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RESEARCH ARTICLE

COMPARATIVE REACTIVITY OF ORGANIC MATTER DURING HYDROPYROLYSIS OF OIL SHALE EFFECT OF SEDIMENTATION CLIMATE

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Abstract

The thermogravimetric analysis during the hydrotreatment in dynamic regime of the organic matter for Tarfaya's oil shale of the different layers and the layer M of Timahdit was the object of this study, several results obtained allowed us to describe this energetic matter of non-estimable value that it is to extract the matter or to use it as fuel. By processing the curves in TG, $DTG=f(T_{max})$ and their surfaces we were able to show that the concentration of mineral and organic matter and the climate of the sedimentation have a great influence on the reactivity of the organic matter. The Z_4 layer (Cenomanian) was the most reactive layer, the Z_3 layer (Turonian) being the most concentrated in light organic matter. These two layers were the subject of in situ pyrolysis. Hydrogen also plays a very important role in the reaction, it decreases the difference of the maximum temperature of the DTG peaks, as it is the case between the Z_4 layer and the M layer of Timahdit, this difference goes from 60°C (under nitrogen) to 8°C (under H_2) due to its reactivity.

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Introduction:-

Oil shale is considered the largest energy resources in the world. Morocco, in terms of clean resources, has a potential in non-renewable energy (green energy) considerable and large reserves of oil shale, whose most important deposits are in Tarfaya, Timahdit, and Tangier.

In this report we will study the Tarfaya deposit which is made up of marl of organic matter dating from the Upper Cretaceous and early Tertiary era (Z_0). A large part of the Upper Cretaceous series is constituted by oil shale with variable organic matter contents. This deposit has been divided into 5 layers, Z_0 , Z_1 , Z_2 , Z_3 and Z_4 . The reserves of the Z layer go down to a depth of 125 m over its entire extent with a total of 795 million m^3 . The estimated global reserves of this deposit amount to about 80 billion tons of rock at the most, containing 22 billion barrels of oil at an average grade of 60 liters/ton. Some layers may contain up to 100 L/t. (M.Saadi; 1981). The M layer of the Timahdit deposit was also studied for comparison.

The thermogravimetric analysis (TG) and the thermogravimetric derivative (DTG) were used to quantify the change in mass of the samples as a function of temperature and heating rate, under controlled atmosphere (hydrogen).

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In this work, we were interested in analyzing the results obtained from thermogravimetry and its derivative of the different layers of Tarfaya deposit and identify the classification according to the climate of the geological stage of sedimentation of organic matter in the layers of this deposit.

Literature Review:-

Morocco is one of the non-oil producing African countries and its energy needs are almost entirely dependent on external sources. Nevertheless, several oil shale deposits with significant potential have been discovered in different parts of the country, but they remain untapped. According to a 2010 report by the World Energy Council, Morocco ranks seventh in global oil shale reserves, with an estimated total oil content of 50 billion barrels. Recently, several exploration programs have been conducted with the aim of making oil shale one of Morocco's future energy sources. The three main Moroccan oil shale deposits that come up to the ground are those of Tangier (Rif region), Timahdit (Middle Atlas) and Tarfaya (Southern Morocco)

Oil shale are broadly defined as grained sedimentary rocks of low permeability, capable of generating a significant amount of oil similar in appearance to crude oil when exposed to heat and pressure.

The potential for oil production is directly related to the nature, volume and composition of the organic matter in the oil shale and its thermal maturity. The organic matter is mainly kerogen, which consists of organic macromolecules with a three-dimensional structure that is insoluble in ordinary solvents and has a low content of soluble organic substances called bitumen.

The thermal behavior of oil shale is more complex and many reactive processes occur simultaneously due to a complex heterogeneous mixture of organic components bound to a mineral matrix. (Ely CheikhMoine et al; 2016)

The kinetic analysis of the complex process of oil shale pyrolysis in the Moroccan Rif was studied by thermogravimetric analysis (TG) and its derivative (DTG) under non-isothermal conditions. The investigated pyrolysis region, located between 325 and 600° C.

The main pyrolysis step of the Moroccan Rif oil shale concerns the volatilization of organic matter, especially bitumen and kerogen, and the subsequent decomposition of the pyrite mineral FeS₂. The first process represents the main pyrolysis kinetics as a function of the dominance of bituminous products in the studied oil shale. By applying nonlinear least squares analysis to the kinetic data, it was found that all processes were well described by the nth order kinetic equations, with (n = 1) for the first and third processes and n = 1.67 for the second process. In addition, the thermodynamic functions of the activated complexes (DS *, DH *, and DG *) for the pyrolysis step of the studied oil shale were calculated and discussed.

In general, the pyrolysis of oil shale can be divided into three essential stages. According to many researchers (Sun YH et al; 2014) the first stage, observed at low temperature, corresponds to water release with highly volatile products. The second stage, at a temperature between 200 and 600°C, corresponds to the volatilization of organic matter and the production of oil and gas hydrocarbons. The last stage appearing at high temperature is attributed to the decomposition of minerals.

Many studies have been conducted to evaluate the decomposition kinetics of complex kerogen in oil shale and most of them state that the pyrolysis mechanism is not a simple process and may involve various parallel reactions (Jiang XM et al; 2006) Kerogen pyrolysis thermograms generally exhibit overlapping behavior characterized by the presence of multiple poorly resolved peaks related to the existence of several processes. This makes it difficult to accurately evaluate all the kinetic parameters and subsequently obtain the proper model to describe the reaction scheme of each process step.

Many works have addressed the kinetic complexity of solid-state reactions involving multiple multi-step processes, such as pyrolysis of activated sludge from industrial waste (Yang XY et al 2009), thermal degradation of cellulose/starch derivative mixtures (Alvarez VA et al; 2004), thermal decomposition of Zn (II) 2-chlorobenzoate Complex with caffeine, and pyrolysis of Brazilian and Chinese oil shale (JankovicB; 2013). According to the recently published recommendation of the Kinetics Committee of the International Confederation of Thermal Analysis and Calorimetric (ICTAC), it is practical to fully separate the overlapping peaks and analyze their kinetics individually (Vyazovkin S et al;2011). The separation method consists of peak convolution from the global

differential kinetic curves, using various conventional mathematical fitting functions such as Lorentz and Gauss distributions and their logistic mixing models (**Wang Q et al;2013**). Alternatively, other fitting functions, including Weibull and Fraser-Suzuki models, have recently been used mainly to fit asymmetric behaviors. In fact, the organic geochemical and mineralogical characterizations of the Moroccan Rif oil shale have been the subject of several studies in previous research(**Groune K et al;2013**).

Thermogravimetry and its derivatives (TG / DTG) have been used to evaluate the kinetics of the studied oil shale. Based on the complexity of the pyrolysis mechanism, a multi-peak fitting method was applied to separate the overlapping processes using the asymmetric Fraser-Suzuki function. For each separated process, the activation energies were determined by the Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) integral methods and the Friedman differential isoconversion (FR) method. The Coats-Redfern fitting method was used to ensure the activation energy and thus to confirm the proposed kinetic model.

Thermogravimetric analysis was used to quantify the mass change of a sample as a function of temperature and time, under controlled atmosphere, simultaneous TG / DTG / DTA analyses were performed on a LabsysTMEvo (1F) Setaram instrument. The ICTAC Kinetics Committee recommendations for collecting experimental data and performing kinetic calculations were followed to evaluate the kinetic parameters (**Vyazovkin S et al; 2011**). Prior to analysis, the thermal analysis system was calibrated for temperature readings with reference metals of 99.99% purity.

In addition, it is essential to calibrate the microbalance by minimizing buoyancy effects for better estimation of mass changes. Experiments were conducted under non-isothermal conditions in a 30 ml/min pure nitrogen flow atmosphere from room temperature to 800°C, at different heating rates (5, 10, 15 and 20 °C/ min).

Measurements were repeated three times to ensure reproducibility. An initial sample mass of approximately 10.0 ± 0.2 mg was placed in an alumina dish. The sample was well dispersed with negligible depth to reduce heat and mass transfer.

Figure 1 show the non-isothermal TG and DTG experiments performed at heating rates between 5 and 20°C / min for the decomposition of the Moroccan Rif oil shale crude samples.

The samples show similar thermal curves with increasing temperatures from room temperature to 800 ° C, for all heating rates explored. Three basic stages can be distinguished in the TG curves.

The first, where the weight loss curves decrease from room temperature to 325°C, is attributed to evaporation of moisture, intercalated water from the clay minerals and the free organic component present in the shale.

The second stage occurring between 325 and 600°C constitutes a significant weight loss (6%) of the entire pyrolysis process. This is attributed to the decomposition of organic matter, including bitumen and complex kerogen, into oil, gaseous products and residual carbon (**Groune K et al; 2013**), probably accompanied by the decomposition of a small amount of pyrite (FeS₂).

The third stage, between 600 and 800°C, shows a small weight loss and corresponds to the thermal decomposition of minerals, in particular clay minerals, in small proportions. It should be noted that the mineral part of the raw sample is mainly formed by quartz and traces of chlorite and illite clays (**Vantelon JP et al 1990**).

Concurrently, the DTG curves show the same trends characterized by the presence of three stages and their maximum velocities systematically pass at higher temperatures as a function of the heating rate.

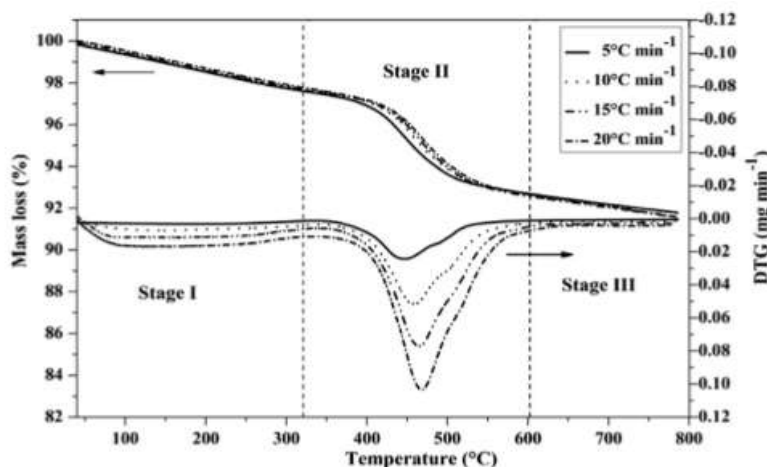


Figure 1:- TG-DTG curves of non-isothermal pyrolysis of Moroccan Rif oil shale at different heating rates, under a nitrogen atmosphere.

On the other hand, the existence of partial overlapping behavior in the DTG curves at the temperature between 325 and 600 °C (Fig. 1, stage II), indicates that the pyrolysis of an oil shale sample is a complicated mechanism consisting of several processes due to the presence of complex organic materials. This finding was also made by Sun and Wang in the kinetic studies of Chinese oil shale and its kerogen.

As can be seen in Figure 1, the existence of multiple overlapping peaks at the major stage of oil production (325-600°C) (stage II) can be interpreted by the occurrence of multicomponent reactions. According to several authors, oil shale pyrolysis is a complex thermal behavior due to the structural complexity of the organic matter that involves a series of independent parallel reactions. For this purpose, the Fraser-Suzuki multi-peak fitting method can be applied to differential curves of different heating rate conditions to separate overlapping peaks. This mathematical fitting algorithm has the advantage of fitting all kinetic models correctly. Recently, it has been shown that conventional functions such as Gaussian and Lorentzian functions, commonly used to fit many complex solid state reactions, are inadequate due to the fact that in most cases the kinetic curves have behaviors

According to the basic kinetic concepts of solid-state chemistry, the determination of the activation energy at different degrees of conversion can provide valuable information about the processes involved in the reaction mechanism. In this regard, three conversion methods were used: the Friedman differential analysis (FR) and the FlynnWalleOzawa (FWO) and Kissinger-Akahira-Sunose (KAS) integral analyses

The comparison of the average E_a value evaluated by the FR, KAS and FWO methods, for each process, It was noted that the energy values calculated from the Friedman method are slightly higher than those from the KAS and FWO methods. This may be due to the inaccuracy created by the application of numerical differentiation of the conversion method of The activation energy values obtained from the KAS method for all discrete processes were found to be slightly higher than those previously reported for other oil shale, but were in near agreement with recent results from pyrolysis studies performed on Brazilian and Chinese oil shale (JankovicB; 2013). The high activation energy values depend mainly on the nature, composition and organic content of the oil shale rocks. Indeed, the Moroccan Rif deposit contains a low proportion of organic matter consisting mainly of aliphatic compounds (bitumen), strongly bound to the mineral matrix. The mineral part is thought to play an important role in the thermal conversion of the organic matter and has catalytic or inhibiting effects during the pyrolysis process of oil shale. The presence of silica as a major mineral component in the Moroccan Rif oil shale results in resistance to heat transfer and subsequently increases the required energetic decomposition of the organic matter.

The pyrolysis characteristics of the Moroccan Rif oil shale of ArbaaAyacha were studied by thermogravimetry and derived thermogravimetry (TG / DTG), at different heating rates. The main oil-producing region (325-600°C) shows a partially nested character, followed by kinetic analysis. Kinetic parameters and appropriate reaction models were established. The calculation of the activation energy shows a small variation in the range of E_a values. The kinetic results were correlated to the decomposition mechanism of bitumen, kerogen and pyrite for the respective processes.

Multi-step parallel reaction modeling using the Fraser-Suzuki algorithm is considered an effective procedure to explore the thermal kinetics of a solid fuel with complex behaviors.

The organic matter evolution and combustion kinetics of Tarfaya and Timahdit oil shale were examined by thermogravimetry (TG) and differential thermal analysis (DTA).

An agreement is observed between the two techniques where it was found that the combustion of organic matter occurs in two stages. The Kissinger method applied to the experimental results gives an activation energy of the same magnitude for the first stage of both oil shale (103 kJ mol⁻¹) while the second is 148 kJ mol⁻¹ for Timahdit and 118 kJ mol⁻¹ for Tarfaya.

Oil shale has long been recognized as a potential source of hydrocarbon products, which are now produced from crude oil and natural gas. Their thermal decomposition to produce oil is generally carried out between 200 and 500°C, at temperatures where considerable degradation occurs, giving rise to a volatile fraction, part of which is condensable and a residual organic carbon fraction, which remains in the solid residue. In shale oil extraction methods, heat is provided by burning a portion of the residual organic matter in the oil shale to thermally decompose it and distill the organic matter in the oil shale (Barkia.H et al;2004).

Previous studies have been conducted on the thermal oxidation of shale using TG, DTG, and DTA thermal analysis techniques. Lee and Sohn studied the kinetics of kerogen oxidation in Colorado oil shale using the TG technique. They assumed that at the relatively low temperatures, at which the kinetics was measured, the oxidation reaction occurred at the surface of the solid kerogen and that decomposition of the kerogen was not significant. It has been demonstrated by the DTA technique that the combustion of kerogen is a complex multi-step process indicated by largely interlocking exotherms. This was confirmed by Earnest when he used TG / DTG to study the oxidation profiles of some American and Australian oil shale. It was assumed that in the presence of O₂, two processes were developing simultaneously: a simple thermal degradation process and a thermochemical process combining temperature and O₂ effects. Infrared emission spectroscopy was used to monitor the chemical changes occurring during the oxidation of raw kerogen and oil shale in the range of 50-700°C. With increasing temperatures, a steady decrease in the signals due to aliphatic hydrocarbons, as well as carbonyl/carboxyl and carbonyl signals, and an increase in anhydride signals. The changes in mass and heat loss are accompanied, upon thermal decomposition, by a change in the physical and chemical properties of the solid. Specific surface area is one of these physical properties. The reactivity of a solid material towards gases is governed, among other things, by its active surface. Measurements of the specific surface area at different stages of the reaction can provide useful information about the reactivity of a material (Barkia.H et al; 2004).

The oil shale samples used were obtained from the Timahdit and Tarfaya deposits (Morocco), Table 1 gives the general characteristics of the two varieties of shale:

Characteristics	Tarfaya	Timahdit
density	2,20	2,02
P.c.s kJ kg ⁻¹	5133	4640
Co2%	33.00	21.80
Organic matter %	16.25	12.83

Table 1:- Characteristics for Tarfaya and Timahdit deposit.

Thermal analyses were performed on a simultaneous Stanton - Red Croft STA 781 TG / DTA unit using 10 mg samples in dry and dry air atmospheres (dried with MgClO₄) and a flow rate of 34.8 cm³ min⁻¹.

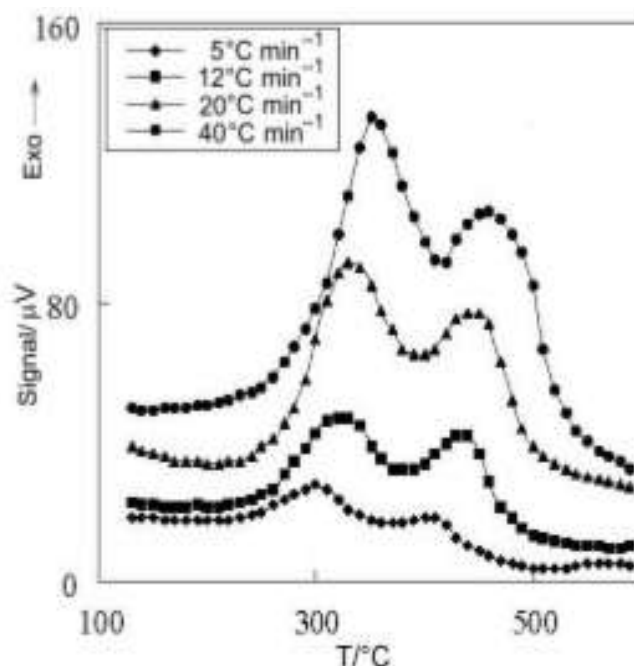


Figure 2:- DTA curves of Timahdit oil shale.

Figures 2-5 show the DTA and TG curves at different heating rates of 5, 12, 20, and 40 ° C min⁻¹. The first plot shows the variation of energy changes and the second illustrates the fractional mass loss, as a function of the temperature of the Timahdit/air and Tarfaya/air system. The DTA results indicate that the system gives two successive exothermic reactions where the first is more exothermic than the second. This is also observed by TG, which gives a curve characterized by two steps. Both data sets (Figures 2 and 3) were recorded simultaneously under the same experimental conditions. Analysis of the two plots (5°C min⁻¹) shows that the first and second DTA peaks correspond to mass losses of 2.1 and 8.9%, respectively

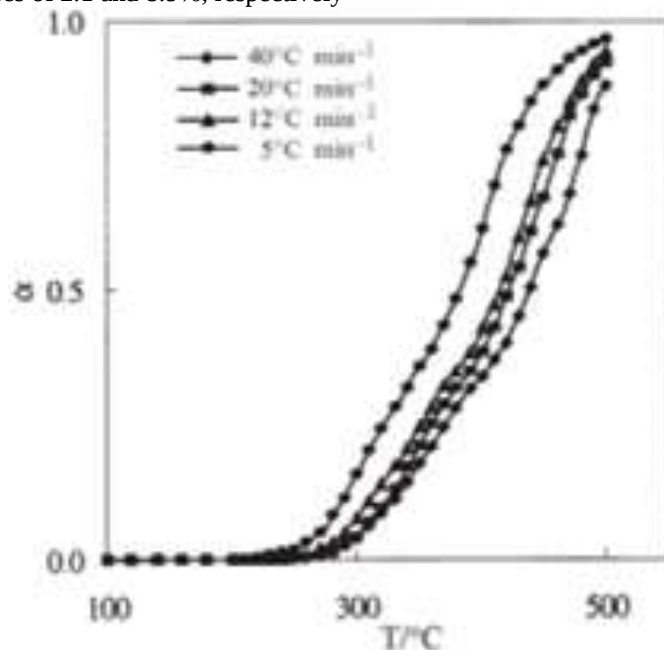


Figure 3:- Mass loss (TG) of Timahdit oil shale in a dynamic air atmosphere.

Therefore, the peaks are well defined and it is possible and simpler to apply the Kissinger method to our data. The results obtained will be compared with those obtained by applying the Coats - Redfern method to the TG data.

Similar studies by TG and DTA (Figures 4 and 5) were conducted on Tarfaya oil shale under the same experimental conditions. These show that the combustion of organic matter occurs in two stages, between 200 and 500 °C, and that the first stage is more exothermic than the second.

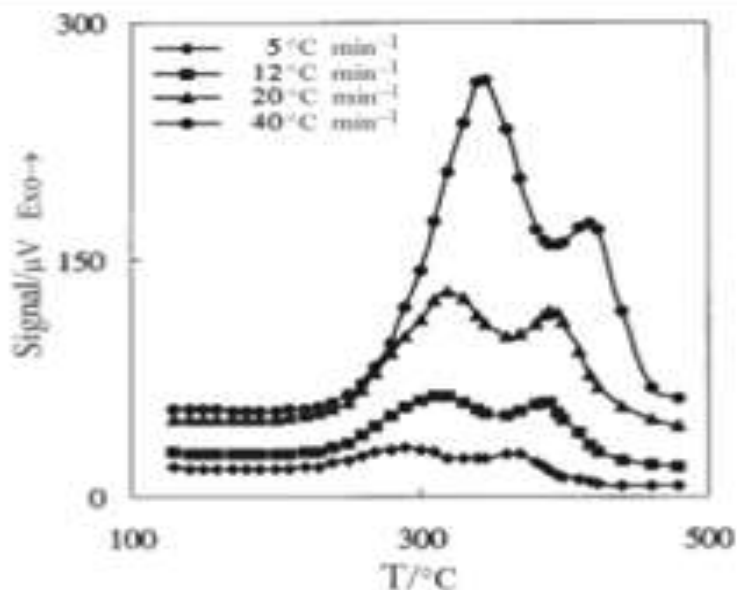


Figure 4:- DTA curves of Tarfaya oil shale in a dynamic air atmosphere.

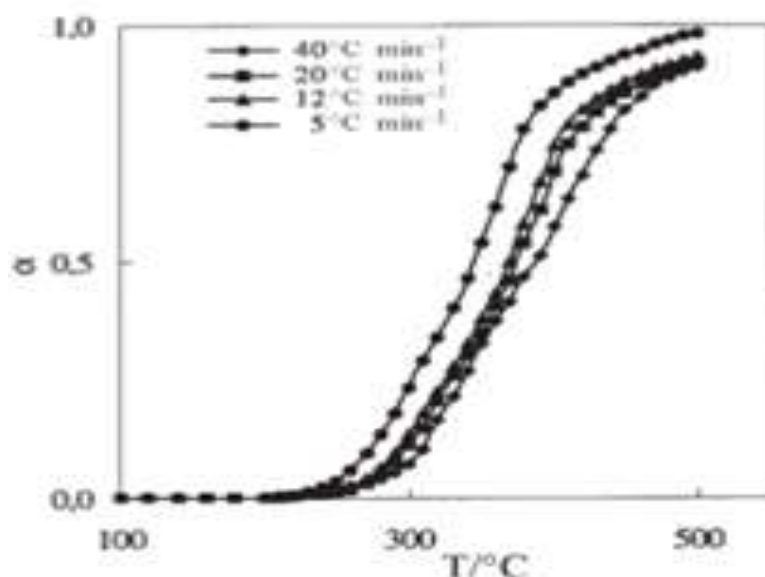


Figure 5:- Mass loss (TG) of Tarfaya oil shale in a dynamic air atmosphere.

Comparison between the TG and DTA curves shows that, for example at 12°C min⁻¹, the temperature corresponding to the final decomposition of the first type of organic matter is 380°C. The second part of the organic matter starts its decomposition after this temperature.

As shown in many studies, the Coats - Redfern method is applied to the data. The results obtained are shown in Figure 5, which shows that no real straight line was obtained. This non-linearity of the points leads us to look for another model that must fit the oxidation of oil shale. Future studies will examine all parameters accompanying oil shale decomposition to postulate a better model. Despite having a very high and complex heterogeneous nature, the Tarfaya oil shale share some similarities (and have some differences) to the Timahdit oil shale

They have almost the same activation energy (103 kJ mol^{-1}) for the first stage. While they are different in the second stage: 148 kJ mol^{-1} for Timahdit against 118 kJ mol^{-1} for Tarfaya. Thus, during combustion, the Tarfaya oil shale is more reactive than the Timahdit oil shale. This difference also corresponds to a drop of about 50°C in the temperature of the DTA peaks. The two exothermic peaks, where their maximums are located at about 300 and 400°C , correspond to the combustion of organic matter. This is in good agreement with research on oil shale oxidation, which has confirmed the existence of both peaks. The first is attributed to the complete or near-complete combustion of aliphatic components to yield an aromatic char-containing fragment (Barkia.H et al; 2004).

A comparison between the reactivity of the two shale during the organic oxidation step concluded that the Tarfaya oxidation products exhibit higher reactivity, which is explained by the shift in the maximum temperature of the DTA peaks and the TG mass loss profile at lower temperatures. Thus, the reactivity of a solid material towards gases is governed by its active surface area. In light of the two specific surface area data, the second stage starts at about 312°C for Tarfaya, while for Timahdit it is 420°C . This difference in temperature is most likely related to the lower reactivity obtained for Timahdit oil shale compared to Tarfaya during combustion under air.

Experimental techniques

Thermogravimetry

The thermal analysis technique of thermogravimetry (TG) is one in which the change in mass of the sample (loss of mass or gain) is determined as a function of temperature and/or time. Three modes of thermogravimetry are commonly used, isothermal thermogravimetry in which the mass of the sample is recorded as a function of time at a constant temperature; quasi-isothermal thermogravimetry, in which the sample is heated to a constant mass at each of a series of increasing temperatures; and dynamic thermogravimetry in which the sample is heated in an environment whose temperature undergoes a change in a predetermined way, preferably at a linear rate. Most of the studies reviewed will refer to dynamic thermogravimetry, which is referred to as the resulting mass change versus temperature curve (which has various synonyms such as thermoanalysis curve, pyrolysis curve, thermograms, thermogravimetric curve, thermogravimetric analysis curve, etc.) it gives information regarding the thermal stability and composition of the starting sample. The thermal stability and composition of all the intermediate compounds that can be formed, and the composition of the residue, this being to provide useful information with this technique.

The sample must evolve to a volatile product, which can come from various physical and chemical processes. Much of the information obtained from the TG curve is empirical in nature and that the transition temperatures depend on the instrumental parameters and the sample. The following picture shows a thermobalance from the Setaram series called Red-Croft, which is a flail thermobalance with a compensation system based on a photoelectric source to keep the sample at the same position in the oven, avoiding the temperature gradient due to a displacement of the sample in the oven.



Figure 6:- Photo of thermobalance Red-Croft.

Experimental studies

Thermograms $\Delta m = f(T)$

We performed experiments in hydrotreating (H_2 flow rate=20 cc /min) in dynamic regime (at the three heating rates $9^\circ\text{C}/\text{min}$, $15^\circ\text{C}/\text{min}$ and $21^\circ\text{C}/\text{min}$) for the five layers of Tarfaya deposit and the M layer of Timahdit in $\Delta m = f(T)$. The initial mass is 15 mg.

The thermograms corresponding to the organic matter decomposition stage are shown in the following figures:

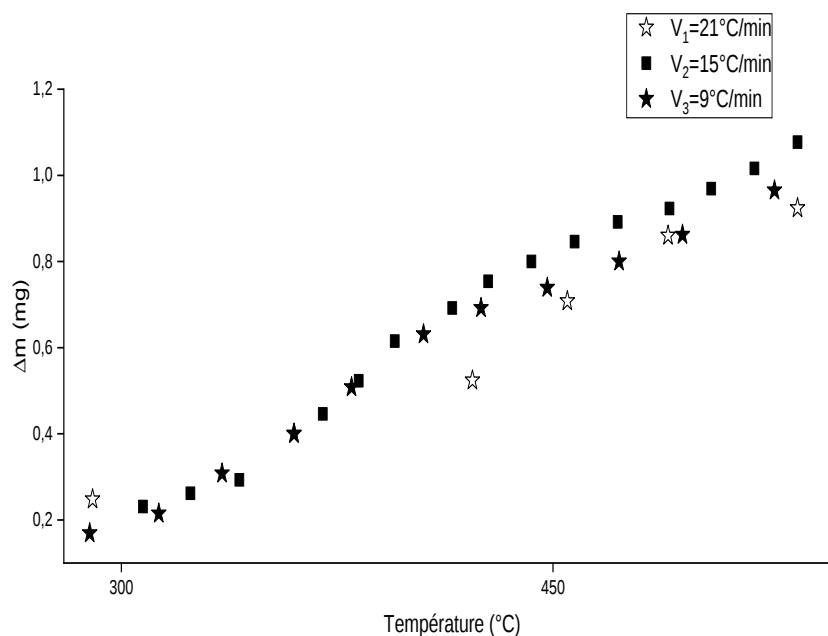


Figure 7:- Thermograms in TG of the hydrotreatment of the Z_0 layer of the Tarfaya deposit.

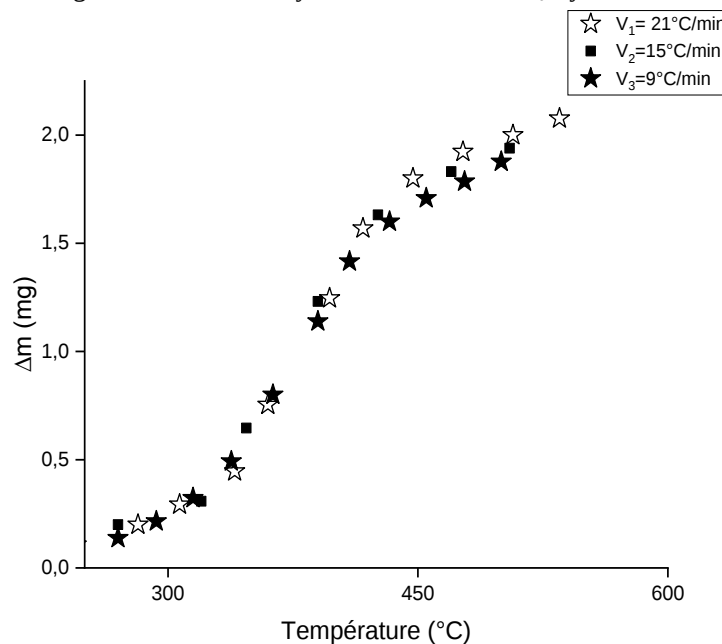


Figure 8:- Thermograms in TG of the hydrotreatment of the Z_1 layer of the Tarfaya deposit.

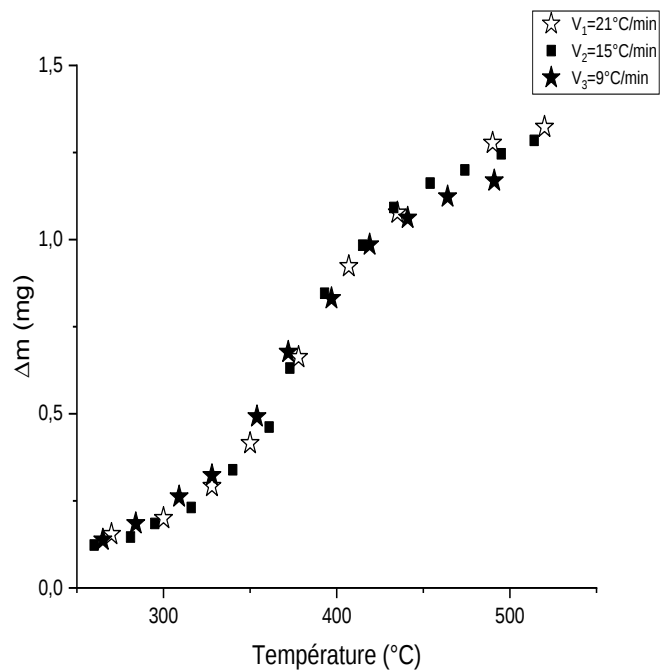


Figure 9:- Thermograms in TG of the hydrotreatment of the Z_2 layer of the Tarfaya deposit.

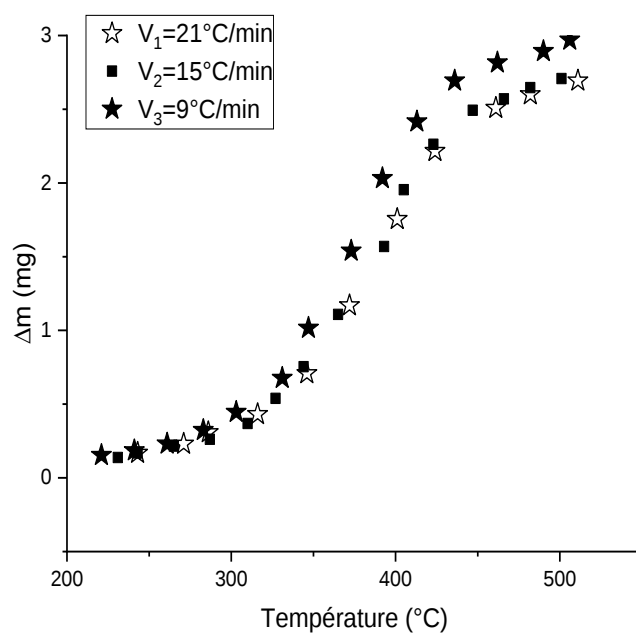


Figure 10:- Thermograms in TG of the hydrotreatment of the Z_3 layer of the Tarfaya deposit.

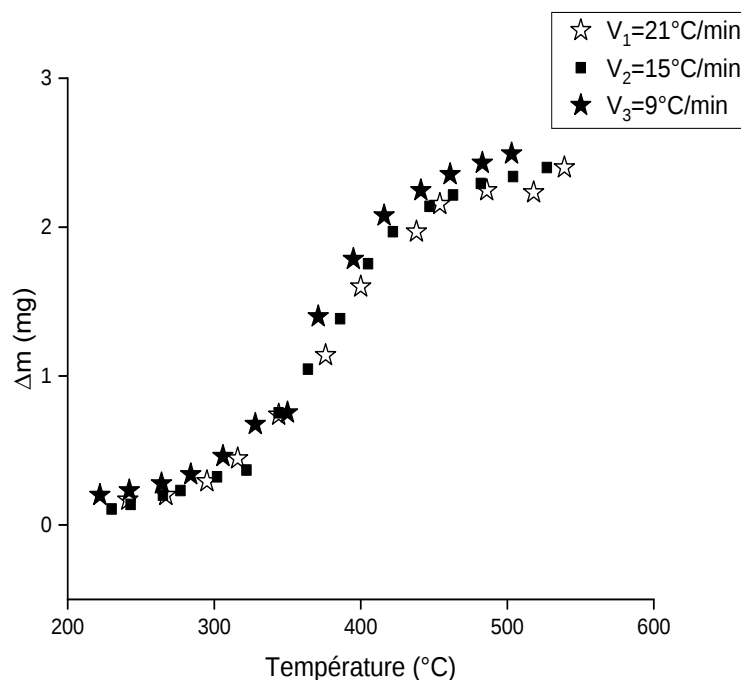


Figure 11:- Thermograms in TG of the hydrotreatment of the Z_4 layer of the Tarfaya deposit.

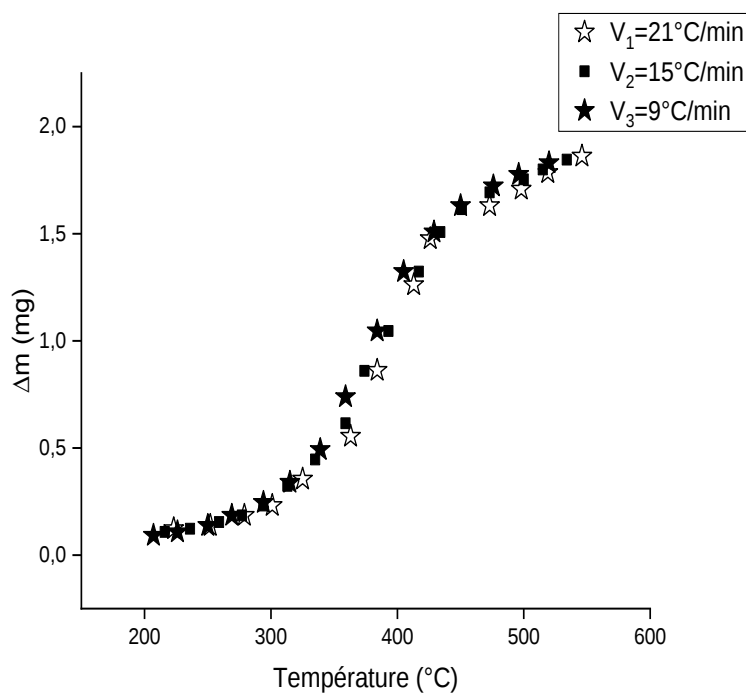


Figure 12:- Thermograms in TG of the hydrotreatment of the M layer of the Timahdit deposit.

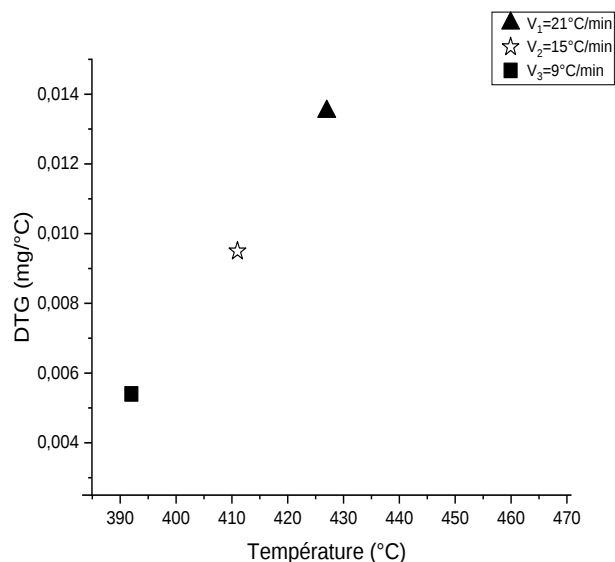
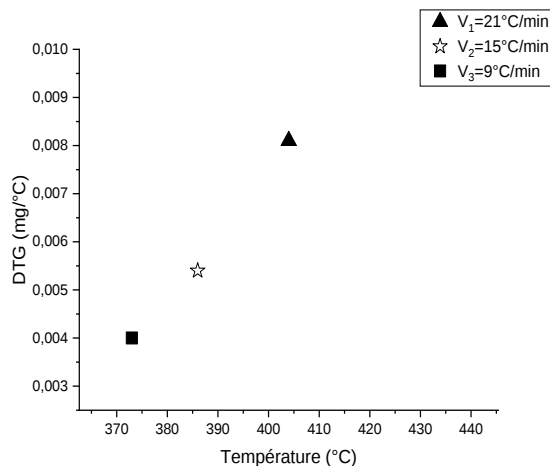
We have collected the different percentages of composition (organic matter) as well as the DTG peak temperatures for all samples in the following table:

Table 2:- Percentage loss (MO) and DTG peak temperatures for thehydrotraitement reaction.

Heating rate (°C/min)	Characteristics	samples					
	origin	Tarfaya					Timahdit
	Zone	Z ₀	Z ₁	Z ₂	Z ₃	Z ₄	Ti
21	Percentage loss	6,5	12,3	7,4	16,4	14,4	11,49
	DTG peak temperature	-	427	404	401	398	406
15	Percentage loss	5,6	11,6	7,7	18,09	15,59	11,48
	DTG peak temperature	-	411	386	390	377	380
09	Percentage loss	5,0	11,59	6,89	18,4	15,1	11,4
	DTG peak temperature	-	392	373	379	368	372

Heating rate variation for each sample during hydro treating:

We performed hydro treating tests by changing the rate of 9°C/min, 15°C/min and 21°C/min the following figures represent DTG=f(Tmax) at different heating rate for each sample:

**Figure 13:-**Hydrotreating of sample Z1 at different heating rates (the primary stage).**Figure 14:-**Hydrotreating of sample Z2 at different heating rates (the primary stage)

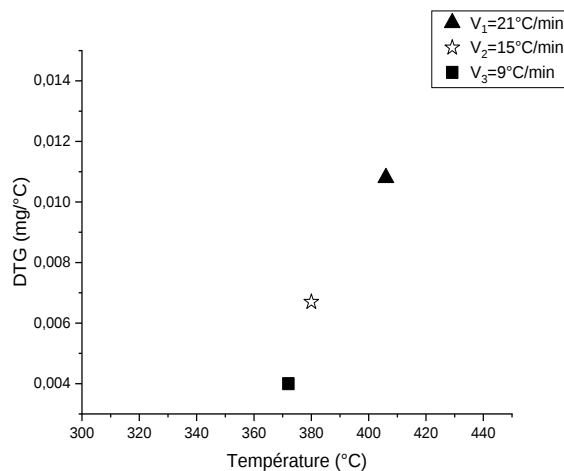


Figure 15:- Hydrotreating of sample Z3 at different heating rates (the primary stage)

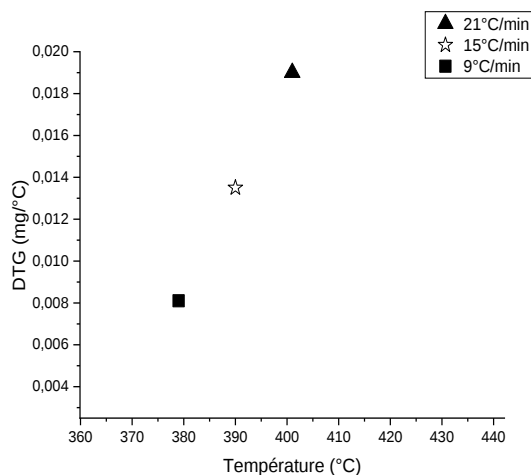


Figure 16:- Hydrotreating of sample Z4 at different heating rates (the primary stage).

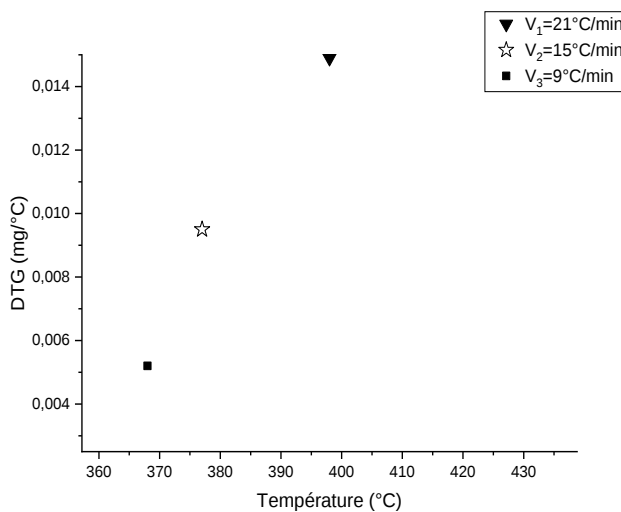


Figure 17:- Hydrotreating of sample M (Timahdit) at different heating rates (the primary stage).

When we observe the curves $DTG = f(T_{max})$ we see a high reactivity, when the heating rate increases the temperature of the peaks increases and conversely the reactivity decreases as well as the DTG peak increases in the same direction as the heating rate, this is verified for all samples.

So in summary when the heating rate increases the reactivity decreases and the temperature of the reaction step increases as well as the DTG peak.

Comparative study of the five samples by DTG

We were able to identify the DTG for each sample by plotting the maximum DTG peak versus temperature.

We have gathered in the following figures according to the heating rates:

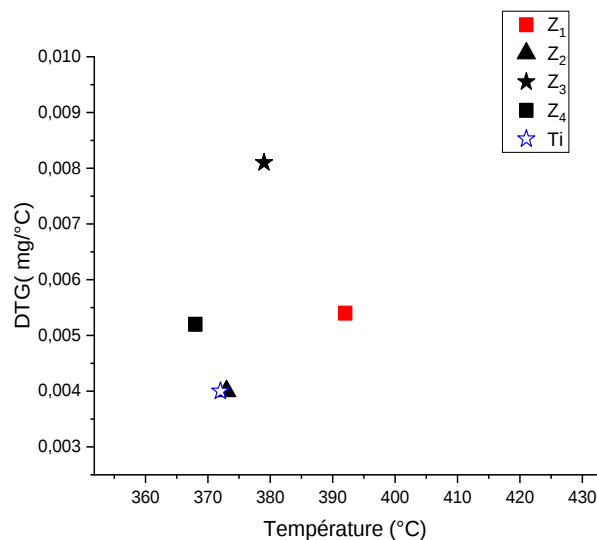


Figure 18:- DTG peak for the different layers as a function of temperature at 9°C/min.

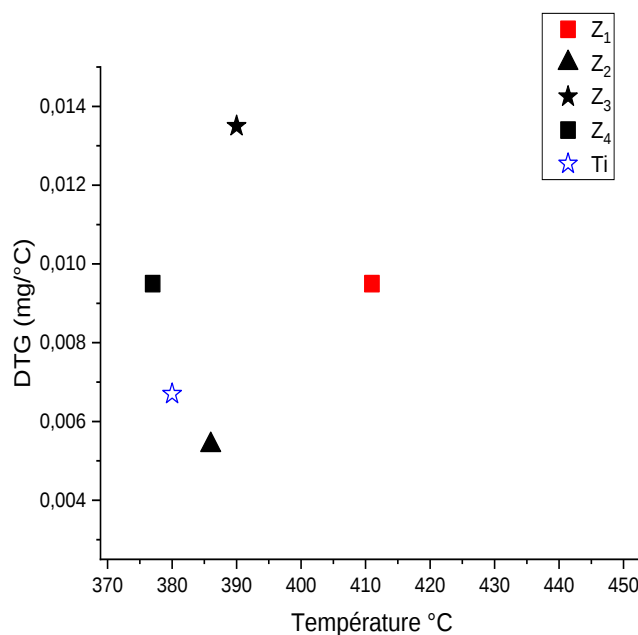


Figure 19:- DTG peak for the different layers as a function of temperature at 15°C/min.

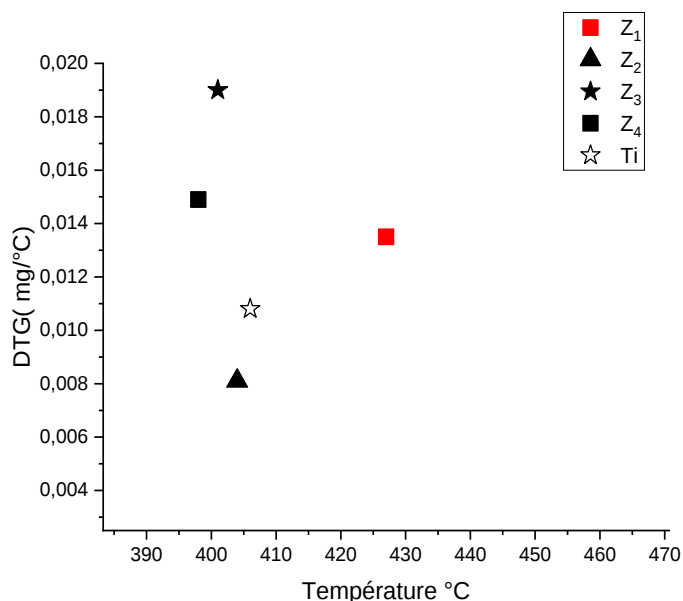


Figure 20:- DTG peak for the different layers as a function of temperature at 21°C/min.

Statistically the order of reactivity in decay for the layers is as follows: Z₄, Z₃, Z₂, Ti, Z₁

The maximum temperature difference between the DTG peaks is 8°C between the Z₄ layer and the M layer of Timahdit and if we adopt the pyrolysis under nitrogen this temperature difference was 60°C (**Attaoui.A et al; 1992**) thus we notice the sensitive activity of the hydrogen gas. Hydrogen is a fairly reactive gas for several reasons: firstly, its electropositivity to form the H⁺ cation and its small size, it reacts with ease and is introduced into the compounds. All these properties make quite reactive and it acts on the oil shale as a quite sensitive delimiter during the hydrotreating reaction compared to the inert gas N₂.

The pyrolysis reaction only highlights the reactivity of different layers depending on the era of the geological formation, while the hydrogen element of quite sensitive reactivity adds to this.

Let's take the Z₃ (Turonian) and Z₄ (Cenomanian) layers, the size of the peak of the first one is quite intense while the maximum temperature of the reaction of the second one is reduced, so we have two opposite phenomena. This is explained by the corresponding mineral concentration. It should be noted that the mineral content is 40.7% for Z₄ and 49.7% (**Mokhlis .H; July 2014**) for Z₃, so the mineral composition also has an influence on the reactivity even though we have not yet reached the decomposition range of the latter.

We move on to the Z₁ (Maestrichtian, warm climate) and Z₂ (Senonian; cold climate) layers, the Z₂ layer is quite reactive given the position of T_{max} while the DTG peak is large for Z₁, we note that the dolomite concentration is quite high (**Mokhlis .H; March 2014**) for Z₁, this reverses the position of T_{max} of the decomposition as dolomite is a more stable compound in the solid state.

Study of the surface of DTG peaks during hydrotreating of different shale samples:

The stages of the geological eras of sedimentation succeed each other with a rather high influence on each other. In the Turonian (Z₃), in the secondary, pyrolysis occurred in situ (**Malal.A; 2009**), since the temperature was high, but this does not prevent the consequences on the layer before (Z₄), which was formed in the stage before (Cenomanian), hence its sensitive reactivity.

We will try to give a suitable order concerning the surface dimension of the DTG peaks depending on the climate and sometimes on the composition of the mineral matter stored within a given layer. The following table gathers the dimension of the surfaces in mm² of the various DTG peaks for the five layers according to the three heating rates.

Table 3:- DTG peak area of different samples at different heating rates.

θ (°C/min) DTG peak area	9°C/min	15°C/min	21°C/min
Z ₁	55,56	66,67	66,67
Z ₂	66,67	44,44	33,33
Z ₃	144,44	177,67	155,56
Z ₄	100	111,11	133,33
Ti	77,78	77,78	100

The heating rate increases the DTG peak surface area in contrast to the reactivity decreases, for the Z₂ layer the surface area decreases when the heating rate increases, this is due to the low organic matter concentration (cold sedimentation climate).

Concerning the Z₃ layer, we observed a fluctuation in the order of the surface area of the peak, in fact this layer is subject to in situ pyrolysis and it is formed especially by light organic matter (**Amal.M;2010**).

As for the comparison of different layers, we will discuss the mutual effects two by two. For the layers Z₁ and Z₂, Z₁ and Z₃, Z₁ and Z₄, Z₂ and Z₃ as well as Z₂ and Z₄ the surface area increases and so does the reactivity.

We have noticed that the previous order does not apply to the Z₃ and Z₄ layers for the simple reason that these layers have undergone pyrolysis in situ (Turonian, Cretaceous) (**Malal.A; 2009**), in fact the Z₃ layer has only light organic matter and the reaction is accelerated hence the area of the DTG peaks is high.

Conclusion:-

The thermogravimetric analysis and its derivative (DTG) are used to identify the reactivity of organic matter in oil shale of different layers of Tarfaya and layer M of Timahdit (for comparison) during the reaction of hydro treating (hydrogen flow) according to several parameters such as the heating rate, the concentration of organic and mineral matter, Tmax of the DTG peak and the surface area of these peaks

From the observation and analysis of the curves DTG=f(Tmax) we could notice that when the heating rate increases from 9 to 21°C/min passing by 15°C/min the reactivity of the organic matter decreases and the temperature of the reaction stage increases as well as the DTG peak.

We were able to compare the five samples by DTG by plotting the maximum temperature of these peaks, and we deduced that hydrogen plays a very important role in the reaction, it decreases the maximum temperature of the DTG peak it is the case between the Z₄ layer and the M layer of Timahdit whose difference going from 60°C (under nitrogen) (**Attaoui.A et al; 1992**) to 8°C (under H₂) this is due to its reactivity. It was also deduced that the concentration of mineral matter in general and dolomite have reversed the statistical order of reactivity concerning the layers Z₃, Z₄ and Z₁, Z₂.

We were able to determine the surface area of the DTG peaks and we found that the heating rate increases the surface area except in the case of the Z₂ layer this is due to the low concentration of organic matter and the case of the Z₃ layer where there is a fluctuation in the order which is explained by its composition of light organic matter although it is the layer with the highest concentration of this material (**Amal.M; 2010**).

Comparing the different samples by discussing the mutual effects two by two for the layers Z₁ and Z₂; Z₁ and Z₃; Z₁ and Z₄; Z₂ and Z₃; Z₂ and Z₄ the surface area increases and the reactivity likewise, we could notice that this order does not apply in the case of the layers, Z₃ and Z₄ this is due to the phenomenon of in situ pyrolysis which is presented in these layers.

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