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Kinetic Analysis of the Oil Shale Pyrolysis using Thermogravimetry and Differential Scanning Calorimetry

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The organic and mineral matter are directly linked to the oil shale, allowing multiple reactions in parallel that may result in different behaviors. An in-depth study using the techniques of Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) non-isothermal were performed. The oil shale was extracted from Basin Irati being supplied by Petrobras/SIX located in the city of Sao Mateus do Sul, Parana, Brazil. The parameters analysed through shale pyrolysis kinetics were evaluated using the ASTM E-698 and Flynn-Wall-Ozawa (FWO) methods, with analysis and a comparison of parameters the activation energy and exponential factor. The experiments were done at different heating rates, from 298 K - 1,173 K for TGA and 298 K - 873 K for DSC both with nitrogen atmosphere flow of 50 mL/min. The results showed a correlation between TGA and DSC and that, for both processes, the shale underwent thermal decomposition in three steps. Activation energy values decreased throughout the process due to the decrease in the amount of organic matter.

1. Introduction

The oil shale decomposes to generate oil and gas by a thermochemical conversion. The consumption of products generated through the pyrolysis process is beneficial to alleviating the depletion of fossil fuels and promoting the development of society, (Li, 2017). Although shale can be found all over the world, Brazil has the second largest reservoir containing deposits of various geological periods. However, due to factors such as the thickness and the average organic matter content of the deposits, only the deposits of Permian age (278 mia) are explored, (Ribas et al., 2017).

Thermogravimetric analysis (TGA) is often used to evaluate the decomposition of the shale by the heat treatment process in a controlled environment. Performing several experiments, measuring the mass loss, temperature and varying the heating rates, is possible to getter sufficient information to calculate the Kinect parameters. Among the numerous applications of thermogravimetry, stand out: thermal decomposition or pyrolysis of organic, inorganic and biological materials; evaporation and distillation of liquids; determining the vapour pressure and enthalpy of vaporization of volatile additives; determination of moisture, volatile, and composition of ash, kinetic study of reactions involving volatile species.

According to (Kissinger, 1957), the differential scanning calorimetry (DSC) technique, based on the linear relationship between peak temperature and heating rate, can be used to determine the kinetic parameters (Activation energy, for example). These methods and their modified versions are widely used for the investigation of the thermal decomposition of organic materials, polymers and petroleum products. Non-isothermal calorimetry experiments are much faster and can provide information not only on the first oxidation step (observed in conventional isothermal methods), but also other oxidation steps from a single run.

2. Material and Methods

For this study, the shale used was extracted from the Irati Formation and supplied by Petrobras / SIX, located in Sao Mateus do Su, Parana, Brazil, with particle range size -42 +48 Mesh (0.354 mm – 0.297 mm). Parameters kinetics as activation energy (E) and the pre-exponential factor (k_0) were determined using thermogravimetric analyser (TGA) and the Differential Scanning Calorimetry (DSC) non-isothermal. For

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analysis 9.5 mg of shale was weighed and put inside alumina crucible. All the analyses were performed using the equipment model TGA/DSC1 with a microbalance model MX5 of measuring range 5 g and resolution 1 µg and Stare software from Mettler Toledo. TGA was heated under nitrogen flow of 50 mL/min, atmosphere since 373K - 1,173K with a heating rate (β): 2, 5, 10, 15, 20, 25, 40 and 50 K/min. The final weight was considered to be ash (oxidized mineral matter), i.e. all material that did not form gaseous combustion products. For DSC, he same methodology with heating rates were adapted, with exception of the temperatures were between 298K-843K. The samples of oil shale were prepared according to ASTM E-698. The equipment used was DSC Star model, Gas Controller GC10 of Mettler Toledo manufacturer.

3. Model Free and ASTM 698-11 Methods

3.1 Model Free

The definition of Kinetics parameters was determined by relating the mass loss versus temperature response at different heating rates to the oil shale pyrolysis kinetics. The kinetics of decomposition analysis are based on the Arrhenius equation (Equation 1), and kerogen transformation rate for the volatile product (Equation (2):

$$k = k_0 . e^{\left(-\frac{E}{RT}\right)} \tag{1}$$

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \tag{2}$$

To calculate the pyrolysis kinetics from the TGA data, it was considered the method of Flynn–Wall–Ozawa Table 1, which is associated with model-free descriptions of the kinetics.

Table 1: Approximate equation of the kinetic method. Adapted from (Bai et al., 2015)

Method	Equation	X	Y
FWO	$\ln(\beta_i) = \ln\left(\frac{k_0.E}{R.g(\alpha)}\right) - 5.331 - 1.052\frac{E}{RT}$	$\frac{1000}{T}$	$\ln(\beta_i)$

Wherein: k_0 is the pre-exponential factor, E the Arrhenius activation energy, R the gas constant and T the absolute temperature in K. The equation was used for the calculation of Arrhenius kinetic parameters and the activation energy.

3.2 ASTM 698-11

The definition of Kinetics parameters for DSC was determined the ASTM method E698-11. This method considers the linear regression of log B versus 1/T, were T is the peak temperature at that heating rate, which the slope of the curve is used to calculate the activation energy.

The calculation of activation energy an interactive process to refine the value of Activation energy. After the initial calculation of Activation Energy (E’), this result is used to find the corresponding value of D, identified according ASTM 698-11, to recalculate the Activation Energy (E’’) by Eq(3). This process is replicated until the value of D are the same in two sequential calculations.

For each heating rate, the peak for the DSC represents a system in the state of the same constant conversion, (Ozawa, 1992). The advantage of the FWO method is that the activation energy can be determined without knowing the kinetic model of the reaction: (Opfermann, 1992). The activation energy of Arrhenius for the process and the pre-exponential factor A can be written as:

$$E = -2.19R\frac{d\log\beta}{dT_p^{-1}} \tag{3}$$

The pre-exponential factor could be calculated by Eq(4). The values of Heating Rate and Peak temperature considered should be the ones of the middle of the range.

$$k_0 = \frac{\beta \exp[E/RT]}{RT^2{}_p} \tag{4}$$

4. Results

The Figure 1 shows of mass loss as a function of temperature. The mainly results were that in the region I between 373 K and 573 K the mass loss is attributed to moisture. In region II, between 623 K and 823 K is identified variations due to the hydrocarbon compounds (alkanes, alkynes, aromatics). At this region, most of the weight loss occurs in result of the decomposition of kerogen in oil shale. In Region III, a slightly variation into the curve behavior which is observed between 823 K and 1,023 K, an effect of the amount of mineral material into the desvolatilization process, i.e. dolomite, calcite, according Lee (1991). Although oil shale has his particularities in different basins, they have a similar content of carbonate, which affects the loss of mass with elevation of the temperature.

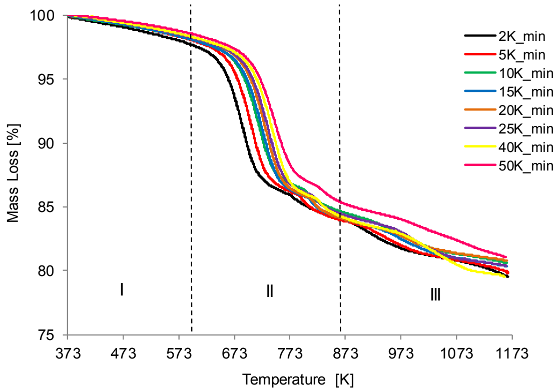

Figure 1: Mass loss data obtained by the temperature TGA.

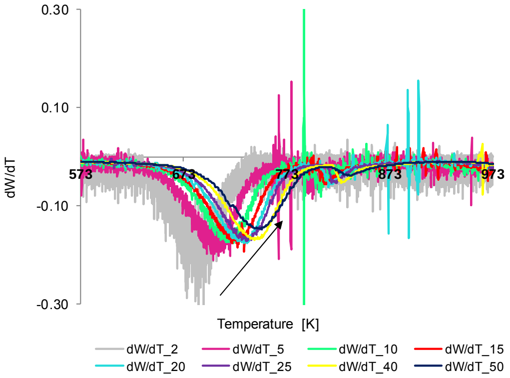

Figure 2: DTG curves of shale at varying heating rates.

Table 2: Peak temperatures used for the DSC for different heating rates

Heating rate (K/min)	Temperature (K)
2	786.5
5	800.2
10	814
15	823.2
20	829.7
25	838.2
40	842.9
50	845.6

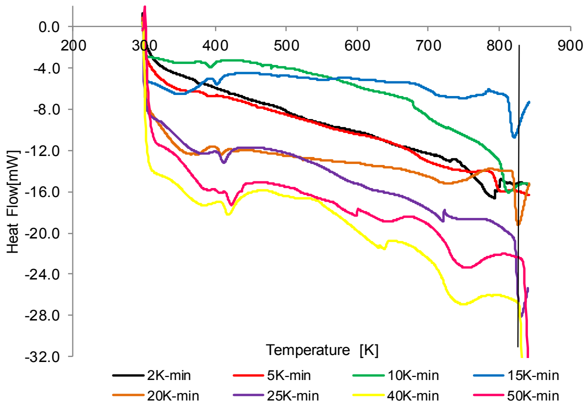

Figure 3: Heat flow for different heating rates.

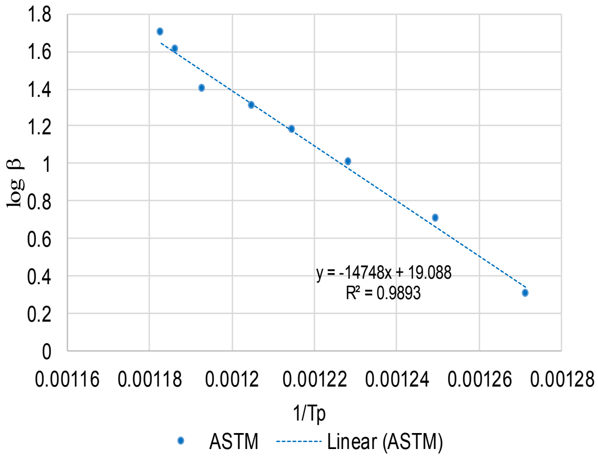

Figure 4: Kinetic analysis of DSC data ASTM Method

The Figure 2 shows the derivative obtained from the analysis of TGA for different heating rates. Note also from Figure 2 that, with the increase of the heating rate the top conversion occurs in a higher temperature. Figure 3 shows heat flow data obtained by DSC. Note that the DSC endothermic reactions indicated by the behavior of the samples shown. The Table 2 present Peak temperatures used for the DSC for different heating rates.

This relationship is show for different heating rates for the model in Figure 4 and the calculated correlation coefficient for linear regression is $r^2 > 0.98$. The calculation of the pre-exponential factor considered the peak temperature of 15 K/min heating rate. The Table 3 present calculated pre-exponential factor (k_0) and activation energy (E) for the pyrolysis reaction using ASTM 698-11 method.

Table 3: Calculated pre-exponential factor (k_0) and activation energy (E) for the pyrolysis reaction using ASTM 698-11 method.

Slope	-14,748.1
E'(kJ/mol)	268.5
E/(RT)	39
D	1.0513
E''(kJ/mol)	268.6
k_0 (min^{-1})	7.9×10^{16}

During the pyrolysis process, the mass loss that occurred in Region I was mainly due to evaporation of lighter material in the kerogen and not due to pyrolysis, Figure 1. The fraction of the total mass loss that took place in Region I was in the range α = 0.10 to 0.15. The kinetic analysis is therefore valid only for values of α ≥ 0.15 and the calculated kinetics at lower conversion has no real meaning. Although Region II represented pyrolysis, literature indicated that this was due to mineral matter catalysis, (Al-Harahsheh et al., 2011). The conversion at the start of Region II was around 65 % and the kinetics analysis of oil shale kerogen pyrolysis was consequently limited to α ≤ 0.65.

The FWO method, resumed in Table 1, is in a linear regression of the conversion with the temperature (1/T). This relationship is show for different levels of conversion for the model in Figure 5.

The pre-exponential factor and activation energy for the first order pyrolysis reaction (n =1) derived at different levels of conversion using the FWO methods. The calculated correlation coefficients for linear regression were $r^2 > 0.97$ in the range 0.15 ≤ α ≤ 0.55, but became worse as the transition from thermal cracking (Region II) to mineral matter assisted cracking (Region II) was approached. A significant increase in the activation energy at 0.65 conversion is indicated by the FWO method, Table 4.

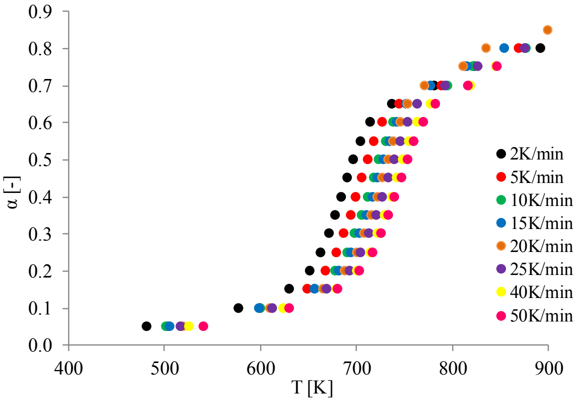

Figure 5: Conversion for different heating rates.

Table 4: Calculated pre-exponential factor (k_0) and activation energy (E) for the pyrolysis reaction using FWO method

α	Flynn–Wall–Ozawa		
	E	k_0	r^2
0.05	121	1.0×10^{11}	0.895
0.10	180	2.7×10^{14}	0.895
0.15	216	1.7×10^{16}	0.977
0.20	219	1.0×10^{16}	0.993
0.25	211	1.8×10^{15}	0.990
0.30	218	4.6×10^{15}	0.996
0.35	240	1.5×10^{17}	0.995
0.40	239	1.1×10^{17}	0.998
0.45	246	3.0×10^{17}	0.992
0.50	237	4.8×10^{16}	0.997
0.55	245	1.7×10^{17}	0.992
0.60	255	5.6×10^{17}	0.982
0.65	301	$5.6x10^{20}$	0.868

4.1 Methods Comparison

Comparing these two methods, is possible to see that the mean activation energy calculated for the FWO method was 230 kJ / mol and the activation energy calculated for the ASTM 698-11 method of 268.6 kJ / mol. For the pre-exponential factor calculated for the FWO method it was 9.0 x 10^{16} min^{-1} and the calculated pre-exponential factor for the ASTM 698-11 method was 7.90 x 10^{16} min^{-1}.

Although the equipment is properly calibrated, the difference found in the activation energy between the methods can be explained by the difference between the measurement process of the equipment used in each method. While the FWO method uses the results of the TGA, which evaluates the variation of sample weight over time, the ASTM method uses the DSC results, which compares the existing energy in the sample when compared to a reference sample. From the literature, we found that the DSC is recommended for the evaluation of endothermic processes and calculated values of activation energy and pre-exponential factor.

For the pre-exponential factor, the variation is explained by the difference in the calculation of the activation energy, since for the FWO method the higher the activation energy the lower the pre-exponential factor presenting a linear relationship whereas for the ASTM 698-11 method. The higher the activation energy the higher the pre-exponential factor with an exponential relation.

5. Conclusions

Differential scanning calorimeter (DSC) and Thermogravimetric analysis (TGA) were used to study the kinetics of shale. The heating rate impacted the pyrolysis process when analyzed in TGA. This is due to the material properties during the process. As the heating rates increase, the peaks move to higher temperatures in the

DSC curves. Note also the reactions that occur due to the decomposition and dissociation of the minerals present. Evaluating the FWO and ASTM methods to calculate the activation energy and the pre-exponential factor of the oil shale we found that the mean activation energy calculated for the FWO method was 14.4 % lower when compared to the ASTM 698-11 method. For the pre-exponential factor calculated for the FWO method it was 13.9 % higher than the pre-exponential factor calculated for the ASTM method.

Nomenclature

E	activation energy (J/mol)
E'	First calculation of activation energy by ASTM 698-11 method (J/mol)
E''	Second calculation of activation energy by ASTM 698-11 method (J/mol)
$f(\alpha)$	reaction model
$g(\alpha)$	integrated reaction model
k	reaction rate constant (units depend on reaction order)
k_0	pre-exponential factor (min^{-1} for 1st order)
m	mass of oil shale (mg)
m_o	mass of oil shale before pyrolysis (mg)
m_f	mass of oil shale after pyrolysis (mg)
n	reaction order
r	correlation coefficient for linear regression
R	universal gas constant (J/mol·K)
t	time (min)
Tp	temperature Peak (K)
α	kerogen conversion as defined by Equation 3 (mg/mg)
β	heating rate (K/min)

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