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Article

Production and Characterization of the Bio-Oil Obtained by the Fast Pyrolysis of Spent Coffee Grounds of the Soluble Coffee Industry

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Agro-industrial wastes are abundant and low-cost sources of energy and chemicals. Biomass account for 14% of the world's energy production. Industrial residues of production of soluble coffee (spent coffee grounds - SCG) have great potential due to its large-scale production and can be transformed by pyrolysis, in liquid, solid and gaseous products with applications from energy to chemicals. This work has the objective of producing bio-oil from the pyrolysis of industrial SCG, characterize it by chromatography and indicate its possible applications. As SGC contains a large amount of glycerides, they were extracted from SGC before the pyrolysis, aiming to obtain a better bio-oil from the residue. The yield in vegetable oil was 5.2% and its analyses showed that 50% are saturated acids (mainly palmitic 27.6%) and other 50% are unsaturated ones (mainly linoleic acid 35.3%). This composition qualifies this oil for biodiesel purposes. The residue (SGC after extraction) was submitted to pyrolysis, yielding 30% in liquid products, being 6% bio-oil. The bio-oil was analyzed by gas chromatography being identified free fatty acids, hydrocarbons, phenols and N-compounds. The heteroatomic compounds limit the use as biofuel but can be interesting for the pharmaceutical, agrochemical and fine chemicals industries.

Keywords: biomass, bio-oil, pyrolysis, spent coffee grounds

Introduction

The increases in energy demand due to the accelerated consume of nonrenewable sources and the abusive dependence on fossil fuels lead the scientific community to seek sustainable sources of energy. The environmental impacts of the emission of pollutant gases, as well as fluctuations in the prices of fossil fuels are the main boosters for the development of research using biomass.[1]

In this context, public policies to encourage the production of biofuels and bio products from alternative sources (to fossil ones) have been gaining strength widely. Among renewable energies, biomass has shown great potential, not only in the conversion of energy, but also in the generation of inputs for the chemical industry.[2]

Biomass is an abundant and low-cost source of chemicals, mainly when it comes from agricultural, industrial and forestry waste.[3] Thus, besides adding value to these residues, the use of lignocellulosic biomass has great importance in the environmental issue, since it provides an ecologically correct destination for these wastes, which are produced in high quantities and not adequately discarded. This concern is still higher in countries such as Brazil, whose raw internal product is largely dependent on agribusiness.[4,5] Among the products of Brazilian agribusiness, coffee stands out, considered the second largest commodity marketed worldwide, behind only oil. The country is considered the largest producer of coffee in the world, moving about 5 million workers for its cultivation and harvest.[6] During the industrial processing of coffee beans for the production of soluble coffee, only 20% of the weight of this grain is converted into coffee, while the rest is discarded as waste,

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called spent coffee grounds (SCG). This is an undesirable residue, with large amounts of nitrogen compounds, which can cause environmental impacts. For this reason, in recent years several studies indicate SCG as a promising biomass for industrial or energy purposes, due to its lignocellulosic composition, pleasant smell and the high heating value in relation to other biomasses.[6-11]

According to Roy and Dias,[12] pyrolysis is the most applied thermo-chemical process in the conversion of a biomass, where the degradation of the biomass occurs in an atmosphere free of oxygen, under high temperatures, producing biochar (charcoal), bio-oil (pyrolytic liquid) and gases.[13-15] The yield of each of these products is directly related to the type of pyrolysis chosen, with fast pyrolysis being recommended for a higher liquid yield.[16]

Bio-oil is a dark-colored liquid, characteristic odor and is considered chemically a complex mixture of various organic compounds. In its composition more than 300 compounds have already been identified, such as acids, alcohols, aldehydes, esters, ketones, phenols, furans, hydrocarbons and N-compounds.[17] Therefore, bio-oil has great potential for application as a source of raw material for chemicals as well as in the fuel industry.[18]

Some authors have performed the pyrolysis of coffee grounds and reported a bio-oil with a high content of fatty acids (around 10% in weight),[19-24] due to the thermal degradation of glycerides presented in the vegetable oil. Aiming its energetic application, Vardon *et al.*[23] performed pyrolysis of the biomass after the process of extracting the vegetable oil and noticed a considerable decrease in the content of fatty acids.

According to Phimsen *et al.,*[25] the vegetable oil extracted from SCG can be transesterified for biodiesel production, once their composition is similar to other vegetable oils used for this purpose. The presence of fatty acids such as linoleic, palmitic and oleic, make it considered a high quality raw material in comparison to other sources of waste, because it is less expensive, more stable, besides having a pleasant odor.[26]

The characterization of biomass and bio-oil are of great importance in order to determine their best uses. Related to biomass, thermogravimetric analysis (TGA) allows the prediction of the kinetic parameters of a thermochemical process, such as pyrolysis,[27] while Fourier transform infrared spectroscopy (FTIR) aiming an initial analysis of its chemical composition.[28]

With regard to vegetable oil and bio-oil, gas chromatography coupled to the mass spectrometry (GC-MS) provides information about the identity of the sample, making possible to prospect for future applications, in the chemical or energy industry.[29]

Considering these parameters and techniques, the goal of this work is the production of vegetable oil (Soxhlet extraction) and bio-oil (fast pyrolysis) from the SCG (industrial residue from the production of soluble coffee) and characterize them, aiming their exploration and possible application for energy and industrial purposes.

Experimental

Materials

The solvents employed in the Soxhlet extraction process and in the chromatographic analyzes were hexane and dichloromethane, (PA, Merck, Dortmund, Germany) and they were bi-distilled. Helium (99.999%, White Martins, Aracaju, Brazil) was used as carrier gas in the chromatographic procedures. A mixture of chromatographic standards of n-alkanes (C_7H_{16} to $C_{33}H_{68}$, Merck, Dortmund, Germany) was used in the calculation of retention indexes.

Sample (SCG)

The SCG from the soluble coffee production process was supplied by Companhia Iguaçu de Café located in the city of Cornélio Procópio (Paraná, Brazil). The SCG is composed by a blend of Arabica and Robusta species of coffee.

The samples were ground in a blender (in the range of 10 to 32 mesh) and oven dried at 60 °C for 24 h.

Extraction of vegetable oil

An exhaustive extraction from SGC (by Soxhlet) was performed according to the Association of Analytical Chemists,[30] using hexane as the extractor solvent. The analysis of the content and quality of fatty acids in the vegetable oil was carried out after a derivatization step, which consisted of the conversion of the glycerides into methyl esters. The methylation process was carried out using BF_3 as catalyst, according to the methodology described by Metcalfe *et al.*[31] widely used for this purpose.

Biomass characterization

Infrared Spectroscopy (FTIR) analyzes of the biomass were performed on the Varian 640-IR (Santa Clara, USA). All spectra were recorded at the range from 4000 to 400 cm^{-1}, with 4 cm^{-1} of resolution and 64 scans.

The thermogravimetric (TGA) and derived thermogravimetric (DTG) curves of the SCG samples (containing 13.0 mg) were obtained using TA Instruments model SDTQ60 (TA Instruments, Lukens Drive, New

Castle, USA). The samples were characterized at a heating rate of 10 ºC min^{-1} until 1000 ºC under a N_2 flow of 100 mL min^{-1} in a platinum crucible.

Pyrolysis

The pyrolysis process was carried out on a bench scale equipment made of stainless steel fixed bed reactor with vertical furnace, which was constructed in the laboratory, with resistances capable of achieving a heating rate above 100 °C min^{-1}, characterizing a fast pyrolysis.

The stainless steel cylindrical reactor (30 × 5.1 cm), with a maximum capacity of 300 g of biomass, has an inert gas inlet (N_2, White Martins, Salvador, Brazil) for carrying the volatiles formed during the pyrolysis of the biomass, and another for a thermocouple, which indicates the temperature at which the process occurs inside the reactor. At the top of the lid is installed the volatiles outlet which connects directly to a stainless steel condenser. This connection is used for the first cooling of the vapors so that later the glass capacitors are adapted, thus avoiding the contact of glass/metal still at high temperatures, which causes very frequent maintenance due to the breaks and dilation.

The condensation of the volatiles occurs by a condensation system composed of six more condensers of glass, arranged in series and connected in pairs by an adapter in its inferior part for the collection of the organic and aqueous fractions. The temperature of the cooling system is maintained by a thermostatic bath, which allows cooling to –4 °C. Figure 1 shows the complete system and the reactor, including an illustration of its internal part.

Approximately 30 g of the sample were subjected to pyrolysis at a N_2 flow of 100 mL min^{-1}. The oven heating, from room temperature to 600 °C (temperature optimized through the TG) was performed at an average heating rate of 100 ºC min^{-1}. At the end of the process, the organic and aqueous fractions were collected. After calculating yield, the bio-oil was separated from the aqueous fraction by liquid-liquid extraction with dichloromethane. The solvent present in the organic fraction was evaporated and the remaining bio-oil underwent drying with anhydrous sodium sulfate to remove residual water.

Chromatographic analysis

The oil extracted from the SCG and the bio-oil produced by the pyrolysis were analyzed by GC-MS, (Shimadzu model GC/MS-QP 2010 Ultra, Japan). The capillary column used for the vegetable oil was a DB-5 (polymethylsiloxane with 5% phenyl groups) 30 m long, 0.25 mm internal diameter and 0.25 µm stationary phase thickness. For the bio-oil analysis, the used column has the same stationary phase, but with a length of 60 m.

For the oil analysis, the injector and interface temperatures were maintained at 280 °C. The initial oven temperature was 40 ºC with a heating rate of 3 ºC min^{-1} until the temperature reached 280 °C, which was held for 10 min. For the bio-oil, the injector and interface temperatures were maintained at 300 °C. The analysis was started at 40 °C, with a heating rate of 3 °C min^{-1}, until 300 °C, and remained at this temperature for 10 min. The carrier gas used was helium (White Martins, Salvador) with 99.999% purity with

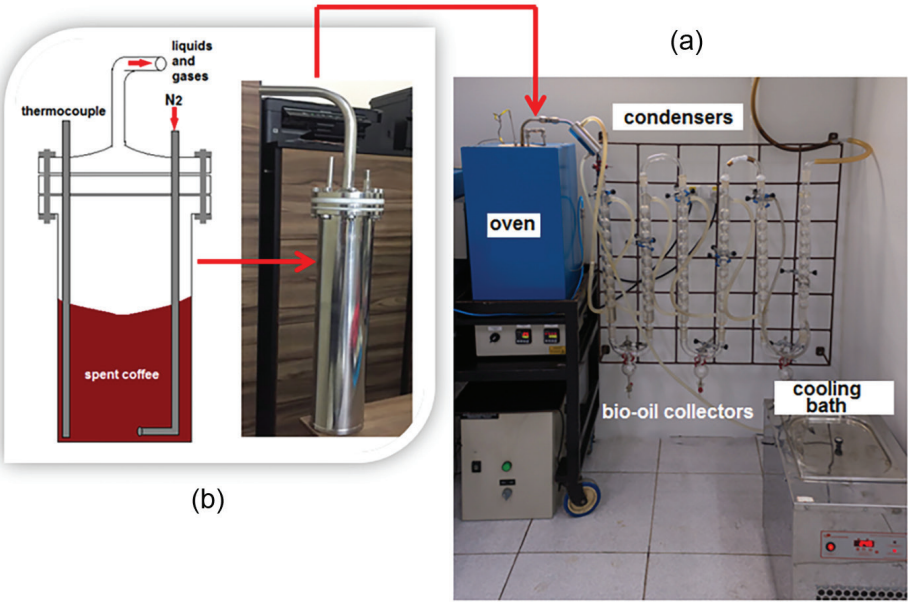

Figure 1. Illustration of the pyrolytic system: (a) Photograph of the whole system (oven, condensers and cooling bath); (b) details of the stainless-steel reactor.

1 mL min^{-1} flow. The analysis mode adopted was the total spectrum scanning for each peak (SCAN) with a range of 45 to 450 Daltons.

Treatment of chromatographic data

The identification of the compounds was performed through a detailed analysis of each component, evaluating their retention time, similarity, area, molecular weight, formula, structure and organic function, comparing with the mass spectra and the generated by the equipment library. Confirmation of the compounds was also performed by comparing the linear programmed temperature retention indexes (LTPRI), obtained experimentally, with those reported in the literature by the National Institute of Standards and Technology (NIST) (NIST-MS Search 2.0). For this, a mixture of linear alkanes (C_7-C_{33}) was injected and the calculations used the Van den Dool and Kratz[32] equation, whose values are calculated automatically by the GC-MS system software.

Results and Discussion

Extraction of vegetable oil from industrial spent coffee grounds

The process of extracting the vegetable oil from the SCG aimed to reduce the glycerides, favoring the quality of the bio-oil obtained after pyrolysis. The presence of glycerides implies in the generation of fatty acids after the pyrolysis, which can increase the acidity and corrosivity of the bio-oil, for energetic purposes.[33] The yields of the extraction are shown in Table 1.

Table 1. Mass yield of the Soxhlet extraction of the biomass (n = 3)

Experiment	Mass yield / %	
	Oil	Solid residue
1	5.14	94.86
2	5.20	94.80
3	5.26	94.74
Average / %	5.20	94.80
Standard deviation / %	0.05	0.05

The mass average yield value of the oil presented in Table 1 is lower than that found by some authors.[7,23] This difference can be due to the origin of the biomass. In the present work the SGC comes directly from the industrial roasting process, while the biomass used in the mentioned works comes from restaurants or domestic households.

Characterization of the solid residue from the Soxhlet extraction

The thermogravimetric analysis of the biomass provides relevant information in order to estimate the kinetic parameters of pyrolysis. Figure 2 shows the thermogram resulting from the thermogravimetric analysis of the sample after the extraction of vegetable oil.

In Figure 2 it is possible to observe the three main stages of mass loss. The first stage, which can be observed at temperatures around 100 °C, can be attributed to the loss of water absorbed and corresponded to about 1%. This value is below that reported by Bispo *et al.*,[16] which also used SCG, but originated from restaurants. Thus, this behavior can be explained due to the origin of the sample of this work (industrial process).

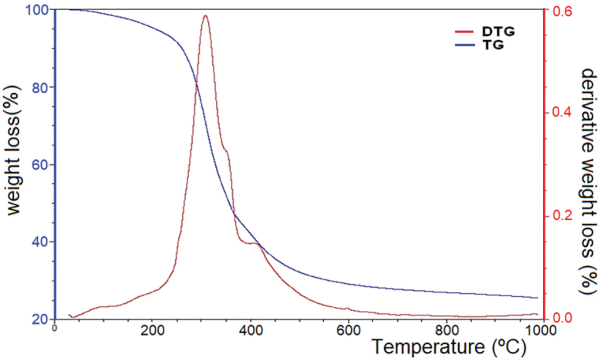

Figure 2. Thermogravimetric analysis of the biomass. Experimental conditions were described in the Experimental section.

The second stage, between 100 and 600 °C, represents the most evident mass loss of the sample, about 70%. In this stage the hemicellulose and cellulose decomposition occurs, releasing a large variety of volatiles. As the thermal decomposition of hemicellulose occurs at a lower temperature, the end of the first peak of this stage is related to the end of the decomposition stage, which occurs at 365 °C and represents about 51% by weight of the mass loss of the sample. Cellulose, with higher decomposition temperatures, is decomposed in the second peak formed at this stage, with a temperature of approximately 400 °C, representing 19% of mass loss. The lignin structure, which decomposes over a wide temperature range (280-550 °C), showed no evident mass loss, indicating a possible contribution to the decomposition peaks of the other two structures (hemicellulose and cellulose) and also for the final solids mass, as already observed by Kelkar *et al.*[21]

The third stage, which occurred at temperatures above 600 °C and at a very low rate of mass loss, represents the formation of the carbonaceous solid. As the objective of this work is the higher yield of the liquid product, pyrolysis

can be suggested to be carried out at temperatures lower than 600 °C, confirming the results of other studies.[2,11,21] In addition, the high content of volatile and semi-volatile compounds indicates that the biomass is a potential source of organic compounds generated through a thermochemical process, such as pyrolysis.

Figure 3 shows the FTIR analyses of the biomass, the solid residue from the Soxhlet extraction and the biochar after the pyrolysis.

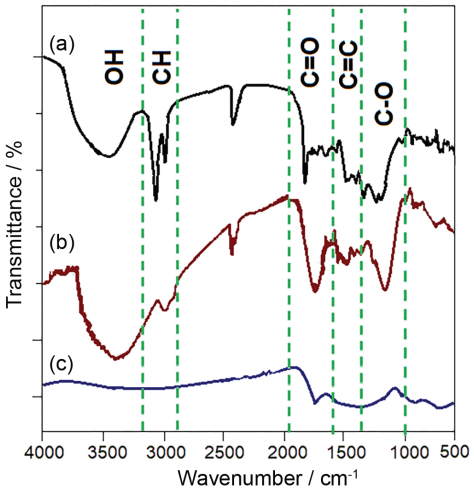

Figure 3. Infrared spectrum of the biomass and the solid residues: (a) original biomass; (b) slid residue after extraction of glycerides and (c) biochar from the pyrolysis. Experimental conditions were described in the Experimental section.

It is possible to observe the bands in the region of 3200-3500 cm^{-1} that correspond to the stretching vibrations of OH or NH functional groups, carboxylic acids, amines, amides, and alcohols. The two narrow bands in the region of 2800-2975 cm^{-1} represented the highest intensity vibrations and are attributed to the methyl and methylene groups. The vibrational stretch of the C=O bond, characteristic of carbonyls of lipids, esters and carboxylic acids can be observed in the range of 1700-1750 cm^{-1}. The region between around 1500 cm^{-1} corresponds to C=C, while region between 1000 and 1100 cm^{-1} corresponds to the C–O and C–C–O bonds and has been attributed to the structure of cellulose, hemicellulose and lignin, according to Lazzari *et al.*[28] On the other hand, Figure 3c shows the FTIR spectrum for biochar and it is possible to observe the absence of all these signals indicating the majority presence of mineral materials or coke, concluding that the pyrolysis was efficient. This spectrum and the representations of each band corroborate with the results found by other authors who analyzed the coffee grounds by FTIR.[2,9,22]

Chromatographic profile of extracted vegetable oil

Figure 4 shows the chromatogram of the derivatized oil (methyl esters). It exhibits good resolution between the peaks, although the retention times of the identified compounds were very close. The chromatogram shows that the major peaks correspond to the methyl palmitate and methyl linoleate esters. Similar results were found by Kondamudi *et al.*[34] and Burton *et al.*[35]

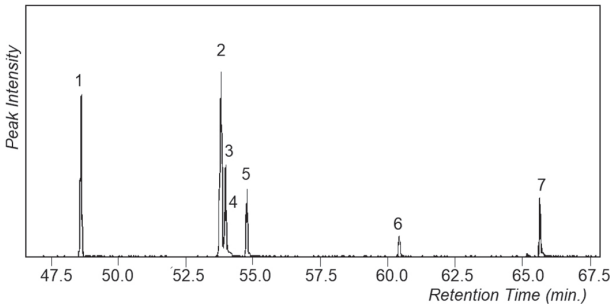

Figure 4. Total ion chromatogram (GC-MS SCAN mode) of the oil extracted from biomass. Peak identifications are shown in Table 2. Chromatographic conditions were described in the Experimental section.

Identification was confirmed through LPTRI, and Table 2 lists the chromatographic parameters (retention time and percentage area) in addition to experimental and theoretical retention indexes (LPTRI) . Relative areas

Table 2. Identification of fatty acid methyl esters (FAME) in the oil extracted from the spent coffee ground

Peak	Identified compunds	Formula	t_R / min	Area / %	LPTRI[a]		
					Experimental	NIST[b]	ΔRI[c]
1	methyl palmitate	$C_{17}H_{34}O_2$	48.63	27.6	1926	1926	0
2	methyl linoleate	$C_{19}H_{34}O_2$	53.83	35.3	2094	2094	0
3	methyl oleate	$C_{19}H_{36}O_2$	53.98	13.9	2099	2098	1
4	methyl linoleate	$C_{19}H_{32}O_2$	54.13	0.8	2104	2105	–1
5	methyl stearate	$C_{19}H_{38}O_2$	54.78	10.0	2126	2128	–2
6	methyl arachidate	$C_{21}H_{42}O_2$	60.43	3.1	2327	2329	–2
7	methyl behenoate	$C_{23}H_{46}O_2$	65.68	9.3	2529	2531	–2

[a]LPTRI: linear programmed temperature retention indexes; [b]NIST: National National Institute of Standards and Technology; [c]$\Delta RI = LPTRI_{experimental} - LPTRI_{NIST}$.

were used as the semi-quantitative determination of the identified esters.

As can be seen from Table 2, all of the methyl esters identified (palmitate, linoleate, oleate, linolenate, stearate, arachidate and behenate) corroborate with those found in other studies[23,36,37] which can be compared to those found in other oil seeds, demonstrating the potential for using the SCG oil for processing into biodiesel.[38,39]

Pyrolysis

Table 3 shows the mass yields (m/m) of the pyrolysis of the SCG. The procedure was performed in triplicate and the standard deviation was calculated.

Table 3. Mass yield of the pyrolysis of the biomass (n = 3)

Experiment	Liquid / %			Solid / %	Gases and losses
	CBO[a]	AP[b]	OP[c]	Biochar / %	
1	29.53	22.87	6.67	25.78	44.69
2	27.74	22.49	5.25	25.83	46.43
3	31.22	24.89	6.33	23.68	45.1
Average	29.5	23.41	6.08	25.1	45.4
STD[d] / %	5.9	5.52	12.13	4.89	2.01

[a]CBO: crude bio-oil (all the liquid phases); [b]AP: aqueous phase; [c]OP: organic phase (bio-oil); [d]STD: standard deviation.

Through these results, it can be seen that the values of biochar are consistent with the literature, ranging from 20-25% for similar experimental conditions.[19,22,24] However, the average yield of the liquid fraction (bio-oil + water) of approximately 30% was in the lower limit of the values found by other authors ranging from 30-55%.[16,20,21] One of the possible reasons for this low value may be related to losses in the condensation system and coke generation, since the literature reports gas yields of 20-30%,[21,23] far below those found in this work.

These losses are related to the sum of the process gases (CO, CO_2 and light hydrocarbons C_1-C_4) and also to the coke content formed. It was not possible to obtain these yields alone due to the experimental limitations to the quantification, since the coke is strongly adhered to the internal walls of the reactor, making difficult its quantitative withdrawal.

Another plausible justification for the low liquid yield of the process may be linked to pyrolysis having been carried out with the biomass after the extraction of the lipids, which generates a much smaller amount of organic fraction, but of superior quality, when compared to pyrolysis of the biomass *in natura*.[23]

Chromatographic profile of the bio-oil

Figure 5 shows the main results of the chromatographic analysis of the bio-oil. In Figure 5a it is shown the total ion chromatogram of the bio-oil obtained in the pyrolysis of the SCG; in Figure 5b it is shown the distribution of the compounds identified according to their chemical class, considering the number of peaks and relative area and in Figure 5c, a comparison between the major compounds found in the bio-oil (area% > 1.0%). Table S1 of the

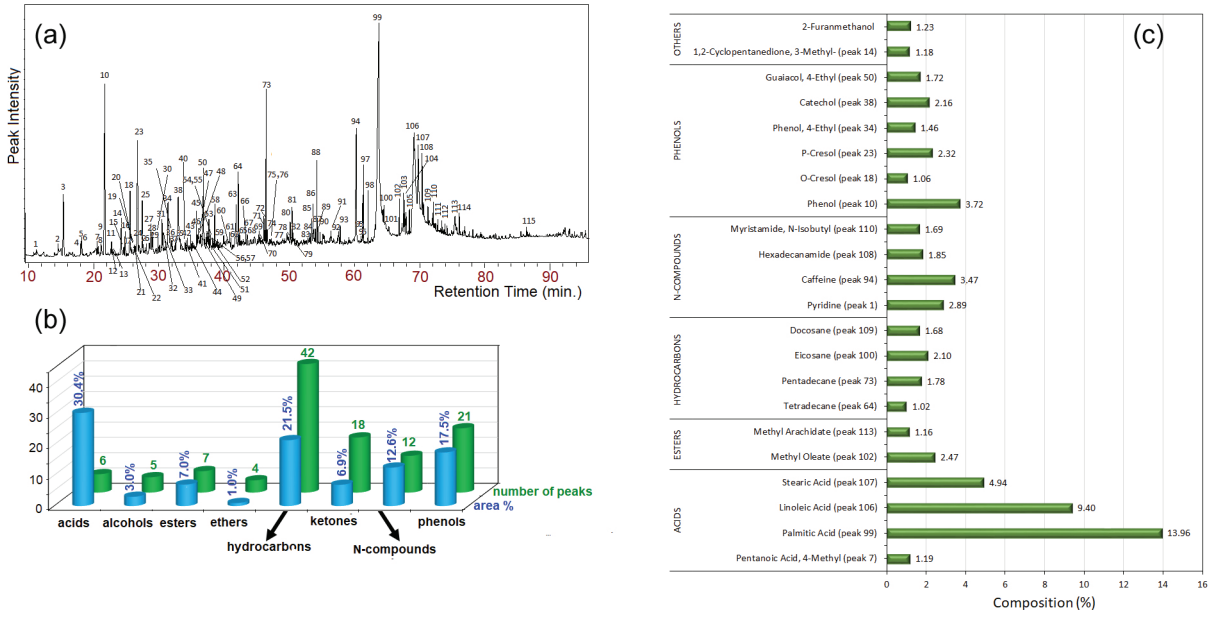

Figure 5. Chromatographic analysis of bio-oil. (a) Total ion chromatogram (GC-MS-SCAN mode) of the bio-oil from the pyrolysis of the biomass. Peak identifications are shown in Table S1 of Supplementary Information section; (b) class distribution of the identified compounds in the bio-oil, using area% and number of peaks; (c) major compounds found in the bio-oil (area% > 1.0%). Chromatographic conditions are described in the Experimental section.

Supplementary Information section shows the complete list of the compounds identified in the sample, classified according to the chemical classes.

One hundred and fifteen (115) peaks were identified, of which 109 were confirmed by the retention index (LPTRI). Despite the high number of compounds found, it was not possible to identify several peaks due to co-elutions of compounds. These co-elutions generate a mass spectrum formed by the fragmentation of all co-eluted compounds, making it difficult to identify.

It can be seen from Figure 5 that despite the previous extraction of the lipids present in the biomass, the major class of compounds in the bio-oil is still that of the acids, even though it is represented by a lower number of peaks. This is due to the high presence of palmitic, linoleic and stearic acids, the three compounds with the highest concentration in the sample, representing 13.96, 9.4 and 4.94% in area, respectively. The presence of these compounds corroborates the results of Yang *et al.,*[24] and is considered a disadvantage for an application as biofuel due to the bio-oil becoming viscous and corrosive. This fact indicates that the initial extraction by Soxhlet, in spite of being considered exhaustive, was in fact not sufficient for the total removal of these compounds. Another consideration to be made is that the glycerides, present in the coffee grounds, were already partially decomposed to generate free fatty acids which would not be extracted by Soxhlet. The process of roasting and extraction of soluble coffee could explain this previous decomposition.

In addition to acids, relatively high levels of hydrocarbons have been found, with special emphasis to tetradecane and pentadecane, also reported by Kelkar *et al.*[21] and Chen *et al.*[11] Those compounds are of great interest to the petrochemical industry. Besides being able to be applied as biofuels, they can be used in the production of polymers.[40]

Also important for the production of polymers, the bio-oil presented a large phenolic composition, with emphasis on phenol (3.72%), *p*-cresol (2.32%) and catechol (2.16%), which were also found by Li *et al.*[22] in high proportions (area > 1%). However, these compounds plus ketones and aldehydes characterize bio-oil with a high content of oxygenates, reducing their quality for energy purposes.[20,24]

Furthermore, high concentration of N-compounds, including caffeine, pyridine, indole, amides and amines was found. Caffeine is cited in several studies[11,20,24] as one of the major compounds found, together with pyridine that was also found as one of the main compounds by Li *et al.*[22] and Bok *et al.*[19]

The amount of nitrogenated compounds is higher than that normally found in bio-oil from other biomasses[23] and is undesired for application as biofuel, since their combustion releases polluting gases into the atmosphere.[41] On the other hand, nitrogenous compounds have great importance in the pharmaceutical and agrochemical industry.[13,42-47]

Conclusions

The present work had the objective of producing and characterizing the vegetable oil and pyrolitic bio-oil from the SCG. The yield and composition of the vegetable oil indicated that it can be used as biodiesel sources, mainly because it is an undesirable industrial residue with no other application. Its chromatographic profile presented mainly fatty acids in the range of 16 to 20 carbon atoms, being able to be compared to other oilseeds such as soy, corn and sunflower, showing that SCG can be reused in this context.

It was observed that the mass yield of the bio-oil was at the lower limit of the results reported in the literature, which may be associated with high losses in the system and the extraction of part of the lipids present in the biomass, which decrease the liquid content formed at the end of the process. Its chromatographic analysis indicated the majority presence of acid and other oxygenated compounds, even after lipid extraction.

The presence of oxygenated compounds is considered a disadvantage for applying the bio-oil as biofuel. Similarly, the high concentration of nitrogen compounds is also undesirable, as it would be responsible for the generation of polluting gases. Nevertheless, the phenolic and nitrogenous composition of the bio-oil can potentiate the use of this bio-oil as a source of inputs for the pharmaceutical, agrochemical and fine chemical industries.

As suggestion for future work, it is recommended to separate the compounds of interest from the above-mentioned industries and the subsequent upgrading for use as biofuel.

Supplementary Information

Supplementary information is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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