

Thermal cracking of poly α -olefin aviation lubricating base oil

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Abstract. Thermal cracking of poly α -olefin (PAO) was conducted under different temperatures among 190 °C to 300 °C. The reacted mixtures were sequentially detected by gas chromatography-mass spectrometer (GC/MS). A series of small molecular normal alkanes, branched alkanes and olefins were identified. PAO perfect structure of aligned comb-like side-chains has been seriously cracked under high temperatures. Property changes about kinematic viscosity and pour point of PAO samples reacted under high temperatures were also investigated. The appearance of small molecular compounds weakened the thermal stability, viscosity temperature performance and low temperature fluidity of PAO samples. Property of PAO samples was deteriorated due to thermal cracking under high temperatures.

1. Introduction

Aviation lubricating oil with special lubricating conditions plays a more important role in aeronautic and astronautic field [1, 2]. As base oil of the aviation lubricating oil, PAO (Poly α -Olefin) is the key element influencing its comprehensive properties. It has special structure of aligned comb-like side-chains as shown in figure 1[3-6]. But as function of aero-engine is improved, working conditions of its lubricating system grow rigorous. Working temperature increases continuously, and working hours of lubricating oil become longer.

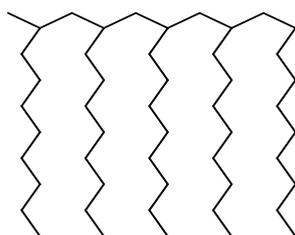


Figure 1. Schematic diagram of PAO.

As introduced by the literature [7], the rise of aviation lubricant's temperature will result in chemical reaction intensified, including oxidation, thermal decomposing, catalytic reaction and polymerization. Therefore, the perfect structure of PAO will be cracked into small molecular groups, and the base oil samples' thermal stability, viscosity temperature property and low temperature fluidity will deteriorate greatly, which seriously affect the normal working of engine and threaten safe flying.

GC/MS (gas chromatography-mass spectrometer) is an effective tool for analysing organic mixtures because of its high sensitivity and good performance in separation. In the present study, we

tried to investigate molecular groups and structure changes of PAO base oil under different high temperatures with GC/MS to study its thermal cracking process and property variations.

2. Experimental section

The PAO base oil was collected from market. All of the solvents used in the experiment were analytical reagents and distilled prior to use.

A Büchi R-134 rotary evaporator was used for distillation of solvents and concentration of fractions. The reactor (stainless steel, magnetic stirred at 800 rpm, 500 mL) was used for reacting experiment of PAO base oil under high temperatures. Put 150 mL PAO base oil into 500 mL reactor. The autoclave was quickly heated to the temperatures of 190 °C, 200 °C, 230 °C, 240 °C, 250 °C and 300 °C, respectively, and hold for 2 h at the corresponding temperature[8]. Then, the autoclave was cooled to room temperature. Finally, the reaction mixtures were analyzed with GC/MS.

The kinematic viscosity (KV) of the thermally treated PAO base oil was detected as standard of GB/T 265 ASTM D445 (40 °C) and GB/T 265 (100 °C) by a KV tester (DKY-301B/DMY-301A). The pour point (PP) of the thermally treated PAO base oil was detected as standard of GB/T 3535-1983 (1991) by multifunctional low temperature instrument (DKY-103A).

The instrument used for quantitative and qualitative analyses of compounds was a Hewlett Packard 6890/5973 GC/MS equipped with a capillary column coated with HP-5 (cross-link 5% PHME siloxane, 60 m × 0.25 mm i.d., 0.25 μm film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode. GC/MS detecting conditions were as follows: a flow velocity of 1.0 mL/s, a diffluent rate of 20:1, and a mass scanning range from 33 to 500 amu. The column was heated at a rate of 13 °C min⁻¹ from 120 °C to 274 °C, and hold at 274 °C for 2 min, then at a rate of 0.5 °C min⁻¹ from 274 °C to 281 °C, and hold at 281 °C for 2 min, finally at a rate of 12 °C min⁻¹ from 281 °C to 300 °C, and hold at 300 °C for 3 min. Data acquired were processed using Chemstation software. The compounds were identified by comparing their mass spectra with NIST05 library data and those beyond NIST05 were determined by referring to related data from available literatures. Finally, the relative content of every component was measured by area normalization.

3. Results and discussion

The products detected by GC/MS were different under high reacting temperatures as exhibited in figure 2. It can be seen that small molecular compounds occurred with the increase in reaction temperature. figure 3 shows the possible cracking mechanism of PAO. figure 4 shows the distributions of every kind of compounds' relative content.

In total, 12 normal alkanes (NAs) with C₁₂ to C₂₃ were distinguished. Especially the small molecular NAs occurred at PAO-200, and increased greatly with temperature going up. The NAs' total relative content increased from 0.02% to 8.60%. Not only NAs but branched alkanes (Bas) and alkenes were reported to be subjected to thermal cracking including chain breaking and dehydrogenation [9]. 25 BAs with C₁₂ to C₂₂ were identified, most of which had the structure of alkane with single methyl side of the chain. As we have known, PAO base oil contains less small molecular BAs. The BAs' relative content decreased firstly from 0.352% to 0.260% before 190 °C, and increased greatly from 0.370% to 3.536% under the temperature from 200 °C to 300 °C. Meanwhile, 46 alkenes with C₁₂ to C₂₃ were detected. Their relative content increased from 0.231% to 9.967%.

Among reacted samples under high temperatures, GC/MS has distinguished not only NAs, BAs or alkenes but many α-polymers (PMs) and less heteroatom containing compounds (HCCs) after retention time of 14 min. From figure 4 it can be easily seen that PMs occupied the most of the products. Its relative content was over 99% before 190 °C, and others were 98.816%, 98.146%, 95.914%, 92.771% and 71.975%, respectively. Meanwhile, the total content of NAs, BAs and alkenes reached to the maximum of 22.14%, while PMs' decreased to 71.975% under the high temperature of 300 °C, suggesting PAO samples was cracked greatly.

It can be seen that PAO base oil had undergone thermal cracking, especially after the high temperature of 200 °C. NAs were reported to have the property of high melting point [9, 10], leading

to their bad low temperature fluidity. Since viscosity index of NAs is lower than BAs, NAs have worse viscosity temperature performance. The appearance of NAs was considered to have lowered the thermal stability of PAO base oil. And as we all know [11-13], good low temperature fluidity should have the structure of multi long side chains located middle of the molecule. PAO has the perfect structure of aligned comb-likely side-chains, while the reacted products of BAs only have more alkanes with single methyl located side of the molecular chain. The occurrence of small molecular BAs worsened the samples' low temperature fluidity and viscosity temperature performance. And the great changes of alkenes had the same efficacy on the samples' thermal stability.

The oxidation of lubricating oils generally occurs through a free radical chain reaction process, which includes chain initiation, chain growth, and chain termination. In the chain-initiation stage, the temperature should be high and thermal radiation and a catalysing metal should be present, to catalyse the generation of free radicals and initiate the free radical chain reaction. Radicals with a high chemical reactivity are particularly unstable. They tend to form saturated electron pairs and react with the surrounding electron cloud.

The results analysed above were further confirmed by kinematic viscosity (KV) and pour point (PP) detecting experiment shown in tables 1 and table 2. It can be seen that KV (40 °C) before 230 °C changed slightly. While from 230 °C to 240°C, it changed greatly from 17.23cst (1cst=1mm²/s) down to 15.68cst. And it was merely 8.279cst at the temperature of 300 °C, which was 53.9% less than original PAO samples. It proves that viscosity index of PAO samples is deteriorated seriously after 230 °C.

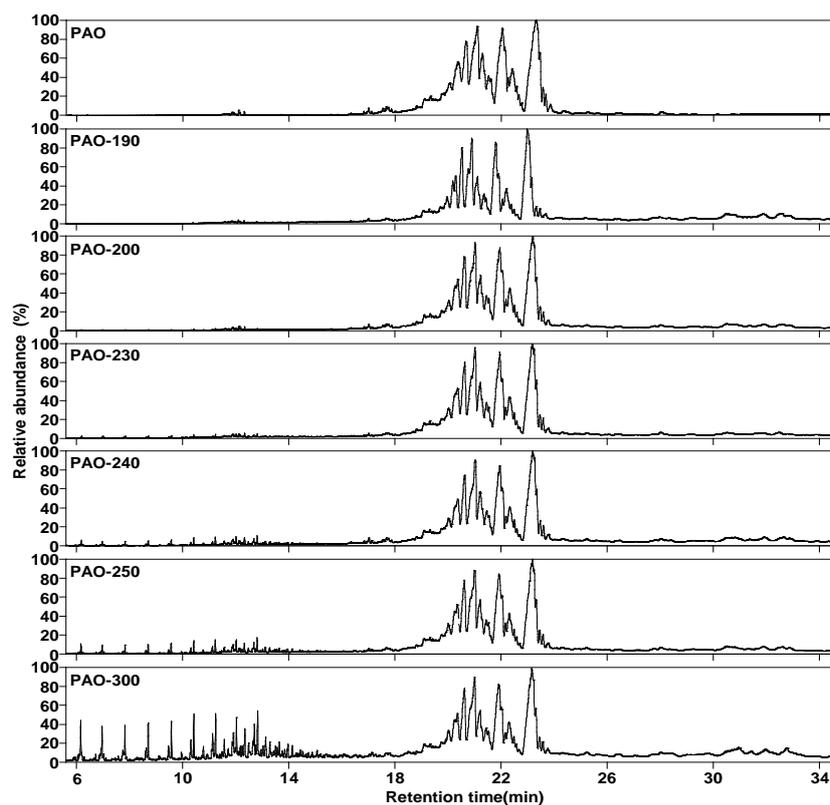


Figure 2. Total ion chromatograms of products from PAO samples.

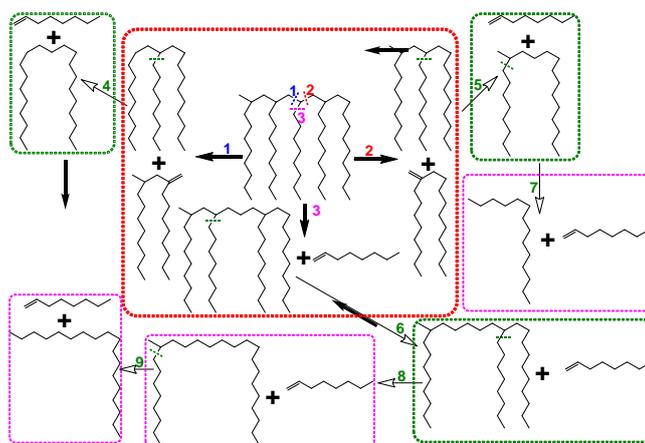


Figure 3. Possible cracking mechanism of PAO.

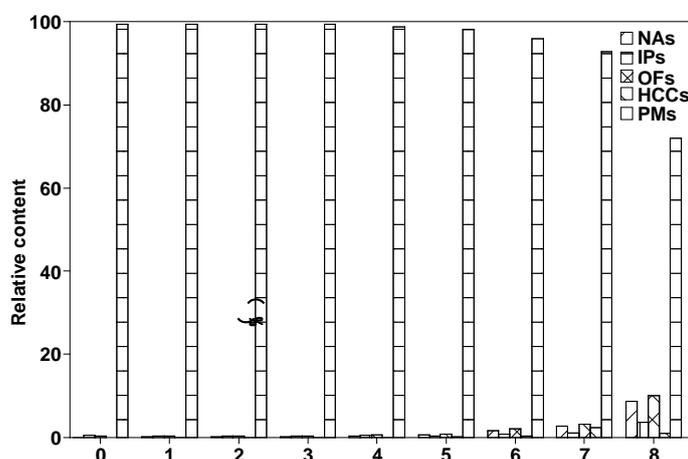


Figure 4. Distributions of every kind of compounds' relative content.

Table 1. Kinetic viscosities of reacted PAO samples.

| Viscosity(mm ² /s) | PAO | PAO190 | PAO200 | PAO230 | PAO240 | PAO250 | PAO300 |
|-------------------------------|-------|--------|--------|--------|--------|--------|--------|
| 40 °C | 17.94 | 17.98 | 17.88 | 17.23 | 15.68 | 14.02 | 8.279 |
| 100 °C | 4.018 | 3.928 | 4.051 | 3.911 | 3.794 | 3.484 | 2.491 |

Table 2. Pour point of reacted PAO samples.

| Samples | PAO | PAO190 | PAO200 | PAO230 | PAO240 | PAO250 | PAO300 |
|-----------------|-----|--------|--------|--------|--------|--------|--------|
| Pour Point (°C) | -68 | -66 | -66 | -64 | -61 | -59 | -24 |

4. Conclusions

PAO perfect structure of aligned comb-likely side-chains has been cracked seriously under high temperatures. A series of NAs, BAs, and alkenes were identified with GC/MS. Their relative content increased with temperature going up. It reached to the maximum of 22.14% under the high temperature of 300 °C. The appearance of NAs, BAs, and alkenes worsened the thermal stability, viscosity temperature performance and low temperature fluidity of PAO samples. Property of PAO samples was deteriorated due to thermal cracking under high temperatures.

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