

Thermogravimetric analysis in the synthetic engine oil 5W-30

Engine oils undergo oxidative degradation and wears out during service. Hence it is important to characterize ageing of engine oils at different simulated conditions to evaluate the performance of existing oils and also design new formulations. This work focuses on characterizing the thermo-oxidative degradation of synthetic engine oils 5W-30. Thermogravimetric analysis of fresh and degraded oil samples at different temperatures and ageing intervals was performed in STA 449 F3 Jupiter® coupled with the FTIR spectrometer. The temperature regime provided that the samples were heated to the temperature of 600°C at the heating rate of 10 K/min. Gases (nitrogen, argon) were used with flow rates of 60 mL/min. The results, along with discussion, are presented in graphs – TG curves and IR spectrum.

Key words: synthetic oil, degradation, oxidation, thermogravimetry, differential scanning calorimetry

1. Introduction

Engine oils are carefully engineered for use in today's sophisticated engines by blending with various additives. Engine oils reduce friction between moving surfaces and also aids in transportation of contaminants and other particles away from moving parts. Oils are prone to thermal and oxidative degradation during service in internal combustion engines as they are exposed to extremely high temperatures (up to ca. 800°C in cylinder walls) and pressures (up to ca. 1000 psi in the bearings) under air environment [6]. The degree of degradation depends on engine conditions, cycle time and duration of its use.

Some of the desirable characteristics of lubricants include reduction of friction, high boiling point, optimum viscosity and thermal stability, corrosion retardation and resistance to oxidation. As engine oils are designed with a mixture of base oil and performance augmented additives such as friction modifiers, antioxidants, dispersants and detergents, and viscosity index improvers [6, 7, 9], it is necessary to understand the thermal stability of engine oils under various operating conditions in order to evaluate the performance of specific additive's package and to design better additive formulations.

Thermo(oxidative) degradation of engine oils in conventional thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) are fundamental techniques to evaluate the stability of engine oils under isothermal and dynamic heating conditions [1, 3, 4, 8]. Importantly, the data obtained from this analysis coupled with the standard engine tests gives a better understanding of the stability of the engine oils [2]. Santos et al. [8] evaluated the rheological and thermo-analytical properties of automotive mineral lubricants and found that increasing the temperature of degradation from 150 to 210°C resulted in thixotropic and pseudo-plastic behavior of the oils. The increase in viscosity of the lubricants was found to be due to the polymerization process along with formation of insoluble high molecular weight products.

Thermogravimetric analysis in air resulted in three decomposition steps while only one decomposition step was observed in nitrogen atmosphere. Gamlin et al. [4] studied the effects of viscosity and base oil class of mineral, fully synthetic and semi-synthetic oils on the thermal stability of base oils. The mechanism of base oil degradation was ex-

amined using isothermal, non-isothermal and modulated TGA analysis. It was concluded that base oils with higher viscosity within the same category tend to degrade at higher temperatures. The base oils of natural/mineral origin were more resistant to oxidation than semi-synthetic and fully synthetic oils due to naturally occurring antioxidants, which can inhibit the oxidation process.

Oxidation is the primary mechanism by which oil degradation occurs in an engine. The process of oxidation occurs in three stages. The first stage corresponds to the depletion of antioxidant and antiwear additives, followed by oxidative degradation of the base oil [7, 9]. During this stage, the formation of polar organic compounds in oil (such as ketones, alcohols, carboxylic acids and esters) is more pronounced. The final stage corresponds to an increase in viscosity of the oil owing to polymerization.

The recombination of long chain radicals, Aldol and Claisen condensation reactions of carbonyl, carboxylic acid and alcohols that are formed via oxidative degradation in the second stage are the main reactions leading to higher molecular weight molecules [10]. Besides oxidation, during combustion, with the engine running at full load or with improper air/fuel ratios, other reactions that lead to the formation of nitrogen oxides and organic nitrates may occur. Similarly, the presence of sulfur may lead to the formation of SO_x, organic sulfones and sulfoxides via oxidation, and sulfurous acid esters when SO_x reacts with organic compounds present in oil. Therefore, a comprehensive understanding of engine oil ageing in terms of oxidation, nitration and sulfation, along with thermal stability and rheological properties is required.

Apparent activation energy of oxidation of oils is usually evaluated using TGA under dynamic heating rate in presence of air. Isoconversional methods are utilized to evaluate the variation of apparent activation energy of oxidative degradation of oils with conversion [3, 4]. Crnkovic et al. [3] evaluated the oxidative degradation kinetics of Brazilian fuel oils using TGA in presence of air, and the apparent activation energy was correlated to the ignition delay.

2. Materials and methods

Thermogravimetric testing of engine oil was conducted on the Simultaneous Thermal Analyser STA 449 F3 Jupi-

ter[®], which was coupled with the FTIR spectrometer. In the analyser mentioned above the samples (S and R) were placed symmetrically in identical measuring vessels (Pt/Rh crucibles) in the same furnace whose temperature was regulated according to an assumed temperature regime, regardless of the changes in the properties of the samples during the measurement. The temperature regime provided that the samples were heated to the temperature of 600°C at the heating rate of 10 K/min. Gases (nitrogen, argon) were used with flow rates of 60 mL/min.

Differential scanning calorimetry (DSC) means a technique in which the change of the difference in the heat flow rate to the sample and to the reference sample is analysed while they are subjected to a temperature regime, or a technique where the change of the difference in the heat flow rate to the sample and to the reference material is measured as a function of temperature.

$$\Delta\Phi_{SR} = \Phi_S - \Phi_R \quad (1)$$

where: *S* – sample, *R* – reference sample.

The thermal analyser measured the difference in temperatures between the samples:

$$\Delta T_{SR} = T_S - T_R \quad (2)$$

When the analyser furnace is heated and the system is thermally symmetric, an identical heat flux flows to both samples and their difference in temperature is then zero. If this state of dynamic equilibrium was disturbed by a change in either sample, or if there was thermal asymmetry of the system caused by a difference in the heat capacity of the samples, the DSC measurement showed differences in temperature, $\Delta T_{SR} \neq 0$, in proportion to the differences in the heat fluxes to the sample and to the reference sample, and then

$$\Delta\Phi_{SR} = -k\Delta T_{SR} \quad (3)$$

where: *k* proportionality constant with the nature of the inverse of thermal resistance.

Used as raw materials in experiments was Engine Oil samples – fully synthetic engine oil 5W-30 (Castrol EDGE) for Audi, VW, BMW, Mercedes-Benz, Porsche, Skoda and Seat cars. This oil with Fluid Strength Technology is most advanced engine oil, engineered with an adaptive strength ready to perform however the engine and drive demands. Weight of the samples, depending on the experiment, the limits ranged from 20–24 mg.

A majority of the TG experiments were repeated three times, and the standard deviation of *T*_{max}, the temperature corresponding to maximum mass loss rate, as observed in the differential thermogram, was within ±2°C for all the runs.

3. Results and discussion

Synthetic engine oil 5W-30 was degraded between 200 and 500°C. Figures 1–4 depicts the thermograms and differential thermograms of synthetic engine oils. The results of the measurement made with the use of the DSC tech-

nique were DSC curves – the dependence of the measured difference in the heat fluxes on time/temperature. The graphs in Fig. 1 present the course of derivatographic curves; the TG curve for fresh full synthetic engine oil are marked in red and the curve for used full synthetic oil are marked with a green.

The graphs in Fig. 2–3 present the DSC curves in a argon and nitrogen atmosphere. And the graph Fig. 4 present DDSC curves for fresh and used full synthetic engine oils in a argon atmosphere.

In the process of thermal decomposition of the full synthetic oils sample in the different atmosphere (nitrogen, argon) the following stages can be isolated:

- evaporation of water with heat absorbed from the system (50.3°C for the oils sample in a argon atmosphere and 70. °C for the oils sample in a nitrogen atmosphere),
- two distinct weight loss regimes are evident from the TGA profiles of the engine oils. The first regime is from 180 to 35 °C and the second regime is from 360 to 500°C for all the types of engine oils (fresh and used). Based on mass spectrometric measurements, Lehrle et al. [5] confirmed that in the temperature range of 180 to 350°C, both evaporation of hydrocarbons present in the low end of the molecular weight distribution, and degradation of base oil components occur. The former occurs at temperatures lesser than 250°C, while the onset of degradation occurs in the range of 275–300°C. The second weight loss regime can be attributed to the decomposition of long chain hydrocarbons.
- as fresh synthetic oils contained a lot of oxygenated organics including alcohols, diols, esters, sulfurous acid esters and other oxygenated functional groups, accelerated degradation of the these organics and base oil stock is justified in the temperature range of 275–300°C.
- in many experiments, fresh the oils pyrolyzed completely before 500°C without any formation of residue, while in certain cases less than 4 wt% residue was observed at 500°C.

The graphs in Fig. 2 and 3 present the TGA curves obtained by means of the DSC method. An exothermic effect with an enthalpy of –77.26 J/g (in a argon atmosphere) and –140.9 J/g (in a nitrogen atmosphere) during the first mass loss step which is due to the release of moisture, was observed. For a sample in nitrogen two overlapping exothermic effects with an entire enthalpy of –4.01 J/g and –9.905 J/g occurred during the remaining mass loss steps which reflect the pyrolytic decomposition of oil sample. Second exothermic effect with an enthalpy of –23.56 J/g (in a argon atmosphere) and –16.81 J/g (in a nitrogen atmosphere) was started at 336.7°C and 368.7°C. Gasification reactions starter above 430°C.

A collection of all detected absorbance a oils sample in a different atmosphere are shown as a 3-dimensional cube in Figure 5. Additionally the TG-signal at the side face of the cube shows the communication between the two software.

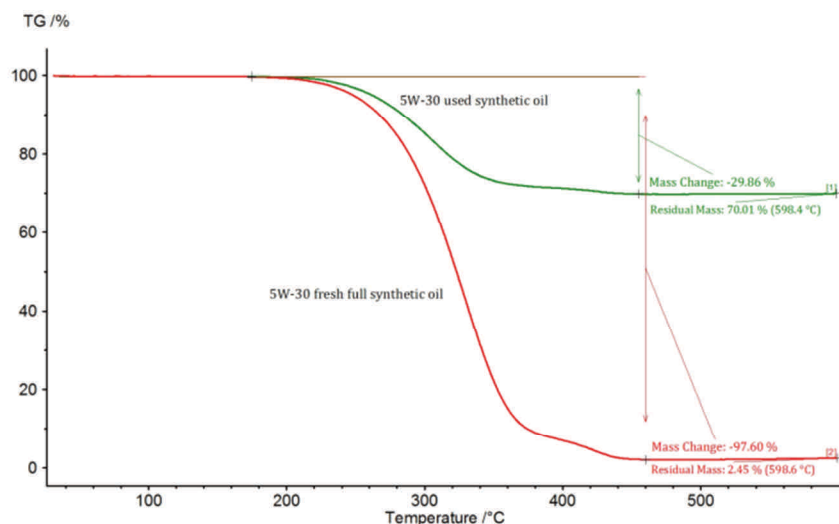


Fig. 1. Thermogravimetric analysis of full synthetic engine oils (fresh and used) conducted in a argon atmosphere

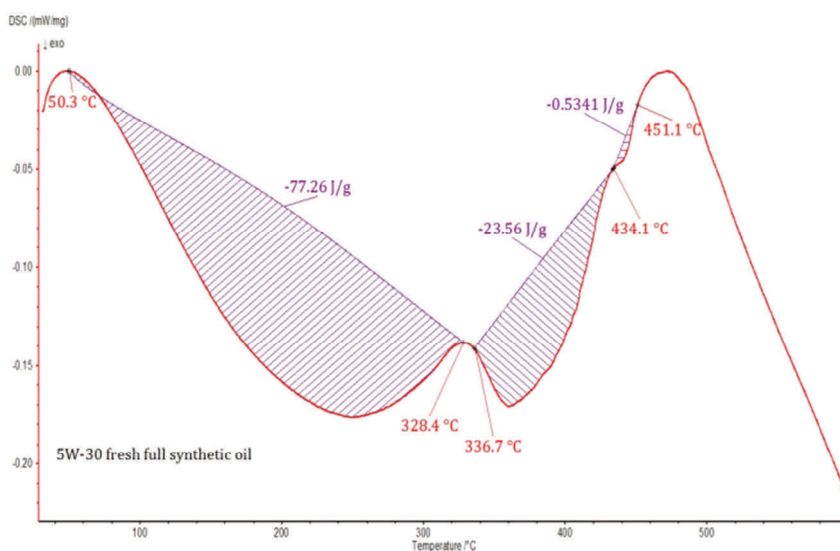


Fig. 2. Thermogravimetric analysis of fresh full synthetic engine oil conducted in a argon atmosphere

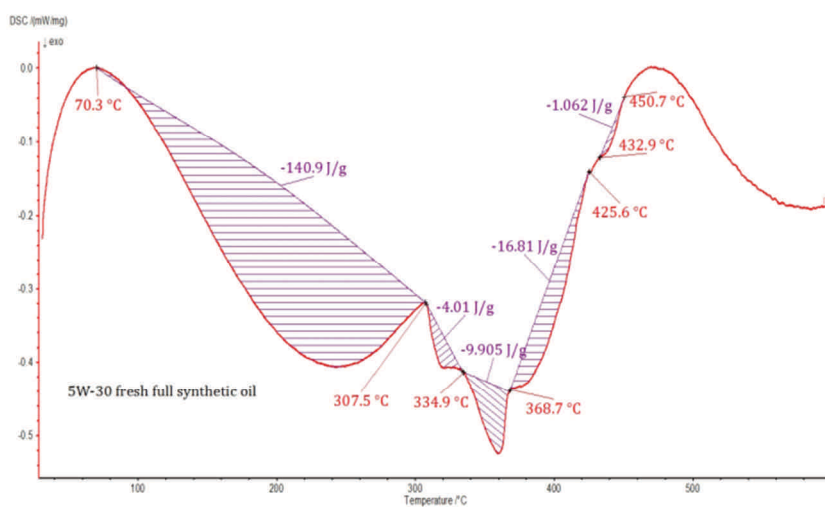


Fig. 3. Thermogravimetric analysis of fresh full synthetic engine oil conducted in a nitrogen atmosphere

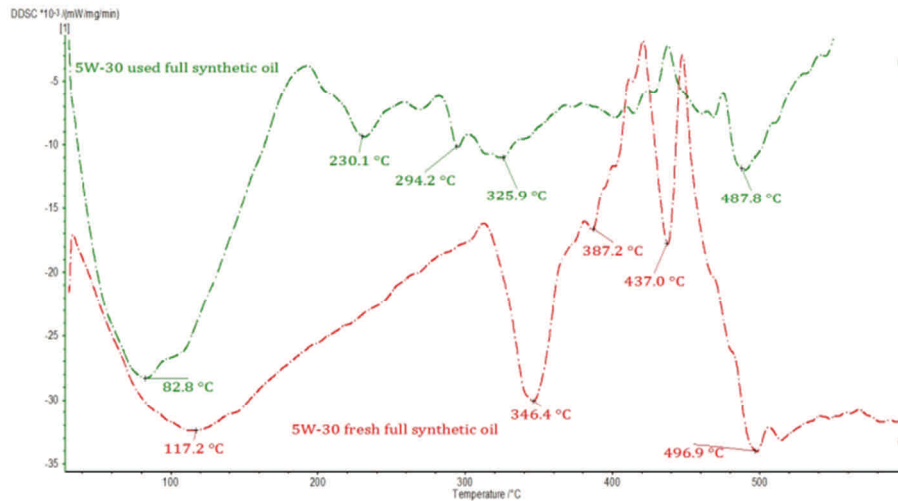


Fig. 4. DDSC curves of fresh and used full synthetic oils conducted in a argon atmosphere

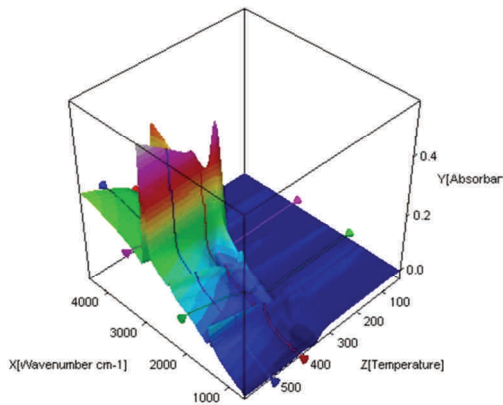


Fig. 5. 3D view of FTIR spectra – wavenumber versus temperature including the TG results at the side face of oils samples conducted in a argon atmosphere

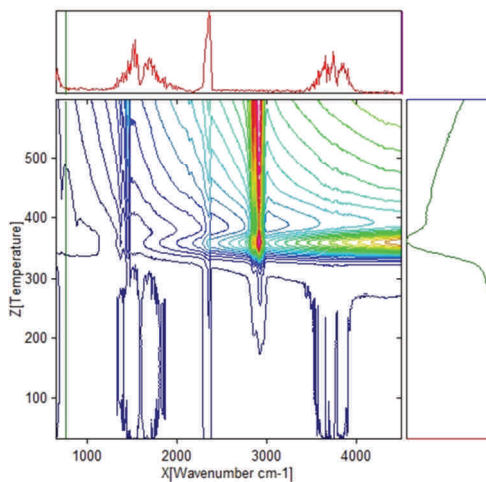


Fig. 6. IR spectrum of the full synthetic engine oil conducted in argon atmosphere

4. Conclusions

In this study, a characterization of oxidative degradation of full synthetic engine oils at different atmosphere. Based on the kinetic analysis of synthetic engine oils degraded at different temperatures, the following conclusions can be drawn:

1. At an oxidation temperature about of 120°C, synthetic oil loses stability in the initial time period, while it gains stability at longer ageing periods.
2. At an ageing temperature of 200°C, both synthetic fresh and used engine oils exhibit similar trends in variation of a E. The oils lose their thermal stability, while the stability is regained at long ageing periods. The gain in stability may be correlated with the decrease in oxidation index of synthetic oil. The increase in viscosity is due to the formation of long chain hydrocarbons.
3. Around 72–96 h, the oils lose their thermal stability, while the stability is regained at long ageing periods. The gain in stability may be correlated with the decrease in oxidation index of synthetic oil after 96 h of ageing and increase in kinematic viscosity of synthetic oil with ageing time. The increase in viscosity is due to the formation of long chain hydrocarbons. The oils rapidly lose their lubricity, as evidenced by the high rate of decrease of viscosity index.
4. The physicochemical characterization of fresh and used engine oils discussed in this work will be useful to develop distributed activation energy models with pseudo components taking part in a multistep mechanism. The apparent activation energies can be used as initial estimates for a more robust semi-mechanistic model of engine oil oxidation.

Nomenclature

DSC differential scanning calorimetry
 DDSC first derivative DSC

FTIR Fourier transform infrared spectroscopy
 TGA thermogravimetric analysis

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