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Article

Process analysis of main organic compounds dissolved in aqueous phase by hydrothermal processing of Açaí (*Euterpe Oleraceae*, Mart.) seeds: Influence of process temperature and biomass-to-water ratio

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Abstract: This work aims to investigate systematically the influence of process temperature and biomass-to-water ration on the chemical composition of aqueous and gaseous phases and mass production of chemical by hydrothermal processing of Açaí (*Euterpe Oleraceae*, Mart.) seeds. The hydrothermal carbonization carried out at 175, 200, 225, and 250 °C, 2 °C/min, biomass-to-water ratio of 1:10, and at 250 °C, 2 °C/min, and biomass-to-water ratios of 1:10, 1:15, and 1:20, in technical scale. The chemical composition of aqueous phase determined by GC and HPLC and the volumetric composition of gaseous phase by using an infrared gas analyzer. For constant biomass-to-water ratio of 1:10, the yields of solid, liquid, and gaseous phases varied between 53.39 and 37.01% (wt.), 46.61 and 59.19% (wt.), and 0.00 and 3.80% (wt.), respectively. The yield of solids shows a smooth exponential decay with temperature, while that of liquid and gaseous phases a smooth growth. By variation of biomass-to-water ratios, the yields of solid, liquid, and gaseous reaction products varied between 53.39 and 32.09% (wt.), 46.61 and 67.28% (wt.), and 0.00 and 0.634% (wt.), respectively. The yield of solids decreases exponentially with increasing water-to-biomass ratio and that of liquid phase increases in a sigmoid fashion. For constant biomass-to-water ratio, the concentrations of Furfural and HMF decrease drastically with temperature, reaching a minimum at 250 °C, while that of phenols increases. In addition, the concentrations of CH_3COOH and total carboxylic acids increase, reaching a maximum at 250 °C. For constant process temperature, the concentrations of aromatics vary smoothly with the temperature. The concentrations of furfural, HMF, and cathecol decrease with temperature, while that of phenols increases. The concentrations of CH_3COOH and total carboxylic acids decrease exponentially with temperature. Finally, for the experiments with varying water-to-biomass ratios, the productions of chemicals (furfural, HMF, phenols, cathecol, and acetic acid) in the aqueous phase is highly dependent on the biomass-to-water ratio.

Keywords: Açaí seeds; hydrothermal carbonization; hot compressed water; process analysis, HMF, Furfural, Acetic Acid, Mass Production.

1. Introduction

. Açaí (*Euterpe oleracea* Mart.) is palm native to the Brazilian Amazon [1]. It has abundant occurrence in the Amazon estuary floodplains [2-3]. The Açaí fruits *in nature* have a great economic importance for the agroindustry, as well as extractive activities of rural communities of the Brazilian Amazonian state of Pará [4]. The fruit is a small dark-purple, berry-like fruit, almost spherical, weighing between 2.6 to 3.0 g [5]. It has a diameter

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around 10.0 and 20.0 mm [5], containing a large core seed/kernel that occupies between 85-95% (vol./vol.) of its volume [3,6].

By processing/extracting the pulp and skin with warm water to produce a thick, purple-colored juice [3, 6], a waste is generated [7-11], the Açaí seeds, a rich lignin-cellulosic residue with great potential to energetic use [8-9, 12]. In the crop years 2016-2017 around 1200-1274 million tons of Açaí fruits were produced in Brazil, being the state of Pará the main producer (94%), generating large amounts of solid residues, consisting of seeds and fibers [4-9].

The residue of Açaí fruits (seeds + fibers) processing has a fibrous outer layer, containing 46.51% (wt.) cellulose and 30.31% (wt.) lignin [11], being the residue (seeds + fibers) composed by 36.13% (wt.) cellulose, 47.92% (wt.) lignin, 1.57% (wt.) ash, and 16.64% (wt.) extractives [11], representing an important biomass renewable source for energetic applications [8-9, 12]. In fact, only a few studies investigated systematically the

The thermo-chemical transformation of lignin-cellulose rich biomass with H_2O in the sub-critical or supercritical state is a promising technique, and the literature reports several studies on the subject [13-46]. *Li et. all.* [13], applied statistical methods to investigate the role of process conditions (temperature, rection time, biomass-to-water ratio) and chemical raw material characteristics on the physical-chemistry properties hydrothermal carbonization products (solid, liquid, and gas). In addition, *Li et. all.* [13], reported that most commonly cited hydrothermal carbonization product parameter was solid (hydrochar) yield (71%), while little attention has been paid to carbon-related information to the liquid and gaseous phases (< 18%), *which includes the analysis of chemical composition*.

In fact, only a few studies investigated systematically the composition of main chemical compounds, such as aromatic-ring compounds (*Furfural*, *HMF*, *Phenols*, *Cresols*, *Cathecol*, *Guaiacol, etc.*) [14, 18, 39-41], carboxylic acids ($HCOOH$, CH_3COOH, CH_3CH_2COOH, $CH_3CH(OH)COOH$, $CH_3C(O)CH_2CH_2COOH$, *etc.*) [14, 18, 39-40, 43], alcohols (CH_3OH, CH_3CH_2OH) [14], and sugars (*Glucose*, *Xylose*, *Galactose*, *Fructose*, *Sucrose*, *Mannosan*, *Levoglucosan*, etc.) [18, 40, 43], and BTEX (*Benzene*, *Toluene*, *Xylenes*, and *Ethyl benzene*) [41], dissolved in the process water by hydrothermal carbonization of biomass, including the hydrothermal processing of corn Stover [14, 18], Tahoe mix, Pinyon/Juniper, and Loblolly pine wood, sugar bagasse, and rice hulls [18], wheat straw, wheat straw digestate, Poplar, Garapa, massaranduba, and pine wood, α-Cellulose, and D-(+)-xylose [39], wheat straw, Poplar, and α-Cellulose [40], wheat straw, wheat straw digestate, Poplar, Garapa, massaranduba, and pine wood [41], and Tahoe mix [43]. Recently, *Poerschmann et. all.* [44], investigated the distribution of main medium molar mass compounds dissolved in process water by hydrothermal carbonization of glucose, fructose and xylose by GC-MS and IC, identifying more than 50 compounds, being the most abundant carboxylic acids (formic, acetic, glycolic, lactic, and levulinic acids) and aromatic-ring compounds (Furfural, 5-(Hydroxymethyl)-2-furfural).

Another process parameter affecting the physical-chemistry properties hydrothermal carbonization products (solid, liquid, and gas) is the water-to-biomass ratio, although only a few studies investigated the influence of water-to-biomass ratio by hydrothermal processing of biomass [], including *tomato-pell-waste* [26], *olive stone* [27], *microalgae* [28], *sawdust* [29]; *banana peels* [30], *wood ships* [25], and *corn Stalk* [19], but no study has examined it´s influence consistently [13], particularly on the composition of main chemical compounds dissolved in the process water.

Açaí (*Euterpe oleracea*, Mart.) seed is the only fruit specie, whose centesimal and elemental composition is completely different from wood biomass (Poplar, Garapa, massaranduba, Tahoe mix, Pinyon/Juniper, Loblolly pine, and pine wood) [18, 39-41, 43], agriculture residues of cereal grains (corn Stover, corn Stalk, rice hulls, wheat straw), agriculture residues of sugar cane (sugar bagasse) [18]. Although, hydrothermal treatment has been applied to enhance enzymatic hydrolysis of Açaí seeds in aqueous-H_2SO_4 at 121 °C [47], until the moment no systematic study investigated the influence of temperature and biomass-to-water ration on the chemical composition of aqueous and gaseous phases and mass production of chemicals by HTC of Açaí seeds in technical scale.

This work aims to investigate systematically the influence of process temperature and biomass-to-water ration on the chemical composition of main chemical compounds, such as aromatic-ring compounds, carboxylic acids, and alcohols, dissolved in process water, the gaseous phase composition, and mass production of chemicals by hydrothermal processing of Açaí (*Euterpe Oleraceae*, Mart.) seeds in technical scale.

2. Materials and Methods

2.1. *Materials, pre-treatment, and centesimal/elemental characterization of Açaí (Euterpia oleraceae,* Mart.*) seeds in nature*

The charges of Açaí (*Euterpe oleracea* Mart.) seeds *in nature* obtained in a small store of Açaí commercialization, located in the City of Belém-Pará-Brazil [12]. The seeds were dried at 105 °C, grinded using a knife cutting mill, and sieved using an 18 Mesh sieve, as reported elsewhere [12]. Afterwards, the seeds were physical-chemistry characterized for moisture (AOAC 935.29), volatile matter (ASTM D 3175-07), ash (ASTM D 3174-04), fixed carbon (ASTM D6316-09), lipids (AOAC 963.15), proteins (AOAC 991.20) according to official methods [12], fibers determined according to a standard norm [48], and insoluble lignin by the modified method of Klason [49].

2.2. *Experimental apparatus and procedures*

2.2.1. Experimental apparatus

The technical scale apparatus illustrated in Figure 1, described in details elsewhere [14].

Figure 1. View of pilot scale stirred tank stainless steel reactor of 18.875 L (Parr, USA, Model: 4555).

2.2.2. Experimental procedures

The hydrothermal processing of dried Açaí (*Euterpe Oleracea*, Mart) seeds carried out with hot compressed at 175, 200, 225, and 250 °C, 240 minutes, biomass-to-water ratio of 1:10, and at 250 °C, 240 minutes, and biomass-to-water ratios of 1:10, 1:15, and 1:20, as described in details elsewhere [14].

2.3. *Compositional analysis of reaction products*

2.3.1. Aqueous phase

The chemical analysis of volatile low-chain length carboxylic acids (R-COOH, with $R_1=CH_3$, $R_2=C_2H_5$, $R_3=C_3H_7$, $R_4=C_4H_9$) and alcohols (R-OH, with $R_1=CH_3$, $R_2=C_2H_5$, $R_3=C_3H_8$), selective cellulose/hemicellulose-derived compounds by hydrothermal processing of biomass, identified by GC while the selective cellulose/hemicellulose-derived phenolic (phenol, cresol, catechol, and guaiacol) and aldehydes (Furfural, HMF) compounds identified by HPLC. The equipment specifications (GC, HPLC) and operating conditions described in details elsewhere [14].

2.3.2. Gaseous phase

The volume of gas, degassed at 25 °C and 1.0 atmosphere, measured with a gas flow meter, while an infrared gas analyzer was used to determine the volumetric composition of gaseous products [14]. The equipment's specifications and procedures described in details elsewhere [14].

2.4. *Steady state material balance by hydrothermal carbonization*

The yields of reaction products (solid, liquid, and gaseous phases) were determined by applying the mass conservation principle within the stirred tank reactor, operating in batch mode, closed thermodynamic system, and the equations described in details elsewhere [14].

3. Results

3.1. *Hydrothermal processing of Açaí seeds*

3.1.1. Material balances, operating conditions, and yields of reaction products:

The material balances, operating conditions, and yields of reaction products by hydrothermal processing of Açaí seeds *in nature* at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10, are summarized in Table 1.

Table 1. Mass balances, process and operating conditions, and yields of solid, liquid, and gaseous products by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10.

	Temperature [°C]			
Process Parameters	**175**	**200**	**225**	**250**
Mass of Açaí Seeds [g]	**300.00**	**299.82**	**299.98**	**300.16**
Mass of H_2O [g]	**2997.60**	**3000.20**	**3001.30**	**2999.90**
Mechanical Stirrer Speed [rpm]	90	90	90	90
Initial Temperature [°C]	30	30	30	30
Heating Rate [°C/min]	2	2	2	2
Process Time [min]	240	240	240	240
Mass of Slurry [g]	**3252.20**	**3240.20**	**3216.50**	**3167.40**
Volume of Gas [mL], T = 25 °C, P = 1 atm	**0**	**5290**	**5590**	**7470**
Mass of Gas [g]	**0**	**7.564**	**8.231**	**11.408**
Process Loss (I) [g]	**45.40**	**59.82**	**84.78**	**132.66**
Input Mass of Slurry (Pressing) [g]	3252.20	3240.20	3216.50	3161.70
Process Loss (II) [g]	**0.00**	**0.00**	**0.00**	**5.70**
Mass of Liquid Phase [g]	2638.53	2615.56	2637.97	2556.96
Mass of Moist Hydro-char [g]	588.10	587.37	557.61	591.29
Process Loss (III) [g]	**25.57**	**37.27**	**20.92**	**13.41**
Mass of Dry Hydro-char [g]	**160.16**	**118.53**	**113.052**	**111.092**
(Mass of Liquid Phase + Σ Process Loss + Mass of Moist Hydro-char - Mass of Dry Hydro-char - Mass of Gas) [g]	3137.44	3173.926	3179.997	3177.52
Process Loss (I + II + III) [g]	**70.97**	**97.09**	**105.70**	**151.77**
Mass of $Liquid_{Reaction}$ [g]	139.84	173.726	178.697	177.62
Yield of Hydro-char [wt.%]	**53.39**	**39.534**	**37.686**	**37.011**
Yield of Liquid Phase [wt.%]	**46.61**	**57.943**	**59.570**	**59.188**
Yield of Gas [wt.%]	**0.000**	**2.523**	**2.744**	**3.801**

Figure 2 shows the effect of temperature on the yields of reaction products by hydrothermal processing of Açaí seeds *in nature* with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10. The exponential function was applied to regress the yields of reaction products, correlating well the experimental data for both the solid and liquid phases, with r^2 (R-Squared) between 0.996 and 0.996. The yield of solids shows a smooth first-order exponential decay behavior, while that of liquid and gaseous phases a smooth first-order exponential growth. At 175 °C hydrothermal carbonization takes places, as the main reaction product is a solid [15]. From 200 °C, hydrothermal liquefaction occurs, as the maim reaction products are liquids [15]. The hydrochar yields are according to those reported in the literature for *Rye straw* [16], *Eucalyptus leaves* [17], *corn Stover* [14], *Sugarcane bagasse* [18]; and *corn Stalk* [19].

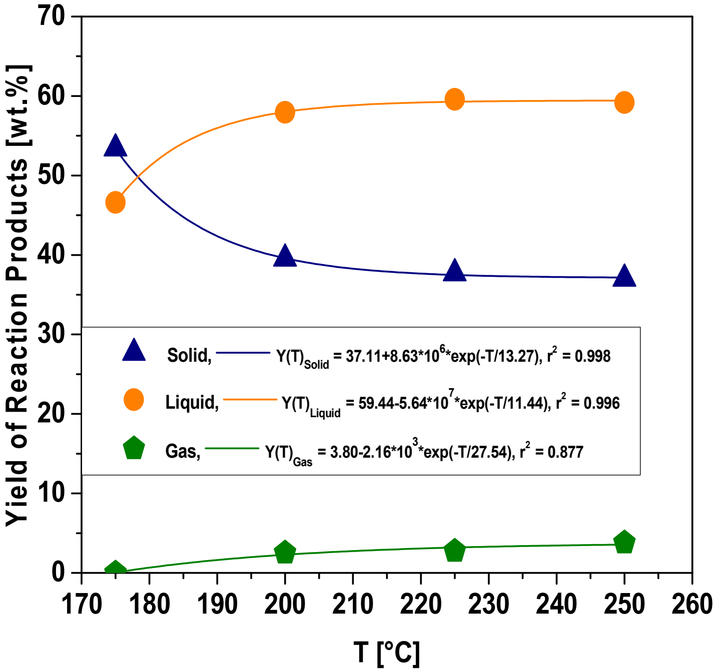


Figure 2. Effect of temperature on the yields of reaction products by hydrothermal processing of Açaí seeds *in nature*.

Based on the centesimal composition of Açaí (*Euterpe oleracea* Mart.) seeds [12], containing 40.29% (wt.) cellulose, 5.5% (wt.) hemi-cellulose, 4.0% (wt.) lignin, 29.79% fibers, as well as 6.25% (wt.) proteins, 0.61% (wt.) lipids, 10.15% (wt.) moisture, 0.5% (wt.) volatile matter, 0.83% (wt.) fixed carbon, and 0.15% (wt.) ash (Supplementary Table TS1), and on the composition of Açaí fibers *in nature*, containing 41.37% (wt.) cellulose, 11.54% (wt.) hemi-cellulose, 40.25% (wt.) lignin, 1.96% ash, and 8.88% moisture, as reported by *Tavares et. all.* [7], that 61.25% (wt.) cellulose and 15% (wt.) lignin decompose by 200 °C, 24 hours, 1:10 biomass-to-water ratio, according to *Falco et. all.* [16], that 5.0% (wt.) lipids and 72% (wt.) proteins decompose at 350 °C, 90 min, 1:5.7 biomass-to-water ratio, as reported by *Teri et. all.* [20], that hemicellulose degrades 65% (wt.) by severity factor between 4.5 and 5.0, as reported by *Borrero-López et. all.* [21], and that approximately 50% (wt.) cotton fibers decompose at 210 °C, 8.0 hours, 1:41 biomass-to-water ratio, as reported by *Zhang et. all.* [22], one may perform a centesimal mass balance to compute the approximate theoretical mass degradation of Açaí seeds at 200 °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10, using the simple equation as follows $Y_{Solid} = \sum \{40.29\%(wt.)*0.3875+4.0\%(wt.)*0.85+5.5\%(wt.)*0.35+6.25\%(wt.)*0.28+0.61\%(wt.)*0.95+[29.79\%(wt.)*0.4137*0.3875+29.79\%(wt.)*0.1154*0.35+29.79\%(wt.)*0.4025*0.85+29.79\%*0.0199(wt.)_{Ash}]+\sum[0.83\%(wt.)_{Fixed\ Carbon}+0.15\%\ (wt.)_{Ash}\} = 41.01\%$ (wt.), very close to the experimental value of 39.534% (wt.), showing a deviation of 3.73%. In addition, the computed amount of Açaí seeds fibers [29.79% (wt.)] degraded at 200 °C, 240 min, and biomass-to-water ratio of 1:10 was 13.03% (wt.), giving a degradation percentual of 43.74%, very close to the results reported by *Zhang et. all.* [22], who stated that approximately 50% (wt.) cotton fibers decompose at 210 °C, 8.0 hours, 1:41 biomass-to-water ratio.

By analyzing the thermal decomposition behavior of cellulose and lignin reported by *Falco et. all.* [16], one observes that decomposition of cellulose is almost constant between 200 °C and 240 °C (38.75→37.00), showing that degradation/depolymerization of cellulose is less intense [19], while lignin loses only 7.5% its initial mass (85%→77.5%), thus making it possible to explain the small differences for the solid phase yields between 200 °C and 250 °C.

Table 2 describes in details the material balances, operating conditions, and yields of reaction products by hydrothermal processing of Açaí seeds *in nature* at 250 °C, 2 °C/min, 240 min, and biomass-to-water ratios of 1:10, 1:15, and 1:20.

Table 2. Mass balances, process and operating conditions, and yields of solid, liquid, and gaseous phases by hydrothermal processing of Açaí seeds with hot compressed H_20 at 250 °C, 2 °C/min, 240 min, and biomass-to-water ratios of 1:10, 1:15, and 1:20.

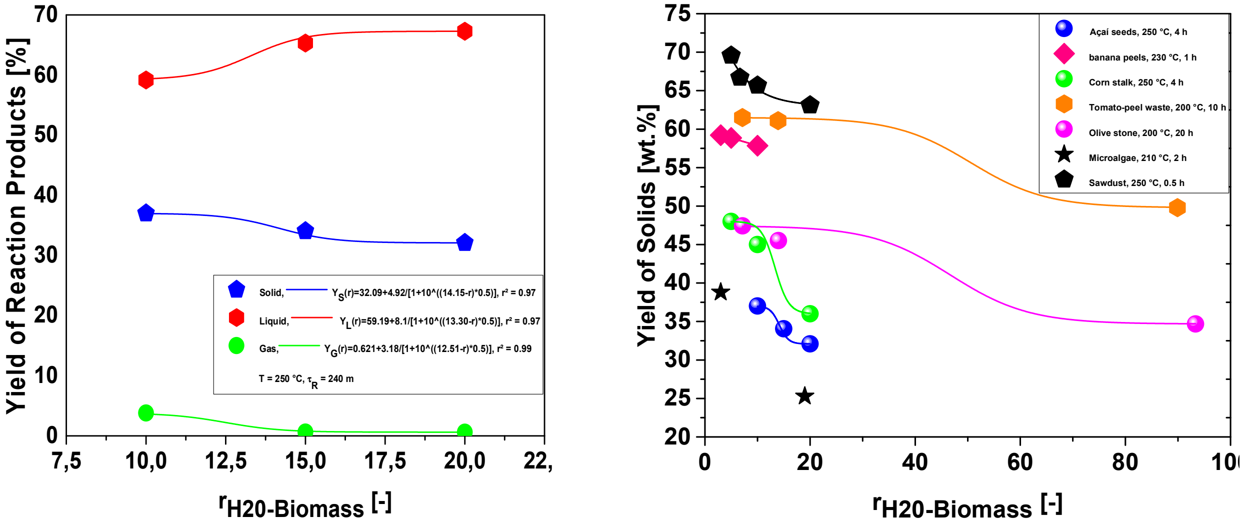
	250 °C		
	Biomass/H_20 [-]		
Process Parameters	**1:10**	**1:15**	**1:20**
Mass of Açaí Seeds [g]	**300.16**	**300.28**	**300.07**
Mass of H_2O [g]	**2999.90**	**4502.90**	**6000.80**
Mechanical Stirrer Speed [rpm]	90	90	90
Initial Temperature [°C]	30	30	30
Heating Rate [°C/min]	2	2	2
Process Time [min]	240	240	240
Mass of Slurry [g]	**3167.40**	**4696.50**	**6217.40**
Volume of Gas [mL], T = 25 °C, P = 1 atm	**7470**	**1240**	**1225**
Mass of Gas [g]	**11.408**	**1.905**	**1.863**
Process Loss (I) [g]	**132.66**	**106.68**	**83.47**
Input Mass of Slurry (Pressing) [g]	3161.70	4696.50	6209.30
Process Loss (II) [g]	**5.70**	**0.00**	**8.10**
Mass of Liquid Phase [g]	2556.96	4077.05	5663.60
Mass of Moist Hydro-char [g]	591.29	585.83	518.45
Process Loss (III) [g]	**13.41**	**33.62**	**35.35**
Mass of Dry Hydro-char [g]	**111.092**	**102.25**	**96.302**
(Mass of Liquid Phase + Σ Process Loss + Mass of Moist Hydro-char - Mass of Dry Hydro-char - Mass of Gas) [g]	3177.52	5000.795	6210.805
Process Loss (I + II + III) [g]	**151.77**	**140.30**	**126.92**
Mass of $Liquid_{Reaction}$ [g]	177.62	196.125	202.535
Yield of Hydro-char [wt.%]	**37.011**	**34.051**	**32.093**
Yield of Liquid Phase [wt.%]	**59.188**	**65.315**	**67.286**
Yield of Gas [wt.%]	**3.801**	**0.634**	**0.621**

The effect of H_20-to-Biomass ratio on the yields of reaction products (solid, liquid, and gas) by hydrothermal of Açaí seeds *in nature*, illustrated in Figure 3 (a) and comparison of hydro-char yields with similar data reported in the literature, shown in Figure 3 (b). At 250 °C hydrothermal liquefaction is dominant, as the main reaction products formed are liquids [15]. The yields of reaction products, illustrated in Figure 3 (a), were regressed using a dose-response function, showing r^2 (R-Squared) between 0.97 and 0.99. The yields of hydro-char and gas decrease with H_20-to-water ratios, while that of liquid phase increases. By increasing the H_20-to-Biomass ratio, the amount of reaction media (hot compressed H_20) increases, increasing the number of hydroxonium ion (H_3O^+) and a hydroxide ion (OH^-) dissociated within the reaction system, thus improving the catalyzes of chemical reactions such as hydrolysis and organic compounds degradation (e.g. depolymerization, fragmentation) without aid a catalyst [23]. In fact, according to the literature [24-25], increasing the H_20-to-Biomass ratio causes a great impact on hydrolysis reactions by hydrothermal processing of biomass.

A compilation of similar data on the effect of H_20-to-Biomass ratio over hydro-char yields illustrated in Figure 3 (b). The behavior of hydro-char yields is similar, showing a decrease on the hydro-char yields as the H_20-to-Biomass ratio increases. The data for *Açaí seeds*, *tomato-pell-waste* [26], *olive stone* [27], and *corn Stalk* [19], were regressed using a dose-response function, showing r^2 (R-Squared) between 0.941 and 0.969.

The experimental data are not only according to similar data reported in the literature for *tomato-pell-waste* [26], *olive stone* [27], *microalgae* [28], *sawdust* [29]; *banana peels* [30], *wood ships* [25], but close to that of *corn Stalk* [19], carried out at 250 °C and 4.0 h.

By analyzing Figure 3 (b), one observes that temperature has a combined effect on the hydro-char yield with varying H_20-to-Biomass ratios. At higher temperatures (250 °C), the effect of H_20-to-Biomass is more intense, playing an important role on hydro-char yield. For low-medium hydrothermal processing temperatures, the effect of H_20-to-Biomass on hydro-char yield is secondary, as reported by [26].

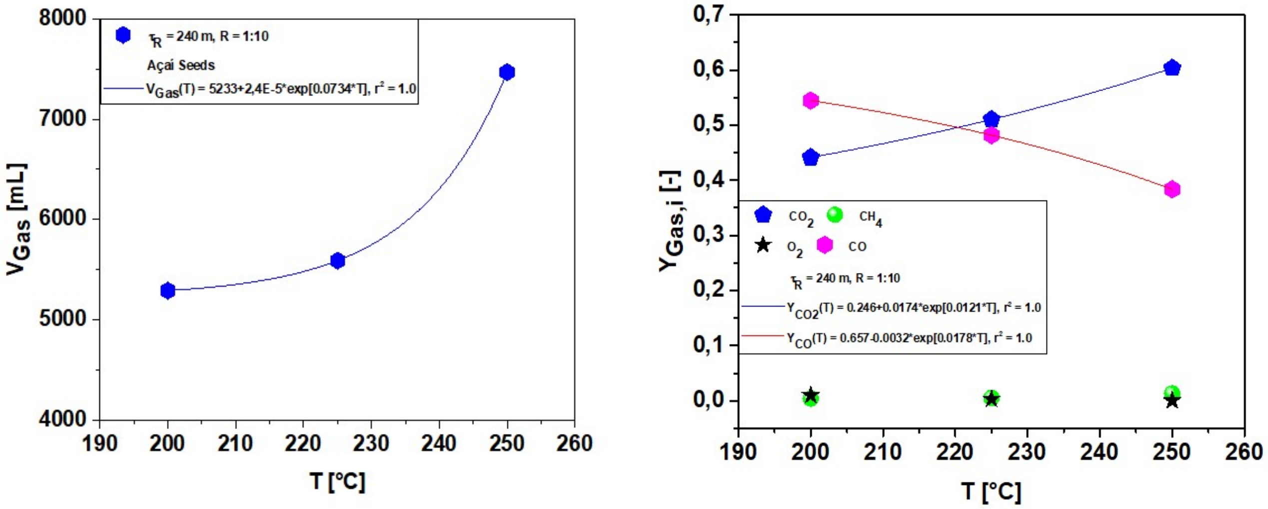


(a) (b)

Figure 3. Effect of H_20-to-Biomass ratio on the yields of reaction products (solid, liquid, gas) (a) and comparison of hydro-char yields with similar data reported in the literature (b).

3.1.1.1. Chemical composition of gas reaction products

The volume of gas degassed at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10 is shown in Figure 4 (a) and the volumetric composition of gaseous products in Figure 4 (b). The volume of gas increases exponentially as the process temperature increases and the same behavior was reported for the hydrothermal carbonization of corn Stover by *Machado et. all.* [14]. Similar studies reported that volume of gaseous products increases with temperature [18, 31-32].



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

Figure 4. Effect of process temperature on the volume of gas degassed at 25 °C and 1.0 atmosphere (a) and on the chemical composition of gas reaction products, expressed in mole fraction (b).

Table 3. Volume of gas and composition of gas products at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10.

		Temperature [°C]		
Composition [vol.%]	**175**	**200**	**200**	**200**
CO_2 [vol.%]	0.00	44.40	51.30	60.60
CH_4 [vol.%]	0.00	0.40	0.50	1.30
O_2 [vol.%]	0.00	1.0	0.30	0.00
100 - Σ (CO_2 + CH_4 + O_2) [vol.%]	0.00	54.20	47.90	38.10
Volume of Gas [mL]	**0.00**	**5290**	**5590**	**7470**
Volume of CO_2 [mL]	0.00	2348.76	2867.67	4526.82
Volume of CH_4 [mL]	0.00	21.16	27.95	97.11
Volume of O_2 [mL]	0.00	52.90	16.77	0.00
$V_{100 - \Sigma (CO2 + CH4 + O2)} \approx V_{CO}$ [mL]	0.00	2867.18	2677.61	2846.07
Mass of Gas[g]	**0.00**	**7.564**	**8.231**	**11.408**
Mass of CO_2 [g]	0.00	4.191	5.117	8.078
Mass of CH_4 [g]	0.00	0.014	0.018	0.063
Mass of O_2 [g]	0.00	0.068	0.022	0.000
Mass of CO [g]	0.00	3.291	3.074	3.267
Composition of Gas [mol.%]				
Y^{CO2}	**0.00**	**0.441410**	**0.510306**	**0.603507**
Y^{CH4}	**0.00**	**0.004055**	**0.004936**	**0.012943**
Y^{O2}	**0.00**	**0.009848**	**0.003017**	**0.000000**
$Y^{100-\Sigma(CO2 + CH4 + O2) \approx Y CO}$	**0.00**	**0.544687**	**0.481741**	**0.383550**

The infrared gas analyzer identified the presence of CO_2, O_2, CH_4, and CO was computed by difference [14], as summarized in Tables 3 and 4, being CO_2, the most abundant gaseous specie produced. This is according to similar studies on the evaluation of gaseous products and compositions by hydrothermal processing of biomass [14, 18, 31, 33-34]. The presence of high volumetric concentrations of CO_2 in the gaseous phase indicates that decarboxylation is probably one of the dominant reaction mechanisms/pathways by hydrothermal processing of Açaí seeds *in nature*, being according to *Li et. all.* [35]. In fact, according to the literature [36], by hydrothermal processing of biomass, decarboxylation takes place, yielding CO_2, but other sources can also produce CO_2, including de decomposition of HCOOH, produced during the hydrothermal degradation of cellulose, and until condensation reactions.

The effect of temperature on the chemical composition of gas reaction products is shown in Figure 4 (b). The mole fraction of CO shows a smooth exponential decay behavior and the mole fraction of CO_2 a smooth exponential growth. An increase on CO_2 concentration in the gaseous phase by hydrothermal processing of biomass may be explained by analogy to the mild torrefaction process of biomass, as reported by *Wannapeera et. all.* [37]. By increasing the process temperature, the oxygen functional groups in the Açaí seeds are decomposed resulting not only in higher amounts of gas formed, but also in higher yields of CO_2.

Table 3. Volume of gas and composition of gas products at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10.

	Temperature [°C]			
Composition [vol.%]	**175**	**200**	**200**	**200**
CO_2 [vol.%]	0.00	44.40	51.30	60.60
CH_4 [vol.%]	0.00	0.40	0.50	1.30
O_2 [vol.%]	0.00	1.0	0.30	0.00
100 - Σ (CO_2 + CH_4 + O_2) [vol.%]	0.00	54.20	47.90	38.10
Volume of Gas [mL]	**0.00**	**5290**	**5590**	**7470**
Volume of CO_2 [mL]	0.00	2348.76	2867.67	4526.82
Volume of CH_4 [mL]	0.00	21.16	27.95	97.11
Volume of O_2 [mL]	0.00	52.90	16.77	0.00
$V_{100 - \Sigma (CO2 + CH4 + O2)} \approx V_{CO}$ [mL]	0.00	2867.18	2677.61	2846.07
Mass of Gas[g]	**0.00**	**7.564**	**8.231**	**11.408**
Mass of CO_2 [g]	0.00	4.191	5.117	8.078
Mass of CH_4 [g]	0.00	0.014	0.018	0.063
Mass of O_2 [g]	0.00	0.068	0.022	0.000
Mass of CO [g]	0.00	3.291	3.074	3.267
Composition of Gas [mol.%]				
Υ_{CO2}	**0.00**	**0.441410**	**0.510306**	**0.603507**
Υ_{CH4}	**0.00**	**0.004055**	**0.004936**	**0.012943**
Υ_{O2}	**0.00**	**0.009848**	**0.003017**	**0.000000**
$\Upsilon_{100-\Sigma(CO2 + CH4 + O2)} \approx \Upsilon_{CO}$	**0.00**	**0.544687**	**0.481741**	**0.383550**

The effect of H_20-to-Biomass ratio on the volume of gas degassed at 25 °C and 1.0 atmosphere by hydrothermal of Açaí seeds *in nature* with hot compressed H_20 at 250 °C, 2 °C/min, 240 min, and biomass-to-water ratios of 1:10, 1:15, and 1:20, illustrated in Figure 5. By increasing the H_20-to-Biomass ratio, the volume of gas depletes, indicating that hydrolysis may be the dominant reaction mechanism [24; 38].

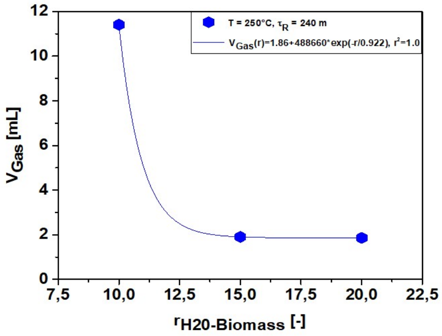


Figure 5. Effect of H20-to-Biomass on the volume of gas degassed at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H_20.

Table 4. Volume of gas and composition of gas products at 25 °C and 1.0 atmosphere as a function of temperature by hydrothermal processing of Açaí seeds with hot compressed H_20 at 250 °C, 2 °C/min, 240 min, and biomass-to-water ratios of 1:10, 1:15, and 1:20.

		250 °C	
		Biomass/H_2O [-]	
Composition [vol.%]	**1:10**	**1:15**	**1:20**
CO_2 [vol.%]	60.60	63.40	59.90
CH_4 [vol.%]	1.30	3.10	1.60
O_2 [vol.%]	0.00	0.00	0.00
Σ (CO_2 + CH_4 + O_2)	61.90	65.50	61.50
100 - Σ (CO_2 + CH_4 + O_2) [vol.%]	**38.10**	**33.50**	**38.50**
Volume of Gas [mL]			
Volume of CO_2 [mL]	4526.82	786.16	**733.775**
Volume of CH_4 [mL]	97.11	38.44	**19.60**
Volume of O_2 [mL]	0.00	00.00	00.00
$V_{100 - \Sigma (CO_2 + CH_4 + O_2)} \approx V_{CO}$ [mL]	**2846.07**	**415.40**	**471.625**
Mass of Gas[g]			
Mass of CO_2 [g]	8.078	1.403	**1.309**
Mass of CH_4 [g]	0.0629	0.0249	**0.0127**
Mass of O_2 [g]	0,00	0.00	0.00
Mass of CO [g]	**3.267**	**0.477**	**0.541**
Composition of Gas [mol.%]			
Y_{CO2}	0.6035	0.6317	0.5966
Y_{CH4}	0.0130	0.0308	0.0159
Y_{O2}	0.000	0.000	0.000
$Y_{100-\Sigma(CO2 + CH4 + O2)} \approx Y_{CO}$	**0.3835**	**0.3375**	**0.3875**

3.1.1.2. Chemical composition of organic compounds in the aqueous phase

The effect of temperature on the concentration profile of aromatic-ring compounds (Furfural, HMF, Phenols, and Cathecol) and carboxylic acids (CH_3COOH, CH_3CH_2COOH) by hydrothermal processing of Açaí seeds, illustrated in Figure 6 (a) and (b), and the data summarized in Table 5.

Table 5. Concentration of aromatics compounds (HMF, furfural, phenol, cathecol), carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) in aqueous phase at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10.

		Temperature [°C]		
Concentration of aromatics [mg/L]	**175**	**200**	**225**	**250**
HMF: CAS: 67-47-0	492.3	474.8	170.1	24.45
Furfural: CAS:98-01-1	227.80	119.50	96.83	5.05
Phenol: CAS: 108-95-2	11.34	-	60.81	81.24
Catechol: CAS: 120-80-9	63.86	-	-	193.8
Concentration of carboxylic acids [mg/L]				
Acetic acid: CAS: 64-19-7	700	1280	1410	1680
Total acetic acid (HAc)	773.2	1394	1540	1859
Propionic Acid: CAS: 79-09-4	90	140	160	220
Concentration of alcohols [mg/L]				
Methanol: CAS: 67-56-1	< 20	< 20	< 20	< 20
Ethanol CAS: 64-17-5	< 20	< 20	< 20	< 20
Propanol CAS: 71-23-8	< 20	< 20	< 20	< 20
Butanol CAS: 71-36-3	< 20	< 20	< 20	< 20

By increasing the process temperature, the concentrations of furfural and HMF, by products of cellulose degradation, decreases exponentially, being present at very low concentrations at 250 °C, while the concentrations of phenols and cathecol, products of furfural and HMF degradation, increase, as shown in Figure 5 (a).

By hydrothermal processing of biomass, as cellulose hydrolyzes, it forms glucose, being transformed by isomerization reactions into fructose [38]. The decomposition of monosaccharides (glucose, fructose) produces volatile carboxylic acids, dissociating within the reaction media, thus producing hydroxonium ion (H_3O^+) and increasing the ionic product of reacting media, improving the degradation of biomass [38]. The monosaccharides (glucose, fructose) also undergo dehydration and fragmentation reaction producing furfural-derived compounds (furfural, HMF), as well as acids and aldehydes [38]. Finally, as temperature increases, furfural-derived compounds (furfural, HMF) suffer degradation, producing acids, aldehydes, and phenols [38]. In this context, based on the reaction mechanism described by Sevilla and Fuertes [38], it is expected that, by increasing the process temperature, the concentrations of Furfural and HMF will decrease, while those of cathecol and phenols increase. The results are according to similar studies reported in the literature [14, 18, 39-41]. *Jung et. all.* [42], studied the growth mechanism of hydro-char and the kinetic model of fructose degradation by hydrothermal carbonization, concluding that HMF degrades forming hydro-char and H_20 (HMF →Hydro-char + H_20), following a first-order kinetics $\frac{d[Hydro-char]}{dt} = K * [HMF]$. This is according to the results for hydro-char yields in Table 1, that is, the higher the concentration of HMF, the higher the yield of hydro-char.

Figure 6 (b) shows that temperature has a great effect on concentrations of carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10. The concentrations of carboxylic acids, particularly CH_3COOH, the most predominant one, as well as the concentration total carboxylic acids (HAc), increase strongly with temperature. By hydrothermal processing of biomass, the monosaccharides (glucose, fructose) produced by hydrolysis of biomass are decomposed forming volatile carboxylic acids, including acetic and propionic acids [38]. As reported by *Hoekman et. all.* [18, 43], and *Machado et. all.* [14], the concentrations of acetic acid and total organic acids produced by hydrothermal processing of different biomass feedstocks increases with temperature. *Poerschmann et. all.* [44], investigated the distribution of main medium molar mass compounds dissolved in process water by hydrothermal carbonization of glucose, fructose and xylose at 180, 220, and 250 °C by GC-MS and IC, reporting acetic acid concentrations of 4560 and 3920 for degradation of glucose and fructose, respectively, at 220 °C and 2.0 h

It is known that monosaccharides (glucose, fructose) decompose, producing not only volatile carboxylic acids, but also undergo dehydration and fragmentation reaction producing furfural-derived compounds (furfural, HMF). According to *Kabyemela et. all.* [45], the reaction mechanism/pathway of Cellobiose decomposition in sub and supercritical H_20 (300 °C/25 MPa, 350 °C/25 MPa, 350 °C/40 MPa, and 400 °C/40 MPa), fallows the sequence: hydrolysis of Cellobiose to form glucose, followed by pyrolysis to form glycosyl-erythrose and glycosyl-glycol-aldehyde, which undergo hydrolysis to produce erythrose + glucose/fructose and glycol-aldehyde + glucose/fructose, that is, glucose/fructose are intermediate-reaction products, *being produced continuously along the hydrothermal process*. However, *Hoekman et. all.* [43], reported that concentrations of glucose/xylose and total sugars decrease with increasing process temperature (215, 235, 255, 275, 295 °C) from 1.02% (wt.) to 0.08% (wt.) and 1.41% (wt.) to 0.22% (wt.), respectively, being not detected at 275 and 295 °C, such that, one may suppose that degradation of monosaccharides (glucose, fructose) are not the only reaction mechanism to produce volatile carboxylic acids by hydrothermal processing of biomass, as glucose, according to *Falco et. all.* [16], starts to be produced at 140 °C, reaching a maximum at 200 °C, where it begins to decomposes.

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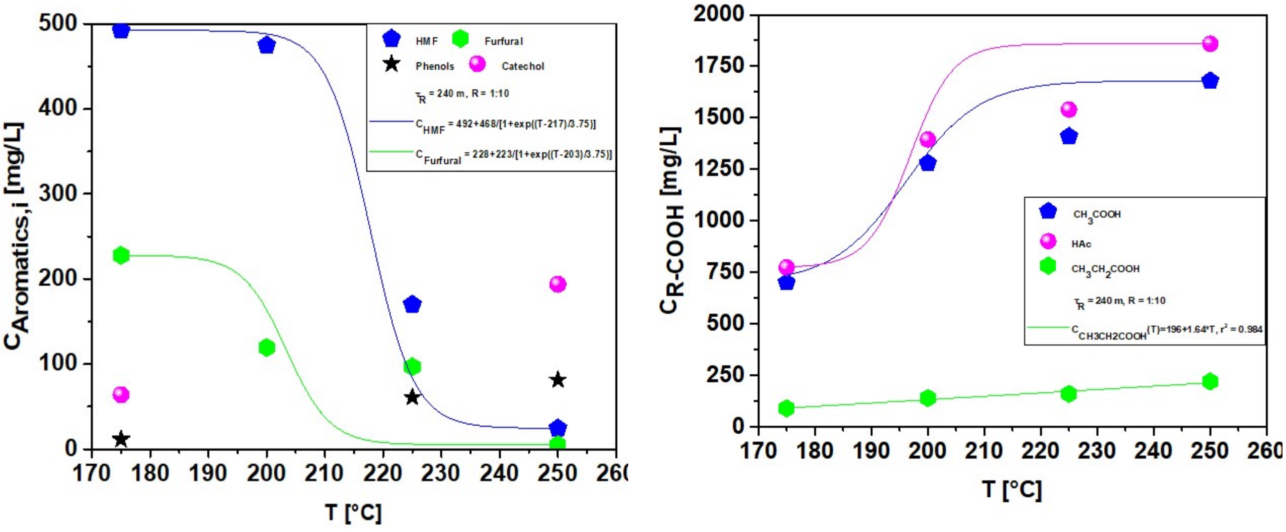


(**a**) (**b**)

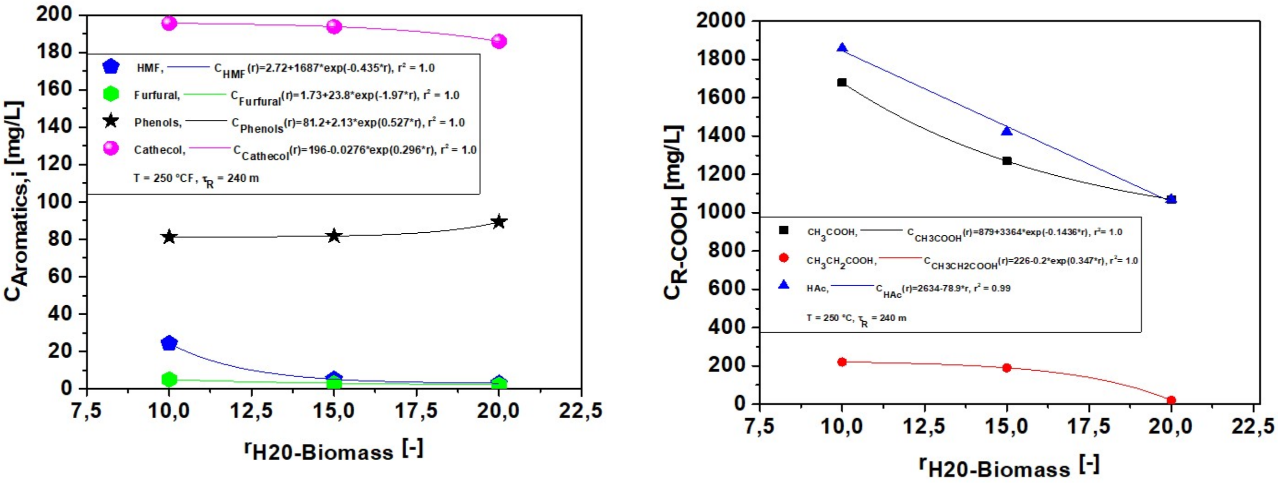
Figure 6. Effect of temperature on the concentration of aromatic compounds (Phenols, Furfural, HMF, and Cathecol) (a) carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) (b).

The effect of biomass-to-water ratio on the concentration profile of aromatic-ring compounds (Furfural, HMF, Phenols, and Cathecol) and carboxylic acids (CH_3COOH, CH_3CH_2COOH) by hydrothermal processing of Açaí seeds, illustrated in Figure 7 (a) and (b), and the data summarized in Table 6.

Table 6. Concentration of aromatics compounds (HMF, furfural, phenol, cathecol), carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) in aqueous phase at 25 °C and 1.0 atmosphere by hydrothermal processing of Açaí seeds with hot compressed H_20 at *175, 200, 225, 250* °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10.

		250 °C	
		Biomass/H_20 [-]	
Concentration of aromatics [mg/L]	**1:10**	**1:15**	**1:20**
HMF: CAS: 67-47-0	24.450	5.188	3.002
Furfural: CAS:98-01-1	5.054	2.972	2.194
Phenol: CAS: 108-95-2	81.24	81.78	89.33
Catechol: CAS: 120-80-9	195.6	193.8	185.9
Concentration of carboxylic acids [mg/L]			
Acetic acid: CAS: 64-19-7	1680	1270	1070
Total acetic acid (HAc)	1859	1424	1070
Propionic Acid: CAS: 79-09-4	220	190	20
Concentration of alcohols [mg/L]			
Methanol: CAS: 67-56-1	< 20	< 20	< 20
Ethanol CAS: 64-17-5	< 20	< 20	< 20
Propanol CAS: 71-23-8	< 20	< 20	< 20
Butanol CAS: 71-36-3	< 20	< 20	< 20

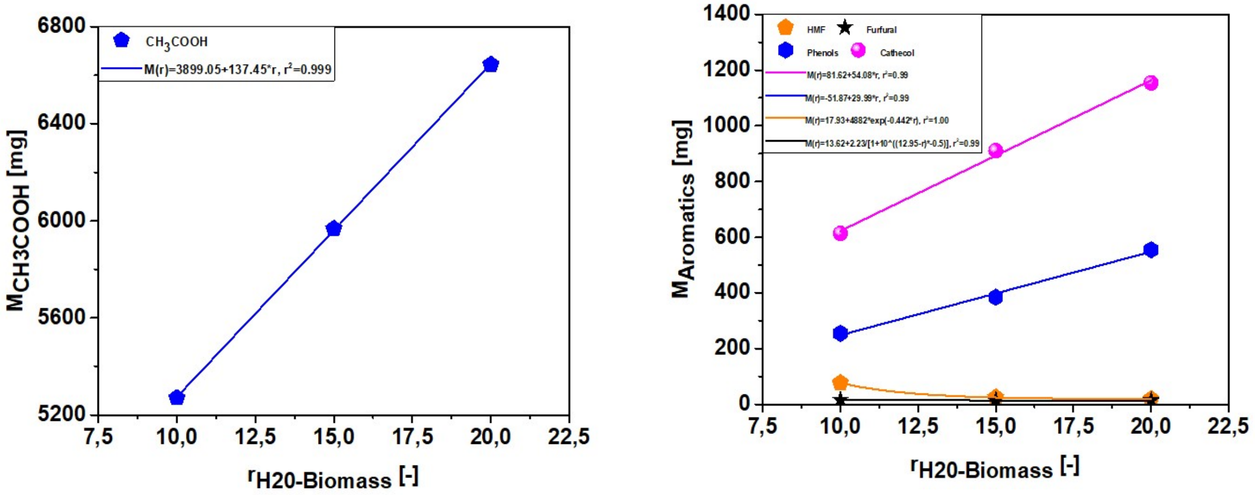
By increasing the H_20-to-Biomass ratio, the concentrations of furfural and HMF are very low and decrease smoothly, while that of phenols shows a smooth first-order exponential growth behavior, as shown in Figure 7 (a). In addition, the carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) also decrease as the H_20-to-Biomass ratio increases, illustrated in Figure 7 (b). In a first look, Figure 7 (a) and (b) do not say much, as the concentration was measured in mg/L, so that, increasing the H_20-to-Biomass ratio, the volume of reaction media increases, and hence it is to expect a decrease on the concentration of main organic compounds dissolved in process water, but performing a mass balance by multiplying the concentration of main organic compounds dissolved in process water, described in Table 6, and the volume of process water (Mass of Liquid Phase + Σ Process Loss + Mass of Moist Hydro-char - Mass of Dry Hydro-char - Mass of Gas), described in Table 2, it can be shown that increasing the H20-to-Biomass ratio has caused an increase on the mass production of chemicals, as shown in Figure 8.



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

Figure 7. Effect of H20-to-Biomass ratio on the concentration of aromatic compounds (Phenols, Furfural, HMF, and Cathecol) (a) carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) (b).

According to the literature [24-25], increasing the H20-to-Biomass ratio causes a great impact on hydrolysis reactions by hydrothermal processing of biomass, so that, the remaining cellulose in biomass is hydrolyzed, producing monosaccharides (glucose, fructose), and the decomposition of monosaccharides (glucose, fructose) produces volatile carboxylic acids, particularly acetic acid, confirmed by Figure 8 (a). It may be concluded that hydrolysis is probably the dominant reaction mechanism, but not the only one, by hydrothermal processing of Açaí seeds with hot compressed H2O at *250* °C, 2 °C/min, 240 min, as biomass-to-water ratio increase from 1:10 to 1:20.



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

Figure 7. Effect of H2O-to-Biomass ratio on the on the mass production of acetic acid (CH_3COOH) (a) and aromatic compounds (Phenols, Cathecol) (b).

5. Conclusions

The yield of solids shows a smooth first-order exponential decay behavior, while that of liquid and gaseous phases a smooth first-order exponential growth. At 175 °C hydrothermal carbonization takes places, as the main reaction product is a solid [15]. From 200 °C, hydrothermal liquefaction occurs, as the maim reaction products are liquids [15].

Based on the centesimal composition of Açaí (*Euterpe oleracea* Mart.) seeds [12], one may perform a centesimal mass balance to compute the approximate theoretical mass degradation of Açaí seeds at 200 °C, 2 °C/min, 240 min, and biomass-to-water ratio of 1:10, obtaining for the solid phase yield 41.01% (wt.), very close to the experimental value of 39.534% (wt.), showing a deviation of 3.73%.

The yields of hydro-char and gas decrease with H_20-to-water ratios, while that of liquid phase increases. Increasing the H_20-to-Biomass ratio causes a great impact on hydrolysis reactions by hydrothermal processing of biomass.

The presence of high volumetric concentrations of CO_2 in the gaseous phase indicates that decarboxylation is probably one of the dominant reaction mechanisms/pathways by hydrothermal processing of Açaí seeds *in nature*, being according to *Li et. all.* [35].

The concentrations of furfural and HMF, decreases exponentially, being present at very low concentrations at 250 °C, as temperature increases, while the concentrations of phenols and cathecol increase.

By increasing the H_20-to-Biomass ratio, the concentrations of furfural and HMF are very low and decrease smoothly, while that of phenols shows a smooth first-order exponential growth behavior. In addition, the carboxylic acids (CH_3COOH, CH_3CH_2COOH) and total carboxylic acids (HAc) also decrease as the H_20-to-Biomass ratio increases. Performing a mass balance, it can be shown that increasing the H_20-to-Biomass ratio has caused an increase on the mass production of chemicals, particularly acetic acid.

It may be concluded that hydrolysis is probably the dominant reaction mechanism, but not the only one, by hydrothermal processing of Açaí seeds with hot compressed H_20 at *250* °C, 2 °C/min, 240 min, as biomass-to-water ratio increase from 1:10 to 1:20.

Supplementary Materials: Table S1: Centesimal and elemental characterization of Açaií (*Euterpe oleracea*, Mart) seeds in *nature*, compared to similar studies reported in the literature [1-4].

Author Contributions: The individual contributions of all the co-authors are provided as follows: Conceição de Maria Sales da Silva contributed with *formal analysis and writing—original draft preparation*, Douglas Alberto Rocha de Castro contributed with *formal analysis and writing—original draft preparation*, Marcelo Costa Santo contributed with *formal analysis and software*, Hélio da Silva Almeida contributed with *formal analysis, software, and visualization*, Ulf Lüder contributed with *investigation and validation*, Maja Shultze contributed with *investigation and methodology*, Jan Mumme contributed with *funding acquisition*, Thomas Hofmann contributed with *resources and project administration*, and Nélio Teixeira Machado contributed with *supervision, conceptualization*, and *data curation*. *All authors have read and agreed to the published version of the manuscript*.

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