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 °C, 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
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 overseas [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 °C, 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 Açaí (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: Vigreux Column (30°C-215°C) | Bio-Oil [g] | Gas [g] | Raffinate [g] | Distillates [g] | Yield [wt.%] |
|-----------------------------------------|-------------|---------|---------------|-----------------|--------------|
|                                        | H₂O G LK K LD | H₂O G LK K LD | H₂O G LK K LD | H₂O G LK K LD | H₂O G LK K LD |
|                                        | 307.53      | 69.87   | 49.48         | 128.27          | 16.16        |

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<sub>Boiling</sub> < 180°C, and 45.3% (wt.) between 180°C < T<sub>Boiling</sub> < 250°C, while vacuum distillation yielded 10.3% (wt.) of an organic phase at 80°C, 5.9% (wt.) between 80°C < T<sub>Boiling</sub> < 160°C, and 40.9% (wt.) between 160°C < T<sub>Boiling</sub> < 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 °C 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/cm³], 30°C             | 0.9146 | 0.9191    | 0.9816   |
| 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    |

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, 0.9191, 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 |
|----------------------------|-------------|------|------|------|------|------|------|----------|
| ρ [g/cm³], 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   |

IA = Acid Value; IR = Refractive Index; ANP: Brazilian National Petroleum Agency, Resolution Nº 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          | α% (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     |
| **Cycloalkenenes**                     |          |              |           |
| 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-ethyliidine               | 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     | % (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   | 526-73-8  | 1.297   |
| Benzene, 1,2,3-trimethyl-              | 9.255   | 538-68-1  | 2.205   |
| Benzene, pentyl-                       | 11.607  | 4544-28-9 | 0.875   |
| Benzene, (1-methyl-2-propynyl)-        | 11.646  | 65051-83-4 | 1.927   |
| Benzene, (1-methyl-2-cyclopropen-1-yl)| 11.685  | 63051-83-4 | 1.441   |
| o-Xylene                               | 6.413   | 95-47-6   | 1.135   |
| 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   |
| Napthalene                             | 12.217  | 91-20-3   | 10.81   |
| 1H-Indene, 2,3-dihydro-4,7-dimethyl-   | 12.533  | 6682-71-9 | 0.760   |
| Benzoisocycloheptatriene               | 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-Furanacarboxylic acid, 3-phenylpropyl ester| 8.536| - | 0.645 |
| Carbonic acid, octadecyl phenyl ester  | 8.616   | -        | 1.937   |
| Acetic acid, 2-methylene-bicyclo[3.2.1]oct-6-en-8-yl ester| 9.379| - | 0.644 |
| 1-hydroxy-1,2,3,4-tetrahydroxynaphthalene 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**                           |         |         |          |
| Compound                                      | Area  | Retention Time (min) | Area. % |
|------------------------------------------------|-------|----------------------|---------|
| 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-   | 12.300| 132316-80-4          | 1.073   |
| Methoxymethoxy-1,5,5-trimethyl-cyclohexene    |       |                      |         |

### Sum (Area. %) = 6.047

#### Furans

| Compound                                      | Area  | Retention Time (min) | Area. % |
|------------------------------------------------|-------|----------------------|---------|
| 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   |

### Sum (Area. %) = 13.239

#### Aldehyds

| Compound                                      | Area  | Retention Time (min) | Area. % |
|------------------------------------------------|-------|----------------------|---------|
| Myrtenal                                      | 10.034| 564-94-3             | 1.724   |
| Cinnamaldehyde                                | 12.654| 104-55-2             | 5.523   |

### Sum (Area. %) = 7.247

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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     | % (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   | 14005-56-7 | 0.562    |
| ∑ (Area.%%)                            |          |         | 32.646   |
| Alkenes                                |          |         |          |
| 1-Dodecene                             | 12.096   | 112-41-4 | 2.077    |
| 1-Tridecene                            | 13.668   | 2437-56-1 | 1.225    |
| 1-Tetradecene                          | 15.157   | 13360-61-7 | 3.279    |
| 1-Pentadecene                          | 16.576   | 13360-61-7 | 2.925    |
| 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    |
| Benzcycloheptatriene                   | 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-Isopropenynaphthalene                | 17.145   | 1855-47-6 | 0.848    |
| Fluorene                               | 18.197   | 86-73-7  | 1.722    |
| 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    |
| ∑ (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- (dodehydro-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 4-(2,4,4-Trimethyl-1-cyclohexa-1,5-dienyl)-but-3-en-2-one | 14.851 | 91531-58-7 | 1.013    |
| 1,2,3b,6,7,8-hexahydro 4-(2,4,4-Trimethyl-1-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 2,4,6-Cycloheptatrien-1-one,2-hydroxy-5-(3-methyl-2-butenyl)-4-(1-methylethenyl)- | 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    |
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: $40^\circ\text{C} < T_{\text{Boiling}} < 175^\circ\text{C}$; light kerosene: $175^\circ\text{C} < T_{\text{Boiling}} < 200^\circ\text{C}$; and kerosene-like fraction: $200^\circ\text{C} < T_{\text{Boiling}} < 215^\circ\text{C}$) 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     | $\omega$ [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             |
| $\sum$ (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%            |
| $\sum$ (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             |
| Napthalene                             | 12.213   | 91-20-3 | 9.719             |
| Napthalene, 1-methyl                   | 14.043   | 90-12-0 | 0.842             |
| Napthalene, 2-methyl                   | 14.290   | 91-57-6 | 0.883             |
| $\sum$ (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             |
| $\sum$ (Area %)                         |          |         | 0.960             |
| **Ether**                              |          |         |                   |
| p-Propargyloxytoluene                   | 12.431   | 5651-90-1| 0.803             |
| $\sum$ (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             |
| $\sum$ (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             |
| $\sum$ (Area %)                         |          |         | 60.794            |
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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