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Bio-gasoline and Bio-kerosene Production by Fractional Distillation of Pyrolysis Bio-Oil Açaí Seeds

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Abstract

The bio-oil obtained by pyrolysis of Açaí (*Euterpe oleracea* Mart.) seeds at 450 ºC, 1.0 atmosphere, in technical scale, submitted to fractional distillation to produce biofuels-like fractions. The distillation of bio-oil carried out in a laboratory distillation column (Vigreux) of 30 cm. The physical-chemistry properties (density, kinematic viscosity, acid value and refractive index) determined by official methods. The chemical functions present in distillation fractions determined by FT-IR and the chemical composition by GC-MS. The distillation of bio-oil yielded gasoline, light kerosene, and kerosene-like fuel fractions of 16.16, 19.56, and 41.89% (wt.), respectively. All the physical-chemistry properties (density, kinematic viscosity, acid value and refractive index) increase with boiling temperature. The gasoline-like fraction is composed by 64.0% (area.) hydrocarbons and 36.0% (area.) oxygenates, while light kerosene-like fraction by 66.67% (area.) hydrocarbons and 33.33% (area.) oxygenates, and kerosene-like fraction by 19.87% (area.) hydrocarbons and 81.13% (area.) oxygenates.

Keywords: Açaí, Residual Seeds, Pyrolysis, Bio-Oil, Distillation, Bio-gasoline, Bio-kerosene.

1. Introduction

Açaí (*Euterpe oleracea* Mart.) is a native palm of natural occurrence in tropical Central and South America [1]. The palm gives a dark-purple, berry-like fruit, clustered into bunches [2]. The fresh fruits are traditionally processed by crushing and/or extracting the pulp and skin

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with warm water to produce a thick, purple-colored beverage/juice or a paste [3-4]. The fruit is a staple food in rural and urban areas of the Amazon River estuary, particularly in the State Pará (Pará-Brazil), with a great economic importance at both rural livelihoods and regional levels [5]. It has become one of the most important export products of the Amazon River estuary to other parts of Brazil [5], as well as oversees [6].

Of the total 1.228.811 tons/year of fruits produced by the State Pará, between 85% [7] and 83% (wt.) [8], is a residue (Açaí seeds), thus producing between 1.019.913 and 1.044.489 tons/year of a residue. The mechanical processing of Açaí fruits *in nature* produces around 175.7 tons residue/day in off-season crop and 448.0 tons residue/day in the season crop in the metropolitan region of Belém (Pará-Brazil), posing a complex environmental problem of solid waste management [9, 10]. The Açaí fruit is a small dark-purple, berry-like fruit, almost spherical, weighing between 2.6 to 3.0 g [11], with a diameter around 10.0 and 20.0 mm [11], containing a large core seed that occupies almost 85% (vol./vol.) of its volume [3]. Açaí (*Euterpe oleracea* Mart.) fruit has an oily-fiber seed, rich in lignin-cellulose material [12–15].

Pyrolysis makes it possible the use of low quality lignin-cellulosic based material to produce not only liquid bio-oils, but also gaseous fuels, and a carbonaceous rich solid phase, as reported in the literature [16-73], and studies include biomass pyrolysis [23-24, 26, 45, 56-57, 62, 67-68], bio-oil chemical upgrading techniques [26, 45, 50], bio-oils physical-chemical properties [21, 25-26, 28, 34-35, 43, 57, 62-63], as well as separation and/or purification processes to improve bio-oils quality [17-22, 30-33, 36-41, 46-48, 51, 53-54, 59-61, 65-66, 70-73].

The bio-oil produced by pyrolysis is a multicomponent liquid mixture presenting water, carboxylic acids, aldehydes, ketones, alcohols, esters, ethers, aliphatic hydrocarbons, aromatic hydrocarbons, anhydrous-sugars, furans, phenols derivatives, among others chemical functions [16-17, 20, 38, 44, 47-48, 53, 60-61, 73]. In addition, its organic fraction has a wide distribution of polarity, molecular weight [47], as well as differences in thermo-physical and transport properties of chemical compounds, as reported by the simulation of organic liquid compounds [74], posing challenges to the efficient separation and/or purification processes [47, 74].

In the last years, several thermal and physical separation processes were applied to remove oxygenates from biomass-derived bio-oils including molecular distillation [30, 33, 36-39, 71], fractional distillation [17-21, 40-41, 46-48, 53, 59-60, 66, 70, 72-73], liquid-liquid extraction [22, 31, 61], and fractional condensation [51, 54, 65]. In addition, chemical methods such as catalytic upgrading of bio-oils vapors have been applied to improve bio-oils quality [19, 29, 64].

The fractional distillation studies were carried out in micro/bench scale [17, 46-47], laboratory scale [41, 53, 66, 70, 72-73], and pilot scale [21], under atmospheric [17-18, 46-48, 53, 66, 70, 72-73], or under vacuum [18-19, 41, 48, 53]. Açaí (*Euterpe oleracea*, Mart.) seeds are the only fruit specie, whose centesimal and elemental composition is completely different from wood biomass (aspen poplar wood, eucalyptus, maple wood, and softwood bark) [17-19, 21, 53], agriculture residues of cereal grains (corn Stover, rice Rusk) [41, 46-47, 66, 70, 72], jatropha curcas [46], and until horse manure and switch-grass [53]. However, until the moment no systematic study investigated the physicochemical properties (density, kinematic viscosity, refractive index, and acid value) chemical composition of Açaí (*Euterpe oleracea*, Mart.) seeds bio-oil distillation fractions [73].

In this work, fractional distillation of bio-oil obtained by pyrolysis of Açaí seeds at 450 ºC, 1.0 atmosphere, in technical scale, has been investigated systematically using a laboratory-scale column (Vigreux) to produce fuels-like fractions (gasoline, light kerosene, and kerosene), as well as to determine the physical-chemistry properties (density, kinematic viscosity, acid value and refractive index) and chemical composition of distillation fractions.

2. Materials and methods

2.1. Materials, pre-treatment, and characterization of Açai (*Euterpe oleracea*, Mart.) seeds in nature

The seeds of Açaí (*Euterpe oleracea* Mart.) *in nature* obtained in a small store of Açaí commercialization, located in the City of Belém-Pará-Brazil [73]. The seeds were submitted to pre-treatments of drying and grinding as reported elsewhere [73]. The dried and grinded seeds were physical-chemistry characterized for moisture, volatile matter, ash, fixed carbon, lipids, proteins, fibers, and insoluble lignin according to official methods [73, 75, 76].

2.2. Fractional distillation of bio-oil

2.2.1. Distillation: Experimental apparatus and procedures

The fractional distillation of bio-oil was performed by using an experimental apparatus and procedures described elsewhere [73, 77-78]. The aqueous phase presented in the distillation fractions was separated from the organic phase by decantation using a 250 ml glass separator funnel. Afterwards, filtration was applied to remove small solid particles present in the organic phase.

2.3. Physical-chemistry analysis and chemical composition of distillation fractions

2.3.1. Physical-chemistry analysis of distillation fractions

The distillation fractions were (gasoline, light kerosene, and kerosene) physical-chemistry characterized for acid value (AOCS Cd 3d-63), density (ASTM D4052) at 25°C, kinematic viscosity (ASTM D445/D446) at 40°C, and refractive index (AOCS Cc 7-25) [81]. The analysis of chemical functions (carboxylic acids, aliphatic and aromatic hydrocarbons, ketones, phenols, aldehydes, furans, esters, ethers, etc.) present in distillation fractions determined by FT-IR [73, 77].

2.3.2. Chemical composition of distillation fractions

The chemical composition of distillation fractions determined by CG-MS and the equipment and operational procedures described in details elsewhere [73].

3. Results and discussions

3.1. Material balances and yields of fractional distillation

Table 1 summarizes the material balance and yields by fractional distillation of bio-oil, and the distillation fractions and bottoms are illustrated in Figure 1. The yields of fuel-like fractions (gasoline, light kerosene, and kerosene) were 16.16, 19.56, and 41.89% (wt.), respectively, giving a total distillation yield of 77.61% (wt.). The results are according to similar studies for distillation of biomass derived bio-oil in the literature [17-19, 21, 41, 46-48, 53, 66, 70, 72]. The yield of distillation fractions, is higher than those reported in the literature for both atmospheric and vacuum conditions [17-19, 21, 41, 46-48, 53, 66, 70, 72].

Table 1: Material balance and yields by fractional distillation of bio-oil.

Distillation:	**Bio-Oil**	**Gas**	**Raffinate**	**Distillates [g]**					**Yield [wt.%]**				
Vigreux Column	**[g]**	**[g]**	**[g]**	**H_2O**	**G**	**LK**	**K**	**LD**	**H_2O**	**G**	**LK**	**K**	**LD**
(30°C-215°C)	**307.53**	**0**	**69.87**	**0**	**49.48**	**59.91**	**128.27**	**0**	**0**	**16.16**	**19.56**	**41.89**	**0**

G = Gasoline, LK = Light Kerosene, K = Kerosene, LD = Light Diesel.

Zheng and Wei [41] reported by distillation of fast pyrolysis bio-oil at 80°C under vacuum (15 mmHg), a distilled bio-oil yield of 61% (wt.). Zhang *et. al.* [47] reported by atmospheric distillation of fast pyrolysis bio-oil, an accumulated distillate of 51.86% (wt.). Zhang *et. al.* [47] observed that as the distillation temperature reached 240°C, condensation reactions take place, generating water, a behavior not observed during the course of distillation as illustrated in Table 1. Capunitan and Capareda [48] reported for the distillation at atmospheric condition, an organic phase (Distillates) yield of 15.0% (wt.) at 100°C, 4.7% (wt.) between 100°C < T^{Boiling} < 180°C, and 45.3% (wt.) between 180°C < T^{Boiling} < 250°C, while vacuum distillation yielded 10.3% (wt.) of an organic phase at 80°C, 5.9% (wt.) between 80°C < T^{Boiling} < 160°C, and 40.9% (wt.) between 160°C < T^{Boiling} < 230°C. Elkasabi *et. al.* [53] reported by distillation of tail-gas reactive pyrolysis (TGRP) bio-oil, yields ranging from 55 to 65% (wt.).

Figure 1: Distillation fractions [gasoline (yellow), light kerosene (red), and kerosene (red dark)-like boiling range temperature fossil fuels] and bottoms [Raffinate (black solid)] obtained by fractional distillation of bio-oil produced by pyrolysis of Açaí (*Euterpe oleracea,* Mart.) seeds at 450 ºC and 1.0 atmosphere, in pilot scale.

3.2. Physical-chemical properties of distillation fractions

The physical-chemical properties of distillation fractions (gasoline, 80-175°C; light kerosene, 175-200°C; and kerosene-like fraction, 200-215°C) of bio-oil are illustrated in Table 2.

Table 2: Physical-chemical properties of distillation fractions of bio-oil.

Physico-chemical Properties	**450 ° C**			**ANP Nº 65**
	G	**LK**	**K**	
ρ [g/cm^3], 30°C	0.9146	0.9191	0.9816	**0.82-0.85**
I. A [mg KOH/g]	14.94	61.08	64.78	
I. R[-]	1.455	1.479	1.497	
ν [mm²/s], 40°C	1.457	3.106	4.040	**2.0-4.5**

I.A=Acid Value, I.R=Refractive Index.

It can be observed that acidity of distillation fractions increases with boiling temperature. However, the acidity of gasoline-like fraction is much lower than that of raw bio-oil (70.26 mg KOH/g), as described in Table 3. The high acid value of bio-oil is due to the presence of 78.48% (area.) oxygenates, as shown in Table 4. The same behavior was observed for the densities, kinematic viscosities, and refractive indexes of gasoline, light kerosene, and kerosene-like like fractions with increasing boiling temperature. This is probably due to the high concentration of higher-boiling-point compounds in the distillate fractions, such as phenols, cresols (*p*-cresol, *o*-cresol), and furans, as the concentration of those compounds in the distillation fractions increases with increasing boiling temperature as reported elsewhere [66, 70, 72], corroborate in Tables 5, 6, and 7.

The gasoline, light-kerosene, and kerosene-like fuel densities were 0.9146, 09191, and 0.9816 g/mL. The gasoline-like fuel density (fractions (40°C < $T^{Boiling}$ < 175°C), higher, but close to the density of distillation fraction of 0.8733 g/mL ($T^{Boiling}$ < 140°C) for jatropha curcas cake pyrolysis bio-oil reported by Majhi *et. al.* [46]. This is probably due to the high lipids content between 14-18% (wt.) and 10-10.9% (wt.) fiber, thus producing a bio-oil similar to lipid-based pyrolysis organic liquid products [77-78]. The gasoline, light-kerosene, and kerosene-like fuel kinematic viscosities were 1.457, 3.106, and 4.040 mm²/s, lower than the distillation fraction kinematic viscosity of 2.350 mm²/s ($T^{Boiling}$ < 140°C) for jatropha curcas cake pyrolysis bio-oil reported by Majhi *et. al.* [46].

The acid value of gasoline, light-kerosene, and kerosene-like fuel fractions were 14.94, 61.08, and 64.78 mg KOH/g, lower than the distillation fraction acid value of 0.05 mg KOH/g ($T^{Boiling}$ < 140°C) for jatropha curcas cake pyrolysis bio-oil distillation reported by Majhi *et. al.* [46], the organic phases (distillates) acid values of 4.1 (100°C < $T^{Boiling}$), 15.1 (100°C < $T^{Boiling}$ < 180°C), and 7.41 (180°C < $T^{Boiling}$ < 250°C) mg KOH/g, for corn Stover bio-oil atmospheric distillation reported by Capunitan and Capareda [48], the organic phases (distillates) acid values of 3.0 (80°C < $T^{Boiling}$), 13.9 (80°C < $T^{Boiling}$ < 160°C), and 5.0 (160°C < $T^{Boiling}$ < 230°C) mg KOH/g, for corn Stover bio-oil vacuum distillation reported by Capunitan and Capareda [48], the acid values of 13.5 mg KOH/g ($T^{Boiling}$ = 192°C) and 5.3 mg KOH/g ($T^{Boiling}$ = 220°C) of distillation fractions F_3 and F_4 of $TGRP_1$, and the acid value of 11.1 mg KOH/g ($T^{Boiling}$ = 235°C) of distillation fraction F_5 of $TGRP_2$, for tail-gas reactive pyrolysis of horse manure ($TGRP_1$), switch grass ($TGRP_2$), and eucalyptus ($TGRP_3$), reported by Elkasabi *et. al.* [53].

The results reported by Elkasabi *et. al.* [53], show that fractional distillation was not effective to diminish the acid values of TGRP bio-oil with initial high acid values, what does not agree with the results reported by Capunitan and Capareda [48], as well as those presented in Table 2, showing that the acid values of distillation fractions are lower than that of raw bio-oil, proving that distillation was effective.

Table 3: Physical-chemical properties of bio-oil, compared to similar studies reported in the literature [21, 25, 28, 47, 69, 79-80].

Physicochemical Properties	**450 ºC**	**[21]**	**[25]**	**[28]**	**[47]**	**[69]**	**[79]**	**[80]**	**ANP Nº 65**
	Bio-Oil	**Bio-Oil**	**Bio-Oil**	**Bio-Oil**	**Bio-Oil**	**Bio-Oil**	**Bio-Oil**	**Bio-Oil**	
ρ [g/cm^3], 30°C	**1.043**	**1.066**	1.250	1.140	1.190	1.1581	1.200	**1.030**	**0.82-0.85**
I. A [mg KOH/g]	70.26	-	-	-	-	-	-		**-**
I. R [-]	ND	-	-	-	-	-	-		**-**
ν [mm²/s], 40°C, *60°C	68.34	38.0	148.0	13.2	40.0*	5.0-13.0	12.0	-	**2.0-4.5**

I.A = Acid Value; I.R = Refractive Index; ANP: Brazilian National Petroleum Agency, Resolution N° 65 (Specification of Diesel S10); ND = Not Determined.

3.3. FT-IR and GC-MS analyses of bio-oil and distillation fractions

3.3.1. FT-IR spectroscopy of bio-oil and distillation fractions

By the FT-IR analysis of bio-oil and distillation fractions (gasoline: 40-175 °C, light kerosene: 175-200 °C, and kerosene-like fraction: 200-215 °C), summarized in Figure 2, the identification of absorption bands/peaks was performed according to previous studies [28, 48, 59, 73, 77-78, 80, 81]. The FT-IR spectroscopy of bio-oil and distillation fraction identify the presence of hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) and oxygenates (phenols, cresols, carboxylic acids, alcohols, ethers, ketones, and furans).

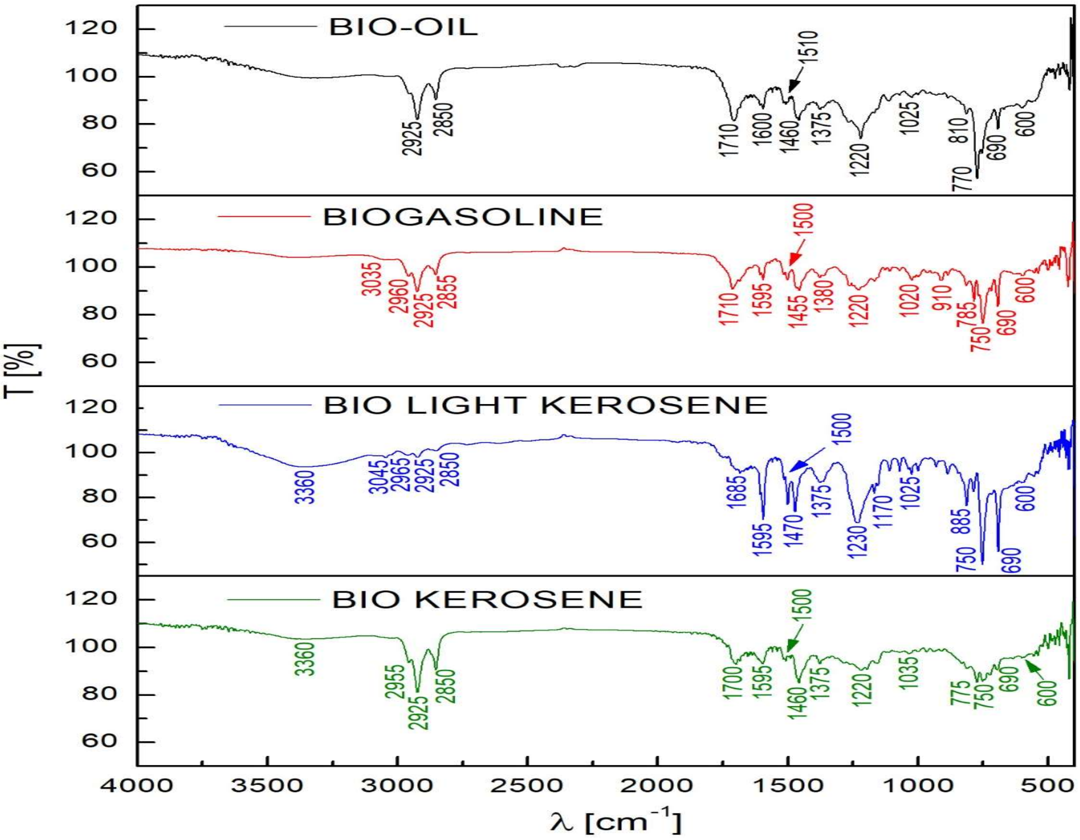

Figure 2: FT-IR of Açaí seeds bio-oil and distillation fractions.

3.3.2. Chemical compositional of bio-oil and distillation fractions by GC-MS

3.3.2.1 Chemical compositional of bio-oil by GC-MS

The chromatogram of bio-oil is shown in Figure 3. The peaks are concentrated between retention times of 8.0 and 22.0 minutes, with the highest one around 12.5 minutes. The GC-MS identified hydrocarbons (alkanes, alkenes, aromatic hydrocarbons, and cycloalkenes) and oxygenates (esters, phenols, cresols, carboxylic acids, ketones, furans, and aldehydes) in bio-oil, being composed of 21.52% (area.) hydrocarbons and 78.48% (area.) oxygenates [73]. The high acidity of bio-oil, described in Table 3, is probably due to the presence of carboxylic acids, ketones, aldehydes, phenols and cresols confer the high acidity of bio-oil.

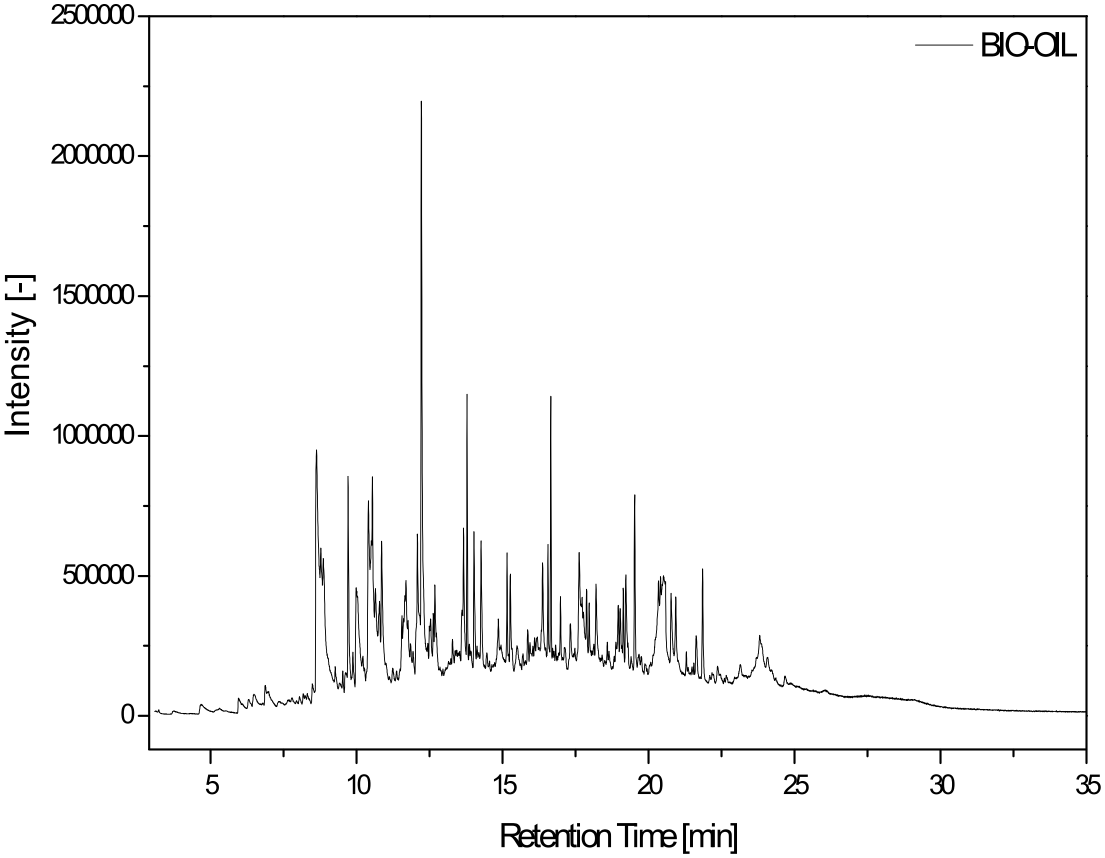

Figure 3: GC-MS of bio-oil.

The composition of bio-oil shows similarity to those reported in the literature [27, 34, 41, 47-48, 53, 61], showing the presence of hydrocarbons, phenols, cresols, furans, carboxylic acids, and esters, among other classes of compounds [73]. The identification of hydrocarbons with carbon chain length between C_{11} and C_{15}, shows the presence of heavy gasoline compounds with C_{11} (C_5-C_{11}), light kerosene-like fractions (C_{11}-C_{12}), and light diesel-like fractions (C_{13}-C_{15}), according to Table 4.

Table 4: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil.

Class of Compounds: Chemical Compounds	RT [min]	CAS	ω_i% (Area)
Alkanes			
Undecane	10.622	1120-21-4	1.124
Tridecane	13.870	629-50-5	2.481
Pentadecane	16.744	629-62-9	2.290
Dodecane, 5,8-diethyl	19.326	24251-86-3	1.626
Σ (Area.%) =			**7.521**
Alkenes			
6-Tridecene, (Z)-	1.626	6508-77-6	2.118
Σ (Area.%) =			**2.118**
Cycloalkenes			
Megastigma-4,6(E), 8 (Z)-trien	13.440	5298-13-5	1.847
Σ (Area.%) =			**1.847**
Aromatic Hydrocarbons			
Naphthalene	12.262	91-20-3	4.399
Naphthalene, 1-methyl	14.046	90-12-0	2.390
1H-Indene, 1-ethylidene	14.296	2471-83-2	3.249
Σ (Area.%) =			**10.038**
Esters			
Undecanoic acid, 10-methyl-, methyl ester	17.049	5129-56-6	1.096
Methyl tetradecanoate	19.620	124-10-7	2.969
Σ (Area.%) =			**4.065**
Carboxylic Acids			
Dodecanoic acid	17.648	334-48-5	4.307
Tetradecanoic acid	20.677	544-63-8	4.216
Σ (Area.%) =			**8.523**
Ketones			
2-Pentanone, 4-hydroxy-4-methyl	5.886	123-42-2	1.878
2-Cyclopenten-1-one, 2,3-dimethyl	9.552	1121-05-7	1.655
Σ (Area.%) =			**3.533**
Phenols			
Phenol	8.469	108-95-2	15.932
Phenol, 2-methoxy	10.446	90-05-1	4.583
Phenol, 2,6-dimethyl	10.805	576-26-1	1.991
Phenol, 2,4-dimethyl	11.469	105-67-9	2.034
Phenol, 2,5-dimethyl	11.502	95-87-4	2.215
Phenol, 3,4-dimethyl	11.821	95-65-8	3.845
Phenol, 4-ethyl-2-methoxy	13.571	2785-89-9	4.567
Σ (Area.%) =			**35.167**
Cresols			
p-Cresol	9.818	108-39-4	6.331
m-Cresol	10.198	106-44-5	11.054
Cresol	12.210	93-51-3	3.141
Σ (Area.%) =			**20.526**
Furans			
Benzofuran, 2-methyl	10.879	4265-26-2	1.879
Furan, 2-(2 furanylmethyl)-5-methyl	11.946	13678-51-8	2.089
Benzofuran, 4,7-dimethyl	12.700	28715-26-6	1.783
Σ (Area.%) =			**5.751**
Aldehyds			
Cinnamaldehyde, β-methyl-	12.654	1196-67-4	0.910
Σ (Area.%) =			**0.910**

3.3.2.2 Chemical compositional of distillation fractions by GC-MS

The chromatogram of bio-oil distillation fractions (gasoline: 40-175°C, light kerosene: 175-200°C, and kerosene-like fraction: 200-215°C) are shown in Figures 4, 5, and 6, respectively. One observes that the spectrum of peaks is moving to the right, showing that distillation was effective to fractionate the bio-oil.

The GC-MS identified in gasoline-like fraction hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) and oxygenates (esters, phenols, alcohols, ketones, furans, and aldehydes). The gasoline-like fraction contains 64.0% (area.) hydrocarbons (13.27% alkenes, 9.41% alkanes, and 41.32% aromatic hydrocarbons) and 36.0% (area.) oxygenates (5.50% esters, 2.61% ketones, 1.35% phenols, 6.05% alcohols, 13.24% furans, and 7.25% aldehydes). The absence of carboxylic acids confers the low acidity of gasoline-like fraction, as summarized in Table 5.

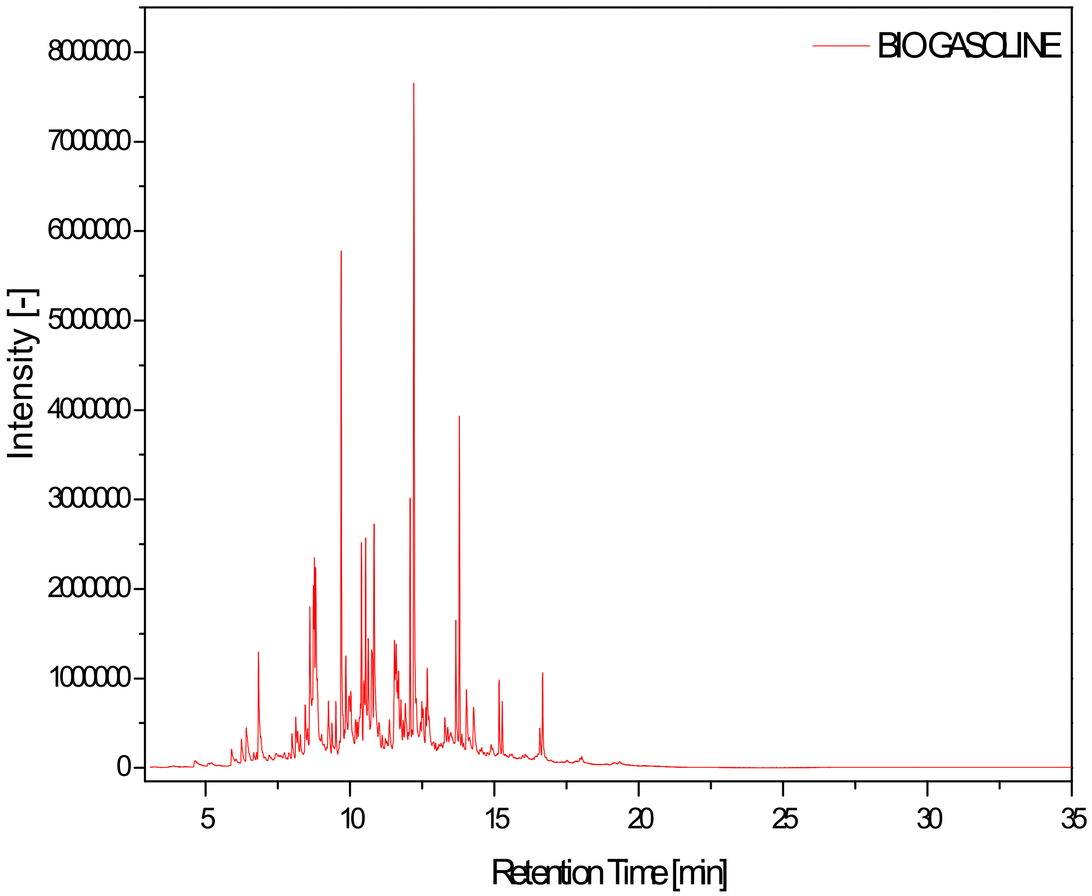

Figure 4: GC-MS of gasoline-like fraction (40°C-175°C).

Table 5: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in gasoline-like fraction (40°C-175°C).

Class of Compounds: Chemical Compounds	RT [min]	CAS	ω_i% (Area)
Alkanes			
Undecane	10.548	1120-21-4	3.19
Tridecane	13.794	629-50-5	3.93
Tetradecane	15.276	629-59-4	0.75
Pentadecane	16.744	629-62-9	1.55
∑ (Area.%) =			**9.41**
Alkenes			
p-Mentha-1,5,8-triene	9.861	21195-59-5	2.254
1-Undecene	10.402	821-95-4	2.776
1-Dodecene	12.088	112-41-4	3.034
Bicyclo[6.4.0]dodeca-9,11-diene	13.291	-	0.614
1-Tridecene	13.672	2437-56-1	2.098
Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	14.286	2443-46-1	1.380
1-Tetradecene	15.167	1120-36-1	1.111
∑ (Area.%) =			**13.267**
Aromatic Hydrocarbons			
Benzene, 1,3-dimethyl-	6.247	108-38-3	0.578
Benzene, propyl-	7.995	103-65-1	0.516
Benzene, 1-ethyl-3-methyl-	8.128	620-14-4	0.686
Benzene, 1-ethyl-2-methyl-	8.193	611-14-3	0.593
Trimethylbenzene	8.283	108-67-8	0.566
Benzene, (1-methylethyl)-	8.454	98-82-8	1.050
Benzene, 1,2,4-trimethyl-	8.738	95-63-6	2.107
Benzene, 1-ethenyl-2-methyl-	8.770	611-15-4	2.709
Benzene, 1,2,3-trimethyl-	9.255	526-73-8	1.297
Benzene, pentyl-	11.607	538-68-1	2.205
Benzene, (1-methyl-2-propynyl)-	11.646	4544-28-9	0.875
Benzene, (1-methyl-2-cyclopropen-1-yl)-	11.685	65051-83-4	1.441
o-Xylene	6.413	95-47-6	1.136
p-Xylene	6.834	106-42-3	2.080
6,7-Dimethyl-3,5,8,8a-tetrahydro-1H-2-benzopyran	10.368	110028-10-9	1.243
2,4-Dimethylstyrene	11.371	2234-20-0	0.703
1H-Indene, 1-methyl-	11.547	767-58-8	1.830
Naphthalene	12.217	91-20-3	10.081
1H-Indene, 2,3-dihydro-4,7-dimethyl-	12.533	6682-71-9	0.760
Benzocycloheptatriene	14.038	264-09-5	1.401
Indane	9.516	496-11-7	0.763
Indene	9.699	95-13-6	6.702
∑ (Area.%) =			**41.322**
Esters			
Hexanoic acid, 2-phenylethyl ester	6.917	72934-12-4	0.494
2-Furancarboxylic acid, 3-phenylpropyl ester	8.536	-	0.645
Carbonic acid, octadecyl phenyl ester	8.616	-	3.193
Acetic acid, 2-methylene-bicyclo[3.2.1]oct-6-en-8-yl ester	9.379	-	0.644
1-hydroxy-1,2,3,4-tetrahydronaphthalene trifluoroacetate ester	11.850	134563-46-5	0.526
∑ (Area.%) =			**5.502**
Ketones			
5H-Inden-5-one, 1,2,3,6,7,7a-hexahydro-	9.975	1489-28-7	1.630
Tricyclo[4.2.1.1(2,5)]deca-3,7-dien-9-one, 10-hydroxy-10-methyl-	11.767	70220-88-1	0.983
∑ (Area.%) =			**2.613**
Phenols			
Phenol	8.704	108-95-2	0.741
2-(2-Hydroxyphenyl)buta-1,3-diene	12.450	90-05-1	0.608
∑ (Area.%) =			**1.349**
Alcohols			

2-heptanol	5.906	543-49-7	0.366
1-Hexadecanol, 2-methyl-	16.583	2490-48-4	0.849
Carveol	10.263	99-48-9	1.259
2-Indanol	9.760	4254-29-9	0.568
2,6,8-Trimethylbicyclo[4.2.0]oct-2-ene-1,8-diol	10.484	-	1.505
1-Naphthalenol, 1,2,3,4-tetrahydro-3-methyl-	13.388	3344-45-4	0.427
2-Naphthalenol, 1,2-dihydro-, acetate\3-Methoxymethoxy-1,5,5-trimethyl-cyclohexene	12.300	132316-80-4	1.073
∑ *(Area.%)* =			**6.047**
Furans			
Benzofuran	8.816	271-89-6	3.746
Benzofuran, 2-methyl	10.838	4265-25-2	4.997
Furan, 2-(2 furanylmethyl)-5-methyl	11.922	13678-51-8	1.209
Benzofuran, 4,7-dimethyl	12.739	28715-26-6	3.287
∑ *(Area.%)* =			**13.239**
Aldehyds			
Myrtenal	10.034	564-94-3	1.724
Cinnamaldehyde	12.654	104-55-2	5.523
∑ *(Area.%)* =			**7.247**

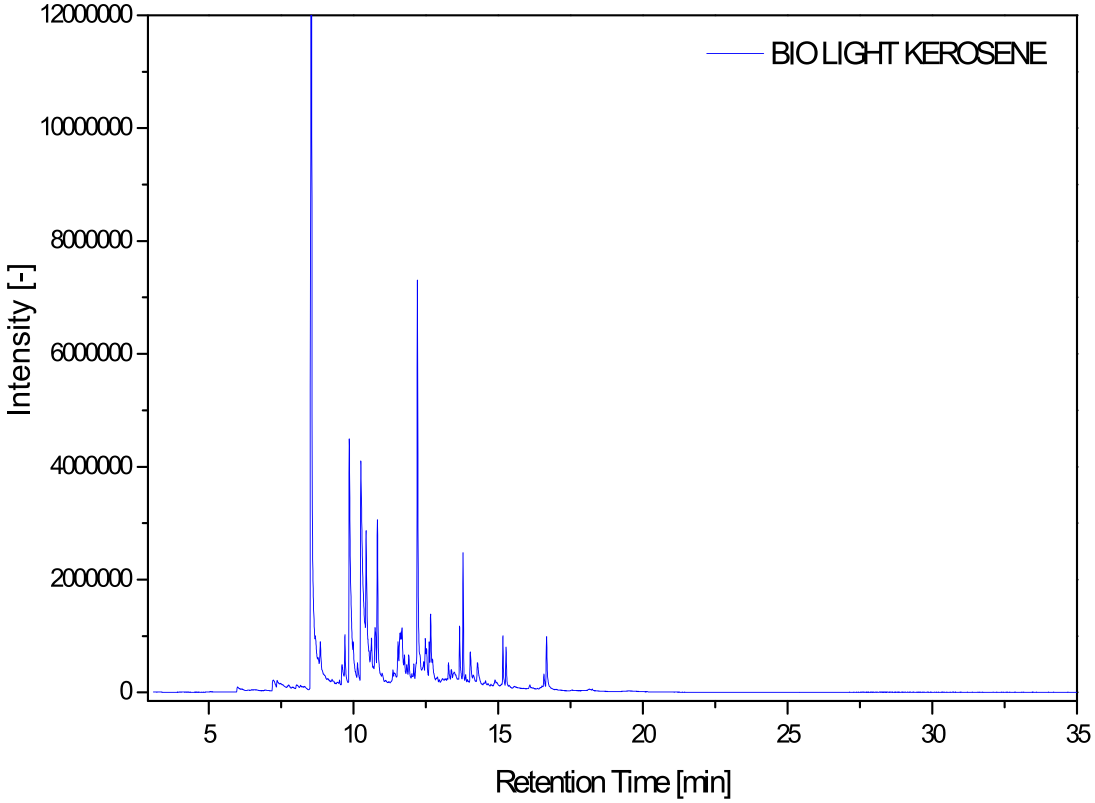

Figure 5: GC-MS of light kerosene-like fraction (175°C-200°C).

The GC-MS identified in light kerosene-like fraction hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) and oxygenates (esters, carboxylic acids, phenols, alcohols, ketones, furans, and aldehydes). The light kerosene-like fraction is composed of 66.67% (area.) hydrocarbons (17.60% alkenes, 32.65% alkanes, and 16.42% aromatic hydrocarbons) and

33.33% (area.) oxygenates (6.16% esters, 4.24% ketones, 3.26% carboxylic acids, 7.13% phenols, 8.30% alcohols, 2.39% furans, and 1.86% aldehydes). The presence of carboxylic acids, ketones, furans, and phenols is associated to the high acidity of light kerosene-like fraction, as shown in Table 6.

Table 6: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in light kerosene-like fraction (175°C-200°C).

Class of Compounds: Chemical Compounds	RT [min]	CAS	ω_i% (Area)
Alkanes			
Undecane	10.558	1120-21-4	2.115
Dodecane	12.222	112-40-3	1.608
Tridecane	13.793	629-50-5	7.177
Tetradecane	15.266	629-59-4	2.550
Pentadecane	16.668	629-62-9	8.424
Hexadecane	17.987	544-76-3	1.236
Heptadecane	19.266	629-78-7	8.974
Tetradacane 2,6,10-trimethyl-	20.485	14905-56-7	0,562
∑ (Area.%) =			**32.646**
Alkenes			
1-Dodecene	12.096	112-41-4 -6	2.077
1-Tridecene	13.668	2437-56-1	1.225
1-Tetradecene	15.157	1120-36-1	1.295
1-Pentadecene	16.576	13360-61-7	3.279
1-Heptadecene	17.896	6765-39-5	1.105
3-Heptadecene,(Z)-	18.991	-	2.914
8-Heptadecene	19.060	2579-04-6	5.701
∑ (Area.%) =			**17.596**
Aromatic Hydrocarbons			
Naphthalene, 2-methyl-	14.023	91-57-6	1.141
Naphthalene, 1-methyl-	14.265	90-12-0	1.582
Benzocycloheptatriene	14.923	264-09-5	1.633
Naphthalene, 1-ethyl-	15.483	1127-76-0	2.301
Naphthalene, 1,3-dimethyl-	15.679	575-41-7	3.739
Naphthalene, 1-(2-propenyl)-	16.732	2489-86-3	1.010
Naphthalene, 2-ethyl-	16.806	827-54-3	1.997
1-Isopropenylnaphthalene	17.145	1855-47-6	0.848
Fluorene	18.197	86-73-7	1.722
9H-Fluorene,9-methyl-	18.415	2523-37-7	0.445
∑ (Area.%) =			**16.418**
Esters			
Dodecanoic acid, methyl ester	16.987	111-82-0	3.801
Methyl tetradecanoate	19.580	124-10-7	2.358
Σ (Area.%) =			**6.159**
Carboxylic Acids			
4,5-Dichlorothiophene-2-carboxylic acid	14.766	**31166-29**-7	1.198
Erucic acid	18.864	112-86-7	0.450
Propanoic acid, 2-methyl-, (dodecahydro-6a-hydroxy-9a-methylene-2,9-dioxoazuleno	19.435	33649-17-1	0.925
Cis-5,8,11,14,17-Eicosapentaenoic acid	20.403	10417-94-4	0.692
∑ (Area.%) =			**3.265**
Ketones			
Cyclopenta[1,3]cyclopropa[1,2]cyclohepten-3(3aH)-one, 1,2,3b,6,7,8-hexahydro	14.851	91531-58-7	1.013
4-(2,4,4-Trimethyl-cyclohexa-1,5-dienyl)-but-3-en-2-one	15.980	-	0.966
Cyclopenta[1,3]cyclopropa[1,2]cyclohepten-3(3aH)-one, 1,2,3b,6,7,8-hexahydro-1,2,3b	16.330	91531-58-7	0.879
2,4,6-Cycloheptatrien-1-one,2-hydroxy-5-(3-methyl-2-butenyl)-4-(1-methylethenyl)-	16.887	552-96-5	1.382

∑ *(Area.%)* =			**4.240**
Phenols			
Phenol, 2,5-dimethyl-	11.725	95-87-4	1.168
Phenol, 3,4-dimethyl-	12.015	95-65-8	1.274
Phenol, 3-ethyl-5-methyl-	13.591	698-71-5	4.686
∑ *(Area.%)* =			**7.128**
Alcohols			
9-Methyltricyclo[4.2.1.1(2,5)]deca-3,7-diene-9,10-diol	14.176	78323-73-6	0.789
1-Naphthalenol, 1,2,3,4-tetrahydro-2,5,8-trimethyl-	16.162	55591-08-7	1.862
Bicyclo[4.1.0]heptan-2-ol,1β-(3-methyl-1,3-butadienyl)-2α,6β-dimethyl-3β-acetoxy	16.378	-	2.696
Cyclopentanol, 3,3,4-trimethyl-4-p-tolyl-, (R,R)-(+)-	16.475	19902-38-6	1.604
1-Hexadecanol, 2-methyl-	19.172	2490-48-4	1.348
∑ *(Area.%)* =			**8.299**
Furans			
Dibenzofuran	17.299	132-64-9	2.387
∑ *(Area.%)* =			**2.387**
Aldehyds			
2-((2R,4aR,8aS)-4a-Methyl-8-methylenedecahydronaphthalen-2-yl)acrylaldehyde	17.791	3650-40-6	1.864
∑ *(Area.%)* =			**1.864**

By the GC-MS analysis of kerosene-like fraction, hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) and oxygenates (esters, ethers, phenols, alcohols, ketones, furans, and aldehydes) were identified.

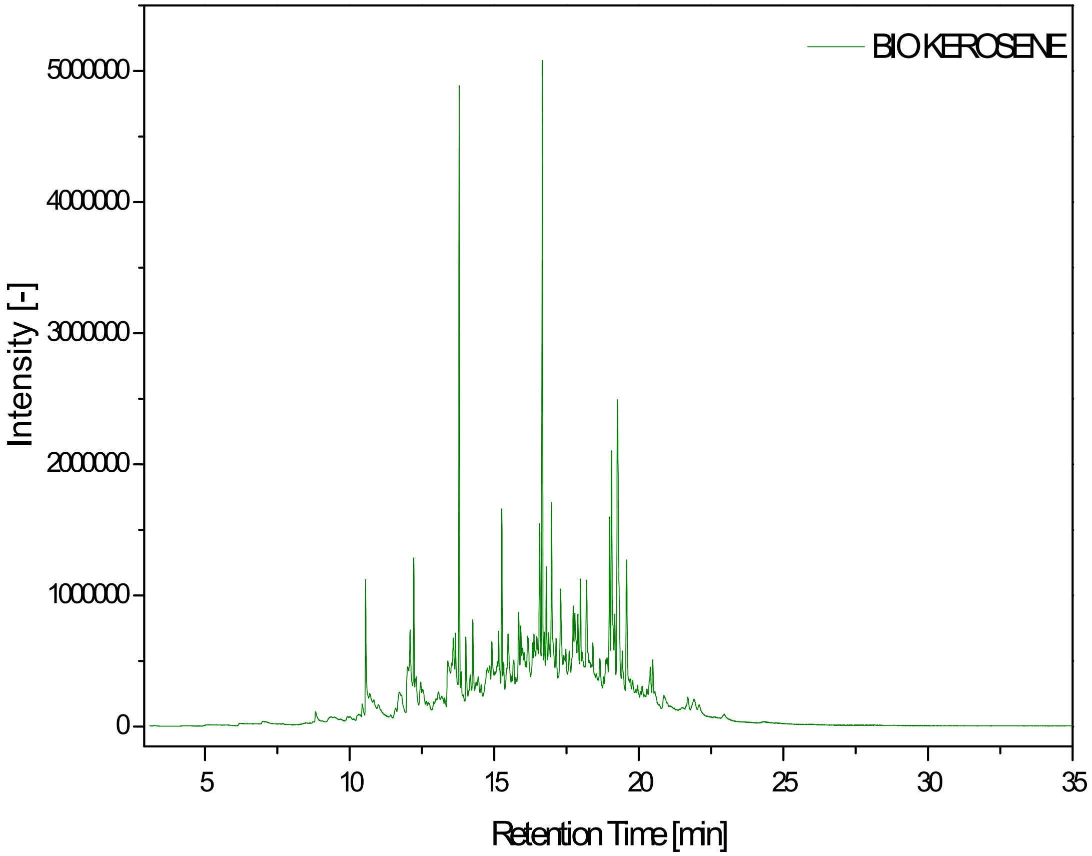

Figure 6: GC-MS of kerosene-like fraction (200°C-215°C).

The kerosene-like fraction is composed of 19.87% (area.) hydrocarbons (2.79% alkenes, 4.20% alkanes, and 12.88% aromatic hydrocarbons) and 81.13% (area.) oxygenates (2.06% esters, 0.80% ethers, 3.50% ketones, 60.79% phenols, 0.96% alcohols, 8.99% furans, and 3.22% aldehydes). The presence of ketones, furans, ethers, esters, aldehydes, and phenols confer the high acidity of kerosene-like fraction, as summarized in Table 7. Finally, the content of hydrocarbons within the distillation fractions (gasoline: 40°C < $T^{Boiling}$ < 175°C; light kerosene: 175°C < $T^{Boiling}$ < 200°C; and kerosene-like fraction: 200°C < $T^{Boiling}$ < 215°C) are higher than those reported in the literature [17-19, 46-48, 66, 70, 72], showing that was effective not only to diminish the acidity, but also to concentrate hydrocarbons.

Table 7: Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in kerosene-like fraction (200°C-215°C).

Class of Compounds: Chemical Compounds	RT [min]	CAS	ω_i% (Area)
Alkanes			
Tridecane	13.792	629-50-5	2.023
Tetradecane	15.276	629-59-4	0.752
Pentadecane	16.675	629-62-9	1.422
∑ (Area.%) =			**4.20**
Alkenes			
Tetracyclo[5.3.0.0<2,6>.0<3,10>]deca-4,8-diene	11.546	34324-40-8	0,981%
Bicyclo[6.4.0]dodeca-9,11-diene	13.288	-	0,389%
1-Tetradecene	15.166	1120-36-1	1,027%
1-Pentadecene	16.586	13360-61-7	0,390%
∑ (Area.%) =			**2.787**
Aromatic Hydrocarbons			
Benzene, 1-ethynyl-4-methyl-	9.708	766-97-2	1.148
1H-Indene, 2,3-dihydro-4-methyl-	11.370	824-22-6	0.288
Naphthalene	12.213	91-20-3	9.719
Naphthalene, 1-methyl	14.043	90-12-0	0.842
Naphthalene, 2-methyl-	14.290	91-57-6	0.883
∑ (Area.%) =			**12.880**
Alcohol			
1,3-Cyclohexadiene-1-methanol, α,2,6,6-tetramethyl-	11.764	102676-97-1	0.773
9-Heptadecene-4,6-diyn-3-ol	13.386	1242413-82-6	0.187
∑ (Area.%) =			**0.960**
Ether			
p-Propargyloxytoluene	12.431	5651-90-1	0.803
∑ (Area.%) =			**0.803**
Ketones			
2-Cyclopenten-1-one, 2-methyl-	7.237	1120-73-6	0.447
Ethanone, 1-(2-furanyl)-	7.366	1192-62-7	0.178
2-Cyclopenten-1-one, 2,3-dimethyl	9.609	1121-05-7	0.735
Benzoin	10.144	119-53-9	0.511
8-Decen-2-one, 9-methyl-5-methylene-	12.090	130876-97-0	0.354
Bicyclo[8.2.0]dodecan-11-one, 12,12-dichloro-, (1R*,10S*)-	13.672	110079-11-3	1.078
∑ (Area.%) =			**3.503**
Phenols			
Phenol	8.860	108-95-2	31.258
Phenol, 2-methyl-	9.861	95-48-7	8.621
Phenol, 3-methyl-	9.995	108-39-4	13.132
Phenol, 2-methoxy	10.442	90-05-1	5.554
Phenol, 2,5-dimethyl	11.645	95-87-4	2.229
∑ (Area.%) =			**60.794**

Ester			
1-hydroxy-1,2,3,4-tetrahydronaphthalene trifluoroacetate ester	11.846	134563-46-5	2.065
∑ *(Area.%)* =			**2.065**
Furans			
Benzofuran, 2-methyl-	10.831	4265-25-2	3.546
Furan, 2-(2 furanylmethyl)-5-methyl-	11.914	13678-51-8	0.750
Benzofuran, 4,7-dimethyl-	12.486	28715-26-6	4.693
∑ *(Area.%)* =			**8.989**
Aldehyds			
2-Propenal, 3-phenyl-	10.753	104-55-2	3.219
∑ *(Area.%)* =			**3.219**

4. Conclusions

The yield of distillation fractions (gasoline, light kerosene, and kerosene-like like fractions), 77.61% (wt.), is higher but according than those reported in the literature for both atmospheric and vacuum conditions [17-19, 21, 41, 46-48, 53, 66, 70, 72]. The acid values of distillation fractions increase with increasing boiling temperature. However, the acidity of gasoline-like fraction is much lower than that of raw bio-oil (70.26 mg KOH/g). The same behavior was observed for the densities, kinematic viscosities, and refractive indexes of gasoline, light kerosene, and kerosene-like like fractions with increasing boiling temperature.

The FT-IR analysis of bio-oil and distillation fraction identify the presence of hydrocarbons (alkanes, alkenes, and aromatic hydrocarbons) and oxygenates (phenols, cresols, carboxylic acids, alcohols, ethers, ketones, and furans). The bio-oil is composed of 21.52% (area) hydrocarbons and 78.48% (area) oxygenates. The presence of carboxylic acids, as well as phenols and cresols is associated to the high acidity of bio-oil.

The gasoline-like fraction is composed by 64.0% (area.) hydrocarbons and 36.0% (area.) oxygenates, while light kerosene-like fraction by 66.67% (area.) hydrocarbons and 33.33% (area.) oxygenates, and kerosene-like fraction by 19.87% (area.) hydrocarbons and 81.13% (area.) oxygenates. The content of hydrocarbons within the distillation fractions are higher than those reported in the literature [17-19, 46-48, 66, 70, 72], showing that distillation was effective not only to diminish the acidity, but also to concentrate hydrocarbons.

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