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THERMODYNAMIC AND KINETIC PARAMETERS ON THERMAL DEGRADATION OF AUTOMOTIVE MINERAL LUBRICANT OILS DETERMINED USING THERMOGRAVIMETRY

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In this work, the thermodynamic activation and kinetic study of mineral lubricant oils was accomplished using isothermal and non-isothermal thermogravimetry based on mass loss as a function of time and temperature. The thermodynamic and kinetic behavior of the mineral lubricant oils depends on the atmosphere and heating rates used in TG analysis. The kinetic and thermodynamic results were satisfactory, presenting good correlation, with a linear correlation coefficient close to unit with a low standard deviation.

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

Introduction

Mineral oils are obtained from petroleum and their properties are not only related to the nature of the raw oil, but also to the refining process. Mineral lubricant oils have very important applications in the decrease of attrition and wear of machines and automotive equipment, besides being responsible for the control of deposits formation, suspended pollutants and also for protection *vs.* erosion [1].

The modern engine lubricant is a carefully designed blend, constituted of base oils and performance enhancing additives, such as pour point depressants, antioxidants, dispersants and detergents [2, 3]. To evaluate these lubricants, bench tests are done, but the majority are slow, man-power intensive, empirical, with a poor reproducibility, and require a large investment in specialized equipment and skilled operators. Some of these tests may be replaced, successfully using conventional thermoanalytical techniques. In recent years, the application of thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) in the study of petroleum derivatives has been widely accepted among researchers [4–8], leading to a meaningful economy.

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 [2]. Thus, this work seeks to characterize the thermal decomposition process of mineral lubricant oils, in relation to its thermodynamic and kinetic properties.

Experimental

A commercial mineral lubricant oil, used in the lubrication of automotive motors, was used in this study. Its API classification is SJ group with SAE viscosity of 40 W. For thermal degradation, lubricants were heated to 150, 170, 190 and 210°C, under air atmosphere, using a system similar to a distillation apparatus. Samples were withdrawn after heat treatment varying from 1 to 48 h. Activation thermodynamic and kinetic parameters were evaluated after thermal degradation.

Non-isothermal TG/DTG analyses were performed in a simultaneous thermobalance (SDT-2960, TA Instruments), under air or nitrogen atmosphere (30 mL min^{-1}) using alumina crucibles, at a heating rate of 5, 10, 15 and 20°C min^{-1}, sample mass of 10 mg, in the temperature range of 25–620°C.

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

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Results and discussion

Kinetic analysis

In the isothermal and non-isothermal studies of thermal decomposition reactions of the mineral lubricant oil, the kinetic parameters – activation energy (E_a), reaction order (n) and frequency factor (A) – were calculated according to Coats–Redfern method [9–11]. The study was accomplished by TG curves, based on mass loss as a function of temperature (Eq. (1)):

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

where α is the decomposed fraction, T is the absolute temperature, R is the gas constant; ϕ is the linear heating rate.

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 [10, 12].

Non-degraded lubricant oils

Decomposition of the non-degraded lubricant is showed by non-isothermal thermogravimetry in different atmospheres and heating rates that led to different profiles, as it is indicated in Fig. 1. Oxidation reactions, leading to decomposition are showed by thermogravimetry in different atmospheres.

TG/DTG curves in air present three main decomposition steps in the temperature range of 170–530°C, while in nitrogen atmosphere, only one main decomposition step is observed in the temperature range of 170–470°C. This result indicates the occurrence of oxidation reactions between lubricant constituents and oxygen present in air atmosphere. In relation to the thermal decomposition steps in air atmosphere, it was observed that the first one (170–360°C) is related to decomposition of low molecular mass compounds. The second step (380–460°C), as well as the third one (450–530°C), are related to combustion of high molecular mass compounds [13].

Concerning to the isotherm experiments, the values of mass losses were increased (22, 29 and 35%) when the temperatures were 190, 200 and 210°C, respectively.

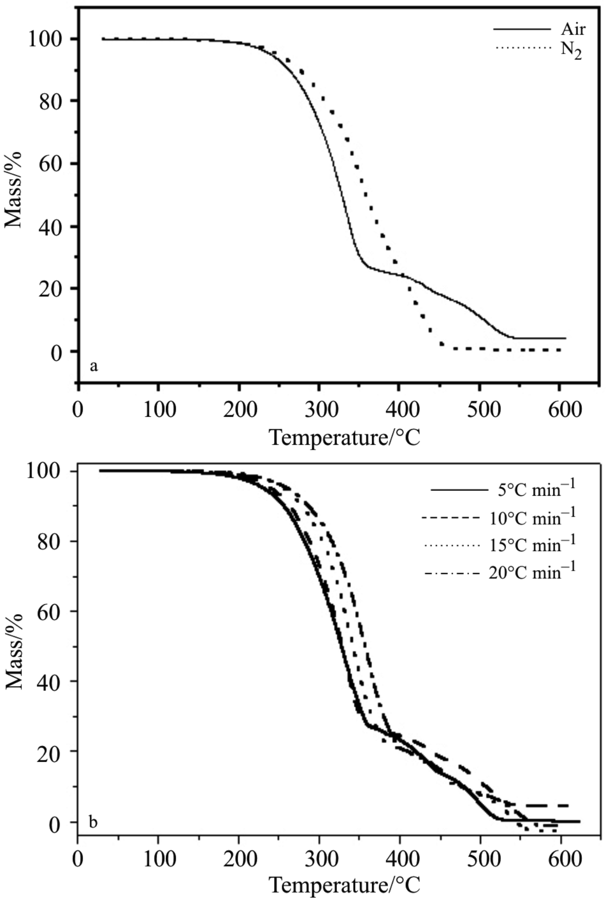

Fig. 1 TG curves of the non-degraded mineral lubricant oil in different: a – atmospheres and b – heating rates

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

In spite of the differences in the decomposition profiles of lubricant in air (oxidant atmosphere) and nitrogen (inert atmosphere), no meaningful difference is observed between the calculated activation energies.

Figure 2 illustrates the influence of atmosphere and heating rate on the decomposed fraction of the analyzed lubricant oil.

Based on these results, a change in the reaction mechanism under different atmospheres can be suggested. The reaction orders of thermal decomposition of the lubricant oil change less with increasing heating rate.

The activation thermodynamic parameters for the thermal decomposition of mineral lubricant oil were evaluated at different conditions from activation energy obtained by Coats–Redfern method, using non-isothermal TG data [12]. Table 2 summarizes the values of the thermodynamic parameters for non-degraded samples at different analysis conditions.

Table 1 Influence of the atmosphere and heating rate on the kinetic parameters

Parameters	Heating rate/°C min^{-1}				
	5 – air	10 – air	10 – N_2	15 – air	20 – air
n	0.68	0.32	1.39	0.52	0.43
E_a/kJ mol^{-1}	64.04	62.36	61.97	71.88	65.99
A/s^{-1}	$6.24\cdot10^2$	$7.06\cdot10^2$	$3.28\cdot10^2$	$5.59\cdot10^3$	$1.41\cdot10^3$
r	0.9999	0.9999	0.9993	0.9999	0.9998
sd	0.0084	0.0022	0.0150	0.0051	0.0060

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

Conditions	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	603.1	59.03	205.46	182.94	1.0000	0.0084
10°C min^{-1}– air	604.6	57.33	204.46	180.95	1.0000	0.0022
10°C min^{-1}– N_2	625.9	56.77	211.12	188.91	0.9992	0.0150
15°C min^{-1}– air	617.9	66.74	187.44	182.56	0.9999	0.0051
20°C min^{-1}– air	634.9	60.71	199.11	187.12	0.9998	0.0060

Thermal decomposition can also be evaluated by isothermal analysis. 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. Results were: $1.88\cdot10^{-8}$ s^{-1} (190°C), $2.92\cdot10^{-8}$ s^{-1} (200°C) and $3.59\cdot10^{-8}$ s^{-1} (210°C), with correlation coefficient of 0.99984 and standard deviation of 0.00208. These results were used to determine activation energy and frequency factor using ln$k$ plotted as a function of $1/T$. Results obtained were: E_a=60.30 kJ mol^{-1} and A=8.16 s^{-1}, with a correlation coefficient of 0.99000 and a standard deviation of 0.06597. Activation energy value is in agreement with the results of non-isothermal method (62.36 kJ mol^{-1}).

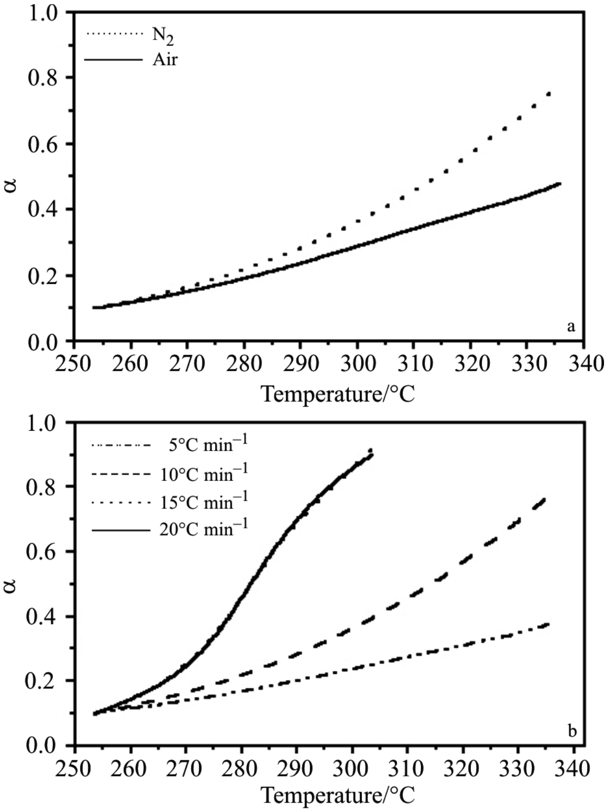

Fig. 2 Decomposed fraction as a function of temperature. a – influence of atmosphere, b – influence of heating rate

Degraded lubricant oils

TG analyses of degraded lubricant were done by means of non-isothermal thermogravimetry in air atmosphere, as presented in Fig. 3 and the TG data were shown in Table 3. It may be observed that, at small degradation times, the higher the thermal degradation temperature, the lower the onset decomposition temperature, indicating that the stability of samples has decreased.

The isothermal TG curves show one decomposition step for degraded lubricants. The isothermal TG data are presented in Table 4.

According to Table 4, a significant increase in the mass loss for the sample degraded at 190°C/48 h was verified. This is due to the formation of polymeric compounds with a long chain and other compounds in suspension. However, the decrease that takes place at 210°C/48 h occurs due to the formation of gums and precipitate materials. The degradation of mineral lubricant oils involves polymerization that can produce compounds with high molecular masses. When this molecular mass is too high, the material may become insoluble, leading to its precipitation.

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

Degradation condition	1st step			2nd step			3rd step		
	T_{on}/°C	T_p/°C	Δm/%	T_{on}/°C	T_p/°C	Δm/%	T_{on}/°C	T_p/°C	Δm/%
150°C/48 h	165.4	328.9	71.76	394.9	428.9	10.15	472.1	505.1	12.75
170°C/48 h	191.5	338.1	69.25	402.8	452.8	13.66	480.1	530.1	11.84
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

Non-isothermal kinetic analysis

Figure 4 illustrates the influence of degradation temperature on the decomposed fraction of the analyzed lubricant oils. The decomposed fraction increases with the temperature of degradation, once as the temperature is raised, more compounds of the lubricant oils are liberated (volatilized). The kinetic and statistical parameters of the first thermal decomposition step of the lubricant oil, degraded at 150, 170, 190 and 210°C for 48 h, are listed in Table 5. Table 5 clearly indicates that the activation energy for the first thermal decomposition step for the degraded samples in relation to non-degraded sample increases about 4.14 kJ mol^{-1}, and after this process, the activation energy is maintained relatively constant throughout the process of degradation. In the thermal degradation of the lubricant oils, the formation of several compounds took place that modified the lubricity capacity these

Table 4 Isothermal thermogravimetric data

Degraded lubricants	Mass loss at isothermal temperature/%		
	190°C	200°C	210°C
150°C/48 h	19.59	28.72	37.78
170°C/48 h	17.56	23.58	29.53
190°C/48 h	31.01	35.24	45.63
210°C/48 h	17.45	22.39	32.16

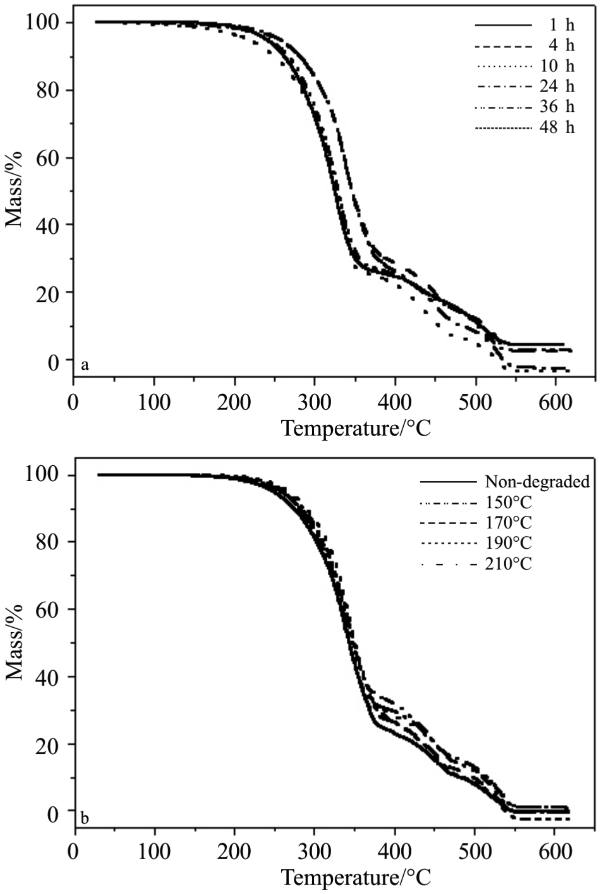

Fig. 3 TG curves of the degraded mineral lubricant
a – at 210°C, for different times and
b – for 48 h at different temperatures

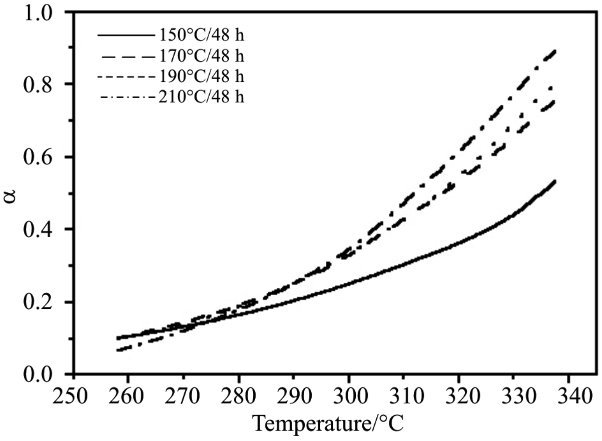

Fig. 4 Decomposed fraction as a function of degradation temperature

Table 5 Kinetic parameters of the lubricant degraded at different temperatures

Kinetic parameters	Non-degraded	150°C/48 h	170°C/48 h	190°C/48 h	210°C/48 h
n	0.32	0.39	0.55	0.22	0.45
E_a/kJ mol^{-1}	62.36	69.66	71.88	66.50	67.73
A/s^{-1}	$7.06\cdot10^2$	$3.41\cdot10^3$	$3.55\cdot10^3$	$1.76\cdot10$	$1.39\cdot10^3$
r	0.9999	0.9999	0.9997	0.9996	0.9995
sd	0.0022	0.0014	0.0075	0.0068	0.0095

oils, and in the elapse of the reaction modify the mechanism, according to modification of the reaction order.

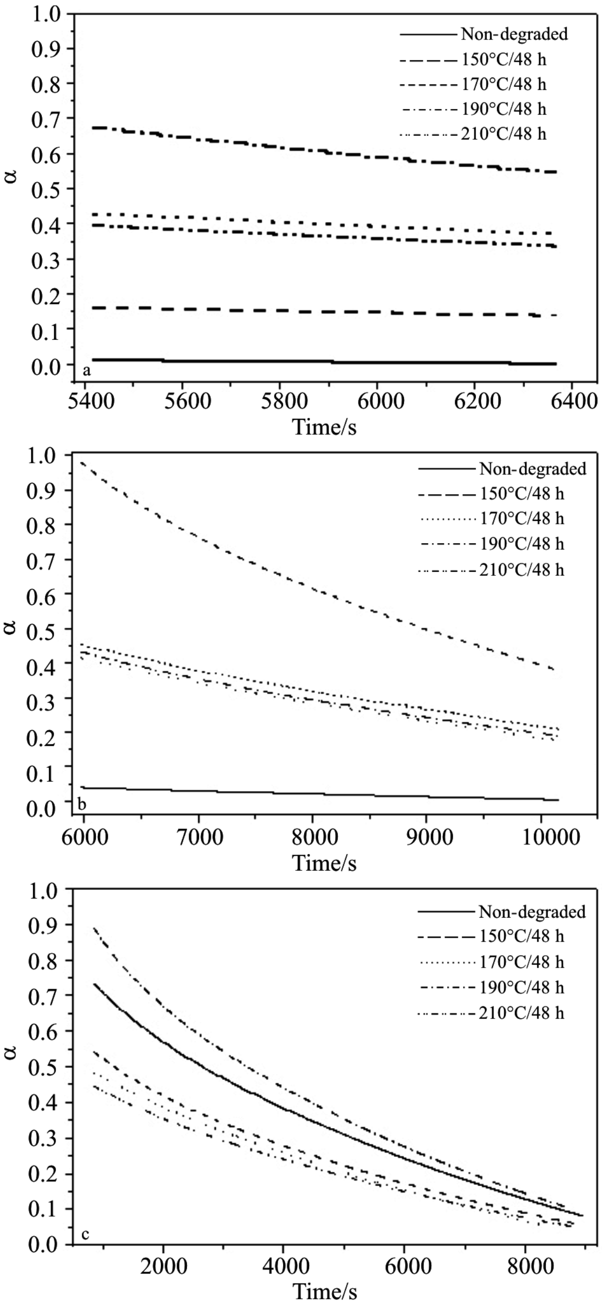

Fig. 5 Influence of degradation time on the decomposed fraction under isothermal conditions: a – 190°C, b – 200°C and c – 210°C

Isothermal kinetic analysis

The plots of decomposed fraction (α), as a function of time are presented in Fig. 5. Results indicate a remarkable change in the reaction mechanism of degraded lubricants. Isothermal curves obtained at 190°C present a nearly linear relationship of decomposed fraction as a function of time, indicating that these oils decompose with an *n*-order mechanism [2]. At 200°C, some samples present a linear relationship, while the sample degraded at 190°C presents an exponential relationship. At 210°C, all samples present an exponential relationship between time and α.

Establishing a relationship between the decomposed fraction and the kinetic models described in [11], the rate constants were calculated (Table 6). The increase in the rate constant values indicated a decrease of the stability of the materials.

A linear relationship between ln$k$ and 1/T was observed, indicating that the rate constants obey the Arrhenius law. Thus, activation energy and frequency factor were calculated and presented in Table 7.

According to Table 7, non-degraded sample and sample degraded at 150°C/48 h present similar activation energy values, indicating that no meaningful degradation occurred at this temperature. At higher degradation temperatures, activation energy values present a cyclic variation. The sample degraded at 170°C/48 h presented a decrease in the activation energy value, while the sample degraded at 190°C/48 h showed high activation energy relative to the formation of intermediary higher molecular mass compounds resulting of the oxidation. The substances formed in the degradation of this type of lubricant, hydrocarbons and esters presenting a high molecular mass, need of high energy values to be decomposed [14]. The considerable decrease of the activation energy of oil samples previously degraded at 210°C, can be attributed to the decomposition of most of the high molecular mass compounds formed during the degradation at 190°C.

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

Degraded lubricants	Isothermal temperature/°C			Statistics	
	190	200	210	r	sd
150°C/48 h	$1.63\cdot10^{-6}$	$2.53\cdot10^{-6}$	$3.15\cdot10^{-6}$	0.99945	0.01378
170°C/48 h	$2.17\cdot10^{-6}$	$2.65\cdot10^{-6}$	$3.22\cdot10^{-6}$	0.99942	0.02369
190°C/48 h	$2.72\cdot10^{-6}$	$3.96\cdot10^{-6}$	$8.38\cdot10^{-6}$	0.99943	0.01406
210°C/48 h	$2.09\cdot10^{-6}$	$2.56\cdot10^{-6}$	$2.88\cdot10^{-6}$	0.99969	0.01669

Table 7 Isothermal kinetic parameters of degraded and non-degraded lubricant oils

Degraded lubricants	E_a/kJ mol^{-1}	A/s^{-1}	r	sd
Non-degraded	60.30	8.16	0.99000	0.06597
150°C/48 h	61.37	$1.40\cdot10$	0.99199	0.05993
170°C/48 h	36.32	$3.70\cdot10$	0.99837	0.01591
190°C/48 h	83.56	$7.11\cdot10^3$	0.98611	0.10803
210°C/48 h	29.80	$2.07\cdot10^2$	0.99615	0.02001

Table 8 Influence of temperature and time of degradation on the thermodynamic parameters

Oil samples	T_{peak}/K	$-\Delta H^*$/kJ mol^{-1}	ΔS^*/kJ mol^{-1}	$-\Delta G^*$/kJ mol^{-1}	r	sd
150°C–48 h	601.9	64.65	191.33	179.81	0.9999	0.0014
170°C–48 h	611.1	66.80	191.12	183.59	0.9997	0.0075
190°C–48 h	612.2	41.41	235.24	185.42	0.9996	0.0068
210°C–1 h	614.5	53.67	214.95	185.76	0.9998	0.0055
210°C–4 h	615.6	64.35	195.54	184.72	0.9998	0.0063
210°C–12 h	612.2	65.43	192.62	183.35	0.9999	0.0046
210°C–24 h	605.4	65.26	192.53	181.82	0.9998	0.0060
210°C–36 h	611.1	67.91	189.12	183.48	0.9998	0.0055
210°C–48 h	613.3	67.73	198.94	184.64	0.9995	0.0095

Thermodynamic activation analysis

Table 8 presents thermodynamic parameters of the samples degraded at different conditions with regard to the temperature and time.

Conclusions

According to the results, degradation reactions are confirmed by isothermal and non-isothermal thermogravimetry using different atmospheres and heating rates that led to different decomposition profiles for the mineral lubricant oils. By means of the kinetic and thermodynamic parameters obtained it was verified that the reaction mechanism of the lubricant oils changes significantly. Using thermodynamic and kinetic parameters of decomposition of mineral lubricant oils, the degradation energies can be evaluated and the lubricant stability degrees can be determined.

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