

## Thermoanalytical and rheological characterization of automotive mineral lubricants after thermal degradation

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### Abstract

This work aims to characterize thermal degradation process of automotive mineral lubricants, in relation to its rheological and thermoanalytical properties. Lubricants were degraded at temperatures varying from 150 to 210 °C, and times of 1–48 h. After degradation, oils were characterized by infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), rheologic measurements and thermal analysis (TG/DSC). IR and NMR spectra indicated oxidation reaction products. TG curves indicated a decrease in the temperature of decomposition start after degradation. DSC curves indicated a decrease in the peak related to hydrocarbon combustion after degradation. In general, the increase in degradation temperature led to an increase of the lubricants viscosity, besides thixotropy appearance for some samples.

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### 1. Introduction

All machines get worn out after some time, due to its own working and to the different contaminants with which it is put into contact. On the other hand its working days may be increased with the use of lubricants. Modern lubricants, with high performance, can do much more than simply reducing attrition and wear. Lubricant oils are really important, presenting different functions, as refrigeration, cleaning, fencing off and protection against corrosive agents [1].

Viscosity is one of the most important characteristics of a lubricant and must be kept in established limits.

Decrease in its viscosity may be due to addition of lower viscosity oils, contamination by fuel and solvents and also due to lubricant degradation. On the other hand, the increase in viscosity indicates the presence of insoluble contaminants, pronounced oxidation and water contamination [1,2].

Lubricant oil degradation under operation conditions is a problem that involves meaningful economical losses. Oxidation is the primary agent of degradation, and has given rise to many studies. Establishing a kinetic mechanism of reaction is difficult due to the complexity of these systems [3–5].

In this work, rheological parameters and thermoanalytical properties were determined after thermal degradation of automotive mineral lubricant oils at different temperatures and times.

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## 2. Experimental

Commercial automotive mineral lubricant oils produced by Brazilian industries were used in this study. According to manufacturer specifications, this mineral lubricant is paraffinic, being used in the lubrication of automotive motors, working with gasoline, alcohol and natural gas. Its API classification is SJ group and SAE viscosity is 40 W. It contains different additives as: antiwear, antioxidant, detergent/dispersing, rust and foam inhibitors and viscosity elevators.

For thermal degradation, lubricants were heat-treated at 150, 170, 190 and 210 °C, with air flux, in a system similar to a distillation one, as presented in Fig. 1. An initial lubricant volume of 300 ml was used. Samples were withdrawn after times that varied from 1 to 48 h. Spectroscopic, rheological and thermoanalytical properties were evaluated for degraded and non-degraded lubricant oils.

Sulfur analysis was done in an X-ray fluorescence spectrometer (XRF-PW 2400, Philips). Equipment calibration was done with pure salts of the respective element.

Infrared spectroscopy (MB Series, Bomem) was done using KBr pellets, in the region 400–4000  $\text{cm}^{-1}$ .

Nuclear magnetic resonance of proton ( $^1\text{H}$  NMR—300 MHz, Gemini) was used in lubricant characterization, at ambient temperature, using relaxation delay of 0.20 s, pulse of 5.0°, acquisition time of 2.667 s, width of 6000 Hz and 16 repetitions. Samples were dissolved in  $\text{CCl}_4$ . A small amount of benzene, at known concentration, was added to each lubricant sample.

NMR analysis (300 MHz, GEMINI) were performed using a broad-band probe set to a radio frequency of 76 MHz, as described for our  $^1\text{H}$  NMR analysis, except that pulse of 48.8°, acquisition time of 0.840 s and width of 19036.7 Hz were used.

Rheological measurements (LV-DVII—Brookfield) were done at 25 °C, in different shear rates, using a small sample adapter.

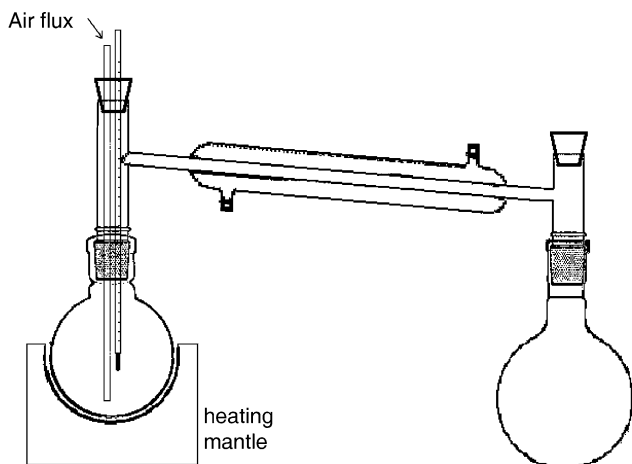


Fig. 1. Schematic representation of the degradation system.

Non-isothermal thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis were done in a simultaneous thermobalance (SDT-2960, TA Instruments), in air and nitrogen atmosphere, with a flux of 100  $\text{ml min}^{-1}$ , using alumina crucibles, heating rates of 5, 10, 15 and 20  $^{\circ}\text{C min}^{-1}$ , sample mass of  $10.0 \pm 0.5$  mg, at a temperature range of 25–600 °C.

## 3. Results and discussion

According to XRF data, non-degraded samples present 0.864% of sulfur in mass. After degradation at 210 °C for 48 h, a decrease to 0.730% is observed, probably due to  $\text{SO}_2$  formation.

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

During thermal degradation, mineral lubricant oils may go under changes in composition. Products, which are harmful to the good working of these oils, may be formed due to oxidation processes, changing its properties. According to Bowman and Stachowiak [6], oil oxidation leads to formation of different compounds as ketones, acids

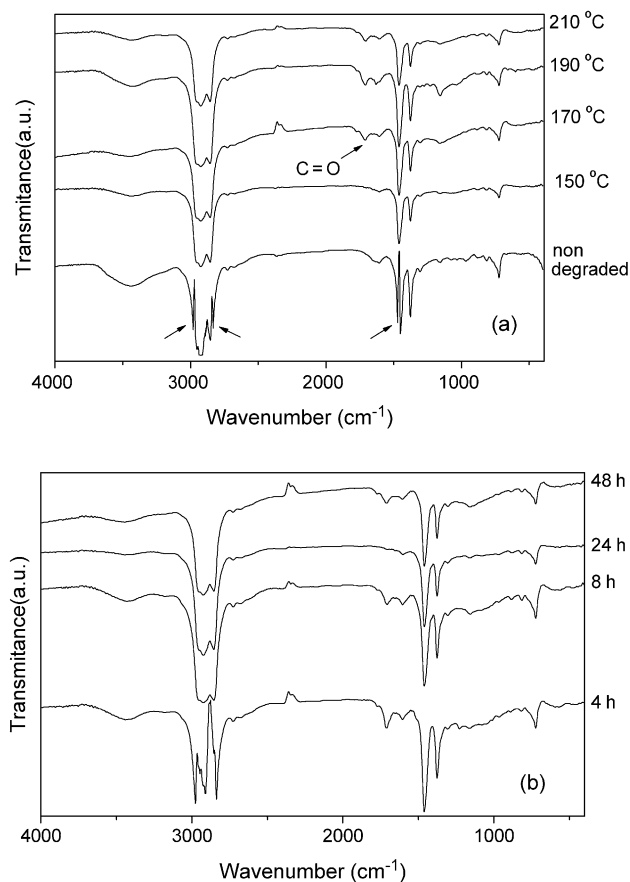


Fig. 2. Infrared spectra of lubricants: (a) samples degraded for 48 h at different temperatures; (b) samples degraded at 170 °C for different times.

Table 1  
Peaks assignment for non-degraded sample in infrared spectra

Non-degraded sample	Assignment
3438	C–H
2980	C–H stretching
2925	CH <sub>3</sub> , CH <sub>2</sub>
2852	CH <sub>3</sub> , CH <sub>2</sub>
2830	C–H alkane
1626 (broad)	C=C or carboxylate (additives) C=O stretching ketone C=O (aldehydes, ketones)
1472–1449	CH <sub>3</sub> , CH <sub>2</sub> and formation of dimers
1377	C–H bending
1157	Axial vibration C–C
721	CH <sub>2</sub>

and aldehydes with characteristic bands between 1500 and 1900  $\text{cm}^{-1}$ , due to carbonyl vibration (C=O).

Fig. 2 contains the infrared spectra for degraded and non-degraded samples. Peaks assignment is presented in Table 1.

A change is observed in peaks related to C–H bond, 2850–3000  $\text{cm}^{-1}$ , being observed the disappearance of the bands at 2980 and 2833  $\text{cm}^{-1}$ . These bands are related to CH<sub>3</sub> and CH<sub>2</sub> in aliphatic chains. With new compounds formation or low molecular weight compounds volatilization, these carbons are the first ones to be changed, while bands related to axial CH<sub>2</sub> (2920  $\text{cm}^{-1}$ ) and asymmetric CH<sub>2</sub> (2850  $\text{cm}^{-1}$ ) do not change.

A consequence of the oxidation is the change observed in the region of 1750–1700  $\text{cm}^{-1}$ . C=O bond absorbs strongly in this range due to its large change in dipole moment. Since the C=O stretching frequency is sensitive to attached atoms, the common functional groups already mentioned absorb at characteristic values. It may also be observed that spectra of ketones bonded to alkyl radicals exhibits a normal, or unconjugated, stretching frequency at 1715  $\text{cm}^{-1}$ . A very weak overtone band related to C=O (1715  $\text{cm}^{-1}$ ) appears at twice the frequency of the C=O absorption (3400  $\text{cm}^{-1}$ ). In the present spectra, bands at 1710  $\text{cm}^{-1}$ , which appear after thermal degradation at 170, 190 and 210 °C, are related to ketones, whose presence is also justified by the change in bands at 1471 and 1450  $\text{cm}^{-1}$  (aliphatic CH<sub>3</sub> and asymmetric CH<sub>3</sub> in alkane) to 1462 (CH<sub>3</sub> present in ketones and esters) and also by the enlargement of the band at 1157  $\text{cm}^{-1}$  (C–C of alkanes), as a consequence of the presence of ketones and alkyl esters characteristic groups bonded to these carbons, by axial and angular deformation, C–C(=O)–C (ketones) and C–C(=O)–O (esters).

Bands between 1000 and 800  $\text{cm}^{-1}$  are related to C–C bonds. As these bands are weak, broad OH bands due to carboxylic acid are usually overlapped. These compounds are generally in dimer form, with a large band at 950  $\text{cm}^{-1}$ . These dimers lead to a dislocation of bands C=O, from 1605 to 1630  $\text{cm}^{-1}$ , as observed for lubricant degraded at 190 °C for 8 h. At 210 °C, this band is not observed, probably due to the compound decomposition.

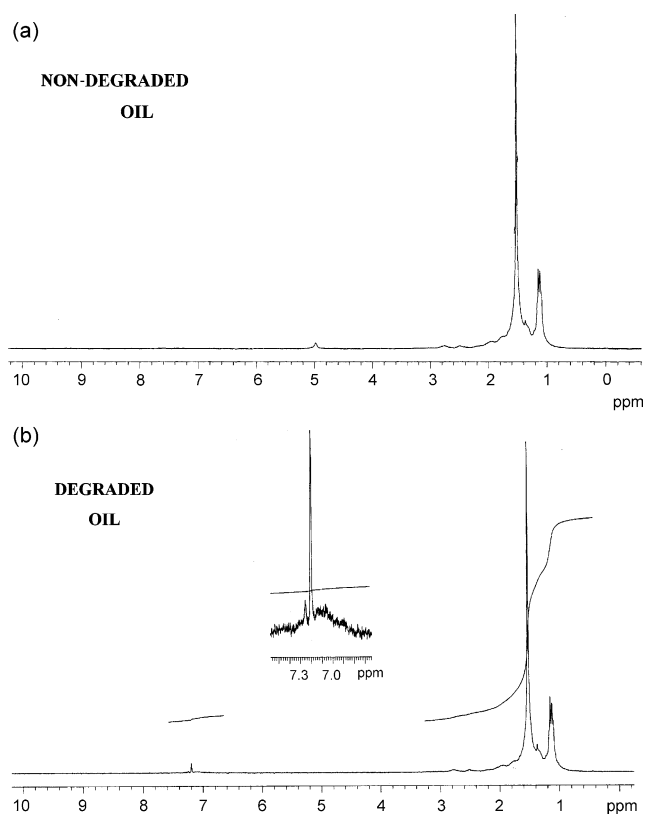


Fig. 3. <sup>1</sup>H NMR spectra of non-degraded and degraded mineral lubricant oils.

This way, IR results indicate that lubricant degradation occurs by oxidation reactions, in agreement to literature results, probably leading to the formation of carboxylic acids and ketones [7,8].

<sup>1</sup>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 7.0–7.4 ppm, which can be attributed to protons in unsaturated ketones.

In relation to <sup>13</sup>C NMR spectra (Fig. 4), the presence of characteristic peaks at 10–30 ppm (CH<sub>3</sub>), 15–55 ppm (CH<sub>2</sub>), 25–60 ppm (CH) and 30–40 ppm (–C–) is observed before and after lubricant degradation. The presence of C–OH and C–O–C bonds may be observed at 45–90 and 55–90 ppm, respectively. In the present spectra, these peaks are observed before and after degradation, with an intensity increase of 75 and 375, respectively. Peak at 120–150 ppm is due to aromatic compounds presence, which may be present in the sample, but may also be due to the solvent used (benzene). NMR results confirm the oxidation of the mineral lubricants, during degradation, leading to ketones and carboxylic acids formation [8].

Viscosity results are presented in Fig. 5. It may be observed that all lubricants present an increase in viscosity, at the beginning of the degradation. This behavior may be due to evaporative loss of lower viscosity components. This evaporation may be related to the disappearance of bands at 2984, 2833, 1470 and 1450  $\text{cm}^{-1}$ , as stated before.

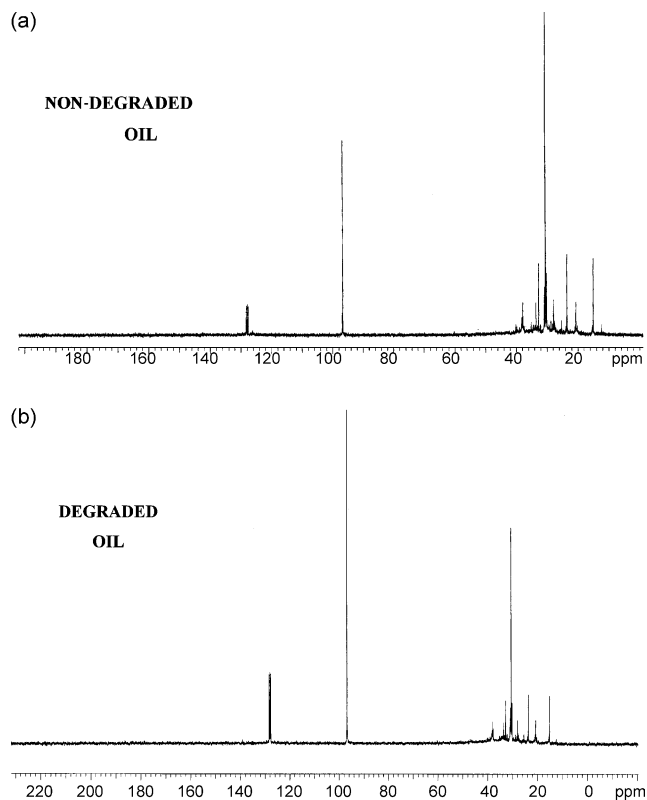


Fig. 4.  $^{13}\text{C}$  NMR spectra of non-degraded and degraded mineral lubricant oils.

For samples degraded at  $150\text{ }^\circ\text{C}$ , after this first increase, viscosity remains constant, indicating that no further degradation occurs.

After the initial increase in viscosity values, samples degraded at  $170$  and  $190\text{ }^\circ\text{C}$  present a viscosity decrease. The highest degradation is observed at  $210\text{ }^\circ\text{C}$ , for 24 h of heat treatment. According to literature data [3] to NMR and infrared spectra, carboxylic acids and ketones are formed after degradation, leading to the formation of hydrogen bonding and dipole–dipole interaction, respectively. As a consequence, higher intermolecular forces are formed, increasing lubricant viscosity. On the other hand, oxidation products are observed in all samples after degradation. This way, we

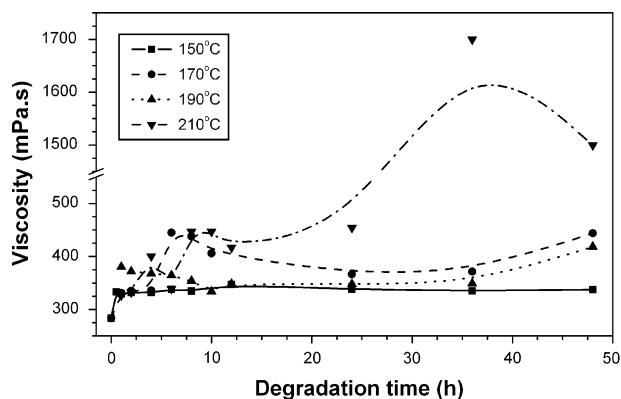


Fig. 5. Viscosity variation as a function of time and temperature.

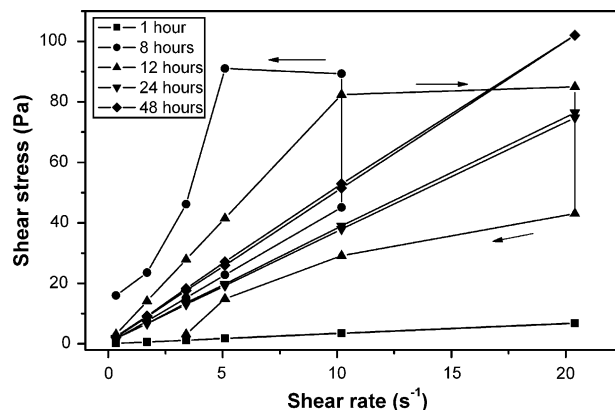


Fig. 6. Rheological behavior, according to shear stress as a function of shear rate of the mineral lubricants after heat treatment at  $170\text{ }^\circ\text{C}$ .

believe that viscosity variation may not be related to these compounds. Another possibility is a polymerization reaction, which may also lead to a viscosity increase, due to the formation of high molecular weight products.

After heat treatment at  $150\text{ }^\circ\text{C}$ , shear stress vs. shear rate curves do not present hysteresis, in contrast to lubricants treated at  $170\text{ }^\circ\text{C}$  for 8 and 12 h, which present the higher viscosities (Fig. 6), associated to anti-thixotropy and thixotropy, respectively. At  $190\text{ }^\circ\text{C}$ , samples do not present thixotropy. At  $210\text{ }^\circ\text{C}$ , only samples degraded for longer times present thixotropy, indicating that a higher degradation is necessary to change rheological properties one more time.

The degradation of mineral lubricant oils involves polymerization that can produce high molecular weight material. When this molecular weight gets too high, the material may become insoluble, leading to its precipitation. This degradation mechanism was observed by Kauffman et al. [9,10] in aircraft turbine engine oils. Viscosity variation, as well as rheological behavior, may be related to the polymerization followed by precipitation of these products. This precipitation is very deleterious, as these products are harmful to machines.

Rheological behavior of mineral lubricant oils was evaluated using Ostwald power law (Eq. (1)), often used to describe highly paraffinic oils, as well as oils of high concentrations of resins and asphaltenes [11]. The  $m$  values were calculated, being presented in Table 2.

$$\sigma = \eta \dot{\gamma}^m \quad (1)$$

Table 2  
 $m$  Values after degradation at different temperatures and times

Time of degradation (h)	Temperature ( $^\circ\text{C}$ )			
	150	170	190	210
1	$0.94 \pm 0.01$	$0.94 \pm 0.02$	$1.00 \pm 0.01$	$1.00 \pm 0.01$
12	$0.93 \pm 0.02$	$0.96 \pm 0.01$	$0.88 \pm 0.04$	$0.88 \pm 0.04$
24	$0.99 \pm 0.01$	$0.90 \pm 0.03$	$1.00 \pm 0.01$	$0.98 \pm 0.01$
48	$0.95 \pm 0.01$	$0.95 \pm 0.01$	$0.97 \pm 0.01$	$0.95 \pm 0.01$

where:  $\sigma$  is the shear stress (Pa),  $\eta$  is the viscosity (Pa s),  $\gamma$  is the shear rate ( $s^{-1}$ ) and  $m$  indicates rheological behavior in the following way:  $m < 1$ : pseudoplasticity (shear thinning);  $m = 1$ : Newtonian flow;  $m > 1$ : dilatancy (shear thickening) [12].

All samples present a behavior varying from Newtonian to pseudoplastic. Samples degraded at 150 °C do not present a considerable variation in rheologic behavior. An important fact is that samples heat-treated at 170 °C for 24 h and at 190 and 210 °C, for 12 h, present an increase in pseudoplasticity (shear thinning). Comparing this behavior to viscosity results (Fig. 5), it may be observed that pseudoplasticity increases when viscosity decreases. According to literature [13–15], anomalous flow properties (structural viscosity, shear thinning and thixotropy) resulting from the aggregation of the paraffin crystallites become increasingly noticeable with increasing paraffin content in the oil and with decreasing temperature. Newtonian flow is observed only at sufficiently high temperatures, such that the paraffins are totally dissolved. This way, pseudoplasticity is probably related to polymerization, being associated to insoluble polymers.

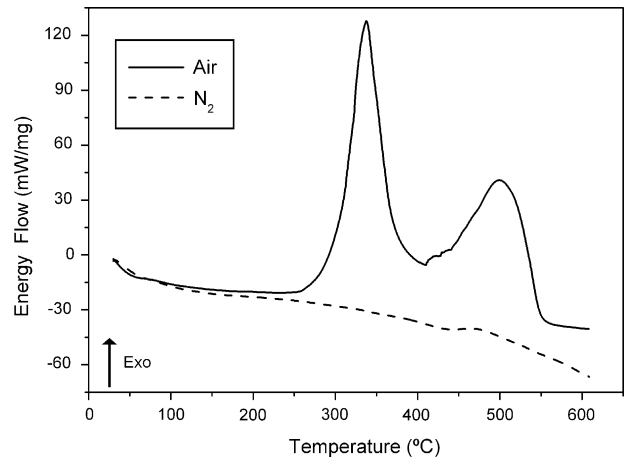


Fig. 8. DSC curves of non-degraded mineral lubricants under different atmospheres.

Oxidation reactions, leading to decomposition, are confirmed by thermogravimetry in different atmospheres. Different decomposition profiles are observed at different atmospheres, for the same lubricant, as indicated in Fig. 7.

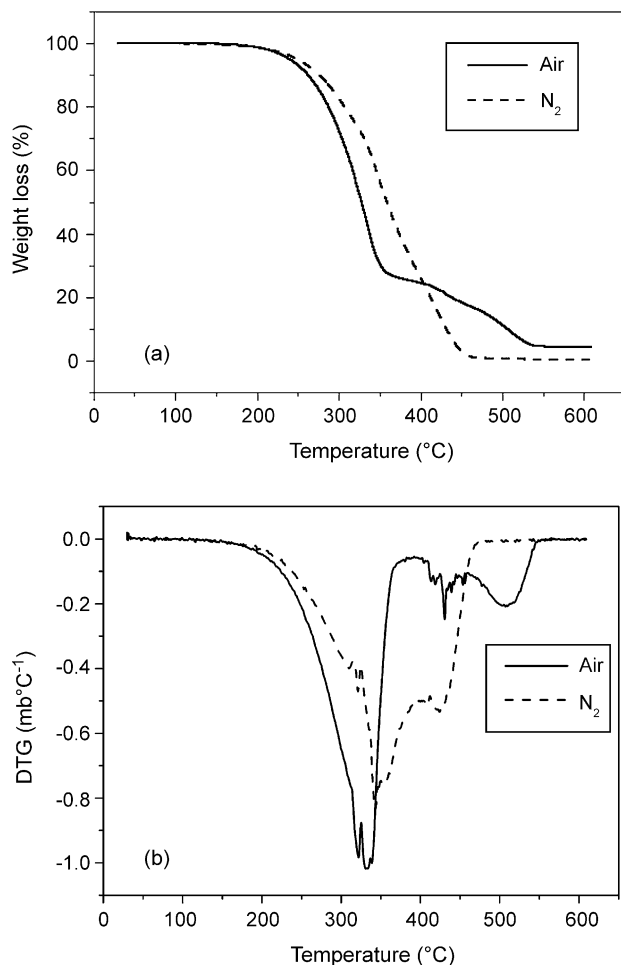


Fig. 7. (a) TG curves of the non-degraded mineral lubricant oil, in different atmospheres; (b) DTG curve of the non-degraded lubricant.

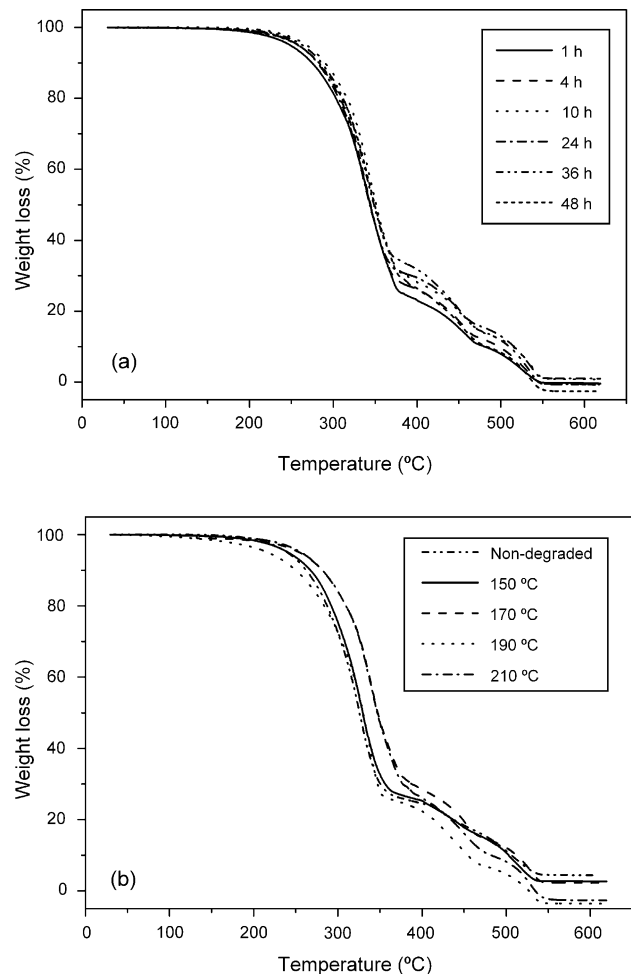


Fig. 9. TG curve of the mineral lubricant (a) degraded at 210 °C, for different times and (b) degraded for 48 h at different temperatures.

Table 3  
Thermogravimetric results of mineral lubricant oils after thermal degradation at different temperatures and times

Degradation conditions	First step			Second step			Third step		
	$T_{\text{onset}}$ (°C)	$T_{\text{peak}}$ (°C)	$\Delta m$ (%)	$T_{\text{onset}}$ (°C)	$T_{\text{peak}}$ (°C)	$\Delta m$ (%)	$T_{\text{onset}}$ (°C)	$T_{\text{peak}}$ (°C)	$\Delta m$ (%)
150 °C—1 h	181.3	338.1	74.41	407.4	455.1	11.88	477.8	523.3	10.55
150 °C—48 h	165.4	328.9	71.76	394.9	428.9	10.15	472.1	505.1	12.75
170 °C—4 h	175.6	335.8	79.12	399.4	447.1	12.62	476.7	523.3	8.47
170 °C—8 h	181.3	341.5	74.33	413.1	447.1	12.29	481.2	524.4	10.70
170 °C—24 h	183.6	336.9	74.35	396.0	432.4	13.14	476.7	528.9	11.81
170 °C—48 h	191.5	338.1	69.25	402.8	452.8	13.66	480.1	530.1	11.84
190 °C—1 h	164.2	335.8	71.78	382.4	447.1	14.32	474.4	531.2	13.49
190 °C—12 h	184.4	316.5	73.64	382.4	423.3	13.67	461.9	510.8	12.15
190 °C—48 h	123.3	339.2	72.63	365.3	439.2	18.86	482.4	532.4	9.008
210 °C—1 h	163.1	341.5	73.93	397.2	450.6	13.13	477.8	521.0	10.56
210 °C—4 h	179.0	342.6	70.94	392.6	456.2	14.24	473.3	527.8	13.14
210 °C—10 h	159.8	339.2	70.74	398.3	452.8	14.08	479.0	528.9	12.74
210 °C—24 h	157.4	332.4	68.20	397.1	444.9	13.37	469.9	531.2	15.07
210 °C—36 h	182.4	338.1	64.80	396.9	449.4	19.32	480.1	532.4	14.57
210 °C—48 h	164.2	340.3	72.37	397.2	452.8	14.53	481.2	533.5	12.00

TG curve in air presents three weight loss steps, in the temperature range 170–530 °C, while in nitrogen atmosphere, only one weight loss step is observed, with one peak followed by one shoulder, in the temperature range 170–470 °C. This result confirms previous ones, indicating the occurrence of an oxidation reaction among lubricant constituents and oxygen present in air atmosphere. This reaction may lead to the formation of compounds as carboxylic acids and ketones, indicated by infrared and NMR spectra. Oxidation may also lead to a polymerization reaction, with formation of higher molecular weight products.

According to Lehrle et al. [16], evaporation of the most volatile components from the lower end of the molecular weight distribution of the oil occurs below 250 °C, followed by the first degradation region, between 250 and 360 °C. In the present work, TG results in air atmosphere present three steps: the first one (170–360 °C) is probably due to elimination of low molecular weight products, followed by hydrocarbons degradation. This step is the most important one to determine the thermal stability of the lubricants. The second mass loss step (380–460 °C) as well as the third one (450–530 °C) are related to decomposition of hydrocarbons of higher molecular weight.

DSC curves (Fig. 8), in air atmosphere, indicate two high exothermic peaks, with temperatures of 338 and 499 °C and an onset temperature of 258 °C. In nitrogen atmosphere, no peaks are observed. These results indicate that peaks observed in air atmosphere decomposition are related to hydrocarbons combustion processes. According to Lehrle et al. [16], evaporation occurs below 250 °C. This transition is not observed in the present analysis, probably due to the small weight loss (~2% up to 200 °C and ~6% up to 250 °C), leading to a low energy transition.

Thermal decomposition profile of lubricants degraded at different temperatures and times are similar, as it may be observed in Fig. 9. All curves present three decomposition

steps in the range 170–530 °C. Table 3 shows the results obtained in TG/DTG curves, in air atmosphere, for degraded samples. It may be observed that, at small degradation times, the higher the thermal degradation temperature,

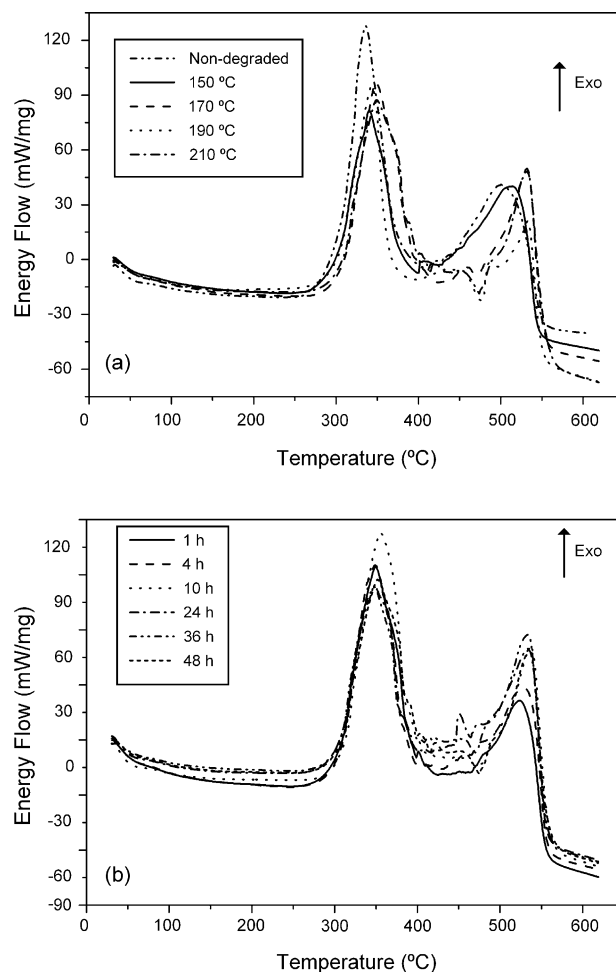


Fig. 10. DSC curves of mineral lubricants (a) after degradation for 48 h and (b) degraded at 210 °C for different times.

the lower the onset decomposition temperature, indicating that samples get less stable.

Samples degraded at 150 and 170 °C present a reduction in the weight loss of the first and second decomposition steps, with an increase in the weight loss of the third step. Formation of higher molecular weight compounds, which decompose at higher temperatures, probably occurs. Samples degraded at higher temperatures do not present this change. For these samples, a gum formation is observed, indicating that compounds with higher molecular weight become insoluble, as indicated in rheological analysis.

Fig. 10a shows the calorimetric results of mineral lubricant oils, degraded at different temperatures. Fig. 10b shows the influence of degradation time in calorimetric behavior of these oils, after thermal treatment at 210 °C. 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.

#### 4. Conclusion

Results indicate that thermal treatment leads to a degradation of lubricants, increasing their viscosity and promoting thixotropy and pseudoplasticity in some samples. These characteristics may be due to the polymerization process, with formation of high molecular weight products, which become insoluble. IR and NMR results indicate oxidation reactions.

Thermogravimetric curves indicate the thermal stability of lubricant oils below 170 °C. Thermogravimetric curve in air presents three decomposition steps while in nitrogen

atmosphere, only one decomposition step is observed. DSC analysis in air atmosphere, indicate two high exothermic peaks, related to hydrocarbons oxidation and combustion processes.

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#### References

- [1] Souza MSM. *Quím e Deriv* 2000;382:20.
- [2] Pedersen KS, Ronningsen HP. *Energy Fuels* 2003;17:321.
- [3] Perez JM. *Thermochim Acta* 2000;357–358:47.
- [4] Keskin C, Kok MV. *Thermochim Acta* 2001;369:143.
- [5] Gamlin CD, Dutta NK, Choudhury NR, Kehoe D, Matisons J. *Thermochim Acta* 2002;392–393:357.
- [6] Bowman WF, Stachowiak GW. *Lubr Eng* 1996;52(10):745.
- [7] Pavia DL, Lampman GM, Kriz GS. *Introduction to spectroscopy*. New York: Harcourt Brace; 1997. 510 p.
- [8] Silverstein RM, Bassler GC, Morrill TC. *Spectrometric identification of organic compounds*, 5th ed. New York: Wiley; 1991. 300 p.
- [9] Kauffman RE, Feng AS, Karasek KR. *Trib Trans* 2000;43(4):677.
- [10] Kauffman RE, Feng AS, Karasek KR. *Trib Trans* 2000;43(4):823.
- [11] Matveenko VN, Kirsanov EA, Remizov SV. *Colloids Surf A* 1995; 101:17.
- [12] Pedersen KS, Ronningsen HP. *Energy Fuels* 2000;14:43.
- [13] Remizov SV, Kirsanov EA, Matveenko VN. *Colloids Surf A* 2000; 175:271.
- [14] Kirsanov EA, Remizov SV. *Rheol Acta* 1999;38:172.
- [15] Farina A, Fasano A. *Math Comput Model* 1997;25(5):75.
- [16] Lehrle RS, Duncan R, Liu Y, Parsons IW, Rollinson M, Lamb G, Barr D. *J Anal Appl Pyr* 2002;64:207.