueous phase obtained by pyrolysis at 350, 400, and 450 °C and 1.0 atmosphere, and 450 °C and 1.0 atmosphere, with 0.5 M, 1.0 M, and 2.0 M KOH, in laboratory scale, performed by Fourier transform infrared spectroscopy (FT-IR) using a spectrometer (BRUKER, Ettlingen-Germany, Model: VERTEX 70v) at the Laboratory of vibrational spectroscopy and high pressure (LEVAP-PPGF/UFPA). The identification of characteristics chemical groups performed as described in the literature [11, 31-34, 37-38].

2.7. Characterization of hidrochar

2.7.1. XRD analysis

The crystalline and/or mineralogical characterization of chemically activated Açaí seeds with 2.0 M KOH solutions, after pyrolysis at 350, 400, and 450 °C and 1.0 atmosphere, and 450 °C and 1.0 atmosphere, with 0.5 M, 1.0 M, and 2.0 M KOH, in laboratory scale, performed by x-ray diffraction using a diffractometer with Bragg-Brentano geometry (BRUKER, Karlsruhe-Germany, Model: D8 ADVANCE), coupled to a detector (BRUKER, Karlsruhe-Germany, Model: LynxEye), at the Laboratory of X-ray Diffraction (PPGF/UFPA) and the equipment specifications described as follows: *generator* (maximum power: 3 kW; tube voltage: 40 kV; tube current: 40 mA; X-ray tube: Cu, $K\alpha 1$=1.540598 Å), *optics* (fixed divergence, scattering and receiving slit; filter: Kβ of Ni; monochromator: graphite; soller slit = 2.5°, divergent slit = 0.6 mm), *goniometer* (model: vertical, scanning range: 5-110° (2θ); scanning speed: 0.2°/min (2θ); accuracy: ± 0.02°). The recording data collected with an angular step of 0.02° and scan rate of 0.2°/min at room temperature. The identification of crystalline phases performed as described in the literature [9, 15-16,39].

2.8. Mass balances by pyrolysis of Açaí 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. A differential mass balance of the considered system is described by the following equation:

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

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:

$$\int_{t_i}^{t_f} \frac{dM}{dt} dt = \int_{t_i}^{t_f} \dot{M}_I dt - \int_{t_i}^{t_f} \dot{M}_O dt$$

$$M_{t_f} - M_{t_i} = \int_{t_i}^{t_f} \dot{M}_I dt - \int_{t_i}^{t_f} \dot{M}_O dt \qquad (2)$$

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:

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

$$M_{feed} - M_{char} = \int_{t_i}^{t_f} \dot{M}_{bio-oil}dt + \int_{t_i}^{t_f} \dot{M}_{aqueous\ phase}dt + \int_{t_i}^{t_f} \dot{M}_{gas}dt \qquad (3)$$

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.

$$M_{feed} - M_{char} - M_{bio-oil} - M_{aqueous\ phase} = M_{gas} \qquad (4)$$

4. Results

4.1. Characterization of catalyst

4.1.1. XRD analysis

4.1.1.1 Effect of pyrolysis temperature

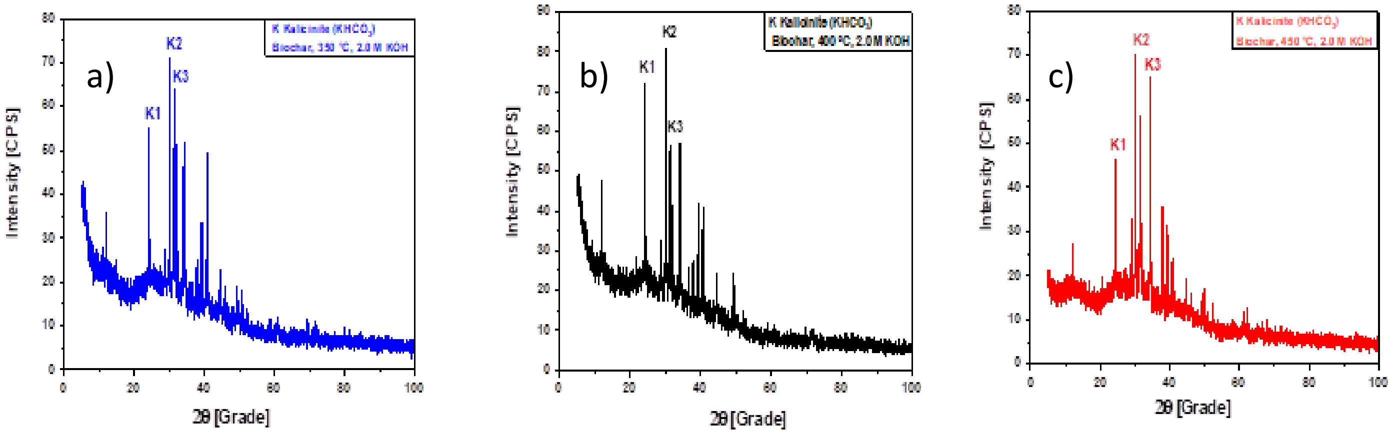

Figure 7. XRD of biochar produced by pyrolysis of Açaí seeds at 350 °C (a), 400 °C (b) and 450 °C (c), 1.0 atmosphere, activated with 2.0 M KOH, in laboratory scale.

Figures 7 illustrate the XRD of biochar produced by pyrolysis of Açaí 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 2θ: 30.0 (100%), and 02 (two) peaks of medium intensity, the first (K1) on the position 2θ: 24.2 (66.8%) and the second (K3) on the position 2θ: 40.6 (68.6%), being all the peaks associated to Kalicinite ($KHCO_3$), the dominant crystalline phase in biochar. This is according to the results of Prakongkep *et. al.* [40], who investigated the chemical properties (pH, conductivity, and ash), elemental analysis (C, N), micro and macro nutrients (Si, Al, Ca, Mg, Na, K, P, S, Fe, Mn, As), as well as morphological (SEM) and crystalline (XRD) characterization of biochar produced by pyrolysis of durian shell at 350 °C, in laboratory scale. Prakongkep *et. al.* [40], reported that Kalicinite ($KHCO_3$) was the dominant crystalline phase in bio-char.

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.* [40]. 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. [40].

Furthermore, Han Lee and colleagues [41] 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. [41], 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. Díaz-Terán et. al. [42], studied the chemical activation of lignocellulosic material with KOH and XRD patterns revealed the presence of K_2CO_3 on the position 2θ: 31.0, demonstrating that peak intensity increases with temperature. Similar results were observed in Figures 7. Díaz-Terán et. al. [42], 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.

4.2. Process conditions, mass balances, and yields of reaction products by pyrolysis of activated Açaí seeds (Euterpe Oleracea, Mart.) with KOH

4.2.1. Effect of process temperature

Table 1 illustrates the process parameters, mass balances, yields of reaction products (bio-oil, bio-char, H_2O, and gas), and acidity of bio-oils by pyrolysis of activated Açaí seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH, using a borosilicate glass reactor, in laboratory scale.

Table 1. Process parameters, mass balances, yields of reaction products (liquids, solids, H_2O, and gas), and acidity of bio-oils by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), at 350, 400, and 450 °C, 1.0 atmosphere, activated with 2.0 M KOH solution, using a borosilicate glass reactor, in laboratory scale.

Process Parameters	**2.0 M KOH**		
	350 °C	**400 °C**	**450 °C**
Mass of Açaí 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_2O (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_2O 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

Pyrolysis experiments were conducted on activated Açaí seeds at 350, 400, and 450 °C and 1.0 atm, after activation with 2.0 M KOH. The experiments were carried out in a laboratory scale borosilicate glass reactor, which resulted in bio-oil yields ranging from 3.19% to 6.79% (wt.), aqueous phase yields ranging from 20.34% to 25.57% (wt.), bio-char yields ranging from 33.40% to 43.37% (wt.), and gas yields ranging from 31.85% to 34.45% (wt.). These bio-oil yields are comparable to those reported by Serrão et al. [43], who studied the pyrolysis of Açaí seeds in nature at 350, 400, and 450 °C and 1.0 atm in pilot scale, and found yields between 2.0% and 4.39% (wt.). They are also consistent with those reported by Castro et al. [11], who investigated the pyrolysis of Açaí seeds in nature at 450 °C and 1.0 atm, in pilot, bench, and laboratory scale, yielding bio-oil between 4.37% and 13.09% (wt.). Furthermore, the experimental data for bio-char yields presented in Table 1 are in agreement with similar data reported in the literature for the pyrolysis of Açaí seeds [9, 11, 18-20, 22], showing bio-char yields ranging from 27.0% to 49.0% (wt.) for the pyrolysis of Açaí seeds in nature [9, 18-20], and bio-char yields ranging from 26.44% to 72.50% (wt.) for the pyrolysis of Açaí seeds chemically activated [11, 22]. Even though most published works show that higher temperatures decrease bio-oil yields, this is observed when range investigated is located above the temperature where maximum decomposition occurs (higher than 450 °C for most organic material). In this range, most original material already decomposed to lighter compounds and the increase in temperature allows for more cracking to molecules of even lower molecular mass (on the gas phase). Since investigated temperatures are on the range of maximum decomposition, where original material is primarily being decomposed to their initial products (present on liquid phase), bio-oil yields tend to increase with increasing temperature around the maximum decomposition.

Figure 8 shows the yields of reaction products, including liquids, solids, H2O, and gas, obtained from the pyrolysis of activated Açaí seeds in a laboratory-scale borosilicate glass reactor, at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH. The yield of bio-oil increases smoothly with temperature and was fitted with a first-order exponential decay model, with an r2 of 1.00. These results are consistent with those reported by Serrão et al. [43], who studied the pyrolysis of Açaí seeds in nature at 350, 400, and 450 °C, 1.0 atmosphere, in pilot scale, and observed an increase in bio-oil yield with temperature. Similar studies on the pyrolysis of biomass also report an increase in bio-oil yield between 200 and 450 °C [44-55].

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 bio-char 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 Açaí 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.

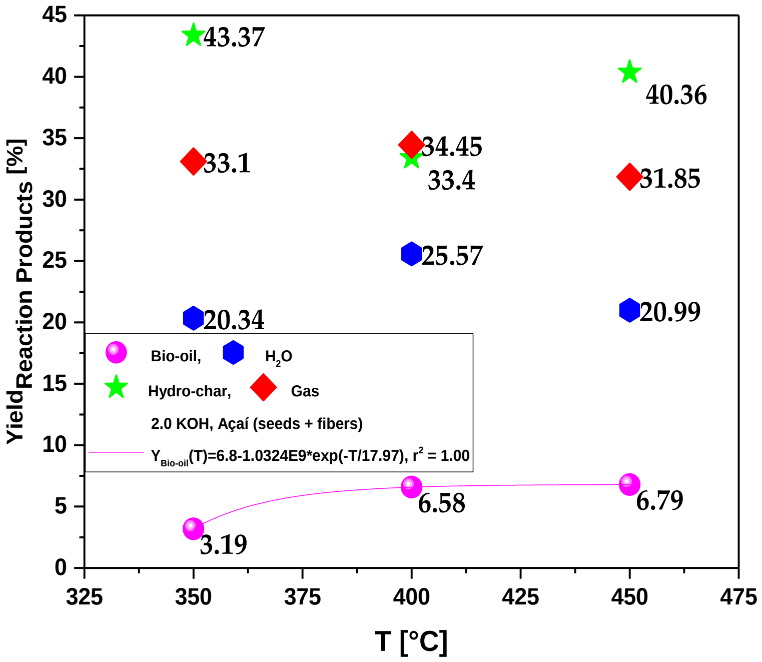

Figure 8. Yield of reaction products (bio-oil, H2O, bio-char, gas) by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

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

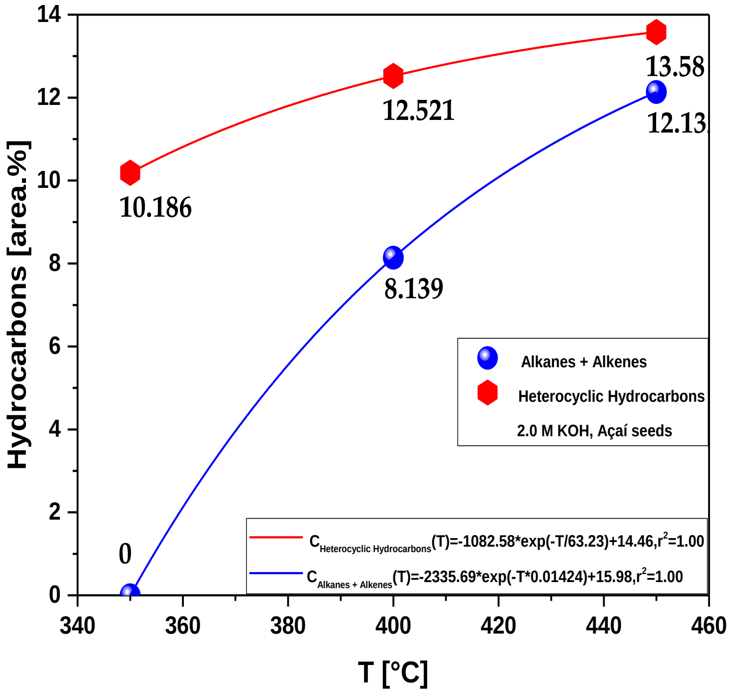

Figure 9. Concentration of acyclic saturated/unsaturated hydrocarbons (alkanes + alkenes) and heterocyclic hydrocarbons (cycloalkanes + cycloalkenes + aromatics) in bio-oil

by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Figures 9 and 10 illustrate the effect of process temperature on the composition of hydrocarbons, expressed in terms of acyclic saturated/unsaturated hydrocarbons (alkanes + alkenes) and heterocyclic hydrocarbons (cycloalkanes + cycloalkenes + aromatics), and oxygenates (phenols, ketones, and esters) in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale. The chemical composition of the liquid fraction was divided in hydrocarbons and oxygenates in order to evaluate designed process for production of chemical compounds that could be adequately used as fuels. Since these oxygenates often are of acidic nature and don't adequately burn (leaving residues in engines) [11], one could use the dichotomy between hydrocarbons and oxygenates as means to evaluate and compare thermochemical conversion processes.

Supplementary Tables S1-S3 present the chemical functions (such as alkanes, alkenes, cycloalkanes, aromatics, esters, carboxylic acids, furans, phenols, aldehydes, alcohols, and ketones), 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 Açaí 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 were found to increase with increasing process temperature. These results were fitted to a first-order exponential growth model, which exhibited a root-mean-square error (r2) of 1.00 for both cases. The findings of this study are consistent with those reported by de Sousa et al. [56], who investigated the impact of process temperature on the concentration of hydrocarbons and oxygenates in bio-oil derived from Açaí seeds in a pilot-scale pyrolysis process conducted at 350, 400, and 450 °C, 1.0 atm. Their study showed that the concentration of hydrocarbons increased, while that of oxygenates decreased with increasing temperature. Moreover, the concentrations of alkanes, alkenes, and aromatics in the bio-oil were found to increase with temperature, indicating that higher pyrolysis temperatures promote the formation of hydrocarbons [56].

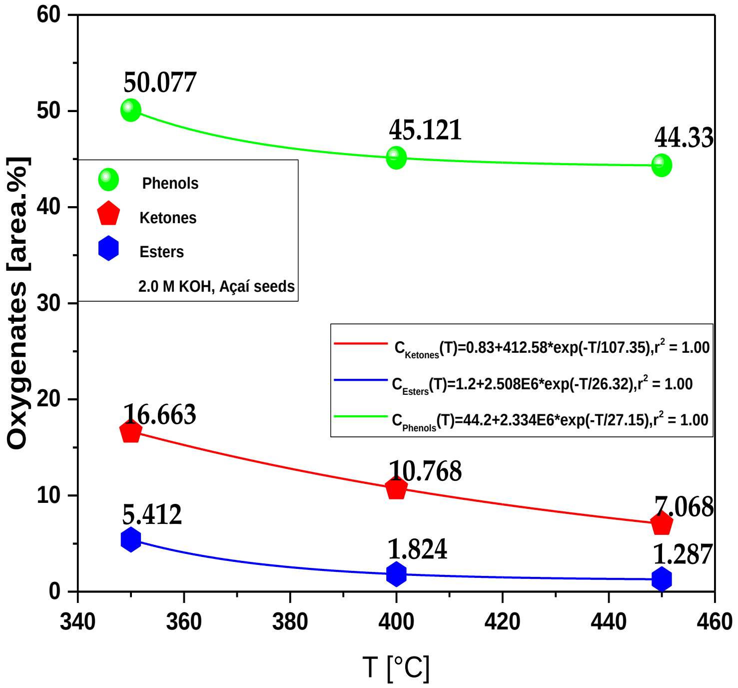

Figure 10. Concentration of oxygenates (phenols, ketones, and esters) in bio-oil by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Figure 10 illustrates the concentration of oxygenates in bio-oil by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale. 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.* [56]. 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.* [56], 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 illustrates the acid value (acidity) of bio-oils obtained from the pyrolysis of Açaí seeds (Euterpe Oleracea, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale. The results indicate a significant decrease in bio-oil acidity with increasing pyrolysis temperature, exhibiting a sharp exponential decay behavior. The acid value of bio-oil ranged between 257.6 and 12.3 (mgKOH/g) and was correlated with a first order exponential decay model, demonstrating a root-mean-square error (r2) of 1.00. These findings are consistent with those presented in Figure 10, suggesting that higher concentrations of oxygenates in bio-oil lead to higher levels of acidity.

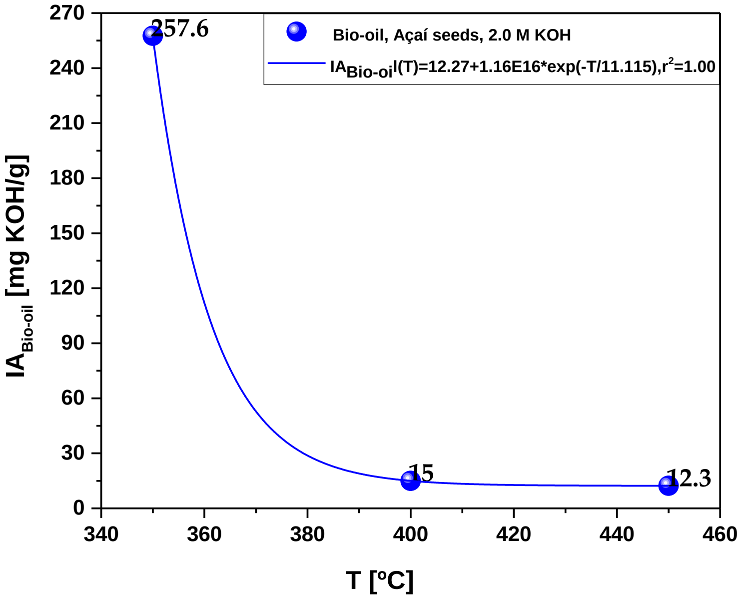

Figure 11. Acidity of bio-oil obtained by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

4.2.1.2. Effect of temperature on the composition of hydrocarbons and oxygenates in the aqueous phase

The chemical composition and acidity of aqueous phase, formed after pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, was determined by GC-MS, as illustrated in Table 2. The chemical functions, sum of peak areas, CAS numbers, and retention times of all the molecules identified in the aqueous phase by GC-MS in the pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, are illustrated in Supplementary Tables S4-S6.

Table 2. Chemical composition and acidity (alcohols, carboxylic acids, ketones, phenols, and other oxygenates) of aqueous phase obtained by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, 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
$\sum_{i}^{n} Ci$	**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. [57] found carboxylic acids, ketones, phenols, and furans in the aqueous phase produced by sawdust pyrolysis, while Torri and Fabbri [58] identified carboxylic acids, aldehydes, phenols, furans, sugars, and N-compounds in the aqueous phase produced by corn stalk pyrolysis. Similarly, Zhou et al. [59] reported the presence of carboxylic acids, aldehydes, phenols, ketones, furans, furfurals, sugars, and amines in the aqueous phase produced by corn stover pyrolysis.

Since alcohols are weak acids, its contribution to the acidity of aqueous phase is small or negligible. On the other hand, the α- hydrogen atoms of ketones are acidic in nature, thus contributing to the acidity of aqueous phase. Finally, low carbon chain length carboxylic acids present in the aqueous phase have a great contribution to the acidity. As the concentration of ketones in the aqueous phase decreases, it is to be expected that acidity of aqueous phase to diminish. The acidity of aqueous correlated with a first order exponential decay

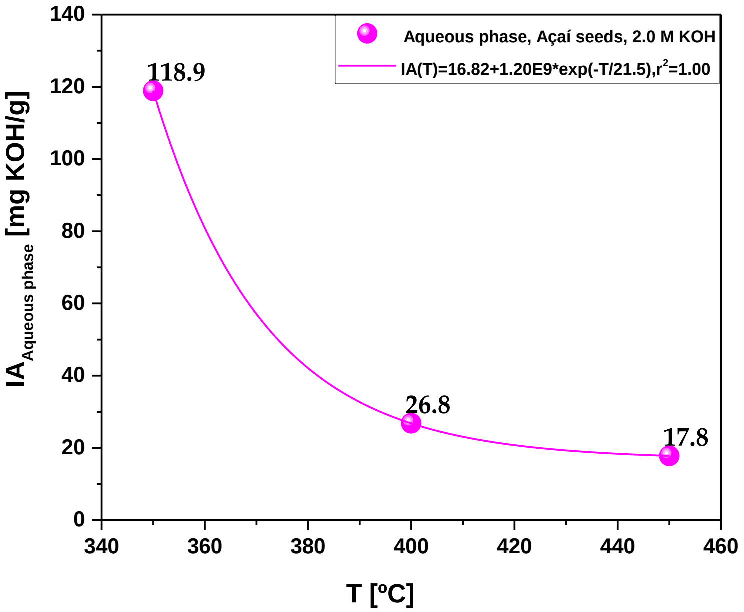

Figure 12. Acidity of aqueous phase obtained by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

4.2.2 Effect of molarity

Table 3 illustrates the process parameters, mass balances, yields of reaction products (bio-oil, bio-char, H_2O, 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, using a borosilicate glass reactor, in laboratory scale.

Table 3. Process parameters, mass balances, yields of reaction products (liquids, solids, H_2O, and gas), and acidity of bio-oils by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH, using a borosilicate glass reactor, in laboratory scale.

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_2O 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_2O 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, bio-char, 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. [43] but similar to those reported by Castro et. al. [11]. The yields of bio-char were also consistent with those reported in previous studies of Açaí seed pyrolysis. Chemical activation of biomass can enhance gas yields and reduce bio-oil yields, 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 bio-char indicated the presence of KOH and its salts, which may have contributed to the observed yields.

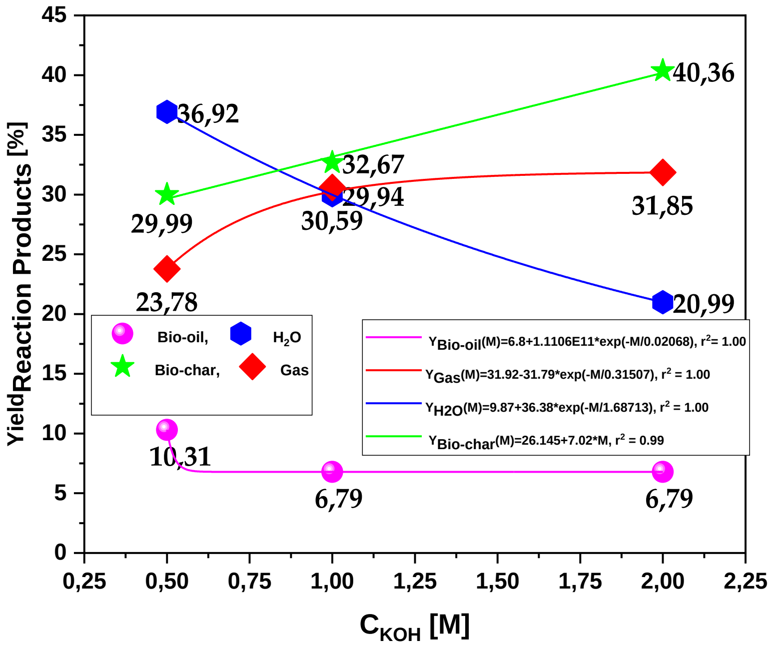

Figure 13. Yield of reaction products (bio-oil, H2O, bio-char, gas) by pyrolysis of Açaí seeds (*Euterpe Oleracea*, Mart), at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH, in laboratory scale.

Figure 13 shows the yields of reaction products (liquids, solids, H_2O, and gas) 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, using a borosilicate glass reactor. The yield of bio-oil shows a smooth decrease with increasing solution molarity, being correlated with a first order exponential decay model, and root-mean-square error (r^2) of 1.00. The yield of bio-char 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.

4.2.2.1. Effect of molarity on the composition of hydrocarbons and oxygenates in bio-oil

Figure 14 demonstrates the effect of different molarities of KOH solution on the concentration of hydrocarbons and oxygenates in the bio-oil produced by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart) at 450 °C, 1.0 atmosphere, in laboratory scale. 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 Açaí 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 [62], 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 (r2) values of 0.999.

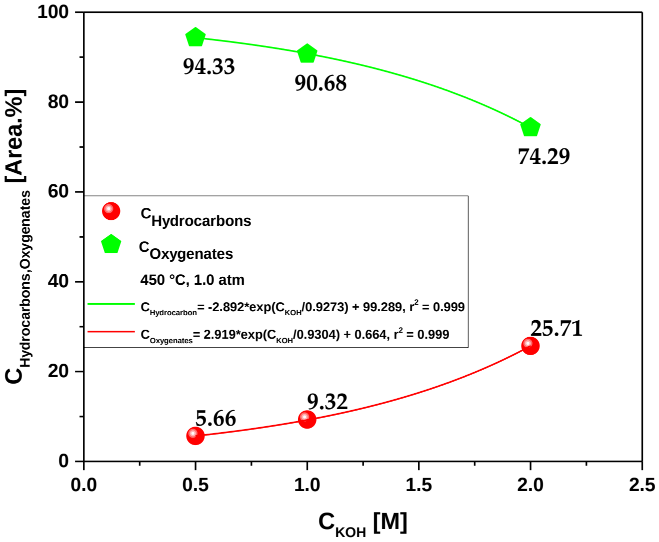

Figure 14. Concentrations of hydrocarbons and oxygenates in bio-oil obtained by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart) at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH solution, in laboratory scale.

Figure 15 displays the acid value (acidity) of bio-oils derived from pyrolysis of Açaí seeds (Euterpe Oleracea, Mart) activated with 2.0 M KOH solution, at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH solutions, in laboratory scale. The data reveal that the acidity of bio-oil reduces with an increase in molarity, exhibiting a sharp exponential decay behavior. The acidity of bio-oil ranged between 113.7 and 12.3 (mgKOH/g) and correlated with a first-order exponential decay model, with a root-mean-square error (r2) of 0.999. This result is in agreement with the findings presented in Figure 14, indicating that the higher the concentration of hydrocarbons in bio-oil, the lower its acidity.

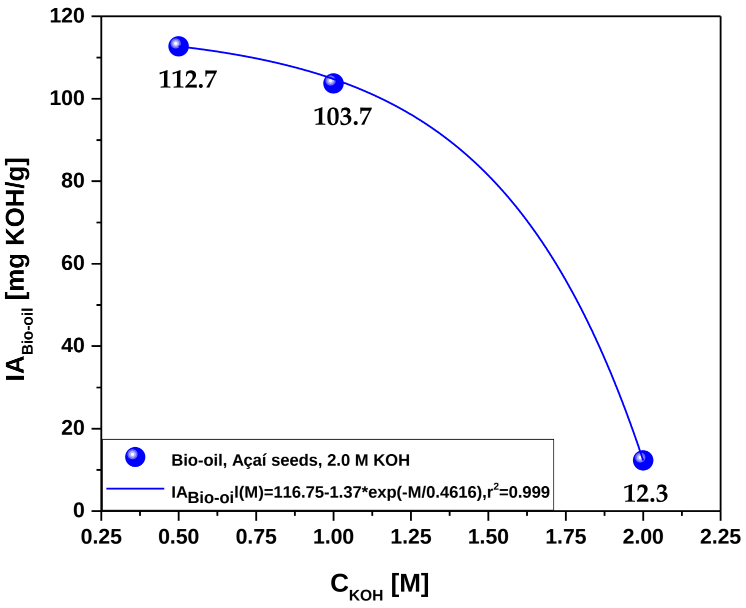

Figure 15. Acidity of bio-oil obtained by pyrolysis of Açaí seeds (Euterpe Oleracea, Mart) at 450 °C, 1.0 atmosphere, activated with 0.5 M, 1.0 M, and 2.0 M KOH solution, in laboratory scale.

5. Conclusions

The X-ray diffraction (XRD) analysis of biochar obtained from pyrolysis of Açaí seeds activated with 2.0 M KOH solution at 350, 400, and 450 °C and 1.0 atm in the laboratory scale, indicates the dominant presence of Kalicinite (KHCO3). The yield of bio-oil increases smoothly with the increase in pyrolysis temperature, which is correlated with a first-order exponential decay model. The concentration of hydrocarbons, especially acyclic saturates/unsaturated hydrocarbons and heterocyclic hydrocarbons, in bio-oil increases with temperature, while the concentration of oxygenates (such as cresols, phenols, and ketones) decreases, indicating that higher pyrolysis temperatures promote hydrocarbon formation but suppress the formation of oxygenates. This is also evident from the sharp decrease in bio-oil acidity from 257.6 to 12.3 (mgKOH/g) with increasing temperature, primarily due to a significant reduction in oxygenate concentration. The aqueous phase generated by the pyrolysis of activated Açaí seeds also shows the presence of carboxylic acids, ketones, alcohols, phenols, and other compounds, and its acidity decreases sharply with temperature as the concentration of ketones in the aqueous phase decreases. The yields of bio-char increase linearly with increasing KOH solution molarity, while those of gas and solid phase (bio-char) increase exponentially and linearly, respectively, with higher molarities favoring gas and bio-char production. At 450 °C and 1.0 atm, the concentration of hydrocarbons in bio-oil increases exponentially with KOH solution molarity, while oxygenate concentration decreases exponentially, indicating that higher KOH solution molarities promotes hydrocarbon formation. Additionally, bio-oil acidity decreases sharply with increasing molarity, exhibiting a sharp exponential decay behavior. These results are consistent with similar studies reported in the literature [57-59].

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, G.D.V. contributed with formal analysis and writing original draft preparation, investigation and methodology, S.J.B. contributed with formal analysis and writing original draft preparation, 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, 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, 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.

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