Article

Light Fatty Acid Methyl Esters in Biodiesel Derived from the Gueiroba (*Syagrus oleracea*) Kernel Oil to Blend with Jet-A1 Kerosene for Aviation Fuel

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The approach proposed here is focused on the separation of light fractions (corresponding to fatty acids with molecular chains between 8 to 14 carbons) from the fatty acid methyl esters (FAMES) of the biodiesel obtained by the reaction of transesterification of triacylglycerols in the kernel gueiroba oil (*Syagrus oleracea*) with methanol. The whole biodiesel was fractionated through atmospheric distillation in a single glass column with thermal insulation. Such a separation produced 59.79% in volume of light biodiesel (LB), which was mixed with the standard mineral Jet-A1 kerosene (cf. ASTM, corresponding to the QAV-1, cf. the Brazilian standard of the ANP) for aviation, in the volumetric ratios LB:Jet-A1 2:98; 5:95; 10:90 and 20:80. The values of density, water content, distillation analysis, flash point, calorific value and freezing point were carefully checked for their compliance with the official recommendations for jet fuel. It was found that the mixtures richest in the Jet-A1 mineral kerosene, that is, those containing no more than 5% LB by volume, well meet the recommended standards and are technologically viable to replace pure Jet-A1 kerosene for the propulsion of turbine aircraft.

Keywords: aviation fuel, blended Jet-A1 kerosene, esters fractioning, gueiroba oil, light biodiesel

Introduction

Widely recognized as a primary factor linking the growth and development of the economy of nations and human life standard, the global availability of promptly usable energy sources is hardly accompanying the population and the economic growths, especially in emerging markets.[1] Conventional energy sources have more often carried along harmful threatens to the natural environment. A parallel run for the development of new cleaner sources, particularly concerning liquid fuels, has been thus on the way, over the last decades.[2]

Chemically, kerosene is a mixture of a petroleum derivative mainly formed by aliphatic hydrocarbons.[3] It is an oily, pale yellow or colorless liquid with a characteristic odorously fraction obtained from the oil distillation column at 150-300 °C; its volatility is intermediate between the gasoline and the diesel fuel.[4] According to American Society for Testing and Materials (ASTM) standard D1655,[5] the aviation fuel is named as Jet-A1 kerosene, and for Brazilian standards, according to Brazilian National Petroleum, Gas and Biofuels Agency (ANP) Resolution No. 37 (2009)[6] the aviation fuel is called QAV-1 (this resolution was later replaced by the ANP Resolution No. 856/2021,[7] which contains also specifications for the alternative kerosene and its mixtures with QAV-1, specifically renamed as JET-C).

The ASTM standard D1655 specifies the recommended limiting values of the physical and chemical features for the Jet-A1 and Jet-A. They are two very similar fuels, but the Jet-A1 is mainly used in the USA, whereas Jet-A is used in other countries; again, the Jet-A1 is formally recognized under the denomination QAV-1, by the Brazilian legislation. The so-named Jet-B (ASTM D6615)[8] consists of a mixture

of gasoline and kerosene, with similar properties as of the Jet-A1, except for its freezing point and density values. The Jet-B is particularly directed for military aircraft.[9]

Using mineral kerosene to sustain the intense global traffic of airplanes adds a lot of environmental consequences through the greenhouse gas (GHG) stock in the Earth's atmosphere, especially carbon dioxide (CO_2).[10] Despite of being a relatively small (2.6%) contributor to total annual anthropogenic CO_2 emissions, the global commercial aviation keeps growing at a rate of approximately 5% a year.[11] Alternatives are sought to mitigate the atmospheric consequences due to emissions from carburant engines. Biofuels are thought to be an effective alternative on this way, as the biomass used as raw material to produce a burnable fuel leads to a very low net balance of the accumulated carbon stock in the environment from its combustion: the photosynthetic crops to produce the industrial biomass feedstocks uptake an amount of CO_2 that ideally should be equivalent to the amount released into the atmosphere, on burning the biofuel. Another favorable characteristic of biofuels is the very low sulfur content in most green biomass: the emission of sulfur dioxide (SO_2) is much lower if compared to the conventional fossil fuels.[12]

The technical regulations for the so denominated alternative jet fuels (AJF) for airplane engines are ruled by the ASTM D7566[13] and by the Brazilian ANP Resolution No. 856/2021,[7] which also specify the chemical-industrial routes to produce aircraft fuels based on synthesized paraffinic kerosene's, namely SPK-HEFA, SPK-FT, SPK-ATJ, SPK-A, and SIP, as overviewed in the literature,[14] or hydrotreated vegetal oil (HVO)[15-18] to aviation fuel.

An intriguing point is that fatty acid methyl (or ethyl) esters, as produced from the catalyzed transesterification of triacylglycerols in vegetable oils, are not formally recognized as AJFs. The so resulting fuel constitutes the conventional biodiesel (chemically, a mixture of fatty acid methyl or ethyl esters), used to power vehicles or stationary engines.[19] The Brazilian ANP 856 essentially basis its recommendations for AJFs on the international ASTM D1655 and ASTM D7566 standards, which make no specific mention to blends with bio-oil-derived esters: paraffinic biokerosene instead must comply with the ASTM D7566 (or with some corresponding parts of ANP 856) recommendations, in order to get compatibility with the existing aircraft fuel.[14]

The main chemical pathway to produce biodiesel is through the transesterification chemical process, which may be performed via alkaline (potassium or sodium hydroxide), acid or enzymatic homogeneous catalysis. The reaction rate under homogeneous alkaline catalysis is approximately 4,000 as fast as the same reaction catalyzed with the same amount of acid; the alkaline catalyst is therefore the most industrially used process. The transesterification reaction still requires short molecular chain alcohol, which is most commonly methanol, even though ethanol, propanol, butanol and amyl alcohol may be alternatively used.[20]

Even though some essays regarding the use of palm (*Elaeis guineensis*)[21,22] and macaúba (*Acrocomia aculeata*)[21,23] oil-derived FAMEs (fatty acid methyl esters), followed by atmospheric distillation to fraction and separate esters of shorter molecular chains, have been earlier reported in the scientific literature, this alternative still requires further rigorous checking for the physical and chemical characteristics of the resulting blends of Jet-A1 kerosene with light FAMEs, in order to assure its compliance with the officially recommended standard characteristics of airplane fuels.

The prospects in having FAME admixed to the mineral kerosene Jet-A1 as a fuel to propel turbine airplanes imply some critical technological developments. For instance, the freezing point must stay below −47 ℃, according to the ASTM D1655 (or ANP 856), and this may be hardly attainable for sole ester-rich mixtures.

The fractioning by distillation to obtain light FAME from the babassu palm (*Attalea speciosa*) oil reportedly met the main ASTM D1655 recommendations for blends with up to 6% light FAME by volume.[24] Similar results were reported for the use of FAME from *Jatropha curcas*,[25] camelina (*Camelina sativa*),[26] palm[22] and macaúba.[21] Those studies were based on distillation processes with variable technical complexities. Procedures involving molecular distillation and vacuum distillation are techniques that involve considerable cost, as well as require controlling critical variables, such as pressure and temperature. Differently from those, the present research relied on an atmospheric distillation,[21] which is a well dominated and is a widely used industrial unit operation and is not especially dependent on more rigorous control of specific variables.

This proposed alternative to preparing blends formed by Jet-A1 (QAV-1) and light biodiesel implies some interesting challenges to cope with, as the physical and chemical features of these prepared blends must be rigorously evaluated to check for their compliance with the ASTM D1655 or ANP 856 standards, more specifically: values of density, water content, flash point, calorific value, and freezing point as well as a distillation analysis and standard chemical profiles from the gas chromatography analysis of the product. The ASTM D7566, which deals with AJF's, and the ANP 856 Brazilian standards do not mention specifically about blends of Jet-A1 kerosene with esters.

This report describes the production of a light FAME (fatty acids with short-molecular chain, ranging from C8 to C14)[27-29] obtained through the methanolic transesterification (catalyzed with KOH) of triacylglycerols from the kernel oil of *Syagrus oleracea* (Mart.) Becc., a Brazilian native plant, commonly known as gueiroba, to be blended, in variable proportions, with the Jet-A1 mineral kerosene as a new approach to getting fuels fully complying with the standard international recommendations for usable fuel to turbine-propelled airplanes.

Experimental

About 5,000 coconuts from native gueiroba (*Syagrus oleracea* (Mart.) Becc.) palm trees were purchased from a local producer, in the municipality of Monte Carmelo, Minas Gerais, Brazil. The fruits were exposed for drying under the direct sunlight for 15 days, from a month following their harvesting date. The coconuts were then manually broken, and the endocarp was removed. The gueiroba coconuts with a yellowish appearance or those visibly affected by any phytopathological agent or plague were discarded. A simple sieve was used to separate the endocarp mass from the remaining fibers or any eventual impurity. The obtained endocarp material was packed in a plastic bag and stored in a freezer at approximately −10 °C.

Oil extraction

The gueiroba kernel oil was extracted with a Soxhlet setup, by using *n*-hexane as the solvent, in the following steps: (*i*) the raw oily feedstock was ground in a blender; (*ii*) a 24 cm-diameter, 0.16 mm thick qualitative filter paper was used to remove any remaining 4-12 mm particles from the oily biomass; (*iii*) the oil extraction itself, with the heating blank control, meaning the sole *n*-hexane solvent temperature above 68 °C, and the condenser water temperature at approximately 10 °C. The average extraction took 4 h. By completing this first phase of the oil extraction, all residual material and the used glassware were washed in-place with *n*-hexane. About 20 L of the solvent was used in the whole extraction process, including the final washing. The after-used leaching *n*-hexane was filtered in a Büchner funnel coupled to a vacuum pump, in a set used to finally separate the residual oil from washing the Soxhlet extractor glassware. The so-filtered residual oil along with the oil from the primary Soxhlet extraction were poured into a rotary evaporator (60 °C; 60 rpm and 650 mm Hg) for a complete oil-solvent separation. The recovered clean *n*-hexane could thus be cyclically used as a solvent for new oil extraction.

Analysis of vegetable oil

The extracted bio-oil obtained from the gueiroba kernels was evaluated for its viability as a material containing the precursor triacylglycerol for the transesterification process: (*i*) relative density analyses at 20 °C (ASTM D1298);[30] (*ii*) water content (ASTM D6304);[31] (*iii*) acidity index[32,33] and (*iv*) peroxide index.[34]

Transesterification and distillation

The chemical process of the methylic transesterification with potassium hydroxide as a homogeneous catalyst followed the conventional methodology, as reportedly used by Harter *et al*.[23]

The fraction of light esters (meaning esters of fatty acid with molecular chain length ranging from 8 to 14 carbons), or, for short, light biodiesel, was obtained from atmospheric distillation of the biodiesel. The conventional distillation with some modifications was used following the methodology earlier described by Harter *et al*.,[23] with a steadily increasing temperature of the biodiesel flask. The distilled fractions were collected from an outlet at about 25 cm from the bottom and about 5 cm from the top of the condenser column, starting at 180 °C and continued up to 270 °C, according to readings on a glass thermometer at the top of the column. The total volume of the collected fractions light esters corresponded to 60% of the initial volume.

Biofuel blends and analysis

The blends were prepared simply by admixing the equivalent of 2, 5, 10 and 20 vol% of the light biodiesel to the mineral Jet-A1 kerosene.

The so obtained blends and the sole individual fuels (i.e., the light biodiesel or the Jet-A1 mineral kerosene) were subjected to analyses for the (*i*) pycnometer relative density (according to the ASTM D1298[30] standard at 15 °C and 20 °C); (*ii*) water content, by the Karl Fischer method (ASTM D6304);[31] (*iii*) distillation at atmospheric pressure (ANP Brazilian standard, according to the ABNT NBR 9619);[35] (*iv*) flashpoint (ANP Brazilian standard, ABNT NBR 7974);[36] (*v*) calorimetry (calorific value) by ASTM D4529[37] and (*vi*) freezing point determination, by interpreting data from exploratory differential calorimetry analysis (DSC), which informed about the melting temperature profile for the samples.

The gas chromatography analyses according to the European standard EN 14103:2003[38] of the whole biodiesel, of the light biodiesel and of the distillation residue were

performed to allow breaking down their composition in esters and to confirm the reliability of the distillation process. The chromatograms were obtained with a Thermo™ gas (Uberlandia, Brazil) chromatograph Focus® GC model, equipped with a Carbowax® capillary column 30 m × 0.32 mm × 0.25 μm. Oven setting: initial temperature, 110 °C; heating rate, 20 °C min⁻¹, up to 190 °C (4 min). The carrier gas was nitrogen, at a flow rate of 1.5 mL min⁻¹. Injection at a flow split ratio, 30:1; injector temperature, 250 °C. Detection with flame ionization detector at 250 °C.

Melting point

Differential scanning calorimetry analyses were performed on a Universal V4.5A TA Instruments equipment Model TA Q20 (Uberlândia, Brazil), in an aluminum hermetic flask under an inert atmosphere, by reading at every 5 °C min⁻¹, with the temperature ranging from −60 to 10 °C. Samples were initially frozen at −60 °C in propanone and liquid nitrogen. Thereafter, heating was started at a rate of 5 °C min⁻¹ until reaching the preset limit of 10 °C. Two runs were performed. Only data from the first run were effectively used.

Results and Discussion

Transesterification

The density for this gueiroba kernel oil was found to be 0.895 g cm⁻³; water content, 651.2 ppm (or 0.06512% v/v) acidity index, 2.240 mg KOH g⁻¹ and peroxide index, 0.378 meq kg⁻¹. As far as the biodiesel production is concerned, there is no reported reference value[19,39,40] for density. However, it is recommended of low density. Except for the acidity index, which was slightly higher than the reference values (maximum of 2.0 mg KOH g⁻¹), these values are well within the recommended range for an oil feedstock for the transesterification process with significant esters yields: water content should be < 0.5% v/v and peroxide index limited to 10 meq kg⁻¹.

Through the transesterification reaction of triacylglycerols with methanol, 2.90 kg (corresponding to ca. 3.24 L) of oil produced 2.21 kg or (ca. 2.54 L) of biofuel

and 0.50 kg (ca. 0.40 L) of crude glycerol, as a byproduct of the reaction.

To determine the reaction mass balance in biodiesel from this reaction, the formula proposed by Gabriel[41] led to a chemical yield of 76.3% biodiesel, 17.3% glycerin and chemical losses of 6.4%. The yellowish and clear appearance of the biodiesel obtained at this stage indicates that the transesterification and washing processes were indeed effective, rendering a product reasonably clean.

Biodiesel distillation

The atmospheric distillation of the produced biodiesel yielded 1,435 mL, from a starting volume of 2,400 mL. This distilled volume corresponded to 59.79 vol% of the initial volume, a result that confirms the effectiveness in planning to stop the distillation at the stage corresponding to ca. 60 vol% of the initial volume.

The composition in fatty acid methyl esters of this kernel gueiroba biodiesel, its distilled biodiesel, and the distillation residue are presented in Table 1.

Density

These results evidence that for all blends prepared by admixing gueiroba light biodiesel to the Jet-A1 kerosene, the density at both temperatures, 15 and 20 °C, are below the maxima values recommended by both ANP (771.3 to 836.6 kg m⁻³) and by the ASTM (775 to 840 kg m⁻³) (Figure 1). Only the values for the sole light biodiesel are above the maximum recommended limits, both at 15 and 20 °C (Figure 1).

The density values for the samples increase by increasing the proportion of light biodiesel. In its single form, the light biodiesel is denser than the kerosene; the density value for the blend is linearly proportional to its biodiesel content (Figure 1). It is also clear that the density of the samples steadily decreases as the temperature increases, and this is well evident for these samples: values at 20 °C are systematically about 0.5% lower than those at 15 °C.

Similar results were reportedly found by Llamas *et al.*,[22,26] regarding the camelina and babassu,[26] and coconut[22] oils, and also by da Silva *et al.*,[21] for FAMEs from the palm and the

Table 1. Composition in fatty acid methyl esters of kernel gueiroba biodiesel, distilled biodiesel, and distillation residue

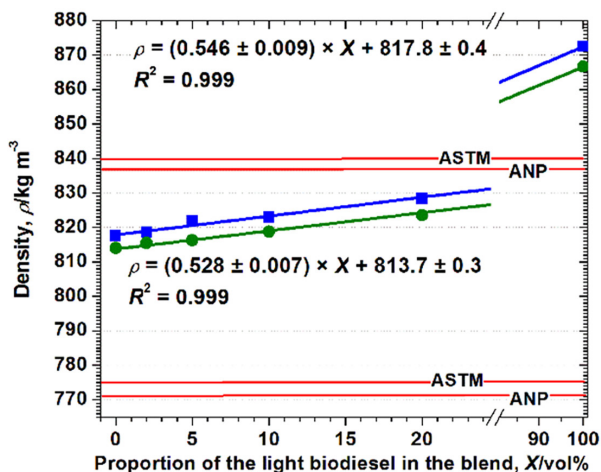| Sample	Fatty acids forming the methyl esters / mass%								
	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Gueiroba biodiesel	10.5	5.5	23.3	4.7	7.0	3.2	15.9	27.3	2.5
Distilled (light) biodiesel	22.5	9.9	43.3	11.1	3.7	2.1	6.3	1.2	–
Distillation residue	0.9	1.0	25.7	21.5	11.9	8.5	26.1	4.3	–

Figure 1. Values of density (ρ) for the blend samples at 15 °C in blue and 20 °C in green. The ASTM and ANP recommended maximum and minimum values are indicated in red, as horizontal dot lines.

macaúba oils: the density values are directly proportional to the biodiesel contents in the blends with Jet-A1 kerosene.

The density values for these blended biofuels (Figure 1) reflect the additive contribution of their components with good reliability and mean that admixing the light biodiesel implies no important intermolecular attraction or repulsion to significantly affect the linear behavior of the blend density, in this range of concentrations.

The sole light biodiesel does not meet the recommended standards. The same remark was reported by Llamas *et al.*,[26] and by da Silva *et al.*[21] However, for these blends, it is plausible to state that, as far as only the relative density (or specific mass) is concerned, the light biodiesel admixed to the Jet-A1 at up to 20 vol% points to good prospects towards the development of aviation fuels.

Water content

Recommended limiting values for water contents are not clearly explicit, either in the ASTM or in the ANP regulatory standards, for blends of FAME kerosene jet fuel. According to the ASTM D7566 and ANP No. 856/2021,[7] the water is limited to 75 mg kg^{-1} for the SPK-ATJ, SPK-A, SIP, SPK-FT, and SPK-HEFA only. The water content may be critical to the normal engine work, as the long run water can lead to corrosion problems, wear and clogging of filters and other parts.[22]

FAMEs are more hygroscopic than the Jet A-1 fuel: in the blended fuels, the moisture is expected to be, to some extent, higher than that of the sole kerosene.[22] Any water in the airplane fuel may form ice, due to the low temperature in high altitude flying, and this may result in aircraft's engine working problems.[22,42] The water can appear in three forms in a jet fuel: (*i*) dissolved in the fuel, from the

atmosphere, and typically exists in jet fuels at levels of 50-100 ppm at typical ground ambient temperatures; (*ii*) in suspension, following the cooling of relatively warm fuel, which releases water as fine droplets, and can form super-cooled droplets and (*iii*) in the form of free water, coming primarily from water condensing from air entering the tank from the vent system during aircraft descent.[43] These circumstances point hygroscopicity to be a critical point regarding the direct use of FAMEs as fuel itself or a fuel component to propel aircraft turbines.

The water content should be kept below the maximum acceptable level, even if the engine is well able to burn the mixture of fuel containing some water to power the aircraft engine. The recommended maximum is 90 ppm-v water (or, roughly, 110 mg kg^{-1} water, for a density of 0.8175 kg L^{-1} for the Jet-A1 kerosene at 15 °C), for normal system operations and up to 260 ppm-v water for emergency system operations, according to Baena-Zambrana *et al.*,[44] and Holmes *et al.*,[42] for the jet fuel.

The linear relationship between the volumetric composition and the water content of the blend agrees with elsewhere reported results.[21,22,26] Using the linear equation 1 and Figure 2, the maximum mixture would be 3.6 vol% FAMEs (X, in %) for a limit of 75 mg kg^{-1} water (y_{H_2O}, in mg kg^{-1}), and 11.9 vol% FAMEs for a limit of 110 mg kg^{-1} water.

$$y_{H_2O} = (4.2 \pm 0.11) \times X + 60 \pm 4 \qquad (1)$$

Controlling the water content for an airplane biofuel composed of biodiesel blends is a challenge. Viable strategies must be created to overcome this disadvantage, an alternative being the route of chemical alterations in the molecular structures of FAMEs to decrease their hygroscopicity.
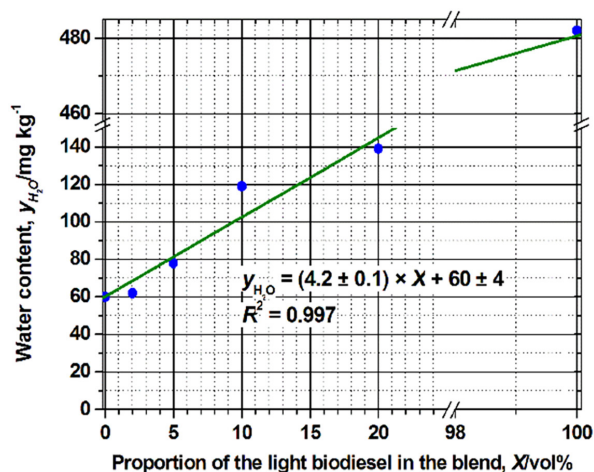

Figure 2. Water content for the samples of Jet-A1 kerosene, the light biodiesel, and their blends.

Distillation of the biodiesel

The efficiency to separate fractions of light FAMEs from the whole biodiesel through atmospheric distillation may be drawn from data presented in Table 2.

These results show compliance to the recommended limits by ASTM D1655 and ANP 856 standards, for all blends, as shown in Table 3. However, the values for the sole light biodiesel is once again slightly outside of the recommended limits.

From the Figure 3, the temperature gap between the 10% evaporated and the final boiling point increases by increasing the proportion of biodiesel in blends. It is interesting to notice that the distillation analysis parameters showed two different aspects: (*i*) the final boiling point increases with the temperature, and (*ii*) the points of 10% evaporated have no significant differences: all points had similar results and the behavior of the biofuel mixtures remains almost the same at different temperatures.

It is observed an increase of the final boiling temperature on increasing the proportion of light biodiesel in the blends: the sole biodiesel sample exceeds by relatively few the officially recommended limit.

The individual boiling points for the methyl esters (length Cn, in which n means the number of carbon atoms in the molecular chain of the corresponding fatty acid) composing this biodiesel are relatively high: 194-195 °C
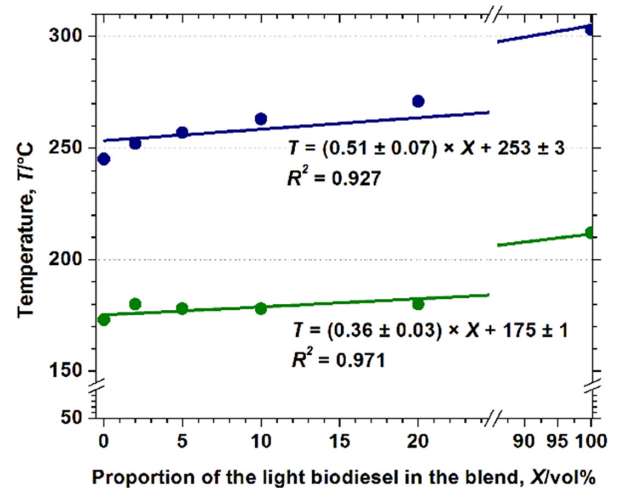

Figure 3. Final boiling points and points of 10% evaporated for the blends and pure samples of kerosene and the light biodiesel. The blue solid line represents the final boiling points; the green line represents the points of 10% evaporated.

for C8;[45] 223-225 °C for C10;[46] 261-262 °C for C12[47] and 296-300 °C for C14.[48] Thus, these boiling points may have influenced the behavior of the final boiling point curve, which increases as the proportion of the light biodiesel in the blend increases. This behavior is in accordance with the remarks by Yang *et al.*,[14] who reportedly stated that the chain length is a dominant factor for the boiling point, also influencing the distillation unit operation.

The mass proportion of residue remaining from

Table 2. Breakdown of the ester in the distilled fractions (according to percent volumetric FAMEs:Jet-A1 ratios) and in the samples of sole kerosene and light biodiesel. The recommended limits are according to the ASTM D1655[5] and to the ANP No. 856/2021[7]

Property	Recommended limit (ANP and ASTM)	Sole kerosene	2%	5%	10%	20%	Sole light biodiesel
10% evaporated / °C	max. 205.0	173.0	180.0	178.0	178.0	180.0	212.0
50% evaporated / °C	–	202.0	207.5	206.0	206.5	211.0	249.0
90% evaporated / °C	–	233.0	234.0	231.0	239.0	247.0	272.0
Final boiling point / °C	max. 300.0	245.0	252.0	257.0	263.0	271.0	303.0
Residue / %	max. 1.5	1.5	1.2	1.3	1.4	1.4	1.8

Table 3. Essential physical and chemical characteristics of the fuels: density (at 15 and 20 °C), water content, flash point, and calorific values for the blends, the sole kerosene, and the sole light biodiesel. Recommended limiting values, according to the international ASTM D1655[5] and to the ANP No. 856/2021[7] are also presented

Property	ASTM D1655 standard limits	ANP 856/2021 standard limits	Jet-A1 kerosene	2	5	10	20	100 Light biodiesel
			Light biodiesel proportion in the Jet-A1 + light biodiesel blends / vol%					
Density 15 °C / (kg m^{-3})	775 to 840		817.5	818.6	821.9	822.9	828.4	872.5
Density 20 °C / (kg m^{-3})		771.3 to 836.6	814.0	815.5	816.2	818.7	823.5	866.7
Water / (mg kg^{-1})			60	62	78	119	139	482
Flash point / °C	38	38 or 40	47	53.5	52	51	49	60
Calorific value / (MJ kg^{-1})	≥ 42.8	≥ 42.8	45.5	44.9	44.5	44.4	43.5	34.8

distilling the whole biodiesel is important to evaluate the tendency of the fuel to form lint, nozzle clogging, or related problems on burning during the jet engine operation. da Silva *et al.*[21] reported higher residue values for light biodiesel from macaúba and palm oils (2.0% of residue for all blends), which have not met the officially recommended standards. da Silva *et al.*[21] found no clear influence of the mass ratio Jet-A1 kerosene:light biodiesel on the proportion of the distillation residue.

From our data (Table 3 and Figure 3), the volumetric FAMEs:Jet-A1 ratio is only slightly correlated to the residue parameter. Again, the pure light biodiesel sample does not comply with the official limits set by regulatory standards, but the sole light biodiesel (LB) sample yielded less distillation residue (1.8%) than the blends (2% residue for all mixtures) and pure samples (2.4% residue for pure light biodiesel from both macaúba and palm oils), comparatively to the data reported by da Silva *et al.*[21]

Flashpoint

The results from Table 1 and Figure 4 evidence that for all blends and for the sole light biodiesel sample, the flashpoint values are well above the recommended critical minimum limit recommended and comply with both the ASTM and the ANP standards. It is important to notice that the flashpoint value decreases by increasing the proportion of light biodiesel in the blend, which is in line with reported data in literature.[49]

Calorific value (enthalpy of combustion)

The calorific value can be understood as the energy available in the fuel and is qualitative information of an
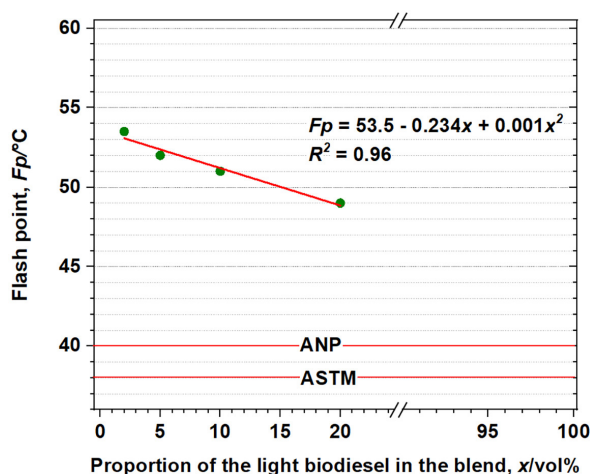
essential value determining the yields of power or heat, according to Francesquett *et al.*[50]

For aviation fuels, the ASTM and ANP standards recommend the same minimum limit of 42.8 MJ kg^{-1} for the kerosene calorific value (q_v), as represented by the solid red horizontal line in Figure 5. The calorific value for any blend can be obtained from the linear equation 2, where X means the volumetric FAMEs:Jet-A1 ratio, in %:

$$q_v = (-0.105 \pm 0.003) \times X + 45.4 \pm 0.1 \qquad (2)$$

Except for the sole light biodiesel sample, the values for these blends well comply with the official recommendations stated by both ASTM and ANP standards. From this linear behavior and the lower officially recommended limit (Figure 5) of 42.8 MJ kg^{-1} for the calorific value of the fuel, the expected composition limit, as the blend volumetric FAMEs:Jet-A1 ratio corresponds to a maximum of 37 vol% light FAMEs.
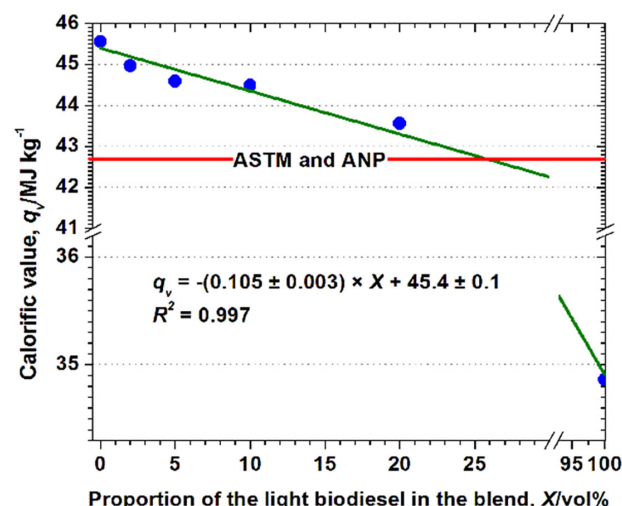

Figure 5. The calorific value for each blend and for the sole samples of kerosene and light biodiesel. ASTM and ANP recommended minimum value (42.8 MJ kg^{-1}) is indicated in red, as a horizontal line.

The calorific value is related to the molecular H:C:O ratio. This explains the higher calorific value of the commercial kerosene, which contains essentially hydrocarbons in its composition.[14] Being a mixture of esters, the calorific value of this biofuel tends to be lower than that of the kerosene. The water content obviously also influences the calorific value of a fuel. However, the values of water contents for these biofuels were found to be relatively low.

The sole Jet-A1 kerosene has a much higher calorific value than its blends with light biodiesel, which may impart a loss of power efficiency in an aircraft with the blended fuels. Specifically, the sample of the sole light biodiesel

Figure 4. The linear flash point behavior of the blends. The minimum recommended values by the ASTM D1655 and ANP 856 standards are indicated as red horizontal lines.

does not meet the recommended parameters, regarding the calorific value.

Freezing point

The values of the melting point were determined by identifying the phase change in the enthalpy DSC (differential scanning calorimetry) curve. The beginning of the fusion was characterized at the peak of the obtained curve, and the end at the left base of the curve, after the main peak of the endothermic reaction. With the purpose of estimating the freezing points, the final value of the melting process temperature was recorded.

Determining the melting point for fuel samples is not actually deduced from promptly reading the DSC pattern. Regarding the chemical nature of the fuel, the DSC pattern may show thermic events corresponding to the components of the mixture, each of them melting at different temperatures.[51]

The DSC curves for these blends, particularly those with higher biofuel contents, are even more complex: the kerosene itself contains several alkanes, including aromatics; the biodiesel is characteristically a mixture of fatty acid methyl esters.

There are some reportedly strategies to determine the melting point from the DSC pattern.[51-53] In the present case, the melting temperature was found by identifying the point just after the minimum of the endotherm valley on the half maximum at the right, corresponding to the side of the highest temperature of the peak, following the methodology described by Moynihan *et al.*,[51] The results are shown in Figure 6.

From the DSC data, there are significant differences between the curve for the Jet-A1 kerosene and that of the light biodiesel. For the kerosene itself, the DSC curve presents a complex profile, with a first low-temperature thermal event occurring close to −58 °C. This appears next to a broader event close to −52.1 °C temperature. The latter event is linked to the fusion of the kerosene, as it melts from −55 to −45 °C, depending upon its origin and degree of purity.

For this light biodiesel itself, two events are observed: one at −47.7 °C and other at −9.4 °C. Both events are associated with the fusion of fatty acid methyl esters, depending on the fractions of different numbers of atoms of carbon of the molecular structure of the esters and on their proportions in the mixture.

These results evidence that only blends with up to 5 vol% light biodiesels are potentially suitable for application as aviation fuel, regarding the freezing temperature of the mixture, which cannot be higher than −47 °C, according to both ASTM and ANP standards. A similar result was
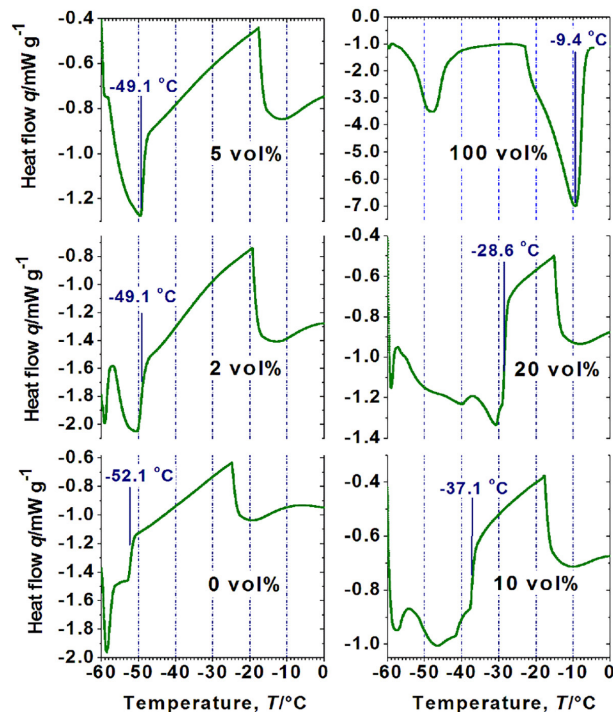

Figure 6. DSC curves and freezing points of pure samples (sole kerosene, 0 vol%; sole light biodiesel, 100 vol%) and blends of 2, 5, 10 and 20 vol% FAMEs.

reportedly achieved by da Silva *et al.*,[21] for biodiesel from the fruits of the macaúba palm tree.

It is expected to be possible to use this biodiesel produced from gueiroba source in this limit as aviation fuel. From the point of view of biodiesel application, it is interesting to look further for oil sources that present in their composition a higher proportion of short-chain, and eventually also unsaturated esters.

In comparison with results reported in the scientific literature, the studies by Llamas *et al.*[22,26] revealed similar values of the freezing point, where only mixtures of 5 and 10% responded to the maximum −47 °C limit for biofuels from camelina, babassu, palm, and coconut. To summarize, the freezing points of the blends are closely related to the biofuel content and on the chemical nature of the esters composing the biodiesel. For SPKs, the freezing point is also strongly related to three main factors: iso-paraffin content, alkylated aromatic content and carbon chain length of the bio-paraffins.[14] Zhang *et al.*[54] also state that the freezing point is strongly dependent on the number of carbons and the *n*-paraffin fraction.

The freezing point of pure light biodiesel is high if compared to that of the mineral kerosene, making it unfeasible for use on high altitude flights.[55] Dunn[56] reported that the long-chain saturated FAMEs have higher melting points than unsaturated FAMEs with the same length. This light biodiesel from the kernel oil of *Syagrus oleracea*

does contain 92.6% of saturated FAMEs (Table 1) and this contributes to substantially raise the freezing temperature of the blended fuel. The freezing points for some methyl (Me) esters (MeCn) of saturated fatty acid (Cn; n = number of carbon atoms of the molecular chain) are: MeC10, −21.4 °C; MeC12, −2.2 °C; MeC14, −12.4 °C; MeC16, +25 °C and MeC18, +34.5 °C.[57] The melting point for the MeC8 is reported to be −40 °C,[57] but Dunn[56] recalls that the freezing points from DSC cooling curves are slightly lower than the melting points from melting curves, due to hysteresis effects.

Conclusions

The atmospheric distillation was efficient enough to separate the light FAMEs fraction of the whole biodiesel derived from the gueiroba (*Syagrus oleracea* (Mart.) Becc.) kernel oil, to reach 86.8% fatty acid methyl esters with molecular length in the range of C8 to C14, in the distilled fraction.

This underdevelopment technological alternative to produce technically suitable blended air fuels, derived from such light FAMEs with the standard Jet-A1 mineral kerosene, has revealed the real potential for further advancements towards an economically interesting and an industrially feasible, by taking benefits from the existing conventional biodiesel plants, and environmentally safer jet fuel, relatively to the conventional fossil derivatives.

These results point to some critical challenges that must be planned, in this continuous effort towards new scientific attempts, to pave the foundations of this technological development, and ensure that the properties of such mixtures fully comply with the international technical recommendations. Two main characteristics must be immediately addressed from now on: (*i*) the water content in such a blended fuel, implying to chemically modify the hygroscopicity of the FAMEs, and (*ii*) the freezing temperature. The use of esters showed here should meet the following steps: (*i*) ester production (*ii*) light fraction separation by atmospheric distillation and (*iii*) deoxygenation. That last step should be based in a chemical way technically consistent and economically beneficial, to obtain the compounds with no oxygen.

At this stage, it can be stated that mixtures containing up to 5% by volume of this light biodiesel from the fruit kernel oil of the gueiroba palm (*Syagrus oleracea* (Mart.) Becc.) are suitable fuels for air transport, as the essential properties of these blended fuels meet recommended features, as regulated by the ASTM D1655 and ANP 856 standards, to propel jet aircraft engines.

Author Contributions

S. P. Chagas was responsible for conceptualization, investigation, formal analysis, data curation, laboratory analysis, writing-original draft preparation; D. Q. Santos for supervision, project administration, investigation, laboratory supervision; J. D. Fabris for conceptualization, investigation, revision, writing supervision, scientific analysis; L. V. L. Harter for investigation, laboratory support; J. Q. da Silva for investigation, visualization, laboratory support.

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