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Chromatographic characterization of pyroligneous liquid obtained from carbonization of peach stone

The peach stone is considered an agroindustrial residue originating from the industrial process of peach in halves in syrup. It does not have an adequate destination, its final disposal is incorrect and may cause contamination in the environmental compartments. In this way, the burning of this raw material as biomass enables its reuse, besides adding value to the residue. Among the processes used for the application of this residue is the carbonization process, which allows to obtain co-products with higher added value, such as pyroligneous liquid, which represents a fraction of organic compounds condensed from the smoke emitted during carbonization. The quality of the liquid depends on the process conditions and the biomass used. Therefore, the objective of this study was to characterize the sample of pyrolignous liquid obtained from the carbonization of the peach stone, on an industrial scale, qualitative and semi quantitative. Preliminary characterization (pH, conductivity, color, density and contents of tar, organic matter and acidity) and a chemical characterization by gas chromatography coupled to mass spectrometry (GC-MS) were performed. The liquid presented satisfactory results for the physico-chemical evaluations. Regarding the qualitative determination, it was possible to identify 49 compounds. Highlighting the phenols, with 44.90% of the number of compounds, mainly methoxyphenols. These are compounds with significant added value and industrial importance, indicating their use as raw material in the production of polymer resins, among other purposes.

Keywords: Biomass; Carbonization; Agroindustrial waste; Chromatography.

Caracterização cromatográfica do líquido pirolenhoso obtido da carbonização do caroço de pêssego

A pedra de pêssego é considerada um resíduo agroindustrial originário do processo industrial de pêssego em metades em calda. Não possui um destino adequado, seu descarte final é incorreto e pode causar contaminação nos compartimentos ambientais. Dessa forma, a queima dessa matéria-prima como biomassa possibilita sua reutilização, além de agregar valor ao resíduo. Entre os processos utilizados para a aplicação desse resíduo está o processo de carbonização, que permite obter co-produtos com maior valor agregado, como o líquido pirolímero, que representa uma fração dos compostos orgânicos condensados pela fumaça emitida durante a carbonização. A qualidade do líquido depende das condições do processo e da biomassa utilizada. Portanto, o objetivo deste estudo foi caracterizar a amostra de líquido pirolímero obtido a partir da carbonização da pedra de pêssego, em escala industrial, qualitativa e semiquantitativa. Foram realizadas caracterização preliminar (pH, condutividade, cor, densidade e conteúdo de alcatrão, matéria orgânica e acidez) e caracterização química por cromatografia em fase gasosa acoplada à espectrometria de massa (GC-MS). O líquido apresentou resultados satisfatórios para as avaliações físico-químicas. Quanto à determinação qualitativa, foi possível identificar 49 compostos. Destacando os fenóis, com 44,90% do número de compostos, principalmente metoxifenóis. São compostos com significativo valor agregado e importância industrial, indicando seu uso como matéria-prima na produção de resinas poliméricas, entre outros fins.

Palavras-chave: Biomassa; Carbonização; Resíduos agroindustriais; Cromatografia.

Topic: **Desenvolvimento, Sustentabilidade e Meio Ambiente**

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INTRODUCTION

The amount of carbon gas emitted into the atmosphere is directly influenced directly by the of fossil fuels, consumption growth, industrial activities and methane gas production from the decomposition of the solid residues (DIAS, 2015). Among these activities, the energy generation from non-renewable sources has been the main cause of emission of greenhouse gases, elevating the risks of global warming. Starting from this fact, the search for alternative renewable and cleaner energy sources has been focus of several studies (SENA et al., 2014).

In this scenario, the biomass used as source of energy becomes a viable alternative for the substitution of the fossil fuels. The biomass is the biodegradable fraction of products or residues coming from the agriculture, forestry, industry or residences (DIMAKIS et al., 2011). Which contains energy stored in the form of carbohydrates that is released and used for generation of heat, electricity and production of liquid and gaseous fuels (FERREIRA et al., 2016).

Residues of the agribusiness have been widely studied in order to obtain co-products with higher added value, as the pyroligneous liquid, coal and gas (KOPP et al., 2015; HEYLMANN et al., 2015). In the southern area of Rio Grande do Sul, the woody endocarp (pit) of the fruit of *Prunus persica* (peach) (Fig. 1) constitutes an agroindustrial residue generated in large scale: about 4.048 tons a year of pit.

Fig 1: (a) Representation of the structure of the fruit *Prunus persica*; (b) The whole fruit; (c) Structure of the fruit in nature.

However, the core (peach stone) is not used industrially and has been discarded improperly, being exposed to the environment and suffering slow degradation, which can provoke contamination of the soil and the water resources. Considering the environmental impacts and the abundance of this biomass, the woody endocarp has been used in the generation of charcoal (HEYLMANN et al., 2015). In this case, the main chemical process used to convert biomass into a more useful energy form is carbonization. According to Bridgwater (2006) and Bae et al. (2011), in this technique, yields and quality are influenced by the process operating conditions, with degradation of organic constituents forming products in the gaseous, solid and liquid states.

According to SENA et al. (2014) approximately 30% volume of the burnt biomass is converted to coal with the remainder emitted into the atmosphere, aggravating the concentration of pollutant gases. The almost 70% residual obtained in the process of carbonization of biomass consists of a non-condensable (gases) and a condensable part, from which the pyroligneous liquid originates (TORRES et al., 2014). This is composed of the organic acid fraction, aqueous fraction and tar (MORVOVÁ et al., 2003; VIEIRA et al., 2015). The proportion of co-products generated varies according to the temperature, the type of process, the type of biomass and the equipment used. However, the pyroligneous liquid usually represents about 35% of the final product, but its economic potential has not been studied very well (SENA et al., 2014).

The use of this by-product causes a significant reduction of gaseous emissions from the carbonization technique and it has been becoming attractive as a source of chemical compounds and generation of new environmental impact reducing products. Aiming at the definition of different uses for products obtained in the carbonization process, such as: fuels; aromas; binders and resins; with emphasis on fertilizer production; and the importance of a quality liquid, it is necessary to know the characteristics of the pyroligneous liquid (GAJIĆ et al., 2012).

Chemically, the pyroligneous liquid is formed by several compounds, among them: ketones; esters; aldehydes; acids; methanol; soluble and insoluble tar; phenolic chains and water (CAMPOS, 2007; RODRIGUES et al., 2016). These compounds are derived from the depolymerization and fragmentation reactions of the three main chemical constituents of the biomass: cellulose, lignin and hemicellulose, being constituted by different branches and sizes (ALMEIDA et al., 2015; EICHLER et al., 2015). In this context, the objective of this work was to qualitatively and quantitatively characterize the chemical compounds that make up the pyroligneous liquid obtained from the industrial scale carbonization of the peach stone.

METHODOLOGY

Materials and reagents

The dichloromethane (DCM), anhydrous sodium sulfate and sodium hydroxide reagents were of analytical grade. The standards of oleic acid, benzofuran, cresols (2-methylphenol, 3-methylphenol and 4-methylphenol), guaiacol (2-methoxyphenol), phenol, 2-ethylphenol, 3-ethylphenol, 4-ethylphenol, 2-methoxyvinylphenol, vanillin and the N-methyl-N-trimethylsilyltrifluoracetamide derivative (MSTFA), were all purchased from Sigma Aldrich.

Raw material

The biomass used was the *Prunus persica* fruit core (peach stone) of different cultivars used in the production of canned peaches by industries in the region. This was provided by two canneries located in the city of Pelotas, in the state of Rio Grande do Sul, Brazil. The cores were first separated from impurities, stored in a waterproofed and covered place, and used in the carbonization process without previous grinding.

Carbonization/generation of pyroligneous liquid

The furnace used for the generation of charcoal has the capacity to burn 100 tons of biomass, working in batch and its structure is represented in accordance with Fig. 2 (a). The heat flow occurred in the upward direction and from the outer layer to the inner layer in the radial direction, with the help of pipes that allow the air to enter, Fig. 2 (b). The carbonization process was carried out on an industrial scale using the biomass without previous drying. The oven was fed by a rotary conveyor. The residence time in the kiln was about 20 hours, while the average carbonization temperature was 500°C ± 20%.

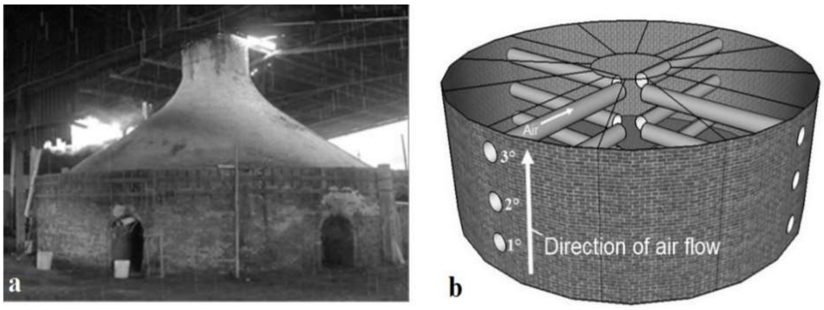

Fig. 2: (a) Kiln where carbonization occurs; (b) Internal representation of the carbonization furnace with the respective in lets and direction of the air flow.

The pyroligneous liquid was collected in 12 distinct points, which composes the condenser system and was collected in 1000 L capacity decantation tanks. The obtained liquid remained at rest for six months in order to separate a high molecular weight organic phase (tar) from the liquid fraction that constitutes the pyroligneous extract.

Preliminary characterization

For the preliminary characterization of the pyroligneous liquid the following parameters were evaluated: potential of hydrogen (Marconi pH meter MA 522/P); conductance (Conductivity meter Instrutherm CD 830); density (densimeter); color (visually); content of organic matter, through liquid-liquid extraction with DCM and gravimetric analysis (APHA, 2008); the titratable acidity (% acetic acid) and tar content followed the methodology described by the Association of Producers of Natural Agriculture (APAN, 2018).

Optimization of sample preparation for chromatography

To optimize the extraction of organic fraction, 10 g of the pyroligneous liquid were extracted with 10 mL of distilled dichloromethane, for three consecutive times, totaling 30 mL of dichloromethane. Each 10 mL extract was percolated into columns with anhydrous sodium sulfate in order to remove the remaining aqueous fraction. The volume of each portion was separately reduced in a rotary evaporator and the final organic fraction had its volume corrected to 1 mL with distilled dichloromethane. Then, the extracts, without derivatization, were analyzed by gas chromatography coupled to mass spectrometry (GC-MS), injected in splitless mode.

Derivatization of the sample

The extracts were derivatized according to Orata (2015), with modifications, where 100 µL of the organic fraction (diluted to 1 mL in DCM) was transferred to a 1 mL vial. Next, 20 µL of the MSTFA derivatizing agent was added by shaking carefully and keeping in a sand bath at 80 °C for thirty minutes. Then, when the sample reached the room temperature, its volume was corrected to 1mL with distilled dichloromethane.

Recovery of samples

In order to evaluate the recovery of the optimized liquid-liquid extraction, the procedure was repeated under the same conditions, however, the samples were fortified with 50 µL of the standards vanillin, guaiacol, oleic acid, cresols and phenol, with a standard stock solution of 100 g L^{-1} in dichloromethane and bringing together all extracts from the three steps. At the end of the procedure, the concentration of the added standards corresponded to 500 mg L^{-1}. According to the following equation, the recoveries were determined by discounting the quantities of the analytes present in the sample without fortification of the fortified samples: (analyte concentration in the fortified sample - analyte concentration in the non-fortified sample/500) x 100.

Chromatographic analysis

The derivatized extract was analyzed on GC/MS-Shimadzu QP2010 Ultra using an RTX-5MS (30 m x 0.25 mm x 0.25 µm) column with the helium entrainment gas. 1 µl of the sample was injected in split mode (1:20), with injector temperature of 280 °C. The following temperature program was used: initial temperature of 60 °C (10 min), at a rate of 5 °C min^{-1} to 200 °C, then the rate was increased to 10 °C min^{-1} to 300 °C where it remained for 12 minutes.

The mass spectrometer was operated in scan mode with the mass-to-charge ratio between 43-500 m/z with the total cycle time of 0.3 s. The temperature of the ion source was 200 °C, and the electron ionization potential at 70 eV. The GC/MS interface was maintained at 280 °C. Identification of the extracted organic fraction compounds was accomplished by comparing the mass spectra of the analytes found with those of the library (NIST/EPA/NIH - Mass Spectral library) of the equipment and by coincidence of the retention times with the standards. Only the peaks that showed similarity above 80% and area greater than 0.1% were considered.

For the quantification of the analytes, the calibration curves were constructed using the concentration range between 50 and 500 mg L^{-1}. The 100 mg L^{-1} standard was analyzed eleven times to determine the accuracy of the method, while the mean value was used to evaluate the relative error. The limit of detection (LoD) was calculated using the sum of the mean of the blank signal plus three times its standard deviation, while the limit of quantification (LoQ) was obtained by adding the mean of the blank signal plus ten times its deviation standard, being considered 100% recovery and 10 g of sample (IUPAC, 1997). All procedures were performed in triplicate and accompanied by blank solutions.

To evaluate the accuracy of the method developed in this experiment RSD was estimated through five injections of the standard of phenols at concentrations of 100mg.L-1 for the derivatized standards (RIBANI et al., 2004; INMETRO, 2007). The accuracy of the method was estimated by the relative error through five injections of the standard mixture of phenols at concentrations of 100 mg L^{-1} for the derivatized standards (INMETRO, 2007).

RESULTS AND DISCUSSION

Table 1 presents the results for the preliminary characterization of the pyroligneous liquid of this study, as well as the values specified for pyroligneous extracts of wood or bamboo marketed under the guidance of the APAN (2018).

Table 1: Physico-chemical characteristics of the pyroligneous liquid obtained from the peach stone and values recommended by APAN for extracts of wood or bamboo.

CHARACTERISTIC	VALUES OBTAINED	RECOMMENDED VALUES
pH	2.89 ± 0.11	3.50 ± 1.20
Condutance (µS cm^{-1})	1190.67 ± 2.52	> 3000.00
Density (kg m^{-3})	1.01	1.002 – 1.010
Color	Light yellow	Light yellow to red chocolate
Acidity (%acetic acid)	2.98 ± 0.07	2.90 – 6.00
Tar (%)	5.47 ± 0.34	----------

The values found for density and acidity are in agreement with the values stipulated by the APAN (2018). However, the conductivity indicates low presence of dissociated salts in the sample in the form of ions or a more diluted extract (ABRATES, 2016). The pH of 2.89 ± 0.11 was below the value recommended by the APAN (2018), but agrees with Campos (2007), which cites the pH range around 2.3 to 3.0. The sample had a characteristic smoky odor, agreeing with Bridgwater (2003) and Campos (2007).

Fig. 3 shows the chromatograms for the three liquid-liquid extraction steps with dichloromethane. The reduction of the intensity and number of peaks are observed when comparing the first, second and third extraction batch indicating that the optimized procedure was sufficient to obtain the exhaustion of the organic fraction of the sample.

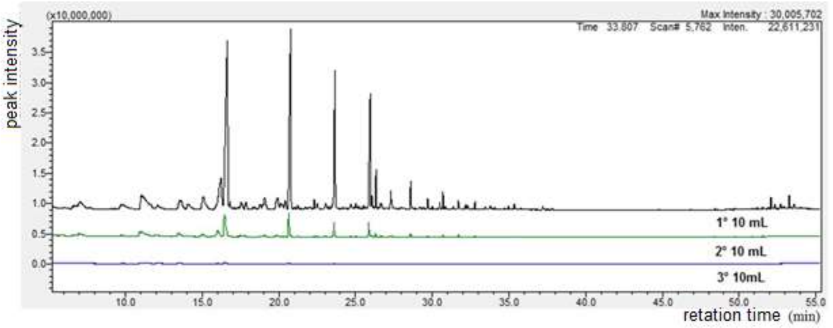

Fig 3: Chromatograms for the three sequential liquid-liquid extractions with DCM to non-derivatized sample.

After the optimization of the extraction process, it was possible to determine the organic matter content through the total mass of the extracts after the evaporation of the DCM, which was 1.81% ± 0.09. The literature reports average levels of the 10% of organic phase in the pyroligneous extract (ALVES et al., 2007). Therefore, the organic matter content in the sample studied is below the expected value, which again suggests that the extract is diluted, a result that agrees with the low conductivity and acidity. These results can be justified by the inefficient condensation system resulting in the loss of organic compounds to the atmosphere. The furnaces in which the pyroligneous liquid (PL) of this study was produced are structured and operated under the conditions for maximum charcoal yield. In this way, the PL appears in the process as a residue and its characterization can lead to a re-sizing of the carbonization process to produce a PL richer in organic compounds. The Table 2 presents the merit figures for the quantitative method of the organic fraction derivatized with MSTFA of PL analyzed by GC/MS.

Table 2: Figures of merit of the quantitative method.

ANALITO	**a**	**b**	**r²**	**RSD**	**Rec.** (±RSD%)	**RE**	**LoQ**	**LoD**
Benzofuran	21740.9	-827451.9	0.996	2.3	--------	7.5	0.7	0.2
Phenol	72328.0	-2652397.6	0.995	5.0	61.7±21.1	6.9	0.2	0.1
2-methylphenol	2357.7	-91751.7	0.993	2.6	74.8±19.4	0.4	6.8	1.6
4-methylphenol	40351.6	-1943595.3	0.988	4.3	111.0±17.8	4.9	0.5	0.1
3-methylphenol	21581.7	-1037318.0	0.988	4.7	113.8±16.9	2.2	0.9	0.2
2-ethylphenol	91633.8	-4981706.3	0.989	4.9	--------	7.9	0.2	0.1
4-ethylphenol	82342.8	-4969581.8	0.989	4.6	--------	9.7	0.3	0.1
2-methoxyphenol	125919.7	-6695826.9	0.989	3.9	71.6±23.5	7.8	0.2	0.1
3-ethylphenol	123997.3	-6920743.7	0.989	3.1	--------	10.0	0.2	0.1
2-methoxyvinylphenol	9789.4	-463304.2	0.989	1.3	--------	6.5	1.7	0.4
Vanillin	75405.8	-4603721.7	0.987	1.8	114.5±12.9	8.4	0.4	0.1
Oleic acid	29908.7	-58266.4	0.996	2.5	113.4±8.9	4.5	0.5	0.2

a. Angular coefficient. B. Linear coefficient. r^2. Coefficient of correlation. RSD. Relative standard deviation in %. Rec (%). Recovery in percentage. RE (%). Relative error. LoD. Detection of limit (mg Kg^{-1}). LoQ. Limit of quantification (mg Kg^{-1}).

It is possible to observe, through the angular coefficient, that the chromatographic method is more sensitive for 2-methoxyphenol and 3-ethylphenol, which is the result of the higher response factor generated in the mass detector by TMS (trimethylsilyl) derivatives. The response factor also contributed to the lower values of detection and the quantification limits. The linear correlation coefficients for all the analytes were close to 0.99, indicating that the method behaves linearly for the concentration range studied. The derivatization process with the generation of trimethylsilyl derivatives promoted a higher interaction between the analytes with the stationary phase of polydimethylsiloxane with 5% of phenyl groups generating more symmetrical peaks, separation of different isomers and increase in the response factor, as observed in Fig 4.

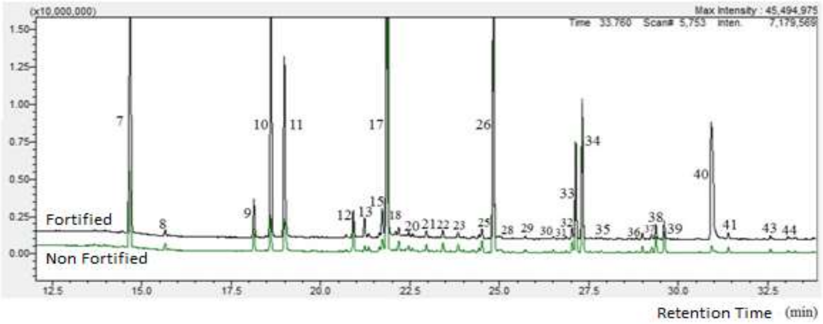

Fig 4: Partial chromatogram obtained by GC/MS analysis for the fortified and non-fortified samples of the organic fraction of the PL.

The recovery values were found to be between 61.7% ± 21.1% for phenol and 114.5 ± 12.9% for Vanillin. According to Pihlström et al. (2008) and Aragão et al. (2009), values above 70% are considered satisfactory. The low recovery presented by the phenol can be associated with its greater polarity, which makes it difficult to extract the aqueous matrix by dichloromethane, and also related to the losses in solvent evaporation stages (DOREA et al., 2017). Figure 4 shows the comparison between the chromatogram of a fortified sample and a non-fortified sample. It also demonstrates the increase in the peaks areas - 7, 9, 10, 11, 17, 40; as identified in Table 3 which corresponds to the fortified compounds. Relative errors were below

10% and the relative standard deviation was less than 5% of an accurate and precise method (OLIVEIRA et al., 2015). Table 3 presents the results for the qualitative and semiquantitative analyzes for the organic fraction of the pyroligneous liquid.

Table 3: Semi quantitative composition and compounds identified in the organic fraction of the PL.

Peak	RT	Name	FORMULA	% AREA	CLASS
1	5.23	2-methylpropan-1-ol	$C_4H_{10}O$	1.02	Alcohol
2	5.62	Butanoic acid	$C_4H_8O_2$	1.24	Acid
3	5.69	Hydroxybutanone	$C_4H_4O_2$	0.16	Ketone
4	7.63	Butenoic acid	$C_4H_7O_2$	0.33	Acid
5	7.70	Pentanic acid	$C_5H_{10}O_2$	0.17	Acid
6	9.59	2,2-dimethylpropanol	$C_5H_{12}O$	1.12	Alcohol
7	14.65	Phenol	C_6H_5OH	6.62	Phenol
8	15.64	2-butoxyethanol	$C_6H_{14}O_2$	0.53	Alcohol
9	18.12	2-methylphenol	C_7H_8O	1.69	Phenol
10	18.59	4-methylphenol	C_7H_8O	2.90	Phenol
11	18.97	3-methylphenol	C_7H_8O	3.29	Phenol
12	20.90	Hexadienoic acid	$C_6H_8O_2$	2.29	Acid
13	21.22	2,3-dimethylphenol	$C_8H_{10}O$	0.36	Phenol
14	21.33	Trihydroxybenzene (isomer 1)	$C_6H_9O_3$	0.30	Phenol
15	21.64	4-ethylphenol	$C_8H_{10}O$	0.30	Phenol
16	21.72	Dimethylphenol (isomer 1)	$C_8H_{10}O$	1.10	Phenol
17	21.84	2-methoxyphenol	$C_6H_5O_2$	23.62	Phenol
18	22.17	3-ethylphenol	$C_8H_{10}O$	0.68	Phenol
19	22.45	Benzoic acid	$C_7H_6O_2$	0.28	Acid
20	22.56	Dimethylphenol (isomer 2)	$C_8H_{10}O$	0.19	Phenol
21	22.95	Dimethylphenol (isomer 3)	$C_8H_{10}O$	0.51	Phenol
22	23.41	Trihydroxybenzene (isomer 2)	$C_6H_9O_3$	0.68	Phenol
23	23.84	Maltol	$C_6H_6O_3$	0.56	Enol
24	24.42	Methoxymethylphenol (isomer 1)	$C_8H_{10}O_2$	0.36	Phenol
25	24.50	Methoxymethylphenol (isomer 2)	$C_8H_{10}O_2$	0.91	Phenol
26	24.82	Methoxymethylphenol (isomer 3)	$C_8H_{10}O_2$	21.66	Phenol
27	24.99	2-propylphenol	$C_9H_{12}O$	0.52	Phenol
28	25.04	2-Methylbenzoic acid	$C_8H_8O_2$	0.22	Acid
29	25.71	Nona-3,6-dien-1-ol	$C_9H_{16}O$	0.22	Alcohol
30	26.50	Dimethoxyphenol (isomer 1)	$C_6H_4O_3$	0.18	Phenol
31	26.86	Vanilina (isomer 1)	$C_8H_8O_3$	0.16	Aldehyde/phenol
32	27.03	4-methyl-benzene-1.2-diol	$C_7H_9O_2$	0.82	Phenol
33	27.13	Vanillin (isomer 2)	$C_8H_8O_3$	7.54	Aldehyde/phenol
34	27.31	Dimethoxyphenol (isomer 2)	$C_6H_4O_3$	10.87	Phenol
35	27.82	Vanillin (isomer 3)	$C_8H_8O_3$	0.14	Aldehyde/phenol
36	28.99	o-hydroxyethylphenol	$C_8H_{10}O_2$	0.45	Phenol
37	29.25	Eugenol	$C_{10}H_{12}O_2$	0.41	Phenol
38	29.37	N.I.	------	1.12	Others
39	29.60	N.I.	------	1.53	Others
40	30.93	Vanillin	$C_8H_8O_3$	0.65	Aldehyde/phenol
41	31.40	3,5-dimethoxy-4-hydroxybenzaldehyde	$C_9H_{10}O_4$	0.35	Aldehyde/phenol
42	31.44	Methyl 3-hydroxy-4-methoxybenzoate	$C_9H_{10}O_4$	0.15	Ester/phenol
43	32.57	2-Hydroxy-3-methylbenzoic acid	$C_8H_8O_3$	0.25	Acid/phenol
44	33.04	4-hydroxy-3-methoxyphenylethanone (apocynin)	$C_9H_{10}O_3$	0.19	Ketone
45	35.62	N.I.	------	0.44	Others
46	35.63	N.I.	------	0.40	Others
47	36.67	N.I.	------	0.12	Others
48	37.03	Methyl 2 (3-hydroxy-4-methoxyphenyl) -2-hydroxyethanoate	$C_{10}H_{12}O_5$	0.12	Ester/phenol
49	37.6	3 (4-hydroxy-3-methoxyphenyl) propane-1-ol	$C_{10}H_{14}O_3$	0.20	Alcohol/phenol

[a]RT (min): Retention time in minutes.

A total of 49 peaks with areas greater than 0.1% were detected. In the organic fraction of the pyroligneous liquid, 44 compounds were identified with the similarity of 80%. Fig. 5 shows the percentage in area and number of compounds of each chemical class constituent of the organic fraction of pyroligneous liquid studied. In the class, other denominates were reunited functions whose compounds presented similarities inferior to 80%.

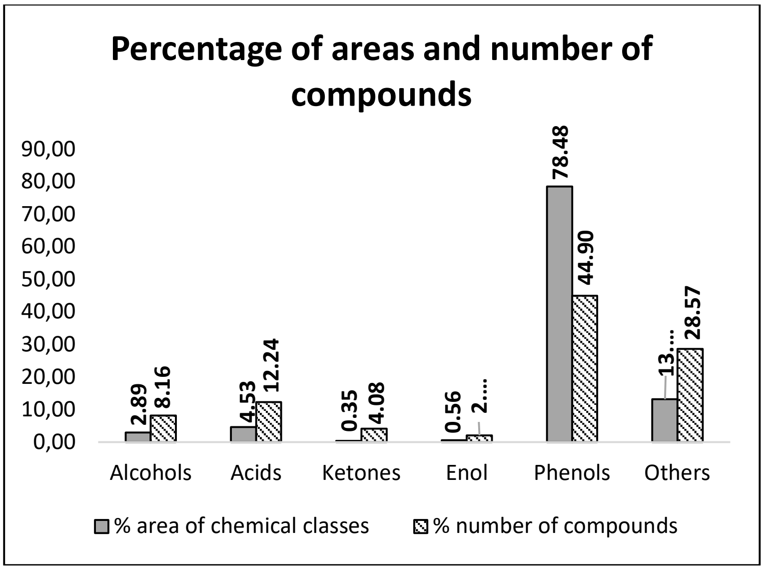

Fig 5: Percentage of areas and number of compounds present in each chemical class identified in PL.

It is found that the phenols are major in both area (approximately 80%) and in number (44.90% of the identified compounds). This fact occurs due to the high content of lignin present in the biomass used (MIGLIORINI et al., 2013; ZHANG et al., 2013; BISPO et al., 2016). According to Souza, et al. (2012), woody materials such as peach stone are rich in lignin and cellulose and when carbonized, they are thermally degraded in ketones, alcohols, furan derivatives and phenolic compounds. Among the phenols identified in this study, two of them stand out: 2-methoxyphenol and methoxymethylphenol (isomer), with 23.62% and 21.66% respectively. According to Migliorini et al. (2013), phenols substituted by methoxy groups originate from lignin. These results agree with those described by Moraes et al. (2012) in the peach stone bio-oil obtained by rapid pyrolysis, Özbay et al. (2008), who performed the bio-oil characterization of the peach pulp using the GC-MS and Migliorini et al. (2013) who found 277 compounds in the bio-oil sample of pyrolysis of the peach stone by GC × GC / TOFMS.

The chemical composition of the extracts obtained depends on the characteristics of the source material, and also on the conditions under which the biomass is exposed. In addition, different biomasses produce bio-oils with different constituents and/or quantities (MA et al., 2013). It should be noted that for this study the pyroligneous liquid was obtained by carbonization, while the studies presented for comparison were obtained by pyrolysis. From the totality of compounds identified in the qualitative analysis, the phenolic compounds that presented the highest percentage of relative area were quantified. The concentrations of the analytes in mg.kg $^{-1}$ in the organic fraction of pyroligneous liquid are shown in Fig 6.

Among the quantified compounds, 2-methoxyphenol with 237.6 mg Kg^{-1} ± 10.3% was the majority, followed by phenol and cresols. Among their chemical properties, the phenols present a great versatility of use as starting material and as intermediates in the production of molecules of greater complexity, as well as in the production of phenolic resins (MIGLIORINI et al., 2013). However, in the concentration ranges detected and considering it to be an aqueous matrix, some studies have proposed its application as a fungicide (SUMANATRAKUL et al., 2015).

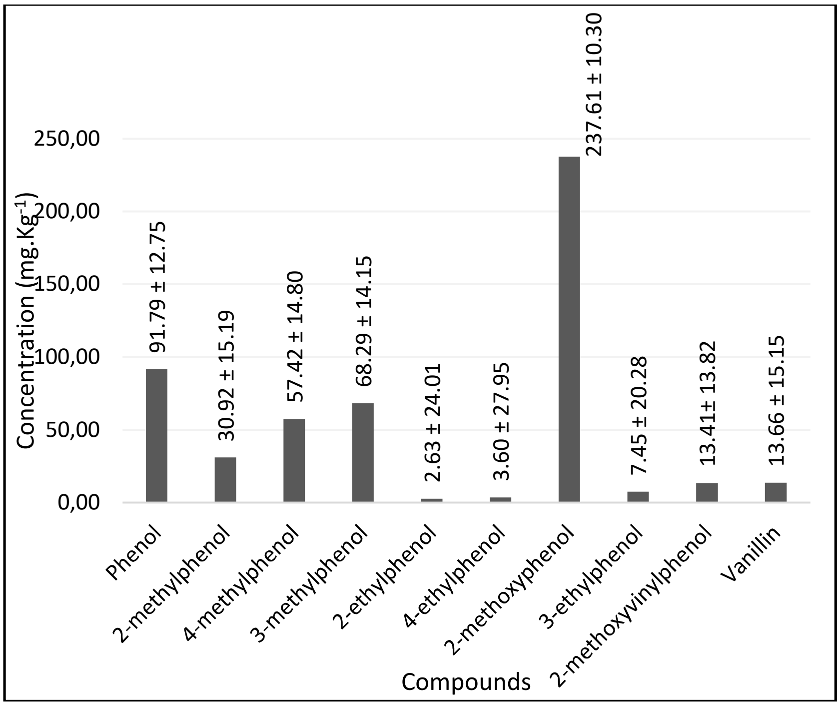

Fig 6: Concentration, in mg Kg^{-1} ± RSD (%) of the main compounds present in the PL sample.

Guaiacol (methoxyphenol) causes darkening in the sample when exposed to air and light and can be used as an indicator for enzymes, expectorant, antiseptic and anesthetic. In addition, hydroxybutanone and maltol, compounds identified in the qualitative analysis are widely used as additives in food production to enhance flavors and in medicinal products (HUANG, 2011).

In the case of the major compound 2-methoxyphenol with 237.61 $mg.Kg^{-1}$, the amount of woody endocarp produced in the year (4,048 tons) and the estimate of the pyroligneous liquid generated (35%) cited by Sena et al. (2014), the average yield of only this compound would be about 336 tons/year. Aiming at the possible industrial applications for this compound and verifying that there is a direct and beneficial influence on the aggregation of the value of the agroindustrial residue, it is verified that the production of the studied co-product has great relevance, when the process used occurs within the expected standards.

However, there are not specific definitions yet or standards for obtaining pyroligneous liquid from peach stone, which specify the constituents, characteristics and benefits of the compounds, to be accepted in the consumer market. For this, it is necessary to implement quality control to ensure the safety and efficiency of this product. However, to apply standards that quantify the components of the PL, it is necessary to evaluate a greater number of samples obtained by different methods and conditions of production and types / quality of the biomass.

CONCLUSIONS

The analysis of the pyroligneous liquid derived from the carbonization allowed us to conclude that this biomass has the potential to obtain chemical compounds of economic interest, such as: phenols, ketones, acids and alcohols. With a predominance of phenols (approximately 80%), it has important applications as raw materials and in the development of commercial products. This justifies its production and use and consequently reducing the environmental impact and adding value to the agroindustrial residue.

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