



Hydrogenated orange oil: A waste derived drop-in biojet fuel

David Donoso^a, David Bolonio^b, Rosario Ballesteros^a, Magín Lapuerta^{a,*},
Laureano Canoira^b

^a Grupo de Combustibles y Motores, ETS Ingeniería Industrial, Universidad de Castilla-La Mancha, Avda. Camilo José Cela s/n, 13071, Ciudad Real, Spain

^b Department of Energy & Fuels, ETS Ingenieros de Minas y Energía, Universidad Politécnica de Madrid, Ríos Rosas 21, 28003, Madrid, Spain

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ABSTRACT

Orange oil was extracted by steam distillation from the peels of oranges produced as waste in the orange juice factories. This raw orange oil, a potential source for biojet fuel, was analysed by FT-IR and GC-MS, and compared with distilled orange oil and pure D-limonene, which is its main chemical constituent. Both distilled orange oil and D-limonene were hydrogenated under reaction conditions (from 3 to 18 bar) which are mild enough to be industrially feasible, to improve its properties, especially to reduce their sooting tendency. Some important properties such as density, viscosity, heating values, lubricity, flash point, crystallization onset temperature, and smoke point were measured for hydrogenated orange oil and D-limonene (as a reference for comparison) at different conversions. These hydro-biofuels were blended with Jet A1 to check their suitability as biobased blending components for aviation. Based on the results obtained for the main aviation fuel properties, it is concluded that up to 15 vol% of partially hydrogenated orange oil could be blended with Jet A1 without any significant drawback for the performance of the actual airplanes. Flammability reduction systems would be needed to further increase the blend proportion of this drop-in biofuel in Jet A1.

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1. Introduction

The aviation fuels sector is facing from few years back the necessity to incorporate biofuels to its portfolio. The unsteady jet fuel prices, the instability of the geopolitical areas where the main crude oil reserves are located, the increasing social demand of less polluting and sustainable fuels, the inclusion of aviation sector in the new carbon dioxide trade emissions system established by EU Directive and the evidence that the aviation sector is difficult to electrify are some of the reasons for this incorporation [1]. Therefore, the International Air Transport Association (IATA) jointly with the American Society for Testing and Materials (ASTM) have approved the blend of six types of biofuels in different amounts (mostly up to 50 vol%) with the conventional jet fuel [2]. However, all approved biofuels share a common drawback in production because some quite complex biological/chemical transformation steps are required to become a “drop-in” biofuel, i.e. a biofuel that could be blended with the conventional jet fuel without any modification of the airplane tanks and turbines [3].

Orange oil is extracted from the orange, *Citrus sinensis*, peels (the orange peel part named flavedo, in opposition to the white peel part called albedo) by three main methods: cold pressing, solvent extraction and steam distillation [4]. This orange oil, used either as net raw oil [4], as raw oil blended with karanja oil methyl ester (KOME) [5,6], as raw oil blended with both KOME and alcohols [7], or after transesterification and emulsification [8], has been tested in diesel engines with limited success. However, to the best of our knowledge, it has never been tested as a blend component for aviation fuels despite its promising physical characteristics [9]. Chuck and Donnelly [9] reported that the blends of 20 and 50 vol% of D-limonene with Jet A1 accomplish the required values of density at 15 °C, kinematic viscosity at –20 °C, cloud point, freezing point, flash point and volatility (distillation curve). However, D-limonene (main component of orange oil) cannot be used in aviation fuels because of its high sooting tendency, which can be reduced by hydrogenation [10], among other processes [11,12]. Another terpenic biofuel tested as blend component for aviation fuel was turpentine (mostly composed by α - and β -pinene, with a small

* Corresponding author.

E-mail address: Magin.Lapuerta@uclm.es (M. Lapuerta).

proportion of α -limonene) at different hydrogenation levels, showing promising results when blended with Jet A1 up to 50 vol% [13]. Also, orange seed oil has been used as a diesel fuel component, although this is not a terpenic oil but a fatty acid oil [14].

Orange tree is the most commonly grown fruit tree in the world, constituting about 60% of the total citrus world production, which accounts for 100 Mt per year [15]. The orange juice industry generates worldwide 30 Mt of waste per year [16], which ends up in landfills and can generate severe environmental and economic problems [17,18], mainly in tropical and temperate climates (such as Indonesia [19] or Brazil [20,21]), where this agricultural production is predominant. Spain produces around 3.7 Mt of oranges per year, mainly in the Valencia and Andalusian regions (being first European and sixth world producer), generating around 1.2 Mt of waste [22]. With a non-optimized extraction yield (0.51 wt% on wet basis), this process could produce 6120 t of orange oil in Spain, which represents around 0.1% of the Jet A1 fuel consumed in Spain in 2019 (6921 kt) [23]. Clearly, this feedstock alone could not accomplish with the EU mandate of incorporation of biofuels to the aviation sector [24], but in the future energy scenario, a single source of biofuel will never satisfy the market objective, and instead, many sources should join to accomplish this objective.

Orange juice industry generates a large amount of waste, including orange peels. Fig. 1 shows a scheme of the processing of orange peels to obtain orange oil, among other products [25]. The main component of raw orange oil is α -limonene with minor amounts of long chain alkanes, alkenes, aldehydes, and fatty acid ethyl esters (FAEE). The majority of these compounds belong to the terpenoids, a family class of natural products also present in the pine resin and many other natural sources [26]. The term terpenoids is preferred over terpenes because terpenes are hydrocarbons and terpenoids may have oxygen or other elements, thus terpenoids is actually the most encompassing term [27]. The molecular structure of α -limonene suggest that this compound is well suited “a priori” as a blend component for Jet A1 because: (i) the carbon

number is within the usual carbon range of aviation kerosene, C_9 – C_{16} . (ii) it is a cyclic alkene (naphthene) and thus, probably its cold flow behaviour is expected to be much better than that of linear alkenes. Moreover, the production process of orange oil from orange peels is a very simple one as shown in Fig. 1, already carried out by the orange fruit companies, and it does not require complex chemical transformations as those necessary to obtain the aviation biofuels already approved by ASTM.

The main drawback of orange oil as blend component for Jet A1 is that this non-toxic compound, despite its waste origin from orange peels, is used in the nutraceuticals industry as an additive [27] and in the plastic industry as a monomer [28]. The actual production rate could be insufficient to satisfy simultaneously all markets, including aviation biofuels industry. However, some recent studies on genetic engineering with bacteria are directed to increase the production of α -limonene by fermentation of waste materials [29].

The purpose of this work is to revise the feasibility of blending orange oil, α -limonene (main component of essential orange oil [30]), and their partially hydrogenated products with Jet A1, and to measure some of their most demanding properties, thus assessing them as new drop-in biofuels.

2. Materials and methods

2.1. Fuels and reagents

α -limonene (98.0% purity) was supplied by the company Industrial Resinera Valcan SA (Cuenca, Spain). Commercial Jet A1 was supplied by Exolum, i.e. CLH (Madrid, Spain). Catalyst 1% Pt/ Al_2O_3 was purchased from Sigma-Aldrich. Dichloromethane and anhydrous ethanol (from Panreac) were used without further purification.

Navel late oranges of juice type were bought from a local market, with an average weight of 0.165 kg for each orange. The external parts of the orange peels (orange flavedo) was cut and

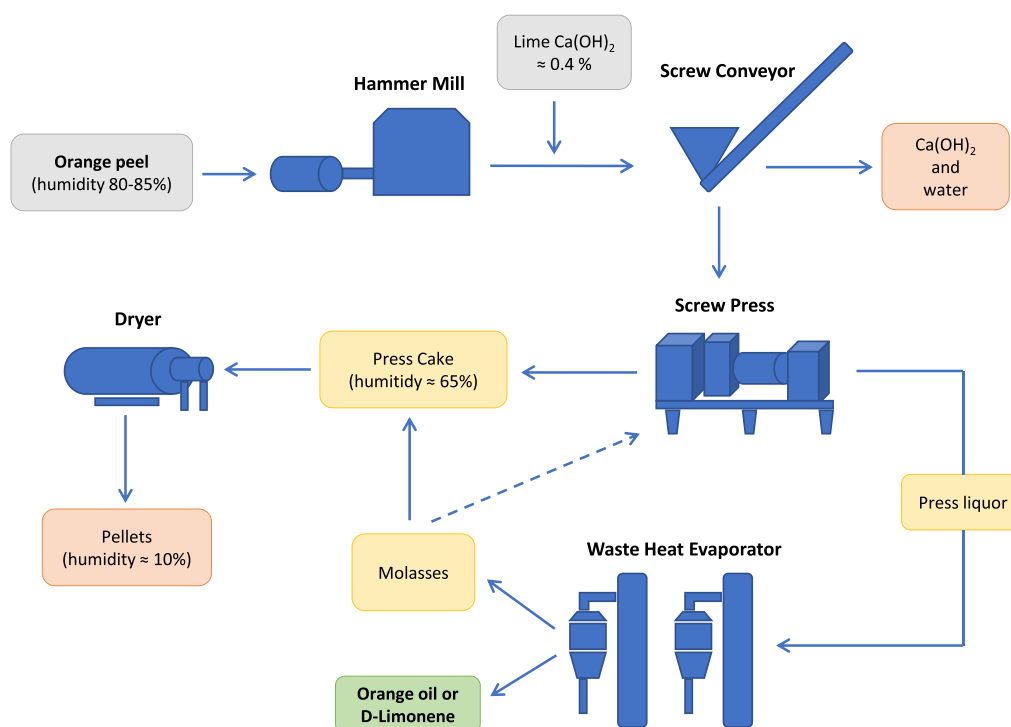


Fig. 1. Industrial process of production of orange oil.

separated from the white part (albedo) with a potato peeler. Between 150 and 192 g of flavedo orange peels were introduced in a 2 L flat bottomed flask with 1.5 L of warm distilled water. After soaking (1 h), this flask was connected with a silicone rubber tubing to a 2 L steam generation flask filled also with 1.5 L of distilled water and the flask was stopped with a safety valve. The flask containing the orange flavedos was connected to a Liebig refrigerant cooled by running water using a distillation head, and finally the refrigerant was connected to a 500 mL receiving flask (see apparatus in Fig. 1S of Supplementary Material). This steam distillation equipment was kept running at least 8 h, being necessary to refill the steam generation flask at least once during each distillation run. The raw orange oil was recovered in the receiving flask with a lot of water, and it was extracted with three successive 25 mL portions of dichloromethane and was decanted each time in a decanting funnel. The combined dichloromethane extracts were dried with anhydrous sodium sulphate, the solution was filtered, and the solvent was removed in a rotary evaporator Büchi 461 (Switzerland). The raw orange oil extraction yield was 1.1 g (0.6–0.7 wt% yield on a wet basis, 3.8–4.9 wt% yield on a dry basis, considering that the orange flavedo has 85 wt% humidity) and it contains 44.6 wt% of *D*-limonene (as shown in Table 1S). Two-fold steam distillation was done to increase the purity of *D*-limonene to 94.0 wt%. This product is denoted hereinafter as distilled orange oil [4].

2.2. Fourier transform infrared spectroscopy (FT-IR) and gas chromatography – mass spectrometry (GC-MS) analysis

FT-IR spectroscopy was done in a Nicolet 6700 instrument (Thermo Electron Corporation, USA) with the software Omnic version 8.0, placing a small drop of product between two circular sodium chloride disks (Aldrich, USA, 5.40 mm thick, 24.97 mm o.d.). Fig. 2S in Supplementary Material shows the FT-IR spectra of raw and distilled orange oil and *D*-Limonene.

The different chemical components of the products were identified in an Agilent 6890 series II gas chromatograph equipped with a mass selective detector (MSD5973) (Agilent, Madrid, Spain) and splits/splitless injector. The samples were run through a HP-5MS 5% Phenyl Methyl Siloxane column (30 m × 0.25 mm i.d. × 0.25 µm) using the following analytical conditions: injector temperature, 275 °C; split ratio, 50:1; injection volume, 1 µL; constant flow mode (He), 1 mL/min; oven program: remain 10 min at 40 °C, heat at 5 °C/min up to 250 °C and keep this temperature for 10 min. In each case, 10 µL of the sample were added in 990 µL of dichloromethane. The conditions of the mass detector were: electronic impact, 70 eV; *m/z* scan from 50 to 800 Da; resolution, 1000. The chromatograms and mass spectra of the compounds were analysed by the MSD ChemStation Data Analysis Application software of Agilent using the spectral library NIST. Fig. 3S in Supplementary Material shows the chromatogram for raw orange oil. The chromatograms of all products are shown in Section 3.2, except for raw orange oil which is shown in Fig. 3S in Supplementary Material (Tables 1S–6S show the chemical characterization of all products).

2.3. Fuel characterization

Density was measured using a 10 mL glass pycnometer inside an Ineltec climatic chamber at 15 °C and 45% relative humidity.

Kinematic viscosity was measured with viscosimeter (Cannon Fenske series 75) at –20 °C using an Ineltec climatic chamber and at 40 °C inside a Tamson (TV 2000) thermostatic visibility bath, following standard EN ISO 3104.

Higher heating value (HHV) was measured in a calorimetric bomb Parr 1351 (USA) following standard ASTM D240. The lower

heating value (LHV) was obtained from the measured HHV and the elemental composition of each fuel (see Table 7S in Supplementary Material), as described in Ref. [13].

Lubricity was measured with a HFRR (PCS Instruments) following the standard EN ISO 12156-1. The wear scar diameter (WSD) on the ball surface, which is inversely proportional to the lubricating efficiency, was obtained with a stereomicroscope Optika SZ-CTV equipped with 100x magnification lens. The ambient temperature and humidity were controlled using a climatic chamber with the use of salts. Repeatability was shown to be less than 20 µm [31], complying with the European standard, which requires a repeatability lower than 50 µm.

Flash point was measured following standard EN ISO 2719 and using SETA PM-93, an automated Pensky-Martens Closed Cup Flash Point Tester.

Cold flow behaviour was studied by differential scanning calorimetry (DSC). Crystallization Onset Temperature (COT) was determined as the temperature at which the peak of heat release from crystallization starts, using a Differential Scanning Calorimeter Q20 from TA DSC Instrument. DSC study comprises two heating-cooling cycles. First, the sample (approx. 30 mg) was heated to 40 °C and kept at this temperature for a period of 5 min. Second, the sample was cooled from 40 to –90 °C. After this temperature was reached, the sample was maintained at –90 °C for 5 min. The rate of temperature was chosen as 5 °C/min following previous studies which reported a good combination of resolution characteristics and timeliness [32].

Smoke point was measured in a standardized lamp as required in standard ASTM D1322. Two calibration blends of toluene and isooctane were prepared, with 20 and 40 vol% of toluene. Smoke points obtained for these calibration blends allowed calculating a calibration correction factor for the lamp of 1.01, applying the standard. Threshold Sooting Index (TSI) was calculated to compare sooting tendency between fuels, as proposed by Calcote and Manos [33] for diffusion flames. TSI was established within a 0–100 scale, with 0 corresponding to ethane and 100 to naphthalene.

2.4. Hydrogenation of distilled orange oil and *D*-limonene

Distilled orange oil or *D*-limonene as reagent (1 mol), absolute ethanol as solvent (ranging from 100 to 200 mL) and 1% Pt/Al₂O₃ as catalyst (4.0 g, powdered) were placed in a 1 L stainless steel autoclave Burton Corblin (Autoclave Engineers USA). The autoclave was evacuated with a vacuum pump KNF and filled with hydrogen three times up to the hydrogen pressure set for the experiments. Before experiments, 1% Pt/Al₂O₃ catalyst was activated (1 h, 2 bar H₂). The reaction mixture was stirred at 300 rpm throughout the experiment (5.5 h), which was carried out monitoring pressure (ranging from 3 to 18 bar H₂) and temperature (60 °C). Afterwards, the hydrogen was vented off and the catalyst was filtered through a 1.6 µm glass microfiber filter GF/A (47 mm o.d.) from Whatman (USA). Ethanol was removed using a rotary evaporator Büchi R-210, under 2000 Pa and 40 °C. To evaluate the conversion efficiency of hydrogenation, the bromine number of the hydrogenated terpene was measured following standard ASTM D1159. This property is defined as the mass of bromine (in grams) that react with 100 g of sample under the test conditions, and it allows to quantify the degree of unsaturation of the sample. The potentiometric titration was carried out stirring (650 rpm) the sample in a stirring plate Nahita-Blue 692/1 and measuring the potential with a platinum electrode ORP Crison 5056 and a potentiometer Crison microPH 2002. The conversion in the hydrogenation was quantified by Equation (1), where *BN*_i is the initial bromine number, and *BN*_f is the final bromine number.

$$\text{Conversion(\%)} = \frac{BN_i - BN_f}{BN_i} \cdot 100 \quad \text{Equation 1}$$

2.5. Experimental matrix

Density, viscosity at $-20\text{ }^{\circ}\text{C}$ and $40\text{ }^{\circ}\text{C}$, heating values, lubricity, flash point, crystallization onset temperature, and smoke point were measured on hydrogenated orange oils (0, 18, 51% conversion, denoted as O, HO1 and HO2, respectively), hydrogenated α -limonene (0, 26, 47% conversion, denoted as L, HL1 and HL2, respectively), and on Jet A1 (denoted as J) (see Table 8S in Supplementary Material). At least two repeats were done for each property. The six terpenic biofuels were blended (2.5, 5, 10, 20, 30% v/v) with Jet A1 and the same fuel characterization was performed (see Table 9S in Supplementary Material), except for viscosity and lubricity. Moreover, mean molecular formula, molecular weight, H/C ratio, stoichiometric fuel/air ratio, and Threshold Sooting Index were calculated for these fuels (including raw orange oil) based on their chemical composition (see Table 7S in Supplementary Material).

3. Results and discussion

3.1. Chemical characterization of orange oil

The chemical identity of orange oil products was characterized by FT-IR spectroscopy, with some differences between raw orange oil and distilled orange oil and very good match between distilled orange oil and pure α -limonene (see Fig. 2S in Supplementary Material), consistently with the high content of α -limonene in essential orange oils [30]. The bands between 2800 and 3100 cm^{-1} are characteristic of CH stretching vibrations for both sp^2 and sp^3 hybridized carbon atoms. The frequency of the small sharp peak at 3100 cm^{-1} is indicative of a $=\text{CH}_2$ group. In addition, a sharp $\text{vC}=\text{C}$ mode can be seen at $\sim 1645\text{ cm}^{-1}$. The bands at 1376 and 1437 cm^{-1} are assigned to deformation modes of CH_3 groups, the one at 887 cm^{-1} to the $=\text{CH}_2$ out-of-plane bending mode of vinylidene groups, and at 797 cm^{-1} to the $=\text{CH}$ out-of-plane mode of a trisubstituted alkene. The O–H vibration bands between 3000 and 3500 cm^{-1} denotes that raw orange oil has a lot of water, due to the extraction process of raw orange oil. However, distillation of orange oil to increase the content of α -limonene entails water removal as can be checked in distilled orange oil and pure α -limonene.

The raw orange oil was also analysed by GC-MS and the resulting molecular composition is summarized in Table 1S of Supplementary Material. The main component is α -limonene (44.6 wt%) and the following component is ethyl linoleate (10.4 wt%). The remaining components are long chain alkanes, alkenes, aldehydes, and fatty acid ethyl esters, and also other terpenoids whose molecular structures are shown in Fig. 2. However, since the ASTM does not allow any oxygenated compounds in jet fuels due to their oxidative tendency [34], distillation of orange oil was necessary to reduce presence of oxygen, increasing the presence of α -

limonene. Once distilled, orange oil was mainly composed by α -limonene (94.0 wt%) and by other mono- and sesquiterpenes, such as β -myrcene and α -pinene, and some terpenic alcohols (in very low mass fractions), such as linalool or α -terpineol, since fatty acid ethyl esters were removed (see Table 2S of Supplementary Material). Higher distillation of orange oil resulted in an almost pure α -limonene (98.0 wt%). Therefore, hydrogenation process was carried out with distilled orange oil and with pure α -limonene, the last one as a reference. Hydrogenated products of both distilled orange oil and α -limonene were also analysed by GC-MS (see Fig. 3) and explained in Section 3.3.

3.2. Hydrogenation of orange oil and α -limonene

Orange oil and α -limonene typically show a high sooting tendency because of their high olefinic character [13], which avoid their direct application as a blending component for aviation jet fuel. Consequently, hydrogenation was proposed to saturate double bonds of these compounds. The hydrogen pressure and ethanol volume used in distilled orange oil and α -limonene hydrogenations are detailed in Table 10S in Supplementary Material. The rest of parameters remained constant, as described in Section 2.4.

The hydrogenation results were moderate since the internal double bond remained almost unchanged in all reactions (see Fig. 4). As expected, the exocyclic double bond of this terpenoid (α -limonene) was more easily hydrogenized on 1% Pt/ Al_2O_3 than the endocyclic one [35]. At the conditions applied, hydrogenation of orange oil or α -limonene produced mainly 1-p-menthene and only minor amounts of p-menthane. However, no rings appeared to be scissed since these are more chemically stable. Medium hydrogen pressure (6 bar) resulted in a significant improvement of conversion with respect to low pressure (3 bar), but no relevant increase in

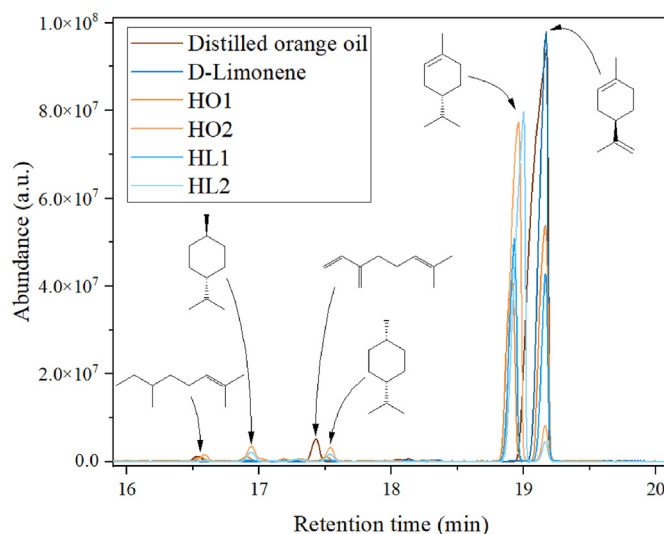


Fig. 3. Chromatogram of pure and hydrogenated biofuels.

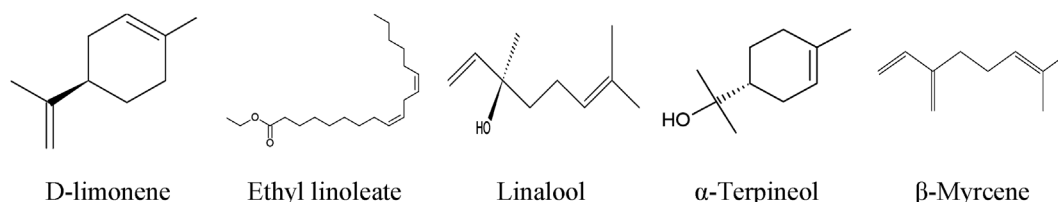


Fig. 2. Main terpenoids in orange oil.

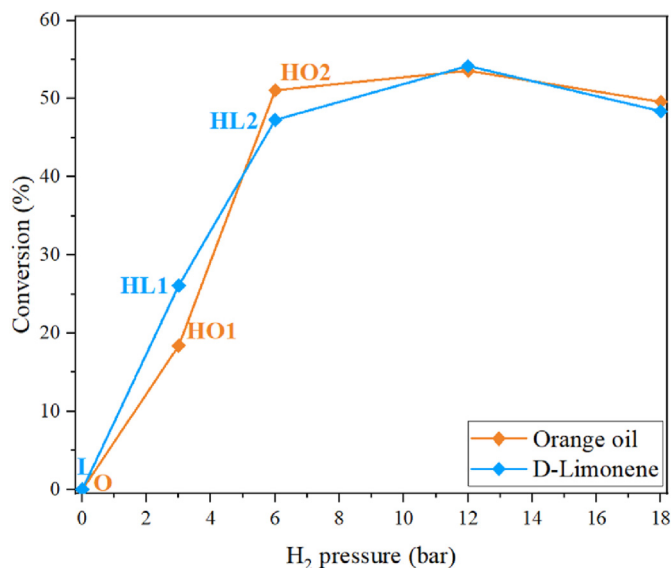


Fig. 4. Conversion vs H₂ pressure in orange oil and D-limonene hydrogenations (1 mol terpenoid, 100–200 mL ethanol solvent, 4.0 g catalyst, 60 °C, 300 rpm, 5.5 h).

conversion was obtained when higher pressure (12–18 bar) was applied. In summary, conversion is improved as pressure increases but only until 6 bar. The solubilization of hydrogen in the solvent increases with pressure, which increases the number of hydrogen molecules exposed to the catalyst, thus allowing to increase the hydrogenation of unsaturated compounds. However, we hypothesize that further hydrogenation including that of the endocyclic unsaturation or the cycle scission would require much more aggressive conditions, which would be industrially unfeasible.

With low pressure (3 bar), D-limonene was partially saturated to 1-p-menthene in case of HO1 and HL1 (see Tables 3S and 4S of Supplementary Material), obtaining a small amount of *trans*- and *cis*-p-menthane in both cases (0.8 and 1.8 wt%, respectively). With medium pressure (6 bar), D-limonene was completely hydrogenated to 1-p-menthene in case of HO2 and HL2 (see Tables 5S and 6S of Supplementary Material), and *trans*- and *cis*-p-menthane were obtained in higher amounts (3.5 and 4.4 wt%, respectively).

Other minor compounds of distilled orange oil, such as β -myrcene (2.4 wt%) and α -pinene (0.9 wt%), were also partially hydrogenated with both low and medium pressure. β -Myrcene (with three double bonds) was partially hydrogenated to 2-ethyl-6-methyl-1,5-heptadiene and *cis*-2,6-dimethyl-2,6-octadiene (1.0 wt%, with two double bonds) and 2,6-dimethyl-2-octene (1.0 wt%, with one double bond), when low pressure was applied, and it was also partially hydrogenated to 2,6-dimethyl-2-octene (1.3 wt%) when medium pressure was used. Finally, α -pinene was hardly hydrogenated to *trans*-pinane, obtaining only traces of the latter in both HO1 and HO2.

High yields were obtained in all hydrogenations, with an average yield of 92% in both distilled orange oil and D-limonene. Distilled orange oil and D-limonene hydrogenation products (O, HO1, HO2 and L, HL1, HL2) were characterised to check if the partial hydrogenation improved properties as sooting tendency (main property to upgrade), without affecting other ones (e.g. flash point, cold flow behaviour ...). Moreover, these biofuels were blended with Jet A1 (as explained in Section 2.5) to quantify the volume fractions that fulfil the limits established in ASTM D7566 standard.

3.3. Density

Hydrogenated orange oil and hydrogenated D-limonene resulted in values of density at 15 °C between limits (775–840 kg/m³) established by ASTM D7566 standard (see Fig. 5, left), since the hydrogenation process reduced the density of orange oil and D-limonene (higher and almost equal than the maximum limit, respectively), as expected. Densities of pure and hydrogenated biofuels were higher than that of Jet A1. All blends with Jet A1 fulfilled the limits and showed a linear trend respect to volume fraction, except in blends with low concentrations of biofuel, in which a small anti-synergistic effect (positive excess volume) was observed (see Fig. 5, right).

3.4. Kinematic viscosity

Orange oil, D-limonene and their hydrogenated ones showed a kinematic viscosity at –20 °C below the upper limit (8.0 mm²/s) for Jet A1 (Fig. 6, left). Therefore, any blend of hydrogenated orange oil and hydrogenated D-limonene (up to around 50% conversion) with Jet A1 would expectedly fulfil the limit, since fossil fuel resulted in 3.09 mm²/s at –20 °C. Kinematic viscosity increased as the

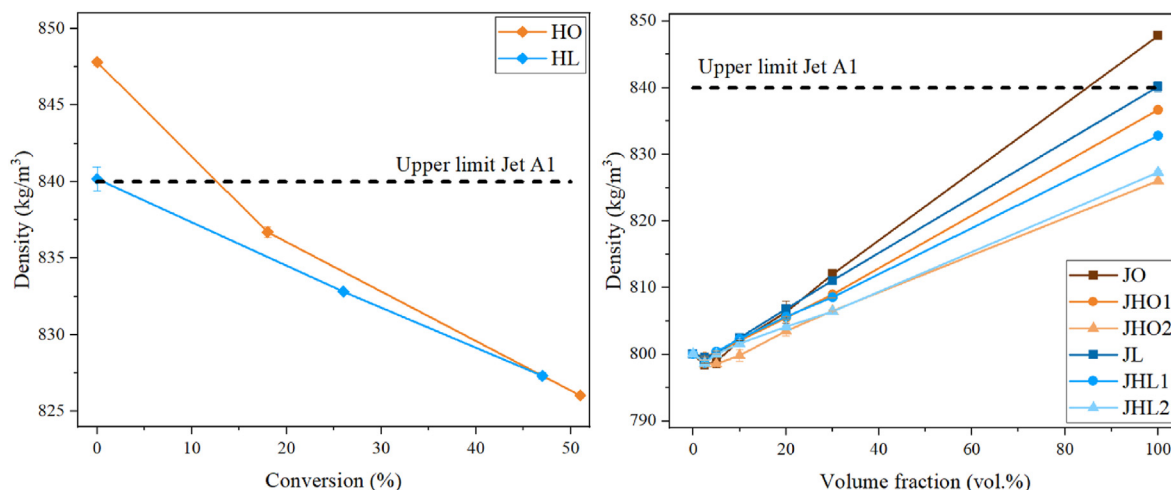


Fig. 5. Density of hydrogenated orange oil and D-limonene vs conversion (left) and of these hydro-fuels blended with Jet A1 (right).

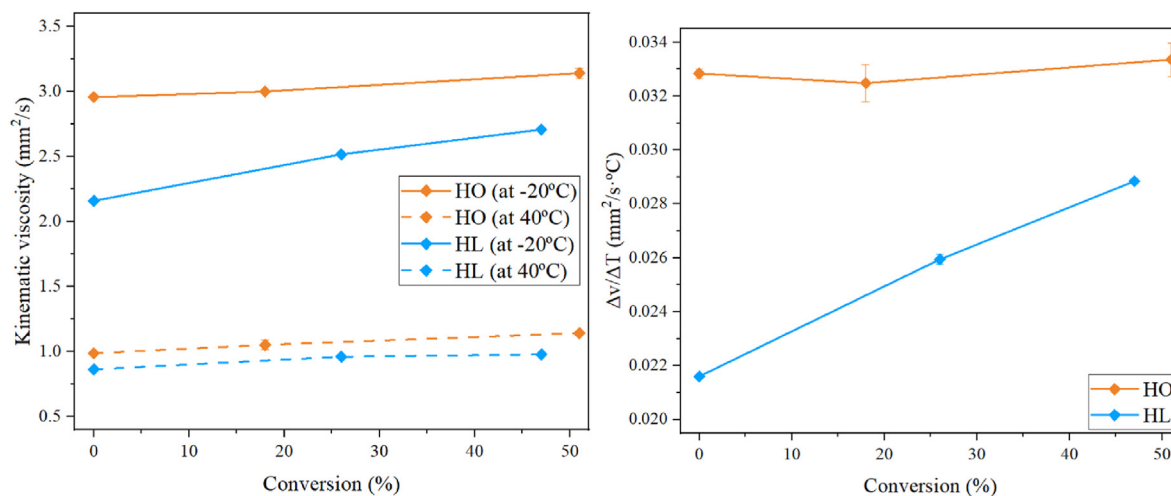


Fig. 6. Kinematic viscosity at -20°C and 40°C of both hydrogenated orange oil and D-limonene and Jet A1 (left) and absolute rate of decrease of viscosity with temperature vs. conversion (right).

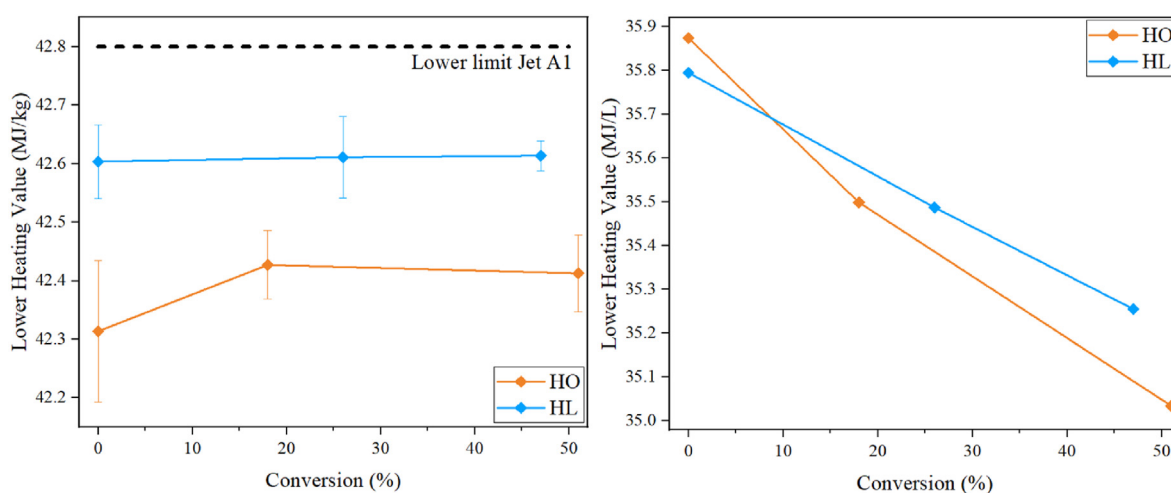


Fig. 7. LHV in mass basis (left) and in volume basis (right) of hydrogenated orange oil and D-limonene vs conversion.

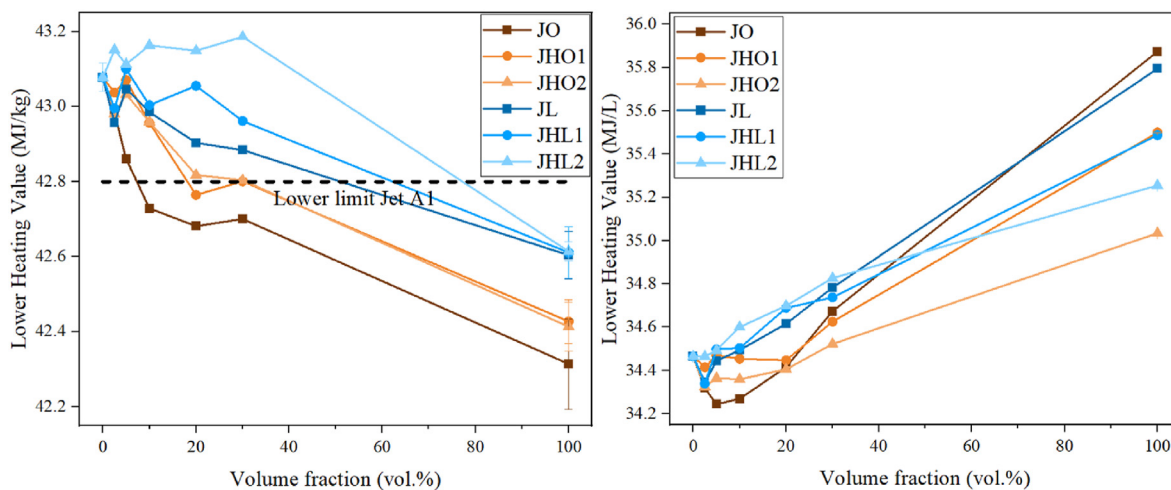


Fig. 8. LHV in mass basis (left) and in volume basis (right) of blends of both hydrogenated orange oil and D-limonene with Jet A1.

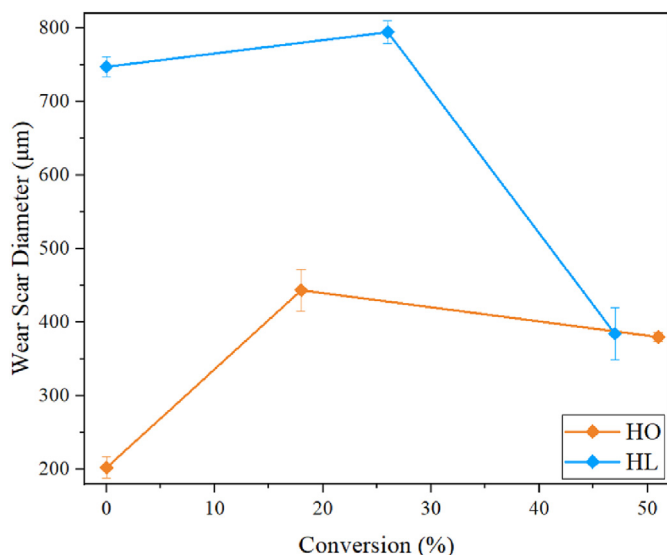


Fig. 9. WSD of hydrogenated orange oil and D-limonene vs conversion.

conversion progressed. The absolute rate of decrease in viscosity with temperature remained constant with conversion in case of hydrogenated orange oil, and thus showing similar values than Jet A1 ($0.033 \text{ mm}^2/\text{s} \cdot ^\circ\text{C}$), but this rate increased slightly and linearly as hydrogenation did in D-limonene (Fig. 6, right).

3.5. Heating values

Lower Heating Value (*LHV*) of orange oil resulted in 42.3 MJ/kg , which is quite similar to the value reported by Purushothaman [4] of 42.0 MJ/kg and much higher than the value reported by Senthilkumar [5] of 34.7 MJ/kg . Orange oil, as well as D-limonene (42.6 MJ/kg), showed slightly lower *LHV* than the minimum required in ASTM D7566 standard (42.8 MJ/kg). Hydrogenated orange oils (both 42.4 MJ/kg) and hydrogenated D-limonenes (both 42.6 MJ/kg) showed similar *LHV* in mass basis than pure biofuels. Consequently, they also resulted in slightly lower *LHV* than the

minimum, despite showing higher H/C ratio than non-hydrogenated compounds (see Fig. 7, left). However, all biofuels (either hydrogenated or not) showed higher *LHV* in volume basis than Jet A1, despite *LHV* decreased linearly with conversion (see Fig. 7, right). All blends (up to 30 vol%) with Jet A1 resulted in higher *LHV* in mass basis than minimum limit, except blends of orange oil with Jet A1 (see Fig. 8, left). Moreover, blends beyond 20 vol% biofuel showed similar *LHV* in volume basis or higher than Jet A1 (see Fig. 8, right). Therefore, hydrogenation enables increasing the volume fraction to be blended with Jet A1 that complies with the minimum required. Thus, similar levels of airplane range are expected, although detailed calculations of payload vs. range [36] are required to optimize the energy supply.

3.6. Lubricity

Orange oil, D-limonene and their hydrogenated products showed lower WSD than the maximum limit established by standard ASTM D7566 ($850 \mu\text{m}$). All biofuels resulted in lower WSD than Jet A1 (with $722 \pm 25 \mu\text{m}$), except D-Limonene and HL1 (see Fig. 9). The two-fold steam distillation of orange oil, which led to an almost pure D-limonene (98 wt%), affected this property very negatively. Related to hydrogenation, hydrogenated orange oil and D-limonene showed higher WSD than non-hydrogenated ones, except HL2. In both sets, maximum of WSD is observed in the first partial hydrogenation (around 22% conversion). HL1 resulted in worse lubricity than HO1 due to its higher content in 1-p-menthene (56 vs. 41 wt%). This compound (1-p-menthene) is expected to have worse lubricity than pure D-limonene, since HL2 (with 94 wt% of 1-p-menthene) showed higher WSD than distilled orange oil (with 94 wt% of D-limonene).

3.7. Flash point

Orange oil, D-limonene and their first hydrogenated level compounds comply the minimum flash point for jet fuels (38°C) established in standard ASTM D7566 (see Fig. 10, left). All these compounds show higher flash point than Jet A1, except HO1. However, both second hydrogenated level of orange oil and D-limonene fall below this minimum, because of the higher presence of more volatile compounds (i.e. 1-p-menthene and p-menthane). Similar tendency is observed in blends with Jet A1 (see Fig. 10,

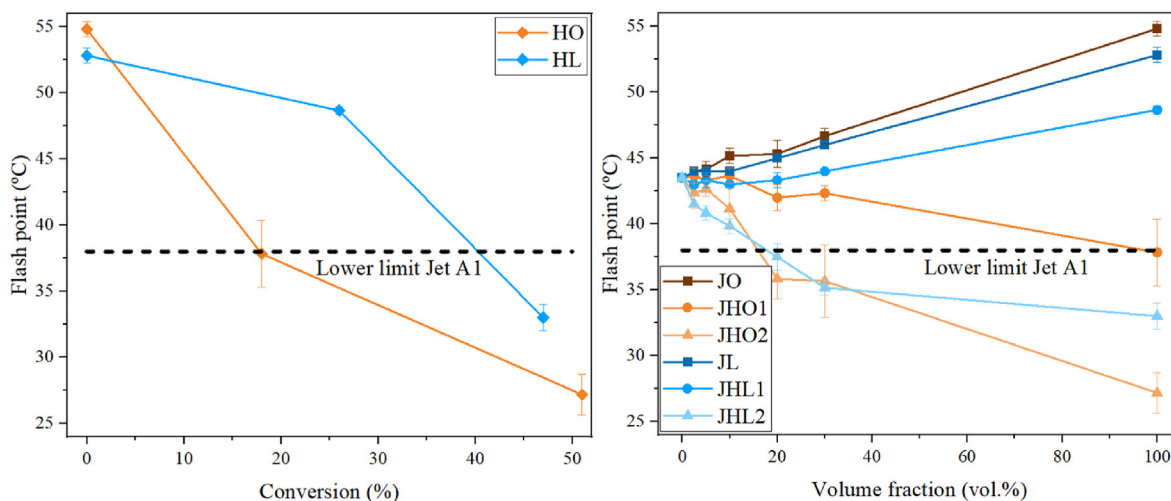


Fig. 10. Flash point of hydrogenated orange oil and D-limonene vs conversion (left) and of these hydro-fuels blended with Jet A1 (right).

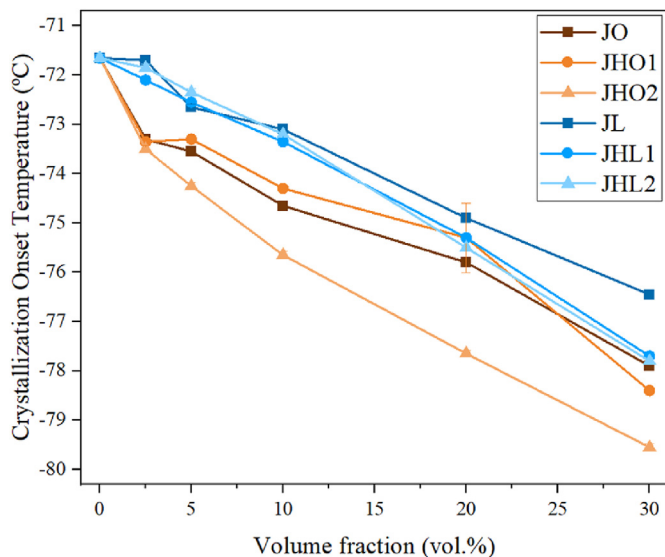


Fig. 11. COT of blends of both hydrogenated orange oil and D-limonene with Jet A1.

right), because pure and first hydrogenated level compounds fulfil the limit for all volume fraction, but second hydrogenated level compounds only fulfil the limit up to around 15 vol%. Consequently, blends with higher content than 15 vol% would not avoid fire hazard unless flame inhibition systems are applied [37].

3.8. Cold flow behaviour

Hydrogenation improves the cold flow behaviour of orange oil and D-limonene, as can be inferred from Fig. 11. Thus, all biofuels would present lower COT than Jet A1, better in case of hydrogenated ones. As the level of hydrogenation of the biofuels increases, the blends of these with Jet A1 show slightly lower COT. No problems for the turbine performance at high flying heights would be expected with any blend since the freezing point required for aviation fuels (max. -47°C) is fulfilled.

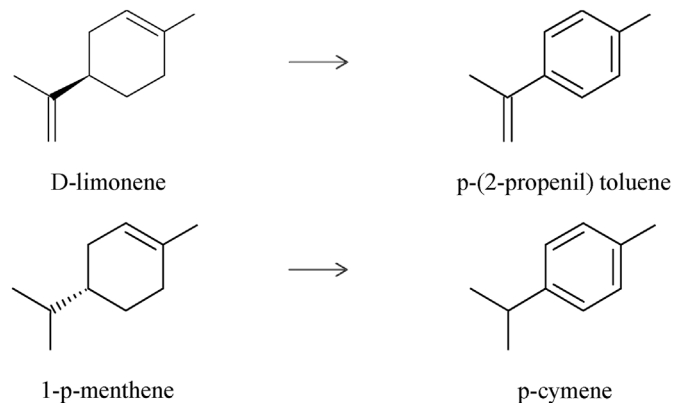


Fig. 13. Aromatization of D-limonene and 1-p-menthene.

3.9. Smoke point

Sooting tendency of fuels has been demonstrated to be inversely proportional to smoke point [38]. One of the following minima for smoke point should be fulfilled according to ASTM D7566 standard: (1) 25 mm, or (2) 18 mm (when the naphthalene content remains below 3.0 vol%). The hydrogenation process substantially improves the smoke point of orange oil and D-limonene, as shown in Fig. 12 (left). Despite this improvement, partially hydrogenated orange oil and D-limonene still show lower smoke point than Jet A1. D-limonene and 1-p-menthene are supposed to suffer an aromatization reaction when entering the flame, and it is well known that aromatic compounds have lower smoke points than naphthenic or aliphatic hydrocarbons (Fig. 13) [39]. Fig. 12 (right) shows the decrease in the smoke point of the blends when the amount of biofuel increases. However, blends of hydro-limonene at low concentrations show a positive synergistic effect, especially for blends of HL2 which shows similar or slightly higher smoke point than Jet A1 up to 30 vol%. The clear increase in smoke point after hydrogenation would allow blending up to almost 100 vol% HO2 or HL2, both still maintaining the smoke point above 18 mm. In practice, this is the minimum required because a naphthalene content below 3.0 vol% is guaranteed as an additional requirement by the company Exolum in its logistics distribution network. Blends of HL1 with Jet A1 allow fulfilling the limit with higher content of biofuel

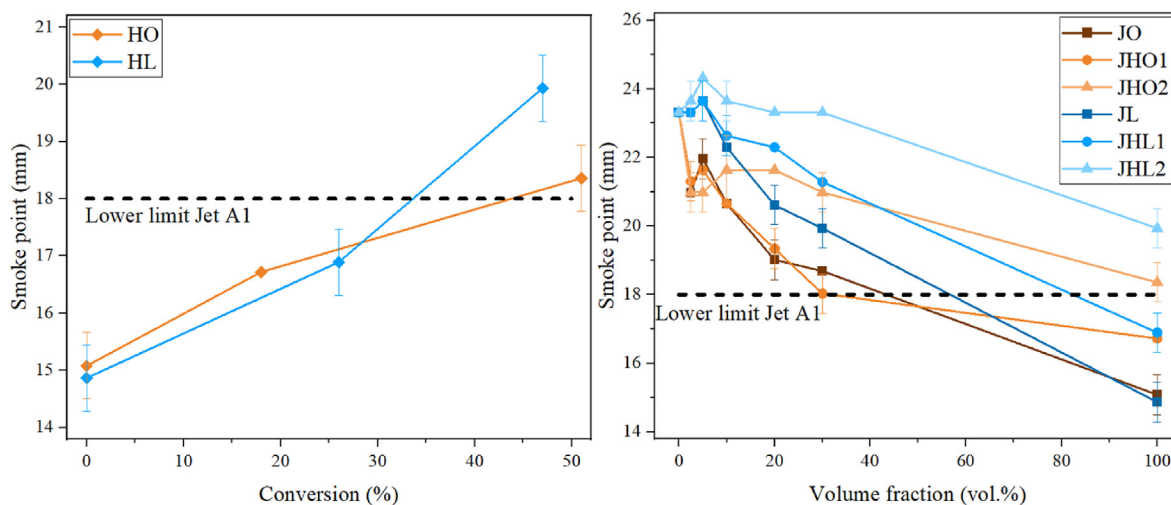


Fig. 12. Smoke point of hydrogenated orange oil and D-limonene vs conversion (left) and of these hydro-fuels blended with Jet A1 (right).

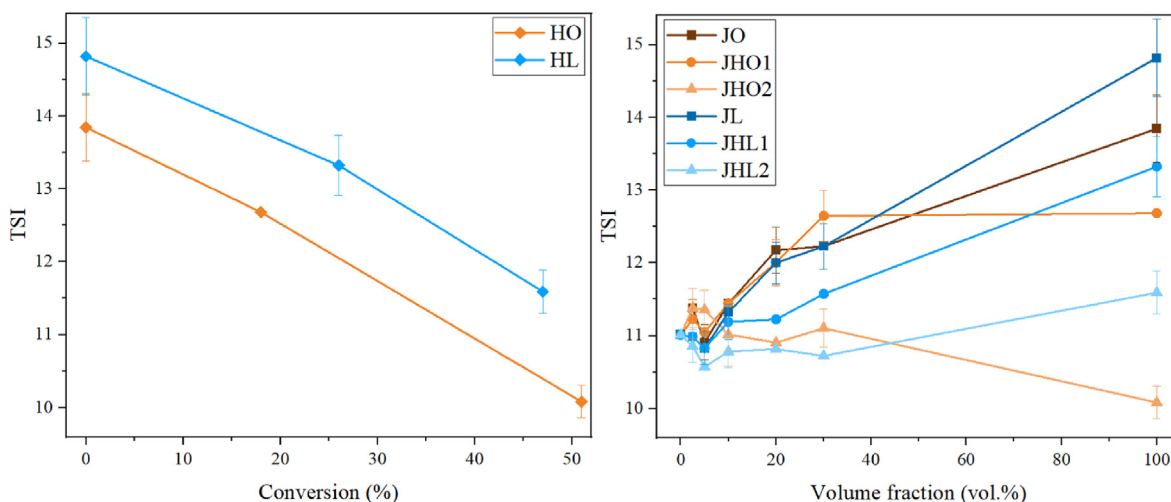


Fig. 14. TSI of hydrogenated orange oil and D-limonene vs conversion (left) and of these hydro-fuels blended with Jet A1 (right).

(up to 80 vol%) than blends of D-Limonene (up to 55 vol%). However, blends of HO1 fulfill the limit with lower content of biofuel (up to 30 vol%) than blends of orange oil (up to 40 vol%). Fig. 14 (left) confirms the decrease in sooting tendency upon hydrogenation, since it shows the clear improvement in the soot-forming tendency. Consequently, any volume fraction of HO2 or HL2 in Jet A1 leads to similar sooting tendency than Jet A1 (see Fig. 14, right). In summary, both hydrogenated orange oil and D-limonene could be used with increasing content in blends with Jet A1 as the hydrogenation level increases, thus obtaining cleaner combustion processes in aircraft turbines. Therefore, blending ranges higher than those specified in ASTM D7566 (50 vol%) for other biofuels could be proposed for both hydrogenated orange oil and D-limonene.

3.10. Summary of properties

Considering the properties measured for all hydrogenated products, no significant differences were found between distilled orange oil and pure D-limonene. Both products showed similar density and crystallization point after hydrogenation. However, hydrogenated orange oil resulted in higher viscosity than hydrogenated D-limonene, both fulfilling the maximum limit at -20°C . Also, HO showed slightly worse LHV (in both mass and volume basis) and flash point than HL, both below the corresponding limits. Nevertheless, HO resulted in better lubricity than HL. Moreover, sooting tendency, which is the main property to be improved in terpenic compounds, was lower in case of HO. Sooting tendency was reduced linearly with conversion in both HO and HL. Therefore, purification of D-limonene from distilled orange oil did not provide any fuel property improvement. However, hydrogenation of orange oil was clearly beneficial to reduce the sooting tendency.

4. Conclusions

Raw orange oil was extracted from orange peels (flavado) by steam distillation. When compared to the existing chemical/biological processes to produce blending components for aviation fuels, this process may result attractive due to its simplicity and the already existing infrastructure in orange juice producing companies. However, this product should be distilled to eliminate oxygenated compounds, since these are not allowed in jet fuel ASTM standards. Once distilled, orange oil (with contents of 94.0

and 98 wt% D-limonene), without hydrogenation, shows appropriate properties to become drop-in biojet fuel except for its high sooting tendency, which can be reduced by partial hydrogenation (mainly converting D-limonene in 1-p-menthene and, afterwards, in p-menthane). Both hydrogenated distilled-orange oil and pure D-limonene maintain the acceptable LHV of pure fuels but their flash point are reduced, especially when increasing conversion level. Nevertheless, these potential biojets would not need addition to keep its freezing point below -47°C as required for aviation fuels since their crystallization points are lower than -90°C . In addition, hydrogenation of orange oil and D-limonene notably improves their smoke points since the aromatization of the naphthenic ring in the monoterpenes is reduced. Therefore, the properties of both partially hydrogenated products (with conversions around 50%) are similar, indicating that D-limonene purification does not lead to additional benefits in front of two-fold distilled orange oil. The good properties of hydrogenated orange oil demonstrate that this is a potential alternative to be blended up to 15 vol% with Jet A1, fulfilling all the requirements in ASTM D7566. Flame inhibition systems would be needed to further increase the blend proportion of biofuel in Jet A1 and to approximate to the approved limits for aviation biofuels.

CRediT authorship contribution statement

David Donoso: Investigation, Data curation, Writing – original draft. **David Bolonio:** Resources, Investigation, Data curation. **Rosario Ballesteros:** Visualization, Data curation, Formal analysis. **Magín Lapuerta:** Funding acquisition, Supervision, Validation, Writing – review & editing. **Laureano Canoira:** Resources, Formal analysis, Writing – original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2022.02.078>.

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