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Pyrolysis of Agroindustrial Residues of Coffee, Sugarcane Straw and Coconut-Fibers in a Semi-pilot Plant for Production of Bio-oils: Gas Chromatographic Characterization

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Abstract: Microbial, vegetal or animal organic matter, which has potential to be transformed into energy, is considered biomass. Among the various alternative energy sources, biomass is the only one with the possibility of generating a class of substances of interest for fine chemistry (ketones, aldehydes, alcohols, phenols, etc.). From biomass, it is possible to produce bio-oil using pyrolysis, a thermodegradation process. The quality of the bio-oil depends on the process conditions (pyrolysis temperature, heating temperature, etc.) and biomass used. In this paper, the pyrolysis (using a fixed bed reactor) of three biomasses (coconut fiber, coffee grounds and sugar cane straw) is studied. The results indicated that the bio-oil yields for all biomass were similar, approximately 37%. The chemical profile obtained by gas chromatography coupled with mass spectrometry (GC/qMS) showed high amounts of fatty acids in the coffee grounds bio-oil and aliphatic and aromatic hydrocarbons in coconut fiber bio-oil, whereas guaiacols were the predominant components of the sugar cane straw bio-oil.

Key words: Pyrolysis, GC/qMS, Biomass, coconut fiber, coffee grounds, sugarcane straw.

1. Introduction

The use of agroindustrial sub-products is of great interest considering economic and environmental factors, as it reduces the contamination potential of rivers and ground water and enables the production of higher aggregated-value products [1, 2]. The agroindustrial and domestic residues have been highlighted as biomass sources for bio-oil production, as they do not compete with food and present an elevated amount of lignocellulose in their constitution [3].

Brazil is considered the largest worldwide producer of coffee, sugar cane and green coconut, which are intensely used agro-products that release a great amount of residues after their use.

The northeast region of Brazil represents 83% of the total cultivated area of coconut and is responsible for 69% of all coconut produced in the country [4, 5]. The fiber generated in this agroindustry represents 80% to 85% of the raw weight of the fruit and approximately 60% of the waste discharged in Brazilian beaches. The study of the reuse of the coconut fibers enables the reduction of inadequate disposition of these solid residues and indicates a new social-economic option for raw materials at the production sites.

Another abundant residue that could be used for bio-oil production is coffee grounds, which represents 50% of the total industrial processing of the coffee, contributing to large amounts of solid residues in

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landfills. This residue contains mainly nitrogen and is rich in lignocellulosic compounds, which indicates that it might primarily be used as a raw material for pyrolysis or liquefaction processes [6].

Increased sugar cane cultivation has contributed to the elevated amounts of residues from this agroindustry. It is estimated that 220 million tons of sugar cane straw are annually produced, and it is known that 50% are left in fields in order to prevent erosion [7]. Some investigations reveal that this lignocellulosic residue could be a potential biomass for thermochemical processes [8].

Pyrolysis is a promising route to convert the biopolymer constituents of biomass (cellulose, hemicellulose and lignin) into substances that can be used as biofuels and as raw material for chemical industries [9]. Two approaches are primarily used for pyrolysis biomass conversion: slow and fast or flash pyrolysis [10, 11]. Slow pyrolysis is used to maximize the gas combustible production and enhance the biochar production [12]. Fast pyrolysis is a process leading to maximized production of bio-oil [13, 14].

In addition to the remarkable volume of these biomasses disposed in landfills, there is a prominent to develop technologies that can contribute to aggregate social and economic values to these residues and minimize their environmental impact. In this context, the aim of this work is to produce and characterize bio-oils from these three residual biomasses using pyrolysis in a fixed bed reactor and, for the first time, to compare the results of simultaneous production of these bio-oils. This comparison can allow the development of processes for the production of different compounds from different biomasses, which could feed into distinct chemical industries.

2. Materials and Methods

2.1 Raw Materials

The biomasses used in this work were sugar cane straw, coffee grounds and green coconut fiber, obtained from a farm located in the city of Carmopolis in the state of Sergipe, Marata Industry and the Brazilian Company of Agricultural and Livestock (EMBRAPA Tabuleiros Costeiros de Aracaju/SE), respectively. Samples were first manually separated from physical impurities, dried in an oven (Arsec model AE5001), and then ground in a mill (SPLABOR Model MA-340) to obtain particle sizes between 32 and 60 mesh. After that, samples were stored in a glass vial under refrigeration, protected from light and in a nitrogen atmosphere until the analysis.

2.2 Raw Material TGA (Thermogravimetric Analysis)

The TGA and its derivate (DTG) of samples were conducted in a thermo-balance (Shimadzu mod. TGA—60 H, Japan) following the methodology described by Almeida [15] and coworkers. Briefly, samples were heated from 26 to 900 ºC, with a heating rate of 10 ºC min^{-1}, in a nitrogen atmosphere.

2.3 Pyrolysis

Fig. 1 shows a scheme of the pyrolysis unit used in the present work. The system was designed in a laboratory-scale (Model SDSLL, Bioware, Campinas, Brazil) with the aim of producing high rates of heat transfer in an annular space of 2 cm inside the fixed bed reactor with capacity of approximately 250 g, where the biomass undergoes the process of pyrolysis. The heating rate can be controlled between two levels defined by the resistance and ranging from 3,000-6,000 W. The heat flux occurs in the radial direction of both the outer and inner surface to center.

The three condensers of the system, as shown in Fig. 1 (C1, C2, C3), allow the collection of the bio-oil. The separation of the first fraction of bio-oil occurs in the first condenser as a function of temperature decrease. In the second condenser, there is also a vacuum pump system with a centrifuge, which separates the second fraction, consisting of compounds not condensed in the first step. Finally, there is another condenser for

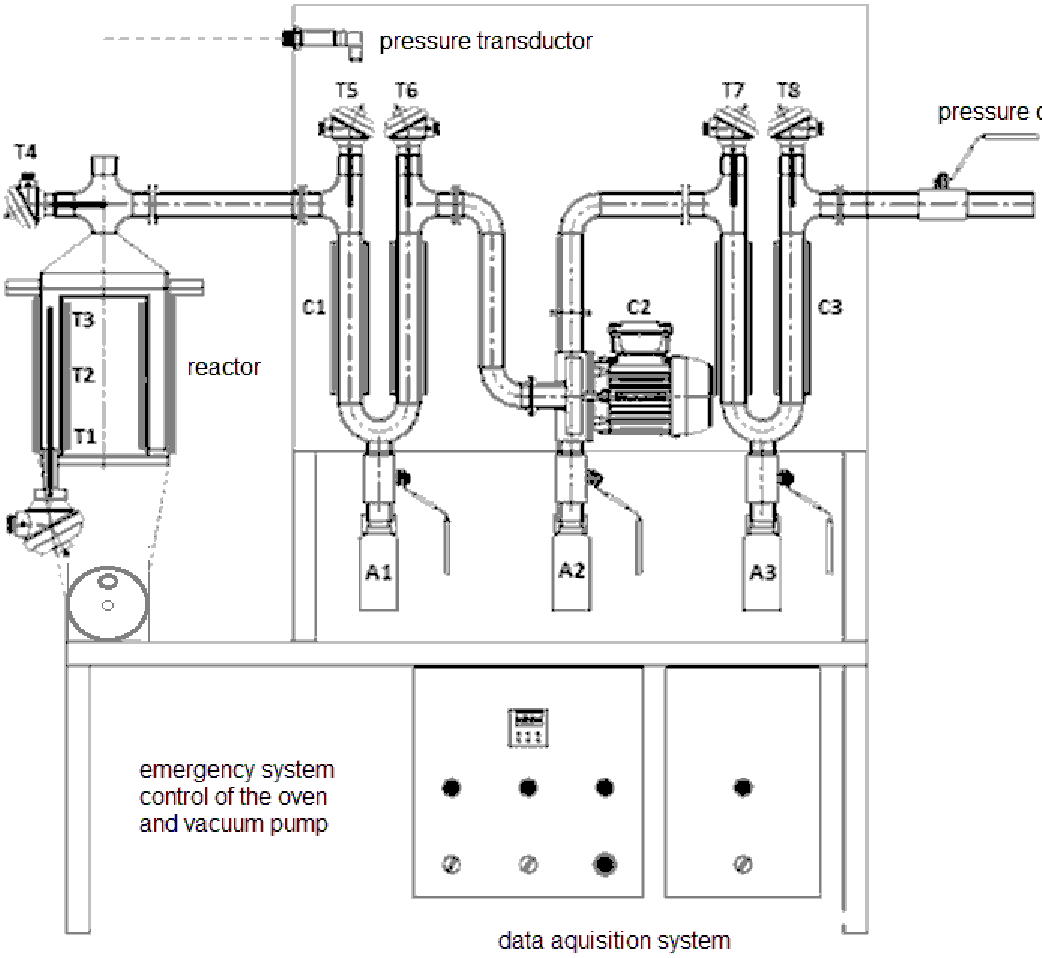

Fig. 1 Schematic diagram for the experimental setup used in the pyrolysis experiments. T1 to T8: K type thermocouples; C1 to C3: condensers; B1 vacuum pump; A1 to A3: collectors.

collecting the fractions of bio-oil that did not separate in the previous steps.

A thermostatic bath (Marconi model MA-184) facilitates the condensation of bio-oil and water. Temperature measurements can be made at the inlet and outlet of each condenser using type K-thermocouples, simple and multipoint, as illustrated in Fig. 1 (T1-T8). A pressure transducer indicates the pressure within the reactor. The complete structure has a length of 1.1 m, height of 1.2 m and depth of 0.5 m, fixed in a metal block and having a control panel in the side.

Field Chart software and Field Logger took the acquisition of data and created charts and tables, respectively, in appropriate on-line process monitoring.

The experimental conditions for the pyrolysis reaction were as follows: heating rate of 30 ºC/min until 700 ºC and residence time from 15 to 30 min in the final temperature. The products generated in the pyrolysis were condensed in the condensers maintained at 1 ºC using thermostatic recirculating baths. Yields of the condensed products (bio-oils) were calculated based on the collected liquid fraction and related with the total raw material fed into the reactor.

An amount of 250 g of each studied biomass was placed in the annular space of the reactor. The temperatures of the condensers are initially kept at 1 °C. After connecting the software for data acquisition and monitoring, the temperature on the control panel of the equipment, the resistance and the vacuum pump are connected and the process of pyrolysis is started. As the temperature increases, the pyrolysis of biomass begins and the steam and the raw bio-oil are transported by the vacuum system, condensed and collected in vials (Fig. 1, A1, A2 and A3).

2.4 Chemical Characterization

Bio-oils were analyzed by one-dimensional gas chromatography coupled to the quadrupole mass spectrometry technique on a GC/qMS (GC/qMS-Shimadzu QP2010 plus, Shimadzu, Tokyo, Japan) that was equipped with an auto injector AOC20i. The chromatographic separation was carried out using a DB-5 column (30 m × 0.25 mm i.d. × 0.25 mm). The oven temperature was programmed as follows: 45 ºC for 2 min, followed by a heating rate of 5 ºC/min up to 280 ºC, remaining for 2 min. The injection and detector temperature was 280 ºC, the injection was conducted in splitless mode and gas flow (Helium, ultrapure, from Air products, Aracaju—SE, Brazil) was 1 mL min^{-1}. All data were treated by GCMS 2.6 solution software (Shimadzu, Japan) and the compounds were identified using the NIST08 and WILEY spectral database. Only the peaks presenting a match to the libraries of over 85% were considered.

3. Results and Discussion

3.1 Biomass Characterization

3.1.1 TGA

Fig. 2 shows the TGA and DTG curves from the green coconut fiber, coffee grounds and sugar cane straw. As typically shown in TGA curves, the increase in the temperature is accomplished by a weight loss of the samples. At the end of the process, once the cellulose, hemicellulose and lignin were exhausted, the remaining weight corresponds basically to ashes. The dashed curve shows the relative mass loss in terms of temperature applied. Therefore, the mass loss at approximately 100-150 ºC is related to water evaporation, while the second mass loss between 150-550 ºC, is an event due to the decomposition of lignocellulosic material.

The loss-of-weight profile of the sample can be classified in three different stages: i) initial loss of water; ii) decomposition of lignocellulosic material, whose percentages of mass-loss and variation in temperature are observed in each stage of the TGA curve (Fig. 2); iii) carbonization step, in which the remaining mass is formed by the mineral material transformed in ashes (metallic oxides) [16]. Table 1 presents these events for each biomass material investigated.

The nature and composition of the biomass can influence the thermodecomposition profile and, therefore, affects the final product of pyrolysis [17]. The decomposition of hemicellulose and cellulose occurs in temperature ranges from 210 to 550 ºC. Lignin, however, is harder to decompose, presenting a wider range of temperature (160-900 ºC) for producing the corresponding weight loss [17, 18]. These observations are in agreement with previous works and were used to determine the final temperature of the pyrolysis (700 ºC) [15, 19].

3.2 Yield and Chemical Characterization

All of the biomasses presented similar yield of liquid products in the pyrolysis (~ 37%), which is the same range as those found in the literature [11, 20, 21].

The liquid products (bio-oils) from the pyrolysis of coconut fiber, sugar cane straw and coffee grounds presented an appearance and odor common to all of the liquid products of pyrolysis from other biomasses cited in the literature [22]. In this study, the chromatographic analysis by GC/qMS indicated over one hundred compounds for each bio-oil. Fig. 3 presents the typical chromatograms for the three bio-oils.

The chromatograms in Fig. 3 indicated a variety of chemical classes present in bio-oils, such as ethers, esters, aldehydes, phenols, ketones, carboxylic acids,

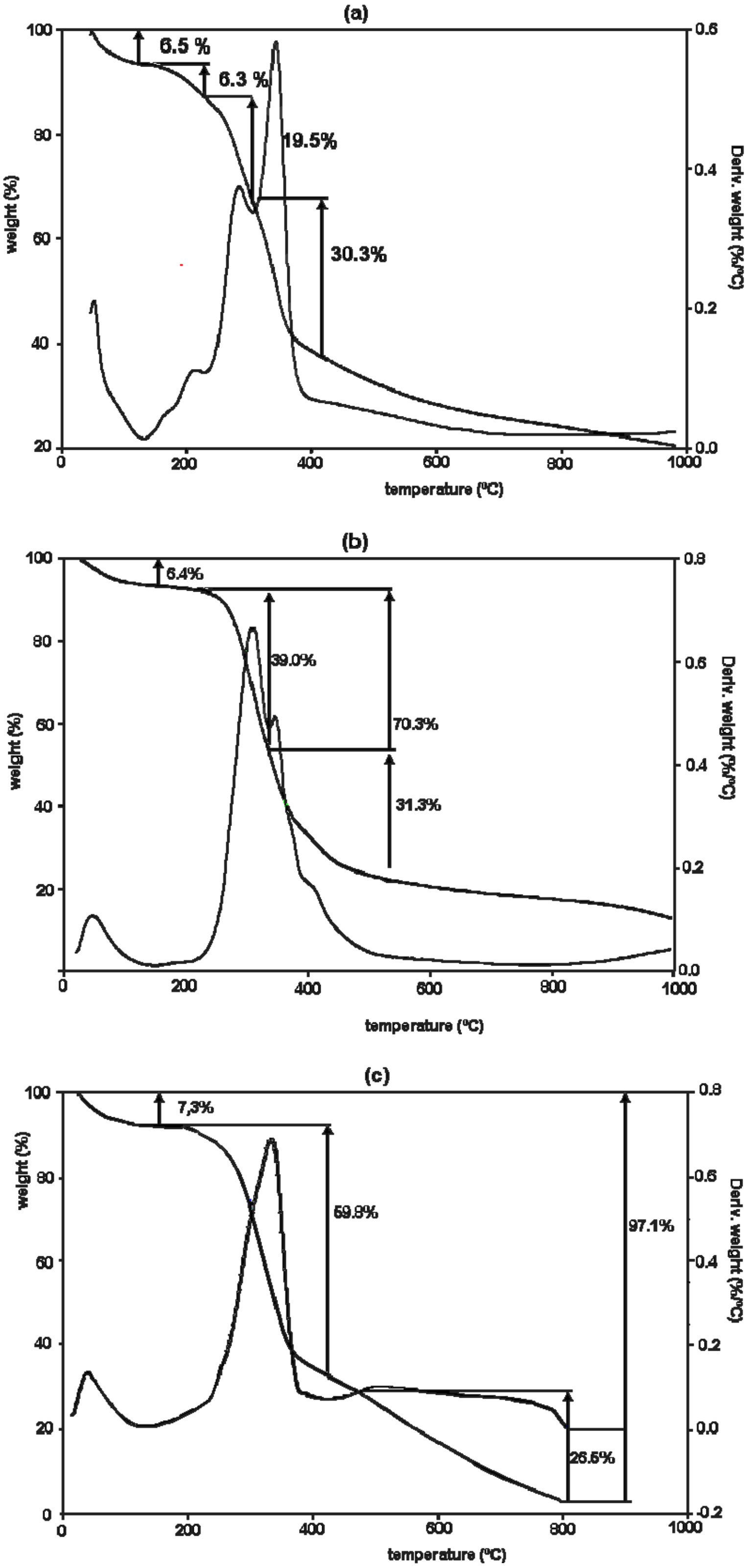

Fig. 2 TGA curves for the biomass investigated in this work (a) CCF (coconut fiber), (b) CFG (coffee ground), and (c) SCS (sugar cane straw).

Table 1 Thermal events and percentage of weight loss for coconut fiber, coffee ground, and sugar cane straw analyzed by TGA.

Stage	Thermal event	Temperature gap (~°C)	Weight loss (%)
Coconut fiber			
1º	H_2O loss	0.0-120	6.50
2º	Fiber decomposition	210-410	56.0
3°	Carbonization (residue)	> 410	37.5
Coffee grounds			
1º	H_2O loss	0.0-110	6.4
2º	Fiber decomposition	250-550	31.3
3°	Carbonization (residue)	> 550	23.3
Sugar cane straw			
1º	H_2O loss	0.0-110	7.3
2º	Fiber decomposition	110-480	70.3
3°	Carbonization (residue)	> 480	26.5

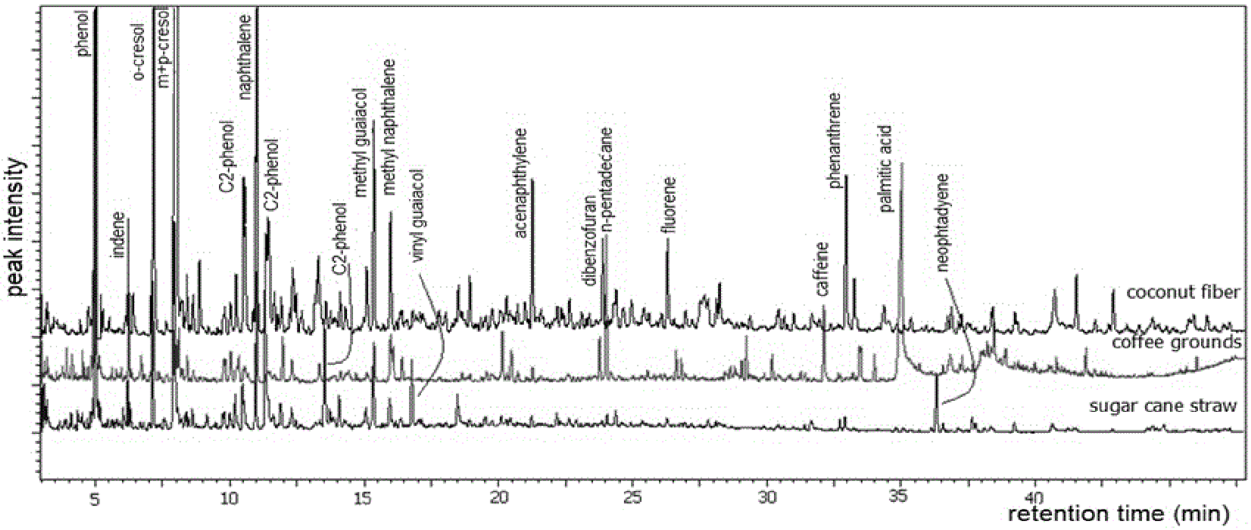

Fig. 3 Total Ion Chromatogram of the three bio-oils from the pyrolysis of CCF, CFG and SCS.

nitro compounds, aromatic hydrocarbons and olefins. It can be noted in Fig. 3 that for each bio-oil studied, there are several quantitative differences in the classes of compounds found. Table 2 lists the chemical classes and the number of compounds identified in the chromatograms, while Fig. 4 depicts the distribution of compounds and area in each class.

By analyzing Fig. 4 and Tables 2 and 3, it can be seen that the compounds in the bio-oils are qualitatively similar. Phenols are the predominant class in the bio-oils, which is in agreement with the literature [14, 23-26], being a characteristic of biomasses with higher lignin content [22, 27].

A high percentage of carboxylic acids was found in the bio-oil from coffee grounds, most likely due to the glycerides content in this biomass, which was already noted by Bok [23] and coworkers.

A high percentage of area and number of peaks of hydrocarbons (aromatic) was observed in the bio-oils from coconut fiber, while phenols were predominant in sugar cane straw bio-oil.

Few studies are described in the literature concerning the characterization of bio-oil obtained from coconut fiber and coffee grounds. However, recent research discusses other bio-oils with similar composition to those studied here, supporting the discussion of the results found in this work [1, 14, 28, 29].

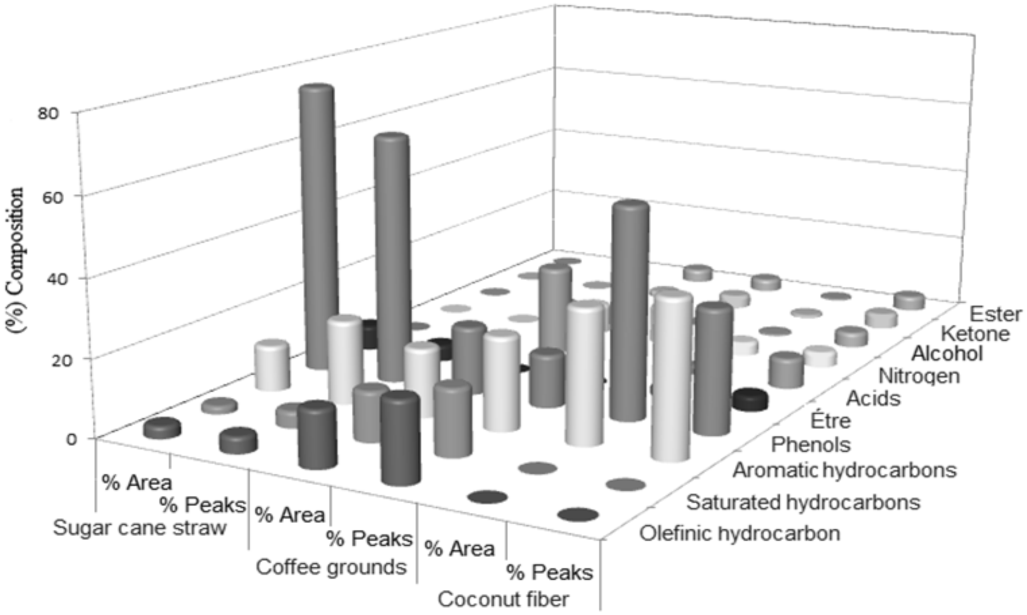

Fig. 4 Semi quantitative distribution of the compound classes for the three bio-oils studied: (a) Distribution according to the percentage of peaks in each class and (b) distribution according to the percentage of chromatographic peak area in each class.

Table 2 Summary of the results obtained by the characterization by GC/qMS.

Compound class	RT (min)	Components	% area		
			Coconutfiber	Sugar canestraw	Coffeegrounds
Alcohol	14.3	Phenyl Pentanol	14.3	——	——
Ácids	33.8	Tetradecanoic acid	14.1	——	——
	35.0	Hexadecanoic acid	——	——	20.73
	38.2	Octadecadienoic acid	——	——	0.44
	38.3	Octadecenoic acid	——	——	2,27
	40.1	n-hexadecanoic acid	2.61	——	——
Ketones	6.4	C2-cyclopentanone	2.61	——	——
	35.3	Octadecanone	——	——	1.62
Ester	7.1	Phenyl acetate	0.50	——	——
	36.8	Ethyl Stearate	——	——	3.67
Ether	13.5	Dihydro Benzofuran	——	6.54	——
	23.9	Dibenzofuran	2.82	——	——
Phenol	5	Phenol	14.53	18.74	9.10
	7.2	Methyl Phenol	10.59	6.01	2.68
	7.9	Methyl Phenol	20.38	5.12	3.91
	7.9	Methoxy Phenol	——	9.62	——
	10.5	C2 Phenol	2.89	2.01	——
	11.3	C2 Phenol	——	10.84	——
	11.4	C2 Phenol	3.48	1.83	——
	11.9	Methyl-methoxyphenol	——	2.14	——
	12.3	C2 Phenol	0.92	1.62	——
	14.1	C3 Phenol	0.60	2.43	——
	15.1	Methoxyindanol	1.39	——	——
	15.4	C2 methoxyphenol	——	4.67	——
	16.8	Vinyl methoxyphenol	——	4.22	——
	38.0	Hydroxy-pyrene	——	——	2.15

Table 2 continued

Compound class	RT (min)	Components	% area		
			Coconutfiber	Sugar canestraw	Coffeegrounds
Aromatic hydrocarbons	6.2	Indene	1.15	1.87	2.95
	10.0	Methyl Indene	——	1.57	——
	10.0	Dihydroxynaphthalene	——	——	2.98
	10.3	C5 Benzene	——	——	1.61
	11.0	Naftalene	12.58	4.59	4.60
	15.4	Methyl Naphthalene	4.58	2.36	2
	16.0	Dihydro Methyl Naphthalene	3.13	——	——
	18.9	Biphenyls	0.92	——	——
	21.3	Acenaphthylene	3.44	——	——
	26.3	Fluorene	2.61	——	——
	33.0	Phenanthrene	4.21	——	——
	41.5	Fluoranthene	1.04	——	35.7
	42.9	Pyrene	0.82	——	——
Saturatedhydrocarbons	5.1	Decane	——	——	1.65
	12.3	Dodecane	——	——	1.61
	20.5	Tetradecane	——	——	1.78
	24.0	Pentadecane	——	——	6.17
	24.4	n-Pentadecane	——	2.13	——
	29.2	Hexadecane	——	——	1.78
Olefinichydrocarbons	4.9	Decene	——	——	4.17
	8.1	Undecene	——	——	4.17
	12.0	Dodecene	——	——	2.07
	16.1	Tridecene	——	——	1.66
	20.2	Tetradecene	——	——	2.53
	23.8	Pentadecene	——	——	1.90
	36.3	Neophytadiene	——	3.22	——
Nitrogenous	8.9	C4 piperidinone	1.07	——	——
	13.3	Isoquinoline	2.5	——	——
	32.1	Caffeine	——	——	3.49
	38.4	Hexadecanamide	——	——	4.42

Table 3 Number of compounds obtained in the CG/MS analysis of the bio-oil from coconut fiber, coffee ground, and sugar cane straw pyrolysis.

Compound class	Coconutfiber	Sugar canestraw	Coffeegrounds
	Number of compound		
Alcohols	1	nd	nd
Acids	2	nd	3
Ketones	1	nd	1
Esters	1	nd	1
Ethers	1	1	nd
Phenols	8	12	4
Aromatic hydrocarbons	10	4	6
Saturated hydrocarbons	nd	1	5
Olefinic hydrocarbons	nd	1	6
N-compounds	2	nd	2
Total	26	19	28

nd = not detected.

Bok [23] and coworkers semi-quantitatively characterized the coffee grounds bio-oil by GC/MS and identified 40 compounds of different classes of hydrocarbons, ketones, phenols, with a considerable acid and olefins percentage. In a recent study using GC/MS and GC×GC/MS, Cunha et al. [24] identified (comprehensive two-dimensional gas chromatography with mass spectrometry) an elevated percentage of aliphatic hydrocarbons after the fractionation of sugar cane straw bio-oil. Almeida et al. [15] found that phenols and aldehydes corresponded to 71% of the bio-oil from the pyrolysis of green coconut fibers.

The hydrocarbons, carbohydrates and furans are the main products of holocellulose pyrolysis, while guaiacols and syringols are the main products of lignin fragmentation [30]. The acids, alcohols, aldehydes, ketones and esters are most likely derived from primary cellulose and hemicellulose decomposition products [10].

These results indicate that high aggregate value compounds can be recovered from these residues by simple pyrolysis processes, which also result in considerable reductions in the volumes of waste material. This approach can make the activity of cultivating and using of these materials a sustainable option allowing an improvement of the environmental quality.

4. Conclusion

The pyrolysis of the biomass from coffee grounds, coconut fiber and sugar cane straw produced bio-oils with similar yields but slightly different composition. The GC/qMS analysis allowed the identification and semi-quantification of the bio-oils indicating the presence of carboxylic acids, phenols, alcohols, ketones, ethers and esters, N-compounds and hydrocarbons (aromatic, saturated and olefinic) in these biomasses.

The predominant class of biomasses produced from the coconut fiber bio-oil was the aromatic hydrocarbons, while in coffee grounds bio-oil, the major compounds were carboxylic acids and in the sugar cane straw bio-oil, phenols predominated.

These compounds have important industrial applications that justify the use of the pyrolysis for their industrial production, solving two social and economic problems by the reducing the volume of wastes that aggress the environment and adding value to a residual agroindustrial material that is normally rejected.

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