Study on Thermal Oxidation and Viscosity Degradation for Synthetic Aviation Lubricant Fluids

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Abstract: The thermal oxidation and viscosity degradation for poly-α-olefins (PAO) and di-esters (DOS) was studied under the GC/MS investigation. Through the oxidative pyrolysis conditions, these two synthetic base fluids were characterized to get their simulated “aero-engine” conditions for thermal stability, such as oxidative and kinematic viscosity variation. The experimental results suggest that the oxidation products generated from oxidation reactions of DOS is mainly single esters, di-esters, ketone, ether, organic acids and alcohol, which results much bigger total acid values than that of PAO treated in similar conditions. The substantial increment of the kinematic viscosity of DOS reveals its limited thermal oxidation stability compared to PAO.

1. Introduction

The synthetic lubricating fluids, poly-α-olefins (PAO) and synthetic esters (DOS) are formulated to suit the aviation applications. Compared to the mineral fluids, PAO and DOS have unique properties of high viscosity, low corrosive and volatility and toxicity, etc. The excellent viscosity index property of PAO and DOS allows the synthetic lubricants to be used at extended operation temperature ranges. However, the PAO and DOS base oils are gradually hard to meet the increasing standards of next generation aviation lubrication oils, due to the limited application properties and promoting demands of high-performance aero-engine at conditions of ultra temperature, revolving speed and catalyst of transition metal ions [1]. In particular, viscosity thinning and colour deepening of in-use oil embarrass normal usage of the aero-engine, which influences lubricants’ comprehensive properties severely, such as lubricity, viscosity and volatility, so as to understand the molecular composition through the oxidative pyrolytic process.

Sophisticated detection strategies have been developed to identify the molecular information of the lubricants. The gas chromatography/mass spectrometer (GC/MS), has been widely accepted for evaluating the molecular change of lubrication oils, is effective for analysing the most volatile species, through which we could monitor the thermal-oxidative stability of lubricants. Nowadays, the GC/MS method has been successfully applied in deep analysis of medicine molecules [2], special steroids [3], common contaminants [4], mainly species of crude oils [5] and synthetic polymers used in petroleum products [6].

Both the PAO and DOS base oils are important synthetic lubricating fluids [7-9], which is need further investigations to understand the chemical reactions occurs under extreme condition that simulated the aviation engine operated at harsh condition. In this paper, the molecular structure analysis of the PAO, DOS and their oxidation products were characterized through viscosity testing experiments and GC/MS.
2. Experimental

2.1 Fluid Sample and Reagents
The PAO and DOS base oil are purchased from Yiping Lubrication Company of SINOPEC. Other reagents used in this paper like petroleum ether, acetone, n-hexane and so on are analytical pure degree, and the reagents applied while they are received without any further treatment.

2.2 High temperature oxidation of the oil samples
All of the received oil samples including PAO and DOS are oxidized at 170°C, 200°C and 300°C, respectively, in a 300mL stainless-steel, mechanically stirred autoclave with the stirring rate of 800r/min. The oxidation time lasted for 2 hours, then the products are allowed to cool down to room temperature and collected for the kinematic viscosity examination according to ASTM D445 standard to evaluating the deterioration of the viscosity properties of the oxidized oil samples. For convenience in description, the PAO, DOS and the oxidized oil samples treated at 170°C, 200°C and 300°C are named as P0, P1, P2, P3 and E0, E1, E2, E3, respectively.

2.3 Analytical Methods
PAO, DOS and their degraded samples were analyzed with a Frontier Fourier transform infrared (FTIR, Perkin Elmer Company) spectrometer by collecting 64 scans at a resolution of 8 cm⁻¹ in reflectance with measuring region from 4000 to 400 cm⁻¹.

Afterwards, fluid samples were analyzed with a Perkin Elmer GC/MS (GC Clarus 680 and MS Clarus SQ 8 T), which was equipped with a capillary column coated with MS-5 and a quadrupole analyzer with a m/z range from 45 to 550 and operated in EI mode. The capillary column was heated from 50°C to 280°C at a rate of 10°C/min and held at 280°C for 8 min.

3. Results and Discussion

3.1 FTIR Analysis
The FT-IR method is applied to study the functional groups variation in the base oils used in this paper after oxidation reactions. As studied before, the synthetic lubricant oils are used to be changed both in chemical composition and physical properties. Their oxidation products, which are mainly harmful to the physicochemical performances of these lubrication oils, should be formed during the oxidative thermal cracking process \[10\].

![Fig.1 Infrared spectra of PAO and their reacted samples](image)

As shown in Figure 1 and 2, the functional groups of PAO and DOS are changed during oxidation reactions based on the FTIR analysis of PAO and DOS oil samples according to the experimental conditions. The IR absorbance peaks centered at around 2844-2963 cm⁻¹ and 1461 cm⁻¹ are assigned...
the energetic absorption of aliphatic moieties (AMs) from Pn species (n=0-3), which is much stronger than those of En species, indicating that AM-rich species in P_n are predominant species. The AM-rich species in P_n is mainly from the oxidation reaction of the special structure of PAO, which is the multi-aligned side-chains comb-like and straight chain alkynes skeleton bones molecular structure. The strong absorption peak at ~3431 cm^{-1} and 3462 cm^{-1} could be attributed to stretching vibration of −OH group. The stretching vibration of −OH groups in E_n is also stronger than that in P_n. As shown in Figure 1, the relative weak absorption peak at ~1640, 1642, 955 and 891 cm^{-1} could be attributed to the absorbance effect of C=C group that might be β-elimination reactions occur in the P_n, indicating the existence of olefins in P_3.

![Infrared spectra of DOS and their reacted samples](image)

Figure 2 Infrared spectra of DOS and their reacted samples

Relatively absorption peak at ~1735 cm^{-1} could be assigned to the −C=O bond of carboxyl groups in En, which is nearly weak in P_n, which is also proved that the -C=O is the dominate group in the esters of DOS base oils. The characteristic absorption peak of the carbonyl group of the aldehydes, ketones and carboxylic acids appear at ~1718 cm^{-1}. Such absorption peaks of PAO are very weak, suggesting that fractional substances are oxygenized. The absorbance of more -(CH2)n- at 754 cm^{-1} of but the DOS oil samples are much stronger, which indicates that the DOS has been thermal oxidized and generated many small oxidation products.

3.2 GC/MS Analysis

The GC/MS analysis is applied to investigate the molecular structure of the oxidized oil samples to further research the thermal cracking effect of high temperature oxidation atmosphere. As shown in Figure 3, as much as 94 micro chemicals (MCs) were found in the GC and MS results. Both the PAO and DOS oil samples are tested. The chemicals include 13 n-alkanes (NAs), 26 iso-paraffins (IPs), 51 olefins (OFs) and 4 other compounds (OCs) shown in the left graph in Figure 3 PAO reacted oil samples. For the DOS oil samples, 53 MCs were identified, includes 24 small esters (SEs), 13 micro-di-esters (MDEs), 9 ketones, 3 alcohol, 1 organic acids (OAs), 1 alkane and 2 ethers. The results indicate that the chemical composition of oxidation products in oxidation reactions of PAO is much more complicated than DOS, which also generates more oxidation products during oxidation process of the base oils.

As shown in figure 3a, the main products from chemical pyrolysis reactions of PAO are IPs, NAs and OFs. The carbon number of the backbone of oxidation products of NAs is from 12 to 24, and the C20 chemical species are dominant compounds. The relative content of RC and OFs are equivalent to that of NAs, which the carbon number the backbone of oxidation products of DOS is from 12 to 23, indicates that oxidative molecular recombination reactions happened with increasing oxidation temperature. This result is quite similar to the oxidative molecular composition of the former PAO products. The results give the higher content of long-chain macromolecular species and quite less oxygen-containing organic compounds (OCOCs) in the oxidation products. The results also show that
the existence of OCOCs is coincident with the results from the FTIR analysis in figure 1 and 2. However, the RC of OCOCs is nearly 1.03 % and only show in the oxidative products in PAO. The existence of RC of OCOCs indicates the higher oxidation degree of PAO base oils which is depicted in Scheme 1.

![Relative abundance of PAO (a), DOS (b) and their reacted samples](image1)

Fig. 3 Relative abundance of PAO (a), DOS (b) and their reacted samples

The first oxidation cracking of PAO is such as –CH2- bonds in the backbone in the comb-like molecular to produce large amounts of olefins in the process. Thus some of the olefins are oxidized and rearranged by further reactions. According to oxidation mechanism, the oxidation of NAs or IPs could be described to the cleavage of weak covalent bonds at the tertiary carbon atom.

![Scheme 1 Mechanism for PAO oxidative pyrolysis reactions](image2)

Scheme 1 Mechanism for PAO oxidative pyrolysis reactions

The formation of di-alkenes or vinyl radicals is the part of vial dehydrogenation of the further decomposition of OFs and OCOCs. However, the oxidation of dialkenes and vinyl radicals could efficiently destroy the C-C bonds to produce very small aromatic products at higher emperatures exceed 300°C, the materials could results the darken oils colour.

As depicted by figure 2b, the order: E3 >> E2 > E1 > E0 is found in the RC of SEs decreases order. With carbon number of the backbone from 13 to 16, the SEs in E1, E2 and E3 are mainly short-chain species, gives the RC of SEs from E3 (1.36%) is triple more than that from E2 (0.39%). The yields of short-chain SEs indicates that the thermal oxidation dramatically increased. Much lower than that from E3 is founded, few significant differences could be described in the results of the RC of MDEs (0.27%), ketone (0.11%), OAs (0.019%), ether (0.004%) and alcohol (0.04%) between E1 and E2. Special chemical, such as 6-(2-ethylhexyloxy)-6- oxohexanoic acid are found in the oxidation products, however, the detection of the species might be rarely accurate. Moreover, the products in OCOCs from E3 is related to the fact that the acid value of E3 is 12.598 mgKOH/g, with 0.02% of RC, which is much higher PAO, chemicals likes 2-cyclopentenylethenylpentanonone is very small in ketone from E1, E2 and E3, might contributing to the darkened colour in oxidized oil samples.
Seven OCOCs were confirmed in the oxidation products from the oxidation reactions of DOS oil samples, which are demonstrated in figure 4. Few reports have been reported on the detection of OCOCs in the products from DOS oxidation reactions which produce various compounds were identified from fluid oxidation.

The results show the positive oxidation effect due to the oxidation atmosphere, which leading to the formation of oxygenated species. The oxidation reactions of benzyl and alkyl radicals indicate the observed increase in OCOCs formation at higher oxidation temperatures. The intermediate oxidation products formed from the reactions between the ketone through the dialkenes and vinyl radical and oxygen containing species.

Fig. 4 Mass spectrums of some chromophore detected from DOS reacted samples

Then, some highly condensed groups (solids phase) are produced into the black deposit, which may further polymerize with the same free radicals to generate aromatic radicals, to performed as building blocks to synthases the heavy species by consecutive reactions and highly condense.

After oxidized at high temperature, the compounds are much more than the detected species in the GC/MS results. The evidence of the light black solid deposit stay in the oil samples has very high molecular weight and contain some smaller molecules in the pore structures to release at certain conditions like the higher temperature and better solvent were applied. It is impossible to analysis the entire chemical compounds in the solid deposit since the GC/MS analysis can not perform while the analytes can not be vaporized.

3.3 Viscosity Analysis.

The certain sulfur and nitrogen containing species would substantially deteriorate the viscosity properties of the oxidized oil samples. According to the standards, lubricating oils should relative clean and has proper viscosity. In this paper, kinematic viscosity is measured according to the ASTM D445 standard to predict the actual service life of lubricant while served at high temperature. And less tendency it has to viscosity increases during the usage results more resistant a lubricant in thermal-oxidation resistance[10].
Fig. 5 Trend in viscosity of PAO and DOS reacted samples

Each point shown in figure 5 represents the viscosity variation of the oxidized base oil samples, which shows the thermal stability properties of the PAO and DOS, respectively. The higher content of long-chain AMs than DOS could be found in the viscosity of the two synthetic lubricants including PAO and DOS, which is follows the PAO > DOS rules as shown in figure 5. However, DOS shows better oxidative thermal stability at temperatures lower than 200°C, which only has 23.8 % of RC in MCs. Species such as methyl and ethyl di-ester, which is more thermal stable than PAO oxidation products with a higher NAs content than DOS.

4. Conclusion

Oxidation thermal treatments is an effective method to evaluating the base oils of PAO and DOS base on the GC/MS analysis and kinematic viscosity testing. The results also provide solid evidences to understand oxidative mechanism of the PAO and DOS base oil. The experimental results suggests that the oxidation products generated from oxidation reactions of DOS is mainly single esters, di-esters, ketone, ether, organic acids and alcohol, which results much bigger total acid values than that of PAO treated in similar conditions. The substantial increment of the kinematic viscosity of DOS reveals its limited thermal oxidation stability compared to PAO. The significant decrease of viscosity in PAO reveals its lower thermal stability compared to DOS.

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