DISSERTAÇÃO DE MESTRADO - PPGESA

CARACTERIZAÇÃO DA FASE AQUOSA E BIO-ÓLEO PRODUZIDOS NA PIRÓLISE DAS SEMENTES E FIBRAS DE AÇAÍ (EUTERPE OLERACEA MART.)

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UNIVERSIDADE FEDERAL DO PARÁ
INSTITUTO DE TECNOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO EM ENGENHARIA SANITÁRIA E AMBIENTAL

BELÉM (2024)

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Dissertação apresentada ao Programa de Pós-Graduação em Engenharia Sanitária e Ambiental da Universidade Federal do Pará (PPGESA-UFPA), como parte dos requisitos para obtenção do título de Mestre em Engenharia Sanitária e Ambiental.

Linha de Pesquisa: Planejamento, Monitoramento, Operação e Controle de Sistemas de Saneamento.

Orientador: Prof. Dr. -Ing. Nélio Teixeira Machado

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Article

Characterization of the Aqueous Phase from Pyrolysis of Açaí Seeds and Fibers (Euterpe Oleracea Mart.)

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Abstract: Açaí (Euterpe oleracea Mart.) is a native fruit of the Amazon, and its production chain is centered in the state of Pará. The processing of açaí fruits generates large amounts of solid waste, which can pose serious risks to the environment if not used and managed properly. The novelty of this research lies in the fact that until this moment, no research had been reported in the literature on the pyrolysis of açaí fibers and the chemical composition of the aqueous phase, making possible a broad set of applications including biogas production. The present research proposes a study of the pyrolysis of açaí seeds and fibers and the physicochemical and compositional characterization of the aqueous phase products. In this way, açaí processing residues were collected in the city of Belém, PA. The seeds and fibers were dried and impregnated with NaOH solutions, and subsequently subjected to pyrolysis on a laboratory scale. The liquid products from pyrolysis were characterized through acidity index analysis, FT-IR, and gas chromatography. The increase in the concentration of the impregnating agent led to an increase in bio-oil yield from both the seeds (ranging from 3.3% to 6.6%) and the fibers (ranging from 1.2% to 3.7%). The yield in the aqueous phase showed an inverse behavior, decreasing as the concentration of NaOH increased, both in the seeds (ranging from 41% to 37.5%) and the fibers (ranging from 33.7% to 21.2%). High acidity levels were found in the liquid products studied, which decreased as the concentration of the impregnating agent increased. The increase in the concentration of the impregnating agent (NaOH) influenced the chemical composition of the obtained liquid products, leading to a decrease in oxygenated compounds and an increase in nitrogenous compounds in both experimental matrices, which was also evidenced by the reduction in acidity.

Keywords: biomass wastes; açaí seeds and fibers; chemical activation; pyrolysis process; characterization of aqueous phase

1. Introduction

Euterpe oleracea Mart. is one of the most well-known commercial plant species, native to the Eastern Amazon, and is very important for human populations, with the main product being the fruit (açaí), which is essential to the diet of people living in the Amazon. The production chain of açaí fruits is centered in the state of Pará, largely supplied by extractivism [1–3].

Table 1. Description of the variables used in the study.

Symbolism	Variable Description	Unit
mi	mass of the material before the drying process	g
mf	mass of the material after the drying process	g
mc	mass of the component (seed or fiber)	g
mt	total mass before the component separation process	g
$m2$	biomass before calcination at 900 °C	g
$m3$	biomass after calcination at 900 °C	g
$m4$	biomass before calcination at 575 °C	g
$m5$	biomass after calcination at 575 °C	g
AC	ash content	%
VC	volatile content	%
$Toperation$	operating temperature of the pyrolysis process	°C
$Tambient$	temperature around the reactor before the pyrolysis process	°C
TA	operating rate	°C/min
mp	mass of the pyrolysis product (bio-oil, aqueous phase, or biochar)	g
mbi	biomass used in the pyrolysis process	g
$mbiochar$	mass of biochar obtained after the pyrolysis process	g
$mfaq$	mass of aqueous phase obtained after the pyrolysis process	g
$mbiooil$	mass of bio-oil obtained after the pyrolysis process	g
VA	volume of titrant used in the titration of the analyte	ml
VB	volume of titrant used in the titration of the blank	ml
N	normality of the titrant solution	n°Eqg/L
Cf	titrant solution correction factor	-

The açaí is processed with warm water to produce a juice of high nutritional value, and the non-edible part of this fruit is the residue resulting from this processing [4,5]. In the city of Belém, PA alone, tons of seeds from pulp processing are discarded daily, which can pose serious risks to the environment if not utilized and managed properly [6]. Due to the gradual depletion of non-renewable energy sources and high processing costs in developing oil fields, the volume of waste generated from açaí processing could become an alternative for energy conversion [4,7].

Global concern about climate change, largely associated with fossil fuel consumption, has driven increasing interest in renewable energy sources [8]. The pyrolysis of lignocellulosic biomass is a thermochemical process with significant potential to convert waste into energy and fuel, primarily producing an aqueous phase, a gaseous phase, bio-oil, and biochar. Bio-oil is a complex organic mixture containing hydrocarbons and oxygenated compounds, including volatile carboxylic acids, phenols, ketones, aldehydes, and other oxygenated compounds, while the aqueous phase is the product of intermediate condensation reactions containing dissolved oxygenated compounds such as ketones, phenols, and volatile carboxylic acids [9–11].

Table 2 was synthesized based on bibliographic research covering the period from 2020 to 2024 aimed at exemplifying the published research on açaí pyrolysis [10–19]. It can be observed that most studies focused on investigating the pyrolysis of comminuted seeds rather than fibers. Additionally, bio-oil was the most addressed pyrolysis product within the mentioned context, and until this moment, no research was found in the literature comparing the pyrolysis of açaí seeds with fibers or examined the influence of impregnated solution molarity on aqueous phase composition obtained by pyrolysis of açaí fibers, which is the novelty of this research. The impact of this research lies in the fact that new applications can be addressed based on the physical chemistry and compositional characterization of the aqueous phase, such as production of biogas by anaerobic digestion

Table 2. Studies reported in the literature on açaí pyrolysis between 2020 and 2024 [10–19].

Publications	Experimental Matrix	Impregnating Agent	Pyrolysis Temperature	Biomass Comminution	Featured Products
[10]	Seeds	KOH 0.5 M, 1.0 M, 2.0 M	350 °C, 400 °C, 450 °C	Yes	Bio-oil, aqueous phase, biochar
[11]	Seeds	HCl, KOH	350 °C, 450 °C	Yes	Bio-oil, aqueous phase, biochar
[12]	Seeds	NaOH 2 M	400 °C, 450 °C	Yes	Biochar
[13]	Seeds	-	450 °C	Yes	Bio-oil
[14]	Seeds	-	350 °C, 400 °C, 450 °C	Yes	Bio-oil
[15]	Seeds	-	350 °C, 400 °C, 450 °C	Yes	Bio-oil
[16]	Seeds	-	450 °C	Yes	Bio-oil
[17]	Seeds	$ZnCl_2$	650 °C	Yes	Biochar
[18]	Seeds	-	400 °C, 450 °C	Yes	Biochar
[19]	Seeds	KOH 0.5 M, 1.0 M, 2.0 M	350 °C, 400 °C, 450 °C	Yes	Bio-oil, aqueous phase

There is a scarcity of studies characterizing the aqueous phase obtained from the pyrolysis of açaí fibers and seeds without comminution process, and from a technical-scientific standpoint characterizing such a product can provide a basis for new forms of reutilization of these residues. Thus, this work aims to conduct the pyrolysis of açaí seeds and fibers on a laboratory scale under different experimental conditions and to characterize the aqueous phase resulting from the pyrolysis physiochemically.

2. Materials and Methods

2.1. Methodology

Figure 1 illustrates the entire research process methodology employed in this work. Initially, the biomass discarded after the artisanal processing was collected, and the residues were dried in an oven until constant weight. Subsequently, the fibers were separated from the seeds in a rotating drum, and the materials were impregnated with NaOH at concentrations of 0.5 M, 1.0 M, and 2.0 M. After impregnation, the biomass was washed with distilled water, filtered, and left to dry at room temperature for 24 h. Then, the raw and chemically treated fibers and seeds were pyrolyzed in a borosilicate glass reactor at 450 °C and 1 atm. The liquid and solid products were weighed to determine the yields. The characterization of the bio-oils and aqueous phases was conducted by determining the acidity (acid value), the chemical functions present within the liquid phase products as determined by FT-IR analysis, and the chemical composition via gas chromatography coupled with mass spectrometry.

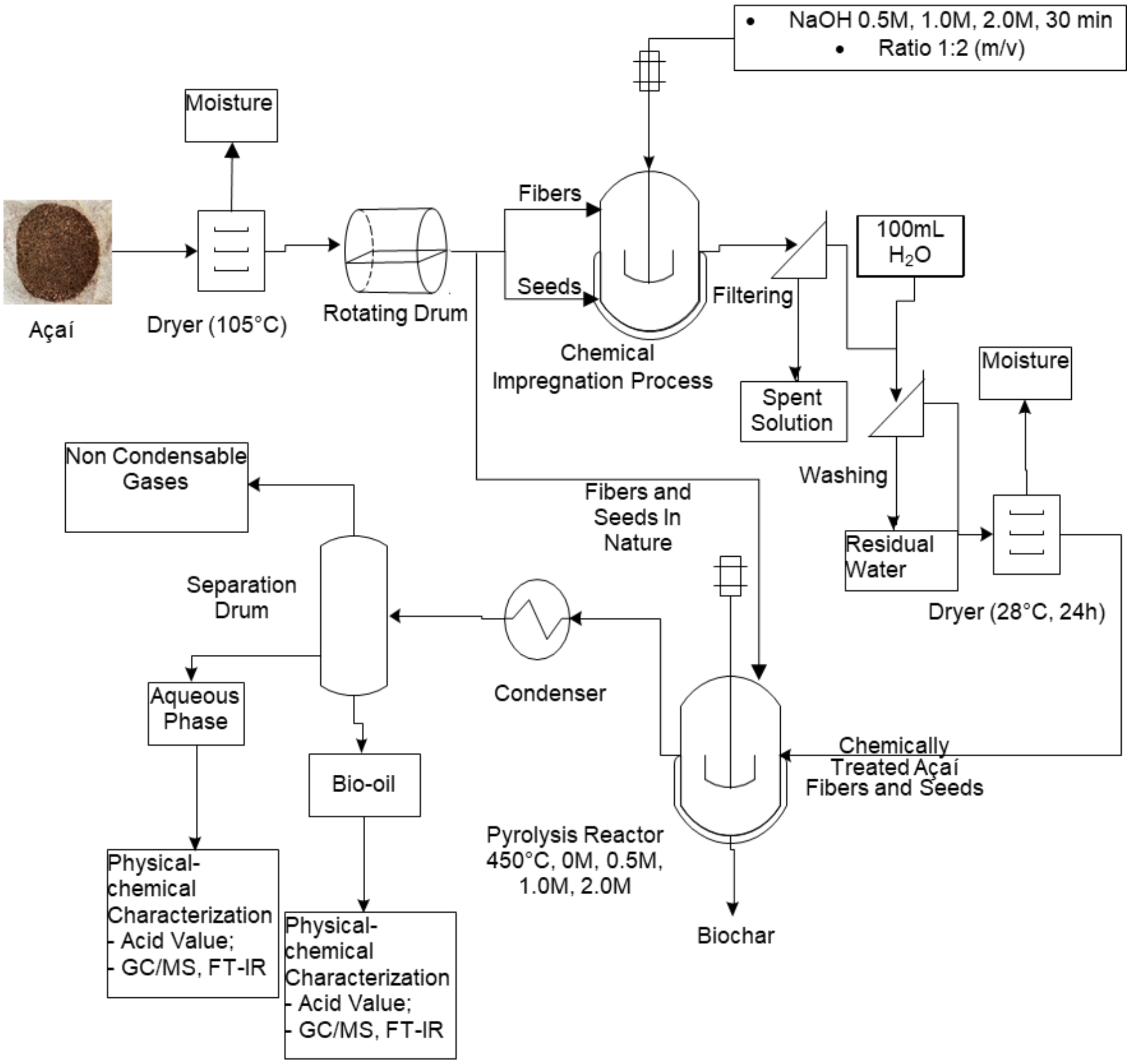


Figure 1. Methodology used for obtaining and characterizing the liquid products from the pyrolysis of açaí seeds and fibers. Source: adapted from Valdez [11].

2.2. Collection, Drying, and Mechanical Separation of the Fibers

The açaí seeds were collected from a commercial establishment located on Cesário Alvim Street in the old town neighborhood of Belém–Pará–Brazil. After collection, the material was placed in aluminum trays and dried in an oven at 105 °C until constant weight. The quantification of the biomass before and after the drying process was performed by gravimetry, and the moisture content was determined according to Equation (1).

$$Moisture\ (\%) = \frac{mi - mf}{mi} x100 \tag{1}$$

After drying in the oven, the fibers were separated from the seeds using a rotating drum with a length of 56.5 cm and a height of 120 cm. The separation occurred using loads of around 1.35 kg of biomass which was placed inside a mesh basket that was then inserted into the rotating drum at 60 rpm for 40 min. The yield of the process was determined using Equation (2).

$$Process\ yield\ (\%) = \frac{mc}{mt} x100 \tag{2}$$

After determining the yield of the separation process, the samples were weighed on a Marte brand semi-analytical balance model AD330 and stored in hermetic plastic bags for later use.

2.3. Determination of the Volatile, Ash, and Fixed Carbon Contents of the Seeds and Fibers

2.3.1. Volatile Content

The determination of volatile content was conducted according to ASTM D 3175 07 [20]. The entire procedure was conducted in triplicate, and the volatile content was calculated according to Equation (3).

$$Volatile\ content\ (\%) = \frac{m2 - m3}{m2} x100 \quad (3)$$

2.3.2. Ash Content

The determination of ash content was performed according to ASTM E1755 01 [21]. The entire procedure was conducted in triplicate, and the ash content was calculated using Equation (4).

$$Ash\ content\ (\%) = \frac{m5}{m4} x100 \quad (4)$$

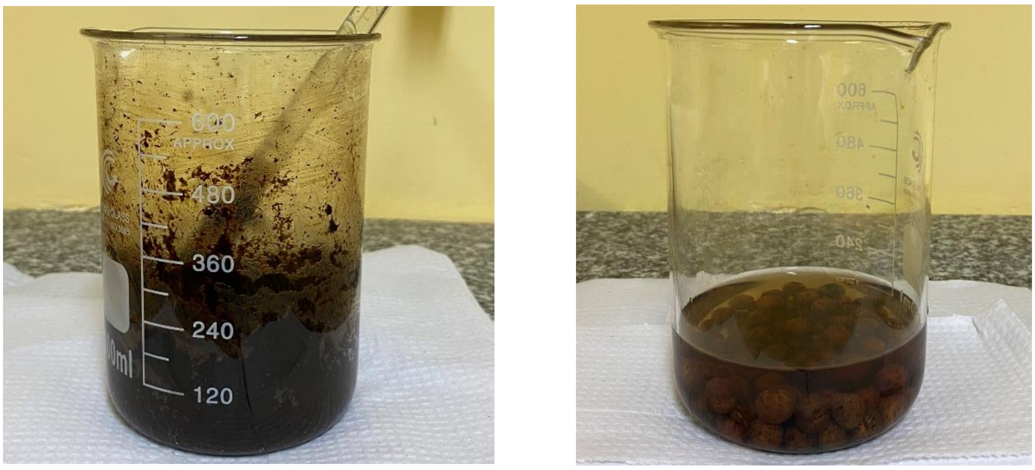
2.3.3. Fixed Carbon Content

The fixed carbon content was determined according to ASTM D3172-89 [22] methodology from the volatile content (VC) and ash content (AC) using Equation (5).

$$Fixed\ carbon\ content\ (\%) = 100 - AC - VC \quad (5)$$

2.4. Chemical Impregnation

The selected impregnating agent for this research was NaOH, as studies have shown that chemical activation of biomass with this agent increases the yield of bio-oil as well as the hydrocarbon content [23]. Additionally, by testing impregnation with 0.5, 1.0, and 2.0 M, we aim to investigate the influence of molarity on the yield and chemical composition of the liquid products. Investigation with higher molarities was discarded due to economic viability concerns. In this way, for the chemical impregnation process of the fibers and seeds, NaOH solutions with concentrations of 0.5 M, 1 M, and 2 M were used. Approximately 57 g of biomass was placed in 600 mL beakers, and the NaOH solutions were added in a ratio of 2:1 (volume of solution in mL/mass of sample). The system was manually stirred for 30 min with the aid of a glass rod (Figure 2). The samples were placed in a simple filtration system and washed with 115 mL of distilled water. After 24 h, the biomass was dried in a Deleo brand oven at 105 °C for an additional 24 h.



(**a**) (**b**)

Figure 2. (**a**) Chemical impregnation of açaí fibers with NaOH solution. (**b**) Chemical impregnation of açaí seeds with NaOH solution.

2.5. Laboratory-Scale Pyrolysis

2.5.1. Description of the Experimental Apparatus

The pyrolysis unit was made up of a borosilicate reactor in a cylindrical (1) shape with a volumetric capacity of approximately 200 mL. The reactor was placed in a cylindrical furnace (2) with a ceramic heating element rated at 800 W. The heating element was connected to a digital temperature and a heating rate controller (THERMA, Model TH90DP202 000) that had a type K temperature sensor (Ecil, Model: QK. 2). A straight borosilicate condenser (Liebig) was coupled to the reactor (3), connected to a cooling system (4) consisting of a thermostatic recirculation bath (VWR) with water as the refrigerant fluid. Above the reactor, a curved connection was attached. The condensed products were collected in a borosilicate glass separation funnel (5). The non-condensable gaseous products and the carry-over gas were directed through an opening in the 90° curve, which was connected between the condenser and the separation funnel. Figure 3 shows the assembled experimental setup.

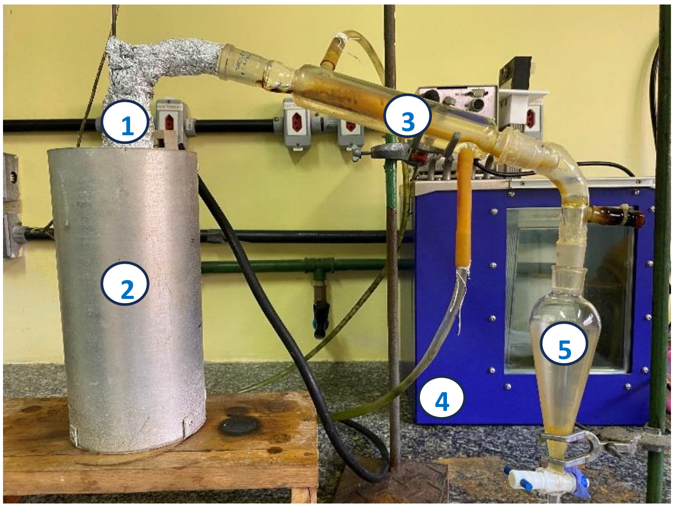


Figure 3. Experimental setup of the pyrolysis process.

2.5.2. Pyrolysis Experiments

The pyrolysis reactions were conducted using açaí fibers and seeds as feedstock. The experiments were performed at a temperature of 450 °C and at 1.0 atm. Approximately 20 g of biomass was weighed for each experiment using a semi-analytical balance (Marte model AD330). Next, the reactor was inserted into the jacketed cylindrical furnace, and with the help of the temperature controller, the reaction time, heating rate, and final process temperature (set-point) were programmed, based on Equation (6). Given the established parameters, a time of 30 min was set to maintain each final operating temperature constant. The pyrolysis process started at room temperature with a heating rate of 10 °C/min.

The solid and liquid products from the reactions were weighed on a semi-analytical balance, and the yield per product was calculated using Equation (7).

$$t = \frac{Toperation - Tambient}{TA} \quad (6)$$

$$Product\ yield\ (\%) = \frac{mp}{mbi} x100 \quad (7)$$

The mass of gaseous products and process losses was obtained through a simple mass balance using Equation (8).

$$Gas + losses = mbi - mbiochar - mfaq - mbiooil \quad (8)$$

2.6. Physicochemical Characterization of the Aqueous Fractions and Bio-Oils Obtained

The physicochemical characterization of the aqueous fractions and bio-oils produced on a laboratory scale aimed to evaluate the acidity index. The assessment was conducted through the analysis of the acidity index (AI) and the comparison of the Fourier-transform infrared (FT-IR) spectra of the samples.

2.6.1. Acidity Index

The acidity index was determined using an adaptation of the official AOCS method Cd 3d-63 (AOCS, 2001). The acidity index, in mg of KOH/g of sample, was calculated using Equation (9).

$$AI\ (\%) = \frac{(VA - VB)N.56{,}1.Cf}{mA} x100 \quad (9)$$

2.6.2. Fourier-Transform Infrared Spectroscopy (FT-IR)

Fourier-transform Infrared Spectroscopy (FTIR) analysis was applied to determine which functional groups were present in the samples. The spectra were obtained using a BRUKER Fourier-transform Infrared Spectrometer (FTIR), model: VERTEX 70v, located in the vibrational and high-pressure spectroscopy laboratory (LEVAP-PPGF/UFPA).

2.6.3. Gas Chromatography Coupled with Mass Spectrometry (GC-MS)

The identification of all compounds present in the liquid products of pyrolysis was performed by GC-MS, using a gas chromatograph (Agilent Technologies, Santa Clara, CA, USA, Model: GC-7890B) coupled with an MS-5977A mass spectrometer with a SLBTM-5 ms (30 m × 0.25 mm × 0.25 mm) fused silica capillary column. The temperature conditions used in the GC-MS were injector temperature: 250 °C; split: 1:50; detector temperature: 230 °C; and quadrupole: 150 °C; injection volume: 1.0 mL; oven: 60 °C/1 min; 3 °C/min; 200 °C/2 min; 20 °C/min; 230 °C/10 min. The intensity, retention time, and compound identification were recorded for each peak analyzed according to the NIST (Standard Reference Database 1A, V14) mass spectra library, which is part of the software. Identification is based on the similarity of the obtained peak mass spectrum with the spectra within the library database included in the software.

3. Results and Discussion

3.1. Moisture and Mechanical Separation of Fibers

Table 3 shows the yields related to the drying and mechanical separation processes of the fibers. The results indicate that the moisture content of the collected material is approximately 35% (wt.), which may be associated with the depulping process of the fruit as well as the improper disposal of seeds that were exposed to the environment.

As expected, the yield of fibers after the mechanical separation process was significantly lower compared to the yield of seeds, as the composition of the residue indicates a smaller percentage of fibers. The losses during the mechanical separation process can be attributed to the small-sized fibers that inevitably got trapped in the mesh basket and other parts of the equipment used to assist in the separation process.

Table 3. Yields after the pre-treatment of drying and mechanical separation processes of the fibers.

Data	Drying	Separation - Seeds	Separation - Fibers
Initial mass (kg)	7.35	1.35	1.35
Final mass (kg)	4.80	1.10	0.20
Yield (%)	65.31	81.48	14.54
Moisture (%)	34.69	-	-

3.2. Ash Content, Volatile, and Fixed Carbon

Table 4 shows the results obtained from the physical characterization of açaí seeds and fibers. It can be observed that the volatile content for the materials in question was quite similar, with 77.39% in the seeds and 77.69% in the fibers. These values are consistent with the study by Cortez and Lora [24], which describes the volatile content ranging from 65% to 83% for raw materials.

According to Silva et al. [25], the ash content depends directly on the amount of inorganic compounds present in the material to be incinerated. In the present study, it was found that the ash content for the seeds was 2.77%, while for the fibers this value was 10.92%. Seye et al. [26], investigating açaí seeds as a source for electricity generation, found an ash content of 1.15%, while Castro [23], studying the pyrolysis of açaí seeds, reported an ash content of 0.42% for the raw material. Santos et al. [27], conducting the physico-chemical characterization of açaí seeds and fibers from a species cultivated in Bahia, found ash contents of 1.4% and 3.41% for the fibers and seeds, respectively. Such differences can be explained by the chemical composition varying according to the cultivation region, soil types, and climatic conditions (Mesquita, [28]).

Table 4. Physical–chemical characterization of raw açaí seeds and fibers.

Data	Seeds	Fibers
Ash content (%)	2.77	10.92
Volatile content (%)	77.39	77.69
Fixed carbon (%)	19.84	11.39

From Table 3, we can also observe that the fixed carbon content in the seeds was 19.84%, while in the fibers the value was 11.39%. The fixed carbon content found by Silva [29] for raw açaí seeds was 21.63%, while Seye et al. [26] and Nagaishi [30] reported values of 18.5% and 20.95%, respectively. In the present study, the fixed carbon content in raw seeds falls within the range described by the mentioned authors.

3.3. Chemical Impregnation

Table 5 illustrates the results after the chemical impregnation process of the seeds and fibers. With the chemical treatment there was a mass loss in both the fibers (around 6%) and the seeds (around 4%). This process generated an aqueous phase with a characteristic color resembling the fruit pulp (Figure 4), indicating that there was extraction and/or solubilization of the chemical constituents. The variation in mass is attributed to the loss of components from the biomass structure such as hemicellulose and lignin. According to Leão [31], treatment with NaOH directly influences the reduction of hemicellulose and lignin by activating the hydroxyl groups of cellulose.

Table 5. Yields after chemical treatment of seeds and fibers with NaOH.

Material	NaOH (mol/L)	Initial Mass (g)	Final Mass (g)	Mass Loss (%)
Fiber	0.5	57.500	53.853	6.343
Fiber	1.0	57.500	53.729	6.558
Fiber	2.0	57.500	54.160	5.809
Seed	0.5	57.500	55.187	4.023

Seed	1.0	57.500	55.558	3.377
Seed	2.0	57.500	55.086	4.198

Figure 4. Wash water after chemical impregnation.

3.4. Laboratory-Scale Pyrolysis

Tables 6–8 show the results obtained during and after the pyrolysis process of raw seeds (S) and fibers (F), both untreated (IN) and impregnated with NaOH solutions at 0.5 M, 1.0 M, and 2.0 M at 450 °C.

Table 6. Process parameters, mass balances, and product yields by pyrolysis of açaí fibers activated with NaOH at 450 °C, 1 atm, and at laboratory scale.

Process Parameters	450 °C		
	NaOH 0.5 M	**NaOH 1.0 M**	**NaOH 2.0 M**
Mass of açaí fibers (g)	20.003	20.007	20.007
Cracking time (min)	70	70	70
Initial cracking temperature (°C)	285	278	218
Mass of solid (coke) (g)	7.519	7.967	7.841
Mass of liquid (bio-oil) (g)	0.303	0.491	0.741
Mass of H_2O (g)	6.089	4.843	4.242
Mass of gas (g)	6.092	6.706	7.183
Bio-oil yield (wt.%)	1.51	2.45	3.70
Aqueous phase yield (wt.%)	30.44	24.21	21.20
Biochar yield (wt.%)	37.59	39.82	39.19
Gas yield (wt.%)	30.46	33.52	35.90
Acidity H_2O (mg KOH/g)	148.2	81.7	19
Acidity bio-oil (mg KOH/g)	130.7	76.4	26.4

Table 7. Process parameters, mass balances, and product yields by pyrolysis of açaí seeds activated with NaOH at 450 °C, 1 atm, and at laboratory scale.

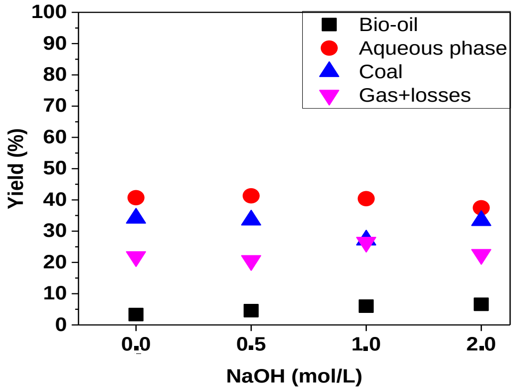
Process Parameters	450 °C		
	NaOH 0.5 M	**NaOH 1.0 M**	**NaOH 2.0 M**
Mass of açaí seeds (g)	20.008	20.74	20.066
Cracking time (min)	70	70	70
Initial cracking temperature (°C)	255	270	280
Mass of solid (coke) (g)	6.710	5.450	6.696
Mass of liquid (bio-oil) (g)	0.910	1.202	1.322
Mass of H_2O (g)	8.264	8.107	7.519

Mass of gas (g)	4.124	5.315	4.529
Bio-oil yield (wt.%)	4.55	5.99	6.59
Aqueous phase yield (wt.%)	41.30	40.39	37.47
Biochar yield (wt.%)	33.54	27.15	33.37
Gas yield (wt.%)	20.61	26.48	22.57
Acidity H_2O (mg KOH/g)	77.4	73.6	68
Acidity bio-oil (mg KOH/g)	47.3	23.1	18.4

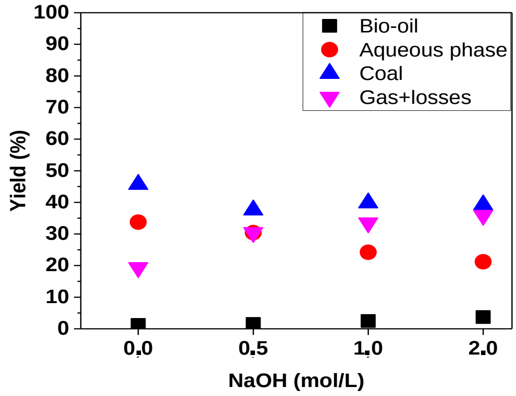
Table 8. Process parameters, mass balances, and yields of reaction products (liquids, solids, H_2O, and gas) by pyrolysis of açaí fibers and açaí seeds *in nature* at 450 °C, 1.0 atmosphere, and at laboratory scale.

Process Parameters	450 °C	
	Fibers	**Seeds**
Mass of açaí seeds (g)	20.000	20.034
Cracking time (min)	70	70
Initial cracking temperature (°C)	300	290
Mass of solid (coke) (g)	9.134	6.836
Mass of liquid (bio-oil) (g)	0.245	0.663
Mass of H_2O (g)	6.747	8.155
Mass of gas (g)	3.874	4.380
Bio-oil yield (wt.%)	1.23	3.31
Aqueous phase yield (wt.%)	33.74	40.71
Biochar yield (wt.%)	45.67	34.12
Gas yield (wt.%)	19.37	21.86
Acidity H_2O (mg KOH/g)	184.3	78.4
Acidity bio-oil (mg KOH/g)	202.6	71.5

From the data in Tables 5–7 and Figure 5, it is observed that there was a change in the production of some pyrolysis products. Notably, in the pyrolysis of seeds, the yield of bio-oil increased with the higher chemical impregnation of the biomass, rising from 3.3% in the raw material to 6.6% in seeds impregnated with a 2 mol/L NaOH solution. A similar trend was observed in the yields of bio-oil during the pyrolysis of fibers, increasing from 1.2% in the raw material to 3.7% in the material impregnated with 2 M NaOH. Castro [23], investigating the pyrolysis of raw açaí seeds at 450 °C at bench, semi-pilot, and pilot scales, reported bio-oil yields of 13.09%, 5.6%, and 4.4%, respectively. When the same author impregnated the seeds with 2 M NaOH, an increase in the yield of bio-oil was observed, reporting 15.59%, 13.38%, and 7.20% for this product obtained at bench, semi-pilot, and pilot scales, respectively. However, when we compare the bio-oils obtained from the two experimental matrices in quantitative terms, it is evident that the seeds provided a larger quantity of this product.



(a)



(b)

Figure 5. (**a**) Yield of reaction products by pyrolysis of açaí seeds. (**b**) Yield of reaction products by pyrolysis of açaí fibers.

It can be observed that the yield of the aqueous phase after the pyrolysis of the fibers exhibited an inverse behavior compared to the yield of bio-oil, decreasing as the concentration of the impregnating agent increased, from 33.7% (raw fiber) to 21.2% when the fiber impregnated with 2.0 M NaOH was processed. After the pyrolysis of the seeds, an aqueous phase yield of around 41% was obtained for both the raw biomass and that impregnated with 0.5 M NaOH, which decreased after the material was impregnated with 1.0 M (40.4%) and 2 M (37.5%) NaOH.

In the pyrolysis of the fibers, the yield of activated charcoal had slight variations, remaining between 33% and 34% (for raw material and that impregnated with NaOH at 0.5 and 2.0 M), and decreasing to 27% in the material impregnated with 1.0 M NaOH. In the pyrolysis of seeds, activated charcoal yields ranged from 38% to 40% (for material impregnated with NaOH at 0.5, 1.0, and 2.0 M) and a yield of 45.7% was obtained for the raw material.

3.5. Physicochemical Characterization of the Obtained Liquid Products

3.5.1. Acidity

The results obtained for the acidity index in the aqueous fractions and bio-oils of the raw fibers showed high values, reaching 184.3 and 202.6 mg KOH/g sample, respectively (Figure 6). It was observed in the fiber samples that as the concentration of the impregnating agent increased, the acidity index decreased significantly in both the aqueous fraction (a reduction of 89.6%) and in the bio-oil (a reduction of 86.9%). A similar behavior was observed in the acidity of the pyrolysis products of the seeds, decreasing from 78.4 mg KOH/g sample to 68.0 mg KOH/g sample (aqueous fraction) and from 71.5 mg KOH/g sample to 18.4 mg KOH/g sample (bio-oil).

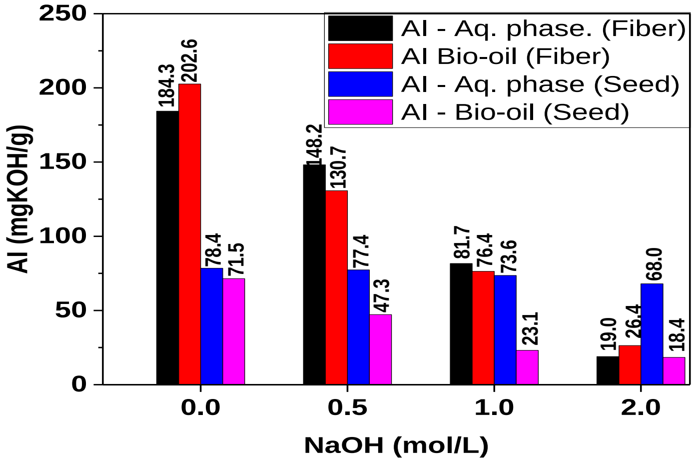


Figure 6. Acidity index of the aqueous fractions and bio-oils from açaí seeds and fibers.

Serrão et al. [14], studying the pyrolysis process of açaí seeds at pilot scale at 450 °C, identified an acidity index of 70.26 mg KOH/g, close to that identified in this work (71.5 mg KOH/g). Castro [23], investigating the pyrolysis process of raw açaí seeds at bench, semi-pilot, and pilot scales, reported that at 450 °C the acidity values found in the bio-oils were 70.25, 68.31, and 70.26 mg KOH/g, respectively. For the seeds impregnated with NaOH at 2 mol/L, the acidity values in the bio-oils obtained at bench, semi-pilot, and pilot scales were 9.21, 15.42, and 19.44 mg KOH/g, respectively.

3.5.2. Fourier-Transform Infrared Spectroscopy

Figure 7 shows the infrared spectra of the bio-oils and aqueous phases obtained from the pyrolysis at 450 °C of raw seeds (SIN) and those impregnated with NaOH.

The bio-oil spectra showed peaks in the ranges between 2853 and 2924 cm^{-1}, associated with axial deformation vibrations, indicating the presence of hydrocarbons [32] in all experiments. It was also observed that for the bio-oils obtained from raw seeds and those impregnated with NaOH, the spectra exhibited characteristic peaks of CO groups, which may be associated with aldehydes, ketones, carboxylic acids, esters, amides, among others (1643, 1710, 3340, 3360, 3361, 3390 cm^{-1}) [32]. The peaks at 1514 cm^{-1} and 1460 cm^{-1} present in all bio-oils indicated the presence of aromatic nuclei (C=C) and methylene groups $(CH_2)n$, respectively [32]. The peaks at 1373 cm^{-1} correspond to the symmetric angular deformation of C-H bonds in the methyl group (CH_3) [32]. The peaks between 1072 and 1225 cm^{-1} may be associated with the presence of alcohols, phenols, and ether and ester groups in the analyzed samples, while the peaks at 729 cm^{-1} may be associated with methyl (CH_3, CH_2) groups [32].

By examining the spectra of the aqueous phases obtained from raw seeds and those impregnated with NaOH (Figure 7), we can infer the presence of CO bonds (1639, 3350 cm^{-1}), hydrocarbons (1394 cm^{-1}), alcohols, phenols, and ether and ester groups (1076, 1273 cm^{-1}) [32]. Castro [23], studying the pyrolysis of açaí seeds at 450 °C, found bio-oil spectra similar to those shown in Figure 7. Similar results were found in the bio-oil obtained from the pyrolysis at 450 °C of açaí seed impregnated with 2.0 M KOH [11].

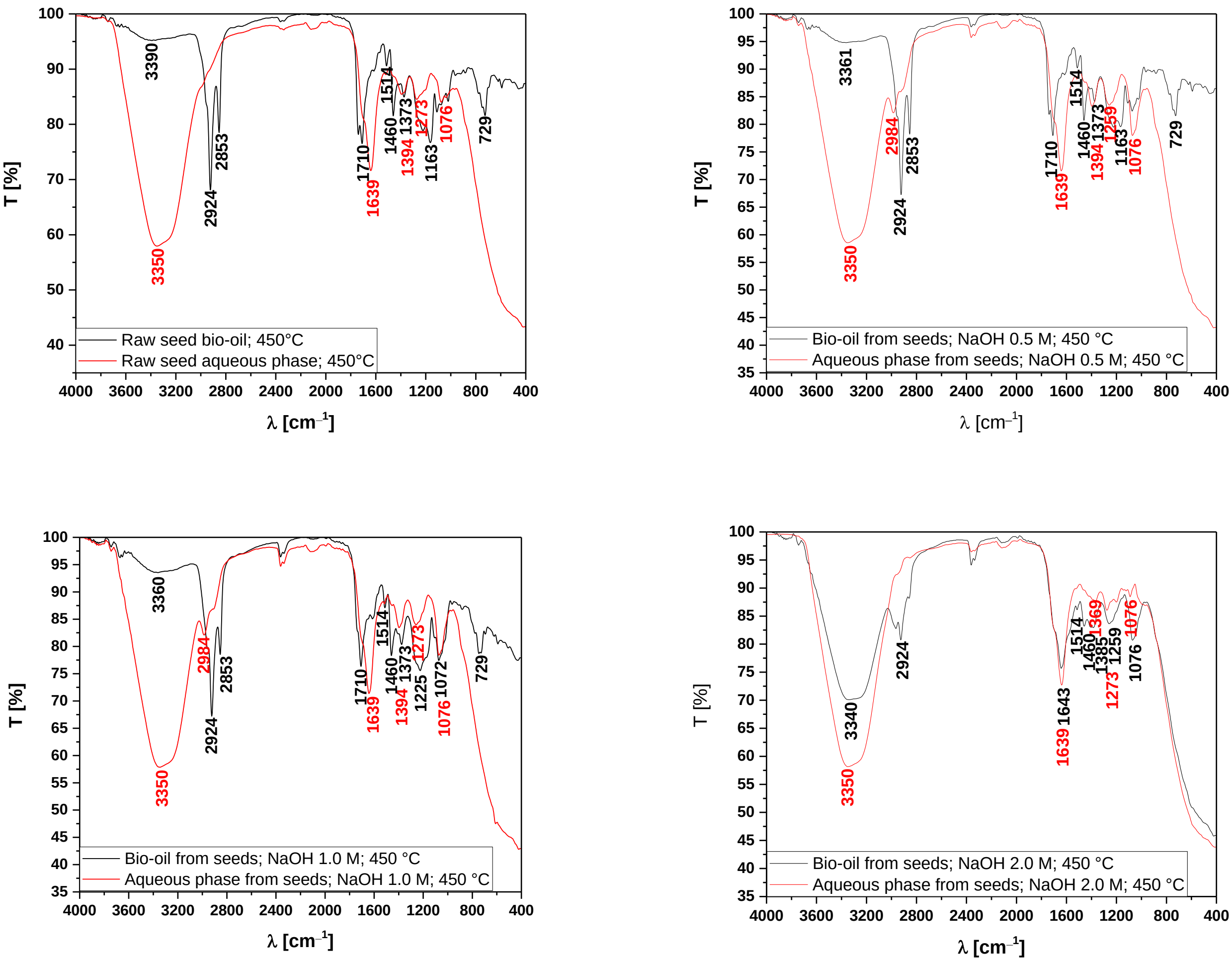


Figure 7. Infrared spectra of bio-oils and aqueous phases by pyrolysis of in nature seeds and NaOH-impregnated seeds.

In the analysis of Figure 8, it can be observed that chemical impregnation influenced the variation in the presence of functional groups, especially in the peaks between 3200 and 3600 cm^{-1}, 2800 and 3000 cm^{-1}, 1600 and 1800 cm^{-1}, and 1200 and 1400 cm^{-1}. This corroborates the data obtained from the acidity index, as the peaks observed, particularly in the range of 1710 cm^{-1}, may be associated with carboxylic acids [32].

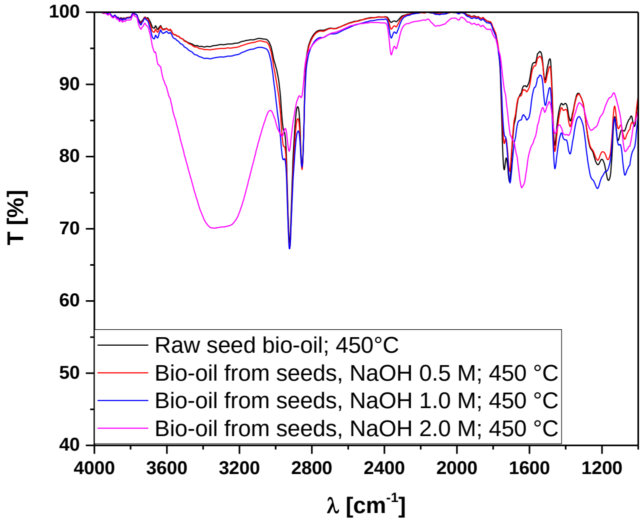
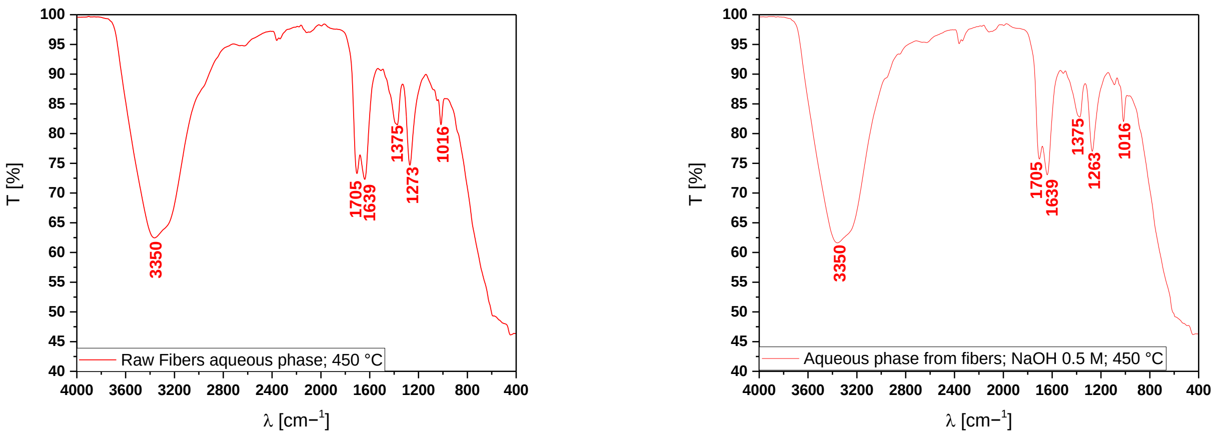


Figure 8. Comparison of the infrared spectra of bio-oils obtained by pyrolysis of in nature seeds and seeds impregnated with NaOH at 0.5, 1.0, and 2.0 M.

Figure 9 shows the infrared spectra of the aqueous phases and bio-oil obtained from the pyrolysis at 450 °C of raw fibers (FIN) and those impregnated with NaOH.

We can observe from the spectra of the aqueous phases peaks at 3350 cm^{-1} indicating the presence of hydroxyl (OH) bonds that may be associated with alcohols and phenols, evidence of carbonyl (C=O) bonds at peaks of 1705 cm^{-1} and 1639 cm^{-1}, hydrocarbons (1375 cm^{-1}), CO bonds (1263 cm^{-1} and 1273 cm^{-1}), sulfoxide or sulfone groups (1090 cm^{-1}), as well as alkanes and ethers (1016 cm^{-1}) [32].

Due to the low yields of bio-oil after the pyrolysis of the fibers, only the spectrum of the sample impregnated with NaOH at 1.0 mol/L could be obtained. This spectrum shows characteristic peaks of OH groups (3340 cm^{-1}), carbonyl groups (1639 cm^{-1}), hydrocarbons, and ethers (1558 cm^{-1}, 1412 cm^{-1}, 1269 cm^{-1}, 1107 cm^{-1}, and 1116 cm^{-1}) [32].



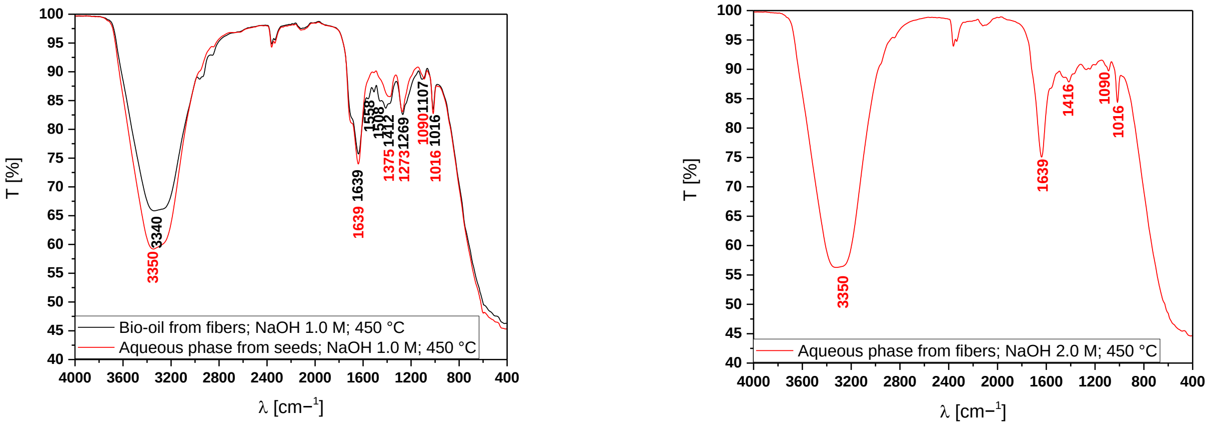


Figure 9. Infrared spectra of the aqueous phases and bio-oil obtained by pyrolysis of in nature fibers and NaOH-impregnated fibers.

In the analysis of Figure 10, it can be observed that chemical impregnation influenced the variation in the presence of functional groups in the aqueous phases obtained from the pyrolysis of the fibers, especially in the peaks between 3000 and 3500 cm^{-1} and in the peaks indicative of the presence of hydrocarbons and carbonyls [32].

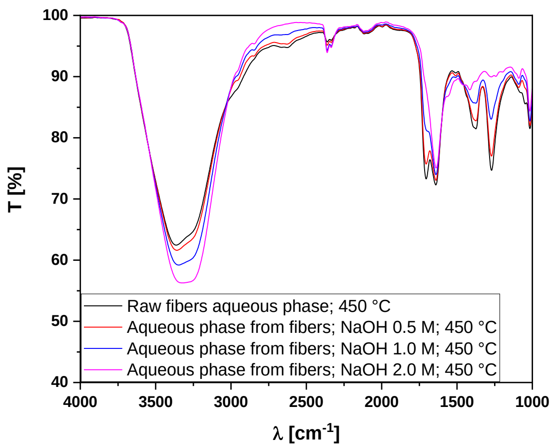


Figure 10. Comparison of the infrared spectra of the aqueous phases obtained by pyrolysis of in nature fibers and fibers impregnated with NaOH at 0.5, 1.0, and 2.0 M.

From the analysis of Figure 11, it is possible to observe significant differences in the peaks of the bio-oil spectra obtained from the two experimental matrices (seed and fiber), especially in the characteristic regions of OH groups, hydrocarbons, and in the ranges between 1070 and 1710 cm^{-1} [32]. This suggests a change in the chemical composition when comparing the bio-oils obtained from the seeds and fibers under the same experimental conditions.

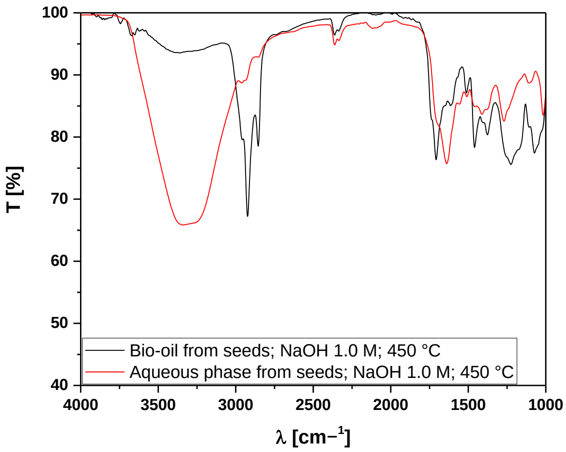


Figure 11. Comparison of the infrared spectra of bio-oils obtained by pyrolysis of açaí seeds and fibers impregnated with NaOH at 1.0 M.

3.5.3. Gas Chromatography

Due to the small amount of biomass used as raw material in all the pyrolysis experiments and the fact that bio-oil yield was low, it was only possible to identify the compounds present in the bio-oil from seeds impregnated with 2.0 M NaOH (S-2.0 M). Table 9 shows the chemical compounds, along with their respective retention times (RT), that are present in the oil in quantities ≥ 3%.

It can be observed that tetradecanoic acid was the major compound (8.91%), followed by dodecanoic acid (4.46%), n-hexadecanoic acid (3.93%), and then phenol (3.24%) and 2-furanmethanol (3.17%). Castro [23], studying the pyrolysis of açaí residues at 450 °C, identified phenols (6.79%) as the major compound in raw seeds, followed by p-cresol (6.68%), tridecane (5.14%), and 1-tridecene (4.32%). For seeds impregnated with 2.0 M NaOH, the same author found naphthalene (7.26%) as the major compound, followed by 5-octyl-4-one, 2,2,7,7-tetramethyl (6.45%), and 7-tetradecene (5.15%).

Table 9. Compounds ≥3% identified in the bio-oil after pyrolysis at 450 °C of açaí seeds impregnated with 2.0 M NaOH.

RT	Compounds	S-2.0 M
4041	2-Furanmethanol	3.17
6689	Phenol	3.24
22845	Dodecanoic acid	4.46
27619	Tetradecanoic acid	8.91
32124	n-Hexadecanoic acid	3.93

Figure 12 shows the total area percentage of the compounds identified in the aqueous phases' GC-MS, obtained from pyrolysis of açaí seeds. For more details of the individual compounds see Supplementary Table S1. It can be observed that the oxygenated compounds decreased as the concentration of the impregnating agent increased. There is also a slight increase in the ketones and nitrogen-containing compounds present in the aqueous phases when the seeds were impregnated with 1.0 M and 2.0 M.

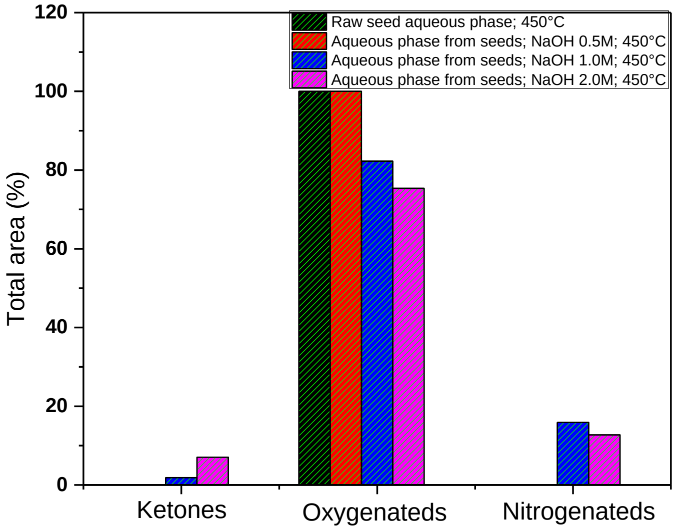


Figure 12. Total area percentage sum of the compounds identified in the aqueous phases obtained by pyrolysis of in nature seeds and NaOH-impregnated seeds.

Table 10 shows the constituents ≥ 5%, along with their respective retention times (RT), present in the aqueous phases after the pyrolysis of the seeds. It can be observed that levoglucosan (beta-D-Glucopyranose, 1,6-anhydro-) was identified in all analyzed samples, varying between 52% and 65%. Furfural was identified in the aqueous phases of the raw seeds and those impregnated at 0.5 M with contents of 18.52% and 15.47%, respectively, while 3,5-dimethylpyrazole was identified only in the samples impregnated with NaOH at 1.0 M and 2.0 M, with contents of 15.88% and 12.74%, respectively. It was observed that the constituent butyrolactone increased with the rise in chemical impregnation, from 0% in the aqueous phases of raw seeds to 12.55% when the seeds were impregnated with 2.0 M NaOH.

Table 10. Compounds ≥5% identified in the aqueous phases after pyrolysis at 450 °C of raw seeds and NaOH-impregnated seeds with 2.0 mol/L NaOH.

RT	Compounds	S-IN	S-0.5 M	S-1.0 M	S-2.0 M
3.742	Furfural	18.52	15.47		
3.746	3,5-Dimethylpyrazole			15.88	12.74
5.119	Butyrolactone		6.4	9.57	12.55
20.820	beta-D-Glucopyranose, 1,6-anhydro-	55.43	65.53	59.04	52.34

Figure 13 shows the total area percentage of the compounds identified in the aqueous phases' GC-MS, obtained from pyrolysis of açaí fibers. For more details of the individual compounds see Supplementary Table S1. It can be observed that there is significant variation in the oxygenated compounds, mainly due to the decrease of the phenol compound, which diminished as the concentration of the impregnating agent increased. This corroborates the acidity index data, as the phenolic compound imparts acidic characteristics to the aqueous phase. An inverse behavior was observed in the nitrogen-containing compounds, which increased as the concentration of NaOH increased.

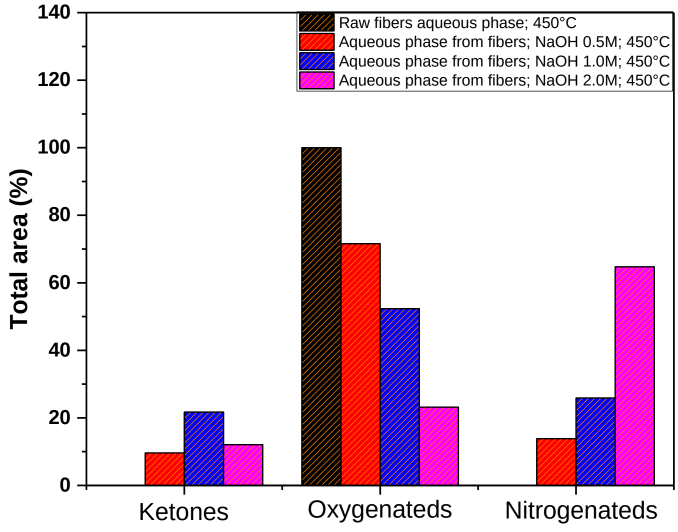


Figure 13. Total area percentage sum of the compounds identified in the aqueous phases obtained by pyrolysis of in nature fibers and NaOH-impregnated fibers.

Table 11 shows the constituents identified in the aqueous phases after the pyrolysis of raw fibers (F-IN) and NaOH-impregnated fibers. It can be observed that phenol was the major constituent in the aqueous phase of the raw fibers, which decreased as the concentration of the impregnating agent (NaOH) increased, from 33.08% (F-IN) to 14.86% in the fibers impregnated with 2.0 M NaOH (F-2.0 M). A similar trend was observed for 2-methoxyphenol, which decreased from 11.76% (F-IN) to 8.34% (F-2.0 M). Meanwhile, the concentration of 4,5-dihydro-2,4,4-trimethyl-oxazole increased from 0% (F-IN) to 48.31% in the fibers impregnated with 2.0 M NaOH.

Table 11. Compounds ≥ 5% identified in the aqueous phases after pyrolysis at 450 °C of NaOH-impregnated fibers.

RT	Compounds	F-IN	F-0.5 M	F-1.0 M	F-2.0 M
3.134	Oxazole, 4,5-dihydro-2,4,4-trimethyl-		5.01	16.76	48.31
6.702	Phenol	33.08	37.28	28.19	14.86
9.613	Phenol, 2-methoxy-	11.76	26.11	15.86	8.34

4. Conclusions

The increase in the concentration of the NaOH impregnating solutions has influenced the formation of pyrolysis products, resulting in an increase in bio-oil yield both from the pyrolysis of seeds (an increase of 3.3%) and fibers (an increase of 2.5%). An inverse behavior was observed in the yield of the aqueous phases, which decreased as the concentration of NaOH increased. The yield of activated carbon showed slight variations, ranging from 27% to 34% after the pyrolysis of fibers and from 38% to 45% after the pyrolysis of seeds.

The acidity of the bio-oils decreased as the concentration of NaOH increased, with a reduction of 74.3% in the treatment of the seeds and a reduction of 86.9% in the treatment of the fibers. A similar behavior was observed in the acidity of the aqueous phases, showing a reduction of 13.3% in the products derived from the seeds and 89.6% in the aqueous phases derived from the fibers.

Tetradecanoic acid (8.91%) was the major compound identified in the bio-oil from seeds impregnated with 2.0 M NaOH, whereas in the aqueous phase of this experimental treatment, the major compound was β-D-Glucopyranose, 1,6-anhydro- (52.34%). In the aqueous phase derived from the raw fibers, phenol was the major compound, which decreased as the concentration of the impregnating agent increased, going from 33.08% (raw fibers) to 14.86% (fibers impregnated with 2.0 M NaOH). An inverse behavior was observed with the compound Oxazole, 4,5-dihydro-2,4,4-trimethyl-, which increased with the concentration of NaOH, rising from 0% (raw fibers) to 48.31% (fibers impregnated with 2.0 M NaOH).

Chemical impregnation influenced the chemical composition of the liquid products, as it causes a decrease in oxygenated compounds and an increase in nitrogen-containing compounds in the aqueous phases derived from the fibers.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, Figure S1: title; Table S1: title; Video S1: title.

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Supplementary table of chemical compounds identified in the liquid products from the pyrolysis of açaí seeds and fibers

RT	Compounds	Fibers				Seeds			
		0M	0.5M	1.0M	2.0M	0M	0.5M	1.0M	2.0M
3.134	Oxazole, 4,5-dihydro-2,4,4-trimethyl-		5,01	16,8	48,3				
3.285	3-Hydroxy-3-methyl-2-butanone				4,86				
3.745	Furfural	47,4				18,5	15,5		
3.750	3,5-Dimethylpyrazole		8,85					15,9	12,7
3.750	2-Cyclopenten-1-one			6,72					
3.929	1,2-Ethanediol, monoacetate		3,22	3,91					
4.110	1,3-Dioxolane, 2,2,4-trimethyl-	5,94					2,19		
4.221	2-Propanone, 1-(acetyloxy)-		3,05						
4.230	1,2-Ethanediol, diacetate	1,86							
4.315	Aziridine, 2-(1,1-dimethylethyl)-1,3-dimethyl-				16,4				
4.320	Aziridine, 2-tert-butyl-1,3-dimethyl-, trans-			9,14					
4.645	2-Furanol, tetrahydro-2-methyl-								2,41
4.826	4-Hydroxy-3-hexanone		3,23	7,06	7,2				
5.022	2-Cyclopenten-1-one, 2-methyl-			3,43					
5.114	2-Furancarboxylic acid, 2-ethylcyclohexyl ester					8,01			
5.125	Butyrolactone		4,98	4,4			6,4	9,57	12,6
5.426	2,5-Hexanedione							1,88	
6.286	2-Furancarboxaldehyde, 5-methyl-							2,83	2,58
6.702	Phenol	33,1	37,3	28,2	14,9				
7.155	Methanone, dicyclopropyl-			4,53					
7.869	1,2-Cyclopentanedione, 3-methyl-		3,36				3,8	2,95	4,1
8.673	1-Octene, 4-methyl-		4,9						
9.613	Phenol, 2-methoxy-	11,8	26,1	15,9	8,34				
9.827	Cyclopropyl carbinol								2,4
10.435	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-								2,95
12.818	1,4:3,6-Dianhydro-,alpha,-d-glucopyranose					3,73	3,45	3,97	4,65
18.311	Sulfurous acid, nonyl 2-pentyl ester					4,83	3,15	3,89	3,27
20.330	,alpha,-D-Glucopyranose, 4-O-,beta,-D-galactopyranosyl-					9,49			
20.820	,beta,-D-Glucopyranose, 1,6-anhydro-					55,4	65,5	59	52,3
	TOTAL	100	100	100	100	100	100	100	100

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