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Production of Fuel-Like Fractions by Fractional Distillation of Bio-Oil from Açaí (*Euterpe oleracea* Mart.) Seeds Pyrolysis

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Abstract: This work investigates the effect of production scales (laboratory, bench, and pilot) by pyrolysis of Açaí (*Euterpe oleracea* Mart.) seeds at 450 °C and 1.0 atmosphere, on the yields of reaction products and acid value of bio-oils. The experiments were carried out in batch mode using a laboratory scale reactor of 143 mL, a bench scale reactor of 1.5 L, and a pilot scale reactor of 143 L (≈1:10:1000). The bio-oil was obtained in pilot scale, fractionated by distillation to produce biofuel-like fractions. The distillation of bio-oil was carried out in a laboratory column. The physical-chemistry properties (density, kinematic viscosity, acid value, and refractive index) of bio-oils and distillation fractions were determined. The qualitative analysis was determined by FT-IR and the chemical composition by GC-MS. The pyrolysis showed bio-oil yields from 4.37 to 13.09 (wt.%), decreasing with reactor volume. The acid value of bio-oils varied from 68.31 to 70.26 mg KOH/g. The distillation of bio-oil produced gasoline, light kerosene, and kerosene-like fuel fractions, and the yields were 16.16, 19.56, and 41.89 (wt.%), respectively. The physical-chemistry properties of distillation fractions increase with temperature. The FT-IR analysis of bio-oils and distillation fractions identified the presence of functional groups characteristic of hydrocarbons (alkenes, alkanes, aromatics, and aromatics rings) and oxygenates (carboxylic acids, ketones, esters, ethers, alcohols, phenols). The GC-MS identified 48.24 (area.%) hydrocarbons and 51.76 (area.%) oxygenates in the bio-oil produced in bench scale and 21.52 (area.%) hydrocarbons and 78.48 (area.%) oxygenates in the bio-oil produced in pilot scale. The gasoline-like fraction was composed by 64.0 (area.%) hydrocarbons and 36.0 (area.%) oxygenates, 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; gasoline; light kerosene; kerosene-like fuel

Table S1. Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in bio-oil obtained by pyrolysis of Açaí seeds at 450 °C and 1.0 atmosphere, in pilot scale.

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**

Table S2. Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in gasoline-like fraction (40–175 °C) after distillation of bio-oil obtained by pyrolysis of Açaí seeds at 450 °C and 1.0 atmosphere, in pilot scale.

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**

Table S3. Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in light kerosene-like fraction (175–200 °C) after distillation of bio-oil obtained by pyrolysis of Açaí seeds at 450 °C and 1.0 atmosphere, in pilot scale.

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**

Table S4. Classes of compounds, summation of peak areas, CAS number, and retention times of chemical compounds identified by CG-MS in kerosene-like fraction (200–215 °C) after distillation of bio-oil obtained by pyrolysis of Açaí seeds at 450 °C and 1.0 atmosphere, in pilot scale.

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**