

Kinetic on Thermal Decomposition Reactions of Mineral Lubricant Oils by Thermogravimetry

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Abstract: This study seeks to characterize the thermal decomposition process of automotive mineral lubricant oils in relation to its kinetic properties. Using kinetic study of decomposition of automotive mineral lubricant oils, degradation energy can be evaluated. The kinetic study was accomplished using thermogravimetric curves based on weight loss as a function of temperature. The kinetic behavior of the analyzed lubricant oils depends on atmosphere and heating rates used in TG analysis. On the other hand, the results were satisfactory, presenting good correlation, with a linear correlation coefficient close of the unit with a low standard deviation.

Key words: Mineral lubricant, kinetic, thermogravimetry, activation energy, thermal analysis

INTRODUCTION

The mineral oils are obtained from petroleum and consequently, its 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 reducing of attrition and waste of materials and automotive equipments, besides being responsible for the control of deposits formation, suspended pollutants and also for protection against erosion by Carreiro and Moura^[1]; Perez^[2].

Formulation of an automotive lubricant is a complicated process. 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 described by Gamlin *et al.*,^[3]. As engine testing is an expensive process, a number of bench tests have been developed to evaluate the lubricant throughout the formulation and performance process described by Souza,^[4]. Many of these bench tests are slow, man-power intensive, empirical, with a poor reproducibility and require a large investment in specialized equipment and skilled operators and may be replaced, with advantage, by conventional thermal analysis techniques.

Thermal Analysis is defined as the measurement of change in chemical and physical properties of a sample as a function of temperature or time. In recent years, the application of Thermogravimetry (TG/DTG) and Differential Scanning Calorimetry (DSC) for the study of petroleum derivatives has gained wide acceptance among research studyers presented by Zanier and Jackle^[5], Bermejo *et al.*,^[6], Perez^[2], Govin *et al.*,^[7], Kok and Keskin^[8] and is of exceptional significance for economy.

The lubricants can suffer several changes with the increase of temperature, as oxidation, altering its chemical and physical-chemical properties. Through the kinetic study of thermal decomposition reactions of mineral lubricant oils, degradation energy can be evaluated, stability degree of the lubricant can be established by Ganlim *et al.*,^[3]. This way, this study seeks to characterize the process of thermal decomposition of automotive mineral lubricant oils, in relation to its kinetic properties. The kinetic study was accomplished using thermogravimetric curves, based on weight loss as a function of temperature. The calculation of the kinetic parameters, as activation Energy (E_a), reaction order (n) and frequency factor (A), was accomplished using the kinetic equation developed by Coats-Redfern and

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the Non-Linear Regression method, for all the stages of thermal decomposition of the lubricant oil samples.

MATERIALS AND METHODS

In this study, automotive mineral lubricant oils were evaluated. Commercial lubricants of different marks and SAE classifications were used.

Thermogravimetry: The non-isothermal thermogravimetric curves (TG/DTG) were obtained in a simultaneous thermobalance (TA Instruments, model SDT-2960), in air and nitrogen atmospheres (100 mL min⁻¹), using alumina crucibles, heating rates of 5, 10, 15 and 20°C min⁻¹, sample mass of 10.0±0.5 mg, in a temperature range of 25-600°C.

Kinetic study: In the kinetic study of the thermal decomposition reactions of the automotive mineral lubricant oils, kinetic parameters, as activation Energy (E_a), reaction order (N) and frequency factor (A), were calculated using the integral method proposed by Coats-Redfern by Santos *et al.*^[9] and the Non-Linear Regression method from Santos *et al.*^[10], based on the mass variation of the samples as a function of temperature.

The calculation of kinetic data by thermogravimetry is based on the Eq. 1:

$$\frac{d\alpha}{dt} = k\alpha^n \quad (1)$$

where, α is the amount of sample undergoing reaction, n is the reaction order and k is the specific rate constant. The temperature dependence of k is expressed by the Arrhenius Eq.

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where: A is the Arrhenius constant, E_a is the activation energy and R is the gas constant.

From Eq. 1 and 2:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (3)$$

where: $f(\alpha) = \alpha^n$.

The linear Eq. is:

$$\frac{dT}{dt} = \phi \quad (4)$$

Combining Eq. 3 with Eq. 4:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\phi}\right) \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (5)$$

Integrating Eq. 5, the theoretical basis for kinetic calculations by non-isothermal methods (integral and approximations) is obtained:

$$g(\alpha) = \frac{A}{\phi} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (6)$$

where: A is the frequency factor, T is the temperature, R is the gas constant, ϕ is the heating rate and E_a is the activation energy.

Coats and redfern method: Coats and Redfern Santos *et al.*^[9] 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 equations used for analysis of thermal decomposition reactions of the mineral lubricant oils are presented below:

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log\frac{AR}{\phi} - \frac{E_a}{2.303(RT)} \quad \text{for } n=1 \quad (7)$$

$$\log\left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right] = \log\frac{AR}{\phi} - \frac{E_a}{2.303(RT)} \quad \text{for } n \neq 1 \quad (8)$$

Non-linear regression method: In this method presented by Santos *et al.*^[10], dynamic TG/DTG curves for lubricant oils were used, besides the following values: $g(\alpha)$, that is just function of α ; T, the absolute temperature; T₀, the initial temperature and ϕ , the heating rate. Substituting these values in the Eq. 9, k (T) may be estimated, as a function of T, a value of k is found for each value of substituted T.

$$g(\alpha) = k(T) \frac{T - T_0}{\phi} \quad (9)$$

With the values of calculated k and its respective temperature values, a graph of lnk versus 1/T is plotted and the kinetic parameters E_a (activation energy) and A (frequency factor), are calculated according to the Eq. 10.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (10)$$

RESULTS AND DISCUSSION

Thermogravimetric analysis: The thermal decomposition profile of the different automotive mineral lubricant oils presented similar characteristics, as observed in Fig. 1. Three stages of thermal decomposition are present, in the temperature range of 200 to 600°C.

In relation to the stages of thermal decomposition, it was observed that the first one (175-300°C) corresponds to the distillation or exit of volatile compounds. This stage is the most important one for proposition of the thermal stability of lubricant oils, as lubricant is commonly used in this temperature range. The second stage (300-420°C) corresponds to the decomposition of the hydrocarbons present in these oils. The third stage of thermal decomposition, whose temperature range is around 420-570°C, corresponds to the combustion of some compounds.

Kinetic analysis: The determination of the kinetic parameters for the two principal stages of thermal

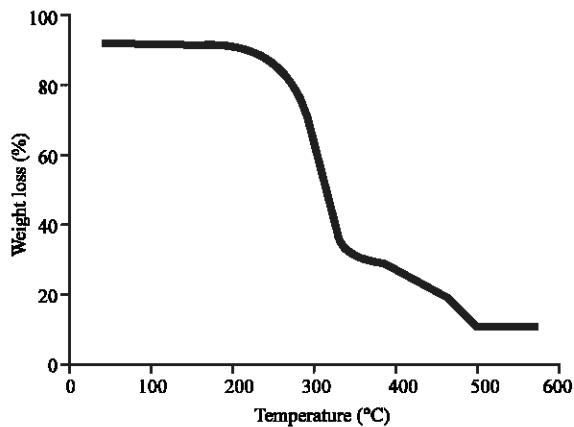


Fig. 1: Typical TG curve of a mineral lubricant oil

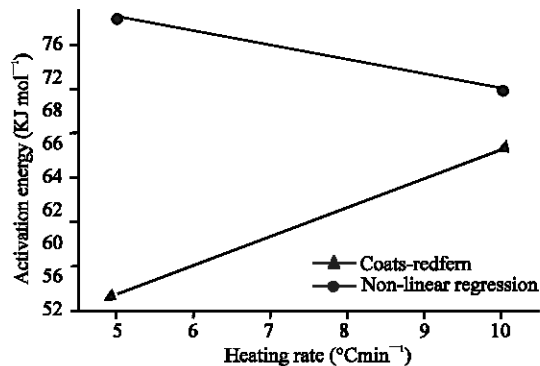


Fig. 2: Influence of the heating rate in the activation energy of the first stage of thermal decomposition of the mineral lubricant oil

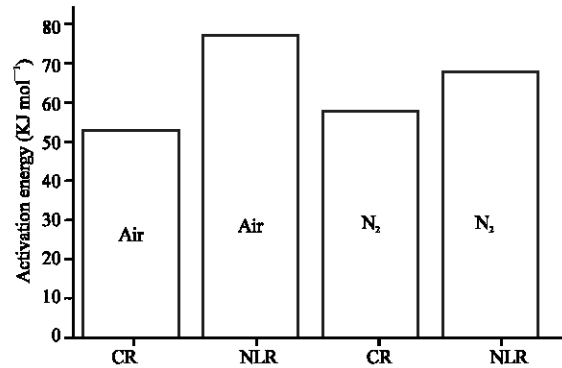


Fig. 3: Influence of the atmosphere in the activation energy of the mineral lubricant oil obtained by Coats-Redfern method (CR) and Non-Linear Regression method (NLR) at 5°C min⁻¹

Table 1: Average values of kinetic parameters of the thermal decomposition reactions of the automotive mineral lubricant oil obtained by coats-redfern method

Heating rates	Stages	Kinetic parameters	Atmosphere	
			Air	Nitrogen
5°C min ⁻¹	1	E _a (kJmol ⁻¹)	53.35	58.75
		A (s ⁻¹)	1.33×10 ³	1.28×10 ³
		n	0.90	0.98
	2	E _a (kJmol ⁻¹)	186.13	311.57
		A (s ⁻¹)	2.12×10 ¹²	3.24×10 ¹³
		n	1.05	1.16
10°C min ⁻¹	1	E _a (kJmol ⁻¹)	66.52	69.967
		A (s ⁻¹)	1.84×10 ³	2.55×10 ³
		n	0.88	0.94
	2	E _a (kJmol ⁻¹)	257.36	311.57
		A (s ⁻¹)	1.43×10 ¹⁵	2.01×10 ¹⁹
		n	1.27	1.36

decomposition of the automotive lubricant oils (volatilization and combustion), was accomplished, using a range of decomposed fraction from 0.10 to 0.90. The calculated kinetic parameters were reaction order (n), activation Energy (E_a) and frequency factor (A), using the integral method of Coats-Redfern and Non-Linear Regression method.

Figure 2 illustrates the influence of the heating rate in the average values of the activation energy obtained by the average different kinetic methods used in the analysis. Fig. 3 illustrates the influence of the atmosphere in the average values of the activation energy obtained using the different kinetic methods. The kinetic parameters, for all the stages of thermal decomposition of the mineral lubricant oils obtained in different heating rates and different atmospheres, are presented in Table 1 and 2. These tables clearly indicate that the activation energy for first stage of thermal decomposition of lubricant oils is relatively constant throughout the degradation process for analyzed oils. Fig. 4 shows a

Table 2: Average values of kinetic parameters of the thermal decomposition reactions of the automotive mineral lubricant oils obtained by Non-Linear Regression method

Heating rates	Stages	Kinetic parameters	Atmosphere	
			Air	Nitrogen
5°C min ⁻¹	1	E _a (kJmol ⁻¹)	74.18	68.48
		A (s ⁻¹)	4.56×10 ⁷	2.84×10 ⁵
		n	0.99	0.98
	2	E _a (kJmol ⁻¹)	182.59	243.78
		A (s ⁻¹)	2.84×10 ⁹	3.240×10 ¹¹
		n	1.09	1.10
10°C min ⁻¹	1	E _a (kJmol ⁻¹)	71.87	69.65
		A (s ⁻¹)	3.12×10 ⁵	1.54×10 ⁴
		n	0.98	0.94
	2	E _a (kJmol ⁻¹)	249.63	247.57
		A (s ⁻¹)	1.28×10 ¹²	1.12×10 ¹³
		n	1.21	1.20

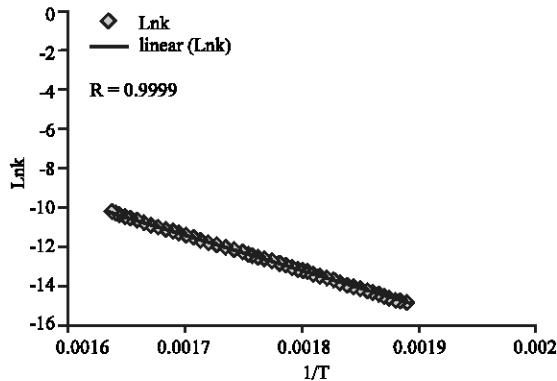


Fig. 4: Comparison between the Arrhenius graphs by Coats-Redfern (Red) and Non-linear Regression (Blue) methods

comparison between the arrhenius graphs obtained using the Coats-Redfern (Linear) and Non-linear Regression methods for to first stage of the thermal decomposition reactions of the lubricant oils. The reaction orders of thermal degradation of lubricant oil change less with temperature, in calculation using Non-Linear Regression method than calculations done with Coats-Redfern method. In the first case, average values increased from 0.94 to 1.20. When Coats-Redfern method was used, it changed from 0.88 at 5°C min⁻¹ in first stage to 1.36 at 10°C min⁻¹ in second stage. These results indicate a possible change in mechanism for thermal degradation reactions of the lubricant oil.

CONCLUSION

The study demonstrated that thermal characterization of automotive mineral lubricant oils by Thermogravimetry is a novel technique. Based on the results, it can be verified that the thermal analysis methods, especially thermogravimetry, are basic to the science of formulating

lubricants. Kinetic parameters of the lubricant samples were obtained using two different methods and indicate that the activation energy increases with the increase of the temperature of degradation of the samples.

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REFERENCES

- Carreteiro, R.P. and C.R.S. Moura, 1989. Lubrificantes e Lubrificação, Makron Books.
- Perez, J.M., 2000. Oxidative properties of lubricants using thermal analysis. *Thermochim. Acta*, n, pp: 47-56.
- Gamlin, C.D., N.K. Dutta, N.R. Choudhury, D. Kehoe and J. Matison, 2002. Evaluation of Kinetic parameters of thermal and oxidative decomposition of base oils by conventional, isothermal and modulated TGA and pressure DSC. *Thermochim. Acta*, n.3 92-393, pp: 357-369.
- Souza, M.S.M., 2000. Métodos analíticos para lubrificantes e isolantes. *Quím. e Deriv.*, n. 382, pp: 20-28.
- Zanier, A. and H.W. Jachle, 1996. Heat Capacity measurements of petroleum fuels by modulated DSC. *Thermochim. Acta*, n. 287, pp: 203-212.
- Bermejo, J., M. Granda, R. Menendez, R. García and J.M.D. Tascón, 1997. Thermal Behavior of extrographic fractions of coal tar and petroleum pitches. *Fuel*, v. 76, n. 2, pp: 179-187.
- Govin, O.V., V.V. Diky, G.J. Kabo and A.V. Blokhin, 2000. Evaluation of the chemical exergy of fuels and petroleum fractions. *J. Therm. Anal. Cal.*, v. 62: 123-133.
- Kok, M.V. and C. Keskin, 2001. Comparative Combustion kinetics for in situ combustion process. *Thermochim. Acta*, n. 369, pp: 143-147.
- Santos, J.C.O., A.G. Souza, A.V. Santos, S. Prasad and I.M.G. Santos, 2002. Thermal Stability and kinetic study on thermal decomposition of commercial edible oils by thermogravimetry. *J. Food Sci.*, v. 67, n. 4, pp: 1393-1398.
- Santos, J.C.O., A.G. Souza, A.V. Santos and M.F.S. Trindade, 2001. Kinetic Study on Thermal decomposition of vegetable edible oils by thermogravimetry using non-linear regression method. In: 5th Mediterranean Conference on Calorimetry and Thermal Analysis, Santiago de Compostela, Espanha: GECAT, set.