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Bio-oil from coconut fibers: fractionation by preparative liquid chromatography for phenols isolation

Bio-óleo de fibra de coco: fracionamento por cromatografia líquida preparativa para isolar fenóis

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ABSTRACT

The great potential of bio-products generated from agro-industrial residues from the biomass processing, as is the case with the green coconut fibers (*Cocos nucifera* L. var. dwarf), makes Brazil stand out in the field of transformation of these residues, mainly due to its high biodiversity and favorable climatic conditions. In this work, residual green coconut fibers were used in the production of bio-oil by pyrolysis. The bio-oil was fractionated using preparative liquid chromatography (PLC) in silica using solvents of different polarities: hexane, hexane/toluene, toluene/dichloromethane, dichloromethane/acetone, and methanol. Bio-oil and its fractions were analyzed by gas chromatograph /quadrupole mass spectrometer (GC/qMS). The concentration of each compound was carried out by multiplying the percentage area of the corresponding peak by the mass yield of the respective fraction. PLC of bio-oil increased the number of compounds identified by about 170% compared to the original bio-oil (non-fractionated), besides allowing the isolation of nonpolar compounds (mostly hydrocarbons) from polar compounds (mainly phenols, aldehydes, and ketones). Another advantage of PLC was the increase in the number of hydrocarbons identified in the fractions, as opposed to the crude bio-oil analysis. Among the major compounds, phenols can be highlighted, besides furfural derivatives and hydrocarbons, which indicates the potential use of bio-oil mainly for industrial purposes.

Keywords: agricultural waste; biomass; fast pyrolysis; PLC; gas chromatography.

RESUMO

O grande potencial de bioprodutos gerados de resíduos agroindustriais provenientes do processamento de biomassa, como é o caso das fibras verdes de coco (Cocos nucifera L. var. anã), destaca o Brasil no campo da transformação desses resíduos, principalmente por sua alta biodiversidade e pelas condições climáticas favoráveis. Neste trabalho, fibras residuais verdes de coco foram utilizadas na produção de bio-óleo por pirólise. O bio-óleo foi fracionado usando cromatografia líquida preparativa (PLC) em sílica com solventes de diferentes polaridades: hexano, hexano/tolueno, tolueno/diclorometano, diclorometano/acetona e metanol. O bio-óleo e suas frações foram analisados por cromatografia gasosa com espectrometria de massas quadripolar (GC/qMS). A concentração de cada composto foi realizada multiplicando a área percentual do pico correspondente pelo rendimento em massa da respectiva fração. A PLC do bio-óleo aumentou o número de compostos identificados em cerca de 170% em comparação com o bio-óleo original (não fracionado), além de permitir o isolamento de compostos não polares (principalmente hidrocarbonetos) dos compostos polares (principalmente fenóis, aldeídos e cetonas). Outra vantagem da PLC foi o aumento do número de hidrocarbonetos identificados nas frações em oposição à análise do bio-óleo bruto. Entre os principais compostos, podem ser destacados os fenóis, além de derivados de furfural e hidrocarbonetos, o que indica o potencial uso do bio-óleo principalmente para fins industriais.

Palavras-chave: resíduos agrícolas; biomassa; pirólise rápida; PLC; cromatografia gasosa.

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Introduction

The global demand for energy has driven extensive research into alternatives to fossil fuels, with a particular emphasis on biomass utilization. However, biomass has garnered significant attention, not only as an energy source but also in the production of non-energy-related materials for industries such as chemicals, food, and pharmaceuticals (Qiu et al., 2022; Vuppaladadiyam et al., 2023). Industries traditionally reliant on fossil fuels stand to benefit from the integration of biomass into their processes. Bioplastics, pharmaceuticals, food additives, and various other products, typical derivatives of the petrochemical chain, can be synthesized in a biorefinery using diverse biomass sources (Yaashika et al., 2022). Optimal sustainability can be achieved by utilizing agro-industrial residues, such as sugarcane straw, bagasse, coconut fibers, rice husks, and others. This approach not only contributes to environmental preservation by reducing discarded materials but also offers economic benefits associated with their utilization (Zhang et al., 2023).

To advance the utilization of biomass, it is imperative to develop technologies for its comprehensive characterization (Opia et al., 2020; Srivastava et al., 2023). Information regarding the physical and chemical properties of biomass is crucial for assessing its toxicity, quality, and stability, ultimately guiding the definition of conversion and application parameters. The characterization of biomass, essential for its proper handling, involves understanding key physicochemical properties such as moisture content, volatile compounds, fixed carbon, elemental composition, and characteristics related to thermal degradation (Cai et al., 2017). An effective method for converting residual biomass is through the production of bio-oil via pyrolysis. Bio-oil, a complex mixture encompassing various classes of compounds like ketones, phenols, aldehydes, and hydrocarbons, requires upgrading to enhance its quality. This process is particularly important for the production of high-value chemical products or applications such as biofuel (Kanaujia et al., 2016; Michailof et al., 2016; Lazzari et al., 2018; Figueirêdo et al., 2022; Machado et al., 2022).

Among the various upgrading processes employed to isolate specific compounds from bio-oil, methods focused on separating compound classes, such as fractionation and extraction, are particularly noteworthy (Schena et al., 2020).

The upgrading of bio-oil through extraction/fractionation encompasses diverse techniques, including organic solvent extraction, supercritical fluid extraction, ionic liquid extraction, fractional distillation, preparative liquid chromatography, membrane separation, electrosorption, and others (Onorevoli et al., 2017; Chan et al., 2020; Schena et al., 2020). Preparative liquid chromatography (PLC) involves the isolation of chemical classes through elution with organic solvents of varying polarities. This method allows for improved qualitative and quantitative analysis, particularly when coupled with gas chromatography/quadrupole mass spectrometry (GC/qMS).

The extensive consumption of green coconuts on the beaches of northeastern Brazil, primarily for their renowned "coconut water", raises ongoing environmental concerns due to the substantial volume of waste, particularly coconut fibers, disposed of improperly. Addressing the urgent need to reduce the amount of this material becomes imperative. Moreover, integrating the utilization of these residues not only aids in waste reduction but also contributes to resolving both environmental and economic challenges.

Against this backdrop, the current study aims to perform rapid pyrolysis on green coconut fibers generated in Aracaju, a city of Sergipe (SE) state, in northeastern Brazil. The objective is to produce and analyze the resulting bio-oil. Additionally, we propose the application of a PLC fractionation methodology on this bio-oil to streamline the analysis of its constituents, employing GC/qMS. This fractionation method allows for the isolation of chemical classes of significant interest, paving the way for potential industrial applications.

Methodological procedures

Materials and reagents

The biomass employed in this study consisted of green coconut fibers (*Cocos nucifera* L. var. dwarf) sourced from a private farm in São Cristovão, Sergipe, Brazil (latitude 10°57'28"S and longitude 37°8'54"W). The green coconut fibers underwent grinding in an industrial mill (Fortalmag) and subsequent drying in an electric furnace (SPLabor Model SP-100) at 70°C for three days. Following the drying process, the fibers underwent further grinding using a knife mill of the Willye type (SPLabor model SP-31), resulting in particle sizes ranging from approximately 32 to 60 mesh. Thereafter, the crushed fibers were stored in a sunlight-protected glass vial until the pyrolysis process. The samples were assigned the designation "CF" (coconut fibers).

For PLC, analytical-grade dichloromethane, hexane, acetone, toluene, and methanol (Sinth, Brazil) were employed. Anhydrous sodium sulfate and silica gel 60 (0.063–0.200 mm, 70–230 mesh) were procured from Merck (Darmstadt, Germany). To prevent contamination, all solvents underwent distillation prior to use. Ultra-pure-grade gases (helium and nitrogen) with purity exceeding 99.999% were supplied by White Martins (Aracaju, SE, Brazil).

Biomass characterization

The proximate analysis of the biomass was conducted following the American Society for Testing and Materials (ASTM) standard methods, and elemental analysis was carried out using LECO CHN-628 equipment, operating at 950°C, with data processed using CHN-628 software version 1.3. Oxygen content was determined by the difference method. The higher heating value (HHV) was determined employing the correlation proposed by Sheng and Azevedo (2005) based on the main elemental composition, as per the Equation 1:

$$\boldsymbol{HHV}\ (\mathrm{MJ\ kg^{-1}}) = -1{,}3675 + 0{,}3137.\boldsymbol{C} + 0{,}7009.\boldsymbol{H} + 0{,}0318.\boldsymbol{O} \quad (1)$$

Where ***C***, ***H***, and ***O*** are the weight percentage (w%) of carbon, hydrogen, and oxygen, respectively.

Pyrolysis conditions

The pyrolysis process, conducted in triplicate, utilized a bench-scale fixed-bed reactor equipped with a vertical furnace. A 3,000 W resistance was employed to heat the stainless-steel reactor at a rate of 100°C min^{-1}. Details of the reactor and the comprehensive pyrolysis system were previously described by Barros et al. (2021). The stainless steel reactor, 30 cm long and 5.1 cm in internal diameter, has a maximum mass capacity of 300 g of biomass.

The pyrolysis process was conducted within a system comprising a vertical oven, wherein the reactor, housing a 3,000 W power resistance, is inserted. Nitrogen served as the carrier gas and was conveyed to the system via a steel connection that traversed the internal part of the oven for preheating. This connection maintained direct contact with the electrical resistance.

For product collection, seven condensers were employed. The initial condenser, constructed from stainless steel, facilitates a secure connection between the reactor and the glass condensers . This design enabled efficient cooling of the pyrolysis gases, preventing thermal expansion in the glass condensers and subsequent breakage. The other condensers are made of glass and have three adapters for collecting bio-oil at the bottom. Temperature control of the condensers was achieved through a thermostatic bath (Marconi model MA-184), maintaining a temperature of approximately 4°C. This control was accomplished using a water and ethylene glycol mixture.

Procedure: The pyrolysis methodology was developed and optimized based on previous works by the research group (Barros et al., 2021), with the pyrolysis temperature set at 700°C and residence time 15 minutes. Initially, 40 g of green coconut fiber biomass was utilized, but after the process optimization, the amount was adjusted to 20 g due to challenges in compacting the green coconut fibers and reducing volume. The heating rate was determined by the maximum power of the 3,000 W resistors, set at 100°C min^{-1}. The variable optimized in the process was nitrogen flow, with two conditions tested: 100 and 200 mL min^{-1}. All analyses were conducted in triplicate, resulting in six pyrolysis runs. After each pyrolysis, the liquid fractions, comprising crude bio-oil and an aqueous fraction, were collected in pre-weighed test tubes. The organic fraction of the bio-oil adhering to the condenser walls was removed by washing with acetone. Following acetone evaporation, this fraction was combined with the original liquid fraction. The solid fraction, referred to as biochar, was also collected. The crude bio-oil samples for the nitrogen flow condition were labeled BO100 at 100 mL min^{-1} and BO200 at 200 mL min^{-1}.

The separation of crude bio-oil from the liquid fraction was achieved through decanting. Dichloromethane (DCM) was employed to dissolve the bio-oil, ensuring complete separation of the aqueous phase. The organic extracts, representing bio-oil diluted in DCM, underwent filtration through a funnel with glass wool and anhydrous sodium sulfate to ensure the complete removal of water. The excess solvent (DCM) was evaporated using a gentle stream of nitrogen gas until a constant weight was achieved. All fractions obtained in the process were weighed to facilitate yield calculation and mass balance.

Yields for the solid fractions (biochar) and bio-oil and aqueous fraction were determined through direct weighing, while the gaseous fraction was calculated by difference. Losses in the process, such as coke production and incrustations, were accounted for alongside the gaseous fraction.

Preparative liquid chromatography

After determining the optimal pyrolysis conditions, the bio-oil underwent a preparative-scale liquid chromatography fractionation process. This procedure aimed to simplify the sample, facilitating a more detailed identification of the compounds of interest. Silica served as the stationary phase in a glass column (20 × 1 cm), employing five solvents with varying polarities, resulting in the production of five fractions. The fractionation approach was inspired by the work of Da Cunha et al. (2013), but with an open system and without column pressurization

Procedure: Approximately 200 mg of bio-oil were dissolved in 5 mL of DCM and added to 1 g of pre-activated silica gel, with vigorous mixing. After complete solvent evaporation, the silica impregnated with bio-oil was transferred to the top of a glass column (20 × 1 cm), previously packed with 10 g of activated silica using n-hexane. Subsequently, the bio-oil was eluted using solvents of varying polarities, and the respective fractions were collected:

Fraction 1 (FR1): eluted with 25 mL of n-hexane.

Fraction 2 (FR2): eluted with 20 mL of a n-hexane/toluene mixture (1:1).

Fraction 3 (FR3): eluted with 25 mL of a dichloromethane/toluene mixture (4:1).

Fraction 4 (FR4): eluted with 25 mL of an acetone/dichloromethane mixture (4:1).

Fraction 5 (FR5): eluted with 25 mL of methanol.

The procedure was conducted in triplicate, and yields in each fraction were calculated after solvent evaporation.

Chromatographic analysis (GC/qMS)

Bio-oils and fractions were subjected to chromatographic analyses using a gas chromatograph coupled to a mass spectrometer (GC/qMS), specifically the model GC/qMS-QP 2010 Ultra by Shimadzu, Japan. The capillary column employed was DB-5 (polydimethylsiloxane with 5% phenyl groups), J&W Scientific, Agilent Technologies, USA, measuring 60 m in length, 0.25 mm in internal diameter, and 0.25 µm of thickness phase. Helium with a purity of 99.999% (White Martins, Aracaju, SE) served as the carrier gas at a flow rate of 1 mL min^{-1}. The oven was programmed to heat from 40°C at a rate of 3°C min^{-1} until 300°C, when it was held for 10 minutes. The injector, detector, and interface

were maintained at 280°C, with electron impact ionization energy set at 70 eV and electron multiplier set at 0.82 kV.

Injection was performed in splitless mode, with a 1 µL injection volume of the solution at a concentration of 10,000 mg L^{-1} in DCM. Detection occurred in full scan mode, covering a range from 45 to 400 Da. All data were processed using GCMS-Solution version 2.6.1 (Shimadzu, Japan).

For compound identification, MS data (comparing the spectra of each peak with the equipment's spectra library), GC data (retention time), and LPTRI (linear programmed temperature retention indexes) were employed. The LPTRI was calculated by the software after injecting a mixture of linear alkanes ranging 6–30 carbon atoms, following the method of van den Dool and Kratz (1963).

Results and discussion

Biomass characterization

Table 1 shows the main properties of the coconut fibers used in this work.

The average moisture content of green coconut fiber was estimated at 10.59% standard deviation ±0.77%, a level considered satisfactory for biomass transformation through thermochemical pyrolysis. Higher moisture contents can impede volatilization speed, requiring greater energy input to initiate the pyrolysis process and resulting in increased aqueous phase production (Aboulkas et al., 2017).

The elevated volatile content and low ash values observed are characteristic of biomass derived from agricultural residues (Vassilev et al., 2010). In pyrolytic processes, a low ash content is desirable to minimize issues related to clogging and incrustation (Serapiglia et al., 2015). Keeping ash levels below 3.0% is recommended to prevent phase separation of bio-oil during aging. Conversely, high ash content can diminish pyrolysis efficiency, causing corrosion and contamination in thermochemical processes. Additionally, high ash content may catalyze undesirable reactions, leading to increased water and gas formation at the expense of liquid organics (Varma and Mondal, 2017).

Table 1 – Preliminary analysis of coconut fibers biomass.

Proximate analysis		Elemental analysis		Others	
Moisture (%)	10.59±0.77	Carbon (%)	46.34	H/C (atomic ratio)	1.55
Volatiles (%) (d.w.)	83.22±1.42	Hydrogen (%)	6.02	HHV (MJ kg^{-1})	18.58
Ashes (%) (d.w.)	1.85±2.70	Nitrogen (%)	0.30		
Fixed Carbon (%) (d.w.)	14.93±5.94	Oxygen (%) (by diff.)	47.34		

d.w.: dry basis; H/C: hydrogen/carbon; HHV: higher heating value; diff.: difference method.

Thermogravimetric analysis (TGA) was employed to determine the optimal temperature and estimate the thermal stability of the material. Figure S1, presented in the Electronic Supplementary Material, illustrates the TGA and the derivative of the thermal gravimetric (DTG) curves for the coconut fibers utilized in this study.

The pyrolytic decomposition of woody plant tissues in inert atmospheres typically initiates at mild temperatures for hemicelluloses (250–300°C), followed by cellulose (315–400°C), and concludes with lignin (mainly between 300–500°C). After 400°C, there is minimal solid residue remaining. Among these components, lignin proves to be the most challenging to decompose, exhibiting slow decomposition over a broad temperature range, extending from ambient temperatures to 900°C (Song et al., 2004; Yang et al., 2007).

Three distinct stages can be observed in the TG curve: the first stage at 100°C, representing the loss of water (6.5%); the second stage from 200 to 900 °C, indicating a 70% loss of lignocellulosic material; and the third stage from 900 to 1000°C, showing a constant weight due to mineral material (14.4%). However, the portion of lignocellulosic material can be further divided into the loss of cellulose occurring from 200°C to approximately 400°C (49.8%) and the less well-defined loss of lignin, spanning from 400 to 900°C (29.3%). In reality, lignin tends to decompose in parallel with cellulose from 100 to 900 °C.

From this last step, the ideal pyrolysis temperature was determined to obtain better bio-oil yields. Therefore, the maximum temperature selected to carry out pyrolysis in this study was set at 700°C, aligned with findings in the literature on green coconut fiber pyrolysis (Almeida et al. 2013; Bispo et al., 2016).

Pyrolysis yields

Table 2 shows the mass yield of the pyrolysis process. Gases and losses (G&L) of the process were considered together and were not measure directly, that is, they were calculated by difference.

It was observed that the mass yield of liquid products (water phase and oil phase), solid products (biochar), and gaseous products (G&L) did not show significant variation under both conditions. This indicates that the alteration in gas flow was not a predominant parameter influencing the final yield of any studied fraction.

Table 2 – Mass yield of the pyrolysis of coconut fibers.

Sample	Yield %				
	AP	BO (bio-oil)	LP=AP+BO	Biochar	G&L
BO100	25.21±3.83	6.46±0.52	31.66±3.31	29.15±4.36	39.19±1.04
BO200	22.92±0.57	7.22±0.47	30.14±1.04	31.24±0.31	38.62±1.35

BO100: 20 g biomass of coconut fibers with a N_2 flux of 100 mL min^{-1}; BO200: 20 g of biomass of coconut fibers with a N_2 flux of 200 mL min^{-1}; AP: aqueous phase; BO: bio-oil; LP: liquid phase; G&L: gases and losses.

On the contrary, the gas content, including losses, was notably substantial, exceeding 38%, which translates to a significant reduction in the final volume of the solid product (biochar). This reduction can be regarded as an environmental benefit of the process, addressing one of the major challenges associated with residues — their large volumes coupled with extended decomposition times.

Upon analysis of Table 2, the volume of residual solids was reduced by 70.85% in BO100 and by 60.76% in BO200, considering the initially used biomass as 100% and designating the biochar formed as the solid residue. Some works developed using green coconut as biomass achieved bio-oil yields that varied, on average, between 28 and 33% (Almeida et al., 2013; Schena et al., 2020). This variation occurs due to different parameters in the pyrolytic process employed by the authors, such as the flow rate of inert gas, heating rate, temperature, and system layout (Tsai et al., 2006).

After establishing that the carrier gas flow did not significantly impact the yields, the flow of N2 at 100 mL min^{-1} was designated as the standard condition for subsequent use. To assess the extent of organic matter transformation during pyrolysis, the biochar underwent TG analysis, and the corresponding graph is provided in Figure S2 of the Electronic Supplementary Material. Notably, the analysis revealed that the organic matter was almost entirely degraded, as evidenced by the stable DTG curve throughout the analysis. Consequently, only mineralized material in the form of ash, comprising approximately 18.7%, remained. This outcome signifies the efficiency of the pyrolysis process.

Characterization of bio-oil by GC/qMS

The chromatograms (GC/qMS – SCAN mode) for the two bio-oils (BO100 and BO200) are shown in Figure 1.

Only peaks whose mass spectra exhibited a similarity greater than 70% with the equipment library and had a maximum difference between calculated and theoretical LPTRI values not exceeding ten units (according to the National Institute of Standards and Technology–NIST) were tentatively identified. Table 3 provides a summary of the results obtained after the identification and semi-quantification of compounds, categorizing them into chemical classes, for the two analyzed samples. Semi-quantitative assessment at this stage was solely based on evaluating the percentage area of identified peaks, with unidentified peaks being disregarded.

Table 3 – Identification of classes of compounds in terms of number of peaks and relative areas for both samples.

Chemical classes	Number of peaks	Area %	
		BO100	BO200
Alcohols	4	1.13	1.60
Aldehydes	8	4.68	5.38
Anhydrous sugar	1	0.56	0.82
Esters	4	2.05	2.62
Ethers	4	2.17	2.75
Hydrocarbons	4	6.10	4.89
Ketones	17	11.91	12.33
Phenols	32	71.39	69.61

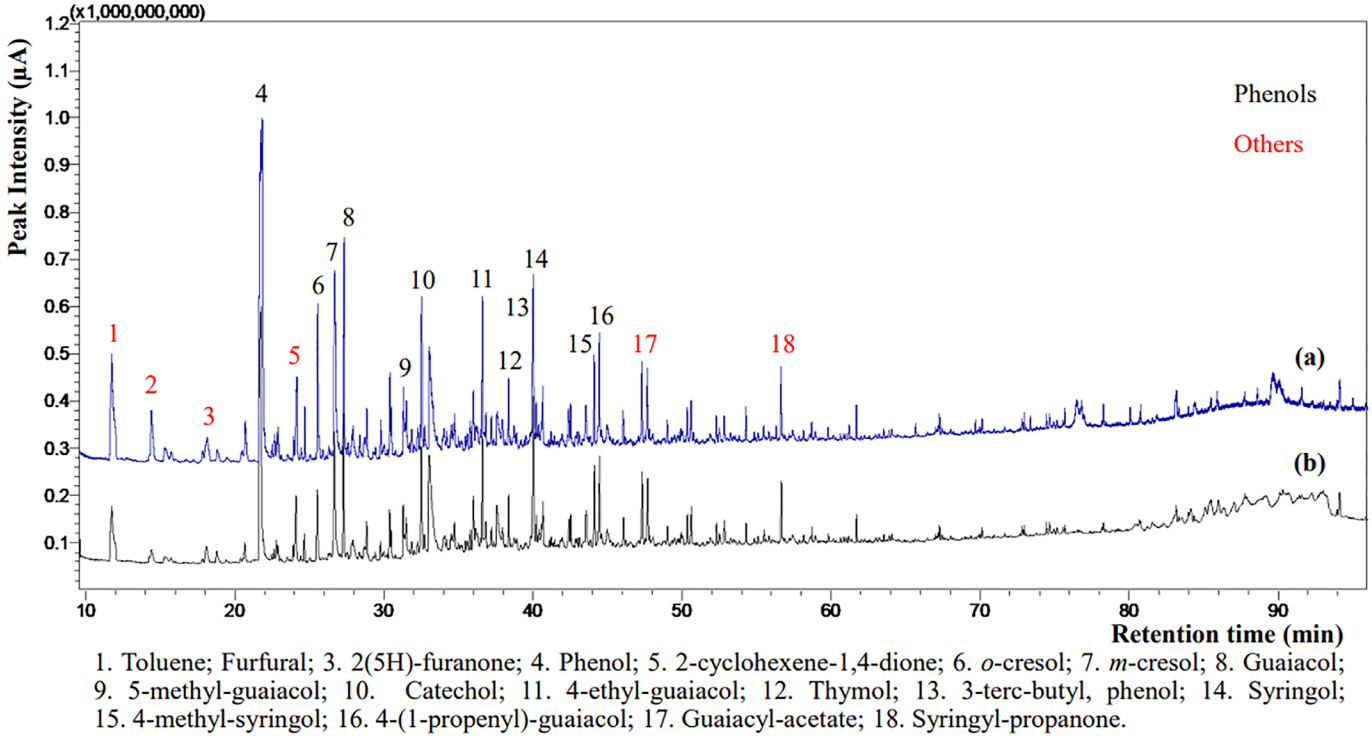

Figure 1 – Chromatographic profile of the bio-oils (GC/qMS SCAN mode) from coconut fibers: (A) BO100 and (B) BO200. Experimental conditions are described in item 2.5 of the Methodological Procedures Section. Majority compounds are identified in the chromatograms.

Although the bio-oil is composed of a mixture of various organic substances, phenols and their derivatives exhibited larger relative areas among the compounds detected in the studied biomass. In both samples, a total of 75 compounds were identified, with the majority (32 compounds) being phenols, representing approximately 70% of the total area. It is noteworthy that the distribution of compounds is highly similar in the two bio-oils. Phenol, a high-value compound, constitutes over 70% in both bio-oils. This aligns with the literature for comparable conditions studied through gas chromatography for green coconut fiber bio-oil (Bispo et al., 2016; Schena et al., 2020).

Fractionation of BO100

Mass yield of fractionation

The yields of bio-oil (BO100) fractionation products, with their respective standard deviations for three determinations, are presented in Table 4.The recoveries for all experiments exceeded 80%, which can be considered acceptable given the potential for irreversible column retention, even after the passage of a strong solvent like methanol. The distribution exhibited a consistent trend, with a higher percentage observed in the fourth fraction (FR4), eluted with acetone and dichloromethane, and a lower percentage for the first fraction (FR1) eluted with n-hexane. These results affirm the abundance of polar and oxygenated compounds in bio-oil samples, indicating a distribution where more than 80% of the compounds are polar, while less than 5% are non-polar.

These results confirm the significant presence of polar and oxygenated compounds in bio-oil samples and align with findings from a similar fractionation method developed by Da Cunha et al. (2013). The proposed method involved pressurized fractionation of bio-oil produced from sugarcane straw, utilizing solvents with polarities similar to those employed in the open column fractionation with PLC suggested in this study.

It is noteworthy to emphasize the scarcity of studies employing this technique for bio-oil upgrading, aiming at a more effective and efficient separation of chemical compounds. This underscores the importance of our study in contributing valuable insights into the potential of PLC fractionation for bio-oil refinement, addressing a current research gap, and highlighting the significance of exploring alternative methods in this field.

Table 4 – Mass yield for the fractions obtained for the studied bio-oil (BO100).

Fraction/solvents	Mass yield (%)*
FR1: n-hexane	3.21±0.91
FR2: n-hexane/toluene	19.04±3.36
FR3: dichloromethane/toluene	19.18±1.47
FR4: acetone/dichloromethane	31.31±5.04
FR5: methanol	27.26±7.84
Recovery**	86.46±9.65

*mass yield plus standard deviation considering three replicates; **total recovery considering the total of 100%.

Chromatographic analysis of fractions by GC/qMS

The total ion chromatograms in the SCAN mode of the bio-oil before fractionation and its respective fractions are illustrated in Figure 2. Notably, some key compounds are highlighted in the chromatograms, providing insights into the composition and distribution of chemical constituents in the bio-oil samples.

The comprehensive identification of compounds in the fractions is provided in the Electronic Supplementary Material (Table S1), showcasing their distribution based on peak relative area% (utilized for semiquantitative analysis) and LPTRI data. A total of 240 compounds were tentatively identified in the bio-oil fractions. It is noteworthy that some compounds with lower intensities exhibited suboptimal chromatographic resolution, displaying partially co-eluted peaks and underscoring the complexity of the sample. Nevertheless, a significant number of peaks could be successfully identified through retention indices and mass spectra.

As some compounds appeared in more than one fraction and for a better semiquantitative interpretation of data after the fractionation of bio-oil, the concentration of each compound was calculated by multiplying the percentage area of each compound by the mass yield of the respective fraction (Table 4). Subsequently, the final concentration of each compound corresponds to the sum of these values found in each fraction. For instance, the compound Vanillin (4-Hydroxy-2-methoxybenzaldehyde, RT=39.11 min) was detected in the fractions FR2 (0.55% or 0.55 × 0.1905=0.10 g/100 g), FR3 (4.98% or 4.98 × 0.1918=0.96 g/100 g), FR4 (0.92% or 0.92 × 0.3131=0.29 g/100 g), and FR5 (0.20% or 0.20 × 0.2726=0.06 g/100 g). The total concentration of this compound corresponds to the sum of these individual concentrations (0.10 + 0.96 + 0.29 + 0.06=1.41g/100 g of bio-oil).

These values are presented in the Ci column (g/100 g) in Table S2, and compounds with higher concentrations (Ci>1.0%) can be found in Table 5. These compounds are considered the most significant in bio-oil and can characterize this type of bio-oil, indicating potential uses.

Following the fractionation, it is evident that catechol and its derivatives stand out as major compounds, holding a considerable industrial interest in this sample, totaling 23.06 g/100 g of bio-oil. Among the phenols, alkyl phenols are also prominent at a concentration of 2.77 g/100 g of bio-oil, while syringol derivatives appear at 7.81 g/100 g of bio-oil. In addition to phenols, the presence of hydroxymethylfurfural (HMF) at a concentration of 3.81 g/100 g of bio-oil is noteworthy.

It is important to highlight that certain lighter compounds, particularly phenol and alkyl-phenols, do not appear in the fractions but are prominent in the crude bio-oil, possibly due to their loss during solvent evaporation (Figure 1). This aspect represents an area for improvement in achieving a more comprehensive characterization of bio-oil.

Another common challenge in fractionation processes is the simultaneous presence of some compounds in more than one fraction. It is conceivable that certain fractions can be considered collectively, such as FR2, FR3, and FR4, for example, given their similar composition.

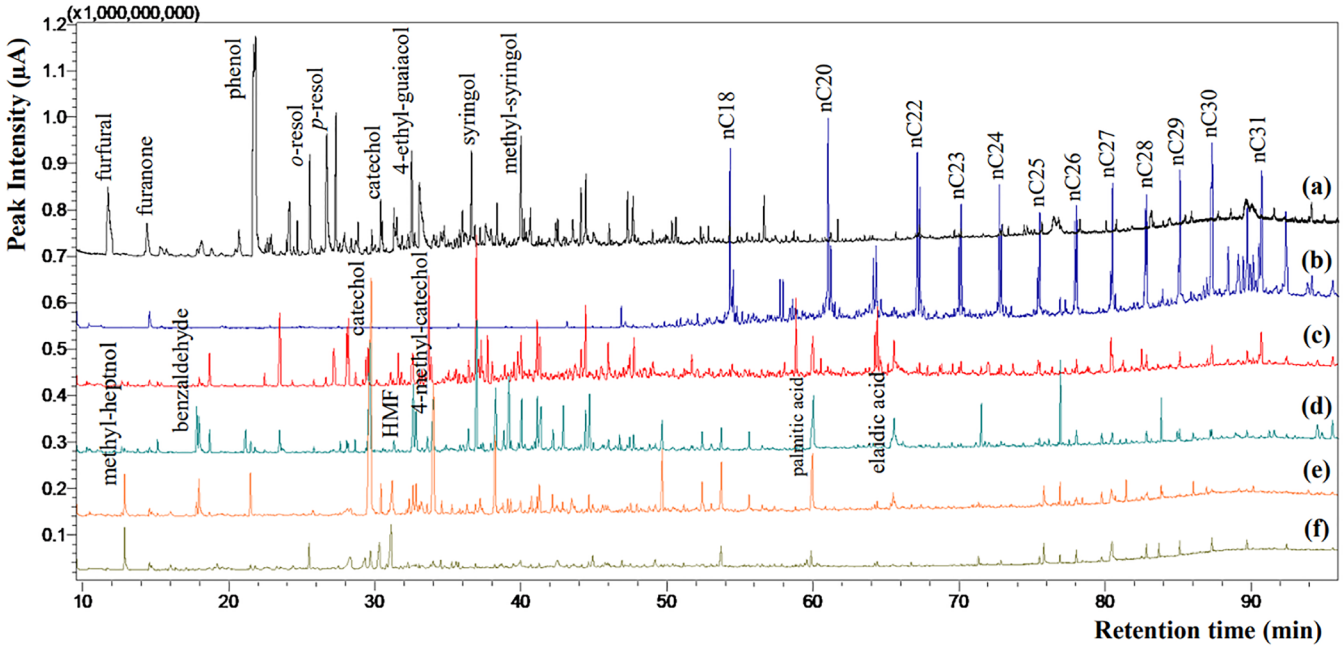

Figure 2 – Total ion chromatogram of the (A) bio-oil before fractionation; (B) FR1 — n-hexane; (C) FR2 — n-hexane/toluene; (D) FR3 — dichloromethane/toluene; (E) FR4 — acetone/dichloromethane; and (F) FR5 — methanol, in the SCAN mode. Chromatographic conditions are described in item 2.5 of the Methodological Procedures Section.
nC: n-alkanes identified in the samples.

To facilitate data comparison, a summary of the semi-quantitative data is presented in Figure 3, where the composition of chemical classes is distributed based on peak relative area (%) multiplied by the yield of the respective fraction. The compounds are grouped into three major classes: phenols, oxygenated non-phenolics, and hydrocarbons.

Analyzing this figure, it can be observed that the hydrocarbon content (represented by the red line) is higher in FR1 and FR5, decreasing significantly for the other fractions. In contrast, the phenol content is practically zero in these fractions, with higher values in FR2 and FR4. The distribution of other oxygenated compounds (non-phenolic) mainly occurs in FR2 and FR5.

The fractionation of bio-oil facilitated the identification of a large number of hydrocarbons in FR1 and FR5. In FR1, 94.67% of the sample is represented by hydrocarbons, with 49.11% being alkanes, 36.95% alkenes, and 8.61% aromatics. However, it is essential to note that this fraction had a very low yield (around 3%), and therefore, the presence of hydrocarbons was not as significant. This fraction presented 72 peaks.

It was observed that the hydrocarbons found mainly in FR1 and FR5 had high molecular weights, ranging from 15 to 33 carbon atoms. The absence of light hydrocarbons is probably due to evaporation together with the solvent after fractionation.

FR2 presented a higher yield and larger number of compounds (109) compared to FR1, and the content of hydrocarbons was low (~10%), with a prevalence of oxygenated compounds (~90%), including 54.23% phenols. From FR2 to FR4, one can observe that phenols are also the majority of compounds, suggesting that they can be mixed and analyzed as a single fraction.

In FR3, there were some co-elutions and contaminations; however, a total of 76 identified peaks were obtained, distributed among phenols (47.63% of the percentage area), ketones (14.04%), acids (11.17%), aldehydes (9.59%), esters (7.38%), and hydrocarbons, mainly alkanes (5.49%).

FR4 was characterized as one of the most polar, presenting 44 identified peaks, with phenols being the most prominent chemical class. Despite having the lowest number of identified peaks, the profile of the FR4 was the one most similar to crude bio-oil in terms of the percentage area of chemical groups, presenting a pre-concentration of phenols (60.14%), followed by aldehydes (10.47%), ketones (9.02%), acids (9.32%), alcohols (5.50%), and esters (4.91%).

The last fraction (FR5) presented 63 identified peaks, with more heterogeneous results in percentage area. The highest value was represented by sugar derivatives, indicating that complete pyrolysis had not yet occurred, as these compounds come from the primary decomposition of biomass components and suggest a partial decomposition of carbohydrates. Regarding ketones, most of them are aromatic (acetophenones) or cyclic, belonging to the classes of cyclopentanones and cyclopentenediones, and are concentrated in FR4 and FR5. Fura-

Table 5 – Major compounds (Ci>1%) for the coconut fibers sample after the fractionation procedure.

Classes	RT (min)	Compounds	Ci (*)
Acid	28.32	Benzoic acid	1.05
	59.97	n-Hexadecanoic acid	3.30
	65.48	Trans-9-Octadecenoic acid (elaidic acid)	1.10
Alcohol	12.86	5-Methyl-2-heptanol	2.55
	21.48	Benzyl alcohol	1.00
Aldehyde	31.15	5-(hydroxymethyl)-2-furfural (HMF)	3.81
	39.11	Vanillin (4-Hydroxy-2-methoxybenzaldehyde)	1.40
	49.66	Syringaldehyde	1.64
Ester	40.05	Benzoic acid, 3-hydroxy-, methyl ester	1.08
	41.33	Methylparaben	1.23
	75.83	Monopalmitin	1.20
Phenol	23.48	Phenol, 3-methyl-	1.08
	29.71	1,2-benzenediol (Catechol)	13.69
	32.61	Phenol, 4-propyl-	1.69
	32.83	1,2-Benzenediol, 3-methoxy-	1.16
	34.02	1,2-Benzenediol, 4-methyl-	5.40
	36.94	Phenol, 2,6-dimethoxy-(syringol)	3.69
	38.24	1,4-benzenediol, 2-(1-methylpropyl)-	2.81
	41.12	4-methylsyringol (2,6-dimethoxy-4-methylphenol)	1.35
Others	80.49	n-heptacosane	1.83
	30.37	Anhydro-sugar 2	1.96
	25.50	Maltol	1.07
	44.42	Toluene, 2,3,5-trimethoxy	1.09

*Ci (curie): concentration of each compound in g/100 g of bio-oil, considering the relative area on the chromatogram and the mass yield of each fraction; RT: retention time.

nones were also classified as ketones, being actually lactones found in bio-oil as well as in FR4 and FR5. Cyclopentanones and cyclic ketones are derived from the degradation of cellulose and hemicellulose, which make up biomass.

Among the main compounds found in bio-oil fractions, especially in FR2, FR3, and FR4, phenolic compounds are predominant. These compounds have numerous applications in different chemical and pharmacological industries due to their antioxidizing and antimicrobial activities. Fractionation proves to be a viable alternative for isolating and recovering these valuable compounds (Albuquerque et al., 2021; Del Olmo et al., 2021).

Preparative liquid chromatography fractionation (PLC-5) increased the total number of identified compounds: from 99 compounds found in unfractionated bio-oils to 240 in FR1, FR2, FR3, FR4, and FR5. Therefore, the fractionation applied in this work demonstrated its efficiency in analyzing bio-oil through GC/qMS, reducing co-elution and, thereby, increasing the concentration of all compounds in the different fractions.

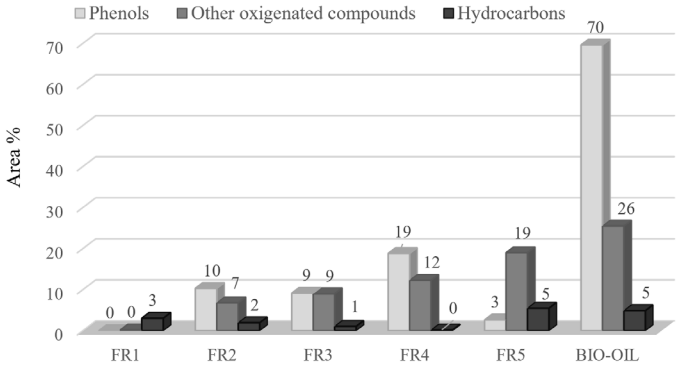

Figure 3 – Distribution of chemical classes: phenols, hydrocarbons, and other oxygenated compounds in the fractions and in the crude bio-oil analyzed by GC/qMS related to the yield of each fraction (yield corresponding to the chemical class x yield of the fraction).
FR1: n-hexane; FR2: n-hexane/toluene; FR3: dichloromethane/toluene; FR4: acetone/dichloromethane; FR5: methanol.

A study conducted by Bordoloi et al. (2016) using PLC-4 fractionation on silica (solvents: hexane, toluene, ethyl acetate, and methanol) for the bio-oil generated from the pyrolysis of the microalga *Scenedesmus dimorphus* found aromatic hydrocarbons and phenols as the major compounds. In the first fraction (hexane), saturated compounds were predominant (n-alkanes, olefins, and branched hydrocarbons). There are few studies in the literature that address this bio-oil upgrading technique, which is why the chemical composition of the fractions obtained in the mentioned study differs from the present work, in addition to the use of different organic solvents.

Conclusion

In the present study, it has been confirmed that the pyrolysis of agro-industrial residues, such as green coconut fiber, proves to be an efficient process for the production of chemical compounds with significant industrial value. Bio-oils obtained from this process contain valuable chemicals, including phenols and methoxyphenols, showcasing excellent potential for the production of derivatives crucial in the chemical, pharmaceutical, and food industries.

The utilization of PLC-5 (silica) fractionation resulted in five distinct fractions, strategically distributed based on solvent polarity. GC/qMS analysis of these fractions not only demonstrated the efficiency of the fractionation process but also revealed that several compounds, especially hydrocarbons, were not identifiable in the original sample and only became apparent after fractionation. Additionally, a reduction in some lighter compounds, notably phenols, was observed following fractionation.

The bio-oils exhibited high concentrations of phenols and a complex composition, which was effectively simplified through the fractionation process. This separation of fractions facilitated a more detailed characterization of the compounds, leading to an increased number of identified compounds. Furthermore, the fractionation process unveiled new compounds that would have remained unidentified without this essential step.

Authors' Contributions:

FARRAPEIRA, R.F.: conceptualization, data curation, writing – original draft, writing – review & editing. ANDRADE, Y.B.: conceptualization, data curation, writing – original draft, writing – review & editing. CONRADO, N.M.: conceptualization, data curation, writing – original draft, writing – review & editing. SCHNEIDER, J.K.: supervision, writing – original draft, writing – review & editing. KRAUSE, L.C.: supervision, writing – original draft, writing – review & editing. CARAMÃO, E.B.: supervision, writing – original draft, writing – review & editing.

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