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Improving the Bio-Oil Quality of Residual Biomass Pyrolysis by Chemical Activation: Effect of Alkalis and Acid Pre-Treatment

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Abstract: In this study, we investigated the acid (HCl) and alkali (KOH) chemical activation of açai seeds (*Euterpe Oleraceae*, Mart.) pre-treatment before pyrolysis at temperatures of 350–450 °C in order to assess how reactions proceed when affected by temperature. Chemical composition of bio-oil and aqueous phase were determined by GC-MS and FT-IR. The bio-char is characterized by XRD. For the activation with KOH, the XRD analysis identified the presence of Kalcinite (KHCO₃), the dominant crystalline phase in bio-char, while an amorphous phase was identified in bio-chars for the activation with HCl. The experiments have shown that bio-oil yield increases with temperature for the KOH activated biomass and decreases for the acid activated one. The KOH bio-oil is primarily composed of alcohols and ketones, showing the lowest acid values when compared with the HCl one, which is composed mainly of carboxylic acids and phenols. An increase in alcohol content and a decrease in ketones in the KOH bio-oil with temperature suggests conversion reactions between these two functions. For HCl bio-oil, carboxylic acid concentration increases with temperature while phenols decrease. For production of hydrocarbons, KOH activated biomass pyrolysis is better than acid-activated one, since no hydrocarbons were produced for HCl bio-oil.

Keywords: açai seeds; chemical activation; pyrolysis; acidity; liquid hydrocarbons

1. Introduction

The population growth and increasing waste generation in low-, medium-, and high-income lands pose a huge challenge concerning waste management and its final destination [1]. Lignin-cellulosic-based biomass is a class of waste to be considered for energy conversion due to the volume generated, particularly those associated with agricultural activities [2], as non-renewable energy sources are not only depleting gradually but also new developing oils fields have high content of paraffin, which increases the processing costs [3].

There exist several technologies for producing renewable fuels (biofuels) from lipid-base materials, including hydro-treating, transesterification, esterification, and catalytic cracking [4,5], but those are not appropriate for the thermo-chemical conversion of lignin-cellulosic materials, except catalytic cracking and pyrolysis [5].

Açaí (*Euterpe oleracea*, Mart.), a palm of native occurrence in the floodplains of the Amazon [2,5–7], has great economic importance not only for the agroindustry, but also for rural communities whose economic income is based on extractive activities in the state of Pará-Brazil [6]. Açaí fruits are processed with warm water to produce a thick juice of high nutritional and cultural value, but also generate a residue, the seeds [2,5]. Similar to other types of biomasses, the seeds are mainly composed of hemicelluloses, celluloses, and lignin connected into an intricate structure matrix and can be burned or subjected to other thermochemical processes to convert it to energy or fuels [8–12]. Besides being an urban solid waste problem, the internal market for açaí generates millions of tons of waste each year in Brazil, including 94% in the State of Pará and a considerable amount of renewable energy could be generated from açaí seeds [6,13].

Pyrolysis is a thermo-chemical process with great potential to convert biomass into energy and fuel [8,11]. By pyrolysis of lignin-cellulosic biomass an aqueous phase, a gaseous phase, a bio-oil and a bio-char are formed [8,11]. The yield and properties of reaction products is a function of biomass characteristics, type of pyrolysis process, type of reactors, operating mode, and process parameters, particularly the temperature, type of catalyst, and catalyst-to-biomass ratio [14–16].

In the last years, studies on the pyrolysis of residual Açaí seeds, most of them aiming to produce a carbonaceous solid with activated carbon characteristics, were reported in the literature [8,11,17–29].

Despite studies on the pyrolysis of residual Açaí seeds in nature [17–19], and activated residual Açaí seeds [8,20–29], as far as we know, there is no study analyzing and comparing the effect of acid and alkalis activation of residual Açaí seeds on the yield, chemical composition, and acidity of the bio-oil and aqueous phase. This was achieved by investigating the effect of temperature and acid (HCl) and alkalis (KOH) chemical activation of residual Açaí seeds on the yield, hydrocarbon content, and acidity of bio-oil, as well as on the chemical composition and acidity of the aqueous phase, by pyrolysis of residual Açaí seeds at 350, 400, and 450 °C and 1.0 atmosphere, activated with aqueous solutions of 2.0 M KOH and HCl, in the laboratory scale.

2. Materials and Methods

2.1. Methodology

The process flow sheet shown in Figure 1 summarizes the whole research scheme used to produce bio-oil by pyrolysis of Açaí seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH and HCl, using a fixed bed reactor, on a laboratory scale. Initially, the Açaí seeds are discharged/disposed on the sidewalks and streets after the processing of Açaí fruits in nature. Afterwards, it is subjected to pre-treatment drying, milling, and sieving. The powder biomass is chemically activated with KOH and HCl, followed by H₂O washing and drying. The experiments were completed in a lab-scale glass reactor. The effect of acid and alkalis activation analyzed. The physical-chemistry properties and chemical composition of the bio-oil and aqueous phases were determined.

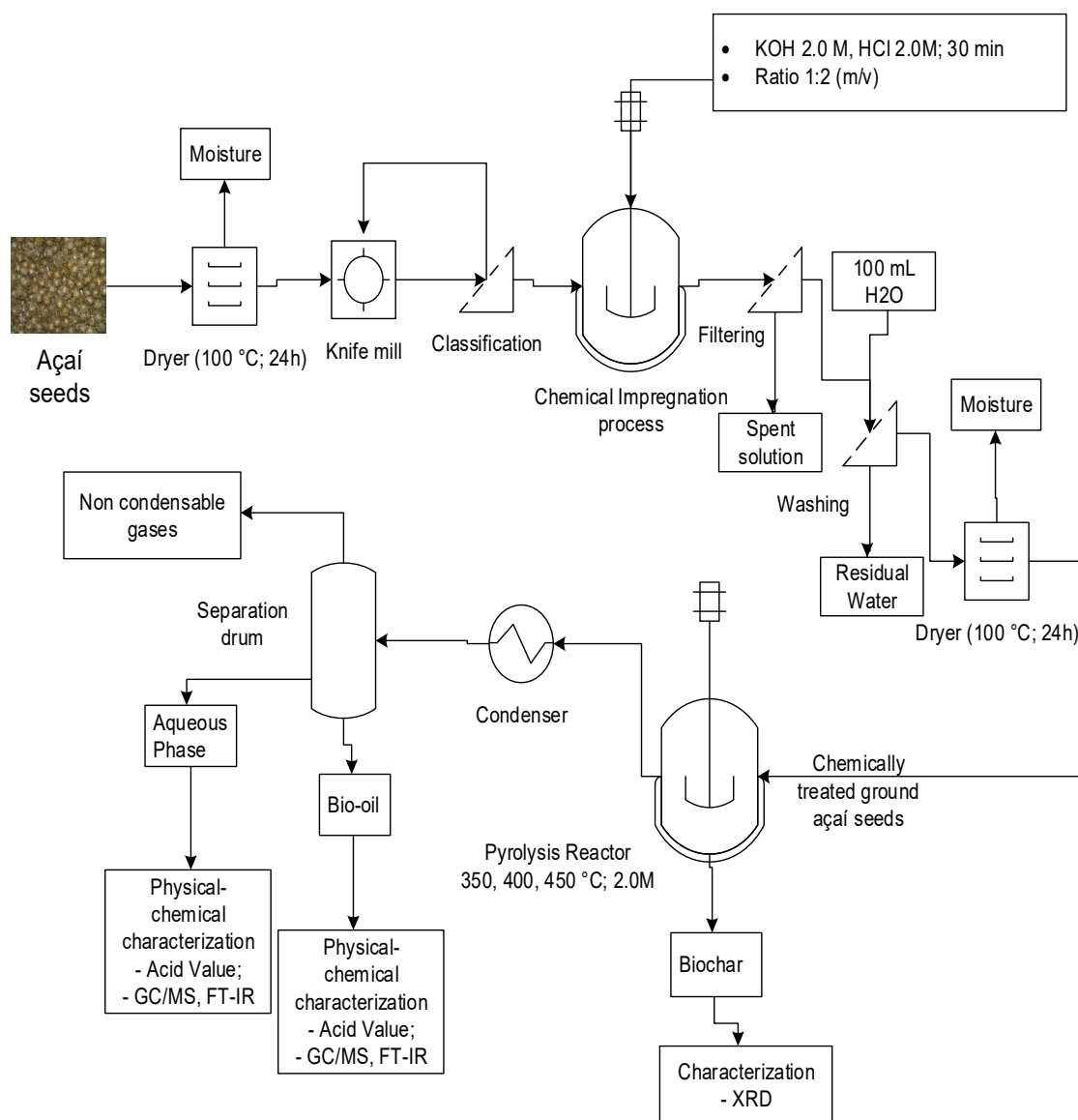


Figure 1. Process flow schema of bio-oil production by pyrolysis of Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH and HCl, using a fixed bed reactor, in laboratory scale.

2.2. Materials

The seeds of Açai, discharged/disposed on the sidewalks and streets by a small store of Açai commercialization located in the District of Jurunas, Belém-Pará-Brazil, were collected and conditioned in plastic bags.

2.3. Pre-Treatment of Açai Seeds

The seeds of Açai were submitted to physical pre-treatment drying, grinding, and sieving. The centesimal analysis of Açai seeds performed in a previous study [30]. Afterwards, the dried, ground, and sieved seeds were activated chemically using solutions of 2.0 M KOH and 2.0 M HCl, and the procedures described in detail in Sections 2.3.1 and 2.3.2.

2.3.1. Physical Pre-Treatment of Açai Seeds

The seeds were dried at 105 °C for 24 h in a temperature-controlled oven (DeLeo, Porto Alegre, Brazil, Model: DL-SE), ground to powder in a knife mill (TRAPP, Jaraguá do Sul, Brazil, Model: TRF 600), and classified in different particle diameters by a set of sieves (28, 35, 48 and 60 Mesh) in order to remove excess fiber material and decrease specific

particle diameter. A charge of Açai (*Euterpe oleracea*, Mart.) seeds in nature weighting approximately 5.0 kg was collected for the pyrolysis experiments.

2.3.2. Chemical Activation of Açai Seeds

After the physical pre-treatment described in Section 2.3.1, the dried, ground, and sieved Açai seeds were activated chemically with 2.0 M KOH or 2.0 M HCl solutions, and the procedures were described as follows: Approximately 120 g of dried, ground, and sieved Açai seeds were mixed manually with 240 mL of a 2.0 M HCl solution or 240 mL of a 2.0 M KOH (1:2 mass/volume ratio) for 30 min, using a Becker of 500 mL. The addition of 2.0 M HCl or 2.0 M KOH solutions into the fine powder of Açai seeds produced a moisture sludge. Afterwards, the moist sludge was placed into a paper filter and washed with 100 mL distilled water for 24 h, as described elsewhere [9]. Furthermore, the retained moist sludge is again submitted to drying over 24 h.

2.4. Experimental Apparatus and Procedures

2.4.1. Experimental Apparatus

The experimental apparatus is composed of a cylindrical glass reactor of approximately 200 mL, a tube condenser, 800 W electric furnace, and a separating funnel. Heating is controlled by temperature controller (THERMA, São Paulo, Brazil, Model: TH90DP202-000) connected to a k-type thermocouple (Ecil, São Paulo, Brazil, Model: QK. 2) inserted in the electric furnace near the glass reactor. The Liebig condenser is cooled by water circulation from a digital thermostatic recirculation bath. For more details, see ref. [31].

2.4.2. Experimental Procedures

For a typical pyrolysis run, approximately 40.0 g of chemically activated açai seeds is loaded into the pyrolysis reactor. The cooling system is turned on, and the water temperature is set to 10 °C. Depending on the setpoint temperature, a different heating program is applied, maintaining the heating rate at 10 °C/min. After reaching setpoint, reactor temperature is maintained over 30 min more. Feed weight and products weight were recorded in order to calculate yields and the amount of gas produced using a global mass balance.

2.5. Physical-Chemistry Analysis and Chemical Composition of Bio-Oils and Aqueous Phase

2.5.1. 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].

2.5.2. Chemical Composition of Bio-Oils and Aqueous Phase

GC-MS Analysis

The chemical composition of bio-oils and aqueous phases obtained by pyrolysis at 350, 400, and 450 °C and 1.0 atmosphere, and 450 °C and 1.0 atmosphere, with 2.0 M KOH and HCl, on laboratory scale, was determined by GC-MS and the equipment and procedures described in detail in the literature by Castro et al. [8,11,15,16,35–38]. The peak intensity, retention times, and compound identification were analyzed according to the NIST mass spectra library. The concentrations were expressed in area, as no internal standard was injected to compare the peak areas.

FT-IR Analysis

The identification of chemical groups (carbonyl, carboxyl, hydroxyl, phenyl, etc.) present in bio-oils aqueous phase obtained by pyrolysis at 350, 400, and 450 °C and 1.0 atmosphere, and 450 °C and 1.0 atmosphere, with 2.0 M KOH and HCl, in laboratory scale, was 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].

2.6. Characterization of Bio-Char

XRD Analysis

Crystalline phases present on the bio-char were detected by x-ray diffraction technique (diffractometer Rigaku, Tokyo, Japan, Model: MiniFlex600) at the Laboratory of Structural Characterization (FEMAT/UNIFESSPA). Equipment specification and detailed parameters were described in detail in previous works [15,16] and are of minor importance for the present discussion. Briefly, bio-char samples are ground with Agatha mortar and pestle. Two to three small spoonfuls of the ground sample are added to a mold and pressed to form tablets ready to be read in the diffractometer. A scan range of 100° was used. The identification of crystalline and/or amorphous carbonaceous phases present in bio-char performed as described in the literature [39,40].

2.7. Mass Balances by Pyrolysis of Açai Seeds

The global material balance mentioned in Section 2.4.2 is realized in order to be able to calculate the gas produced during the reaction. Since all the feed is loaded into the reactor and there is no stream or flow being added into the reactor, the global material balance, considering the whole pyrolysis system as control volume, is represented by Equation (1).

$$\dot{m}_{Feed} = \dot{m}_{solid} + \dot{m}_{gas} + \dot{m}_{bio-oil} + \dot{m}_{aqueousphase} \quad (1)$$

Yields are calculated based on feed weight using Equations (2)–(5).

$$Y_{bio-oil}[\%] = \frac{M_{Bio-oil}}{M_{Feed}} \times 100 \quad (2)$$

$$Y_{Aqueousphase}[\%] = \frac{M_{Aqueousphase}}{M_{Feed}} \times 100 \quad (3)$$

$$Y_{solids}[\%] = \frac{M_{Solids}}{M_{Feed}} \times 100 \quad (4)$$

$$Y_{gas}[\%] = 100 - (Y_{bio-oil} + Y_{solids} + Y_{Aqueousphase}) \quad (5)$$

3. Results

3.1. Characterization of Bio-Char

3.1.1. XRD Analysis

Effect of KOH Activation

The XRD of bio-char samples is shown in Figure 2, and the analysis of peaks characteristics (Intensity, Position: 2θ , Percentage: %) of crystalline phases identified by XRD in bio-chars by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, is illustrated in Table 1.

The diffractogram of bio-chars illustrated in Figure 2 identified peaks of medium and high intensity associated to Kalicinite (KHCO_3), the dominant crystalline phase in bio-char. 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. Moreover, Han Lee et al. [41] studied the XRD patterns of chemically modified biochar by K agents and found similar behavior, showing striking similarity to the diffractograms of biochar illustrated in Figure 2.

Díaz-Terán et al. [42], studied the chemical activation of lignocellulosic material with KOH and XRD patterns revealed the presence of KHCO_3 (Kalicinite) and K_2CO_3 crystalline, demonstrating that peak intensity increases with temperature, as confirmed in Table 1.

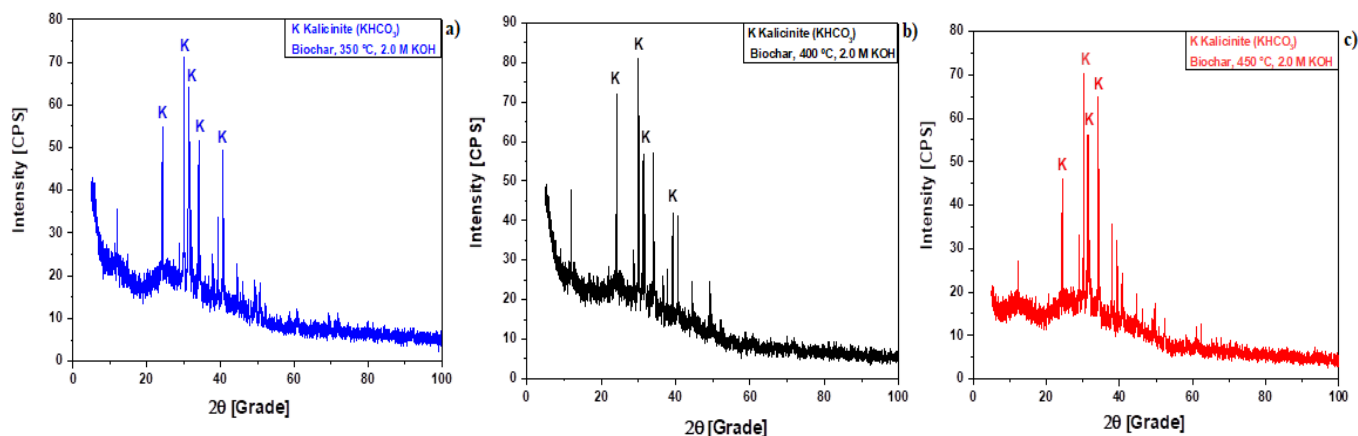


Figure 2. XRD of biochar produced by pyrolysis of Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH, in laboratory scale. (a) 350 °C; (b) 400 °C; (c) 450 °C.

Table 1. Analysis of peaks characteristics (Intensity, Position: 2θ , Percentage: %) of crystalline phases identified by XRD in bio-chars.

Temperature	Peaks Intensity, Position (2θ), and Percentage (%)					
	Medium		Medium		High	
350 °C	2θ	(%)	2θ	(%)	2θ	(%)
	24.2	66.8	40.6	68.6	30.0	100
400 °C	Medium		High		High	
	2θ	(%)	2θ	(%)	2θ	(%)
	31.3	62.2	24.1	81.73	30.0	100
450 °C	High		High		High	
	2θ	(%)	2θ	(%)	2θ	(%)
	30.2	100.0	31.3	79.9	34.2	92.1

Effect of HCl Activation

The XRD of HCl bio-char samples is shown in Figure 3. In fact, the pre-treatment of Açai seeds in nature with HCl, a strong Arrhenius acid, leachates all the inorganic compounds present within the biomass, so that pyrolysis of de-mineralized Açai seeds at 350, 400, and 450 °C, 1.0 atmosphere, produces a solid phase (bio-char) containing significant amount of highly disordered material, amorphous carbon, responsible for the back ground intensity of the diffractograms [39], as illustrated in Figure 3. This is according to the results presented by Manoj and Kunjomana [39], who study the X-ray diffraction of de-mineralized coal with HF, a strong Arrhenius acid, showing back ground intensity in the diffractograms due to a significant amount of amorphous carbon.

3.2. Pyrolysis of Activated Açai Seeds

3.2.1. Process Conditions, Mass Balances, and Yields of Reaction Products by Pyrolysis of Activated Açai Seeds with KOH

Table 2 illustrates the process parameters, mass balances, yields of reaction products (liquids, solids, H_2O , and gas), and acidity of bio-oils by pyrolysis of activated Açai seeds at 350, 400, and 450 °C in 1.0 atmosphere, activated with 2.0 M KOH, using a borosilicate glass reactor, in laboratory scale.

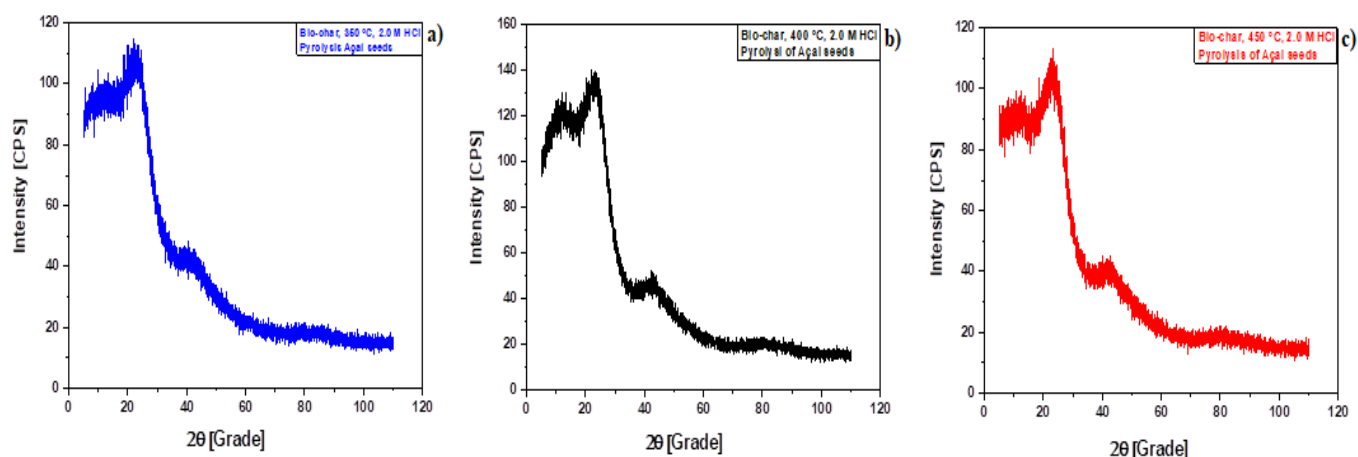


Figure 3. XRD of HCl activated biochar at different temperatures. (a) 350 °C; (b) 400 °C; (c) 450 °C.

Table 2. Process parameters, mass balances, yields of reaction products (liquids, solids, H₂O, and gas), and acidity of bio-oils by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, using a borosilicate glass reactor, in laboratory scale.

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)	72	72	72
Yield of Bio-oil (wt.%)	3.19	6.58	6.79
Yield of H ₂ O (wt.%)	20.34	25.57	20.99
Yield of Hydro-char (wt.%)	43.37	33.40	40.36
Yield of Gas (wt.%)	33.10	34.45	31.85
Acidity (mg KOH/g)	257.6	15.0	12.3

The pyrolysis experiments of activated Açai seeds at 350, 400, and 450 °C, 1.0 atmosphere, activated with 2.0 M KOH, using a borosilicate glass reactor, in laboratory scale, show yields of bio-oil between 3.19 and 6.79% (wt.), aqueous phase yields between 20.34 and 25.57% (wt.), hydro-char yields between 33.40 and 43.37% (wt.), and yields of gas between 31.85 and 34.45% (wt.). The yields of bio-oil are similar to those reported by Serrão et al. [43], who studied the pyrolysis of Açai seeds in nature at 350, 400, and 450 °C, 1.0 atmosphere, in pilot scale, showing yields between 2.0 and 4.39% (wt.), as well as those reported by Castro et al. [11], who studied the pyrolysis of Açai seeds in nature at 450 °C, 1.0 atmosphere, in pilot, bench, and laboratory scale, showing bio-oil yields of 4.37, 6.60, and 13.09% (wt.), respectively. In addition, the experimental data for biochar yields illustrated in Table 2 is according to similar data reported for the pyrolysis of Açai seeds reported in the literature [9,11,18–20,22], showing biochar yields between 27.0 and 49.0% (wt.) for the pyrolysis of Açai seeds in nature [9,18–20], and biochar yields between 26.44 and 72.50% (wt.) for the pyrolysis of Açai seeds chemically activated [11,22].

The yields of reaction products (liquids, solids, H₂O, and gas) by pyrolysis of activated Açai seeds at 350, 400, and 450 °C, 1.0 atmosphere, activated with 2.0 M KOH, using a borosilicate glass reactor, in laboratory scale, are shown in Figure 4. The yield of bio-oil shows a smooth increase with temperature, and was correlated with a first order exponential decay model, exhibiting a root-mean-square error (r^2) of 1.00. The results are according to those reported by Serrão et al. [43], who investigated the pyrolysis of Açai seeds in nature at 350, 400, and 450 °C, 1.0 atmosphere, in pilot scale, showing an increase in bio-oil yield with increasing pyrolysis temperature. Moreover, the results are in agreement with similar studies for the yield of bio-oil by the pyrolysis of biomass reported in the literature [44–55], whereas the yield of bio-oil increases between 200 and 450 °C [44–55].

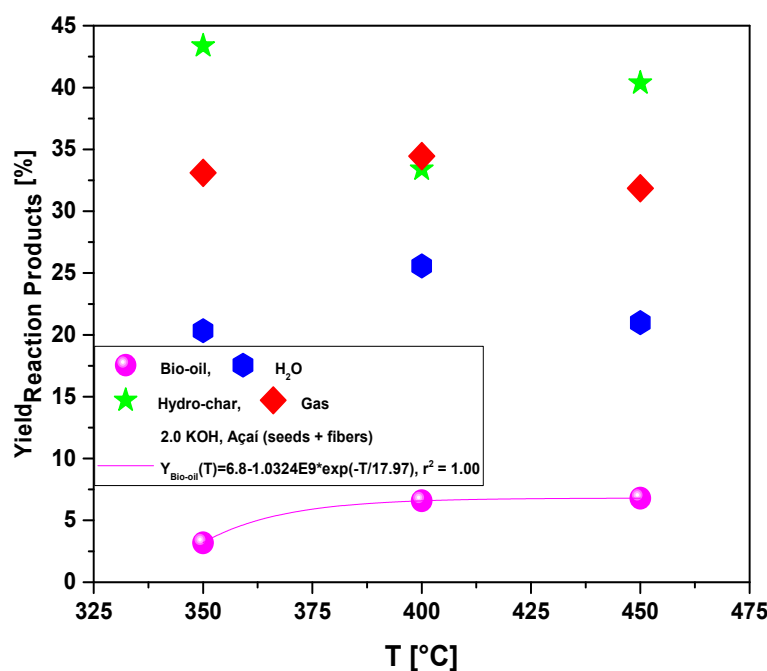


Figure 4. Yield of reaction products (bio-oil, H₂O, hydro-char, gas) by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Effect of Temperature on the Composition of Hydrocarbons and Oxygenates in Bio-Oil

The effect of process temperature on the composition of hydrocarbons and oxygenates in bio-oil obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, is shown in Figure 5.

The chemical functions (alkanes, alkenes, cycloalkanes, cycloalkenes, aromatics, esters, carboxylic acids, furans, phenols, aldehydes, alcohols, and ketones), sum of peak areas, CAS numbers, and retention times of all the molecules identified in bio-oil by GC-MS by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, are illustrated in Supplementary Tables S1–S3. By increasing the temperature, the concentration of hydrocarbons increases, while that of oxygenates decreases. The concentrations of hydrocarbons were correlated with a first order exponential growth model, exhibiting a root-mean-square error (r^2) of 1.00, showing that higher pyrolysis temperatures favor the formation of hydrocarbons. The results are according to those reported by de Sousa et al. [56], who investigated the effect of process temperature on the concentration of hydrocarbons and oxygenates in bio-oil by the pyrolysis of Açai seeds in nature at 350, 400, and 450 °C, 1.0 atmosphere, in pilot scale. According to de Sousa et al. [56], the concentration of hydrocarbons increases, while that of oxygenates decreases with increasing temperature. According to de Sousa et al. [56], the concentration of oxygenates decreases with increasing temperature, showing that higher pyrolysis temperatures do not favor the formation of oxygenates [56]. The concentration of oxygenates in bio-oil was correlated with a first-order exponential decay model, exhibiting in all cases a root-mean-square error (r^2) of 1.00.

The acid value (acidity) of bio-oils obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, is shown in Figure 6. The acidity of bio-oil decreases with increasing pyrolysis temperature, showing a sharp exponential decay behavior. The acidity of bio-oil varied between 257.6 and 12.3 (mgKOH/g) and correlated with a first-order exponential decay model, exhibiting a root-mean-square error (r^2) of 1.00, corroborating with the results presented in Figure 5, that is, the higher the concentration of oxygenates in bio-oil, the higher the acidity of bio-oil.

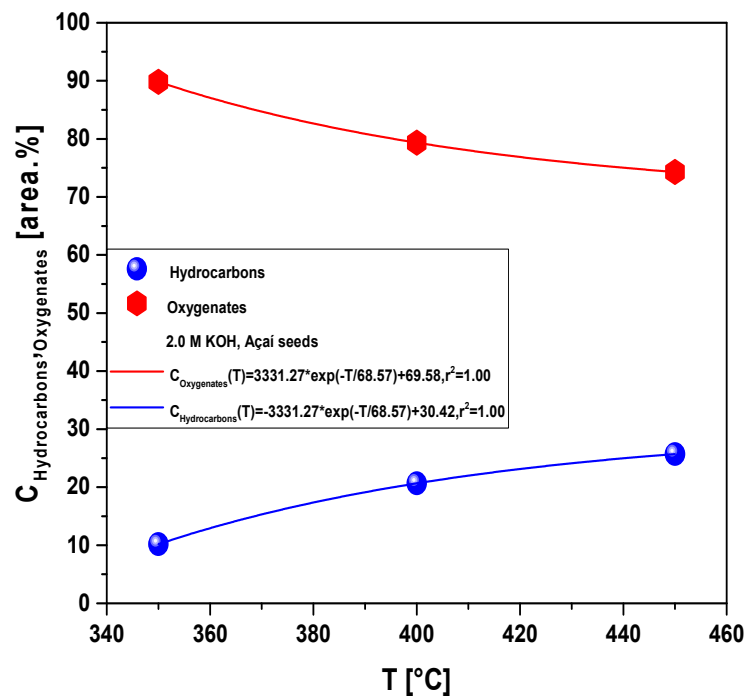


Figure 5. Concentration of hydrocarbons and oxygenates in bio-oil by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

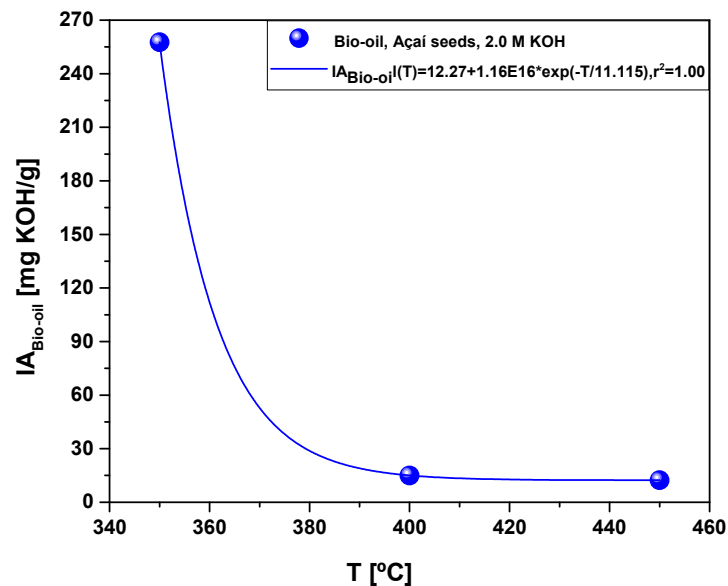


Figure 6. Acidity of bio-oil obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

The chemical function characteristics of hydrocarbons and oxygenates identified by FT-IR analysis of bio-oils obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, are illustrated in Figure 7. The FT-IR identified adsorption bands characteristic of chemical functions/chemical bonds as shown in Table 3, confirming the presence of aliphatic hydrocarbons, carboxylic acids, alcohols, as well as the presence of H₂O in bio-oils, according to similar analysis described elsewhere [11,31–34,57,58].

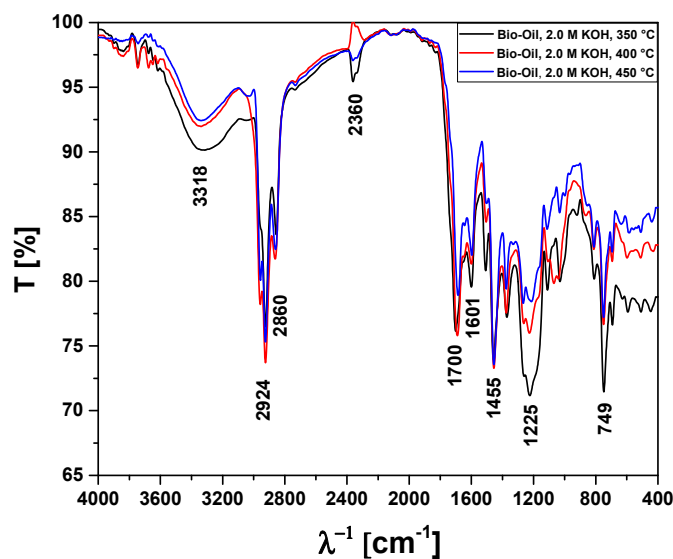


Figure 7. FT-IR analysis of bio-oils obtained by pyrolysis of Açai seeds (*Euterpe Oleracea*, Mart), activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Table 3. Absorption bands and chemical functions/groups identified by FT-IR analysis of bio-oils obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Absorption Bands	Chemical Functions/Chemical Bonds
3400–3200 cm^{-1}	ν -OH, hydrogen bonds of alcohol and H_2O .
2870–2840 cm^{-1}	ν_s - CH_2 , methylene group CH_2 .
2930–2920 cm^{-1}	ν_{as} - CH_2 , methylene group CH_2 .
1709 cm^{-1}	ν -C=O, carbonyl group of carboxylic acids and ketones.
1601 cm^{-1}	ν C=C-C, C=C-C ring-related stretching associated to phenols.
1465–1440 cm^{-1}	δ_{as} CH ₃ , methyl group (C-H).
1200–1125 cm^{-1}	ν -C-O, saturated alcohols (C-O).
1000–650 cm^{-1}	γ =C-H, Alkenes (=C-H).

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 Açai seeds, 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 4.

Table 4. Chemical composition and acidity (alcohols, carboxylic acids, ketones, phenols, and other oxygenates) of aqueous phase obtained by pyrolysis of Açai seeds, 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
$\sum_i^n C_i$	100.00	100.00	100.00
Acidity (mg KOH/g)	118.9	26.8	17.9

The chemical functions, sum of peak areas, CAS numbers, and retention times of compounds identified in the aqueous phase by GC-MS analysis after pyrolysis of Açai

seeds, 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. The major oxygenate compounds identified in the aqueous phase were alcohols, carboxylic acids, and ketones. The remaining oxygen compounds were summed and named oxygenates (phenols, aldehydes, amines, etc.). The composition of the aqueous phase is determined according to similar studies reported in the literature [59–61]. Zhang et al. [59] identified the presence of carboxylic acids, ketones, phenols, and furans in the aqueous phase produced by the pyrolysis of sawdust. Torri and Fabbri [60] investigated the chemical composition of the aqueous phase by pyrolyzing corn stalks, identifying the presence of carboxylic acids, aldehydes, phenols, furans, sugars and N-compounds. Zhou et al. [61], reported the presence of carboxylic acids, aldehydes, phenols, ketones, furans, and furfurals sugars and amines on the composition of the aqueous phase by pyrolysis of corn Stover.

Based on the fact that alcohols are weak acids, their contribution to the acidity of the aqueous phase is small or negligible. On the contrary, the α -hydrogen atoms of ketones are acidic in nature, thus contributing to the acidity of the 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 the acidity of the aqueous phase will diminish, as shown in Figure 8. Figure 8 shows the effect of temperature on the acidity of aqueous phase. The acidity of aqueous correlated with a first-order exponential decay model, exhibiting a root-mean-square error (r^2) of 1.00.

The FT-IR analysis of the aqueous phase obtained by the pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale is illustrated in Figure 9. The FT-IR identified adsorption bands characteristic of chemical functions/chemical bonds of oxygenates, as shown in Table 5, confirming the presence of H₂O, carboxylic acids, ketones, phenols, and alcohols, being according to similar analysis described elsewhere [57,58].

3.2.2. Process Conditions, Mass Balances, and Yields of Reaction Products by Pyrolysis of Activated Açai Seeds with HCl

The process parameters, mass balances, yields of reaction products (liquids, solids, H₂O, and gas), and acidity of bio-oils by pyrolysis of activated Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M HCl, using a borosilicate glass reactor in laboratory scale, are shown in Table 6.

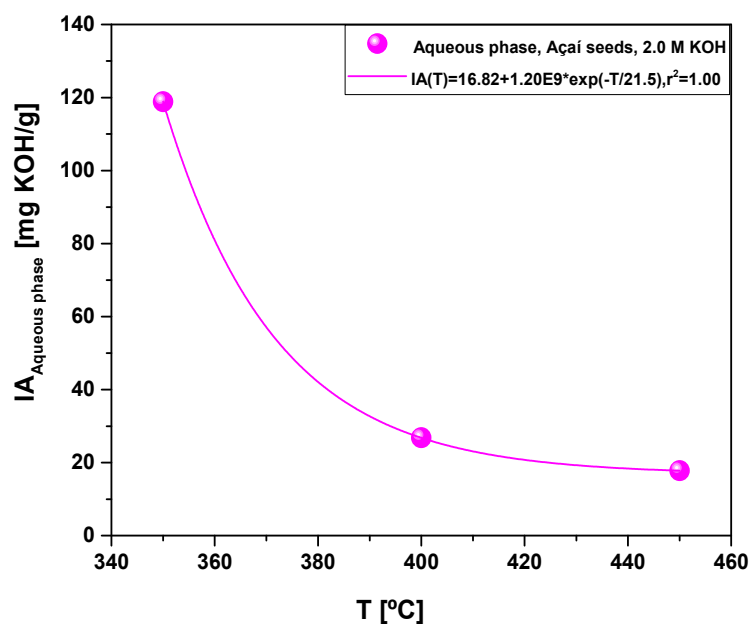


Figure 8. Acidity of aqueous phase obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

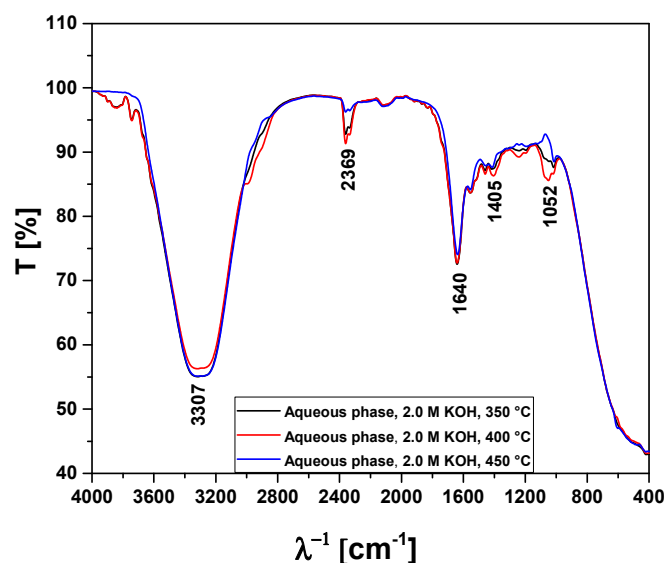


Figure 9. FT-IR analysis of aqueous phase obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Table 5. Absorption bands and chemical functions identified by FT-IR analysis of aqueous phase obtained by pyrolysis of Açai seeds, activated with 2.0 M KOH solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

Absorption Bands	Chemical Functions/Chemical Bonds
3400–3200 cm^{-1}	ν -OH, hydrogen bond of alcohols and H_2O .
2369 cm^{-1}	$\nu_{\text{ass}}\text{-CO}_2$, axial asymmetric deformation of CO_2 .
1648–1636 cm^{-1}	$\nu\text{C}=\text{C}-\text{C}$, $\text{C}=\text{C}-\text{C}$ ring-related stretching associated to phenols.
1052 cm^{-1}	$\nu\text{C}-\text{O}-\text{C}$, $\nu\text{C}-\text{O}$, $\nu\text{C}-\text{H}$, $\text{C}-\text{O}-\text{C}$ bond of esters, $\text{C}-\text{O}$ bonds, and $\text{C}-\text{H}$ bonds of benzene rings.

Table 6. Process parameters, mass balances, yields of reaction products (liquids, solids, H_2O , and gas), and acidity of bio-oils by pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, using a borosilicate glass reactor, in laboratory scale.

Process Parameters.	2.0 M HCl		
	350 °C	400 °C	450 °C
Mass of Açai seeds (g)	42.100	40.480	40.433
Cracking time (min)	72	72	72.0
Yield of Bio-oil (wt.%)	3.37	2.84	2.13
Yield of H_2O (wt.%)	31.19	32.85	22.91
Yield of Hydro-char (wt.%)	47.53	35.08	37.32
Yield of Gas (wt.%)	17.91	29.22	37.64
Acidity (mg KOH/g)	127.1	128.9	218.5

The yields of bio-oil varied between 3.37 and 2.13% (wt.), decreasing with increasing pyrolysis temperature, showing that activation of Açai seeds with 2.0 M HCl did not favor the thermo-chemical transformation of biomass into bio-oil, compared with the chemical activation with 2.0 M KOH, as illustrated in Table 2. This is according to Wang et al. [62], who investigated systematically the effect of acid (H_2SO_4) and basic (NaOH) pretreatment by pyrolysis of corn cob at 500 °C on the yield of reaction products [solid, liquid (bio-oil + aqueous phase), and gas] and chemical composition of the liquid phase, showing that pretreatment of corn cob with NaOH for a constant mass ratio (corn cob-to-acid/alkali) favors the liquid phase yields, compared with the pretreatment with H_2SO_4 . In addition,

Wang et al. [62] identified the presence of carboxylic acids (acetic acid), ketones (butanone), alcohol (methanol), furfural, and an aromatic hydrocarbon (benzene) in bio-oil by pyrolysis of alkali (NaOH) treated corn cobs, while no aromatic hydrocarbon was identified in bio-oil by pyrolysis of acid (H₂SO₄) treated corn cobs, the major identified compounds, acetic acid, furfural, benzofuran, levoglucosan, and guaiacol [62].

The GC-MS analysis of bio-oil produced by the pyrolysis of Açai seeds at 350, 400, and 450 °C in 1.0 atmosphere with 2.0 M HCl, in laboratory scale, has not identified the presence of hydrocarbons, only oxygenates (carboxylic acids, alcohols, ketones, phenols, and furans), as shown in Table 7, proving that pre-treatment of biomass with HCl before pyrolysis did not favor the formation of hydrocarbons, according to the results of Wang et al. [62]. The results for the chemical composition of bio-oils in Table 7 are according to Bru et al. [63], who investigated the main organic compounds in bio-oils obtained by pyrolysis of oak wood, showing that pyrolysis of acid washed oak wood produced bio-oil without hydrocarbons, that is, an acid pre-treatment of oak wood did not favor the formation of hydrocarbons [63]. The chemical functions, sum of peak areas, CAS numbers, and retention times of compounds identified in bio-oil and aqueous phase by GC-MS analysis after pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, are illustrated in Supplementary Tables S7–S9.

Table 7. Chemical composition of major compounds (carboxylic acids, phenols) and oxygenates (alcohols, ketones, aldehydes, etc.) of bio-oil obtained by pyrolysis of Açai seeds, activated with 2.0 M HCl 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 HCl		
	350 °C	400 °C	450 °C
Carboxylic Acids	53.056	43.540	61.175
Phenols	35.945	32.700	28.682
Oxygenates (alcohols, aldehydes, ketones, cresols)	10.999	23.860	10.143
$\sum_i^n C_i$	100.00	100.00	100.00

Figure 10 shows the FT-IR analysis of bio-oils produced by GC-MS analysis after pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale. The FT-IR identified adsorption bands characteristic of chemical functions/chemical bonds of oxygenates, confirming the presence of alcohols, H₂O, carboxylic acids, ketones, and benzene ring probably associated to furans in Figure 10, being according to similar analysis described elsewhere [11,31–34,57,58].

The FT-IR analysis of the aqueous phase obtained by GC-MS analysis after pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale, is shown in Figure 11. The FT-IR identified adsorption bands characteristic of chemical functions/chemical bonds of oxygenates, confirming the presence of alcohols, H₂O, carboxylic acids, and phenols, according to similar analysis described elsewhere [11,31–34,57,58].

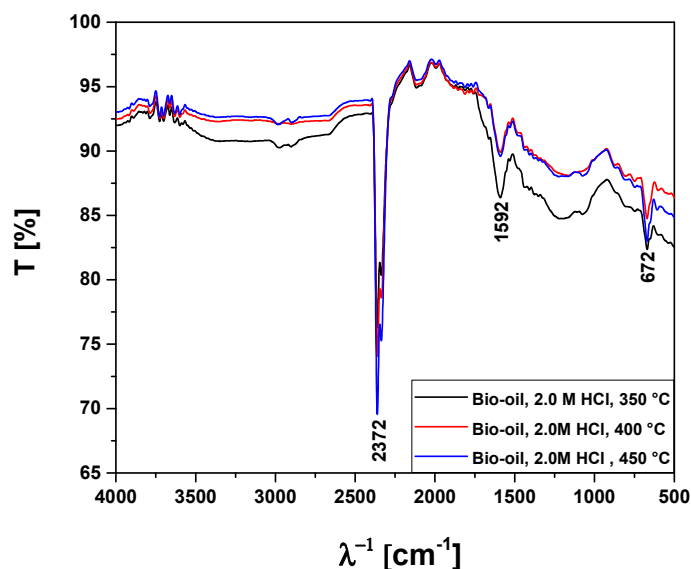


Figure 10. FT-IR analysis of bio-oils obtained by pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

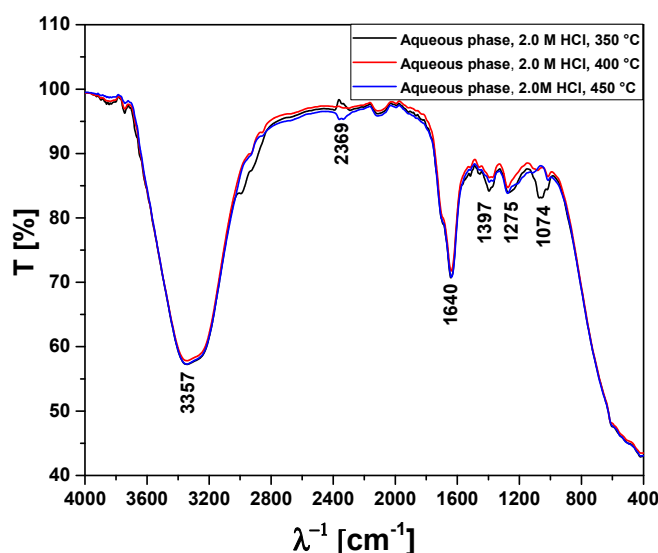


Figure 11. FT-IR analysis of aqueous phase obtained by pyrolysis of Açai seeds, activated with 2.0 M HCl solution, at 350, 400, and 450 °C, 1.0 atmosphere, in laboratory scale.

4. Conclusions

XRD analysis of biochar produced by the pyrolysis of Açai seeds at 350, 400, and 450 °C, 1.0 atmosphere, with 2.0 M KOH, in laboratory scale, shows the presence of Kalicinite (KHCO_3), the dominant crystalline phase in biochar.

The yields of bio-oil by pyrolysis of activated Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH, in laboratory scale, show a smooth increase with temperature, which is correlated with a first order exponential decay model. In addition, by increasing the temperature, the concentrations of acyclic saturated/unsaturated hydrocarbons and heterocyclic hydrocarbons in bio-oil increase, while that of oxygenates (cresols, phenols, and ketones) decreases with increasing temperature, showing that higher pyrolysis temperatures favor the formation of hydrocarbons and disfavor the formation of oxygenates [57], as proved by a sharp decrease in the acidity of bio-oil, from 257.6 to 12.3 (mgKOH/g), due to a drastic decrease in the concentration of oxygenates.

The composition of aqueous phase produced by pyrolysis of activated Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M KOH, in laboratory scale, is according to

similar studies reported in the literature [57–59], being identified the presence of carboxylic acids, ketones, alcohols, phenols, among other compounds. The acidity of the aqueous phase decreases sharply with temperature, as the concentration of ketones in the aqueous phase decreases.

The yields of bio-oil by pyrolysis of activated Açai seeds at 350, 400, and 450 °C, 1.0 atm, activated with 2.0 M HCl, in laboratory scale, decreased with increasing temperature, showing that activation of Açai seeds with 2.0 M HCl did not favor the thermo-chemical transformation of biomass into bio-oil. In addition, it has not been possible to identify the presence of hydrocarbons in bio-oil, only oxygenates, proving that acid (HCl) pre-treatment of Açai seeds did not enhance the yield of bio-oil nor favors the formation of hydrocarbons in bio-oil.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en16073162/s1>. 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 Açai 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 Açai 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 Açai 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 Açai 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 Açai 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 Açai 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 Açai seeds (*Euterpe oleracea*, Mart), activated with 2.0 M HCl solution, at 350 °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 Açai seeds (*Euterpe oleracea*, Mart), activated with 2.0 M HCl solution, at 400 °C, 1.0 atmosphere, in laboratory scale. Table S9: 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 Açai seeds (*Euterpe oleracea*, Mart), activated with 2.0 M HCl solution, at 450 °C, 1.0 atmosphere, in laboratory scale.

Author Contributions: The individual contributions of all the co-authors are provided as follows: G.D.V. contributed with formal analysis and writing original draft preparation, investigation and methodology, F.P.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, L.H.H.G. contributed with chemical analysis, M.C.S. contributed with chemical analysis and methodology, L.P.B. contributed with formal analysis, investigation and methodology, W.P.F. contributed with physicochemical analysis and methodology, L.G.S.M. contributed with chemical analysis, N.M.M. contributed with formal analysis, investigation and methodology, D.A.R.d.C. contributed with investigation and methodology, S.D.J. contributed with resources, chemical analysis, L.E.P.B. contributed with resources, 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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