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Fractional Distillation of Organic Liquid Compounds Produced by Catalytic Cracking of Fats, Oils, and Grease

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Abstract

This work aims to investigate the fractional distillation of organic liquid products (OLP) obtained by catalytic cracking of palm oil (*Elaeis guineensis* Jacq.) at 450°C, 1.0 atm, with 5, 10, and 15% (wt) Na_2CO_3 , using a stirred tank reactor of 143 L. The fractional distillations of OLP were carried out in laboratory scale with and without reflux using columns of different heights, and a pilot-packed distillation column with internal reflux. OLP and distillation fractions (gasoline, kerosene, light diesel, and heavy diesel) were physicochemically characterized for density, kinematic viscosity, acid value, saponification value, refractive index, flash point, and copper strip corrosion. The OLP and light diesel fractions were analyzed by Fourier transform infrared spectroscopy (FT-IR) and gas chromatography-mass spectrometry (GC-MS). For the experiments in laboratory scale, the yields of distillates decrease along with column height, with and without reflux, while those of bottoms products increase. The yields of distillates and gas increase with increasing Na_2CO_3 content, while those of bottoms products decrease. The densities of gasoline, kerosene, and light diesel produced in laboratory scale with reflux superpose exactly those of kerosene, light diesel, and heavy diesel produced in laboratory scale without reflux. The kinematic viscosity decreases with increasing column height for the experiments in laboratory scale. The acid values of distillation fractions decrease along with the column height for the experiments with and without reflux. The FT-IR of distillation fractions in pilot and laboratory scales identified the presence of aliphatic hydrocarbons and oxygenates. The GC-MS analysis identified OLP composition of 92.84% (area) hydrocarbons and 7.16% (area) oxygenates. The light diesel fraction contains 100% hydrocarbons with an acid value of 0.34 mg KOH/g, proving the technical feasibility of OLP de-acidification by the fractional distillation process.

Keywords: palm oil, organic liquid products, fractional distillation, light diesel

1. Introduction

Pyrolysis and/or catalytic cracking is one of the most promising processes to convert triacylglycerides (TAGs), the major compounds of vegetable oils and animal fats [1, 2], into liquid biofuels [3], and the literature reports several studies on the subject [3–47]. Both processes have the objective of obtaining hydrocarbons for use as fuels [3, 4, 6–24, 28–37]. However, the chemical composition of organic liquid products (OLP) shows a significant difference because of the complex cracking mechanism of TAGs [4, 5, 10, 19, 25–27]. Besides the type of cracking mode (thermal cracking and thermal catalytic cracking), other factors that significantly affect the liquid fuel composition are the characteristics of raw material, reaction temperature, residence time, mode of operation (fluidized bed reactor, sludge bed reactor, etc.), and the presence of water in the raw material and/or in the catalyst [6–11, 14, 15, 19, 21–24, 28–30].

The reaction products obtained by pyrolysis and/or catalytic cracking of oils, fats, grease, and fatty acid mixtures include gaseous and liquid fuels, water, and coke [6–8, 14, 15, 17, 21–24, 28–30]. The physicochemical properties and chemical composition of OLP depend on the selectivity of the catalyst used [6, 7, 10, 14–17, 20, 21–25, 28–39]. The OLP consists of hydrocarbons [8, 11, 12, 16, 17, 21–24, 26, 27], corresponding to the boiling point range of gasoline, kerosene, diesel fossil fuels, and oxygenates [6–8, 11, 12, 15–17, 21–25].

One of the advantages of catalytic cracking of oils, fats, greases, and fatty acid mixtures is the possibility of using low-quality lipid-based materials [6, 7, 20, 21–24, 28–35, 41] and the compositional similarities of OLP to fossil fuels [3, 6–8, 10, 21–24]. The OLP obtained by catalytic cracking presents lower amounts of carboxylic acids compared to pyrolysis, because of the catalytic activity in the secondary cracking step, where the carboxylic acids are broken up to form hydrocarbons [10], as reported elsewhere [21–23, 30]. The OLP can not only be stored and transported, but can also be refined and/or upgraded by applying physical (filtration, decantation, and centrifugation) and thermal separation processes (distillation, liquid-liquid extraction, and adsorption) to produce high-quality green fuel-like fractions with the potential to substitute partially fossil fuels [6, 11, 16, 21–23, 40, 44].

The disadvantages and/or drawbacks of OLP obtained by pyrolysis and/or catalytic cracking of oils, fats, greases, and fatty acid mixtures are the high acid value [8, 11, 14, 19, 22, 45, 46] and high concentrations of olefins, making OLP a corrosive and unstable fuel [9, 21]. To increase the yield of OLP and reduce undesired reaction products, as well as the content of oxygenate compounds, a wide variety of catalysts have been tested in catalytic cracking, particularly zeolites [6, 7, 10, 12, 13, 15–18, 21, 22, 28–39]. However, OLP obtained by catalytic cracking using zeolites and mesoporous catalysts still has a high carboxylic acid content [7, 14, 15, 45].

In this context, studies have been investigating strategies to minimize the high acid values and high concentration of olefins in OLP obtained by catalytic cracking of oils, fats, greases, and fatty acid mixtures, including the application of cheap alkali catalysts such as Na_2CO_3 to reduce the acid value of liquid biofuels [7, 21, 23, 24, 30, 47, 51–55]. OLP with lower acid values makes it possible to apply physical (filtration, decantation, sedimentation, and centrifugation) [53–55], chemical (neutralization) [53–55], and thermal separation processes (distillation,

liquid-liquid extraction, and adsorption) to produce high-quality green hydrocarbon-like fuels [21–24, 44, 53–55]. In the last few years, processes have been proposed to remove and/or recover oxygenate compounds from biomass-derived bio-oils including molecular distillation to separate water and carboxylic acids from pyrolysis bio-oils [56–58], fractional distillation to isolate/enrich chemicals and improve the quality of bio-oil [59–64], and liquid-liquid extraction using organic solvents and water to recover oxygenate compounds of bio-oils [40, 65]. Non-conventional separation methods using aqueous salt solutions for phase separation of bio-oils are also applied [66]. Furthermore, the literature reports several studies upon fractionation of OLP by single-stage and multistage distillation to obtain hydrocarbon-like fuels in the temperature boiling point range of gasoline, kerosene, and diesel-like fractions [6, 7, 11, 14, 15, 21–24, 30, 35, 37, 39, 41, 46–55]. However, until now only a few studies have investigated systematically the effect of column height on the chemical composition of OLP [6, 7, 47], but no systematic study has investigated the effect of column height, reflux ratio, and OLP composition on the physicochemical properties of the distillation fraction of OLP.

This work aims to investigate the effect of column height, reflux rate, and OLP composition on the physicochemical properties of distillation fractions and de-acidification of OLP by fractional distillation using laboratory columns of different heights and a pilot-packed distillation column with internal reflux.

2. Materials and methods

2.1. Materials

OLP was obtained by catalytic cracking of crude palm oil (*Elaeis guineensis* Jacq.) at 450°C, 1.0 atm, with 15% (wt) Na₂CO₃ in a stirred tank slurry reactor of 143 L, operating in batch mode, as described in a similar study reported elsewhere [21].

2.2. Physicochemical analysis of palm oil, OLP, and distillation fractions

Palm oil, OLP, and distillation fractions have been physicochemically characterized for acid value (AOCS Cd 3d-63), saponification value (AOCS Cd 3-25), free fatty acid content (ASTM D5555), density (ASTM D1480) at 25°C, kinematic viscosity (ASTM D445/D446), flash point (ASTM D93), copper strip corrosion (ABNT/NBR 14359), and refractive index (AOCS Cc 7-25).

2.3. Fractional distillation of OLP

2.3.1. Laboratory unit

2.3.1.1. Distillation without reflux: experimental apparatus and procedures

The laboratory fractional distillation apparatus was operated without reflux and the procedure is described in detail elsewhere [21].

2.3.1.2. Distillation with reflux: experimental apparatus and procedures

The fractional distillation of OLP with reflux was performed by using an experimental apparatus similar to that described by Mota et al. [21]. The distillation apparatus had a thermostatically controlled electrical heating blanket of 480 W (Fisaton, Model: 202E, Class: 300), and a 500 mL round bottom, three neck borosilicate-glass flask with outer joints, and side joints angled at 20°, 24/40. The side joints used to insert a long thin thermocouple of a digital thermometer and the other used to collect samples, the center joint, 24/40, were connected to a distillation column (Vigreux) of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm). The borosilicate-glass distillation columns (Vigreux) with bottom inner and top outer joints 24/40 were connected to an inverted Y-type glass support, the left side bottom inner joint 24/40 was connected to the distillation column top outer joint 24/40, and the right side bottom inner joint 24/40 was connected to the 250 mL glass separator funnel top outer joint 24/40. The center top outer joint 24/40 was connected to the bottom inner joint 24/40 of a Liebig glass-borosilicate condenser. The right side of the inverted Y-type glass support had a Teflon valve that made it possible to drip only a part and/or fraction of liquid condensates into the glass separator funnel, thus creating a reflux rate. A thermocouple connected to the top outer joint 7/25 of the left side of the inverted Y-type glass support made it possible to measure the vapor temperature at the top of the borosilicate-glass distillation columns (Vigreux). A cryostat bath (VWR Scientific, Model/Series: 913174) provided cold water at 15°C to the Liebig glass-borosilicate condenser. The 500 mL round bottom borosilicate-glass flask and the distillation column (Vigreux) were insulated with glass wool and aluminum foil sheet to avoid heat losses. Initially, approximately 300 g of OLP was weighed, the heating system was switched on, and the distillation time and temperature were recorded. From the time the vapor phase started to condensate, the Teflon valve was regulated to a reflux rate of two drops per second. The mass of distillation fractions (gasoline, kerosene, light and heavy diesel-like fuels) was recorded and weighed. The distillation fractions were submitted to the pretreatment of decantation to separate the aqueous and organic (OLP) phases.

2.3.2. Distillation pilot unit

Figure 1 illustrates the fractional distillation unit (Goel Scientific Glass Works Pvt. Ltd, India, Model: FDU50) with dimensions (height = 370 cm, length = 90 cm, depth = 60 cm), operating pressure –1.0–0.5 bar for process, utility, and vessel sides, and maximum operating temperature of –50–300°C, constructed of borosilicate glass and 100% polytetrafluoroethylene (PTFE). The distillation unit consisted of a distillation vessel of 50 L with a drain valve (DN 25), a heating/cooling system of 6.0 kW, and a heating surface of 0.5 m² (heating medium), as well as copper coils of 0.4 m² heating the transfer area and an operating pressure up to 10.0 bar (steam). A digital display controlled the heating rate and distillation vessel temperature and displayed the temperature at the reflux divider, operating range 0–300°C, $\pm 2.0^\circ\text{C}$ tolerance, PT-100 sensor for the distillation vessel (in built), and reflux divider. The vapor line (H = 100 cm, DN 100) was packed with cylindrical borosilicate-glass raschig rings of 15 mm length and 10 mm diameter, and the vapor condenser (DN 100), cooled with water, had a heating transfer surface of 0.5 m² with a manually operated reflux divider. The product cooler had a 0.2 m² heating transfer area, coupled to two twin receivers of 5 and 10 L with spherical geometry, the 10 L spherical vessel with a drain valve

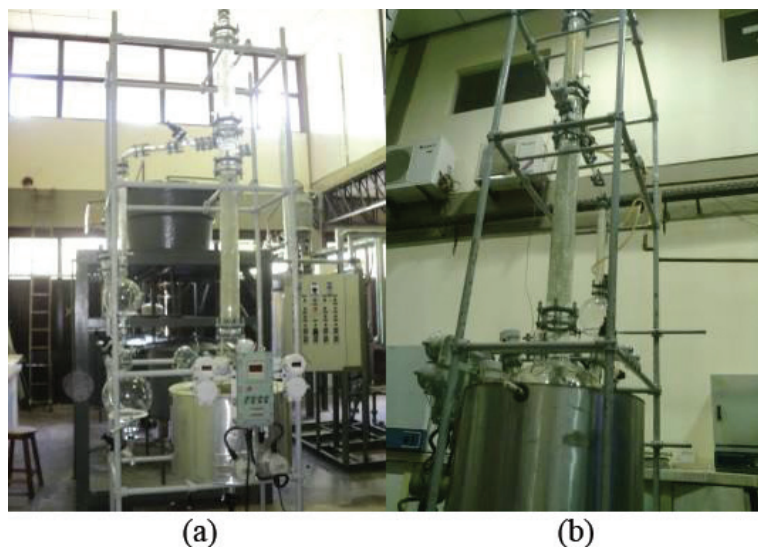


Figure 1. Differential glass packed distillation unit of 50 L: (a) Frontal view, (b) Lateral view.

(DN 25). The 50 L round borosilicate-glass vessel and the distillation column were insulated with glass wool and aluminum foil sheet to avoid heat losses. Initially, approximately 9.50 kg of OLP was weighed and introduced inside the distillation vessel and the electrical heating system switched on for a heating rate of $2^{\circ}\text{C}/\text{min}$, being the distillation time and temperature recorded. Afterwards, the freshwater cooling system valve was opened. From the time the vapor phase started to condensate, the regulating valve between the reflux divider and the product cooler was open. The mass of distillation fractions (gasoline, kerosene, and light diesel-like fuels) was recorded and weighed. The distillation fractions were submitted to the pretreatment of decantation to separate the aqueous and organic (OLP) phases.

2.4. Chemical analysis of OLP and distillation fractions

2.4.1. Physicochemical analysis of distillation fractions

Distillation fractions (gasoline-like fraction: $40^{\circ}\text{C} < T^{\text{b}} < 175^{\circ}\text{C}$; kerosene-like fraction: $175^{\circ}\text{C} < T^{\text{b}} < 235^{\circ}\text{C}$; light diesel-like fraction: $235^{\circ}\text{C} < T^{\text{b}} < 305^{\circ}\text{C}$; and heavy diesel-like fraction: $305^{\circ}\text{C} < T^{\text{b}} < 400^{\circ}\text{C}$) were characterized according to the analysis described in Section 2.2, except for flash point and free fatty acid content. FT-IR of OLP and distillation fractions (gasoline: $40^{\circ}\text{C} < T^{\text{b}} < 175^{\circ}\text{C}$; kerosene: $175^{\circ}\text{C} < T^{\text{b}} < 235^{\circ}\text{C}$; light diesel: $235^{\circ}\text{C} < T^{\text{b}} < 305^{\circ}\text{C}$; and heavy diesel: $305^{\circ}\text{C} < T^{\text{b}} < 400^{\circ}\text{C}$) were performed using an FT-IR spectrometer as described in detail elsewhere [21, 22]. Prior to the chemical analysis by GC-MS, described in detail elsewhere [22, 23], the samples of OLP and light diesel-like fraction ($235^{\circ}\text{C} < T^{\text{b}} < 305^{\circ}\text{C}$) were submitted to a pretreatment of chemical derivatization of free fatty acids.

3. Results and discussions

3.1. CPO and OLP physicochemical properties

Table 1 illustrates the physicochemical characterization of crude palm oil (*Elaeis guineensis* Jacq.) and OLP obtained by catalytic cracking of palm oil at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale. Crude palm oil (CPO) used as raw renewable material on the catalytic cracking experiment was physicochemically characterized in a previous study [21].

3.2. Catalytic cracking of CPO

The process conditions, material balance, and yields of reaction products (OLP, coke, gas, and H₂O) obtained by catalytic cracking of CPO at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃, are shown in **Table 2**. The obtained OLP yield was lower, but in accordance with similar studies reported in the literature [21–24, 30]. The gas yield was lower than that reported in similar studies [21–24], while the yield of coke was higher, but in accordance with that reported elsewhere [21–24, 30].

Physicochemical properties	Palm oil (21)	OLP (wt%) Na ₂ CO ₃			ANP No. 65
		5	10	15	
ρ (g/cm ³)	0.900	0.849	0.834	0.830	0.82–0.85
Acid value (mg KOH/g)	4.80	51.56	4.10	3.55	–
$\frac{(IA_{PalmOil} - IA_{OLP})}{IA_{PalmOil}} * 100$ (%)	–	–	14.58	26.04	–
Refractive index (–)	1.460	1.458	1.458	1.454	–
μ (cSt)	48.05	6.59	5.67	4.82	2.0–4.5
Flash point (°C)	–	87	28	27	>38
Saponification value (mg KOH/g)	179.90	70.95	64.91	54.15	–
$\frac{(IS_{PalmOil} - IS_{OLP})}{IS_{PalmOil}} * 100$ (%)	–	60.56	63.92	69.90	–
Ester index (mg KOH/g)	174.60	19.39	60.81	50.60	–
Content of FFA (%)	2.40	25.78	2.05	1.78	–
Copper strip corrosion (IA)	–	1A	1A	1A	1A

ANP: Brazilian National Petroleum Agency, Resolution No. 65 (Specification of Diesel S10).

IA, acid value; IS, saponification value, Ester index, IS – IA, Free Fatty Acids (FFA).

Table 1. Physicochemical analysis of palm oil and OLP obtained by catalytic cracking of palm oil at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale.

Process parameters	Na ₂ CO ₃ 15% (wt)
	Pilot
Cracking temperature (°C)	450
Mass of palm oil (kg)	34.90
Mass of Na ₂ CO ₃ (g)	5.24
Cracking time (min)	100
Mechanical stirrer speed (rpm)	150
Initial cracking temperature (°C)	320
Yield of OLP (wt%)	58.74
Yield of coke (wt%)	15.47
Yield of H ₂ O (wt%)	13.64
Yield of gas (wt%)	12.15

Table 2. Process parameters and overall steady-state material balance of catalytic cracking of palm oil at 450°C, 1.0 atm, with 15% (wt) Na₂CO₃ in pilot scale.

3.3. Fractional distillation of OLP

3.3.1. Laboratory unit

3.3.1.1. Distillation without reflux: material balances and yields of distillation fractions

Table 3 illustrates the material balances and yields of distillation products (distillates, bottoms, and gas) produced by laboratory fractional distillation of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using Vigreux columns of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm), operating without reflux. For the experiments carried out using columns of different heights, with and without reflux, the yields of distillates (biofuels) and gas decreased in a smooth exponential and linear fashion, respectively, along with the column height, while that of bottoms products increased exponentially with increasing column height, as shown in **Figure 2**. The same tendency was observed by Dandik and Aksoy [6, 7]. The yield of distillates of 66.26% (wt), obtained with a column of 10 cm, was equal to that reported by Almeida et al. [23, 24], higher than that reported elsewhere [6, 7, 61, 64], and lower than that reported by Kumar and Konwer [63]. In addition, the yields of gasoline, kerosene, light diesel, and heavy diesel of 1.55, 11.17, 21.38, and 32.72% (wt), obtained with a column of 10 cm, were in accordance with the yields of distillation fractions reported by Almeida et al. [23, 24] and Kumar and Konwer [63]. For the experiments carried out with OLP obtained with 5, 10, and 15% (wt) Na₂CO₃, using a column of 50 cm height, with and without reflux, the yields of distillates (biofuels) and gas increased in a sigmoid and linear fashion, respectively, with increasing catalyst content, while those of bottoms products decreased in a sigmoid fashion, as shown in **Figure 3**. Dandik and Aksoy [7] observed the same tendency. The yield of distillates obtained with 15% (wt) Na₂CO₃ and 50 cm column height (62.15%) was higher than that reported by Dandik and

Process parameters	Distillation without reflux			Distillation without reflux		
	15% (wt) Na ₂ CO ₃			Column height 50 cm		
	Column height (cm)			(wt%) Na ₂ CO ₃		
	10	30	50	5	10	15
Initial temperature (°C)	26	26	26	26	26	26
Final temperature (°C)	400	400	400	400	400	400
Processing time (min)	85	91	104	102	112	104
Distillation fractions T^{B,1} (°C)						
(40°C < T ^B < 175°C)	158	166	165	–	174	165
(175°C < T ^B < 235°C)	190	185	190	180	188	190
(235°C < T ^B < 305°C)	241	241	244	251	244	244
(305°C < T ^B < 400°C)	310	311	311	308	315	311
Distillation fractions (material balances)						
Mass of feed (g)	694.10	636.05	685.21	692.63	660.69	685.21
Mass distillation fraction (40°C < T ^B < 175°C) (g)	10.75	14.24	12.03	–	4.77	12.03
Mass of aqueous phase (g)	0	0.17	0	–	0	0
Mass distillation fraction (175°C < T ^B < 235°C) (g)	77.55	78.74	79.13	20.71	57.50	79.13
Mass of aqueous phase (g)	0	0	0	4.08	0.92	0
Mass distillation fraction (235°C < T ^B < 305°C) (g)	148.41	136.32	138.60	108.30	106.04	138.60
Mass of aqueous phase (g)	0	0	0	0	0	0
Mass distillation fraction (305°C < T ^B < 400°C) (g)	227.14	186.73	196.14	115.05	203.33	196.14
Mass bottoms products (raffinate) (g)	205.48	197.74	235.84	426.24	269.02	235.84

Process parameters	Distillation without reflux			Distillation without reflux		
	15% (wt) Na ₂ CO ₃			Column height 50 cm		
	Column height (cm)			(wt%) Na ₂ CO ₃		
	10	30	50	5	10	15
Mass of gas (g)	24.77	22.11	23.47	18.25	18.81	23.47
Yield of gasoline-like fraction (wt%)	1.55	2.26	1.75	–	0.72	1.75
Yield of kerosene-like fraction (wt%)	11.17	12.38	11.55	3.58	8.85	11.55
Yield of light diesel-like fraction (wt%)	21.38	21.43	20.23	15.63	16.05	20.23
Yield of heavy diesel-like fraction (wt%)	32.72	29.35	28.62	16.61	30.79	28.62
Yield of biofuels (wt%)	66.83	65.43	62.15	35.82	56.41	62.15
Yield of gas (wt%)	3.57	3.47	3.43	2.63	2.85	3.43
Yield of raffinate (wt%)	29.60	31.10	34.42	61.54	40.74	34.42

$T^{B,I}$, initial boiling temperature; T^B , boiling temperature.

Table 3. Mass balances and yields of distillation products obtained by laboratory fractional distillation of OLP produced at 450°C, 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃, using Vigreux columns of 10, 30, and 50 cm, operating without reflux.

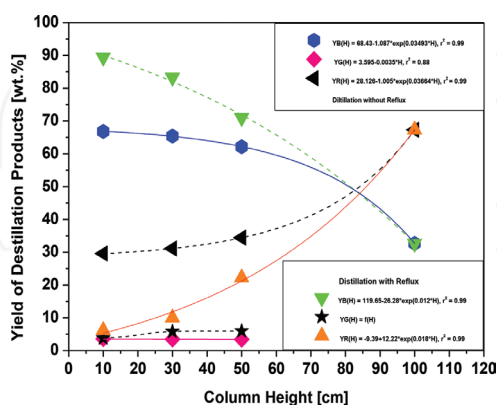


Figure 2. Yield of distillation products (distillates, bottoms, and gas), produced by laboratory distillation with and without reflux (YB, YR, and YG) of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃ in pilot scale, using columns of 10, 30, and 50 cm, and a pilot-packed distillation column of 100 cm height.

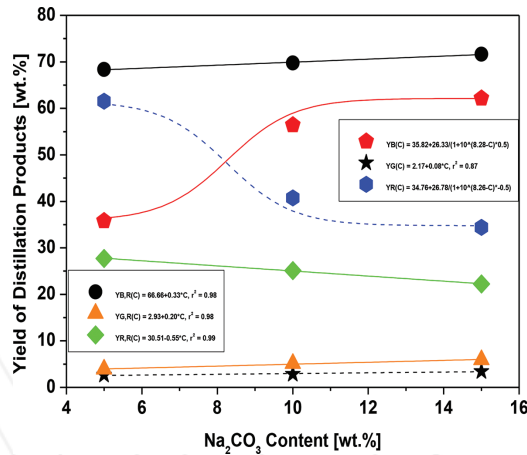


Figure 3. Yield of distillation products (distillates, bottoms, and gas), produced by laboratory distillation with (YB,R, YR,R, and YG,R) and without reflux (YB, YR, and YG) with OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using a column of 50 cm.

Aksoy [7] at 420°C, 1.0 atm, with 10% (wt) Na₂CO₃, using a fractionating column of 54 cm, but lower than the one obtained by Kumar and Konwer [63] using an Oldershaw column of 50 cm.

3.3.1.2. Distillation with reflux: material balances and yields of distillation fractions

Table 4 shows the material balances and yields of distillation products (distillates, bottoms, and gas) produced by laboratory fractional distillation of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using Vigreux columns of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm), operating with reflux. The results show higher distillate yields and lower bottoms products yields compared to the fractional distillation without reflux, as well as the absence of heavy diesel-like fractions. In addition, the same tendency was observed for the variation of distillates, bottoms products, and gas yields with increasing column heights by fractional distillation of OLP obtained with 15% (wt) Na₂CO₃ and with a 50 cm column by fractional distillation of OLP obtained with 5, 10, and 15% (wt) Na₂CO₃. For the experiments with different column heights, a maximum distillate yield of 89.44% (wt) was achieved at 10 cm, much higher than those reported elsewhere [6, 7, 23, 24, 61, 63, 64], showing that reflux has improved the yields of distillates. This is according to the results of Kumar and Konwer [63] for the global yield of distillation fractions collected between 180 and 300°C, 300 and 325°C, and 325 and 370°C, operating with a reflux ratio of 0.2 and 10 mm Hg, obtaining 56.80% (wt). In addition, the yields of gasoline, kerosene, and light diesel of 10.86, 15.38, and 63.18% (wt) were according to the yields of gasoline (14.32%), kerosene (8.67%), and diesel (56.80%) reported by Kumar and Konwer [63]. For the experiments using a column of 50 cm height and OLP obtained with 5, 10, and 15% (wt) Na₂CO₃, a maximum distillate yield of 71.65% (wt) was achieved for OLP obtained with 15% (wt) Na₂CO₃, much higher than those reported elsewhere [6, 7, 23, 24, 61, 64], but lower than those reported by Kumar and Konwer [63].

Process parameters	Distillation with reflux			Distillation with reflux		
	15% (wt) Na ₂ CO ₃			Column height 50 cm		
	Column height (cm)			(wt%) Na ₂ CO ₃		
	10	30	50	5	10	15
Initial temperature (°C)	25	26	25	27	25	25
Initial reflux temperature (°C)	51	53	54	66	60	54
Initial reflux time (min)	10	10	11	18	15	11
Final temperature (°C)	305	305	305	270	305	305
Processing time (min)	270	243	250	257	235	250
Distillation fractions						
<i>T^{B,1}</i> (°C)						
(40°C < <i>T^B</i> < 175°C)	118	113	90	104	84	90
(175°C < <i>T^B</i> < 235°C)	181	187	186	194	186	186
(235°C < <i>T^B</i> < 305°C)	239	240	244	245	236	244
(305°C < <i>T^B</i> < 400°C)	–	–	–	–	–	–
Distillation fractions (material balances)						
Mass of feed (g)	300	200	200	200	200	200
Mass distillation fraction (40°C < <i>T^B</i> < 175°C) (g)	32.60	27.33	20.69	10.30	24.78	20.69
Mass of aqueous phase (g)	0	0.40	0.30	2.60	1.33	0.30
Mass distillation fraction (175°C < <i>T^B</i> < 235°C) (g)	46.16	24.11	24.98	16.35	20.17	24.98
Mass of aqueous phase (g)	0	0	0	1.31	0.15	0
Mass distillation fraction (235°C < <i>T^B</i> < 305°C) (g)	189.56	115.17	97.64	105.00	92.09	97.64
Mass of aqueous phase (g)	1.90	1.37	0	1.20	1.00	0
Mass distillation fraction (305°C < <i>T^B</i> < 400°C) (g)	–	–	–	–	–	–
Mass bottoms products (raffinate) (g)	18.56	20.00	44.49	55.44	50.27	44.49

Process parameters	Distillation with reflux			Distillation with reflux		
	15% (wt) Na ₂ CO ₃			Column height 50 cm		
	Column height (cm)			(wt%) Na ₂ CO ₃		
	10	30	50	5	10	15
Mass of gas (g)	11.22	11.62	11.90	7.80	10.21	11.90
Yield of gasoline-like fraction (wt%)	10.86	13.66	10.34	6.45	13.05	10.34
Yield of kerosene-like fraction (wt%)	15.38	12.05	12.49	8.83	10.16	12.49
Yield of light diesel-like fraction (wt%)	63.18	57.58	48.82	53.10	46.51	48.82
Yield of heavy diesel-like fraction (wt%)	–	–	–	–	–	–
Yield of biofuels (wt%)	89.44	83.30	71.65	68.38	69.77	71.65
Yield of gas (wt%)	3.74	5.81	5.95	3.90	5.10	5.95
Yield of raffinate (wt%)	6.18	10.00	22.24	27.72	25.13	22.24

T^{B,1}, initial boiling temperature; *T*^B, boiling temperature.

Table 4. Mass balances and yields of distillation products produced by laboratory fractional distillation of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using Vigreux columns of 10, 30, and 50 cm, operating with reflux.

3.3.2. Pilot unit

Material balances and yields of distillation products produced by pilot fractional distillation of OLP, obtained at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃ in pilot scale, using a differential distillation apparatus, packed with borosilicate-glass raschig rings of cylindrical geometry (ID = 1.0 cm, L = 1.0 cm), of 100 cm height, with internal reflux, are illustrated in **Table 5**. The results show a distillates yield of 32.68% (wt), higher than that reported by Dandik and Aksoy [7] at 400 and 420°C, column height of 54 cm, with 1, 5, and 10% (wt) Na₂CO₃, but lower than the one obtained by Kumar and Konwer [63], collected between 40 and 140°C, 140 and 180°C, and 180 and 300°C, being the last fraction performed with a reflux ratio of 0.2 and 10 mm Hg. The yield of distillates in pilot distillation scale was lower because of the higher column height, and the fact that distillation was carried out up to 280°C because of equipment instabilities. The distillation of OLP, obtained at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃, using a differential distillation apparatus, packed with borosilicate-glass raschig rings, of 100 cm height, with internal reflux, improved the quality (physicochemical properties) of gasoline, kerosene, and light diesel-like hydrocarbon fractions, particularly the acid values. The acid values ranged between 0.334 and 0.420 mg KOH/g, below the maximum permitted (0.5 mg KOH/g) acid value limit specification for diesel fuel S10 of ANP 65 [67].

Process parameters	Column height (cm)
	100
Initial temperature (°C)	30
Final temperature (°C)	305
Processing time (min)	270
Distillation fractions $T^{B,1}$ (°C)	
(40°C < T^B < 175°C)	94.6
(175°C < T^B < 235°C)	174.9
(235°C < T^B < 280°C)	233.8
Distillation fractions (material balances)	
Mass of feed (g)	6100.00
Mass distillation fraction (40°C < T^B < 175°C) (g)	241.34
Mass distillation fraction (175°C < T^B < 235°C) (g)	631.24
Mass distillation fraction (235°C < T^B < 280°C) (g)	1121.15
Mass bottoms products (raffinate) (g)	4106.27
Yield of gasoline-like fraction (wt%)	3.95
Yield of kerosene-like fraction (wt%)	10.35
Yield of light diesel-like fraction (wt%)	18.38
Yield of heavy diesel-like fraction (wt%)	–
Yield of biofuels (wt%)	32.68
Yield of raffinate (wt%)	67.32

$T^{B,1}$, initial boiling temperature; T^B , boiling temperature.

Table 5. Mass balances and yields of distillation products (distillates and bottoms) produced by pilot fractional distillation of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale, using a differential distillation-packed column of 100 cm, with internal reflux.

3.4. Physicochemical properties of distillation fractions

3.4.1. Density of distillation fractions

Physicochemical properties of hydrocarbon-like fractions, produced by laboratory fractional distillation of OLP, using Vigreux columns of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm), operating with and without reflux, and a pilot differential distillation column, packed with borosilicate-glass raschig rings, of 100 cm height, with internal reflux, are illustrated in **Tables 6–8**. The density of distillation fractions, produced by laboratory distillation of OLP at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 , with and without reflux using columns of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm), and a pilot-packed distillation column of 100 cm, with internal reflux, is shown in **Figure 4**. One may observe that densities of distillation fractions increase with increasing boiling temperature intervals, as reported by Kumar and Konver [63], remaining

Physicochemical properties	Distillation without reflux		Distillation without reflux			
	15% (wt) Na ₂ CO ₃		Column height 50 cm			
	Column height (cm)		(wt%) Na ₂ CO ₃			
	10	30	50	5	10	15
Distillation fraction (40°C < T ^B < 175°C)						
ρ (g/cm ³)	0.7312	0.7389	0.7376	–	0.7311	0.7376
LA (mg KOH/g)	5.29	3.90	1.99	–	4.90	1.99
LS (mg KOH/g)	8.76	12.86	35.81	–	–	35.81
LR (–)	1.400	1.413	1.415	–	1.418	1.415
C (1A)	1A	1A	1A	–	1A	1A
Distillation fraction (175°C < T ^B < 235°C)						
ρ (g/cm ³)	0.7536	0.7497	0.7492	0.7298	0.7418	0.7492
μ (cSt)	0.88	0.84	0.81	0.72	0.76	0.81
LA (mg KOH/g)	1.96	1.65	1.49	78.46	2.96	1.49
LS (mg KOH/g)	10.56	6.39	11.87	95.17	5.27	11.87
LR (–)	1.412	1.412	1.419	1.418	1.425	1.419
C (1A)	1A	1A	1A	1A	1A	1A
Distillation fraction (235°C < T ^B < 305°C)						
ρ (g/cm ³)	0.7887	0.7904	0.7873	0.7945	0.7833	0.7873
μ (cSt)	1.81	1.61	1.59	1.62	1.37	1.59
LA (mg KOH/g)	1.47	1.07	0.98	49.09	2.62	0.98
LS (mg KOH/g)	27.51	3.78	13.63	51.74	9.13	13.63
LR (–)	1.442	1.441	1.442	1.441	1.439	1.442

Physicochemical properties	Distillation without reflux		Distillation without reflux	
	15% (wt) Na ₂ CO ₃		Column height 50 cm	
	Column height (cm)		(wt%) Na ₂ CO ₃	
	10	30	5	15
C (1A)	1A	1A	1A	1A
Distillation fraction (305°C < T ⁿ < 400°C)				
ρ (g/cm ³)	0.8298	0.8470	0.8189	0.8267
μ (cSt)	4.98	4.40	5.07	4.34
LA (mg KOH/g)	3.57	3.37	45.28	3.42
IS (mg KOH/g)	30.42	64.62	64.10	44.61
IR (–)	1.450	1.448	1.445	1.445
C (1A)	1A	1A	1A	1A
1A, acid value; IR, refractive index; IS, saponification value; C, copper corrosiveness.				

Table 6. Physicochemical analysis of hydrocarbon-like fractions produced by laboratory fractional distillation of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using Vigreux columns of 10, 30, and 50 cm, operating without reflux.

Physicochemical properties	Distillation with reflux			Distillation with reflux		
	15% (wt) Na ₂ CO ₃			Column height 50 cm		
	Column height (cm)			(wt%) Na ₂ CO ₃		
	10	30	50	5	10	15
Distillation fraction (40°C < T ^b < 175°C)						
q (g/cm ³)	0.7494	0.7497	0.7492	0.8030	0.7530	0.7492
μ (cSt)	1.373	1.259	1.251	–	–	–
I.A (mg KOH/g)	2.08	2.57	2.96	94.42	3.14	2.96
I.S (mg KOH/g)	5.29	5.29	5.73	36.34	22.45	5.73
I.R (–)	1.421	1.423	1.425	1.449	1.429	1.425
C (I.A)	1A	1A	1A	1A	1A	1A
Distillation fraction (175°C < T ^b < 235°C)						
q (g/cm ³)	0.782	0.787	0.788	0.8090	0.7820	0.788
μ (cSt)	1.845	1.778	1.733	–	–	–
I.A (mg KOH/g)	2.94	2.75	1.65	80.2	3.40	1.65
I.S (mg KOH/g)	9.27	5.28	5.22	48.89	19.82	5.22
I.R (–)	1.439	1.440	1.442	1.445	1.441	1.442
C (I.A)	1A	1A	1A	1A	1A	1A
Distillation fraction (235°C < T ^b < 305°C)						
q (g/cm ³)	0.823	0.824	0.827	0.8190	0.8090	0.827
μ (cSt)	3.610	3.528	3.245	–	–	–
I.A (mg KOH/g)	4.68	3.90	3.39	49.09	5.33	3.39
I.S (mg KOH/g)	38.20	43.60	48.63	39.20	25.18	48.63
I.R (–)	1.451	1.451	1.453	1.454	1.451	1.453
C (I.A)	1A	1A	1A	1A	1A	1A
I.A, acid value; I.R, refractive index; I.S, saponification value; C, copper corrosiveness.						

Table 7. Physicochemical analysis of distillation fractions produced by laboratory fractional distillation of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale, using Vigreux columns of 10, 30, and 50 cm, operating with reflux.

Physicochemical properties	Pilot column
	Column height (cm)
	100
Distillation fraction ($40^{\circ}\text{C} < T^{\text{B}} < 175^{\circ}\text{C}$)	
ρ (g/cm ³)	0.7171
μ (cSt)	0.59
I.A (mg KOH/g)	0.334
I.S (mg KOH/g)	10.52
I.R (–)	1.401
C (1A)	1A
Distillation fraction ($175^{\circ}\text{C} < T^{\text{B}} < 235^{\circ}\text{C}$)	
ρ (g/cm ³)	0.7512
μ (cSt)	0.85
I.A (mg KOH/g)	0.42
I.S (mg KOH/g)	9.25
I.R (–)	1.420
C (1A)	1A
Distillation fraction ($235^{\circ}\text{C} < T^{\text{B}} < 280^{\circ}\text{C}$)	
ρ (g/cm ³)	0.7862
μ (cSt)	1.52
I.A (mg KOH/g)	0.34
I.S (mg KOH/g)	10.56
I.R (–)	1.439
C (1A)	1
I.A, acid value; I.R, refractive index; I.S, saponification value; C, copper corrosiveness.	

Table 8. Physicochemical analysis of distillation fractions produced by pilot distillation with internal reflux, of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale, using a differential distillation-packed column of 100 cm height.

almost constant along with the column height for the experiments carried out in laboratory scale, with and without reflux. For the distillation experiments carried out in laboratory scale without reflux, a total of four hydrocarbon-like fractions were collected (gasoline, kerosene, light diesel, and heavy diesel), while for the experiments under reflux conditions, only three hydrocarbon-like fractions could be collected (gasoline, kerosene, and light diesel). This is probably because of the recycling of part of the distillates back into the distillation column. In addition, the densities of gasoline, kerosene, and light diesel produced by fractional distillation in laboratory scale with reflux superposed exactly those of kerosene, light diesel, and heavy diesel produced by fractional distillation in laboratory scale without reflux, showing the importance of operating under reflux

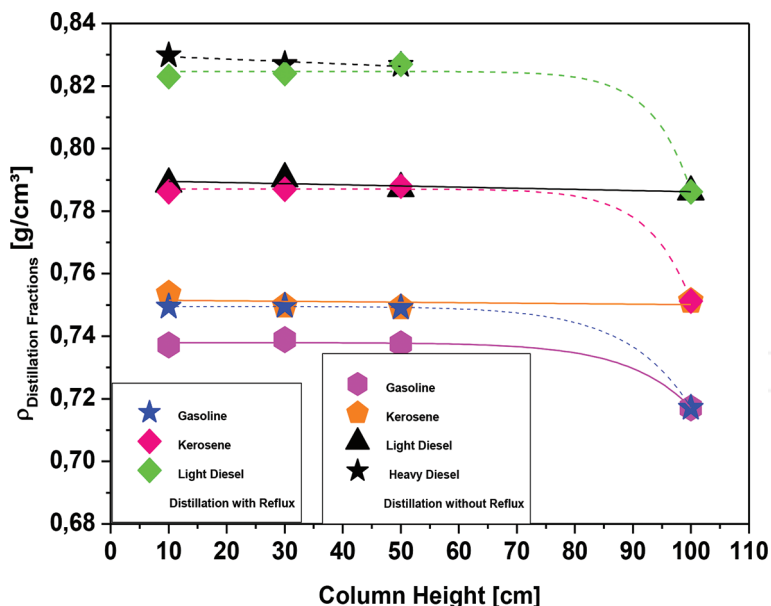


Figure 4. Density of hydrocarbon-like fractions produced by laboratory distillation of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 , with and without reflux using columns of 10, 30, and 50 cm, and a pilot-packed distillation column of 100 cm.

conditions to separate properly the hydrocarbon-like fractions. The densities of hydrocarbon-like fractions produced by fractional distillation in pilot scale, using a differential distillation column, packed with borosilicate-glass raschig rings, of 100 cm height, were lower in comparison to those produced by fractional distillation in laboratory scale, with and without reflux. Finally, the use of reflux made it possible to cut the hydrocarbon-like fractions properly, correcting the lower density limits, as observed by Almeida et al. [22–24], and thus matching the densities of kerosene and diesel fuels according to kerosene aviation specifications (QVA-1/JET A-1) of ANP 37 [68] and diesel S10 specification of ANP 65 [67].

3.4.2. Acid values of distillation fractions

The acid values of hydrocarbon-like fractions, produced by laboratory distillation of OLP (450°C and 1.0 atm, with 15% (wt) Na_2CO_3), without reflux using columns of different heights ($L_1 = 10$ cm, $L_2 = 30$ cm, $L_3 = 50$ cm), and a pilot-packed distillation column of 100 cm, with internal reflux, are illustrated in **Figure 5**. The acid values of hydrocarbon-like fractions decreased in a linear fashion with increasing column height for the experiments carried out in laboratory scale, without reflux, as shown in **Figure 5**. This is probably caused by the concentration of lighter volatile compounds in the vapor phase with increasing column height, so that the chemical compounds conferring the acidity of hydrocarbon-like fractions, particularly those of medium and long carbon chain length present in OLP, cannot reach the top of the distillation column, being present in small concentrations in the gaseous phase. The

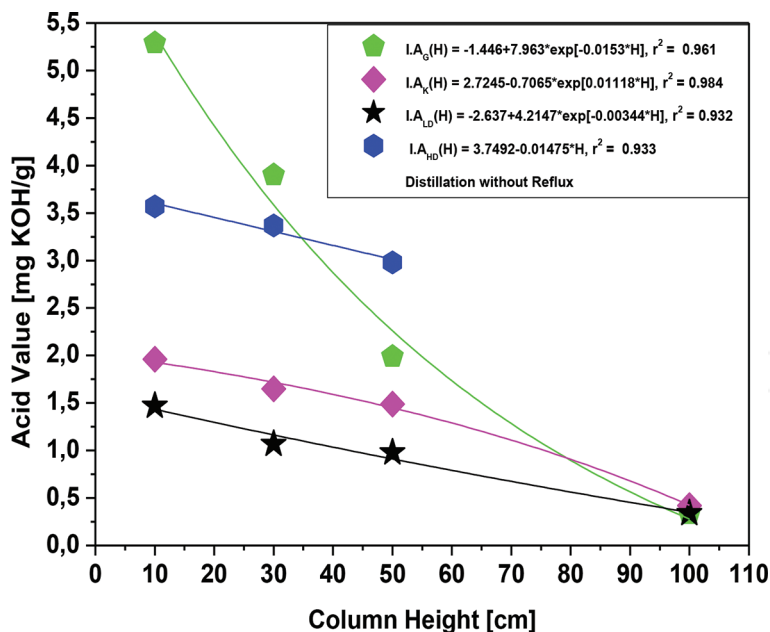


Figure 5. Acid values of distillation fractions produced by laboratory distillation of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 , without reflux using columns of 10, 30, and 50 cm, and a pilot-packed distillation column of 100 cm height.

acid values of distillation fractions also decreased with increasing boiling temperature ranges, except the heavy diesel-like fraction, which is in accordance with the results reported by Elkasabi et al. [64], for acid values of tail-gas reactive pyrolysis (TGRP) distillation fractions. The acid values of hydrocarbon-like fractions decreased with increasing Na_2CO_3 content, for distillation experiments in laboratory scale, using a column of 50 cm, with and without reflux, showing that fractional distillation of OLP with high acid values was ineffective. The acid values of hydrocarbon-like fractions produced by fractional distillation in pilot scale, using a differential distillation column, packed with borosilicate-glass raschig rings, of 100 cm height, were lower in comparison to those produced by fractional distillation in laboratory scale, with and without reflux. This showed that use of packed distillation columns improved not only the de-acidification process, but also the physicochemical properties of distillation fractions.

3.5. Chemical analysis of OLP and distillation fractions

3.5.1. FT-IR of OLP and distillation fractions

Figures 6–8 illustrate the FT-IR analysis of OLP obtained at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na_2CO_3 , hydrocarbon-like fractions, produced by fractional distillation, using a pilot-packed distillation column of 100 cm height, and light diesel-like fractions, produced by laboratory distillation, using columns of 10, 30, and 50 cm height, without reflux. The

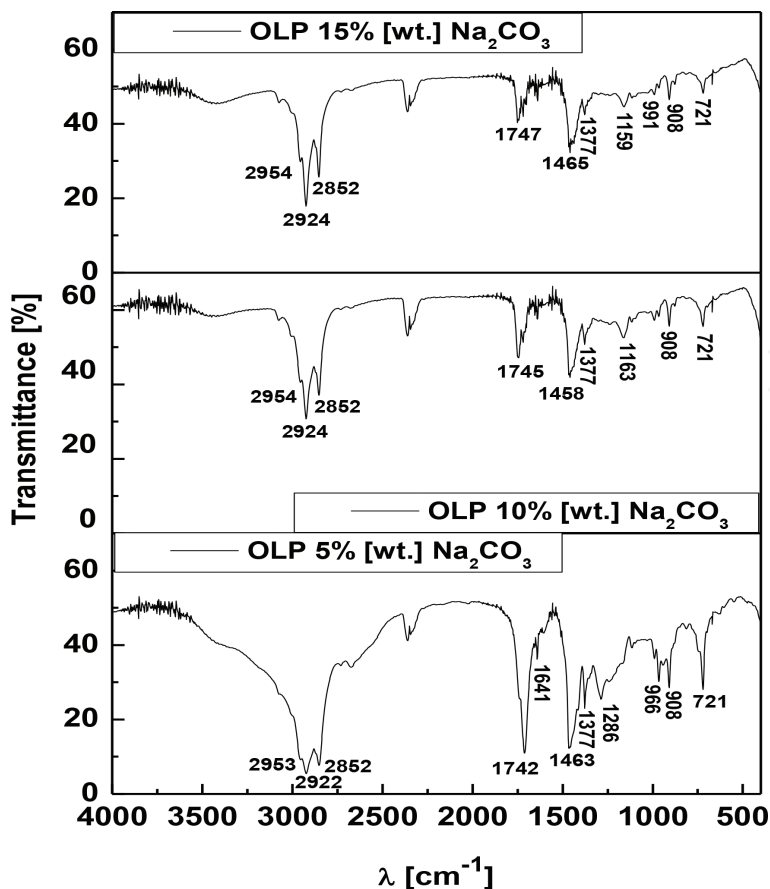


Figure 6. FT-IR of OLP obtained by catalytic cracking of palm oil at 450°C and 1.0 atm, with 5, 10, and 15% (wt) Na₂CO₃ in pilot scale.

identification of absorption bands/peaks was done according to previous studies [21, 24]. The spectrum of OLP obtained with 5% (wt) Na₂CO₃ presented a wide band of axial deformation at 3435 cm⁻¹ compared to OLP obtained with 10 and 15% (wt) Na₂CO₃, characteristic of O–H intramolecular hydrogen bond, indicating probably the presence of fatty alcohols and/or carboxylic acids. This band was also observed for gasoline and kerosene-like fractions, using a pilot-packed distillation column of 100 cm height, as well as light diesel-like fraction, using columns of 10, 30, and 50 cm height, without reflux, both obtained by distillation of OLP at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃. The spectra of OLP and distillation fractions exhibited intense peaks between 2921 and 2964 cm⁻¹ and between 2858 and 2964 cm⁻¹, indicating the presence of aliphatic compounds associated with methylene (CH₂) and methyl (CH₃) groups. This confirmed the presence of hydrocarbons [21–24]. One can also observe for OLP and distillation fractions, except for light diesel-like fraction, produced by laboratory distillation without reflux, using columns of 10 cm, the presence of bands at

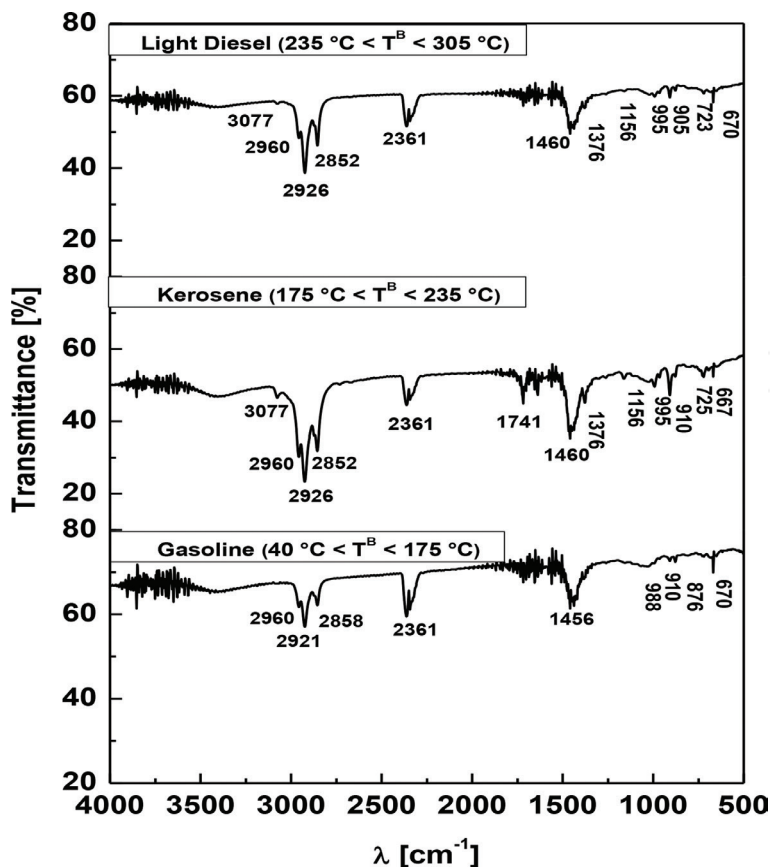


Figure 7. FT-IR of hydrocarbon-like fractions produced in a pilot-packed distillation column with internal reflux of 100 cm height with OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale.

2361 cm^{-1} , characteristic of asymmetrical axial deformation of CO_2 . In addition, both OLP obtained at 450°C and 1.0 atm, with 5% (wt) Na_2CO_3 , exhibited the presence of an intense and larger axial deformation band between 3200 and 2500 cm^{-1} , characteristic of hydroxyl (O–H) groups [39, 40], indicating the absence of carboxylic acids. This is according to the OLP acid value of 51.56 mg KOH/g . An intense axial deformation band has been observed for OLP, whose intensity decreases with Na_2CO_3 content, characteristic of carbonyl (C=O) groups, with peaks at 1742 , 1745 , and 1747 cm^{-1} probably associated with a ketone and/or carboxylic acids [21–24]. This is according to the acid values of OLP presented in **Table 1**, with its highest value obtained with 5% (wt) Na_2CO_3 . These peaks were also observed in kerosene, produced by pilot-scale distillation, and light diesel, produced by laboratory distillation without reflux, using columns of 30 cm. The spectra of OLP and distillation fractions were exhibited between 1455 and 1465 cm^{-1} , a characteristic asymmetrical deformation vibration of methylene (CH_2) and methyl (CH_3) groups, indicating the presence of alkanes [21–24]. The spectrum of OLP and distillation fractions was identified at 1377 cm^{-1} , except for light diesel, produced

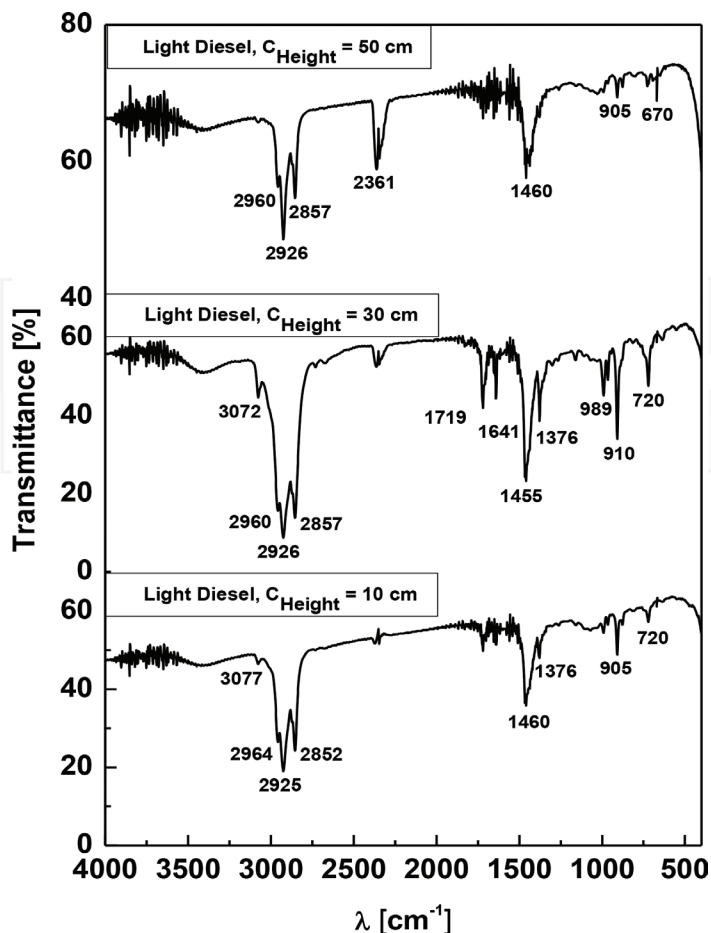


Figure 8. FT-IR of light diesel-like hydrocarbon fraction produced by laboratory distillation without reflux using columns of 10, 30, and 50 cm height with OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale.

by pilot-scale distillation and by laboratory distillation without reflux, using columns of 50 cm, a band of symmetrical angular deformation of C–H bonds in the methyl group (CH_3) [21–24]. The peaks between 995 and 905 cm^{-1} for OLP and distillation fractions were characteristic of an angular deformation outside the plane of C–H bonds, indicating the presence of alkenes [21–24]. The spectra of OLP and light diesel fraction exhibited bands between 721 and 667 cm^{-1} , peaks characteristic of an angular deformation outside the plane of C–H bonds in the methylene (CH_2) group, indicating the presence of olefins [21–24]. The FT-IR analysis of OLP identified the presence of aliphatic groups (alkenes, alkanes, etc.), as well as oxygenates (carboxylic acids, ketones, fatty alcohols), and the presence of aliphatic groups (alkenes, alkanes, etc.) in light diesel fraction.

3.5.2. GC-MS of OLP and light diesel-like hydrocarbon fraction

Figures 9 and 10 illustrate the chromatograms of OLP obtained by catalytic cracking of palm oil at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale and light diesel-like hydrocarbon fraction produced by fractional distillation, using a pilot-packed distillation column with internal reflux of 100 cm height. The classes of compounds, summation of peak areas, and retention times of chemical compounds identified by GC-MS of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 and light diesel-like fraction produced by pilot fractional distillation of OLP, using a differential distillation column of 100 cm height, are described in **Table 9**. GC-MS detected the presence of hydrocarbons such as alkenes, alkanes, alkynes, ring-containing alkenes, ring-containing alkanes, and dienes, as well as oxygenates such as ketones and fatty alcohols. OLP is composed of 92.84% (area) hydrocarbons (52.72% alkenes, 27.53% alkanes, 4.20% ring-containing alkenes, 6.33% ring-containing alkanes, and 1.21% dienes) and 7.16% (area) oxygenates (4.50% ketones and 2.66% fatty alcohols), while the light diesel-like fraction is composed of 100% hydrocarbons (57.08% alkenes, 34.85% alkanes, and 8.07% ring-containing alkanes). In both OLP and light diesel-like fraction, GC-MS had not identified the presence of carboxylic acids. The results were in accordance with the low acid values of OLP (3.55 mg KOH/g) and light diesel-like fraction (0.34 mg KOH/g) presented in **Tables 1 and 8**. The concentration of hydrocarbons in OLP, expressed in % (area), was higher compared to similar studies reported in the literature [21–24]. The chemical composition of OLP indicated the presence of heavy gasoline compounds with C_9 and C_{10} (C_5 – C_{10}), kerosene-like fractions (C_{11} – C_{12}), light diesel-like fractions (C_{13} – C_{17}), and light heavy diesel compounds with C_{18} and C_{19} (C_{18} – C_{25}), as reported in the literature [22–24]. The light diesel-like fraction presented carbon chain lengths between C_{10} and C_{20} with the following carbon chain lengths: alkenes C_{10} – C_{20} , alkanes C_{10} – C_{16} , and ring-containing alkanes C_{11} – C_{12} . It may be observed that

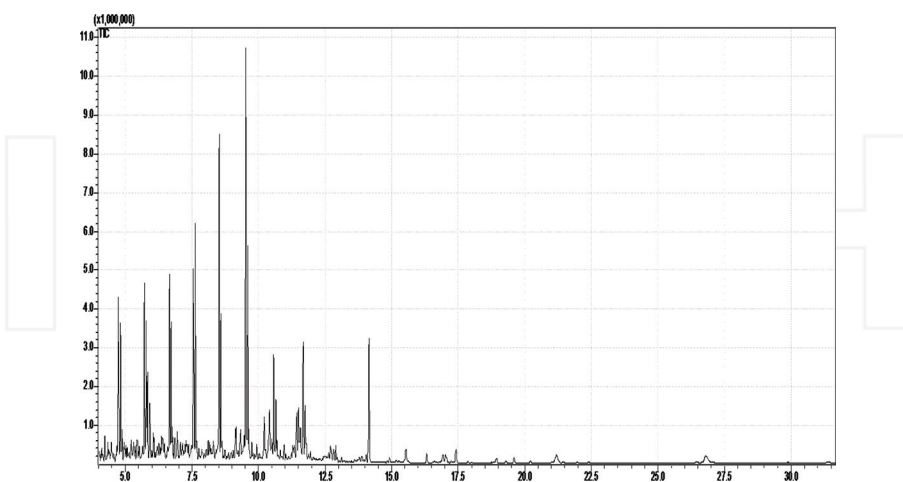


Figure 9. GC-MS of OLP obtained by catalytic cracking of palm oil at 450°C and 1.0 atm, with 15% (wt) Na_2CO_3 in pilot scale.

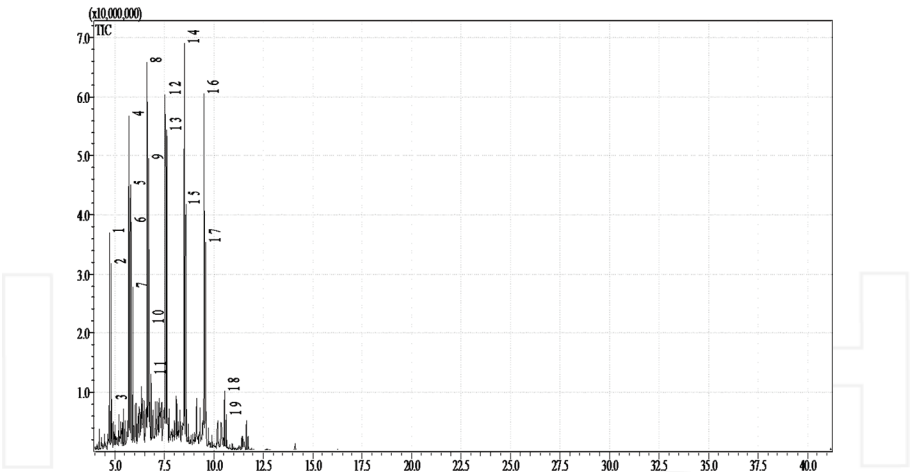


Figure 10. GC-MS of light diesel-like hydrocarbon fraction produced in a pilot-packed distillation column with internal reflux of 100 cm height with OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃ in pilot scale.

OLP, 15% (wt)		Light diesel-like fraction, 15% (wt)	
Class of compounds: chemical compounds	RT (min)	Class of compounds: chemical compounds	RT (min)
<i>Alkenes</i>		<i>Alkenes</i>	
1-Decene	4.74	1-Decene	4.74
4-Decene	4.87	2-Decene	4.87
(3E)-3-Dodecene	5.92	1-Undecene	5.71
1-Dodecene	6.65	1-Dodecene	6.65
(2E)-2-Dodecene	6.76	5-Tetradecene	6.76
1-Tridecene	7.56	1-Tetradecene	7.56
1-Tetradecene	8.51	1-Pentadecene	8.51
(9E)-9-Octadecene	9.46	1-Heptadecene	9.52
1-Pentadecene	9.52	9-Eicosene	10.56
(3Z)-3-Hexadecene	10.49	Σ (Area%) =	57.08
1-Nonadecene	11.58	<i>Alkanes</i>	
1-Heptadecene	11.68	Decane	4.82
Z-5-Nonadecene	12.71	Undecane	5.79
Σ (Area%) =	52.72	Dodecane	6.72
<i>Ring-containing alkenes</i>		Tridecane	7.64
1-Propyl-1-cyclohexene	4.48	Tetradecane	8.58
1-Butylcyclohexene	5.45	Pentadecane	9.59

OLP, 15% (wt)		Light diesel-like fraction, 15% (wt)	
Class of compounds: chemical compounds	RT (min)	Class of compounds: chemical compounds	RT (min)
1-Octyl-1-cyclopentene	8.15	Hexadecane	10.63
1-Hexyl-1-cyclopentene	9.16	Σ (Area%) =	34.85
1-Decyl-1-cyclohexene	9.32	Ring-containing alkanes	
1-Hexyl-1-cyclohexene	10.41	1,2-Dibutyl-cyclopropane	5.83
Σ (Area%) =	4.20	1-Pentyl-2-propyl- cyclopropane	5.92
Alkanes		Nonyl-cyclopropane	6.84
Decane	4.82	Σ (Area%) =	8.07
Undecane	5.79		
Dodecane	6.72		
Tridecane	7.63		
Tetradecane	8.58		
Pentadecane	9.60		
Nonadecane	11.76		
Σ (Area%) =	27.53		
Ring-containing alkanes			
Isobutylcyclohexane	4.23		
1,2-Dimethylcyclooctane	4.96		
Butylcyclohexane	5.22		
1-Pentyl-2- propylcyclopropane	5.83		
Cyclododecane	6.85		
Decylcyclopentane	8.11		
Nonylcyclopentane	9.13		
Cyclopentadecane	9.64		
<i>n</i> -Nonylcyclohexane	10.22		
1-Pentyl-2- propylcyclopentane	11.80		
Σ (Area%) =	6.33		
Dienes			
4,6-Decadiene	5.08		
Z-1,6-Undecadiene	6.04		
(2E,4Z)-2,4-Dodecadiene	6.36		
Σ (Area%) =	1.21		

OLP, 15% (wt)		Light diesel-like fraction, 15% (wt)	
Class of compounds: chemical compounds	RT (min)	Class of compounds: chemical compounds	RT (min)
<i>Alkynes</i>			
6-Tridecyne	6.96		
Σ (Area%) =	0.85		
<i>Ketones</i>			
2-Pentadecanone	14.14		
2-Nonadecanone	17.42		
Σ (Area%) =	4.50		
<i>Alcohols</i>			
Oleyl alcohol	11.43		
Σ (Area%) =	2.66		

Table 9. Classes of compounds, summation of peak areas, and retention times of chemical compounds identified by CG-MS of OLP obtained at 450°C and 1.0 atm, with 15% (wt) Na₂CO₃ and light diesel-like fraction produced by pilot fractional distillation of OLP, using a differential distillation column of 100 cm height.

the presence of gasoline heavy compounds with C₁₀ (C₅–C₁₀), kerosene fractions (C₁₁–C₁₂), and light heavy diesel compounds with C₁₈, C₁₉, and C₂₀ (C₁₈–C₂₅) in light diesel-like fraction, showed that fractional distillation in a pilot-packed distillation column of 100 cm with internal reflux was not capable of proper separation of the hydrocarbon-like fractions. This is probably caused by the limitation of internal reflux.

4. Conclusions

The yields of distillates and gas decreased along with the column height, while that of bottoms products increased, for experiments with and without reflux. The yields of distillates and gas increased with increasing catalyst content, while that of bottoms products decreased. In addition, distillation under reflux conditions showed higher distillates yields and lower bottoms products yields compared to the fractional distillation without reflux, as well as the absence of heavy diesel-like fractions. The densities of distillation fractions increased with increasing boiling temperature intervals, remaining almost constant along with the column height. In addition, the densities of gasoline, kerosene, and light diesel produced by fractional distillation in laboratory scale with reflux superposed exactly those of kerosene, light diesel, and heavy diesel produced by fractional distillation in laboratory scale without reflux, showing the importance of operating under reflux. The use of reflux made it possible to cut the hydrocarbon-like fractions properly, correcting the lower density limits. The acid values of hydrocarbon-like fractions decreased with increasing column height for the experiments with and without reflux. The acid values of distillation fractions showed a tendency to decrease

with increasing boiling temperature ranges. In addition, acid values of distillation fractions decreased with increasing Na_2CO_3 content, for distillation experiments using a column of 50 cm, with and without reflux. The distillation experiments in pilot scale showed gasoline, kerosene, and light diesel-like acid values of 0.33, 0.42, and 0.34 mg KOH/g, proving that use of packed distillation columns improved not only the de-acidification process, but also the physicochemical properties of distillation fractions. FT-IR of OLP and distillation fractions identified the presence of aliphatic hydrocarbons (alkanes, alkenes, etc.) and the absence of carbonyl groups. The light diesel-like fraction was composed of 100% hydrocarbons with an acid value of 0.34 mg KOH/g, density of 0.7862 g/cm^3 , and kinematic viscosity of $1.52 \text{ mm}^2 \text{ s}^{-1}$, proving the technical feasibility of OLP de-acidification by the fractional distillation process.

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