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New Approach for Understanding the Oxidation Stability of Neopolyol Ester Lubricants Using a Small-Scale Oxidation Test Method

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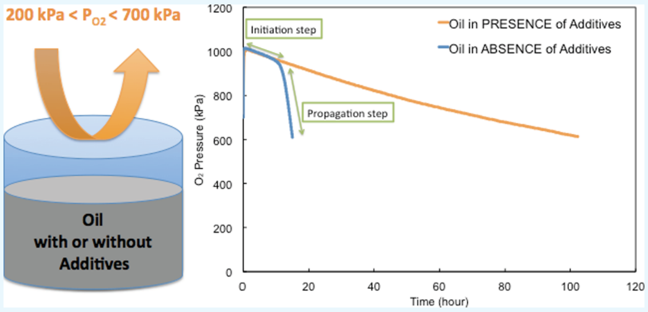
ABSTRACT: This work presents, for the first time, the evaluation on the oxidation stability of synthetic oils for an aircraft engine using the rapid small-scale oxidation test (RSSOT) method. Polyol ester lubricants with and without additives were oxidized at 423 K and 7 bar. The pressure drop plots show that during the first period of thermal degradation, the consumption of oxygen is similar for both samples. This part corresponds to the initiation steps of the mechanism of oxidation. Then, the curve of the oil without additives reveals an increase in the depletion of oxygen, corresponding to the kinetic propagation step. Because of the presence of antioxidants, this phase is not observed for oil-containing additives. The RSSOT method also allows us to quantify the time needed for the ester base to produce enough free radicals in order to propagate the mechanism of oxidation. A methodic comparison with other samples containing the raw oil and one additive is also proposed.



1. INTRODUCTION

Aircraft turbine engines have to be lubricated in order to reduce friction and wear between rotating parts.[1] During operation, oil is exposed to high thermal stress because of severe heating, which leads to continuous oil degradation in the engine due to oxidation. On the other hand, a small part of oil is lost (typically 0.1 L/h) through venting systems. As results, periodic refills are required to keep oil levels, which also contributes to mitigate oil degradation, avoiding the need of complete oil change. However, future generations of aircraft turbine engines will tend to operate at higher temperatures thanks to the use of more efficient materials. At the same time, engine manufacturers are working to reduce oil consumption. In fact, renewal will also be less effective in offsetting oil degradation, whereas oxidation will be more severe, which could ultimately result in a need for complete oil change from the tank and the system.

Typical lubricant oils used in aircraft engines are mainly composed of synthetic esters. Once submitted to high thermal stress, synthetic ester oils suffer degradation because of oxidation, which is characterized by the formation of free radicals. Several studies have been carried out on this subject[2−5] in order to determine the mechanism of radical degradation, which can be described into four main stages: the initiation step corresponding to the formation of free radicals such as $R^\bullet$, the propagation step to the formation of hydroperoxides ROOH, and the autocatalysis step and the termination step to the formation of nonradical products.[6,7] Alcohols are nonradical products, which may be primary, secondary, or tertiary. It is known that in the presence of an excess of oxygen, the primary and secondary alcohols will, respectively, form aldehydes and ketones. Then, the aldehydes will decompose into carboxylic acids, which could raise the total acid number of the oil. The molecules produced are light, oil-soluble, and volatile compounds. As the degradation progresses, the oxidized products will polymerize and form deposits such as sludge and varnish.[8] It is hence very important to follow the changes induced in the oil composition through its oxidation, as well as the evolution of the degradation products, in order to guarantee acceptable lubricant and heat transfer properties and avoid the formation of deposits in the turbine engine lubrication system.

This degradation results in a significant change of colors, viscosity increase, higher acidity, formation of sludge and

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varnish, corrosion, and so forth. The oxidation stability is consequently one of the most important parameters responsible for the ageing of lubricants.[9,10]

Hence, antioxidant agents are used to extend the life of the oil by consuming the free radicals and therefore blocking the propagation step.[6,11] The exchange of a hydrogen atom is fast and takes place intermolecularly. Moreover, the delocalization of electron into the ring compound of the radical formed from the antioxidant is stable, hindering the propagation of this free radical.[12−14] The most commonly used antioxidants in lubricating oil are secondary aromatic amines such as phenyl-1-naphtylamine (PAN, $C_{16}H_{13}N$) and dioctyldiphenylamine (DODPA, $C_{28}H_{43}N$).[15,16]

Several methods have been used to understand the thermal stability of lubricating oil such as the method 5308 of FED-STD-791 (corrosiveness and oxidation stability of light oils) or ASTM D4636 (Standard Test Method for Corrosiveness and Oxidation Stability of Aircraft Turbine Engine Lubricants) which is a combination of techniques 5307.2 and 5308.7 of FED-STD-791.[17−20] However, these methods are extremely time-consuming. In this work, we aimed to accelerate the chemical reactions having access to a high level of oxidation at a laboratory scale. The oxidation of a commercial lubricant has been therefore performed in a PetroOxy device. This innovating study presents the results on the oxidation of aircraft turbine lubricant by rapid small-scale oxidation test (RSSOT). The technique is mainly for automotive fuels (ASTM D7545) in order to study the oxidation stability of the component.[13,21−24] RSSOT oxidation provides a fast determination of the amount of oxygen consumed through the measurement of the total pressure inside the autoclave reactor (PetroOxy).

The goal of this study is thus to use RSSOT oxidation results as a tool leading to a better understanding of the oxidation of a commercial aircraft lubricant, as well as of the role of the different antioxidant agents contained.

2. RESULTS AND DISCUSSION

For a better understanding, the analysis of the oxidation of the ester base of the lubricant was first conducted and then a mixture of the ester base with one additive at the time [PAN, DODPA, and tricresylphosphate (TCP)] was used to complete the formulation of the lubricants. Then, the influence of different parameters such as temperature and pressure on the oxidation of aircraft turbine lubricant was performed using PetroOxy. At the end of each reaction, for each oil sample except for ester base without additives, which was colorless, the color went from orange to brown/black as described in other study.[6] However, no formation of deposits was observed.

2.1. Antioxidant Role of Different Additives. *2.1.1. Oxidation Stability of the Neopolyol Ester Base Oil.* Figure 1 shows the PetroOxy oxidation experiments performed at 700 kPa and 150 °C on the additive-free pristine neopolyol ester (lubricant oil without additives). The extremely fast degradation of the ester in the absence of additives becomes evident by the loss of pressure after 15 h. The oxidation curve of the additive-free ester can be divided into two phases: a first part corresponding to the initiation step of the oxidation reaction, followed by a second step that can be assigned to the propagation of the reaction, also called the acceleration phase, and is typical of free radical involving reaction mechanisms.[13] The initiation part of the curve takes place during the first 9 h of reaction (Figure 1). The rate of oxygen consumption, that is, the slope of the curve, is relatively slow, in comparison to that of the subsequent propagation step. During this initiation period, the first radicals are formed out of the neopolyol ester molecule.[6,7] Moreover, oxygen needs to diffuse from the gas to the bulk of the liquid phase where it will react.[3] Upon approximately 9 h of reaction, this concentration is enough to trigger the propagation phase. When no additives are present, the propagation step occurs rapidly and radicals are consumed and formed again attacking the neopolyol ester molecules.

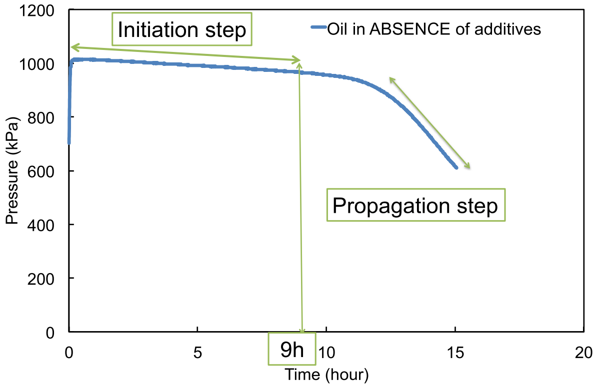

Figure 1. PetroOxy pressure drop curves vs time for oil without additive degradation at T = 150 °C—determination of the time of the initiation step.

Figure 2 contains the Fourier transform infrared spectroscopy (FTIR) spectra recorded for the additive-free pristine neopolyol ester submitted to the PetroOxy experiment compared with the spectra of the fresh oil. The region between 1110 and 1210 and 1550 and 1850 cm^{-1} contains, respectively, the absorbance bands typical of the ester's C−O and C═O bonds.[25] The C−O bond shows the formation of primary alcohols, which might lead to the production of aldehyde because of the change in the carbonyl bond C═O of the ester. The alteration in the peak could show that the ester bond is attacked by free radicals but still remains a C═O bond belonging to an aldehyde or a ketone. As seen previously, if the alcohols produced are primary, the reaction with the excess of oxygen leads to an aldehyde. At the end of the experiment, there is no formation of the C−H bond neither the O−H bond, that is, the aldehydes and the carboxylic acids were not produced.

2.1.2. Single-Additive-Containing Lubricants: PAN and DODPA Roles. For the following experiments, the solutions were oxidized in the PetroOxy device at 150 °C, 700 kPa, until a pressure drop of 40% was attained.

For both antioxidants, the evolution of the pressure drop curve and FTIR results is the same (Figures 3 and 4), pointing that their behavior against oxidation is identical. Moreover, Figure 3 evidences the antioxidant effect of PAN and DODPA by stopping the propagation step (no rapid pressure drops are observed for oxidation of the blends). It is known that secondary aromatic amines are very reactive toward peroxy radicals leading to the formation of amino radical. Nevertheless, on contrary to free radicals generated from the ester, which would propagate the oxidation, amino radicals would increase the oxidation stability by deprotonating hydroperoxyde (which also regenerate a free radical) to generate dimers and trimers which can also react with a free radical.[26]

Kinetic reaction constant k_{app} and the rate of the oxygen depletion noted as v_{O_2moy} corresponding to the slope of the

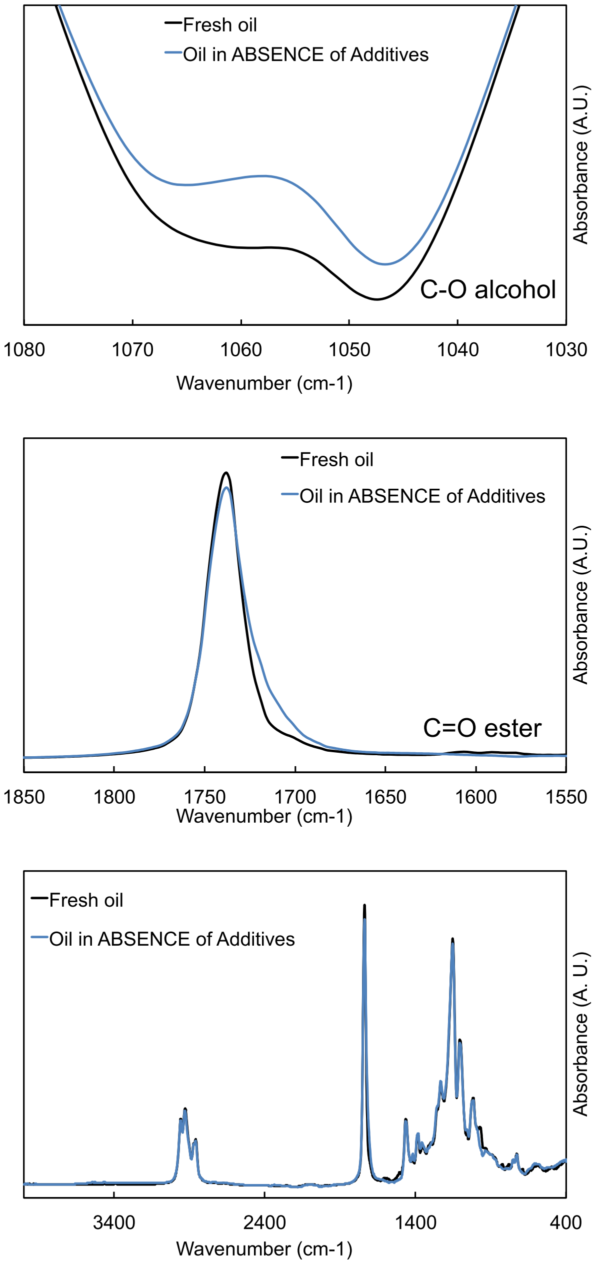

Figure 2. FTIR–ATR for oil without additives ageing in the PetroOxy at T = 150 °C, P_{O_2} = 700 kPa and ΔP = 40%.

oxygen curve were determined for each experiment. The curve of evolution of pressure as a function of the time represents the rate of the reaction between the oil and the oxygen (eq 1).

$$v = k \times [\mathrm{ROOR'}] \times [\mathrm{O_2}] \quad (1)$$

In the PetroOxy device, O_2 is largely in excess so the eq 1 becomes eq 2

$$v \approx k' \times [\mathrm{ROOR'}](1\mathrm{bis}) \text{ with } k' = k \times [\mathrm{O_2}] \quad (2)$$

considering the beginning of the experiment where the concentration of the reactants is stable.

The rate of oxygen consumption of PAN and DODPA is equal. k_{app} was 5.22 kPa/h, slightly higher than the rate measured during the experiment performed for oil without additives, that is, 4.75 kPa/h. This result could be explained by the fact that for the mixture of neopolyol ester with an antioxidant, the structure of the ester undergoes modifications that make it less stable than only the ester. However, it is worthy to mention that the depletion rate of PAN and DODPA is different. Indeed, at the end of the oxidation of the mixtures, PAN was almost completely consumed (only 2% was remaining), whereas only 57% of DODPA was consumed for the same quantity of oxygen depletion (404 kPa) (Table 1). This outcome might indicate that the molecule of DODPA produces active and/or more active compounds, which makes it more efficient than one molecule of PAN. The easiest dissociation of PAN amine bonds may explain this fact, that is, the bond dissociation energy (BDE) of N–H in diphenylamine is 84.7 kcal/mol.[27] However, it seems that pointing to a

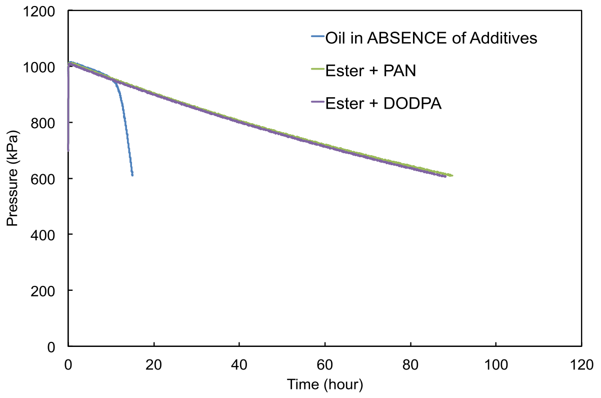

Figure 3. PetroOxy pressure drop curves vs time for oil degradation at T = 150 °C: blue oil without additives, green ester oil with PAN, and violet ester oil with DODPA.

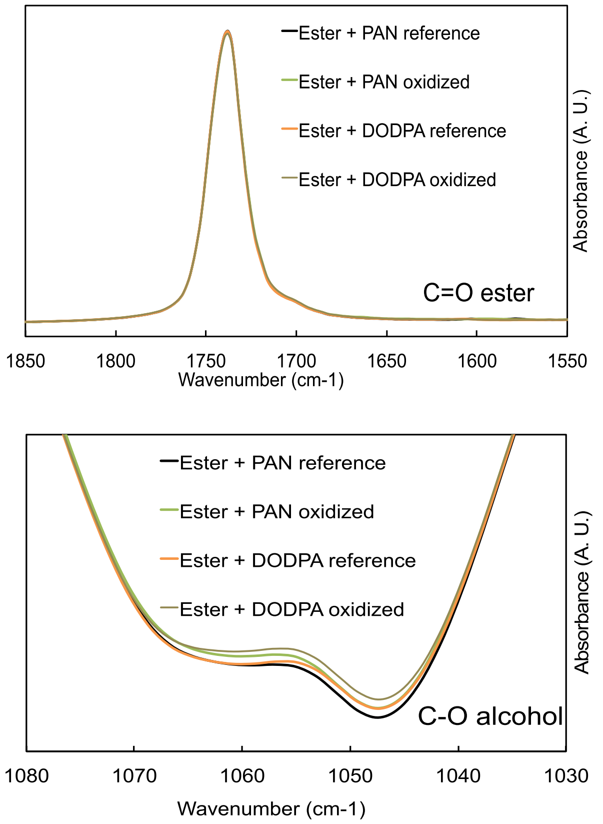

Figure 4. FTIR–ATR for mixtures of ester base with PAN (blue) and DODPA (green) ageing in the PetroOxy.

Table 1. Results of O_2 Depletion, Duration, and Additives Concentration Remaining of All Experiments

								additives concentration (% remaining), HPLC analysis		
type of lubricant	T (°C)	P_i (kPa)	O_2 depletion (kPa)	v_{O_2moy} (kPa/h)	t (h)	k_{app}	E_a (kJ/mol)	PAN (%)	DODPA (%)	TCP (%)
ester	150	700	406	5.44	15	4.75		N/A	N/A	N/A
ester + PAN			405	5.18	90	5.22		2	N/A	N/A
ester + DODPA			404	5.23	88	5.22	N/A	N/A	43	N/A
ester + TCP			405	6.30	17	4.59		N/A	N/A	89
commercial oil			56	7.00	8	6.11		38	87	100
commercial oil			284	5.68	50	5.80		0	52	100
commercial oil	100	700	233	1.59	147	0.70	56.34	33	100	100
	150		396	4.60	102	4.69		0	21	99
	200		444	28.96	17	33.22		0	7	83
commercial oil	150	200	66	2.54	26	2.51	N/A	29	84	100
		700	198	4.60	43	4.66		0	58	100

much weaker BDE for PAN than for DODPA. This being reinforced due to the symmetry of the DODPA molecule.[28]

In line with previous results, FTIR spectra (Figure 4) show no sign of modification of the C═O and C−O bonds of the ester. PAN and DODPA are good antioxidants.

Figure 5 shows the chromatograms obtained for a mixture of neopolyol ester formulated with PAN after oxidation (green) and with DODPA after oxidation (violet). It was possible to quantify the number of products that comes from PAN or DODPA, respectively, 33 and 3 products. None of them comes from both antioxidants. Moreover, for most of the products, their retention time is smaller than the antioxidants, meaning that they are more polar than the antioxidants. Unfortunately, it is the only conclusion that it is possible to know about them without any other characterization.

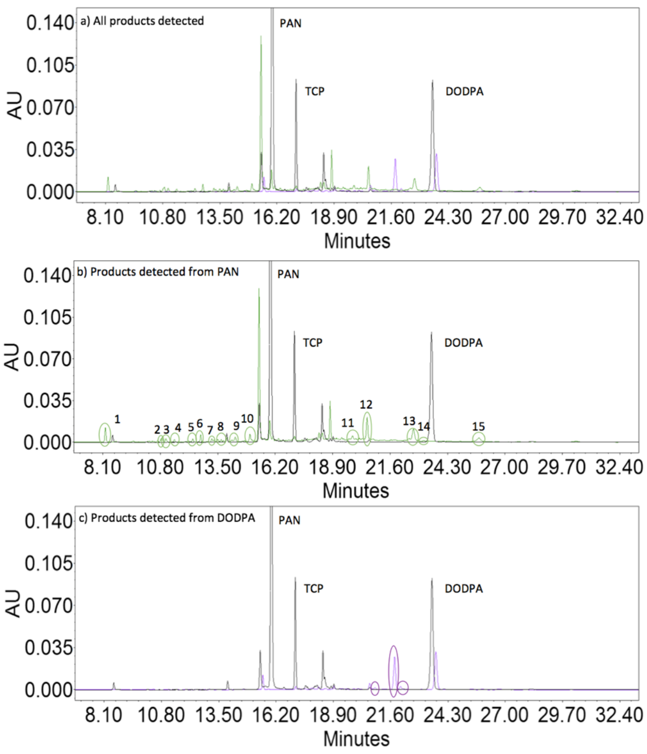

Figure 5. HPLC chromatograms of ester oil with PAN after oxidation (green), ester oil with DODPA after oxidation (violet), and commercial oil before oxidation (black); (a) detection of all of the products formed during the oxidation at T = 150 °C, (b) identification of products from PAN, and (c) identification of products from PAN and DODPA.

For further studies, it would be interesting to analyze theses samples with a mass spectroscopy and to continue the oxidation of the blends of ester + PAN or ester + DODPA to see what would happen in the case where the antioxidant will be completely consumed (if the propagation step will appear or not).

2.1.3. Effect of TCP.

The additive tested in this section is an antiwear: the TCP. Ester base oil was mixed with 3 wt %[29] of it. Then, the solution was oxidized in the same conditions as previously.

Figure 6 presented identical pressure drop curve to the oxidation of the additive-free pristine neopolyol ester. An antiwear is clearly not effective in preventing oxidation. Its role is to limit the wear between parts. These results show the importance of N−H bond to prevent oxidation. High-performance liquid chromatography (HPLC) results show a consumption of TCP of 11% (Table 1) but no product was detected.

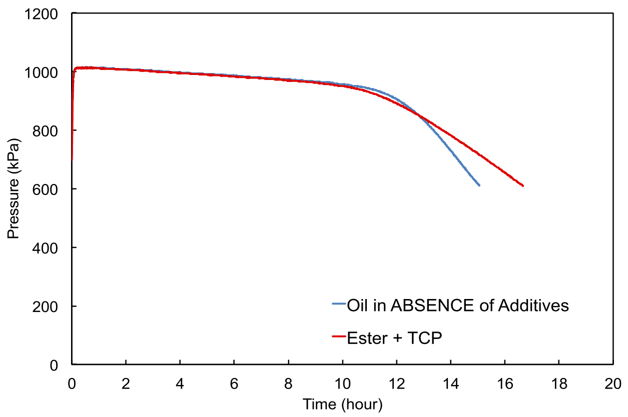

Figure 6. PetroOxy pressure drop curves vs time for oil degradation at T = 150 °C: blue oil without additives and red ester oil with TCP.

Nevertheless, FTIR spectra (Figure 7) show an alteration on the C═O bond, meaning that the degradation produced carbonyl compounds and alcohol products, which should come from the reaction between ester and oxygen. That is the reason why it is not possible to detect these compounds by HPLC (absence of aromatic group in the molecule).

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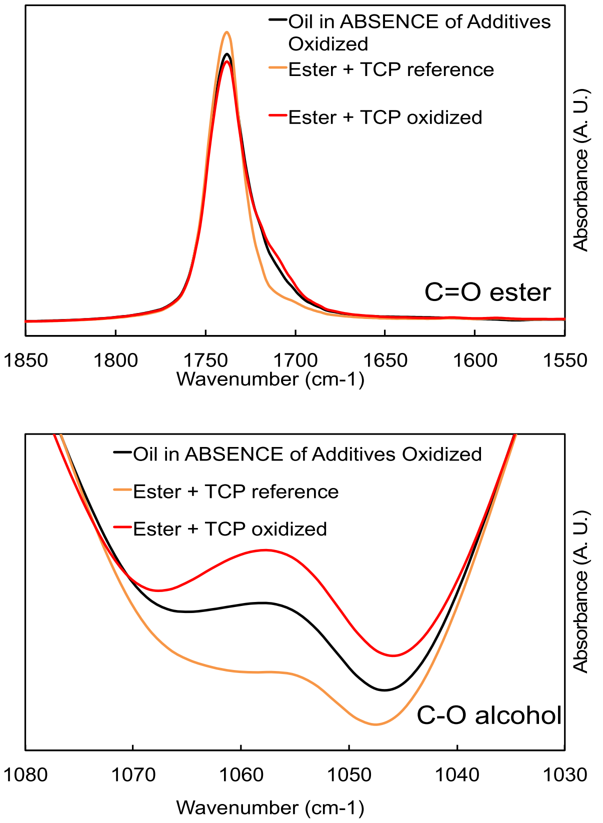

Figure 7. FTIR–ATR for mixtures of ester base with TCP (red) ageing in the PetroOxy.

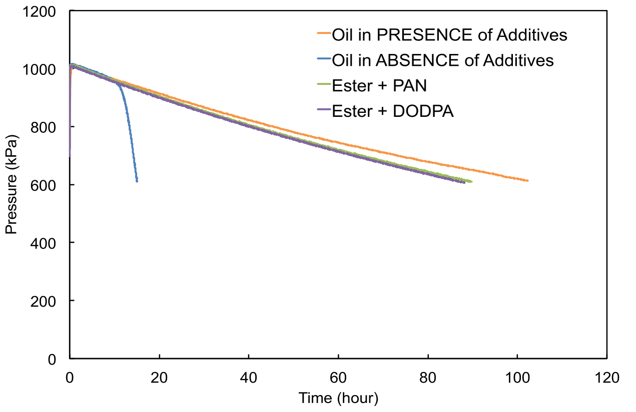

Figure 8. PetroOxy pressure drop curves vs time for oil degradation at T = 150 °C: blue oil without additives, orange oil with additives, green ester oil with PAN, and violet ester oil with DODPA.

2.1.4. Influence of the Presence of Additives. Previous results indicate that PAN and DODPA are satisfying antioxidants and that a mixture with TCP has the same behavior than neopolyol ester against thermo-oxidative degradation. This section is focusing on the oxidation of the commercial lubricant (with all additives) in the same conditions as previously (T = 150 °C, P = 700 kPa, ΔP = 40%).

With the aim of monitoring the remaining concentration of the different additives, two additional PetroOxy experiments were performed during 8 and 50 h (corresponding, respectively, to the initiation and propagation step of the reaction). The results of the HPLC analysis for these tests can be found in Table 1. Figure 9 contains the FITR spectra recorded for the different lubricants submitted to these PetroOxy experiments.

Figure 8 shows that the initiation part of the curve is overlapped for both the commercial lubricant and the additive-free ester. The antioxidant effect of additives remains latent. The concentration of radical species in the media continues increasing.

In the commercial lubricant and thus in the presence of additives, the additive molecules stop the radicals to attack the ester by reacting with them.[11] This results in additive consumption, but at the same time in the protection of the ester against oxidation. Radicals are quenched through reaction with the additive molecules, being no longer involved in the oxidation mechanism. Consequently, the rate of oxygen consumption during the propagation step is considerably slowed down. The presence of the additives is thus the cause of this antioxidant effect that clearly enhances the oxidation stability of the lubricant.[30]

Upon 8 h of reaction, that is, at the end of the initiation phase, the consumption of PAN reaches 62%, whereas DODPA has been consumed to a very small extent, that is, 13%. This means that a certain amount of the radicals formed during the initiation step did already react with PAN molecules. The ester molecules are well preserved from oxidation during this first 8 h of reaction, as confirmed by the almost identical FTIR spectra obtained for the oxidized lubricant and the fresh one (Figure 9). PAN is completely consumed upon 50 h of oxidation, as well as half of the initial amount of DODPA. At this point of the reaction, we are in the

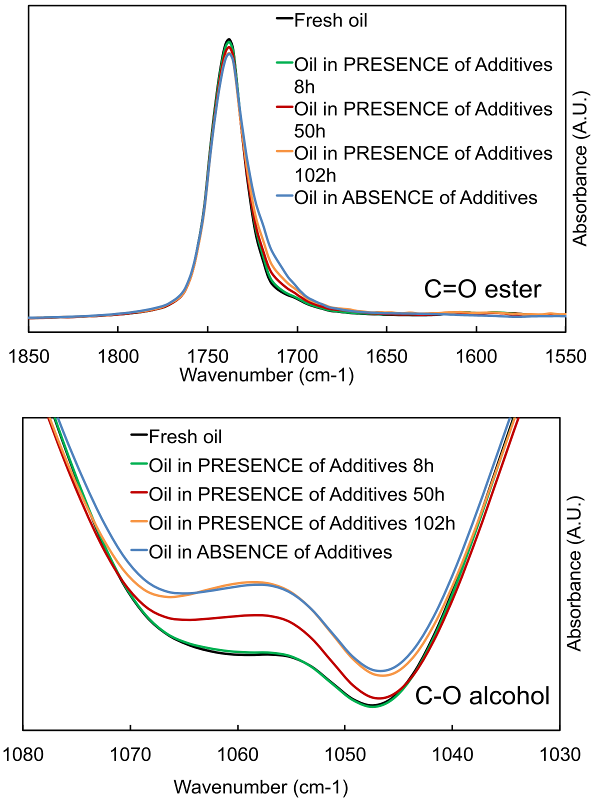

Figure 9. FTIR–ATR for oil with and without additives ageing in the PetroOxy.

propagation step and DODPA follows PAN taking the lead in the neutralization of the radicals. Still, the ester molecule has been already attacked to a certain extent because the FTIR profile already evidences the formation of short chain products and alcohols as degradation products. Upon 102 h of reaction, and corresponding to a pressure drop of 40%, more than 80% of the initial DODPA has been consumed and the oxidation of the ester becomes even more evident in the FTIR spectra. At this point, the peak characteristic of alcohol formation (C−O bond) presents very similar shape and intensity than the one observed in the PetroOxy-oxidized additive-free ester. On the contrary, the carbonyl bond in the ester appears more degraded for this last one than in the additive-containing lubricant oxidized during 102 h. Though a quantitative analysis of FTIR profiles is not straightforward, it may seem that alcohol formation has reached the same limit and that in the absence of additives, the oxidation mechanism follows different pathways not specially leading to the formation of alcohols but of other degradation products.

PAN is the first additive that reacts protecting ester against oxidation. In fact, Hunter et al. showed that PAN reacts in order to limit the formation of radicals and hydroperoxides and thus to limit the initiation step.[25]

Moreover, Table 1 shows that the rate of oxygen consumption k_{app} of the commercial lubricant is slower than one of the mixture of neopolyol ester and PAN or DODPA. This decrease could be explained by the synergistic effects of antioxidants.[31] For oil in the presence of additives, 79% of DODPA was consumed and only 57% for the mixture between neopolyol ester and DODPA, whereas for PAN, the rate of consumption of the additive was equal for the commercial lubricant and the mixture. This shows that oxidation mechanism of PAN in the presence or the absence of other additives is the same, whereas the one with DODPA is different. It is possible that DODPA also reacts with other products formed during the oxidation, which would explain the results obtained.

The comparison of HPLC chromatograms (Figure 10) between standard oil (orange) and the mixture indicates that most of the products formed from PAN or DODPA are present in the commercial lubricant. Four types of product are observed: numbers 3, 4, 6, 8, and 10 from PAN seems to be higher for the lubricant than for the mixture with PAN because of the height of the peaks; 2, 5, 7, 9, 11, and 14 from PAN and 1 and 3 from DODPA look to be in the same proportions, compound numbers 1, 12, and 13 from PAN and 2 from DODPA assume to be higher than if it is formed in the standard oil oxidized and finally some products are present in the lubricant and not in the blends. Those last ones could be from the reaction from both antioxidants. The presence of other additives should have an impact on the formation of these products.

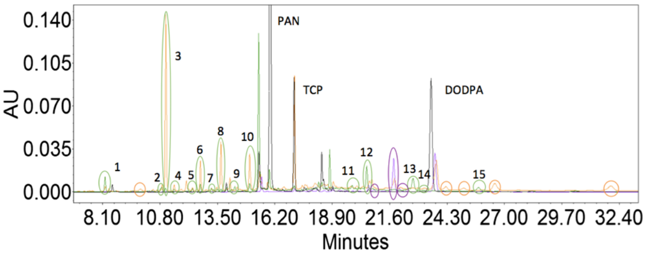

Figure 10. HPLC chromatograms of commercial oil before oxidation (black), after oxidation (orange) and blends of ester oil with PAN (green) and ester oil with DODPA after oxidation (violet).

Furthermore, some of the products detected with standard oil after oxidation were not formed for the mixtures, which should also confirm the synergistic effects of antioxidants.

2.2. Influence of the Temperature on the Oxidation of the Lubricant. Last, after the study on the oxidation of neopolyol ester mixed with additives, this part will discuss about the important parameters that could influence thermo-oxidative degradation.

The commercial lubricant oil was oxidized at three different temperatures (100, 150, and 200 °C), and at an initial oxygen pressure of 700 kPa, until a pressure drop of 40% was reached. Figure 11 shows the evolution of pressure, and thus the oxygen consumption, as a function of time for the oxidation of the lubricant at the three reaction temperatures. It should be mentioned that though the initial pressure at ambient temperature was fixed at 700 kPa, the heating of the autoclave reactor up to each targeted temperature results in an increase of the pressure that can be clearly observed in the curves. The 40% pressure drop threshold was in fact calculated using these oxygen pressures as a reference. The longer heating up period in the case of the PetroOxy experiment performed at 200 °C is moreover the cause of the artifact observed at very incipient reaction times, that is, an initial increase in the pressure can be observed in this case corresponding to the first 10−15 min of the test. In that case, the extent of each reaction is not the same but first conclusions can be drawn by these experiments.

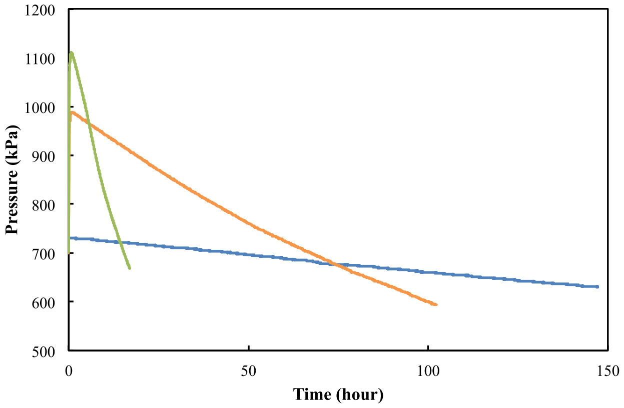

Figure 11. PetroOxy pressure drop curves vs time for oil degradation at T = 100 °C (blue), 150 °C (orange), and 200 °C (green).

It is important to state that because the oxidation implies two reactants in a different physical state, the reaction mostly occurs at the surface of the liquid, which is the contact area of the oxygen and the oil.

At 100 °C, the oxygen consumption decreases slowly with time, corresponding to a long induction phase (Figure 11a). The formation of the oxidation products is also slow because very small differences were observed in the FTIR spectra of the fresh and the 100 °C oxidized lubricant, as will be commented later on. Even though, at the end of the experiment (more than 100 h), the oxidation consumed 70% of the antioxidant PAN (Table 1). PAN starts playing its antioxidant role already at temperatures as low as 100 °C which is not the case of DODPA. No consumption was detected (Table 1). At this

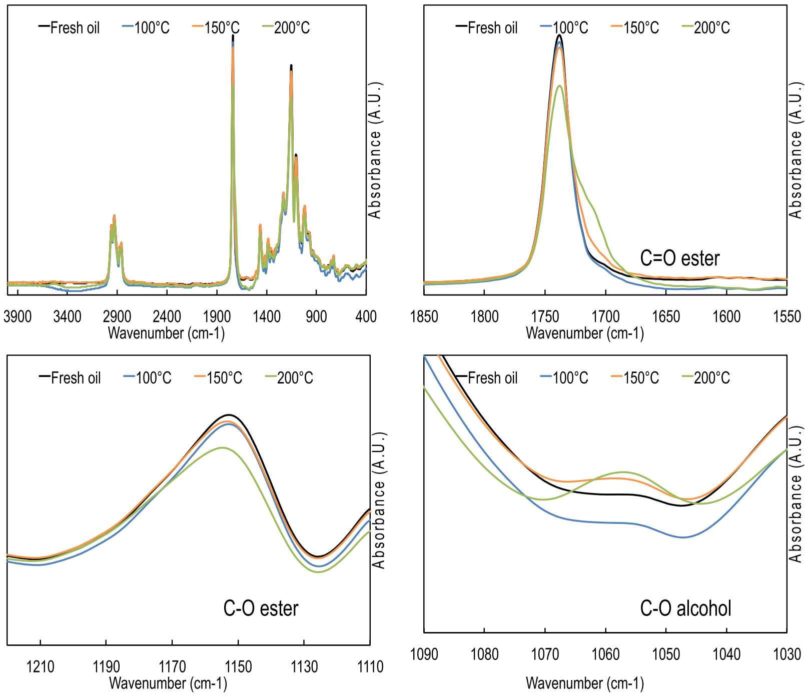

Figure 12. FTIR−ATR results for oil ageing at different temperatures in the PetroOxy.

relatively low temperature, the consumption of PAN seems enough to protect the lubricant against oxidation.

Figure 11 clearly evidences that increasing the temperature results in a reduction of the reaction time, that is, oxygen is consumed significantly faster until the 40% pressure drop threshold is achieved. Temperature boosts the oxidation rate by providing increasing thermal energy. The rate of the oxygen diffusion will also increase. Both facts can contribute to an enhanced deprotonation of the core ester molecule of the lubricant, leading to faster oxidation. Moreover, already at 150 °C (Figure 11b) and even more remarkably at 200 °C (Figure 11c), a change in the oxygen consumption rate, that is, pressure decreases as a function of time—slope of the curve, can be observed. This occurs at about 45 h reaction time for the PetroOxy experiment performed at 150 °C and much earlier, at about 10 h reaction time, for the experiment performed at 200 °C.

Kinetic reaction constant k_{app} determined for each experiment. Table 1 shows that increasing the temperature by 50 °C increases the reaction rate by six to seven times and because of the consumption of the reactants over time, which decrease the frequency of the collisions between molecules. k_{app} is almost equal to v_{O_2moy} at 150 °C. The difference between v_{O_2} and k_{app} observed for 100 and 200 °C implies that there are important parameters which are not consider in eq 1.

Then, in this section, on the basis of the Arrhenius eq 3 describing the temperature dependence of the reaction rate constant, the activation energy of these experiments was determinate by plotting the graph of ln k versus $1/T$. The activation energy obtained equals to 56.34 kJ/mol.

$$k = A \times \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

At the same time, the results of the HPLC analysis (Table 1) point to a complete consumption of PAN at 150 °C, together with an important consumption of DODPA (79% consumed at 150 °C, 93% consumed at 200 °C) and an incipient consumption of TCP, an antiwear additive, which becomes noticeable at 200 °C (17% consumed). This might be the reason why PAN and DODPA are both used as an antioxidant. It is therefore possible that the implication of DODPA in the reaction mechanism, upon the complete consumption of PAN, causes a change in the reaction mechanism that becomes visible in the curves through the change in the slope observed at 150 and 200 °C. Higher reaction temperatures, and thus further acceleration of the oxidation process, are needed thus for activating the DODPA antioxidant and for observing its effect into the overall oxidation mechanism. Once DODPA takes the lead, the oxidation rate is further slowed down, as can be deduced from the decreased slope in this part of the PetroOxy curves. The consumption rates of PAN and DODPA are different. The results presented in Table 1 also evidence a non-negligible consumption of TCP, pointing to a possible antioxidant role of this antiwear additive but confirmed by the first results that TCP does not.

The infrared spectra of the fresh and the oxidized lubricant are presented in Figure 12. Upon PetroOxy oxidation, the intensity of the carbonyl peak decreases as it becomes broader; this being accompanied by the apparition of a shoulder at lower wavenumbers. This becomes particularly evident for the lubricant oxidized at 200 °C, being already remarkable in the FTIR spectrum corresponding to the lubricant oxidized at 150 °C. This shoulder corresponds to the formation of oxidation products, which also contain a carbonyl bond. It should be mentioned that the O−H bond from carboxylic acids was never detected in these FTIR patterns. Shorter chain, lower molecular weight products may be formed as a consequence of the breakdown of the C−O bond because the spectra do not point to a set off of the polymerization phase.[6] Indeed, at temperatures of 150 °C and higher, derived primary alcohol products start to be produced, as pointed out by the presence of a band of increased intensity appearing at about 1064 cm^{-1} as the intensity of the peak C−O decreases.

Even if the extent of the reaction is not the same, all of these results show that below 150 °C, the temperature is too low to initiate the dissociation of the N−H bond in DODPA and PAN is therefore playing the main role as an antioxidant, quite efficiently protecting the core neopolyol ester molecules of the lubricant from oxidation. From 150 °C and on, an important oxidation extent is observed, resulting in the formation of short chain, lower molecular weight oxidation products. Because the temperatures reached in an aircraft turbine engine are rarely as high as 200 °C, a temperature of 150 °C was chosen to perform the study of the influence of the oxygen initial pressure and of the role of the different additives.

Figure 13 shows the chromatograms obtained for oil oxidized at 100, 150, and 200 °C. Each peak corresponds to a product of the oxidation and is an aromatic compound. They come from PAN or DODPA. The number of products increases with the temperature until 150 °C (17 peaks detected for oil oxidized at 100 °C and 25 peaks at 150 °C) and then decreases at 200 °C (22 peaks) but the identification was not possible in this work.

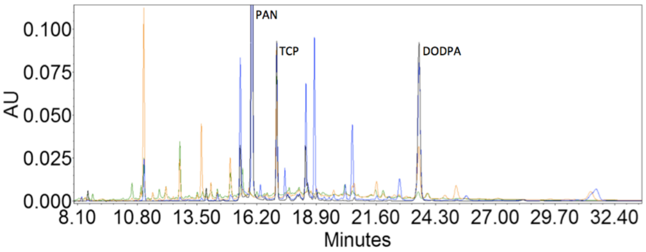

Figure 13. HPLC chromatograms of oil ageing in the PetroOxy: non oxidized oil (black), oxidized oil at 100 °C (blue), 150 °C (orange), and 200 °C (green).

2.3. Influence of the Initial Pressure on the Oxidation of the Lubricant. In order to analyze the influence of the initial oxygen pressure during the PetroOxy oxidation of the commercial lubricant, two experiments were performed at 200 and 700 kPa and at a temperature of 150 °C, setting the pressure drop threshold delimiting the end of the experiment at 20% (instead of 40%). The pressure versus time curves obtained are depicted in Figure 14.

Because of the highest initial pressure registered for the PetroOxy experiment performed at 700 kPa (1010 kPa at 150 °C), the 20% pressure drop threshold was attained upon 43 h reaction, whereas the experiment performed at 200 kPa (289 kPa at 150 °C) was finished after 26 h reaction. The rate of oxygen consumption was also different. With 198 kPa depleted in 43 h, the oxygen consumption rate for the experiment performed at 700 kPa was 4.66 kPa/h, almost two times higher than the rate measured during the experiment performed at 200 kPa, that is, 2.51 kPa/h. This fact points to faster oxidation as the initial oxygen pressure increases. Higher oxygen pressure increases the concentration of the gas inside the autoclave reactor and thus enhanced the oxygen diffusion inside the liquid lubricant sample, thus resulting in increased oxidation rate. Koh and Butt[3] showed that there are three main steps to be considered in the oxidation of a poly(α-olefin) lubricant. Oxygen is first transferred from the gas phase to the interface with the liquid phase, then dissolved into the bulk of the liquid phase, and then consumed in the oxidation reaction occurring in this liquid phase. Oxygen partial pressure in the gas phase might have thus an effect on two parameters concerning the overall oxidation process: the intrinsic rate of the chemical reaction and the transport of the oxygen from the gas phase into the liquid phase.

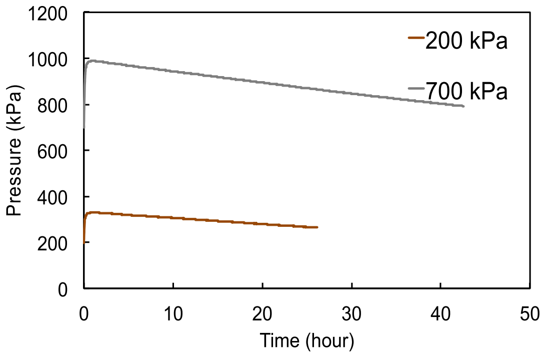

Figure 14. PetroOxy pressure drop curves vs time for oil degradation at P = 200 kPa and P = 700 kPa.

Once again, the extent of each reaction in this section is not the same but what can be noticed is that PAN is the first antioxidant to be consumed, that is, complete consumption upon oxidation at 700 kPa, whereas 29% of the initial amount of this additive still remained in the one oxidized at 200 kPa (Table 1). DODPA consumption was therefore higher when performing oxidation at 700 kPa instead of 200 kPa, though reaction at 200 kPa was already stringent enough to start involving the antioxidant effect (and consumption) of DODPA.

The infrared spectra acquired for this series of oxidized lubricants are shown in Figure 15. Oxidation at 200 kPa does not result in visible chemical changes in the core of the neopolyol ester because the FTIR spectrum obtained for carbonyl bond is practically the same one acquired for the fresh lubricant. However, the decrease of the intensity of the C−O bond from the ester lead to the formation of C−O bond corresponding to the formation of primary alcohols as oxidation products. Moreover, at 700 kPa, the spectrum also evidences the modification of carbonyl bond.

3. CONCLUSIONS

The PetroOxy device can be used to study the oxidation stability of neopolyol ester lubricants. This method combined with HPLC analysis shows that:

- PAN is first to play its antioxidant role at temperatures as low as 100 °C—BDE of PAN is much weaker than that for DODPA;
- 33 products were observed, coming from PAN;
- when DODPA step in the oxidation mechanism that causes a change in the reaction mechanism that could be observed in the curves of oxygen depletion at higher temperatures;
- only three products were detected from DODPA; and
- by combining both antioxidants, it is possible to further increase the oxidation stability of the lubricant because of their synergistic effect.

Moreover mass spectrometry can identify the detection of products from antioxidant degradation by HPLC. This was not investigated in this work but might be the topic of further studies.

FTIR analyses show the degradation of the two main bonds of the ester:

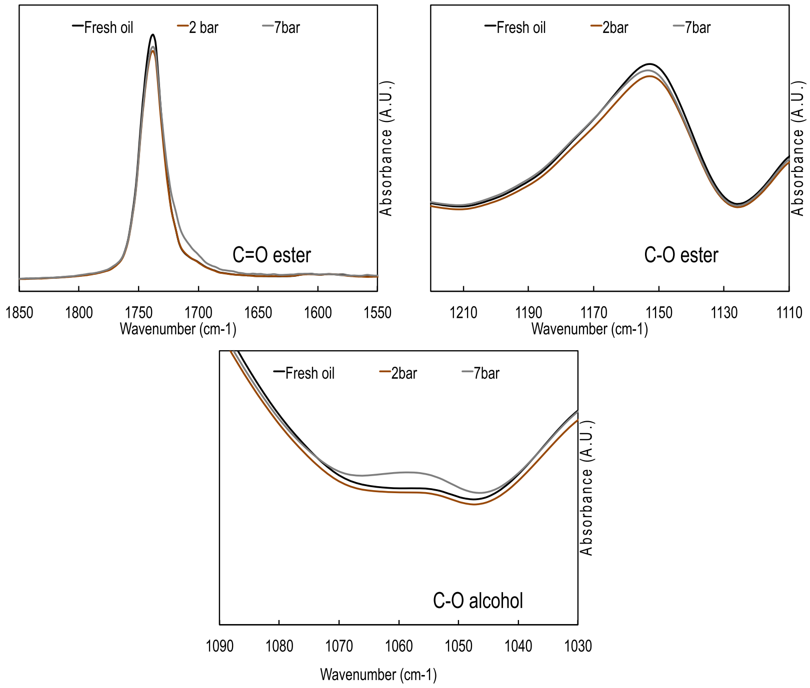

Figure 15. FTIR–ATR results for oil ageing at different pressures in the PetroOxy.

- the carbonyl bond corresponding to the formation of oxidation products such as aldehydes and ketones;
- and the C–O bond, which lead to the generation of alcohol products.
- No other bonds corresponding to carboxylic acids, polymers, or oligomers have been detected.

A correlation could be made between infrared spectrometry and liquid chromatography. Degradation on the neopentyl ester oil could be predicted by the value of remaining concentration in oxidized oil.

Furthermore, PetroOxy can provide the time needed for the oxidation reaction of the synthetic ester to go through his initiation to the propagation step. At 150 °C, 9 h of reaction is necessary to increase the concentration of radical species to trigger the propagation phase. Increasing the temperature would decrease the time before oxygen depletion.

RSSOT is a good alternative method to understand and measure the oxidation stability of the synthetic ester lubricant. It is a fast and simple technique. Monitoring oxygen consumption enables to determine the effect of the antioxidant and the two main steps of oxidation mechanism. In order to confirm these results, it would be necessary to oxidize a sample of oil without additive at 200 °C. Unfortunately, this was not possible in our case because the temperature maximal of use of the PetroOxy device available in our work was 160 °C.

Results obtained can be a step forward toward evaluation of the oxidation stability of synthetic ester lubricant by the RSSOT method. More data are needed to complete the understanding of the behavior of the oil using this device.

4. MATERIALS AND METHODS

4.1. Lubricating Oil and Antioxidants. The compounds used in this work were the same as typically used in a standard aircraft turbine lubricant. The ester base of the oil, obtained by the esterification of pentaerythritol with saturated monocarboxylic acids having carbon atom number from C_5 to C_{10},[31,32] was a commercial ester base oil. Two different antioxidants, PAN ($C_{16}H_{13}N$) and DODPA ($C_{28}H_{43}N$), and also antiwear TCP ($C_{21}H_{21}O_4P$) were supplied by the manufacturer.

The solutions containing neopolyol ester base oil and different additives were stirred together at 80 °C in a beaker until homogeneity. Percentage of the additives was considered in the same proportioned as in the standard oil (1–2 wt % for antioxidants (PAN and DODPA were mixed in the same amount) and 3 wt % for antiwear).[16]

4.2. Accelerated Oxidation Tests. The PetroOxy device was conceived to study the oxidation stability according to three parameters: the temperature, the initial oxygen pressure, and the time of the experiment. The apparatus is well described elsewhere.[33]

In each experience, 5 mL of oil sample was placed into the cell of the PetroOxy apparatus at ambient temperature. A screw cap and a safety hood hermetically seal the cell. In order to drain all the gas inside, pure oxygen (Air Liquide, ALPHAGAZ 1 Oxygen) was injected until the initial pressure of 700 kPa and then evacuated two times. After purging, the cell was pressurized once again with pure oxygen at 700 kPa, the oil sample being heated up to the specified temperature. A data acquisition system monitored the decrease of the pressure during the entire experiment, which last until $\Delta P = P_{max} - P = 40\%$ (stop criterion defined in this work). The PetroOxy experiments were carried out on an oil without additives and solutions of neopolyol ester base oil mixed with each one of the antioxidants at a temperature of 150 °C and a pressure of 700 kPa being the pressure use in the standard normalized tests for the characterization of the oxidation stability of aeronautical and automotive fuels. Finally, the oxidation was carried out on an oil with additives (standard oil) at three different temperatures: 100, 150, and 200 °C, and then at two different initial pressures: 200 and 700 kPa, at a fixed temperature of 150 °C. The fresh and oxidized lubricants were characterized by means of different physico-chemical techniques (FTIR and HPLC). It is essential to monitor the remaining concentration of antioxidant in the oil after oxidation by liquid chromatography as an indicator for the extent of oil oxidation.[29,34]

4.3. High-Performance Liquid Chromatography. The HPLC was performed on Waters e2695 equipped with a diode array detector UV e2998. An oil sample (100 mg) was first diluted in 10 mL of tetrahydrofuran (THF). A 10 μL volume of this solution was then injected into a stainless steel column (Waters XSelect type CSH C18, 250 × 4.6 mm ID, 5 μm particle size). Water and acetonitrile (ACN) were used as the solvent for the mobile phase in a gradient mode. The temperature of the column was maintained at 40 °C and the samples at 4 °C. The pump flow rate was set to 1 mL/min. The wavelength of detection was 254 nm. This technique was used to monitor the quantitative results of antioxidant depletion by a comparison of peak area.

Figure 16 shows a typical chromatograph of the lubricant before ageing. One peak at a specific retention time corresponds to one specific molecule. In our case, PAN is detected at 15.97 min, TCP at 17.14 min, and DODPA at 23.82 min.

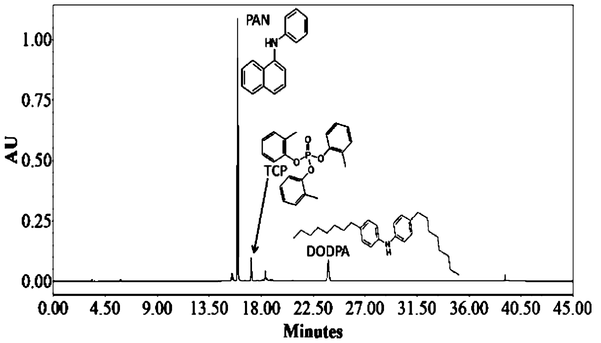

Figure 16. HPLC chromatogram of fresh oil. Retention time of the additives: PAN 15.97 min; (middle) TCP 17.14 min; and (right) DODPA 23.82 min.

4.4. Fourier Transform Infrared Spectroscopy. FTIR was performed using a Bruker spectrometer TENSOR 27. A drop of lubricant was applied on an attenuated total reflectance (ATR) cell equipped with a ZnSe single crystal. The spectra were recorded over the wavelength range of 4000−400 cm^{-1} with a resolution of 4 cm^{-1} using 16 scans. FTIR was utilized for monitoring the changes of the structure of the base oil.

The main chemical bonds of the ester, that is, the carbonyl bond $C{=}O$, appears at 1710 cm^{-1}, and $C-O$ bond is detected at 1200 cm^{-1}, whereas $C-H$ bonds, that is, $C-H_2$, $C-H_3$ can be observed at about 3000 cm^{-1}. The analysis of the FTIR spectra allows therefore detecting the degradation of the ester base of the lubricant, through the simple comparison of the spectra of both oxidized oil and fresh oil. Moreover, after oxidation, the production of primary alcohols should be observed at 1050 cm^{-1} ($C-O$ bond) and 1350−1260 cm^{-1} ($O-H$ bond), aldehydes at 2880−2650 cm^{-1} ($C-H$ bond) and 1740−1720 cm^{-1} ($C{=}O$ bond) and carboxylic acids or also alcohols with a wide band at 3500 cm^{-1} ($O-H$ bond).[35]

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Notes

The authors declare no competing financial interest.

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