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THERMAL, SPECTROSCOPIC AND RHEOLOGICAL STUDY OF MINERAL BASE LUBRICATING OILS

J. C. O. Santos[1*], *L. N. Lima*[2], *Iêda M. G. Santos*[3] *and A. G. Souza*[3]

[1]Unidade Acadêmica de Educação, CES, UFCG, 58175-000 Olho D'água da Bica, Cuité, Paraíba, Brazil
[2]Unidade Acadêmica de Engenharia Química, CCT, UFCG, 58109-970 Campina Grande, Paraíba, Brazil
[3]Departamento de Química, CCEN, UFPB, 58059-900 João Pessoa, Paraíba, Brazil

The thermal degradation process of mineral base lubricating oils was studied in this work by means of thermal, spectroscopic and rheologic analysis. The lubricating oils were degraded at temperatures varying from 150 to 210°C, and for degradation times from 1 to 48 h. After the degradation, the lubricating oils were characterized by X-ray fluorescence, IR and NMR spectroscopies, rheological properties and thermal analyses (TG/DSC). The spectroscopic analyses determined the oxidation reaction products. TG curves indicate that the thermal stability of lubricating oils is below 161°C. TG curves in air present three mass loss stages, whereas in nitrogen there are only two mass loss steps. DSC analyses in air indicate two highly exothermic peaks related to hydrocarbon oxidation and combustion processes, while in nitrogen only two endothermic peaks were observed. The decrease in the degradation temperature led to a decrease of the lubricant viscosity.

Keywords: *degradation, mineral base lubricating oil, rheology, thermal analysis*

Introduction

Formulation of automotive lubricating oil is a complicated process. The modern engine lubricant is a carefully designed blend of base oils and performance enhancing additives, such as pour point depressants, antioxidants, dispersants and detergents [1, 2].

Regardless of the complexity, the lubricating oil formulator must assess the performance of the base oil and the additives, and finally balance the performance and the cost, prior to the full-scale engine testing of the oil. Because engine testing is an expensive process, a number of bench tests have been developed to screen out the lubricating oil throughout the formulation process [3]. Many of these bench tests are time consuming, man-power intensive, empirical, show poor reproducibility and require a large investment in specialized equipment and skilled operators, and may be advantageously replaced by conventional thermal analysis techniques [4, 5].

In this work, thermal, spectroscopic and rheologic properties were determined after the thermal degradation of mineral base lubricating oils at different temperatures and for different degradation times.

Experimental

Oil samples

Mineral base lubricating oils produced by Brazilian petroleum industries were used in this study. According to the manufacturer specifications, this mineral base lubricant is 100% paraffinic, being used in the formulation of the lubricants for automotive engines, working with gasoline, ethyl alcohol and natural gas. Their API classification is SJ group, with a typical analysis from the manufacturer of 0.87 g mL^{-1} density and 30W SAE viscosity.

The thermal degradation of the mineral base lubricating oils were assessed by means of heat treatments at 150, 170, 190 and 210°C, using an apparatus similar to the ones used for distillation, with the oil samples being submitted to an air flow [6]. An initial lubricant volume of 300 mL was used. The samples were withdrawn after degradation times that varied from 1 to 48 h (Fig. 1). Thermal, spectroscopic and rheological properties were evaluated for the degraded and non degraded base lubricants.

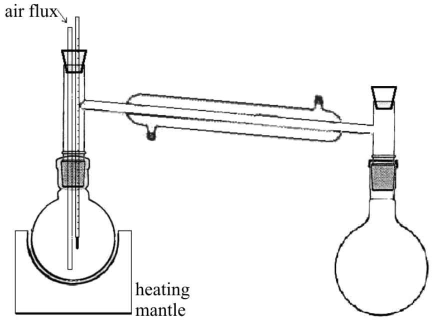

Fig. 1 Schematic representation of the degradation system

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* Author for correspondence: josecos@ufcg.edu.br

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Akadémiai Kiadó, Budapest, Hungary
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Methods

Spectroscopic measurements

Sulfur analyses were performed in an X-Ray fluorescence spectrometer by energy dispersive accessory (Shimadzu, EDX – 800). Infrared spectroscopic measurements (Bomem MB Series) were carried out using KBr pellets in the 400–4000 cm^{-1} region. Proton nuclear magnetic resonance (^{1}H NMR – 300 MHz, Gemini) was used in the lubricating oil characterizations at room temperature using relaxation delay of 0.20 s, pulse of 5.0°, acquisition time of 2.667 s, width of 6000.0 Hz and 16 repetitions.

Rheological measurements

Rheological measurements (Brookfield LV-DVII) were conducted at 25°C, at different shear rates using a small sample adapter. The reproducibility of all the experiments is three tests.

Thermal analysis

Thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) analyses were performed in a simultaneous thermobalance (SDT-2960, TA Instruments) in air and nitrogen with a flow of 110 mL min^{-1}, using alumina crucibles, at heating rates of 5, 10, 15 and 20°C min^{-1}, sample mass of 10.0±0.5 mg in the 25–620°C temperature range.

Specific heat capacity measurements

The specific heat capacities of the mineral base lubricating oils were determined from the data obtained by DSC. The calculations were based on implementation of the temperature program. The oil samples were heated from room temperature at heating rate of 5°C min^{-1} up to 30°C. The samples were kept at such temperature for five minutes. Then, they were heated at heating rate of 10°C min^{-1} up to 190°C and then kept at the end temperature for 5 min.

The following equation was used to calculate the heat capacities:

$$c = \frac{m_0 c_0}{m}\frac{S_3 - S_1}{S_2 - S_1} \tag{1}$$

where c_0 and c are the specific heats of the reference material and of the base oil, respectively; m_0 and m refer to the masses of the reference material and the sample, respectively, and S_1, S_2 and S_3 are the thermal displacements of the DSC in relation to the blank, reference and sample, respectively [7].

Results and discussion

Spectroscopic analyses

According to X-ray fluorescence spectroscopy (XRF) data, non-degraded samples present 0.350 mass% of sulfur. After degradation at 210°C for 24 h a decrease to 0.29% was observed, probably due to SO_2 formation. The samples degraded at 210°C for 36 h were polymerized.

On the other hand, infrared spectra presented a small difference, before and after the thermal treatment, indicating the occurrence of oxidation reactions (Fig. 2).

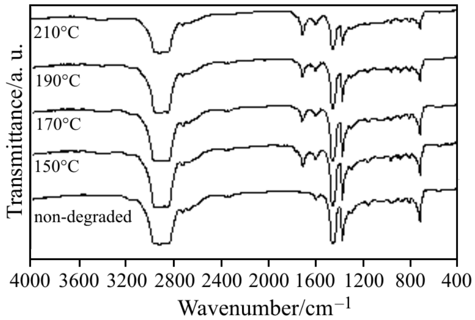

Fig. 2 Infrared spectra of mineral base lubricating oil

Thus, IR results indicate that lubricant degradation occurs by oxidation reactions, in agreement with the literature [8], probably leading to the formation of carboxylic acids and ketones. It is noticed that these spectra indicate that the analyzed oils presented meaningful changes in the spectral regions of the O–H, C=O and C–O groups. This can be attributed to the stronger action of oxygen during the heating period for the degraded samples. The bands observed at 3415 and 1714 cm^{-1} suggest the presence of O–H alcohol and C=O carbonyl groups, respectively, for all the degraded samples. As for the bands found in all the samples at 1157 and 3600 cm^{-1}, they refer to the OH groups, originated from hydrogen bonds and free hydroxyl groups in monomers, respectively. Ketones, aldehydes, carboxylic acids and esters display a band at 1898 cm^{-1}, which originates from the axial deformation of the C=O bond, which is shown to be less intense in the non-degraded sample. As for the C–H bands, no meaningful changes were observed between the degraded and non-degraded samples. The C–H deformation is characterized by the presence of bands at 1463 and 1377 cm^{-1}, which are representative to this group. The C–H asymmetric deformation bands for $–CH_2–$ and $–CH_3$ are noticed at 723 and 1377 cm^{-1}, respectively. The band at 1604 cm^{-1} probably indicates the aromatic C–C bond. The presence of a band at 2670 cm^{-1} in all the samples with the exception of the sample submitted to the highest degradation, 210°C for 24 h, refers to some sulfur compounds. The bands at-

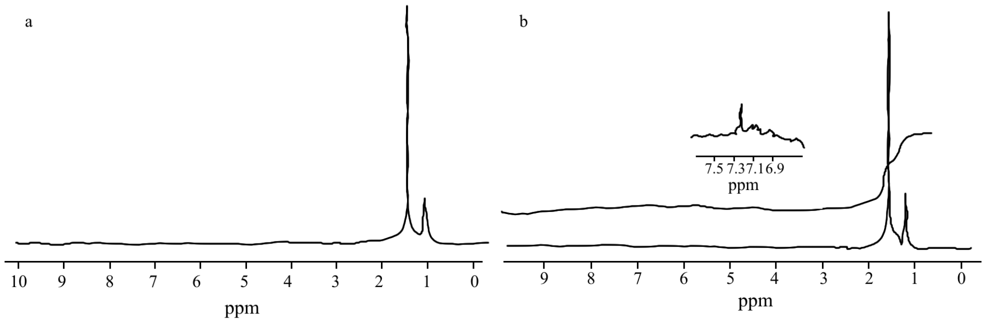

Fig. 3 ^{1}H NMR spectra of a – non-degraded and b – degraded mineral base oils

tributed to the C–C axial vibrations are weak and are noticed at the region between 1200 and 800 cm^{-1}. Bands between 800 and 1400 cm^{-1} presenting several peaks may represent the C–O bonds associated to a variety of oxygenated organic compounds. Some of these bands may be attributed to sulfonated compounds or to other sulfur-containing compounds, either produced upon the degradation or initially present in the lubricating oils [8, 9].

^{1}H NMR spectra of degraded and non-degraded mineral lubricant oils are shown in Fig. 3. The spectra of the degraded lubricants show new peaks at 6.9–7.5 ppm which can be attributed to protons in unsaturated ketones [9, 10].

Rheological behavior

In relation to the viscosity results, it may be observed that at the beginning of the degradation all lubricants present an increase in viscosity. This behavior is due to evaporative losses of lower boiling point and hence lower viscosity components.

For the samples degraded at 150°C after this first increase the viscosity remains constant indicating that no further degradation occurs. After the initial increase in viscosity values samples degraded at 170 and 190°C present a viscosity decrease. According to literature data [9] from NMR and infrared spectra oxidation products are formed after the degradation leading to the formation of hydrogen bonding and dipole–dipole interaction, respectively. As a consequence higher intermolecular forces are formed increasing the lubricant viscosity. On the other hand, oxidation products are observed in all samples after degradation.

The polymerization reaction was observed, what of course leads to a viscosity increase. When the molecular mass of the polymer achieves too high value, the material may become insoluble, leading to its precipitation. This degradation mechanism was observed by Kauffman *et al.* in aircraft turbine engine oils [10, 11]. The viscosity variation, as well as other rheological aspects may be related to the polymerization followed by precipitation of these products. This precipitation is very deleterious as these products are harmful to machines.

Thermal analyses

Oxidation reactions, leading to decomposition are confirmed by thermogravimetry in different atmospheres. Different decomposition profiles are observed at different atmospheres, for the same lubricant at the same heating rate of 10°C min^{-1} as indicated in Fig. 4.

TG results in air atmosphere present three stages: the first one (173–351°C) is probably due to

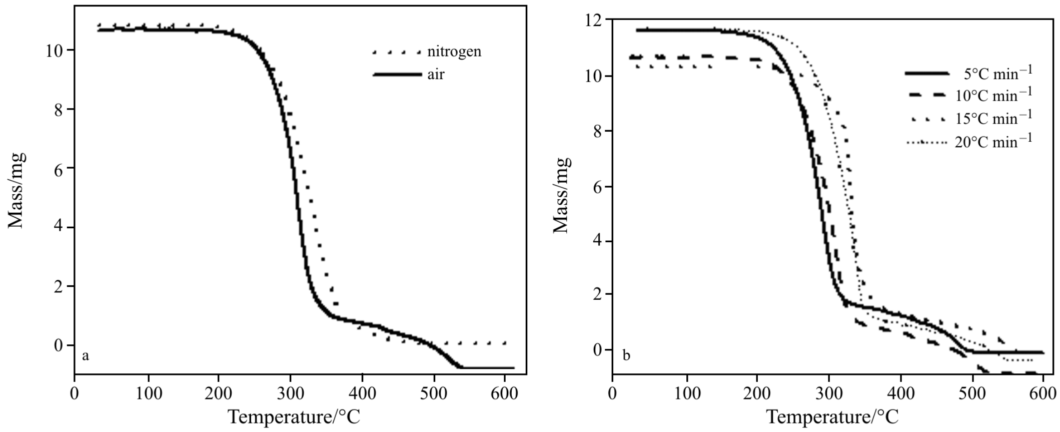

Fig. 4 TG curves of the non-degraded mineral base lubricating oils in different: a – atmospheres, b – heating rates in air

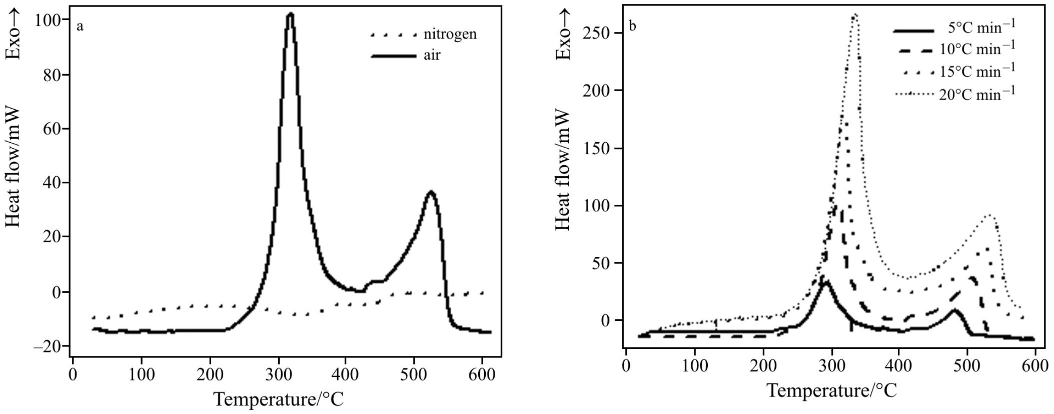

Fig. 5 DSC curves of non-degraded mineral base lubricants under different a – atmospheres and b – heating rates in air

the elimination of low molecular mass products, followed by hydrocarbon degradation. This stage is the most important one to determine the thermal stability of the base lubricants. The second mass loss stage (between 405–431°C), as well as the third one (in the 458–548°C temperature range) are related to decomposition of hydrocarbons of higher molecular mass.

TG curves in nitrogen atmosphere present two stages: the first one (171–390°C) is probably due to the elimination of low molecular mass products, followed by hydrocarbon degradation and the second mass loss stage (390–500°C) is related to decomposition of hydrocarbons of higher molecular mass.

This result corroborates the TG data in an air, indicating the occurrence of an oxidation reaction between the lubricant constituents and the oxygen present in the air. This reaction may lead to the formation of compounds such as carboxylic acids and ketones, indicated by infrared and NMR spectra. Oxidation may also lead to a polymerization reaction, with formation of higher molecular mass products. Table 1 contains the thermogravimetric data of the base mineral lubricating oils.

DSC curves (Fig. 5), in air indicate two remarkable exothermic peaks, with temperatures of 320 and 519°C and a degradation onset temperature of 212°C. In nitrogen two endothermic peaks are observed at 333 and 440°C. These results indicate the occurrence of oxidation reactions. According to Lehrle *et al.* [12], evaporation occurs below 250°C.

Table 2 contains the calorimetric data of the base mineral lubricating oils. Transitions are probably related to oxidation and combustion processes. It may also be observed that the increase in degradation time leads to an enlargement and consequently, an increase in the area of the thermal decomposition peaks.

Specific heat capacity

The heat capacities of lubricants are of practical importance in engineering work related to the petroleum derivative operations and related processes. Not only the design of plant equipment require a knowledge of heat capacity data over wide temperature ranges, but these data are also helpful when prolonged storage or low temperature handling are considered. Heat capacity can then be used in the evaluation of other basic thermodynamic properties of the oils.

In recent years, differential scanning calorimetry (DSC) has been successfully used for the determination of the specific heat capacity of hydrocarbon mixtures and similar compounds [13]. In this work, the same heat flux DSC cell arrangement is used as in conventional DSC, but a different heating profile is applied by the furnace to the lubricant oils and reference (Fig. 6). Differences in the degradation temperature and time of the lubricants may result significant heat capacity differences.

The results obtained in this work for the selected lubricants provide convincing evidence that DSC is a

Table 1 TG/DTG data of mineral base lubricating oils

Conditions	1st stage			2nd stage			3rd stage		
	T_i/°C	T_p/°C	Δm/%	T_i/°C	T_p/°C	Δm/%	T_i/°C	T_p/°C	Δm/%
5°C min^{-1} – air	161	297	85.5	342	398	6.4	450	493	8.5
10°C min^{-1} – air	173	318	90.2	407	422	1.7	458	516	9.0
10°C min^{-1} – N_2	179	331	94.5	396	435	4.9	–	–	–
15°C min^{-1} – air	181	329	86.5	456	537	12.5	–	–	–
20°C min^{-1} – air	188	346	90.8	437	543	9.1	–	–	–

T_i – initial temperature, T_p – peak temperature; Δm – mass loss

Table 2 DSC data of mineral base lubricating oils

Conditions	1st stage			2nd stage			3rd stage		
	T_i/°C	T_p/°C	ΔH/J g^{-1}	T_i/°C	T_p/°C	ΔH/J g^{-1}	T_i/°C	T_p/°C	ΔH/J g^{-1}
5°C min^{-1} – air	212	303	2236	381	385	18.6	444	494	734.4
10°C min^{-1} – air	212	321	2809	425	519	1474	–	–	–
10°C min^{-1} – N_2	253	334	173	399	440	41.7	–	–	–
15°C min^{-1} – air	230	329	2686	467	541	937	–	–	–
20°C min^{-1} – air	233	345	3041	461	549	1075	–	–	–

T_i – initial temperature, T_p – peak temperature; ΔH – decomposition enthalpy

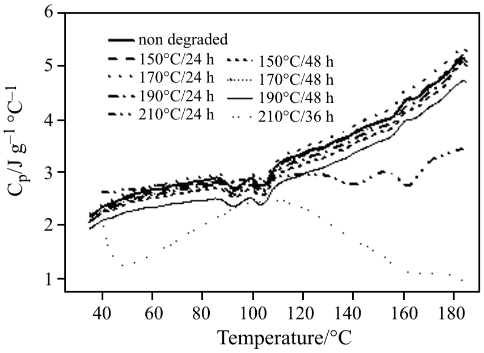

Fig. 6 Evaluation of specific heat capacity of mineral lubricating oil *vs*. temperature

suitable technique for the easy measurement of the heat capacity of lubricants. Once the optimum operation conditions has been established, the heat capacity can be directly determined with great accuracy, within an acceptable period of time.

Conclusions

The thermal, spectroscopic and rheologic results indicate that thermal treatment leads to a degradation of mineral base lubricating oil samples. An increase in the viscosity was observed. These characteristics may be due to oxidation processes, with the formation of high molecular mass products, which become insoluble. Fluorescence, infrared and NMR results indicate oxidation reactions.

TG curves indicate that the thermal stability of lubricating oils is below 161°C. TG curves in air present three mass loss stages, whereas in nitrogen only two decomposition stages can be observed. DSC analyses in air indicate two considerable exothermic peaks related to hydrocarbon oxidation and combustion processes, while in nitrogen only two endothermic effects were observed.

The results obtained in this work for the selected mineral base lubricating oil samples provide convincing evidence that the simultaneous utilization of TG/DTG/DSC is an easy measurement technique of the lubricant degradation.

Acknowledgements

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