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KINETIC STUDY ON THERMAL DECOMPOSITION REACTIONS OF MINERAL LUBRICANT OILS BY THERMOGRAVIMETRY

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Resumo – Através do estudo cinético da decomposição de óleos lubrificantes minerais automotivos, pode-se avaliar a energia necessária para que o óleo se degrade, além de estabelecer o grau de estabilidade do lubrificante. Este trabalho visa caracterizar o processo de decomposição térmica de óleos lubrificantes minerais automotivos em relação às suas propriedades cinéticas. O estudo cinético foi realizado a partir de curvas termogravimétricas com base na perda de massa, em função da temperatura. O comportamento cinético dos óleos lubrificantes analisados é dependente da atmosfera e da razão de aquecimento usada na obtenção das curvas TG. Por outro lado, os resultados foram satisfatórios, pois apresentaram boa correlação, com um coeficiente de correlação linear próximo da unidade e um baixo desvio padrão.

Palavras-Chave: lubrificante mineral, cinética, termogravimetria

Abstract – Using kinetic study of decomposition of automotive mineral lubricant oils, degradation energy can be evaluated, and lubricant stability degree can be determined. This work seeks to characterize the thermal decomposition process 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 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.

Keywords: mineral lubricant, kinetic, thermogravimetry

1. 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 (Carreteiro and Moura, 1989; Perez, 2000).

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 (Gamlin et al., 2002). 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 (Souza, 2000). 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 workers (Zanier and Jackle, 1996; Bermejo et al., 1997; Perez, 2000; Govin et al., 2000; Kok and Keskin, 2001), 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 (Ganlim et al., 2002). This way, this work 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 the Non-Linear Regression method, for all the stages of thermal decomposition of the lubricant oil samples.

2. Experimental

2.1. Material

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

2.2. 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 mLmin^{-1}), using alumina crucibles, heating rates of 5, 10, 15 and $20 \text{ }^\circ\text{Cmin}^{-1}$, sample mass of $10.0 \pm 0.5 \text{ mg}$, in a temperature range of 25 – 600 $^\circ\text{C}$.

2.3. 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 (Santos et al., 2002), and the Non-Linear Regression method (Santos et al., 2001), based on the mass variation of the samples as a function of temperature.

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

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

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 equation:

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

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

From Equation 1 and 2:

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

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

The linear equation is:

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

Combining Equation 3 with Equation 4:

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

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

$$g(\mathbf{a}) = \frac{A}{\mathbf{f}_0} \int_0^T \exp\left(-\frac{E_a}{RT} \right) dT \quad (6)$$

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.

2.3.1. Coats and Redfern Method

Coats and Redfern (Santos et al., 2002) 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:

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

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

2.3.2. Non-Linear Regression Method

In this method (Santos et al., 2001), 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; T_0 , the initial temperature and ϕ , the heating rate. Substituting these values in the Equation 9, $k(T)$ may be estimated, as a function of T, a value of k is found for each value of substituted T.

$$g(\mathbf{a}) = k(T) \frac{T - T_0}{\mathbf{f}} \quad (9)$$

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

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

3. Results and Discussion

3.1. Thermogravimetric Analysis

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

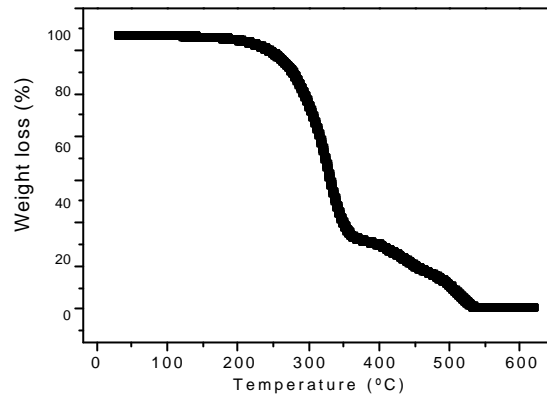


Figure 1. Typical TG curve of a mineral lubricant oil

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.

3.2. Kinetic Analysis

The determination of the kinetic parameters for the two principal stages of thermal 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 different kinetic methods used in the analysis.

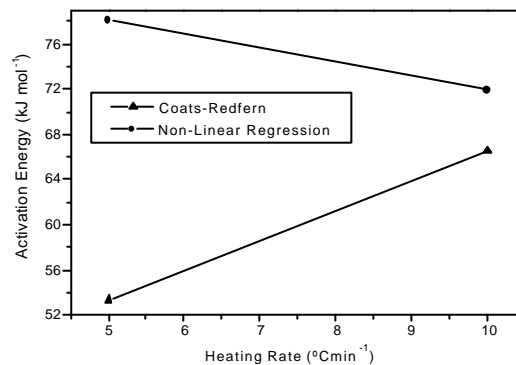


Figure 2. Influence of the heating rate in the activation energy of the first stage of thermal decomposition of the mineral lubricant oil

Figure 3 illustrates the influence of the atmosphere in the average values of the activation energy obtained using the different kinetic methods.

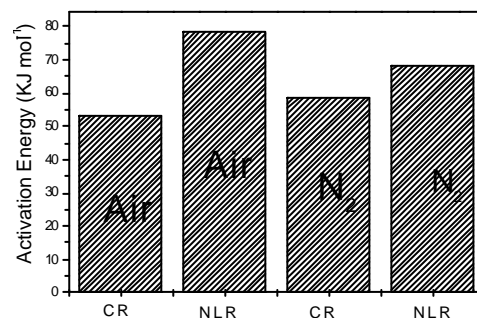


Figure 3. Influence of the atmosphere in the activation energy of the mineral lubricant oil obtained by Coats-Redfern method (CR) and Non-Linear Regression method (NLR) at 5°Cmin⁻¹

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 Tables 1 and 2.

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	E_a (kJmol ⁻¹)	53.35	58.75
		A (s ⁻¹)	1.33x10 ³	1.28x10 ³
		n	0.90	0.98
	2	E_a (kJmol ⁻¹)	186.13	311.57
		A (s ⁻¹)	2.12x10 ¹²	3.24x10 ¹³
		n	1.05	1.16
10°C/min	1	E_a (kJmol ⁻¹)	66.52	69.967
		A (s ⁻¹)	1.84x10 ³	2.55x10 ³
		n	0.88	0.94
	2	E_a (kJmol ⁻¹)	257.36	311.57
		A (s ⁻¹)	1.43x10 ¹⁵	2.01x10 ¹⁹
		n	1.27	1.36

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	E_a (kJmol ⁻¹)	74.18	68.48
		A (s ⁻¹)	4.56x10 ⁷	2.84x10 ⁵
		n	0.99	0.98
	2	E_a (kJmol ⁻¹)	182.59	243.78
		A (s ⁻¹)	2.84x10 ⁹	3.240x10 ¹¹
		n	1.09	1.10
10°C/min	1	E_a (kJmol ⁻¹)	71.87	69.65
		A (s ⁻¹)	3.12x10 ⁵	1.54x10 ⁴
		n	0.98	0.94
	2	E_a (kJmol ⁻¹)	249.63	247.57
		A (s ⁻¹)	1.28x10 ¹²	1.12x10 ¹³
		n	1.21	1.20

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.

Figure 4 shows a 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.

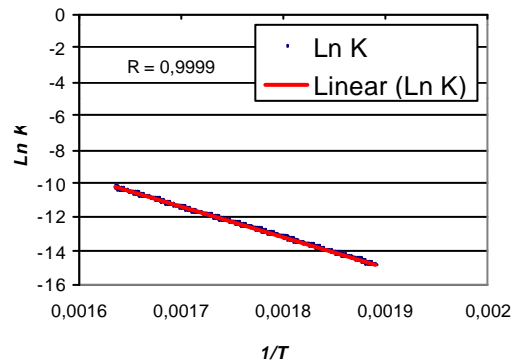


Figure 4. Comparison between the Arrhenius graphs by Coats-Redfern (Red) and Non-linear Regression (Blue) methods

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°Cmin⁻¹ in first stage to 1.36 at 10°Cmin⁻¹ in second stage. These results indicate a possible change in mechanism for thermal degradation reactions of the lubricant oil.

4. Conclusions

The research 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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