

## DETERMINATION OF ACTIVATION ENERGY IN THE COMBUSTION PROCESS BY THERMOGRAVIMETRIC ANALYSIS

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**Abstract.** In this study the activation energies ( $E_a$ ) for combustion in air of three Brazilian fuel oils were determined by thermogravimetry. The thermogravimetric experiments were performed in a Shimadzu TGA-51H analyzer, with oil samples, named A, B and C, supplied by Petrobras-Cenpes. In all experiments three distinct oxidation regions were observed and identified: low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). The activation energies were determined as a function of the conversion degree ( $\alpha$ ) and temperature, following two different procedures, namely ASTM E 1641 and Mode-Free Kinetic. Transient experiments were performed from room temperature (25 °C) up to 600 °C, at heating rates of 2.5, 5.0, 10.0, 15.0, and 20.0 °C min<sup>-1</sup>. Samples of 20.0 ± 0.5 mg were heated inside aluminum crucibles. The reacting atmosphere was synthetic air, which was continuously blown over the samples, throughout the analyzer furnace, at a volumetric rate of 100 mL min<sup>-1</sup>. The calculated activation energies were approximately equal using both methods: 43 kJ mol<sup>-1</sup> ( $\alpha=0.1$  to 0.9) for oil A; 48 kJ mol<sup>-1</sup> ( $\alpha=0.1$  to 0.5) and 65 kJ mol<sup>-1</sup> ( $\alpha=0.5$  to 0.9) for oil B; 58 kJ mol<sup>-1</sup> ( $\alpha=0.1$  to 0.5) and 65 kJ mol<sup>-1</sup> ( $\alpha=0.5$  to 0.9) for oil C. It is concluded that the oxidation activation energy is a suitable parameter to characterize different oils concerning their behavior under combustion, specially in terms of ignition delay in compression ignition engines.

**Keywords:** activation energy, thermogravimetry, fuel oil, combustion.

### 1. Introduction

Fuel oils are widely utilized in the modern industry for heating of ovens and boilers, or in internal combustion engines for generation of heat (Perrone, 1965). Within several features of a fuel oil, it may be showed up the homogeneity in burning that is related with ignition delay (interval between the injection of the fuel and the starting of combustion). In addition, it is important to realize that the longer is the ignition delay, the worst is the fuel. For engines a long ignition delay causes an accumulation of unburned fuel in the combustion chamber. When the fuel enters in autoignition, in some parts of the actual compression process, i.e., outside of the ideal point, an undesirable phenomenon named “combustion knock or diesel knock” occurs (Heywood, 1988 and Obert, 1971). According to Obert (1971), the term “ignition quality” refers to the ease at which fuel oil in the engines is ignited by autoignition. Heywood (1988) further this idea by writing that the ignition quality of a fuel is defined by its cetane number. The engines to ascertain the used in cetane number requires an expensive test, therefore many efforts have been made to correlate a fuel’s physical properties to the cetane ratings, as a way to alleviate this test complementary. The Diesel index number represents one such attempt at deriving this correlation. Empirical data indicates an approximate correlation between the Diesel index and the cetane number contained in most commercial fuels (Obert, 1971). It is based on the fact that ignition quality is linked to hydrocarbon composition: n-paraffins have high ignition quality, and aromatic and naphthenic compounds have low ignition quality (Heywood, 1988). It is defined as:

$$\text{Diesel index} = \text{aniline point (°F)} \times \text{API gravity (60°F)/100} \quad (1)$$

It is possible to correlate the ignition delay with the activation energy ( $E_a$ ). Lichty (1967) proposed that the ignition delay ( $\tau$ ) is a function of  $E_a$  as follows:

$$\tau = f\left(e^{-E_a/RT} / p^b\right) \quad (2)$$

where  $R$  is the universal gas constant,  $p$  is the pressure,  $T$  is the temperature and  $b$  is the reaction order.

In the compression-ignition engines (CI) the starting of the combustion occurs at the end of the compression stroke, in this point, the autoignition of the fuel occurs, the air is aspired to the interior of the cylinder which is compressed by the piston, this process causes the elevation of temperature and pressure in the combustion chamber.

From this principle, the shorter is the ignition delay, the better is the ignition process and, consequently, lower is the activation energy of the combustion reaction.

The  $E_a$  can be obtained experimentally and the thermal analysis is a helpful tool to which enables such determination. However, it is necessary to define descriptive models of these trials.

Previous works applied thermal analysis techniques to study the behavior regarding oxidative degradation of oil derivatives (Drici and Vassoughi, 1985; Verkoczy and Jha, 1986; Kök, 1993; Kök *et al.*, 1996; Kök and Okandan, 1997; Kök and Karacan, 1998; Ali *et al.*, 1998; Kök, 2001; Kök and Keskin, 2001; Gonçalves *et al.*, 2001 and, Kök, 2003).

In recent years, the application of thermal analysis techniques as thermogravimetric analysis (TG/DTG), differential thermal analysis (DTA) and, differential scanning calorimetry (DSC) has been gained acceptance among the researchers (Kök *et al.*, 1997). TG is a technique in which the mass of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. DTA is a technique in which the temperature difference between a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to a controlled temperature program. DSC is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and the reference material are subjected to a controlled temperature program (Mackenzie, 1979).

Traditional kinetics methods for analyze first-order and second-order reactions are often not applicable to complex reaction of practical interest involving, by example, thermal degradation of fuel oils. Consequently, a variety of other mathematical techniques, often called global kinetics analysis, have been developed to characterize the kinetic behavior of these types of reaction (Burnham and Braun, 1998).

Among the kinetics methods we can cited: Arrhenius, Coats and Redfern, Michelson and Eirnhorn (*Ratio model*), Ingraham and Marrier, Freeman and Carroll, Flynn and Wall, Ozawa and, Model-Free Kinetics.

Among the precursors that employed thermal analysis, Tadema (1959) stand out as the first researcher that applied this technique in the study of thermal effects in the combustion mixture of several crude oil and clays. The author showed the feasibility of the utilization of DTA as a tool in the crude oil combustion study.

In recent years, the application of thermal analysis techniques to study the combustion and pyrolysis kinetics of fossil fuels has gained a wide acceptance among researches. These experiments have the advantage over larger scale experiments, they require small samples, and are relatively inexpensive and fast (Millington *et al.*, 1993). Much of the work on thermal analysis of crude oils was directed towards correlation among thermal behavior of the sample and kinetics studies (Kök, 2002).

Ali *et al.* (1998) focused on that thermogravimetry as a technique to study the characteristic of crude oils and other petroleum products.

Verkoczy and Jha (1986) performed thermogravimetric analysis (TG/DTG) and differential scanning calorimetry (DSC) experiments for determination kinetics parameters for four heavy oils. Kinetics and thermochemical data were estimated for low temperature oxidation, high temperature oxidation, cracking and coking.

Kök (1993) characterized pyrolysis and thermo oxidation behavior for two crude oils using TGA and DSC, in air and nitrogen atmosphere. In pyrolysis experiment, when the oils were heated in a nitrogen atmosphere, two different mechanisms causing mass loss were observed, the first region involved distillation and the second region involved visbreaking. In combustion experiments with air, three distinct regions were observed for both crude oils, LTO, FD and HTO. These experiments allowed determining kinetics parameters. The authors obtained the  $E_a$  values between 128.3 and 142.3 kJ mol<sup>-1</sup> for both crude oils, respectively, and they correlated  $E_a$  with °API, i.e., higher activation energies were found as the API gravity of crude oils decreased in the HTO region. According the American Petroleum Institute, the API gravity is a form to express relative density of crude petroleum and petroleum products. The API scale varies inversely with the relative density.

Kök and Okandan (1997) they also correlated the values of activation energies with the API gravity for six crude oils. The authors applied the non-isothermal methods using TG/DTG with excess of air. The authors concluded that these parameters are inversely proportional, while the activation energy varies from 67.4 to 131.9 kJ mol<sup>-1</sup> the °API gravity varies from 26.1 to 11.3, respectively.

Kök *et al.* (1996) utilized high pressure thermogravimetric analyzer (HPTGA) to study the combustion behavior of three crude oils under pressurized conditions (100, 200 and 300 psig). The experiments were performed in oxidizing environment at constant heating rate (10°C min<sup>-1</sup>) and it was observed three different regions from TG curves. The Coats and Redfern method to obtain the kinetics parameters in LTO and HTO region was used. Activation energy values were calculated for three samples, at 100 psig the values were 22.6; 23.9 and 41.1 kJ mol<sup>-1</sup> for LTO region. For HTO region the values were 99.6; 77.9 and 97.1 kJ mol<sup>-1</sup>. For others pressure, no effect of pressure on the kinetics parameters was observed.

Ali *et al.* (1998) utilized TG and DTA to characterize four crude oils, to further investigate the properties of the volatile components of these crude oils and to correlate the characteristics thermal-oxidation behavior of such crude oil. For all samples were observed four regions characteristics, the first region indicates the evaporative loss of free moisture and volatile hydrocarbons (20 to 280°C) and the remainders are characterized by the oxidative degradation of

different types of hydrocarbons, the low molecular weight (280 to 400°C), the medium molecular weight (400 to 510°C) and the high molecular weight (510 to 620°C), respectively.

The main goal of this work is the determination of the activation energy of one of the combustion region by thermogravimetric analysis using both the ASTM E 1641 method and Model-Free Kinetics. To establish the activation energy as a parameter to characterize different oils. The activation energy is proposed as a complementary parameter to the cetane number to determine the quality of a fuel.

## 2. Experimental

The thermogravimetric experiments were performed in a Shimadzu TGA-51H analyzer. Experimental procedures are performed in an environment where temperatures range from room temperature (25°C) up to 600°C, at several heating rates of 2.5, 5.0, 10.0, 15.0, and 20.0°C min<sup>-1</sup>. Samples of 20.0 ± 0.5 mg and aluminum crucibles were used. The reacting atmosphere was synthetic air, which was continuously blown over the samples through the furnace of the analyzer at a volumetric rate of 100 mL min<sup>-1</sup>.

For differentiate thermal analysis (DTA) experiments, a Shimadzu DTA 50 analyzer was used. Transient experiments were performed from room temperature up to 600°C, at heating rate of 5.0°C min<sup>-1</sup>, samples of 20.0 ± 0.5 mg and aluminum crucibles were used. The reacting atmosphere was synthetic air, which was continuously blown over the samples through the furnace of the analyzer at a volumetric rate of 100 mL min<sup>-1</sup>.

Three distinct fuel oils supplied by Petrobras - Cenpes were evaluated: MF-380, Fuel Oil A2 and Fuel Oil A1, denominated in this work by A, B and C, respectively. Table 1 presents the specification and the properties of these samples.

Table 1: Specification and properties of sample A, B and C.

	Sample A	Sample B	Sample C
Classification (Petrobras)	MF 380	Fuel Oil A2	Fuel Oil A1
Kinematic Viscosity	(50°C)300 and 380 cSt	(60°C) maximum of 960 cSt	(60°C) maximum of 620 cSt
Density 15°C/4°C	0.98 a 0.99	0.98 a 1.02	0.98 a 1.02
Ash	~ 0.05%	Not specified by ANP*	Not specified by ANP*
Sulfur	~ 1%	~ 0.8 a 1%	~ 0.8 a 1%

\* ANP – Agência Nacional de Petróleo (Petroleum National Agency)

### 2.1 Kinetics Methods

To determine kinetic parameters, both a method developed by the ASTM committee and Model-Free Kinetics were applied.

The ASTM method as well as Model-Free Kinetics method allows the determination of kinetics parameters by thermogravimetric data. In this work both methods were applied with the purpose of comparing the results. The following presents a short description of these methods.

The standard ASTM E 1641 is based on the method proposed by Flynn and Wall (1966) that utilizes the Equation 3.

$$E_e = -(R/b) * \Delta \log(\beta) / \Delta(1/T) \quad (3)$$

where  $\beta$  is the heating rate,  $E_e$  is the estimate activation energy,  $b$  is iteration variable and  $R$  is the universal gas constant.

The estimate activation energy was calculated using the Eq. (3) applying the slope of the straight line,  $\Delta(\log\beta)/\Delta(1/T)$ , and fixing the value 0.457/K for  $b$  in this first iteration. It was obtained a first value of  $E_e$ . It was possible to calculate the value of  $E_e/RT$  to obtain a new estimation of  $b$  in the Eq. (3). For the subsequent iteration the values of  $b$  tabulated by Doyle (1961 and 1962) was utilized.

The Model-Free Kinetics method based on a Vyazovkin theory (Vyazovkin and Dollimore, 1996; Vyazovkin and Sbirrazzuoli, 1997 e, Vyazovkin, 1999), applies iso-conversional technique to calculate the effective activation energy ( $E$ ) as a function of the conversion level ( $\alpha$ ) of a chemical reaction,  $E=f(\alpha)$ .

The approach follows all points of conversion from multiple experiments instead of a single one. The theory is based on the assumption that:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (4)$$

where  $t$  is the time,  $T$  is the temperature and  $\alpha$  is the conversion,  $f(\alpha)$  represents reaction model and  $k(T)$  the Arrhenius rate constant gives:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

where R is the universal gas constant

Making use the Eq. (4) and dividing by the heating rate  $\beta = dT/dt$  obtains,

$$\frac{d\alpha}{dt} = kf(\alpha) \Rightarrow \frac{d\alpha}{dT} = \frac{k}{\beta} f(\alpha) \quad (6)$$

where  $d\alpha/dt$  is the reaction rate ( $s^{-1}$ ), k is the velocity constant ( $s^{-1}$ ). Substituting the Eq. (6) in the Eq. (5), gives:

$$\frac{1}{f(\alpha)} d\alpha = \frac{A}{\beta} e^{-E/RT} dT \quad (7)$$

Integrating up to conversion,  $\alpha$  (at temperature T) gives,

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{A}{\beta} e^{-E/RT} dT \quad (8)$$

Since  $E/2RT \gg 1$ , the temperature integral can be approximated by,

$$\int_{T_0}^T e^{-E/RT} dT \approx \frac{R}{E} \cdot T^2 \cdot e^{-E/RT} \quad (9)$$

The Equation (9) is defined as dynamic equation, which is used for the determination of the activation energy for all of the values of conversion.

Substituting the temperature integral, rearranging and taking logarithm, gives,

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[ \frac{RA}{E_\alpha g(\alpha)} \right] - \frac{E_\alpha}{R_\alpha} \frac{1}{T_\alpha} \quad (10)$$

Where,

$$\int_0^\alpha \frac{1}{f(\alpha)} d\alpha = g(\alpha) \quad (11)$$

One of the main advantages of this method is the possibility of isolating the function  $g(\alpha)$  of the lineal coefficient, therefore the determination of this function in a complex process is very difficult to determine (Vyazovkin and Wight, 1999).

### 3.1 Results and discussion

Figure 1 shows the TG/DTG curves for sample C at heating rate of  $20^\circ\text{C min}^{-1}$ . However, a similar profile were obtained for other oils studied, A and B. Based on the literature (Kök, 1993; Kök *et al.*, 1996; Kök and Keskin, 2001), three distinct regions were identified. The first region is denominated low temperature oxidation, LTO and up to  $390^\circ\text{C}$ . The second transition takes place between  $390$  and  $490^\circ\text{C}$  and was designated as fuel deposition, FD. The final reaction takes place between  $490$  and  $600^\circ\text{C}$  and it is called high temperature oxidation, HTO.

The Model-Free Kinetics requires at least three dynamic curves with different heating rates and the ASTM method require at least four different heating rates. In this work the five heating rate for both methods were utilized. Figure 2 shows the TG curves for all heating rates utilized.

To determine the kinetics parameters for both methods, it was firstly required to evaluate the conversion degree based on Eq. (11).

$$\alpha = \frac{m - m_0}{m_\infty - m_0} \quad (11)$$

where  $\alpha$  is the conversion, m is the sample mass that varies with the time (t),  $m_0$  is the initial mass sample and  $m_\infty$  is the remaining mass sample.

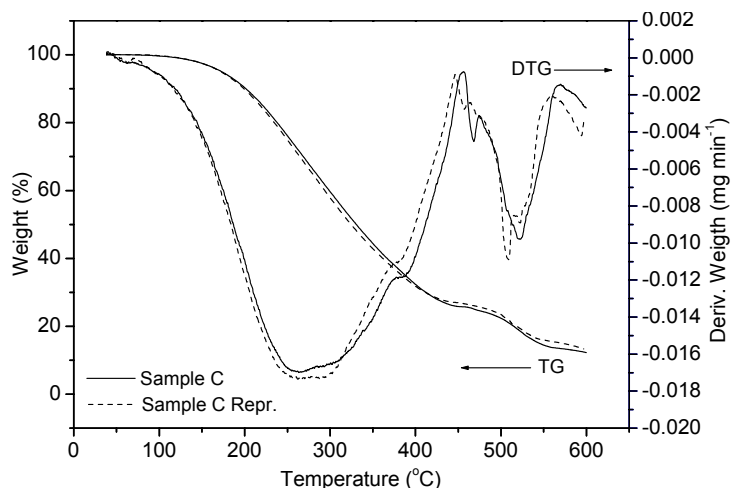


Figure 1: TG/DTG curve for sample C performed at heating rate:  $15^{\circ}\text{C min}^{-1}$ .

This work opted to study the low temperature oxidation region (LTO), which mass loss indicates the evaporative loss of free moisture and volatile hydrocarbons (low molecular weight hydrocarbons) (Ali *et al.*, 1998). The conversion degree was calculated from the TG curves in this region.

Figure 3 shows the conversion curves in function of temperature and, highlights the distinct temperature related to the end of each event ( $\alpha=100\%$ ).

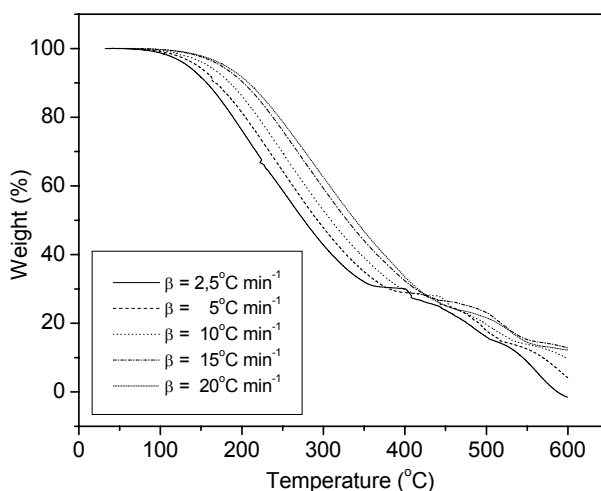


Figure 2: TG curves for sample C performed at different heating rate: 2.5, 5.0, 10.0, 15.0 and  $20.0^{\circ}\text{C min}^{-1}$ .

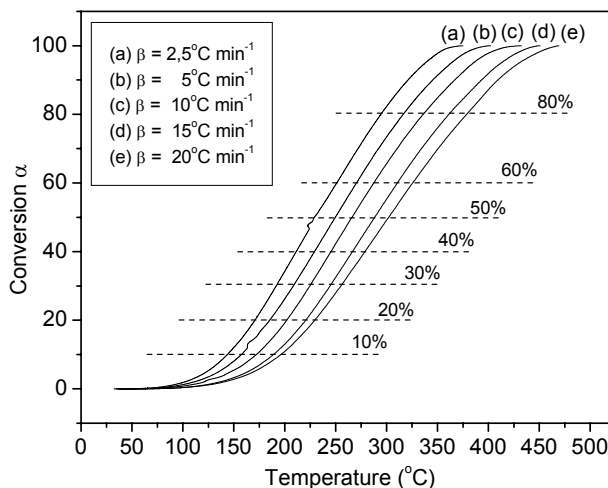


Figure 3: Conversion *versus* Temperature for sample C ( $0 < \alpha < 100$ ).

The activation energy was calculated by ASTM method and some decomposition levels were chosen: 10, 20, 30, 40, 50, 60 and 80% as indicated in Fig.3. It was plotted the logarithm of heating rate ( $\log \beta$ ) against the reciprocal of the temperature which the conversion level was reached ( $1/T_\alpha$ ). A straight line resulted providing a series of lines with slope  $-E_a/R$  represented in Fig. 4.

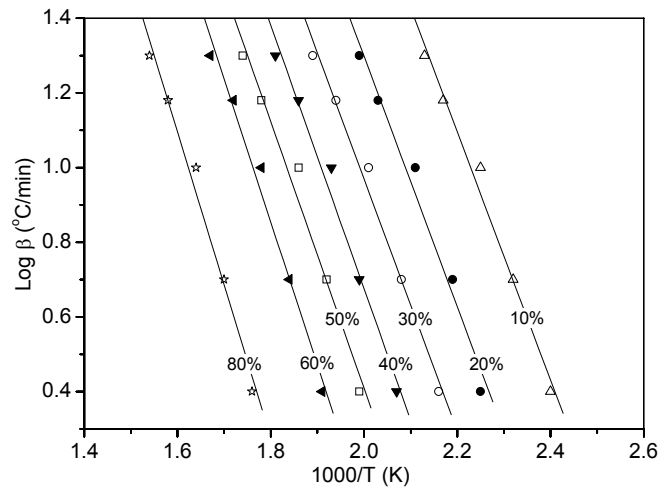


Figure 4: Combustion of fuel oil: heating rate vs.  $1000/K$  at different conversion level for sample C.

To apply Model-Free Kinetics for each conversion  $\alpha$ ,  $\ln \beta/T_\alpha^2$  was plotted versus  $1/T_\alpha$ , providing also a series of straight lines with slope  $-E_a/R$ , therefore the activation energy was obtained as a function of conversion.

The results obtained are presented in Table 2. As it may be seen the values of activation energy are very close for both method and this suggests these methods are adequate to determine this kinetic parameter.

Table 2: Activation energy for some decomposition levels.

	SAMPLE A		SAMPLE B		SAMPLE C	
	ASTM	Model-Free	ASTM	Model-Free	ASTM	Model-Free
Conversion (%)	$E_a$ (kJ/mol)	$E_a$ (kJ/mol)	$E_a$ (kJ/mol)	$E_a$ (kJ/mol)	$E_a$ (kJ/mol)	$E_a$ (kJ/mol)
10	43.44	43.11	48.00	45.49	56.03	55.57
20	43.52	43.28	49.42	47.63	57.58	56.35
30	45.43	43.74	50.40	48.60	57.33	58.18
40	45.94	44.63	49.82	47.49	58.64	59.85
50	44.95	44.13	54.00	50.40	59.62	60.01
60	46.45	44.61	59.41	54.20	63.67	63.60
80	45.50	43.02	82.66	75.69	65.97	66.23

Through out the linear regression is possible to establish  $E_a$  for all conversions levels. Figure 5 shows a group of these  $E_a$  obtained for sample C for the ASTM and Model-Free Kinetics method. It was observed that  $E_a$  varies with the conversion, however the curve profile presented in Fig. 5. represents the feature of the sample C. For samples A and B other profiles were identified.

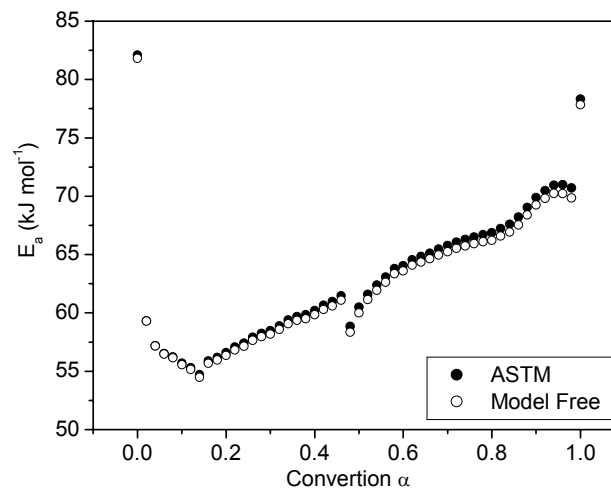


Figure 5: Comparison  $E_a$  versus  $\alpha$  for sample C at five heating rate: 2.5, 5.0, 10.0, 15.0 and 20.0°C min<sup>-1</sup>.

As previously mentioned, the chosen region to determine activation energy corresponds to an oxidation process and it is characterized by an exothermic event. DTA technique characterizes this event and the area under DTA curve is proportional to the heat change involved in this process. However, this value can be used to evaluate semiquantitatively determination of the heat of reaction (Wendlant, 1988).

Figure 6 shows the DTA curve in LTO region for sample C. It can be observed a pronounced exothermic peak around 340 °C. The same procedure was done for samples A and B and then, the corresponding areas of DTA curves of LTO region were calculated: sample A = 817  $\mu\text{V}^\circ\text{C}$ ; sample B = 836  $\mu\text{V}^\circ\text{C}$  and sample C = 916  $\mu\text{V}^\circ\text{C}$ . Concerning activation energy of this region (LTO) for three samples, it was considered the medium value for all conversion degrees between 0 and 100%. Through ASTM method it was determined the following values: sample A = 44.3  $\text{kJ mol}^{-1}$ , sample B = 56.6  $\text{kJ mol}^{-1}$  and sample C = 61.9  $\text{kJ mol}^{-1}$ , and through Model-Free Kinetics the values were: sample A = 44.1  $\text{kJ mol}^{-1}$ , sample B = 57.0  $\text{kJ mol}^{-1}$  and sample C = 63.0  $\text{kJ mol}^{-1}$ .

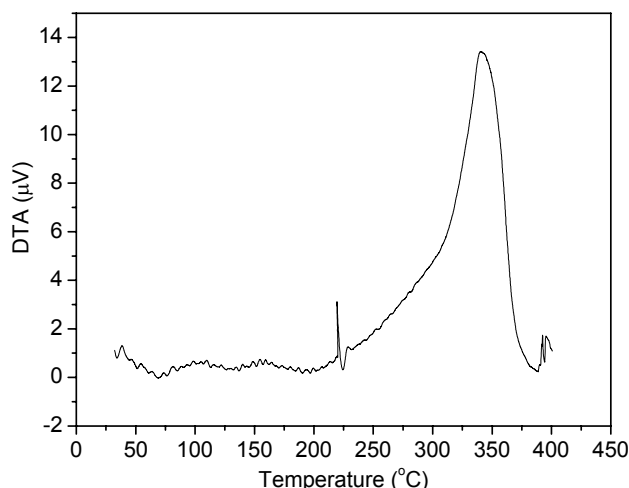


Figure 6: DTA curve for sample C at heating rate: 5.0°C min<sup>-1</sup>.

#### 4.1 Conclusion

The activation energies ( $E_a$ ) of three Brazilian fuel oils were obtained using the ASTM E 1641 and Model-Free Kinetics methods. The  $E_a$  values were approximately equal for both methods, suggesting they are adequate to determine  $E_a$  of the oxidative degradation of fuel oils. It was observed that  $E_a$  is different for each fuel and it is directly correlated with the exothermicity of the event (area under DTA curve), i.e., the lower the  $E_a$ , lower is the heat involved in reaction. These parameters indicate important combustion characteristics of the fuel: higher  $E_a$  values imply longer ignition delays, and, consequently, better the fuel is for use in compression ignition engines. Using this assumption and considering only the low temperature oxidation region (LTO), among the samples studied here, the sample A (MF 380) is the best option as a fuel.

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## 6.1 Responsibility notice

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