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KINETIC AND ACTIVATION THERMODYNAMIC PARAMETERS ON THERMAL DECOMPOSITION OF SYNTHETIC LUBRICANT OILS

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The kinetic and thermodynamic study of synthetic lubricant oils was accomplished in this work, using isothermal and non-isothermal thermogravimetry based on mass loss as a function of time and temperature. The thermodynamic and kinetic behavior of the synthetic lubricant oils depends on atmosphere and heating rates used in TG analysis. The kinetic and thermodynamic results were satisfactory, presenting good correlation.

Keywords: *activation parameters, kinetic, synthetic lubricant, thermodynamic*

Introduction

Lubricants change their chemical and physical fluid properties upon their usage. Since the lubricant is a factor that considerably influences the economic as well as the ecological balance of a machine, the analysis of the aging behavior is extremely important. A characterization of the behavior of the properties of lubricants as a result of utilization is thus the basis for the development of new lubricants [1]. Several properties of the synthetic bases are better than the one of the mineral bases. The superiority of the synthetic bases stand out, above all, in the following aspects: they resist better to the oxidation, they have better thermal stability and higher viscosity index, they are less volatile and they freeze at lower temperatures and some synthetic base oils are biodegradable [2].

Lubricant oil degradation under operation conditions is a problem that involves meaningful economical losses. Oxidation is the primary step of degradation, and was in the scope of many studies. Due to complexity of these systems to establish a kinetic mechanism of this reaction is difficult [3–5]. The degradation of a liquid lubricant is frequently accompanied by deleterious changes in its physical and chemical properties that can adversely affect it a performance [6]. There has been growing interest was paid to understand the details of oxidative degradation processes with respect to the oil composition or types. The adverse effect of temperature has also been an important issue [7]. In recent years, the application of thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) in the study of petroleum derivatives has been widened among researchers [8–12].

Lubricants can be changed with temperature increase altering its chemical and physicochemical properties. By means of the kinetic and the thermodynamic study of thermal decomposition reactions, the degradation energy and the stability degree of lubricants could be evaluated [4]. Thus, this work intends to characterize the thermal decomposition process of synthetic lubricant oils, in relation to its thermodynamic and kinetic properties.

Experimental

Materials

Commercial synthetic lubricating oil, used in automotive motors, was used in this study. Its API classification is SJ group with SAE viscosity of 20–50 W. For thermal degradation, synthetic lubricants were heated to 150, 170, 190 and 210°C, at air atmosphere, using a system similar to a distillation one (Fig. 1). Samples were withdrawn after heat treatments varying of 48 h. Activation thermodynamic and kinetic parameters were evaluated after degradation.

Methods

Thermal analysis

Non-isothermal TG/DTG analyses were done in a simultaneous thermal analyzer (SDT-2960, TA Instru-

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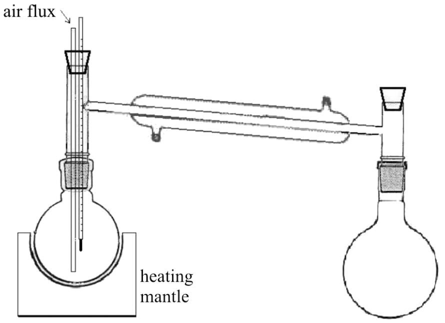

Fig. 1 Heating system used in the synthetic lubricant degradation

ments), using flowing air or nitrogen (110 mL min^{-1}) and alumina crucibles at heating rates of 5, 10, 15 and 20°C min^{-1}, with 10±0.5 mg of sample mass in the temperature range of 25–620°C. Four parallel TG/DTG runs have been done for the sake of reproducibility.

Isothermal TG analyses were done in a thermobalance (TGA-50, Shimadzu), at air atmosphere (30 mL min^{-1}), using alumina crucibles, with a heating rate of 10°C min^{-1}, sample mass of 10±0.5 mg, at 190, 200 and 210°C.

Kinetic analysis

In the isothermal and non-isothermal study of thermal decomposition reactions of the synthetic lubricant oil, the kinetic parameters, as activation energy (E_a), reaction order (n) and frequency factor (A) were calculated according to Coats–Redfern method [13, 14]. The study was accomplished by TG curves, based on mass loss as a function of temperature, using Eq. (1):

$$\log\left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right]=\log\frac{AR}{\phi}-\frac{E_a}{2.303RT} \qquad (1)$$

where α is the decomposed fraction, T is the absolute temperature, R is the gas constant; ϕ is the linear heating rate. Coats and Redfern developed an integral method which can be applied to TG/DTG data, assuming the different reaction orders. The reaction order related to the most appropriated mechanism is presumed to lead to the best linear plot, from which the activation energy is determined.

The thermodynamic parameters were calculated according to Eqs (2)–(4):

$$\Delta H^*=E_a-RT \qquad (2)$$

$$\Delta S^*=R\left(\ln\frac{hA}{k_BT}-1\right) \qquad (3)$$

$$\Delta G^*=\Delta H^*-T\Delta S^* \qquad (4)$$

where ΔH^* is the activation enthalpy, ΔS^* is the activation entropy, ΔG^* is the activation free energy, A is the frequency factor, h is the Plank constant and k_B is the Boltzmann constant [15].

Results and discussion

Non-degraded lubricant oil

Decomposition of the non-degraded synthetic lubricant is showed by non-isothermal thermogravimetry at different atmospheres (Fig. 2) and heating rates (Fig. 3). Different profiles are observed at different atmospheres.

TG/DTG curves at air present two main decomposition steps, in the temperature range of 158–598°C, while in nitrogen atmosphere, only one decomposition step is observed in 178–469°C temperature range. This result indicates the occurrence of oxidation reactions among synthetic lubricant constituents and in oxidative atmosphere. In relation to the thermal decomposition steps in air atmosphere, it was observed that the first one (158–347°C) is related to decomposition of low molecular mass compounds [16]. The second step (348–598°C) is related to combustion of high molecular mass compounds. In nitrogen atmosphere, after evaporation of low molecular mass compounds, carbon chain degradation occurs [16].

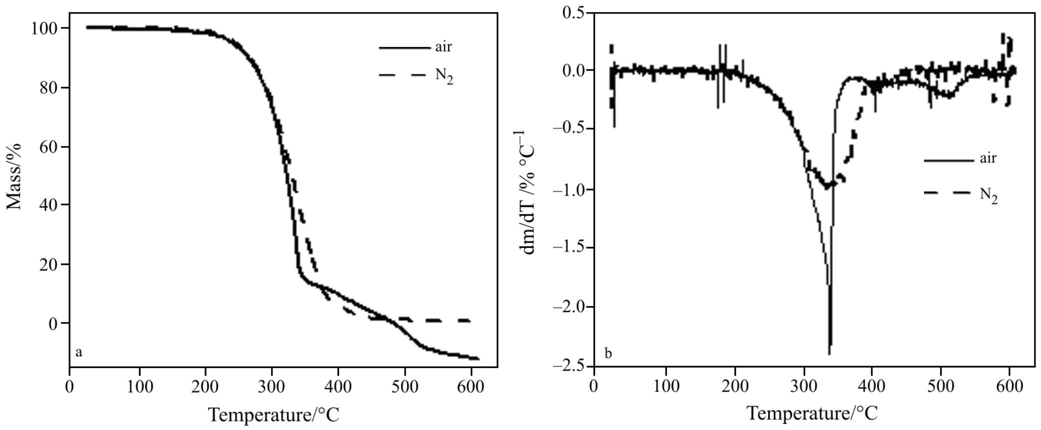

Fig. 2 a – TG and b – DTG curves of the non-degraded synthetic lubricant oil in different atmospheres

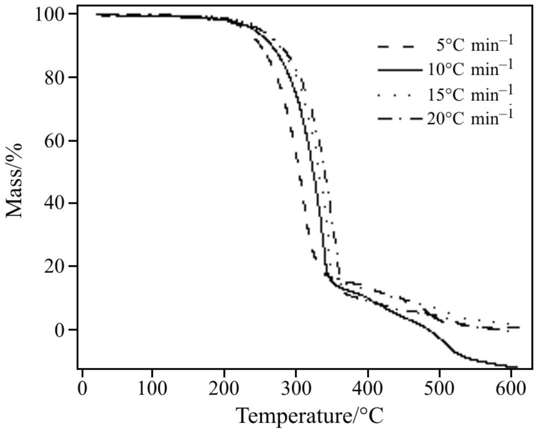

Fig. 3 TG curves of the non-degraded synthetic lubricant oil at different heating rates

The non-isothermal kinetic parameters of the first thermal decomposition step of the non-degraded synthetic lubricant oils are presented in Table 1.

In spite of the difference in the decomposition profiles of synthetic lubricant in air (oxidative atmosphere) and nitrogen (inert atmosphere), no meaningful difference is observed between the calculated activation energies and frequency factor. On the other hand, the reaction order of the thermal decomposition of the lubricant oil changes more pronouncedly with the atmosphere and no meaningful difference is observed as a function of heating rate (Fig. 4), indicating the alteration of the reaction mechanism. These results probably indicate that at the beginning, mass loss process in both atmospheres is related mainly to the evaporation of low molecular mass compounds, leading to similar activation energies. At higher temperatures, different results were obtained, since air atmosphere leads to combustion, while nitrogen atmosphere leads to chain degradation.

The activation thermodynamic parameters for thermal decomposition were evaluated at different conditions, according to Coats–Redfern method, using non-isothermal TG data [15]. Table 2 summarizes the values of the thermodynamic parameters for non-degraded synthetic lubricant samples at different conditions.

Thermal decomposition of synthetic lubricant oils can also be evaluated by isothermal analysis. The mass loss increases with temperature (35.6, 46.1 and 50.4 %, at 190, 200 and 210°C, respectively).

The kinetic parameters were evaluated for non-degraded synthetic lubricant oil by non-isothermal thermogravimetry [13]. The rate constants (k) of the non-degraded oil were calculated according to the angular coefficient of decomposed fraction plotted as a function of time. The results were: $2.94{\cdot}10^{-6}$ s^{-1} (190°C), $3.56{\cdot}10^{-6}$ s^{-1} (200°C) and $4.30{\cdot}10^{-6}$ s^{-1} (210°C), with correlation coefficient of 0.99953 and standard deviation of 0.00299. These results were used to determine activation energy and frequency factor. Results obtained were: E_a=34.48 kJ mol^{-1} and A=43.5 s^{-1}, with a correlation coefficient of 0.99981 and a standard deviation of 0.00518.

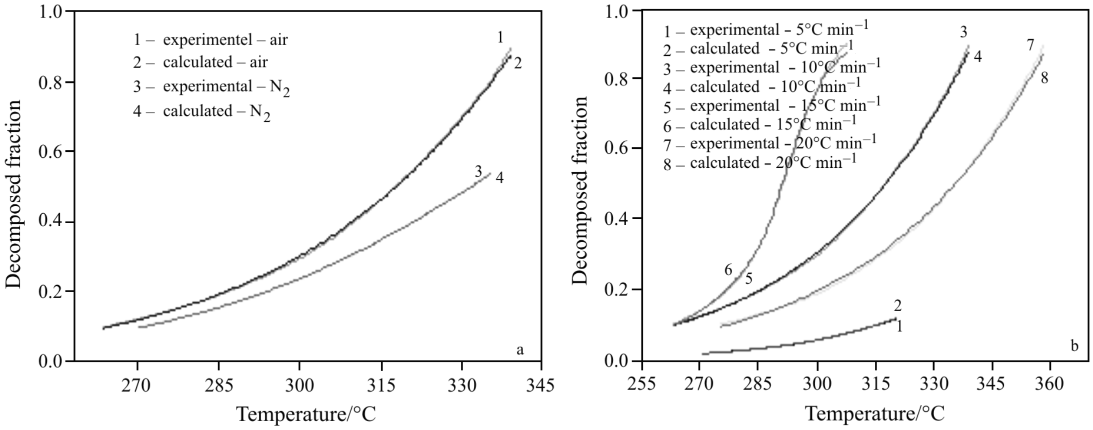

Fig. 4 Decomposed fraction as a function of a – atmosphere and b – heating rate

Table 1 Influence of atmosphere and heating rate in the kinetic parameters of synthetic oil

Parameter	5°C min^{-1} – air	10°C min^{-1} – air	10°C min^{-1} – N_2	15°C min^{-1} – air	20°C min^{-1} – air
n	0.2	0.1	1.0	0.0	0.0
E_a/kJ mol^{-1}	72.3	70.9	73.1	74.8	68.0
A/s^{-1}	$5.0{\cdot}10^3$	$3.8{\cdot}10^3$	$2.0{\cdot}10^3$	$1.1{\cdot}10^4$	$2.5{\cdot}10^3$
r	0.9999	0.9998	0.9998	0.9998	0.9994
sd	0.0027	0.0049	0.0023	0.0043	0.0096

Table 2 Thermodynamic parameters as a function of heating rate and atmosphere of synthetic oil

Condition	T_{peak}/K	$-\Delta H^*$/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}	$-\Delta G^*$/kJ mol^{-1}	*r*	*sd*
5°C min^{-1} – air	584.0	67.4	187.9	177.1	0.9999	0.0021
10°C min^{-1} – air	556.0	66.3	189.8	171.8	0.9998	0.0049
10°C min^{-1} – N_2	612.0	70.0	177.4	176.2	0.9999	0.0022
15°C min^{-1} – air	616.0	69.7	181.8	181.7	0.9998	0.0043
20°C min^{-1} – air	629.0	62.7	194.2	184.8	0.9994	0.0096

Degraded lubricant oils

TG analyses of degraded synthetic lubricant were done by means of non-isothermal thermogravimetry at air atmosphere, as presented in Fig. 5 and Table 3.

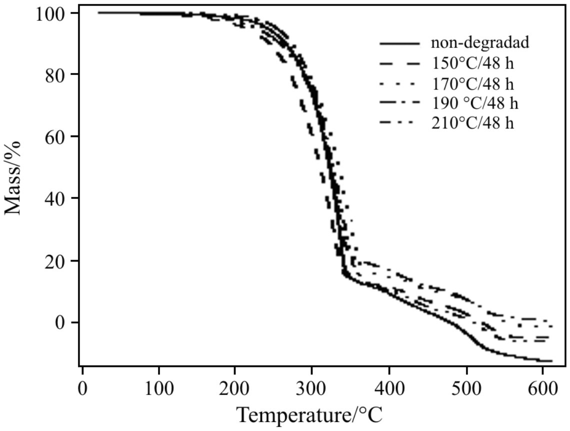

Fig. 5 TG curves of the synthetic lubricant oil after degradation at different temperatures for 48 h

The isothermal TG curves show one decomposition step for degraded synthetic lubricants at 48 h. The isothermal TG data are presented in Table 4. A meaningful increase in the mass loss of the synthetic lubricant sample degraded at 190°C is observed, followed by a decrease after degradation at 210°C. A change in the behavior of samples degraded at different temperatures is also observed in Table 3. The degradation of synthetic lubricant oils involves polymerization that can produce high molecular mass material. When its molecular mass is too high, the substance may become insoluble, leading to gum precipitation, experimentally observed during thermal degradation.

Figure 6 illustrates the influence of degradation temperature in the decomposed fraction of the analyzed lubricant oils. The decomposed fraction increase with degradation temperature, indicating the formation of compounds which evaporate at lower temperatures.

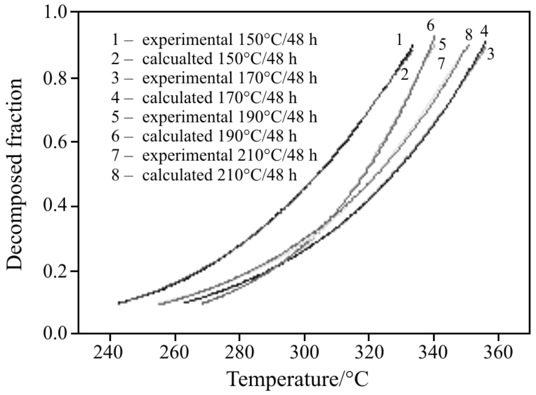

Fig. 6 Decomposed fraction as a function of degradation temperature of synthetic oil

The kinetic and statistical parameters of the first thermal decomposition step of the synthetic lubricant oil, degraded at 150, 170, 190 and 210°C for 48 h, are listed in Table 5.

The activation energy of the first thermal decomposition step of the synthetic degraded samples increases in relation to non-degraded sample except at 190°C, as indicated in Table 5. With degradation temperature the activation energies increase in a small extent. On the other hand, the reaction order presents small variation after degradation at 150°C, with no variation at higher degradation temperatures. During thermal degradation of synthetic lubricant oils, formation of several compounds takes place, modifying

Table 3 TG data of synthetic lubricant oils after thermal degradation

Degradation condition	1st step		2nd step		3rd step	
	T_{on}/°C	Δm/%	T_{on}/°C	Δm/%	T_{on}/°C	Δm/%
150°C/48 h	131.5	83.0	344.3	8.2	474.9	8.8
170°C/48 h	156.2	81.8	380.5	6.4	477.6	10.2
190°C/48 h	151.8	79.6	369.0	8.4	462.6	9.9
210°C/48 h	135.0	78.9	374.3	14.9	–	–

Table 4 Isothermal TG data of degraded synthetic lubricant oil

Degraded lubricant	Mass loss at isothermal temperature/%		
	190°C	200°C	210°C
150°C/48 h	23.38	32.30	40.38
170°C/48 h	23.08	33.63	38.84
190°C/48 h	32.84	34.16	54.29
210°C/48 h	30.35	41.76	54.32

the lubricity capacity and changing decomposition mechanism as indicated by kinetic parameters.

In isothermal conditions, the plots of decomposed fraction (α) *vs*. time are presented in Fig. 7.

According to Fig. 7, results indicate a meaningful change in the reaction mechanism of degraded lubricants. Isothermal curves present a nearly linear relation of decomposed fraction as a function of time, indicating that these oils decompose with a linear relation (n-order mechanism) and an exponential relation [2].

Establishing a relation between the decomposed fraction and the kinetic models described in the literature [14], the rate constants were calculated (Table 6). The increase in rate constant values indicates the stability decrease of lubricant. Samples degraded at 190°C present the lowest stability.

A linear relation between ln$k$ and $1/T$ was observed, indicating that rate constants obey Arrhenius Law. This way, activation energy and frequency factor were calculated, as presented in Table 7.

According to Table 7, sample degraded at 150 and 170°C presents similar activation energy values,

Table 5 Kinetic parameters of the synthetic lubricant degraded at different temperatures

Parameter	Non-degraded	150°C	170°C	190°C	210°C
n	0.1	0.3	0.0	0.1	0.0
E_a/kJ mol^{-1}	70.9	59.3	56.5	79.9	55.4
A/s^{-1}	$3.8\cdot10^3$	$4.4\cdot10^2$	$1.3\cdot10^2$	$2.7\cdot10^4$	$1.2\cdot10^2$
r	0.9998	0.9999	0.9999	0.9999	0.9994
sd	0.0049	0.0036	0.0015	0.0059	0.0089

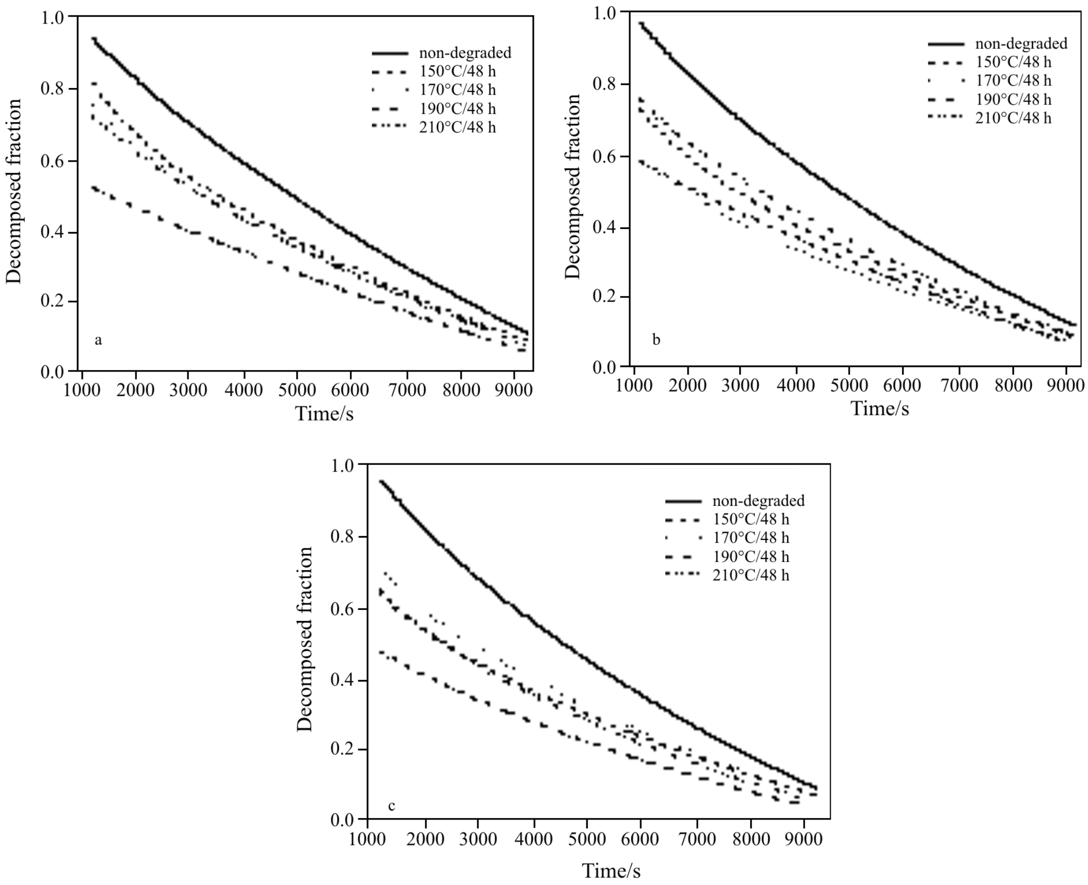

Fig. 7 Influence of degradation time in the decomposed fraction under isothermal conditions: a – 190, b – 200, c – 210°C

Table 6 Reaction rate constant (k) of degraded synthetic lubricant oils

Degraded lubricant	Isothermal temperature/°C			Statistics	
	190°C	200°C	210°C	r	sd
150°C/48 h	$2.70\cdot10^{-6}$	$3.03\cdot10^{-6}$	$3.34\cdot10^{-6}$	0.99941	0.02485
170°C/48 h	$2.63\cdot10^{-6}$	$2.98\cdot10^{-6}$	$3.60\cdot10^{-6}$	0.99951	0.00293
190°C/48 h	$1.83\cdot10^{-6}$	$2.35\cdot10^{-6}$	$3.11\cdot10^{-6}$	099954	0.01257
210°C/48 h	$2.61\cdot10^{-6}$	$3.13\cdot10^{-6}$	$3.54\cdot10^{-6}$	0.99969	0.01998

Table 7 Isothermal kinetic parameters of synthetic lubricant oils

Degraded lubricant	E_a/kJ mol^{-1}	A/s^{-1}	r	sd
Non-degraded	34.48	$4.35\cdot10^{1}$	0.99981	0.00518
150°C/48 h	29.86	$2.27\cdot10^{2}$	0.99988	0.00230
170°C/48 h	28.60	$2.22\cdot10^{2}$	0.98359	0.04032
190°C/48 h	48.68	1.78	0.99532	0.03627
210°C/48 h	19.64	$2.22\cdot10^{3}$	0.97185	0.05318

Table 8 Influence of temperature of degradation in the thermodynamic parameters

Sample	T_{peak}/K	$-\Delta H^*$/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}	$-\Delta G^*$/kJ mol^{-1}	r	sd
150°C/48 h	601.0	54.3	208.3	179.5	0.9999	0.0036
170°C/48 h	625.0	51.3	218.8	188.0	0.9999	0.0015
190°C/48 h	605.0	73.8	174.1	179.1	0.9999	0.0059
210°C/48 h	614.0	50.3	219.3	184.9	0.9994	0.0089

indicating that no meaningful degradation occurred in this temperature range. At higher degradation temperatures, activation energy values present a cyclic variation. The sample degraded at 210°C, present a decrease in the activation energy value, while the sample degraded at 190°C showed high activation energy.

All results relative to isothermal kinetic analysis indicate a differential behavior of synthetic lubricant oil samples degraded at 190°C. This may be due to the formation of intermediate compounds, as a consequence of oxidation reactions. During lubricant degradation high molecular mass hydrocarbons and esters are formed, requiring higher energy for decomposition. These high molecular mass hydrocarbons may become insoluble, leading to gum precipitation, as experimentally observed. This behavior would lead to the decrease in activation energy value, after degradation at 210°C [17].

Table 8 presents thermodynamic parameters of the synthetic lubricant samples degraded at different conditions of temperature and time.

These results are in agreement with the previous ones, indicating a different behavior of samples degraded at 190°C, probable to formation of oxidation intermediary compounds.

Conclusions

According to the obtained results, degradation reactions of the synthetic lubricant oils are confirmed by isothermal and non-isothermal thermogravimetry in different atmospheres and heating rates that led to different decomposition profiles for these lubricant oils. Through the obtained kinetic and activation thermodynamic parameters it was verified that one significant change in the reaction mechanism of the synthetic lubricant oils takes place.

Using thermodynamic and kinetic parameters of decomposition of synthetic lubricant oils, degradation energy can be evaluated, and lubricant stability degree can be determined.

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