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Preliminary Studies of Bio-oil from Fast Pyrolysis of Coconut Fibers

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Supporting Information

ABSTRACT: This work studied fast pyrolysis as a way to use the residual fiber obtained from the shells of coconut (*Cocos nucifera* L. var. Dwarf, from Aracaju, northeastern Brazil). The bio-oil produced by fast pyrolysis and the aqueous phase (formed during the pyrolysis) were characterized by GC/qMS and GC×GC/TOF-MS. Many oxygenated compounds such as phenols, aldehydes, and ketones were identified in the extracts obtained in both phases, with a high predominance of phenolic compounds, mainly alkylphenols. Eighty-one compounds were identified in the bio-oil and 42 in the aqueous phase using GC/qMS, and 95 and 68 in the same samples were identified by GC×GC/TOF-MS. The better performance of GC×GC/TOF-MS was due to the possibility of resolving some coeluted peaks in the one-dimension gas chromatography. Semiquantitative analysis of the samples verified that 59% of the area on the chromatogram of bio-oil is composed by phenols and 12% by aldehydes, mainly furfural. Using the same criterion, 77% of the organic compounds in the aqueous phase are phenols. Therefore, this preliminary assessment indicates that coconut fibers have the potential to be a cost-effective and promising alternative to obtain new products and minimize environmental impact.

KEYWORDS: *biomass, pyrolysis, coconut fibers, GC×GC/TOF-MS, GC/qMS, phenols, ketones*

INTRODUCTION

This paper deals with the pyrolysis of coconut fibers, which are an important agricultural feedstock in northeastern Brazil. The amount of residues generated in the coconut industry and also in its use for the population is very large (around of 20% of all the municipal refuse in Aracaju, SE, Brazil, for instance). Pyrolysis not only reduces the amount of residues but also produces the bio-oil that can be used as a raw material in many processes and also as an alternative fuel.

According to McKendry,[1] "biomass" refers to all organic material that stems from plants (including algae, trees, and crops). As organic matter, it is a resource constituted by carbon, hydrogen, and oxygen conforming molecules in which solar energy is stored.[2,3] Due to its constitution, it is a potential source of renewable and environmentally friendly raw material, constituting an alternative to the declining fossil oil reserves and a cost-effective energy.[2]

Coconut (*Cocos nucifera* L.) cultivation is an example of this situation. Its fruit is formed by the pericarp (involves the seed), epicarp (peel), mesocarp (fiber), endocarp (hard shell around the seed), seed coats, and albumen (endosperm). Brazil is the fourth largest producer of coconut in the world, and this fruit production serves for copra-extraction and coconut water consumption.[3] The use of coconut fibrous residue after removal of the albumen (protein water and solid) is an alternative to reduce the dumping of waste in landfills. There are several studies to explore this waste, because the coconut husks, shells, and their fibers have a wide range of biotechnology applications.[3,4] Coconut shells are an abundant lignocellulosic material with a chemical composition of cellulose, hemicellulose, and lignin, which varies according to seasonal conditions, age, and variety of the plant, etc.

According to Maheswari et al.,[5] after a previous extraction of organic material of the coconut fibers and the analysis of components, the fibers are mainly constituted by 3.1% of extractive materials, 37.3% of cellulose, 20.3% of hemicellulose, 32.2% of lignin, and 6.8% of mineral material (ashes).

As a carbon source, the components of coconut fibrous residue can be converted into solid, liquid, gaseous fuels and chemical feedstock through thermo-chemical and biochemical conversions. Furthermore, the employment of a residue in the production of new products, is a form of to aggregate value to this material.

Pyrolysis is a thermodecomposition process of organic material in an inert atmosphere for converting biomass and its molecules in liquid products and other substances. A pyrolytic process decomposes the organic material, producing vapor, char, ashes, and gas, and then after cooling, it produces a high yield of a dark brown and dense liquid, with a pungent odor, named bio-oil.[6,7] Through this thermochemical transformation it is possible to obtain the maximal energetic valorization of biomass, by carefully controlling some characteristic of the reactions, such as the elemental composition, humidity, and size of the raw material, besides the pyrolysis operating conditions (temperature, humidity, and residence time).[8]

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Table 1. Chromatographic Conditions of GC/qMS and GC×GC/TOF-MS Analyses

parameter	GC/qMS	GC×GC/TOFMS
equipment	Shimadzu QP 2010 plus (Shimadzu, Japan)	Pegasus IV (LECO, St. Joseph, MI, USA) consisting of an Agilent 6890N GC (Palo Alto, CA, USA) with a TOFMS system and a *quadjet* cryogenic modulator
column	DB-5 (60 m × 0.25 mm × 0.25 μm)	1D: DB-5 (60 m × 0.25 mm ×0.25 μm)
		2D: DB-17 ms (2.15 m × 180 mm ×0.18 μm)
injection/ injected volume	splitless/1 μL	split 1:10/1 μL
injector temperature	280 °C	280 °C
MS source temperature	280 °C	250 °C
carrier gas/flow rate	helium/1 mL min^{-1}	helium/1 mL min^{-1}
oven heating	45 °C (2 min) raised at 5 °C/min to 280 °C (2 min)	60 °C (1 min) raised at 3 °C/min to 210 °C (3 min)
modulation period (MP)		8 s
Δ*T* between the ovens		20 °C
duration of hot jet		20% MP
mass acquisition rate	25 Hz	100 Hz
mass range	45−550 Da	45−550 Da

Minimizing the environmental impact generated by agricultural and agro-industrial wastes is one of the goals established by relevant legislation standards, which are defined by the Organization of Environmental Management (ISO 1999). In this context, research groups around the world can and should develop and use technologies to benefit local economies in various stages of production. These studies allow us to understand negative impacts and propose changes to improve the environmental benefits and thus adopt innovations, considering the context in which it should be applied.

With regard to the coconut palm, (*C. nucifera* L. var. nana, Palmae), the object of this study, it is worth noting that this plant is widely distributed and cultivated on a large scale on the Brazilian coast, mainly in the northeastern region, where its cultivation is responsible for a significant environmental liability; for example, 250 mL of coconut water (one glass) generates around 1 kg of waste, which represents 70−80% of the agro-industrial and domestic waste in this region. Also, due to the slow degradation (approximately 8 years) and large amount produced, this residue causes serious problems in landfills.

Due to advances in applications of the technology of pyrolysis, it is possible to convert raw organic biomass into different coproducts, such as bio-oil and/or other higher added-value compounds.[9]

This biomass conversion has been investigated to identify interesting intermediates or chemical products.[8,9] Due to the complex composition of bio-oils and the potential uses of their constituents, several separation methods have been used to obtain bio-oil fractions with different characteristics.

According to Sfetsas[10] and Moraes[11] and their collaborators, high-resolution chromatographic techniques are necessary to analyze the bio-oil especially due its high complexity, high number of isomers, great structural similarity in each chemical class, and large range of concentrations of compounds. The main compounds identified in bio-oils are water, acids, alcohols, aldehydes, esters, ketones, carbohydrates, hydrocarbons, phenols, and other lignin-derived and cellulose-derived substances.

The chemical characterization of bio-oil is necessary for understanding its properties and for determining its composition, aiming for its effective use. The conventional methods for bio-oil analysis include column chromatography, elemental analysis, ^{1}H NMR, and gas chromatography, but most of these methods are time-consuming or require special pretreatments.[12] Thus, the most widely used technique to analyze bio-oils is gas chromatography coupled to mass spectrometry (GC-MS).[12] More recently, two-dimensional gas chromatography with a time-of-flight mass spectrometry detector (GC×GC/TOF-MS) has been used in the characterization of highly complex samples like flavors, petroleum, or essential oils. The bio-oils seem to be potential samples for using this technique, and there are already some papers in the literature applying GC×GC to the analysis of bio-oils.[11,13−18] In all of these papers, the main classes of compounds were oxygenated species, and the GC×GC process promoted a better separation and classification of the compounds, if compared with other analytical techniques.

Many compounds that are commonly found in bio-oils have important uses, such as ketones (chemical synthesis),[19−21] phenols (disinfectant, resins, pesticides, explosives, drugs, dyes),[19,22] and furfurals (lubricants, adhesives, plastics, and nylons).[23]

From the chromatographic profiles of bio-oils and in the potential of coconut fibers for producing higher aggregated value compounds for the industry or for fuel purposes, this study aims to explore the pyrolysis of coconut fibers and the chemical composition of bio-oil and aqueous phase characterization using one-dimensional and two-dimensional gas chromatography for identifying components at major concentration. The main objective of this work is to apply GC×GC in the previous characterization of the pyrolysis products obtained from coconut fibers.

MATERIALS AND METHODS

Sample Preparation. The coconut fibers from green coconut husks (*C. nucifera* L. var. Dwarf) were kindly provided by Embrapa - Tabuleiros Costeiros, Sergipe, Brazil.

The fibers were delivered after grinding, pressing, and fiber/dust separation. The samples were lyophilized (model FR Drying, Thermo Fisher Scientific, Madison, WI, USA).

Pyrolysis Process. The pyrolysis procedure of coconut fibers was performed in a stainless steel vertical oven containing a quartz reactor; more details can be obtained from Moraes et al.[11] After some optimization experiments, the optimal condition for the pyrolysis was found: 5 g of coconut fibers; pyrolysis at 700 °C; heating rate of 100 °C min^{-1}; N_2 flow of 1 mL min^{-1}. The main variables of this process were the temperature and the heating rate. The reactor remained at 700 °C for 5 min until no significant vapor release was observed. The bio-oil was condensed by a chiller and, after weighing, reserved for further analysis. Before each new procedure, the reactor and connections were cleaned with dichloromethane (Merck, Darmstadt, Germany) and dried with a hot air stream at 150 °C.

Mass Balance and Extraction of Aqueous Phase. The collected bio-oil plus aqueous phase (BO+AP) was weighed for a preliminary mass balance. To ensure that there were no losses of volatile compounds, a small portion of dichloromethane was added to the top of the condenser and collected together with the bio-oil. This excess of dichloromethane was quickly evaporated under a gentle flux of N_2 in an ice bath. The amount of BO+AP was registered.

For determining the amount of water, and also to remove the phenols from bio-oil, the BO+AP was submitted to a liquid−liquid extraction (LLE) in alkaline medium (to increase the presence of phenols in ionic form in the water phase). For this purpose, the pH was adjusted to approximately 10 using an aqueous solution of 1 mol L^{-1} NaOH. The LLE was then performed by addition of 5 mL of dichloromethane, stirring, and separation of both phases (organic and aqueous). This procedure was repeated three times, and the organic extracts obtained were mixed in only one fraction. This fraction was washed three times with 5 mL of bidistilled water (the washing water being added to the aqueous alkaline phase) and dried with anhydrous sodium sulfate (Merck), and the solvent was evaporated. The organic extract was weighed (until constant weight), and the yield in dried bio-oil was calculated according to the following equation:

$$\text{yield of dried bio-oil (DBO) (\%)} = \frac{\text{mass of DBO}}{\text{mass of initial coconut fiber}} \times 100 \quad (1)$$

The amount of water generated in the pyrolysis process was calculated by difference:

$$\text{mass of (BO+AP)} - \text{mass of DBO} = \text{mass of AP} \quad (2)$$

(BO+AP) = bio-oil plus aqueous phase, DBO = dried bio-oil, and AP = aqueous phase.

The alkaline aqueous phase obtained was acidified with aqueous 1 M L^{-1} HCl, to pH 4, and the organic compounds were extracted by repeating the same procedure used for the extraction from the organic phase as described above. The yield in dried organic extract of aqueous phase (named AP-LLE, from aqueous phase liquid−liquid extract) was calculated according to the following equation:

$$\text{yield of AP-LLE (\%)} = \frac{\text{mass of AP-LLE}}{\text{initial mass of coconut fiber}} \times 100 \quad (3)$$

It was also possible to calculate the yield of extraction, relating the AP-LLE to the mass of aqueous phase generated in the pyrolysis process (calculated by difference).

Table 2. Mass Yields of the Pyrolysis Procedure

parameter	mass yield (%)
dried bio-oil (DBO)	10.15 ± 1.8
aqueous phase (AP)	27.15 ± 4.9
residual solid	29.22 ± 5.2
volatiles (*losses*)	33.36 (*by difference*)
organic extract from AP (AP-LLE)	17.74 (*related to aqueous phase*)
	4.81 (*related to the original sample*)

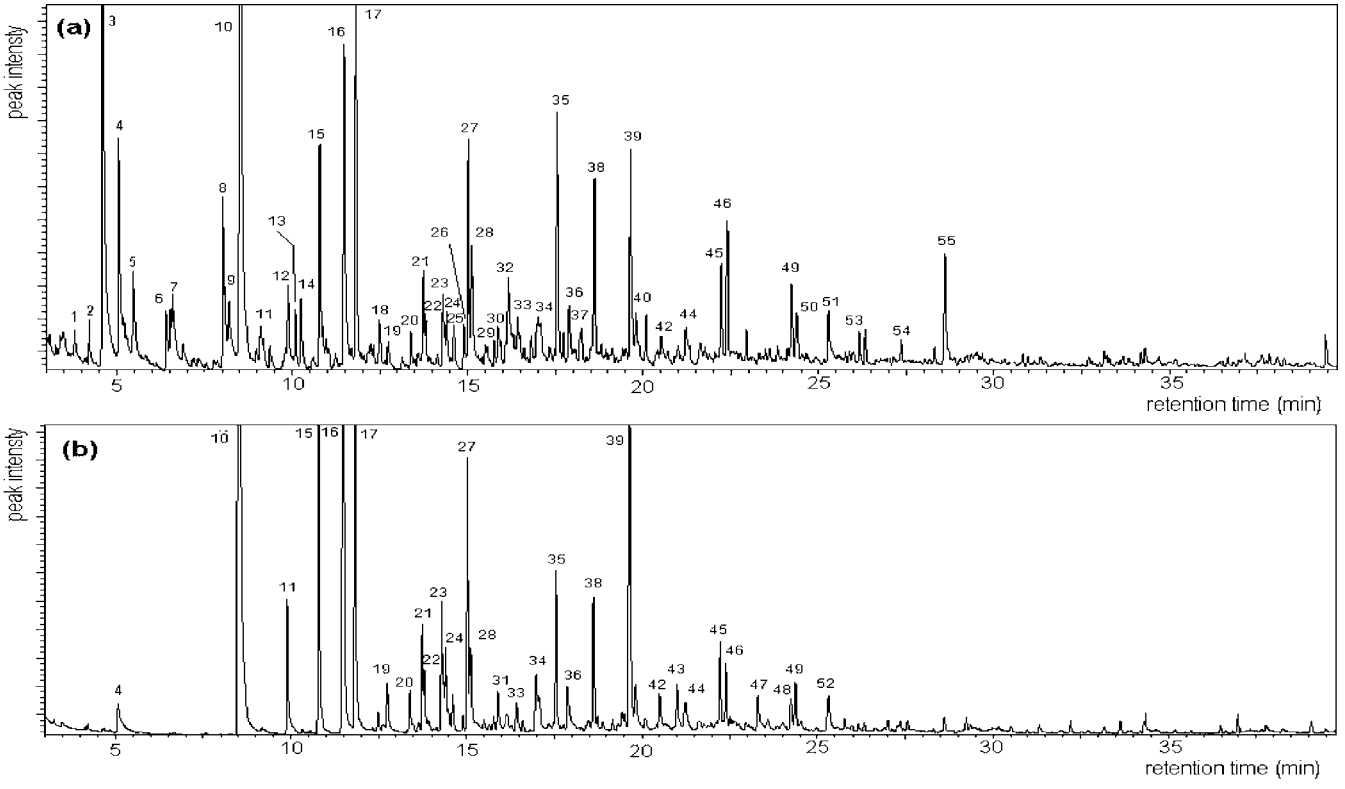

Figure 1. Total ion chromatogram (GC/qMS) of products from the pyrolysis of coconut fibers: (a) dried bio-oil (DBO); (b) liquid−liquid extract of the aqueous phase (AP-LLE). Chromatographic conditions were as described in Table 1, and peak identification is given in Table S1 (Supporting Information).

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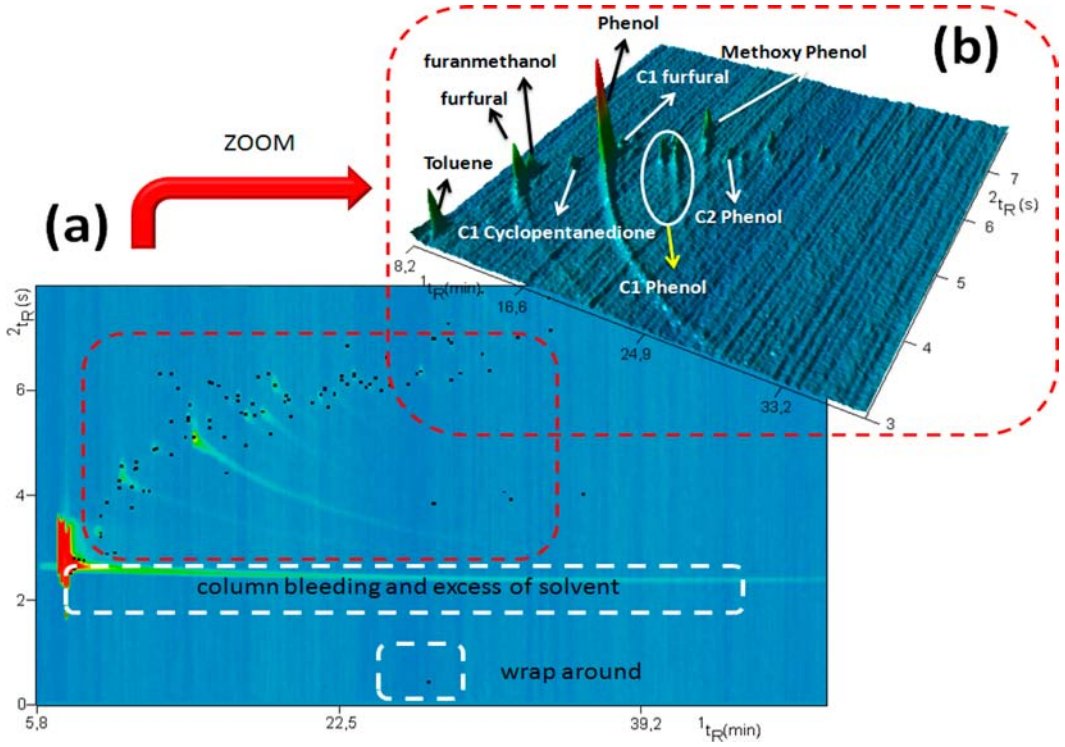

Figure 2. Color diagrams for the GC×GC/TOF-MS analysis of dried bio-oil (DBO) from the pyrolysis of coconut fibers: (a) two-dimensional diagram; (b) three-dimensional diagram of a zoom region. Chromatographic conditions were as described in Table 1, and peak identification is given in Table S1 (Supporting Information).

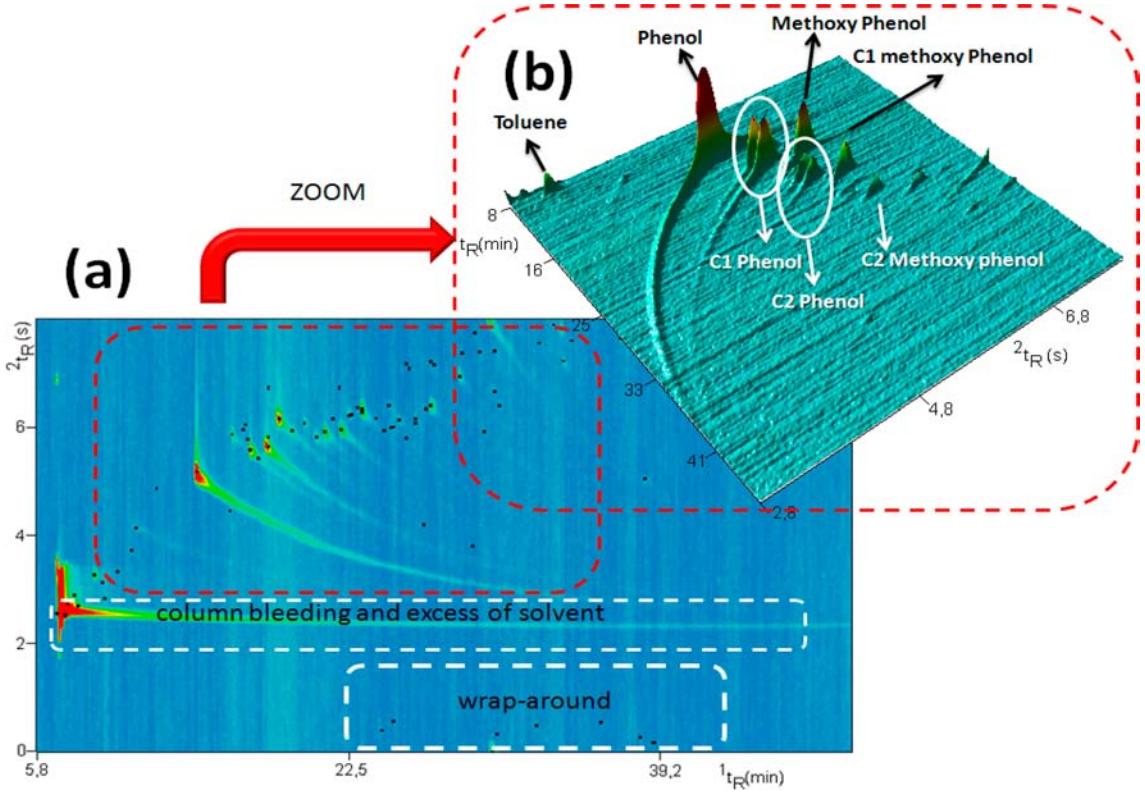

Figure 3. Color diagrams for the GC×GC/TOF-MS analysis of liquid−liquid extract of the aqueous phase (AP-LLE) from the pyrolysis of coconut fibers: (a) two-dimensional diagram and (b) three-dimensional diagram of a zoom region of AP-LLE. Chromatographic conditions were as described in Table 1, and peak identification is given in Table S1 (Supporting Information).

Solutions at 1000 mg L^{-1} of the dried bio-oil, named only DBO, and the AP-LLE were prepared for chromatographic analysis, in dichloromethane.

Chromatographic Analysis. The conditions of analyses for GC/qMS and GC×GC/TOF-MS are described in Table 1. One-dimensional

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Table 3. Summary of the Percent Area and Number of Peaks Identified, According to the Classes of Compounds Found in Both Extracts

	area %				number of peaks				peaks %			
	GC×GC/TOF-MS		GC/qMS		GC×GC/TOF-MS		GC/qMS		GC×GC/TOF-MS		GC/qMS	
class	DBO	AP-LLE	DBO	AP-LLE	DBO	AP-LLE	DBO	AP-LLE	DBO	AP-LLE	DBO	AP-LLE
alcohols	4.1	0.9	4.6	1.0	1	1	4	1	1.1	1.4	7.5	3.0
aldehydes	14.2	0.3	13.3	1.1	7	4	2	1	7.4	5.5	3.8	3.0
ethers	2.6	1.2	3.8	3.2	14	7	4	3	14.9	9.6	7.5	9.1
hydrocarbons	11.5	1.9	1.4	nd	16	5	3.0	nd	17.0	6.8	5.7	nd
ketones	10.2	2.1	10.5	4.7	28	13	11	4	29.8	17.8	20.8	12.1
phenols	55.2	93.2	66.1	88.9	26	37	29	23	27.7	50.7	54.7	69.7
others[a]	2.2	0.5	nd	1.1	2	6	nd	1	2.1	8.2	nd	3.0
totals	100	100	100	100	94	73	53	33	100	100	100	100

[a]Others = acids, anhydrides, esters, sugars.

Table 4. Distribution of Major Compounds Identified in DBO and AP-LLE Extracts, According to Their Area Percent (A% > 1.0%)

			DBO		AP-LLE	
chemical class	compound[a]	isomers[b]	GC	GC×GC	GC	GC×GC
alcohols	furanmethanol	1	3.8	4.1	1.0	0.9
aldehydes	furfural	1	8.3	10.2	nd	0.1
	furfural, C1	1	2.5	3.1	nd	nd
	furfural, hydroxy, C1	1	2.1	nd	nd	nd
	vanillin	1	0.4	nd	1.1	0.2
anhydrides	maleic anhydride	1	nd	2.0	nd	nd
	lauric anhydride	1	nd	nd	1.1	nd
ketones	cyclopentanone	2	0.4	2.2	nd	nd
	cyclopentenone, C1	2	1.6	2.1	nd	nd
	cyclopentenone, C2	4	0.9	1.5	nd	nd
	cyclopentanedione, C1	2	1.7	nd	2.2	1.1
	hexenone	1	1.9	nd	nd	nd
	ethanone, furanyl	1	nd	1.2	nd	nd
	furanone, dihydro	1	1.6	0.2	nd	nd
ethers	benzofuran, C2	3	1.3	0.7	nd	nd
	benzene, trimethoxy	1	1.5	0.1	1.8	0.4
	benzene, trimethoxy, C1	1	1.0	0.2	0.6	0.2
phenols	phenol (*major compound*)	1	22.6	37.6	34.9	37.9
	phenol, C1	3	7.9	6.7	15.6	23.4
	phenol, C2	8	8.2	3.9	9.5	11.0
	phenol, dimethoxy	1	2.7	0.4	5.3	nd
	phenol, methoxy	3	5.2	3.6	nd	13.9
	phenol, methoxy, C1	5	2.1	1.3	3.2	3.6
	phenol, methoxy, C2	2	3.0	1.0	2.4	1.3
	phenol, methoxy, C4	1	1.2	nd	nd	nd
	phenol, methoxypropenyl	4	6.8	0.4	3.9	0.4
	phenol, dimethoxypropenyl	3	2.8	nd	0.4	nd
	benzenediol, C1	4	3.0	nd	3.9	0.4
hydrocarbons	toluene	1	nd	4.6	nd	1.6
	heptane	1	nd	5.2	nd	nd

[a]C*x* represents an alkyl chain linked to a structure, where *x* is the number of carbon atoms. [b]Number of isomers considering both samples and both techniques.

data were processed using the software GCMS Solution, and two-dimensional data were processed using the software ChromaTOF version 3.32. Part of the data was also processed by the software Microsoft Excel.

RESULTS AND DISCUSSION

Yields Obtained in Pyrolysis Procedure. The mass yield of the pyrolysis procedure is described in Table 2. The experiment

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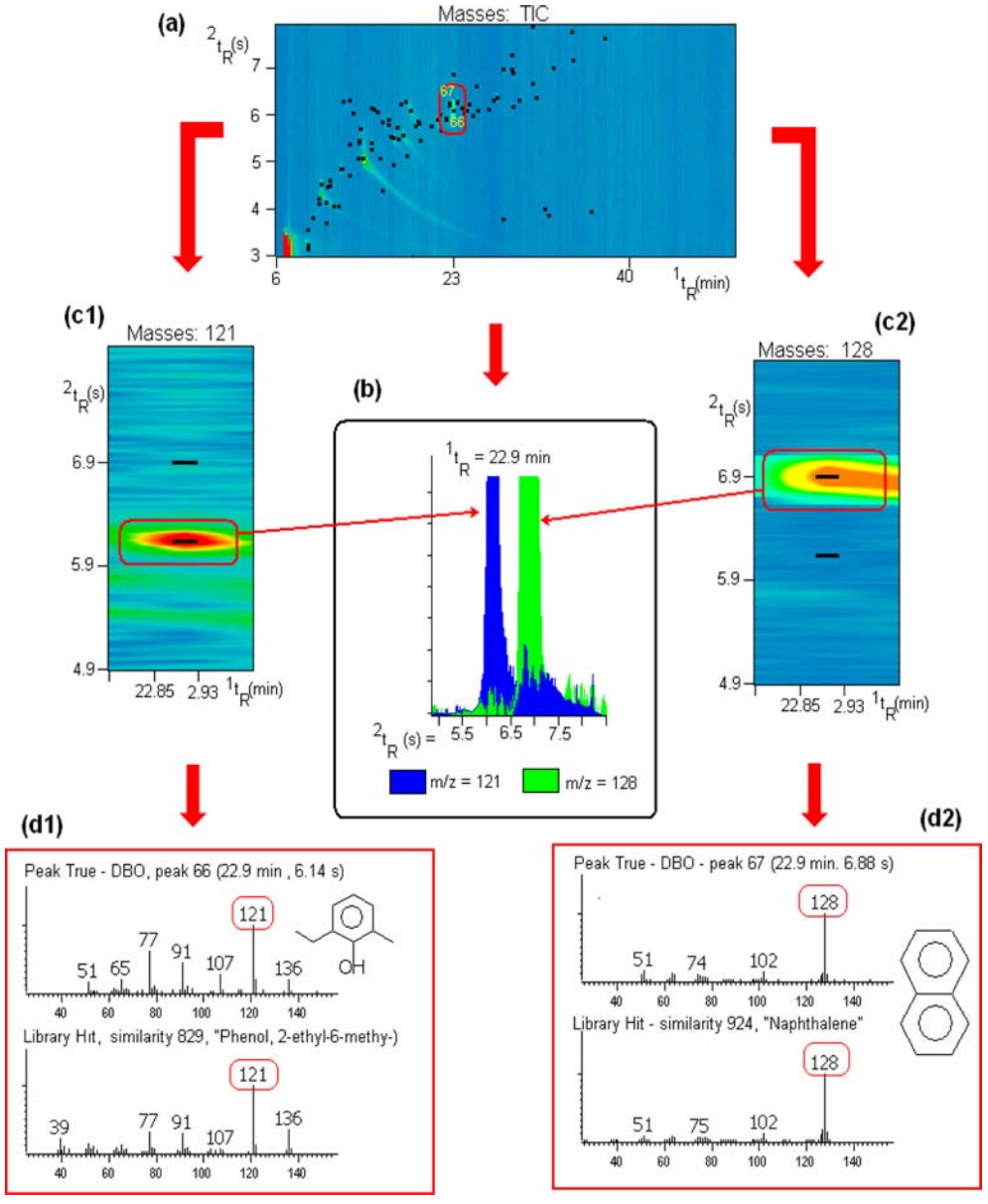

Figure 4. Two-dimensional color diagrams: (a) peak region of interest; (b) reconstructed chromatogram by choosing characteristic ions of each three peaks; (c1, c2) extracted ion mode (EIM) two-dimensional diagrams using one ion chosen for each peak used in the reconstructed chromatogram; (d1, d2) comparison between mass spectra of each peak with the spectrum of the library.

was based in experimental planning (factorial 2^3), and the condition that produced the higher amount of bio-oil was chosen. This experiment was done many times until a sufficient amount of bio-oil was produced for all of the experiments. A standard deviation of 18% was found between 10 replicates of the same experiment. The high standard deviation is probably due to the difficulty in collecting the bio-oil from the reactor. This result does not invalidate the work because the main objective was the qualitative characterization of the bio-oil.

By analysis of Table 2, it can be observed that 15% of the original sample of biomass was transformed in bio-oil (organic phase, named DBO) and organic extract of the aqueous phase (named AP-LLE). It is also important to highlight that approximately 33% of the biomass can be converted to highly volatile compounds, which are not recovered in this process. These compounds will be the object of future research oby our group, which includes a new approach for the equipment for collecting these vapors.

The organic extract of the aqueous phase corresponds to the more polar organic material. The washing of the bio-oil and adding this washing water to the original water produced during the pyrolysis promote a preconcentration of phenols in this phase and an "*up-grade*" in the bio-oil (or a "*de-oxygenation*").

The amount of solid residue (29%, Table 2) corresponds to the ashes formed during the pyrolysis and, probably, some carbon that remains in the form of vegetable coal (which is the residual carbon after the thermal degradation of a vegetable biomass).

Qualitative and Semiquantitative Chromatographic Analysis. Figure 1 shows the total ion chromatogram (TIC, GC/qMS) from the analysis of the DBO and AP-LLE extracts. The same samples (DBO and AP-LLE) were analyzed by GC×GC/TOF-MS, and the color diagrams can be seen in Figures 2 and 3, respectively. The complete tentative identification (obtained by comparison with the library and careful analysis of each mass spectrum) of peaks is presented in Table S1, available as

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Supporting Information. Tables 3 and 4 summarize the main results of this analysis.

As can be seen from these tables and figures, phenols are absolutely the majority of the compounds in both extracts. From the presence of phenolic compounds in the AP-LLE extract, it can be concluded that the alkaline wash procedure did not remove all of the phenols from the aqueous phase, which indicates that the process of removal of the phenols must be improved. On the other hand, the hydrocarbons (saturated and aromatics) were detected only in the DBO extract. The ketones, which are less polar than phenols, remained in the dried bio-oil.

Papers characterizing bio-oils from coconut fibers are not found in the literature, but there are a number of recent publications about other types of bio-oils that have a composition similar to that of the bio-oil studied here.[11,24−27] In these papers, the oxygen-containing compounds are the majority, as occurs in the present work.

As can be seen from Figures 2 and 3 and Table 3, both profiles are very similar with a major presence of phenols, confirming the data from GC/qMS.

One of the main advantage of GC×GC, if compared to GC/qMS, is the greatest peak capacity (that is, the high possibility of finding peaks in the two-dimensional space), resulting in a greater number of peaks resolved, including separation of compounds that do not become separated by one-dimensional gas chromatography (1D-GC).[28] Eighty-one compounds in the bio-oil and 42 in the aqueous phase were identified using GC/qMS and 95 and 68, respectively, in the same samples by GC×GC/TOF-MS. The better performance of GC×GC/TOF-MS was due to the possibility of resolving some coeluted peaks in the one-dimensional gas chromatography. With regard to the semiquantitative analysis of the samples, it was verified that 59% of area on the chromatogram of bio-oil is composed by phenols and 12% by aldehydes, mainly furfural. Using the same criterion, 77% of the organic compounds in the aqueous phase are phenols.

In this work, it was found that the more significant differences between both techniques were related to the number of peaks identified. There is a clear predominance of the phenols in both the DBO and AP-LLE. Probably the high amount of phenols in the DBO was responsible for the bad performance of the LLE procedure. LLE is a well-known procedure of extraction, and its disadvantages are also well described in the literature. Despite this, it is still used as a reference method. Then, as this work had the objective of applying of the GC×GC in the previous characterization of the pyrolysis products obtained from coconut fibers, we opted for using LLE and not searching for another method at this stage. For this reason the LLE procedure was not optimized. In future works other separation procedures will be used, such as adsorption in specific solid phases.

Analyzing Table 4, one can see that the phenol is the major compound in both samples using the two analysis techniques. It is also clear that the class of phenols is predominant among the compounds with an area >1% (>50% in the bio-oil and >89% in the organic extract of the aqueous phase).

The advantage presented by GC×GC can be best explained in Figure 4, which presents a case of coelution in the first dimension of three peaks that are completely separated in the second dimension, with excellent agreement between mass spectra with the library of equipment. Figure 4a shows a part of the two-dimensional diagram; Figure 4b presents the chromatogram reconstructed by choosing characteristic ions of each three peaks; Figure 4c1,c2 shows the extracted ion mode (EIM) two-dimensional diagrams using one ion chosen for each peak

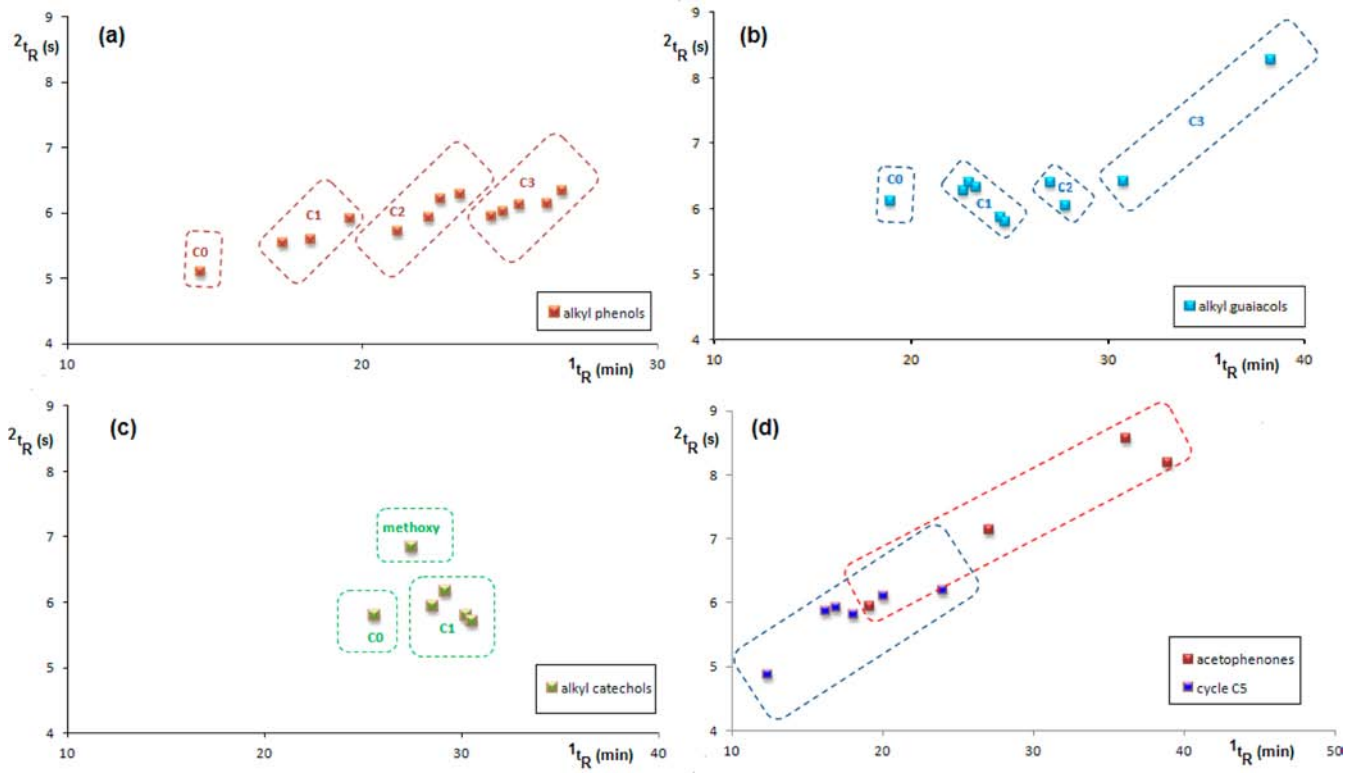

Figure 5. Dispersion diagrams with subclass separation and identification of isomers for (a) alkylphenols, (b) alkylguaiacols, (c) alkylcatechols, and (d) acetophenones and cycle C5 in the dried bio-oil (DBO). C*x* representd an alkyl chain linked to structure where *x* is the number of carbon atoms.

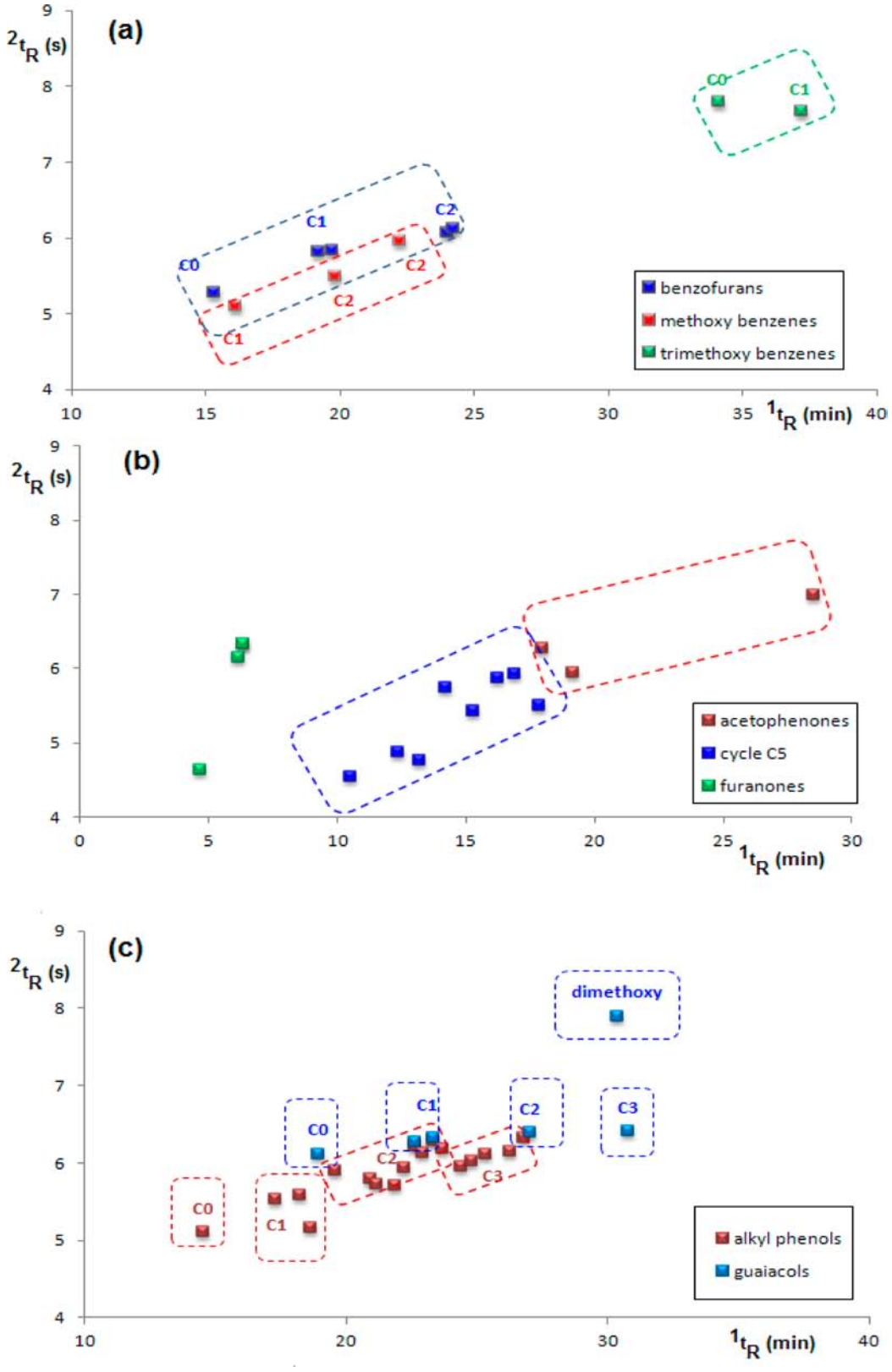

Figure 6. Dispersion diagrams with subclass separation and identification of isomers for (a) benzofuranes, methoxybenzenes, and trimethoxybenzenes; (b) acetophenones, cycle C5 ketones, and furanones; and (c) alkylphenols and guaiacols in the liquid–liquid extract of aqueous phase (AP-LLE). C*x* represent an alkyl chain linked to structure where *x* is the number of carbon atoms.

used for the reconstructed chromatogram; and Figure 4d1,d2 shows the comparison of the mass spectra of each peak with the spectrum of the library with similarity exceeding 800 (80%). It is observed that both compounds have quite different spectra and there is no influence of each spectrum on the other, as would occur in the 1D-GC. The EIM (Figure 4d) allowed a

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considerable increase in sensitivity, as can be seen by the color intensity (which indicates the area under the peak), allowing a better visualization of the shape of the peak, which is important for quantitative measurements.

Another perceived advantage of GC×GC is the ability for ordered distribution of the compounds in the two-dimensional space according to the size of the molecules, number of carbons, and chemical functionality. This may be exemplified in Figures 5 and 6 where are presented the dispersion graphics (DP) for the classes of compounds that are best suited to this type of classification in both samples: ethers, phenols, and ketones. These DP were constructed by using the retention times (first and second dimension) as coordinates of the points in the two-dimensional space. As only the peaks (points) of interest are considered, it becomes easier to visualize the correlation between compounds in the families.

In the specific case of phenols (Figures 5a−c and 6c), this distribution is peculiar, allowing the separation of the subclasses (phenols, methoxyphenols, and benzenediols) by the number of carbons in the side chains of the compounds. This distribution allows a prediction of identification and a confirmation of identity. Another important factor is the reproducibility of retention times, which were virtually the same time in the first and second dimensions for the same compound in both samples (Figures 5a,b and 6c), also functioning as an alternative to aid in the identification of compounds.

In the case of ethers found in the fraction AP-LLE (Figure 6a), a distribution similar to ketones could be observed.

As the number of isomers in the case of ketones is greater than in phenols, the spatial structure is not so evident as in the case of phenols, but it is possible to delimit an area in the graphic (Figure 6b) where all of the different kinds of ketones were found.

According Zhang et al.[29] and Guedes et al.,[30] the furan ring-containing compounds (furfural, furanmethanol, cyclopentanedione, benzofuran), the straight-chain and C═O functional groups (ketones, aldehydes, methyl esters, and acids), and sugars (anhydroglucopyranose) are primarily produced from cellulose (a linear polymer constituted by units of glucose) and hemicellulose (basically formed by hexoses, pentoses, and glucuronic acid). Phenols including methoxy-containing compounds as well as monofunctional phenols (alkylphenols and alkylbenzenediols) are mainly produced from lignin (an aromatic natural polymer formed by guaiacyl, syringyl, and hydroxyphenyl units). When the temperature of pyrolysis is sufficiently high, cellulose and hemicellulose can directly decompose to some anhydrosugars, which can be converted to furans.[31]

This is the first study involving the analysis of pyrolysis products from Brazilian coconuts, especially using GC×GC, and a lot of work still needs to be developed for the complete characterization of this biomass and to develop the appropriate procedure for the use of this material. The results discussed here show that coconut fiber is a raw material that has a promising future in the production of chemicals with higher added value. The use of this raw material (waste material from the coconut industry) presents another advantage, that is, minimizing the environmental impact of the disposal of this residue in sanitary landfills.

In the bio-oil and in the aqueous phase from the pyrolysis of coconut fibers were identified oxygenated compounds such as phenols, aldehydes, and ketones with a high predominance of phenolic compounds. GC/qMS was shown to be a good technique for this analysis, but the GC×GC/TOF-MS was fundamental for the complete characterization of the samples, mainly due to its great advantages, which are high peak capacity, high sensitivity, and the possibility of classifying of compounds in the two-dimensional space.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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