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Bio-Oil Production by Thermal Cracking in the Presence of Hydrogen

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Abstract

This paper describes the bio-oil production process of a mixture of agricultural wastes: discarded soybean frying oil, coffee and sawdust, by pyrolysis and thermal cracking in the presence of hydrogen. The fractions obtained in the pyrolysis and/or cracking processes were divided into a light fraction and a heavy one. All the fractions were analyzed by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry detection (GC×GC/TOFMS). The characteristics of the fractions obtained in from the cracking process in the presence of hydrogen were similar to those of petroleum-based naphtha, while the fractions obtained by pyrolysis contained significant quantities of compounds such as furanmethanol, hexanol, and benzofuran, whose commercial value is high.

Introduction

The recent environmental restrictions on the use of fossil fuels have intensified research into new alternative energy sources. Many alternative technologies to produce cleaner fuels have been developed, including the use of biomass, which offers a promising potential [1-4].

Biomass is a renewable source which has received attention due to various characteristics, particularly its low cost and wide availability. Biomass can be converted into bio-fuel by means of different processes, e.g., reductive combustion, liquefaction, pyrolysis and gasification [5]. The use of biomass is particularly interesting when it involves waste products such as waste vegetable oil, fruit seeds, sugarcane bagasse, sugarcane straw, rice husks, coconut fibers, and coffee grounds, which are also potential sources of energy [6-8].

Bio-oil from biomass pyrolysis, also known as pyrolysis oil, is a dark brown almost black liquid with a characteristic smoky odor, whose elemental composition is analogous to that of the biomass from which it derives. It is a complex mixture of oxygenated compounds with a significant amount of water originating from the moisture of the biomass and from cracking reactions. Bio-oil may also contain small coal particles and dissolved alkali metals coming from the ash. Its composition depends on the raw material and on the operating conditions used in its production. Pyrolysis oil is an aqueous microemulsion resulting from the products of fragmentation of cellulose, hemicellulose and lignin [9,10].

Much attention has focused on pyrolysis, a biomass thermal decomposition process, for which the literature describes numerous different reactors and conditions [11-13]. The presence of oxygen exerts a highly negative impact on the potential uses for bio-oil. For example, oxygen it lowers the heating value, gives rise to immiscibility with petroleum fuels, and leads to corrosiveness and instability during long-term storage and transportation [14]. The biomass pyrolysis process is an economically feasible option for producing chemicals and/or fuels [15,16]. The bio- oil resulting from the pyrolysis process consists of a mixture of more than 300 organic compounds [17], but its processing, separation and characterization pose technological challenges. In the thermal cracking process, the volatile compounds generated during pyrolysis also present a promising potential for energy generation [18]. Moreover, the upgrading process, which involves the reduction of oxygenates and is necessary to improve the quality of bio-oil, normally requires processes such as catalytic cracking, hydrogenation and steam reforming [19-22].

Hydropyrolysis is an important technique for improving the quality of bio-oil produced from biomass pyrolysis. Hydrogen is a reducing gas and cracking biomass in the presence of hydrogen can reduce the oxygen content in bio-oil [23]. This paper discusses the characterization of bio-oil generated from the pyrolysis of a mixture of wastes: discarded soybean frying oil, coffee grounds and sawdust. The thermal cracking process, which was performed in the presence of hydrogen in order to upgrade the bio-oil, resulted in lower molecular weight fractions and substantially reduced the content of oxygenated and nitrogenated species.

Experimental Materials

The bio-oil was obtained by pyrolysis of a mixture (1: 1: 1, in mass) of wastes: discarded soybean frying oil, coffee grounds and eucalyptus sawdust. The frying oil was mixed with the solids after their particle size was reduced to 0.21 mm. To this mixture were added calcium oxide (20 mass %) and sufficient water to produce a malleable mass that could be moulded into cylindrical samples (50 mm × 180 mm). The samples were allowed to dry at room temperature for a week.

Biomass pyrolysis and thermal cracking of the bio-oil

The bio-oil was produced by conventional pyrolysis of the cylindrical samples in an electrically heated stainless steel reactor. Before beginning the pyrolysis, the system was purged for 20 minutes with Argon containing 5% of hydrogen (100 mL min-1). After purging, the pyrolysis started and the system was heated to 850°C at a heating rate of 15°C min-1. The volatiles produced during the process were

treated by isothermal hydrocracking in another reactor (stainless steel, 20 mm in diameter and 600 mm in length) at 850˚C. The final effluent was cooled to 100˚C and the water phase was separated by decantation.

After phase separation, the effluent was condensed at 5˚C and the aqueous phase separation process was repeated, while the gaseous phase was discarded.

For purposes of comparison, the pyrolysis was repeated without thermal cracking. Four samples were thus produced: bio-oil obtained at 100˚C, and bio-oil obtained at 5˚C, both with and without thermal cracking. These samples are hereinafter referred to as: OPH (Oil from Pyrolysis obtained at 100˚C - High temperature) and OPL (Oil from Pyrolysis obtained at 5˚C- Low temperature) for samples obtained only by pyrolysis, and OCH (Oil after Cracking obtained at 100˚C-High temperature) and OCL (Oil after Cracking obtained at 5˚C-Low temperature) for those obtained after thermal cracking. Figure 1 illustrates the production scheme of the four fractions produced, i.e., OPH and OPL by the pyrolysis process and OCH and OCL by the pyrolysis process followed by thermal cracking.2.2. Characterization of the products

The four fractions were analyzed by GC×GC/TOFMS using a LECO Pegasus IV (LECO, St Joseph, MI, USA) system. Experiments were performed in a conventional split/splitless injector (Agilent Technologies) at 320˚C (1μL) with a split ratio equal to 1: 30. Helium (99.999%, Linde Gases, Porto Alegre, RS, Brazil) was used as carrier gas, at 1 mL min-1. The oven temperature was programmed from 40˚C to 300˚C at 3˚C min-1. The difference between ovens 1D and 2D was 15˚C and the modulation period was 8 s (cryogenic quadjet modulator, cooled with liquid nitrogen). The transfer line and electron impact ionization source operated at 300˚C and 250˚C. The acquisition frequency of the detector was 100 Hz, using a mass range of 45 to 400 Daltons. Electron ionization was carried out at 70 eV. The data were processed on the Pegasus 4D platform of the ChromaTOF software. A DB-5 column was used as first dimension, and a DB-17 as second dimension column, using a cryogenic modulator.

The compounds were identified based on the following parameters: retention times, regions of spatial structuration, mass spectral match factor (NIST library), and spectral deconvolution. Given the spatial structure provided by GC×GC, some compounds with similarity below 700 were considered to be identified, since the elution region in the two-dimensional (2D) space, as well as other parameters, provide a higher degree of reliability in the identification of analytes. The data generated in the peak table were transferred to the Microsoft Excel™ program in order to build dispersion graphics to better visualize the distribution of compounds in 2D space.
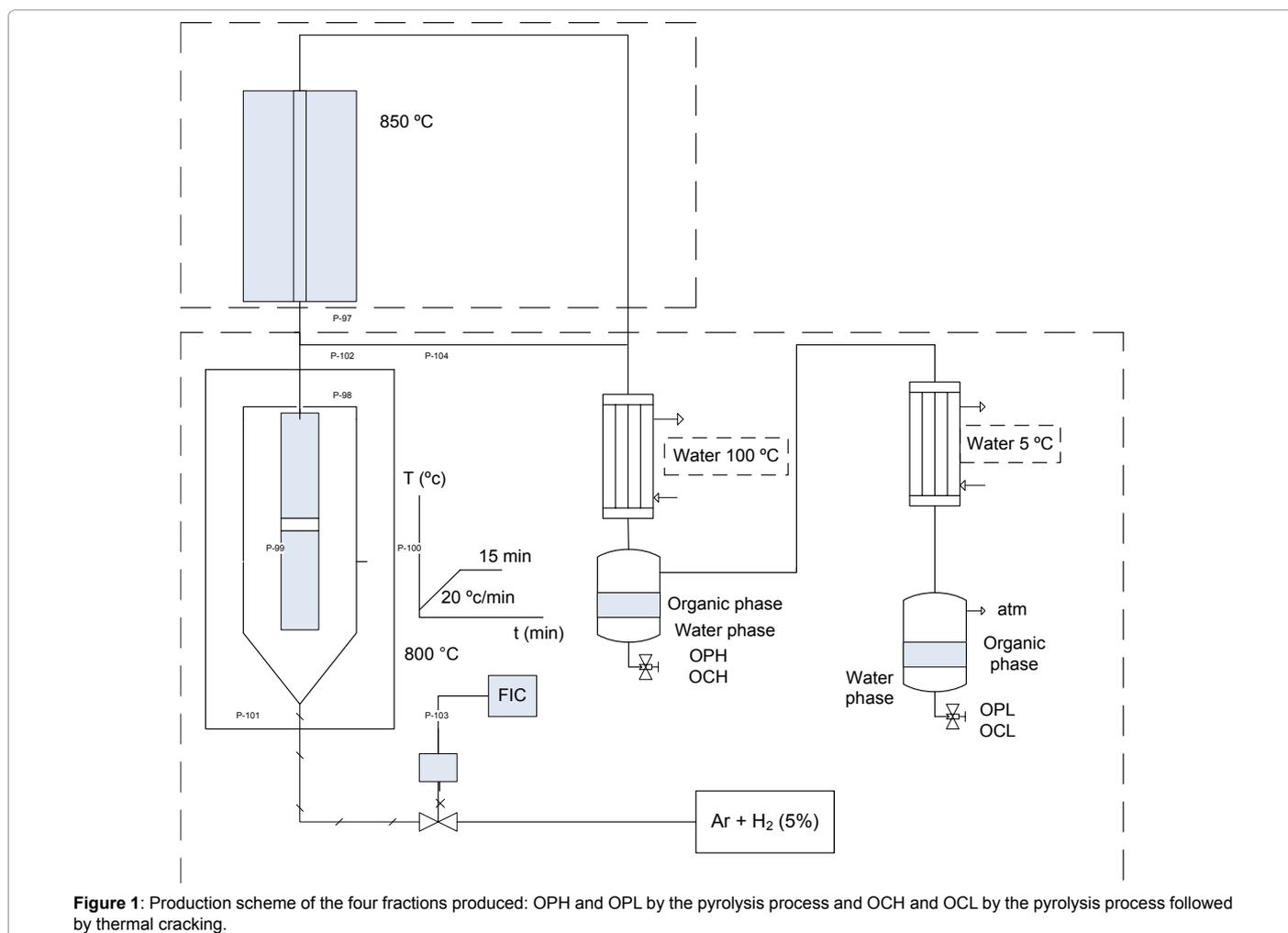
Results and Discussion

Figure 1: Production scheme of the four fractions produced: OPH and OPL by the pyrolysis process and OCH and OCL by the pyrolysis process followed by thermal cracking.

Product yields from pyrolysis and thermal cracking

Pyrolysis product distribution depends on reaction parameters such as temperature, heating rate and reactant particle size, as well as on the starting biomass.

The oil fractions obtained in this work came from the same raw materials and the same operational conditions, but from different production processes. The OCH sample was obtained by pyrolysis followed by thermal cracking, while the OPH sample was obtained solely by pyrolysis. The application of thermal cracking after pyrolysis led to a significant increase in the condensed fraction at the temperature of 5˚C. The average yield of the pyrolysis process is approximately 30% oil fractions, 50% aqueous fractions, and 20% gas phase (uncondensed, obtained by difference). In the pyrolysis process, the oil fraction condensed at a temperature of 100˚C corresponds to approximately 90% of the oil fraction. Pyrolysis process followed by thermal cracking results in a distribution of approximately 40% of the fraction condensed at a temperature of 5˚C (OCL) and 60% of the oil fraction condensed at a temperature of 100˚C (OCH).

Composition of bio-oil fractions

Given that the four bio-oil fractions are very complex mixtures of different chemical species derived from depolymerization and fragmentation of the main components of the biomass, which comprise a wide range of molecular weights, a GC×GC/TOFMS was used for their identification.

The compositions of the four bio-oil fractions shown in Figure 2 are grouped according to types of chemical compounds: acids, aldehydes, ketones, alcohols, phenols, aromatics, cyclic and aliphatic hydrocarbons, ethers and nitrogen compounds. The compounds were tentatively identified when the similarity between a sample's spectrum and that of the library was greater than 750. In total, 214 compounds in OCH, 324 in OCL, 84 in OPH and 312 in OPL were tentatively identified.

Some observations apply both to the bio-oils obtained from thermal degradation and to the light fraction of pyrolysis (OPL-Figure 2). For example, note that there is a high proportion of hydrocarbon compounds, the most important ones being aromatics and aliphatics, representing between 57 and 79 wt % of the products. On the other hand, the OPH sample obtained by pyrolysis and condensed at 100˚C (fraction containing heavy compounds) is composed mainly of ketones and nitrogens, and smaller amounts of alcohols, ethers and phenols. This fraction does not contain hydrocarbons. Nitrogenous compounds in bio-oil originate from the thermal degradation of caffeine derivatives contained in coffee grounds.

As can be seen in Figure 2, the fractions obtained by pyrolysis and thermal cracking (OCH and OCL) consist mostly of aliphatic, aromatic and cyclic hydrocarbons. The OPH fraction is composed mainly of hydrocarbons with nitrogen (46% in area) and oxygen (47% in area) compounds. The oxygen content in pyrolysis bio-oils usually varies from 45 to 50 w/w%, and oxygen is present in most of the more than 300 compounds [10,24,25]. The distribution of these compounds depends mainly on the type of biomass and the process conditions. The presence of oxygenated compounds in bio-oil reduces its calorific value and renders it chemically unstable [9], limiting its use as fuel or in formulations for direct use in diesel cycle engines [9,26,27]. However, when separated, they present high added commercial value [28].

Table 1 lists the main identified compounds and their corresponding percentage area in the bio-oil and fractions (OPH, OPL, OCH and
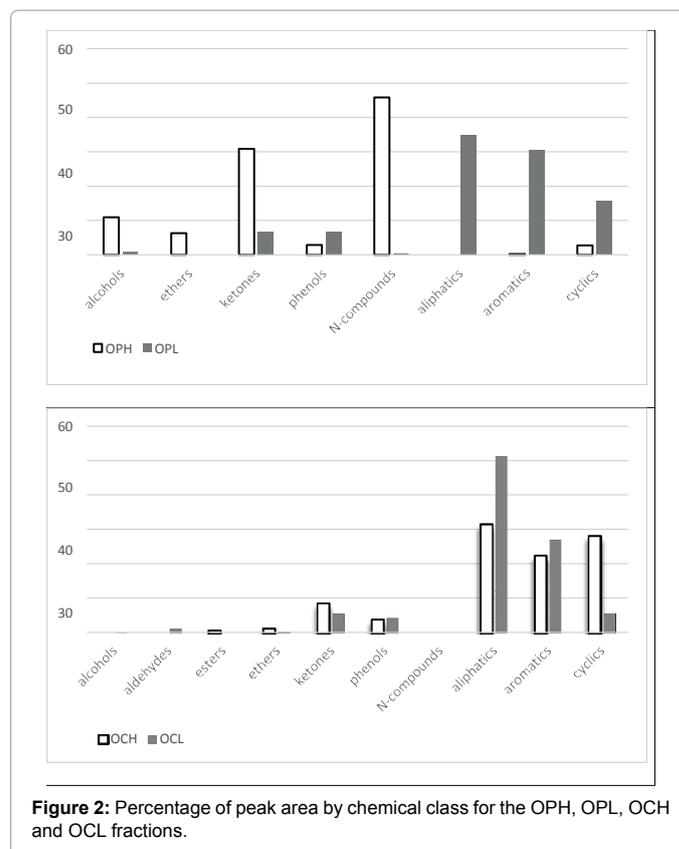

Figure 2: Percentage of peak area by chemical class for the OPH, OPL, OCH and OCL fractions.

OCL). The other compounds contained in the fractions of this study are listed in the Appendix.

As can be seen in Table 1, the oxygenated compounds in the OPH fraction alcohols include furanmethanol (8% in area) and hexanol (2% in area). These two alcohols are important raw materials for the preparation of a wide range of drugs and industrial products of high commercial and industrial value [29]. Benzofuran and dioxyethane ethers are also present in the OPH fraction in percentage areas of 4.0 and 2.0, respectively. Benzofuran is considered an important class of heterocyclic compounds which is present in numerous bioactive natural products and in pharmaceuticals and polymers. Benzofuran is one of the most important heterocyclic rings due to its broad microbiological range. Medicinal chemistry is widely involved in the synthesis of the benzofuran ring owing to its clinical importance. Benzofuran can be used as an enzyme activator and inhibitor, as an antimicrobial, anti-inflammatory, anti-cancer, antiviral, anti-tuberculosis, antioxidant agent, etc. [30].

The four fractions of this study contained phenolic compounds, namely, around 7% OPL, 4% OCH and OCL, and 3% OPH. These compounds are widely employed in the production of phenolic resins [31]. They also have antioxidant and antimicrobial properties that inhibit the proliferation of microorganisms, corrosion and deposits when added to diesel fuel formulations and/or biodiesel for use in engines (use of biomass-derived compounds) [32,33].

Moreover, chemical products containing oxygen are produced mainly from fossil fuels, through the oxidation or hydration of olefins to introduce oxygen containing functional groups. Fortunately, these functional groups are already present in bio-oil. Therefore, obtaining

Major compounds		Area %			
		OCH	OPL	OCL	OPH
Alcohol	Furanmethanol	n.d.	n.d.	n.d.	8.4
	Hexanol	n.d.	0.2	n.d.	2.3
Aldehyde	Propenal, phenyl	n.d.	0.1	1.1	n.d.
Ether	Benzofuran	0.5	n.d.	0.1	4.3
	Ethane, diethoxy-	n.d.	n.d.	n.d.	2.0
Ketone	Hexadecanone	1.5	n.d.	n.d.	n.d.
	Nonanone	n.d.	n.d.	1.4	n.d.
	Cyclopentenone, methyl-	n.d.	n.d.	n.d.	6.6
	Cyclopentenone, C3	0.2	0.5	0.2	6.2
	Cyclopentenone, C2	0.1	0.4	n.d.	5.6
	Cyclohexenone, methyl-	n.d.	0.2	n.d.	1.7
	Cyclopentanone	n.d.	0.1	0.1	1.2
	Cyclopentanone, methyl	n.d.	0.3	0.1	1.1
N-Compound	Pyrrole, methyl-	n.d.	n.d.	n.d.	9.3
	Pyrazine, C5	n.d.	n.d.	n.d.	8.1
	Pyrazine, C3	n.d.	n.d.	n.d.	2.8
	Pyrazole, C4	n.d.	n.d.	n.d.	1.7
	Imidazole, C5	n.d.	n.d.	n.d.	1.6
	Pyrazine, C4	n.d.	n.d.	n.d.	1.5
	Pyridine, methyl-	n.d.	n.d.	n.d.	1.4
	Pentanamide, methyl-	n.d.	n.d.	n.d.	1.0
Phenol	Phenol, ethyl	1.7	1.4	1.1	n.d.
	Phenol, methyl-	n.d.	1.9	n.d.	0.1
	Phenol	0.3	0.6	1.0	2.0

Class	Identification	Area %			
		OCH	OPL	OCL	OPH
HC Cíclicos-C5	Cyclopentadiene, C2	2.6	n.d.	n.d.	n.d.
	Cyclopentadiene, methyl	2.1	n.d.	n.d.	n.d.
	Cyclopentadiene, C3	1.2	n.d.	n.d.	n.d.
	Cyclopentene, C6	n.d.	1.2	n.d.	n.d.
	Cyclopentane, C8	n.d.	n.d.	1.1	n.d.
	Cyclopentadiene, C5	n.d.	n.d.	n.d.	2.2
HC Cíclicos-C6	Cyclohexene, C2	4.2	0.1	n.d.	n.d.
	Cyclohexene, methyl	5.1	0.2	0.5	n.d.
	Cyclohexadiene, C2	4.7	0.4	0.4	n.d.
	Cyclohexadiene, C4	n.d.	1.1	n.d.	n.d.

	Indene, methyl	1.3	1.2	1.3	n.d.
	Indene, C2	1.1	n.d.	n.d.	n.d.
	indene	n.d.	2.4	1.4	n.d.
	Naphthalene, dihydro-	n.d.	1.8	n.d.	n.d.
	Indane	n.d.	1.0	0.5	n.d.
	Naphthalene, methyl	n.d.	0.6	1.1	n.d.
	Heptadiene	2.4	n.d.	0.6	n.d.
	Dodecadiene	n.d.	1.3	n.d.	n.d.
	Toluene	6.2	1.0	0.1	0.2
	Benzene	2.1	n.d.	2.1	n.d.
	Benzene, C3	3.9	2.0	3.4	n.d.
HC diaromatico	Benzene, C4	1.0	3.4	1.9	n.d.
	Benzene, C5	0.1	1.3	0.3	n.d.
	Benzene, C2	n.d.	1.1	6.3	n.d.
	Octene	2.9	2.7	1.3	n.d.
	Decene	1.3	n.d.	1.0	n.d.
	Dodecene	n.d.	1.7	1.0	n.d.
	Undecene	0.6	1.2	0.6	n.d.
	Octane	6.9	1.7	0.4	n.d.
	Nonane	1.0	n.d.	1.5	n.d.
	Tridecane	0.4.	4.4	1.1	n.d.
	Pentadecane	0.6	1.2	0.8	n.d.
	Docecane	03	1.0	0.5	n.d.

Table 1: Main identified compounds and their corresponding percentage area in the bio-oil and fractions (OPH, OPL, OCH and OCL).

value-added chemicals from bio-oil is a potential approach for the efficient use of biomass energy.

With respect to the N-compounds present only in the OPH fraction, pyrazines corresponded to 25% in area. Pyrazine is an important product that participates together with benzene in the synthesis of quinoxaline, also known as benzopyrazine, which is rare in its natural state, but is easy to synthesize. Quinoxaline and its derivatives are very industrially important because of their ability to inhibit metal corrosion [34] in the preparation of porphyrins [35]. The pharmaceutical industry has a potential interest in them because of their broad spectrum of biological properties [36-38].

The composition of the OPH fraction contained practically no aromatic hydrocarbons. On the other hand, the OPL, OCH and OCL fractions each presented approximately 16% in area of alkylbenzenes, which could be isolated and, together with the pyrazines of the OPH fraction, serve as raw material for the synthesis of quinoxaline and its derivatives.

The OCL and OCH fractions obtained by thermal cracking in the presence of a mixture of argon and 5% hydrogen resulted in the elimination of oxygen (deoxygenation) with the formation of water [39], and a stronger breakdown of the heavier organic compounds into lighter organic compounds, as well as the elimination of nitrogen from the nitrogenated compounds. This is illustrated in Figure 2 and in the supplementary material. Because thermal cracking produces various fragments of C-C, they may undergo oligomerization to form olefins, which in turn may undergo aromatization followed by alkylation and isomerization, producing aromatics.

The OCH and OCL fractions presented percentage areas of 82 and 84, respectively, of these hydrocarbons. The OPL fraction obtained by pyrolysis showed a profile similar to that of the OCH and OCL

fractions with respect to hydrocarbons, with 81% in area, but with 8.0% of oxygenated compounds.

Conclusions

In the fractions obtained by pyrolysis, 84 compounds were tentatively identified in the heavy fraction and 312 in the light fraction. The vapors were subjected to thermal cracking in the presence of 5% hydrogen as a way to upgrade the bio-oil, and 214 compounds were identified in the heavy fraction and 324 in the light fraction. The thermal cracking process produced mainly aliphatic, aromatic and cyclic hydrocarbons, yielding approximately 80% in weight of these compounds with characteristics similar to those of naphtha derived from the atmospheric distillation of petroleum with potential applications as fuels. The fractions obtained solely by pyrolysis consisted predominantly of hydrocarbons with nitrogen (46% in area) and oxygen (47% in area) compounds. The oxygenated compounds included furanmethanol and hexanol alcohols, and benzofuran and dioxyethane ethers. All the analyzed fractions contained phenolic compounds. When isolated, these compounds are an excellent potential source of raw material for the preparation of pharmaceutical and industrial products of high commercial and industrial value.

Acknowledgements

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