Oxyfunctionalized turpentine: Evaluation of properties as automotive fuel

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ABSTRACT

Turpentine from pine trees or from Kraft pulping is a complex mixture of monoterpenes, such as: α-pinene, β-pinene, limonene and myrcene. In this work, β-pinene was reacted with paraformaldehyde to synthesize an oxyfunctionalized turpentine (oxyturpentine) composed mainly by α-pinene, nopol and α-terpineol. This oxyturpentine can be a novel biofuel as far as its properties meet the criteria required by automotive fuel regulations. Binary mixtures of oxyturpentine with a diesel fuel (with no oxygen content) and with a conventional biodiesel have been experimentally characterized following the standard methods for each property (density, kinematic viscosity, lubricity, heating value, volatility, etc.) and the results obtained are critically compared using the limit values of European standards as a reference. Results show that the oxyfunctionalization of turpentine improves some relevant properties for fuel applications, such as lubricity, volatility and sooting tendency (wear scar was reduced around 40% and smoke point was increased more than 300%). With respect to other oxygenated compounds used in fuels blends, such as alcohols and esters, oxyturpentine can reduce the problems of high volatility and low viscosity and lubricity of the former ones and the cold behavior of the latter ones, indicating its suitability as a component of diesel fuels.

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1. Introduction

Turpentine is a mixture of terpenes and its composition depends on its origin, but generally α and β-pinene are the major components. The main source of turpentine is a byproduct of paper industry, with a low cost in the market. Besides its renewable character, its residual origin makes turpentine an attractive source for biofuels. Turpentine has been mainly used as a component of additives [1,2], and to a lesser extent, as component of gasoline and diesel fuels [3—6], even in blends with biodiesel [7]. Other applications involve the transformation of the turpentine components. For instance, α-terpineol produced from hydration of α-pinene from turpentine has been used directly in diesel engines and as an octane booster for gasoline fuels, showing improvements in engine performance and reducing some pollutants such as carbon

monoxide [8,9].

In recent years, reducing particulate matter emissions (mainly composed of soot) in internal combustion engines (not only diesel but also spark-ignition) has become a major challenge due to the unceasing shrinkage of regulated emission limits. Besides the generalized use of particle filters, the use of oxygenated components in the fuel, and specifically alcohols, has been widely proposed as an effective way to reduce soot formation [10].

Different alcohols can be derived from turpentine. Furthermore, it has been reported that not only the presence of oxygen but also its position in the molecule plays a key role in combustion reactions. Consequently, different combustion performance can be obtained with molecules such as α- and β-pinene, myrtenol, nopol, terpineol and borneol [11]. In particular, a new application of turpentine-derived compounds is the transformation of β-pinene from turpentine into nopol, which is an alcohol that could improve some engine emissions due to its oxygen content [12].

The market value of turpentine is around 1.3 €/L. Although

almost 30% higher than that of commercial biodiesel, some factors may help reduce this value in the future. On the one hand, traditionally producing countries such as Spain are looking to recover their position in the global production of oleoresin (which decreased notably around three decades ago due to the very high production from China and the low prices of turpentine surrogates obtained from petroleum), and other countries such as Colombia are trying to become new producers, thus enhancing the oleoresin world supply. Additionally, new efforts have focused on improving the yield of oleoresin from pine trees (i.e., the U.S. Department of Energy recently supported work to increase at least five times the current yield of oleoresin from Pinus [13]). On the other hand, if oxyturpentine production is based on the by-product turpentine from the Kraft process, which is considered a waste, the oxy-functionalization of turpentine may become economically feasible due to the low cost of the raw material (although previous desulfurization is required). Based on an economic study of the oxy-functionalization, it was found that the final oxyturpentine cost would be ~0.5 €/L (production cost) plus the turpentine value [14].

The analysis of the main fuel properties of the reaction products from the oxyfunctionalization of turpentine (oxyturpentine) can confirm its actual potential for fuel applications. The fuel properties affect the combustion and emission characteristics in internal combustion engines. This effect is one of the reasons for the standardization and regulation of fuel quality. Thus, ranges have been established for fuel properties such as viscosity, density, lubricity, and flash point, among others, (e.g., standards EN 590:2013+A1 and EN 14214:2013 regulate the limits of diesel fuel properties in the European Union). For instance, it is well-known that the unburned hydrocarbon (UHC), nitrogen oxides (NOx) and particulate matter (PM) emissions in compression ignition engines are related to density, viscosity, volatility and flammability of the fuel, which determine the quality of the mixing process of fuel and air in the combustion chamber [15].

The tendency for autoignition is another important factor affecting combustion and emissions. In the case of diesel fuels, ignitability is often evaluated with cetane number or cetane index. The cetane number of oxygenated molecules is usually lower than that of conventional diesel, leading to high ignition delays [16]. In addition, the lower heating value (LHV, which represents the heat released in a combustion reaction for a specific mass of fuel with the combustion products remaining as vapor) of oxygenated fuels is lower than that for diesel, increasing fuel consumption [16]. Consequently, variations in equivalence ratio and exhaust gas recirculation are often experienced in engines fueled with oxygenated molecules, which can affect the engine performance and emissions [16,17].

Other properties such as lubricity, flash point, volatility and cold-flow ones are not so clearly related to the presence and oxygen content in the fuel. For instance, normal alcohols commonly possess high volatility and low lubricity, with respect to methyl esters from biodiesel, but alcohols have better cold-flow properties than biodiesel. These properties have high relevance because they are directly related to fuel safety, engine durability, and vehicle functionality, among others, demonstrating the importance of analyzing the actual influence of composition in the fuel properties.

In this work, the product of oxyfunctionalization of turpentine without any purification, separately blended with diesel and biodiesel, was compared to raw turpentine, also blended with diesel and biodiesel. Both sets of blends were subjected to measurements of the main fuel properties, and compared to the European standard for diesel fuels, with the aim of investigating the influence of the oxyfunctionalization reaction in the fuel properties and assessing the potential of oxyturpentine as a fuel component.

2. Experimental

2.1. Materials

Turpentine was supplied by Resinas Naturales S.L. (Cuellar, Spain). Oxyturpentine was produced as described in a previous work [18]. Briefly, turpentine and paraformaldehyde in equimolar ratio were added to a flask equipped with a reflux system and temperature control. Sn-MCM-41 was used as catalyst and added at 8 % wt. respect to the turpentine. The reaction conditions were: 1000 rpm, 90 °C and 24 h.

Diesel without any oxygenated molecule, commercialized as first fill diesel, was supplied by Repsol (Spain), whereas biodiesel was supplied by Bio Oils Energy (Spain). Nopol, α- and β-pinene and terpineol in analytical grade were purchased from Sigma-Aldrich (USA). These compounds are among the main components of oxyturpentine, and their properties were measured to analyze their influence on the oxyturpentine ones. The main fuel properties of these substances together with the method used for their corresponding measurement are shown in Table 1.

The identification and quantification of components in turpentine and oxyturpentine were performed by GC and GC-MS in an Agilent 7890 GC system coupled to Agilent 5975C VL MSD triple quadrupole mass detector and flame ionization detector (FID).

Both the injection and detector temperatures were 250 °C. A 1 μL sample was eluted using an DB-1 (30 m × 320 μm x 0.25 μm) capillary column (Agilent J&W). Helium was used as carrier gas. The initial temperature (70 °C) was held for 1 min, and then, a 15 °C/min heating ramp up to 180 °C (held for 1 min) was used, with a split ratio of 25:1. Mass spectra were compared with the NIST database to identify the components of the mixture.

2.2. Blending

Turpentine and oxyturpentine were blended separately with diesel and biodiesel fuels in contents 1%, 2%, 3%, 5%, 10%, 15% and 20% vol. Higher contents were discarded because it was expected that some properties such as the cetane number would be deteriorated notably. Low contents were explored in shorter intervals trying to look for synergistic effects. The main properties for diesel fuel applications were measured to assess the potential of oxyturpentine as a fuel component. The limits for density, viscosity, lubricity, flash point and derived cetane number for European diesel fuels established in standards EN 590:2013+A1 and EN 14214:2013 V2+A1:2018 were used to compare the properties of the blends.

2.3. Property measurements

Density was measured based on standard EN 3675, using a 10 mL glass pycnometer and a climate chamber Ineltec (used to set the temperature and humidity of the sample to 15 °C and 45%, respectively).

Viscosity of the blends was measured based on standard EN 3104 using a Froton viscosimeter 150 series and a thermal bath Tamson Zoetermeer-Holland TV 2000 to keep the samples at 40 °C during the test.

Wear scar diameter was measured to quantify the lubricity of the blends, based on standard EN 12156−1, using a High Frequency Reciprocating Rig (HFRR) from PCS Instruments and a microscope Optika SRZ-1 coupled to Motical 2500 digital camera.

Distillation curves were measured following standard EN 3405 in the automated distillation tester ad-7 from Tanaka. The initial and final heating rates, and the bath and receiver temperatures were optimized for each sample. Barometric pressure for all runs

Table 1
Specifications of fuels.

Property	EN method	Diesel	Biodiesel	α-Pinene	β-Pinene	Terpineol	Nopol	Turpentine	Oxyturpentine
Chemical formula	–	$C_{15.2}H_{29.1}$	$C_{18}H_{34.9}O_2$	$C_{10}H_{16}$	$C_{10}H_{16}$	$C_{10}H_{18}O$	$C_{11}H_{18}O$	$C_{10}H_{16}$	$C_{10.4}H_{16.9}O_{0.5}$
H/C	–	1.83	1.94	1.60	1.60	1.80	1.64	1.60	1.63
Oxygen content (%)[a]	–	0.0	11.3	0.0	0.0	10.4	9.6	0.0	4.9
Molecular weight (g/mol)	–	208.6	283.5	136.2	136.2	154.2	166.3	136.2	149.3
Stoichiometric A/F ratio		14.51	12.51	14.17	14.17	12.51	12.44	14.17	13.29
Density (kg/m³)	3675	829	880	858	868	940	971	862	913
Kinematic viscosity (cSt)	3104	2.5	4.3	1.3	1.4	28.6	13.4	1.3	3.5
Lubricity[b] (μm)	12156−1	443	170	242	758	394	248	484	302
LHV[c] (MJ/kg)	51123	42.94	37.04	42.22	41.48	37.28	37.92	42.34	39.71
DCN[d]	16715	64.4	58.1	22.2	18.5	15.4	19.6	20.2	19.8
Cloud point (°C)	3015	−22.7	7.0	ND	ND	ND	ND	ND	ND
Pour point (°C)	3016	−19.6	7.0	ND	ND	ND	ND	ND	−94.8
CFPP[e] (°C)	6371[e]	−22.6	9.0	ND	ND	ND	ND	ND	−36.0
Crystallization point (°C)	2386	−28.2	−49.6	ND	ND	ND	ND	ND	ND
Flash point (°C)	2719	79.5	130	31	36	88	98	34	37
Vapor pressure (kPa)	3007	~0	1.4	0.5	2.1	~0	~0	1.7	2.7
Smoke point (mm)	3014	22.3	>50	15.7	NM	ND	ND	8.9	33.4

[a] In mass basis.
[b] Wear scar diameter.
[c] Lower heating value.
[d] Derived cetane number; ND not detected; NM not measured.
[e] ASTM method.

was 948.0 + 1.0 hPa.

Vapor pressure was measured according to standard EN 3007 in the vapor pressure tester Eravap model EV01 of Eralytics.

Flash point was measured in a Pensky-Martens closed cup tester SETA PM-93 model 35000−0, which is based on standard EN 2719.

The combustion and ignition delay times (CD and ID, respectively) were measured in a Cetane Ignition Delay 510 from PAC instruments, and the derived-cetane number (DCN) was determined according to standard EN 16715.

Higher heating value (HHV) was measured according to standard method EN 51123 in a Parr 1351 calorimetric pump, while the corresponding lower one (LHV) was obtained by subtracting the heat of vaporization of water in the combustion products from the HHV.

The smoke point was measured in a standard smoke point lamp according to standard ASTM D1322, with previous calibration in accordance to the standard. The oxygen extended sooting index (OESI), proposed in Ref. [19] to evaluate the soot formation tendency in oxygenated fuels, was used according to Eq. (1),

$$OESI = a' \left(\frac{n + m/4 - p/2}{SP} \right) + b' \quad 1$$

where n, m and p are the coefficient of the chemical formula of the fuel ($C_nH_mO_p$), SP is the smoke point and, a' and b' are parameters regarding the experimental setup (43.588 mm^{-1} and -5.7177, respectively, for diffusion flames [20]).

Cloud and pour points, based on standard test methods EN 3015 and 3016, respectively, were measured in an automated cloud and pour points analyzer CPP 5Gs from PAC instruments. Cold filter plugging point (CFPP) was measured in the FPP 5Gs analyzer from PAC instruments, according to standard ASTM D6371.

3. Results and discussion

3.1. Turpentine and oxyturpentine composition

The composition of turpentine and oxyturpentine is shown in Table 2. The composition of oxyturpentine shows a minor

Table 2
Turpentine and oxyturpentine composition.

Compound	Turpentine (% wt.)	Oxyturpentine (% wt.)
α-Pinene	67.3	47.1
β-Pinene	21.5	4.2
Limonene	2.7	0.6
β-Myrcene	1.0	1.3
Longifolene	2.0	0.1
3-Carene	0.4	2.1
Camphene	1.2	1.3
α-Terpineol	0.3	4.7
(+)-Fenchone	0.0	1.1
Isoborneol	0.0	0.7
Nopol	0.0	31.7
α-Phellandrene	0.0	1.6
α-Longipinene	0.2	1.1
Borneol	0.0	0.1
Others	3.4	2.3

amount of unreacted β-pinene and the presence of nopol, α-phellandrene, α-longipinene and borneol as products of the reaction, with nopol as the main product. Other compounds of oxyturpentine remain from turpentine.

3.2. Physical properties

Density profiles for oxyturpentine and turpentine blends with diesel and biodiesel are shown in Fig. 1. The density of oxyturpentine is higher than that for turpentine, diesel and biodiesel, and is above the upper limits for both standards. Oxyturpentine and turpentine blended with diesel at contents below 20% vol. remain between the limits of standard EN 590:2013+A1 (see Fig. 1a), although it must be remarked that the diesel fuel used in this work has a relatively low density with respect to the usual commercial diesel fuel. Similarly, blends of oxyturpentine and turpentine with biodiesel prepared up to 20% vol. are between the limits of standard EN 14214:2013 V2+A1: 2018 (see Fig. 1b).

The oxyfunctionalization reaction of turpentine increases its density. The density of nopol, α-pinene and terpineol (the main components of the reaction product, see Table 2) was measured with the same method. A mixture of these three compounds (with a composition obtained normalizing the composition of Table 2 for
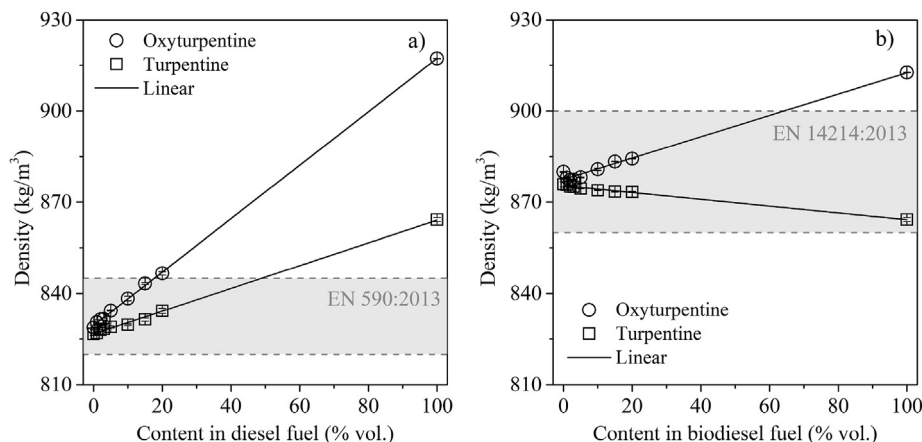
Fig. 1. Density of oxyturpentine and turpentine blended with (a) diesel and (b) biodiesel.

these three compounds only) would lead to a blend with a density of 920.9 kg/m^3, which quite agrees with the value of oxyturpentine (912.6 kg/m^3). The difference is due to the other compounds neglected. The high density of oxyturpentine with respect to that for turpentine is due to the presence of nopol and terpineol. Although the turpentine density is out of range of standard EN 590:2013 for diesel fuels (and closely above the lower limit of standard EN 14214:2013 for biodiesel fuels), the oxyfunctionalization worsened this property, and oxyturpentine went out of range in both EN 540:2013 and EN 14214:2013, which suggests avoiding its use in high contents. For small contents in biodiesel blends, some slight positive excess volumes were observed, which can be explained by the worse molecular packaging between open-chain molecules (esters) and close-chain ones (terpenes and terpenic alcohols).

Viscosity of blends of turpentine and oxyturpentine with diesel and biodiesel are shown in Fig. 2. Viscosity of oxyturpentine is higher than that for diesel but lower than that for biodiesel, whereas the viscosity of turpentine is lower than that for diesel (and therefore lower than that for oxyturpentine and biodiesel). This means that the oxyfunctionalization improved the viscosity of turpentine, leading to a viscosity of oxyturpentine and its blends with diesel and biodiesel according to standards EN 590:3013 and EN 14214:2013, although if compared to the biodiesel standard, oxyturpentine viscosity is close to the lower limit (see Fig. 2b). The viscosity of turpentine is lower than the minimum limit for both

standards, which precludes its use in high contents, in particular, no more than 20% vol.

Measured viscosities for nopol, α-pinene and terpineol (see Table 1) reveal the non-linearity of viscosity with composition. The increase in viscosity of oxyturpentine is due to the presence of nopol and terpineol. In addition, the viscosity of oxyturpentine is barely higher to that of diesel, despite nopol and terpineol possessing a viscosity five and eleven times the value of diesel, respectively, and despite the nopol content being significant. This indicates the importance of the presence of other components in oxyturpentine.

The experimental values were used to obtain the interaction coefficient (G) of Grunberg-Nissan correlation for kinematic viscosity of blends (v), by means of Eq. (2) [21],

$$\ln(\rho v) = x_1 \ln(\rho_1 v_1) + x_2 \ln(\rho_2 v_2) + x_1 x_2 G \qquad 2$$

where x represents the molar fraction, ρ is the density of the blend and subscripts 1 and 2 represent the components of binary blend. The interaction coefficients of Grunberg-Nissan obtained for the blends of oxyturpentine with diesel and biodiesel were −0.605 and −0.100, respectively, whereas those coefficients were 0.230 and 0.454, for the blends of turpentine with diesel and biodiesel, respectively. The estimations of viscosity with this correlation are in good agreement with experimental data (see Fig. 2), and the resulting interaction coefficients are consistent with those obtained
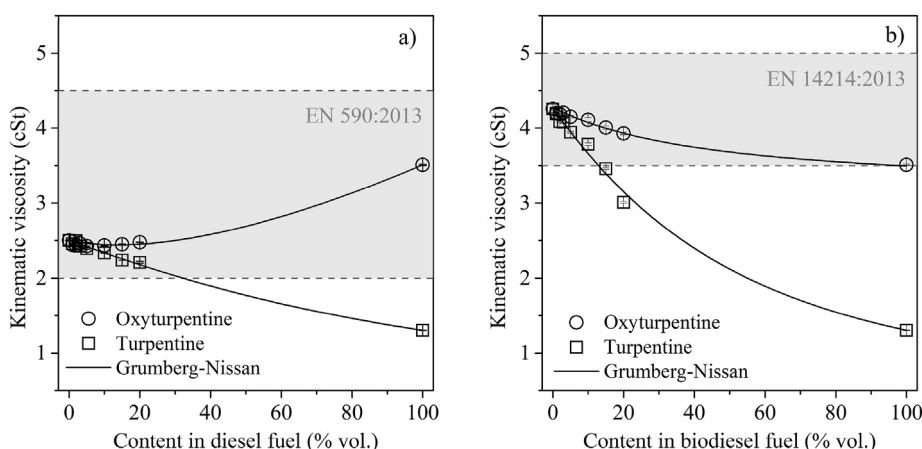

Fig. 2. Viscosity of oxyturpentine and turpentine blended with (a) diesel and (b) biodiesel.

in alcohol blends, which are always higher when alcohols are blended with biodiesel than when they are blended with diesel [22].

Results of wear scar diameter, used to evaluate the lubricity of the blends of oxyturpentine and turpentine with diesel and biodiesel, are presented in Fig. 3. Lubricity is a very important property for the performance and durability of the engine. All wear scar diameters measured for both diesel and biodiesel blended with both turpentine and oxyturpentine are lower than 460 μm, the limit established in standard EN 590:2013+A1 for diesel fuels. Only the wear scar diameter for pure turpentine is higher than the upper limit. At low contents of oxyturpentine, the wear scar diameter of the blend is even lower than that for oxyturpentine and for diesel fuel. This synergistic effect indicates that with the appropriate amount of oxyturpentine (and to a lesser extent of turpentine), the reduction in friction and/or wear can be effectively prevented (see Fig. 3a). Conversely, the wear scar diameter for biodiesel blends always increases with the oxyturpentine and turpentine contents (with convex and concave shapes, respectively) (see Fig. 3b). In any case, all tested blends of biodiesel and oxyturpentine have a wear scar diameter below the limit.

Although the lubricity is far from being directly proportional to blend composition, in this case the experimental value measured for oxyturpentine is similar to that obtained by proportional estimation for a mixture of nopol, α-pinene and terpineol (see Table 1). Since the lubricity of nopol and terpineol is good, they dominate the lubricant properties of the oxyturpentine. Consequently, the lubricity is strongly improved by the oxyfunctionalization of turpentine, as a consequence of the presence of nopol and α-terpineol, and of the decrease in the β-pinene content (with the highest wear scar among terpenes, as shown in Table 1). The oxygen-containing components favor the formation of a protective film onto the metal surfaces, particularly due to their polarity [23]. In summary, oxyturpentine and its blends with diesel and biodiesel possess enough lubricity for diesel and biodiesel fuel applications, while pure turpentine does not.

3.3. Volatility

Distillation curves for diesel, biodiesel turpentine and oxyturpentine are shown in Fig. 4. Distillation curves for turpentine and biodiesel are both quite flat, as a consequence of their homogeneous contents (i.e. fatty acid esters and C_{10} terpenes, respectively). However, diesel fuel and oxyturpentine show much wider range of distillation (consistently with their more scattered
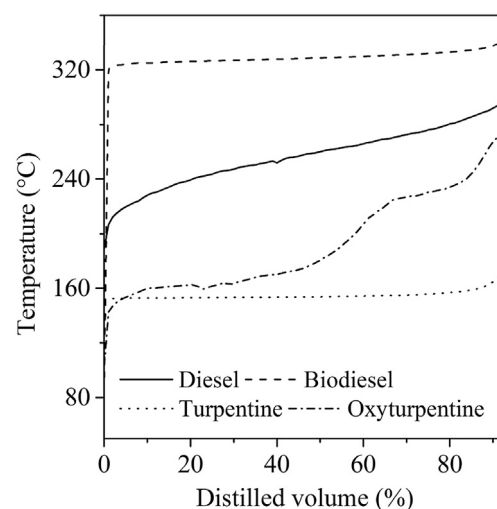

Fig. 4. Distillation curves for diesel, biodiesel, turpentine and oxyturpentine.

composition), both curves being above that of turpentine and below that of biodiesel.

The boiling temperatures to recover 90% vol. of distillate (T90) for diesel and oxyturpentine are 292, and 267 °C, respectively. The presence of nopol and α-pinene confer oxyturpentine distillation curve a s-shape and a broad range of boiling temperature (130 °C), which is much closer to that of diesel fuel (110 °C) than turpentine, especially in the heavy range.

The vapor pressure of blends of oxyturpentine with diesel was measured to evaluate the influence of possible volatile compounds in oxyfunctionalized turpentine in the fuel blend, and the results were compared with turpentine blended with diesel and biodiesel. Fig. 5 displays the Reid pressure and the dry vapor pressure equivalent (DVPE), both obtained following standard ASTM D 4953. Although the vapor pressure of the blends is increased with the oxyturpentine content, experimental values obtained are still very low, and therefore, no volatilization problems are expected when used in diesel engines. In addition, oxyfunctionalization leads to a reaction product with lower volatility than turpentine. Low fuel volatility is highly desirable in diesel and biodiesel fuel applications, because high volatility may contribute to increase hydrocarbon emissions in diesel engines [24,25].

The vapor pressure of turpentine is lower than that of oxyturpentine, Fig. 5, in agreement with the distillation curve at low
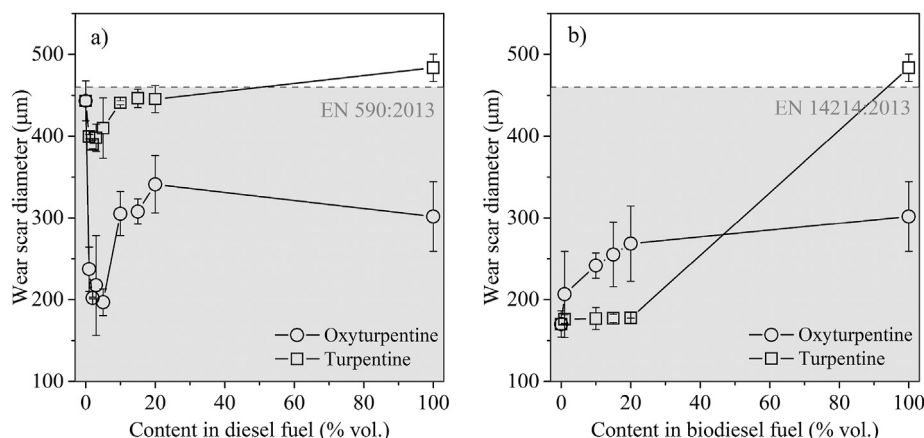

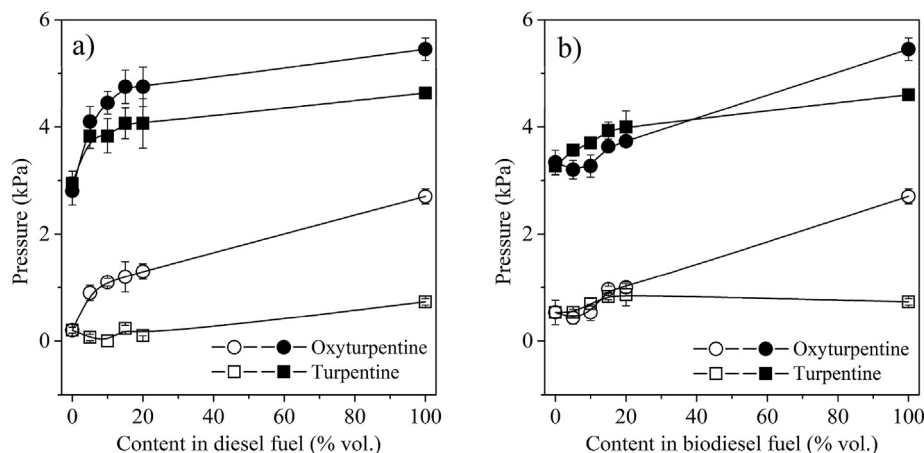**Fig. 3.** Lubricity of oxyturpentine and turpentine blended with (a) diesel and (b) biodiesel.

Fig. 5. Reid pressure (filled symbols) and DVPE (open symbols) of oxyturpentine and turpentine blended with a) diesel and b) biodiesel.

temperatures (see Fig. 4), demonstrating that the most volatile components of oxyturpentine have lower vapor pressure than those of turpentine. This indicates that the components classified as "others" in Table 2 for oxyturpentine are more volatile than those for turpentine. Probably, cracking reactions take place in the oxy-functionalization of turpentine, leading to the presence of some light molecules. In any case, the content of these light molecules is very low, and the vapor pressure still remains far below the lower limit of volatile fuels such as gasoline (standard EN 228). Moreover, the interactions between the added molecules of turpentine/oxy-turpentine (especially of oxyturpentine) and those of biodiesel are apparently higher than those with diesel, leading to flatter vapor pressure curves for biodiesel blends.

3.4. Combustion and thermochemical properties

Flash point is one of the most important properties of fuel regarding safety. Flash point for blends oxyturpentine and turpentine with diesel and biodiesel are shown in Fig. 6.

Typically, light alcohols decrease significantly the flash point of blends with diesel fuels. This is not the case for nopol, whose flash point is higher than that for diesel. However, the flash point of oxyturpentine/diesel blends is reduced by the presence of more volatile compounds in oxyturpentine such as α-pinene. In fact, the flash point of turpentine/diesel remains always lower than that of oxyturpentine/diesel blends, since only around 40% in vol. of

oxyturpentine corresponds to pinenes. In any case, the flash point is improved by the oxyfunctionalziation, and the values of oxy-turpentine/diesel blends are higher than 55 °C, which is the minimum value established in standard EN 590:2013+A1, indicating that the blends of diesel and oxyturpentine at contents lower than 20% in vol. are safe enough (see Fig. 6). In contrast, blends of oxy-turpentine and turpentine with biodiesel possess flash points lower than the minimum value in standard EN 14214:2013 for biodiesel, due to the high volatility of α-pinene, as observed in the distillation curve (see Fig. 4).

The values of flash point for turpentine, nopol, α-pinene and terpineol (see Table 1), measured with the same method, demonstrate that the flash point of oxyturpentine (37 °C) is due to the presence of molecules such as α-pinene. Nopol and terpineol have flash points higher than the minimum value established in standard EN 590:2013 and very similar to that in standard EN 14214:2013. This increase in flash point makes the blends of oxy-turpentine and diesel (at least at 20% vol.) suitable components for diesel application, whereas those blends with turpentine are not. In case of biodiesel blends, both turpentine and oxyturpentine blends would comply with standard EN 14214:2013 in most of the concentration range.

The heating values of oxyturpentine are lower than those for diesel and turpentine, but higher than those for biodiesel, as shown in Fig. 7. Turpentine has a LHV very similar to that of diesel (only 1.4% lower). The addition of oxygen atoms to the turpentine in the
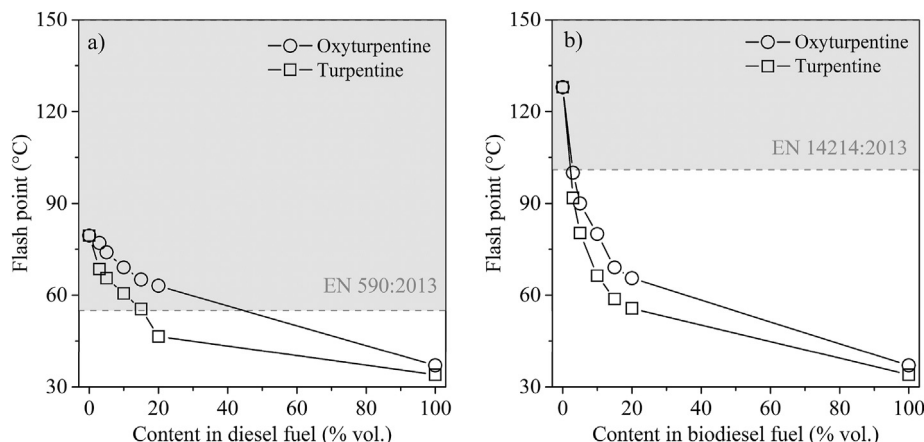

Fig. 6. Flash point of diesel blended with oxyfunctionalized turpentine.
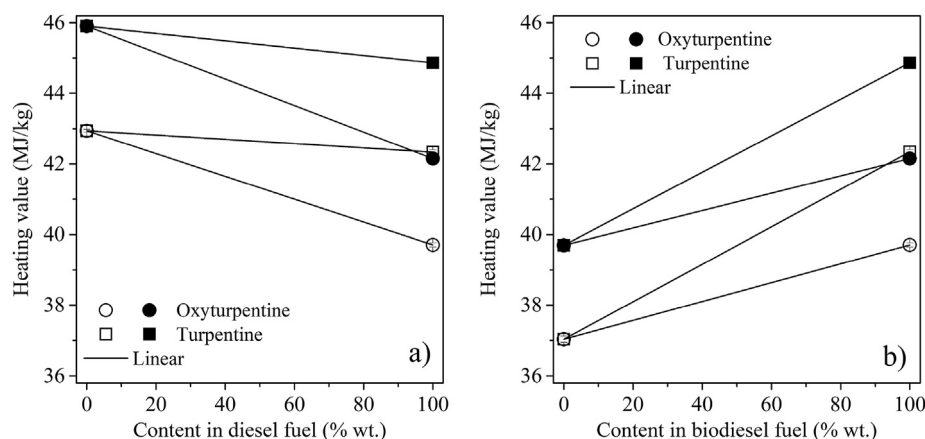
Fig. 7. Higher (filled symbols) and lower heating values (open symbols) of oxyturpentine and turpentine blended with (a) diesel and (b) biodiesel.

oxyfunctionalization (to produce nopol and terpineol), decreases the heating value. The LHV of oxyturpentine is around 6.1% lower than that of turpentine (see Table 1), which means 7.5% lower with respect to that of diesel. However, the high density of oxyturpentine (see Table 1) prevents from reducing the heating value per unit volume, and on the contrary, it is increased around 2% with respect to diesel fuel. In any case, such differences have been proved to affect only slightly the engine performance and emissions [26—28].

The derived cetane number shown in Fig. 8 was obtained as a function of the ignition and combustion delay times from the dynamic pressure curve, following standard EN 16715. The dynamic pressure curves of turpentine and oxyturpentine and their blends with diesel and biodiesel are delayed considerably with respect to diesel and biodiesel ones, as a consequence of the higher ignition and combustion delay times. Consequently, the derived cetane number of oxyturpentine and turpentine blends decrease with increasing contents (see Fig. 8). In any case, blends up to 20% vol. have derived cetane numbers higher than 51 (the limit established in standards EN 590:2013 and EN 14214:2013). Dynamic pressure curves obtained from combustion of oxyturpentine and turpentine are very similar, indicating that the effect of oxyfunctionalization reaction on the ignition time, and consequently on the derived cetane number, is negligible.

Fig. 9a shows the smoke point for blends of diesel with oxyturpentine and turpentine. Tests with biodiesel blends were not

possible due to excessive viscosity [29]. The smoke point of oxyturpentine is around 11 and 25 mm higher than that for diesel and turpentine, respectively, meaning that the sooting tendency of oxyturpentine is significantly lower than turpentine and diesel. With regards to biodiesel, it has a smoke point at least 17 mm higher than that of oxyturpentine, which means that biodiesel has the lowest sooting tendency.

The relation of *OESI* with the oxyturpentine and turpentine content is shown in Fig. 9b. It is evident that the decrease in the sooting tendency of the blends is inversely proportional to the oxyturpentine content, whereas directly proportional for blends with turpentine. This is a consequence of the decrease in molecular weight and the increase in oxygen content as oxyturpentine content is increased [20].

The low sooting tendency of oxyturpentine compared to diesel and turpentine is one of the main reasons to propose its transformation and its fuel application, because a reduction in particulate matter emissions is expected. It has been found that oxygen-containing functional groups, such as those present in oxyturpentine, contribute significantly to reduce soot formation [30]. The smoke point and *OESI* values are proportional to the composition of the mixture, as was observed for diesel blended with oxyturpentine (see Fig. 9). Although the smoke points for nopol and terpineol were not obtained (their high viscosity leads to a high flame attenuation and it was not possible to register a flame length at the smoke breakthrough), the low value obtained for α-pinene
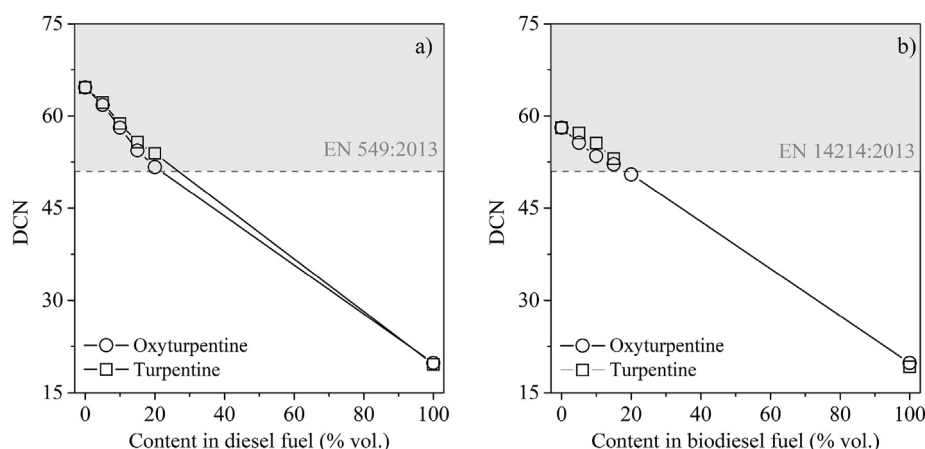

Fig. 8. Derived cetane number as a function of turpentine and oxyturpentine content in (a) diesel and (b) biodiesel.
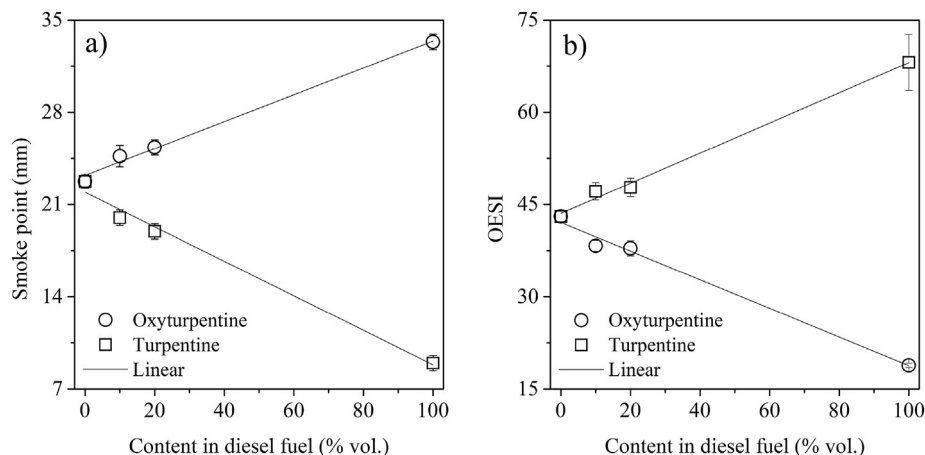
Fig. 9. (a) Smoke point and (b) *OESI* for blends of oxyturpentine and turpentine with diesel fuel.

(see Table 1) suggests that those for alcohols are relatively high, which implies lower *OESI* values. Consequently, a decrease in particulate matter emissions would be expected with oxyturpentine, contrarily to turpentine.

3.5. Cold flow properties

Cold-flow properties have become important properties for biofuels, particularly biodiesel, because their molecular structure and fuel properties negatively influence fuel delivery (i.e., filter plugging) and homogenization at low temperatures. Different tests can reveal the propensity of some fuels to form solid particles such as crystals at low temperatures. Although the crystallization point is indicative of this propensity, this temperature is associated with the bulk phase change of the fuel.

Some amount of crystals may not be problematic, but their accumulation can generate problems. Pour, cloud and cold filter plugging points help identify the temperature at which the fuel can lead to operational problems. These temperatures are shown in Fig. 10. The measured cloud, pour and CFPP temperatures are decreased as oxyturpentine content is increased (with both diesel and biodiesel blends), indicating that the presence of oxyturpentine decreases the trend to form crystals. For instance, with

the blend of diesel and oxyturpentine at 20 % vol., the required temperature to observe filter plugging of crystals was 0.6 °C lower than that for diesel, while those differences for cloud and pour points were 2.5 and 2.6 °C, respectively. The effect of oxyturpentine on biodiesel is stronger than that observed with diesel, obtaining a reduction of 3.5 °C on CFPP and, cloud and pour points, due to the oxyturpentine content.

The cold properties are slightly affected by the oxy-functionalization reaction. For instance, the pour, cloud and cold filter plugging point of the blend of diesel and oxyturpentine at 20% vol. is decreased around 0.5 °C, 1 °C, and 2 °C, respectively, with respect to the blend of diesel and turpentine. The trends observed with turpentine are in agreement with other works [31]. In summary, the addition of oxyturpentine in diesel and, especially, in biodiesel blends can be useful to prepare the base fuel for use in cold weathers.

4. Conclusions

The following conclusions can be drawn on the properties of oxyturpentine as a fuel component:
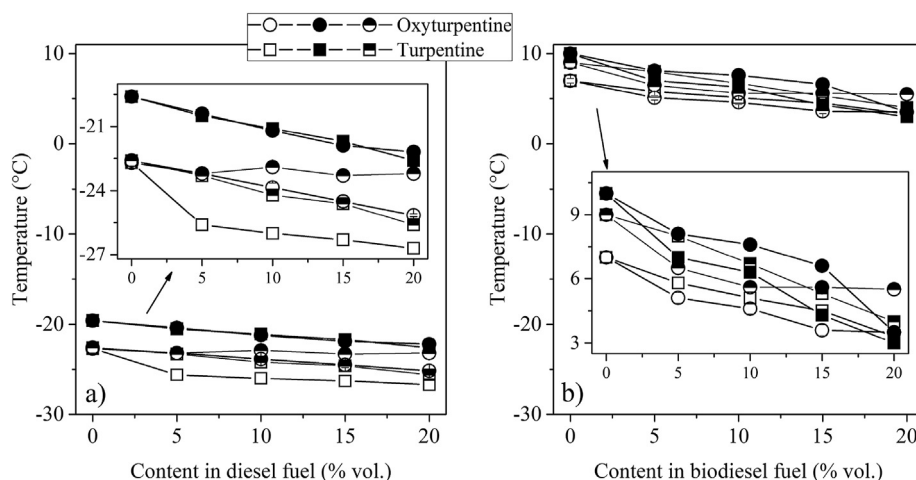

Fig. 10. Cloud (open symbols), pour (filled symbols) and cold filter plugging (half-up filled symbols) points of oxyturpentine and turpentine blended with (a) diesel and (b) biodiesel.

- The main compounds of oxyturpentine (nopol, α-terpineol and, α- and β-pinene) contribute to increase the viscosity of the mixture, although it remains very similar to that of diesel, especially in blends with contents lower than 20 % vol.
- The presence of nopol and terpineol increases the density of the blends, with small excess volume in case of biodiesel blends.
- Lubricity is improved with the presence of oxyturpentine, with synergistic benefits at low contents (1–5% vol.).
- The volatility of oxyturpentine is higher than those of diesel and biodiesel fuels, but lower than that of turpentine, as observed in both vapor pressure and distillation curve results.
- The derived cetane number and flash point of oxyturpentine are both considerably lower than those of diesel and biodiesel, and decrease as a function of the oxyturpentine content. In any case, for contents up to 20% vol., these properties lie within the limits established in European standard. Compared to turpentine, oxyturpentine shows a similar cetane number and an enhanced flash point.
- Oxyturpentine reduces the heating value of diesel blends, but increases that of biodiesel blends. However, the heating value per unit volume increases in both cases, which improves fuel tank autonomy.
- Cloud, pour and cold filter plugging points of diesel and biodiesel decrease linearly with the oxyturpentine content, reducing the occurrence probability of filter plugging by decreasing the temperature in which crystals are formed. Although a deterioration in these properties was evidenced as a consequence of oxyfunctionalization, the influence of oxyturpentine on the cold-flow properties of diesel and biodiesel blends is still positive.
- The sooting tendency of oxyturpentine blended with diesel was reduced in proportion to the oxyturpentine content, and therefore, a reduction in emissions of particulate material from engines is expected.

The oxyfunctionalization reaction performed to turpentine leads to a product with high potential for fuel applications. Some properties such as volatility, viscosity, lubricity, and flash and smoke points were improved due to the oxyfunctionalization, whereas the density, heating value, and cold-flow properties were worsened and derived cetane number remained unchanged. In general, the benefits are more relevant than the drawbacks, and this component can contribute to reduce pollutant emissions, especially particulate matter. Cold-flow properties are improved with respect to those of commercial biodiesel (which has often experienced filter clogging problems) and minor changes in engine performance are expected due to its combustion and thermochemical properties.

CRediT authorship contribution statement

Rosario Ballesteros: Conceptualization, Formal analysis, Methodology, Validation. **Duban García:** Investigation, Data curation, Formal analysis, Methodology, Writing - original draft. **Felipe Bustamante:** Resources, Validation, Writing - review & editing. **Edwin Alarcón:** Funding acquisition, Resources, Supervision. **Magín Lapuerta:** Funding acquisition, Conceptualization, Writing - review & editing.

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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