

Fractional and Chemical Characterization of Green Coconut Fiber Bio-Oil Using Fast-GC×GC/TOFMS

Rafael de Oliveira Farrapeira^{1,2*}, Yasmine Andrade Braga², Jaderson Kleveston Schneider³, Carin von Muhlen⁴, Elina Bastos Caramão^{1,2}

¹Federal University of Bahia - INCT Energy and Environment; Salvador, Bahia; ²Postgraduation Program on Industrial Biotechnology - UNIT; Aracaju, Sergipe; ³Federal University of Pampa; São Gabriel, Rio Grande do Sul; ⁴State University of Rio de Janeiro - UERJ; Rezende, Rio de Janeiro, Brazil

Brazil is renowned for its expertise in utilizing biomass for energy and biomaterials. Notably, in tandem with biomass processing, the country has a high potential for bio-products derived from agro-industrial residues, such as green coconut fibers. This study focused on using green coconut fibers in bio-oil production via pyrolysis (at 700 °C with a heating rate of 100°C/min). The bio-oil underwent fractionation using preparative liquid chromatography on silica (PLC) with solvents of varying polarities. The fractions of bio-oil were then analyzed using fast-GC×GC/TOFMS. This analytical technique significantly reduced the analysis time to 15 minutes per sample. The predominant compounds identified included phenols, furfural derivatives, and hydrocarbons, underscoring the bio-oil's potential for industrial applications. Keywords: Fractionation. Fast Pyrolysis. Chromatography Analysis.

The global energy demand has spurred research into alternatives to fossil fuels, with biomass emerging as a prominent option. However, biomass has found greater prominence in producing alternatives for non-energy uses, notably inputs for the chemical, food, and pharmaceutical industries [1,2]. Industries traditionally reliant on fossil fuels benefit across the board from biomass utilization. Bioplastics, pharmaceuticals, food additives, and other products, typically derived from the petrochemical chain, can be sourced from a biorefinery utilizing various biomasses [3]. Agro-industrial residues like sugarcane straw and bagasse, coconut fibers, rice husks, and others offer the most promising balance, leveraging both environmental impact reduction through waste volume reduction and economic gains [4,5].

Expanding biomass usage necessitates the development of technologies for comprehensive characterization [6,7]. Physical and chemical

data on biomass can inform toxicity, quality, and stability and aid in defining conversion and application parameters. Fundamental physicochemical properties include moisture content, volatile compounds, fixed carbon, elemental composition, and thermal degradation characteristics [8]. A practical route for residual biomass conversion is bio-oil production via pyrolysis. In this process, biomass breaks down in an inert atmosphere, yielding biochar (a porous solid), gases (used for process heat), and a diverse liquid product suitable for various applications.

Bio-oil comprises a complex mix of compounds such as ketones, phenols, aldehydes, and hydrocarbons [9-11], requiring upgrading to enhance quality, particularly for high-value chemical production or biofuel applications [11,12].

Among the upgrade processes aimed at isolating specific compounds from bio-oil, methods such as fractionation and extraction play a significant role [13]. Bio-oil upgrading through extraction/fractionation methods encompasses various techniques like organic solvent extraction, supercritical fluid extraction, ionic liquid extraction, fractional distillation, preparative

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Address for correspondence: Rafael de Oliveira Farrapeira. Avenida Marcelo Deda Chagas, s/n, Rosa Elze, São Cristóvão, Sergipe, Brazil. Zipcode: 49107-230. E-mail: rafael Farrapeira92@gmail.com.

liquid chromatography (PLC), membrane separation, and electrosorption [13-15].

Preparative liquid chromatography (PLC) is particularly effective in isolating chemical classes of compounds by eluting them with organic solvents of different polarities. This method enables a more precise qualitative and quantitative analysis, especially when coupled with fast-GC×GC/TOFMS.

The widespread use of green coconuts for their renowned "coconut water" on the beaches of northeastern Brazil has led to environmental concerns due to the substantial waste produced, primarily coconut fibers that are often disposed of improperly. Reducing the volume of this waste is an urgent necessity, and finding alternative uses for these residues can address both environmental and economic challenges.

Against this backdrop, this study aims to conduct rapid pyrolysis of green coconut fibers from Aracaju (northeast Brazil), analyze the

resulting bio-oil, and employ a PLC fractionation approach to facilitate constituent analysis (fast-GC×GC/TOFMS). This process aims to isolate chemical classes of significant interest, paving the way for potential industrial applications.

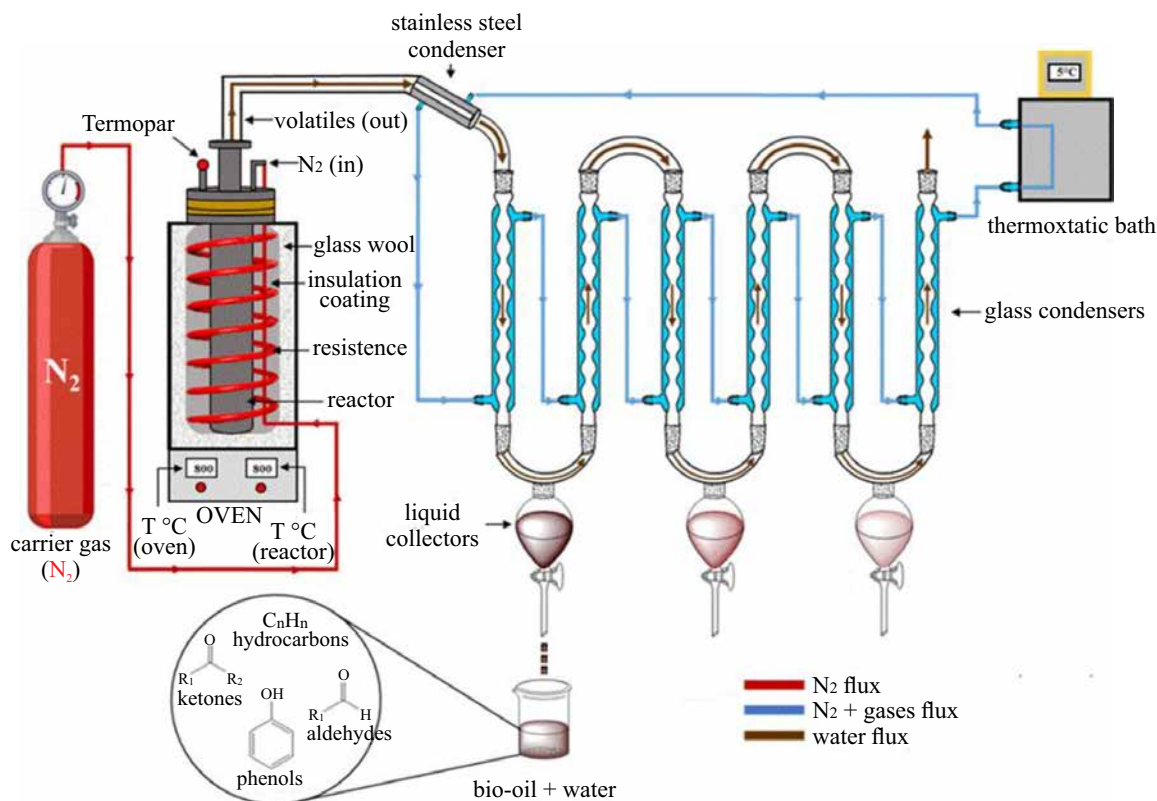
Materials and Methods

Pyrolysis Conditions

The pyrolysis process (triplicate) was carried out using a bench-scale fixed bed reactor and a vertical furnace. A resistance with a power of 3.000 W was used to heat the stainless steel reactor. Figure 1 details a description of the pyrolytic system.

In previous studies by Almeida and colleagues [16] and Bispo and colleagues [17], the biomass pyrolysis process was standardized with specific parameters. The pyrolysis duration was set at 15 minutes at a temperature of 700 °C. Each experiment utilized 20 grams of biomass, and

Figure 1. Pyrolysis system.



the heating rate was determined by the maximum power of the 3000 W resistors, resulting in a rate of 100 °C per minute. The carrier gas flow was maintained at 100 mL per minute while the condensers were kept at approximately 6°C. The mass yields of biochar and bio-oil were calculated based on their respective weights. The gas yield was determined by subtracting the sum of bio-oil and biochar yields from the initial biomass mass. Any losses incurred during the process, such as coke production, were included in the gas yield calculations. These standardized parameters ensure consistency and accuracy in pyrolysis, allowing for reliable comparisons and analysis across experiments.

Preparative Liquid Chromatography (PLC)

After determining the optimal pyrolysis conditions, the bio-oil underwent a preparative-scale liquid chromatography fractionation process. This step aimed to simplify the sample complexity to enable a more detailed identification of target compounds. Silica was employed as the stationary phase in a glass column measuring 20 cm x 1 cm, utilizing five solvents with varying polarities to produce five distinct fractions. This fractionation method was based on the methodology outlined by da Cunha and colleagues [18], albeit in an open system without column pressurization.

The procedure involved dissolving approximately 200 mg of bio-oil in 5 mL of dichloromethane (DCM) and adding it to 1 g of activated silica gel, followed by vigorous mixing. After complete solvent evaporation, the silica impregnated with bio-oil was transferred to the top of the glass column, previously packed with 10 g of activated silica using n-hexane.

Subsequently, the bio-oil was eluted using solvents of varying polarities, and the resulting fractions were collected as follows:

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

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

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

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

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

The entire procedure was performed in triplicate, and the yields of each fraction were calculated post-solvent evaporation using a gentle flow of N₂. This rigorous methodology ensures accurate fractionation and analysis of the bio-oil components, enabling a comprehensive understanding of its chemical composition.

Chromatographic Analysis - fast-GC×GC/TOFMS

The analysis of both the bio-oil and its fractions was conducted using fast GC×GC on a LECO Pegasus 4D instrument, which includes an Agilent Technologies GC 7890A system, a nitrogen-free thermal modulator, and a time-of-flight mass spectrometer (TOFMS). Bio-oil samples were prepared in vials with a 5000 ppm solution, and 1 µL from each sample was automatically injected in splitless mode. The injector temperature was maintained at 280 °C, and helium gas was the carrier gas at a 1 mL/min flow rate. The initial oven temperature was set at 45 °C for 0.20 minutes, then increased to 260 °C at a heating rate of 15 °C/min and held for 5 minutes. Two columns were utilized: RTX-5 (5% diphenyl/95% dimethyl-siloxane) with dimensions of 10 m × 0.18 mm × 0.20 µm in the first dimension, and RXI-17sil MS (50% phenyl-methyl-polysiloxane) with dimensions of 1.0 m × 0.10 mm × 0.10 µm in the second dimension. The data acquisition rate was set at 300 Hz, with the transfer line and ion source maintained at 280 °C and 250 °C, respectively. The modulator chiller temperature was -80 °C, and a modulation period of 3.5 was used, with a 15 °C difference between the primary and secondary ovens. A homolog series of linear alkanes (C7 to C30) was injected under the same conditions as the samples for tentative compound identification. The Linear Temperature Programmed Retention Indexes (LTPRI) method developed by Van Den Dool and

Kratz (1963) was employed, and the equipment software automatically calculated the retention indexes. This comprehensive analysis method accurately identifies and characterizes compounds in the bio-oil samples and their fractions. The data processing was conducted using ChromaTOF software version 451.6 from Leco, USA, which features spectral deconvolution capabilities. The tentative identification of compounds followed a two-step process. Initially, the mass spectra of analytes were compared with the NIST library. Compounds with a similarity lower than 70% and column bleed, solvent peaks, and peak tails were classified as unidentified peaks.

Subsequently, a dispersion graph was generated with the remaining compounds to assess their position in the separation space and classify peaks accordingly. Peaks that did not fit into any classification were considered unidentified. This comprehensive approach ensured a thorough analysis and identification of compounds present in the samples while minimizing the inclusion of erroneous or irrelevant data.

Results and Discussion

Table 1 summarizes the number of peaks and the percentage composition (related to the percentage area of each peak) of each class of chemical compounds found for each fraction of the samples. Figure 2 shows the distribution in terms of the percentage area of the significant constituents of each fraction, considering those compounds that presented a percentage area greater than 1% in at least one of the fractions. 287 different compounds were tentatively identified by summing the bio-oil fractions. The bio-oil fractionation enabled the identification of many hydrocarbon peaks with similar profiles in fractions 1 and 2. Almost all represent hydrocarbons (saturated, 26.69%; unsaturated, 28.53%; and aromatic, 39.96%).

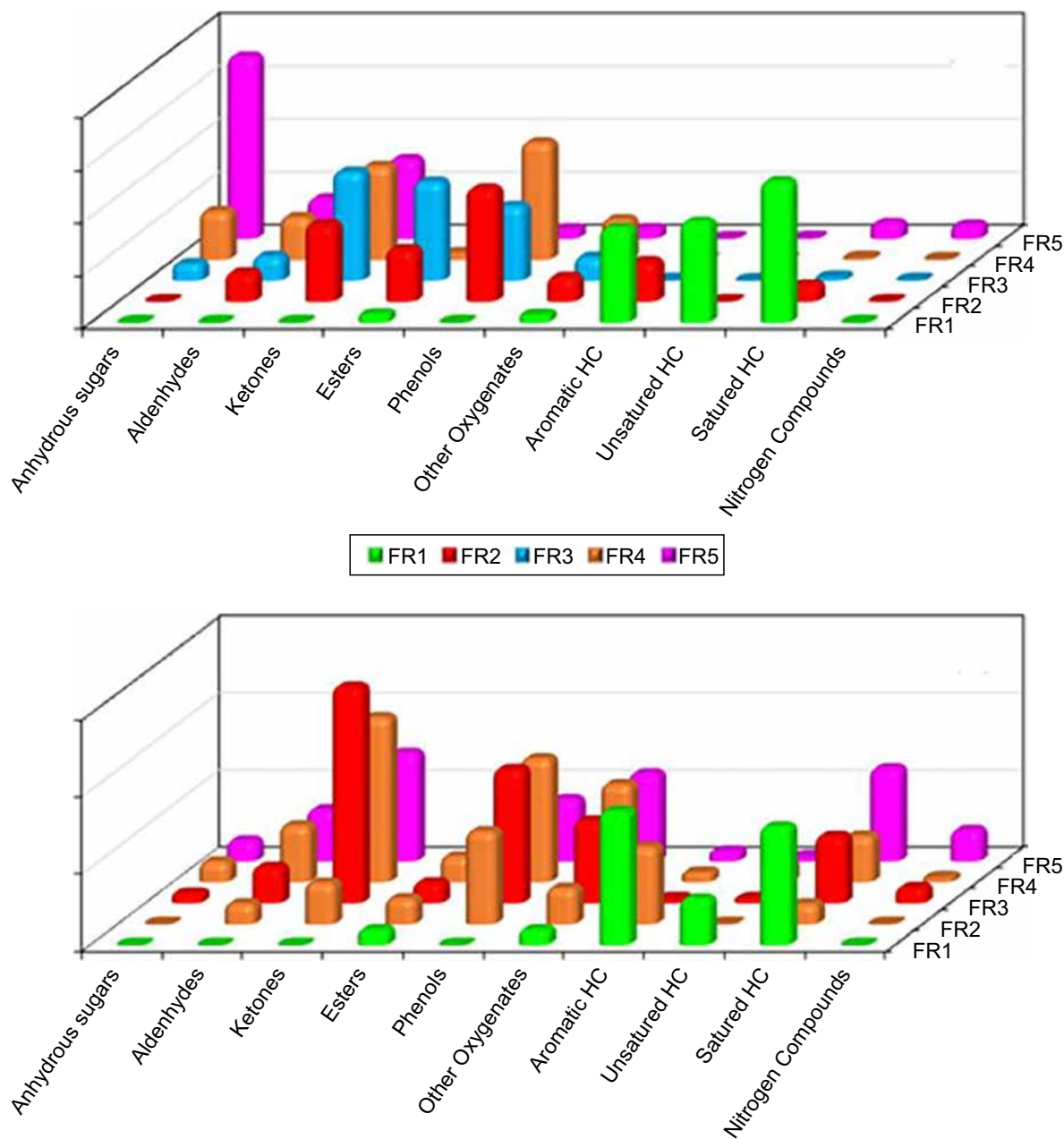
The hydrocarbons identified in Fraction 1 exhibited a high molecular mass, ranging from C17 to C32, with a notable absence of light hydrocarbons, likely due to their evaporation with the solvent post-fractionation, as described in Bordoloi et al.

Table 1. Identification of compound classes regarding the number of peaks and their percentage areas for fractionated bio-oil samples.

Chemical Classes	FR1		FR2		FR3		FR4		FR5	
	Area	Peak	Area	Peak	Area	Peak	Area	Peak	Area	Peak
Anhydrous sugars	n.d.	n.d.	n.d.	n.d.	4.85	2	13.73	4	51.68	4
Aldehydes	n.d.	n.d.	8.15	4	6.91	7	12.06	11	11.32	10
Ketones	n.d.	n.d.	21.89	8	30.87	42	26.52	32	22.56	21
Esters	2.48	3	14.85	5	27.99	4	2.02	5	0.06	1
Phenols	n.d.	n.d.	32.02	18	21.13	26	33.23	24	2.79	12
Other	2.35	3	6.94	7	6.67	16	11.48	19	2.88	17
Aromatic	26.69	26	11.41	15	0.26	1	0.05	2	0.10	2
Unsaturated	28.53	9	n.d.	n.d.	0.03	1	0.28	4	0.29	1
Saturated	39.96	23	4.74	4	1.07	13	0.60	9	4.42	18
Nitrogen	n.d.	n.d.	n.d.	n.d.	0.22	3	0.03	1	3.88	6
Total	100%	64	100%	61	100%	115	100%	111	100%	92

*n.d: not detected

Figure 2. Distribution of compound classes in terms of percentage area (a) and number of compounds (b) of PLC bio-oil fractions.



[19]. Fractions 2, 3, and 4 displayed numerous co-elutions during chromatographic runs. Fractions 3 and 4 exhibited more identified compounds, with phenolic compounds dominating fractions 2 and 4 (32.02% and 33.23%, respectively).

Concerning ketones, the majority were aromatic (acetophenones) or cyclic, falling into classes such as cyclopentanones and

cyclopentenediones, primarily concentrated in fractions 4 and 5. These cyclopentanones and cyclic ketones are derivatives of cellulose and hemicellulose degradation found in biomass. More studies in the literature need to address bio-oil fractionation and chromatographic analysis. Among them, Schneider and colleagues [20] proposed a selective phenolic

compound extraction method from the aqueous phase of bio-oil obtained from sawdust. This method involved alkaline and liquid-liquid extractions using hexane, dichloromethane, and toluene, similar to the extracts used in this study. Analysis was performed using GC×GC coupled with a quadrupole mass spectrometer (qMS), leading to the tentative identification of 130 compounds, predominantly phenols, ethers, ketones, aldehydes, acids, alcohols, and aromatic hydrocarbons. Major compounds included 4-methyl 1,2-benzenediol (12.1%), 1,2-benzenediol (11.1%), C2-benzenediol (7.1%), and phenol (4.8%). Bordoloi et al. [19] utilized PLC-4 fractionation on silica (hexane, toluene, ethyl acetate, and methanol solvents) for bio-oil from *Scenedesmus dimorphus* microalgae pyrolysis. Aromatic hydrocarbons and phenols were identified as major compounds. The first fraction (hexane) predominantly contained saturated compounds (n-alkanes, olefins, and branched hydrocarbons). The results showed notable differences from the present study, particularly in identifying phenolic compounds.

Conclusion

The PLC-5 fractionation on silica yielded five fractions based on solvent polarity. Fast-GC×GC/TOFMS analysis of these fractions demonstrated the efficiency of fractionation, revealing several compounds, particularly hydrocarbons, that were not initially identified in the original sample but were detected post-fractionation. The bio-oils exhibited elevated levels of phenols and a complex composition that was streamlined through fractionation. The separation of fractions significantly improved compound characterization, leading to an increased number of identified compounds and the discovery of new compounds that would have remained undetected without fractionation. In total, 287 compounds were identified, showcasing the substantial impact of fractionation on enhancing the analysis and understanding of bio-oil composition.

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