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RESEARCH ARTICLE

Activation energies by Coast-Redfern approximations of the mineral matter hydropyrolysis for the Tarfaya oil shale (Morocco). Modeling to obtain these energies for the different layers in non-isothermal.

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Abstract

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The hydropyrolysis of inorganic (or mineral) material is also important because most inorganic compounds in the presence of hydrogen form hydrides which are also fuels. In this work, we were interested in heterogeneous kinetics under a dynamic (non-isothermal) regime, with selected heating rates of 21°C/min, 15°C/min and 9°C/min. The oil shale layers studied, Z0, Z1, Z2, Z3 and Z4, come from the Tarfaya deposit (Morocco). The microthermobalance is the Red-Croft **(A.Attaoui et al: 2022)**. In the dynamic regime, several application models are considered, and we adopted the Coast-Redfern approximation to arrive at the activation energies for this reaction. This model enabled us to find these activation energies for the Z2 and Z3 layers for the heating rate of 21°C/min. A development of approach was adapted using also the values of the DTG found in coupling with the TG of the Red-Croft to determine the activation energies of all the layers of the deposit and at all the heating rates.

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Introduction:-

The mineral matter in oil shale is made up of several compounds, most notably carbonates such as calcite and dolomite, which form hydrides in the presence of hydrogen. The heterogeneous chemical kinetics for these reactions is conveniently calculated by applying mathematical models to arrive at activation energies. Several models have been cited previously and are attributed to their authors.

In the non-isothermal regime, several mathematical models have been put forward by authors **(A.W.CoastandD.P.Redfern: 1964, Z.S. Freeman and B. Carroll: 1952, D.B. Anthony and J.B. Howard: 1976, H.L.Friedman: 1965, S.M. Shin and H.Y. Sohn; 1980, M. Suziki et al: 1980)** as well as the extension of Arrhenius'law, for the evaluation of kinetic parameters. Let us recall that all these models have the Arrhenius law as theirmathematical basis and according to the approximate form of its resolution, we obtain the different laws mentionedandwhichareattributedtotheirauthors.Theauthors**(LeeandBeck:1984)**madesomedevelopments andapproximationsbytheintegralmethodandwhichwereproposedearlierbytheauthors**(V.M.Gorbachev:1976,R.K. Agrawal, et al: 1987)** made in the same vision by their approximations, the authors **(S.V. Vyazovkin et al:1987)** made a method of approach, they noted that the nontraditional method gives great information that thetraditional one.

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Authors **(J.E. Cuthrell et al: 1987)** optimized differential systems into algebraic systems by amethod based on finite collocation elements to algebraic equations in the residual nonlinear model knowing thefactorialandadditivecoefficients.Similarlytheauthors**(Z.Smieszekietal:1988)**usedmethodsforthedeterminationofkinetic constantsand notedthe significanteffectofthemethod onthe estimatesofthe results.

In thiswork, wewill use the Coast-Redfern approximation for twolayers of the Tarfaya deposit, Z2 and Z3. Sinceenergyis an extensive quantity, wewillapply a reduced additive model to access the otherenergies.

1/ Bibliographicstudy

The Tarfaya and Timahdit oil shales contain a verysignificantquantity of CO_2,(26.07% and 20.4%). This quantity of carbondioxidecanbeconvertedintomonoxide in the presence of hydrogenaccording to the equilibrium:
$CO + H_2O \rightarrow CO_2 + H_2$

This reaction, whichis in factequilibrium, has been studied by thermogravimetry**(J.E. Kubshand J.A. Dumesic: 1982).** The displacement of the CO_2/CO equilibrium in the presence of the magnet and under the action of the H_2O/H_2gasestakes place at 623°K. The equilibrium and the kinetic data willbedescribed by tworeversibleoxidation and reductionreactions. Thesetworeactionsallow the transformation mechanism, the measurement of the rate and its expression to bemanagedqualitatively. In addition, the hydrogenation of CO cangivemethane by catalyticreaction [BimetallicMo-Fe. and sulphurisedMo-Cofixed on alumina]. By addingmethane, a significantquantity of dimethylether has been produced**(L.T. Thompson/ 1989).**

The rate of the methanationreaction and itsorderindicatethat the entire surface of the catalystis not saturated by CO, unlike the observations concerningconventional CO hydrogenation. The estimates and analysis of the parametersenable the rate of the methanation stage to bedetermined. The proposedcatalytic cycle allows not only the measurement of methane and heavyhydrocarbons but also the dimethyletherproduced first. The absorption of hydrogencanbeexplained by the mixed gastheory**(D.P. Yalenzuela et al: 1985)**whichisextended to the heterogeneousenergeticreactions HIAS; the latter cause segregation in the composition of the absorbed phase whichallows the production of a concentration gradient and thusfacilitates the diffusion of hydrogen.

As mentionedearlier, oil shale around the world varyaccording to theiroil production capacity and quality. The Green River shale in the western United States, for example, contains a high concentration of hydrogen in relation to organiccarbon and yields a high yieldsimply by decomposingitusing the conventionalprocedureinvolving the use of an inertgas. However, muchother shale thatresemble the Devonian shale in the eastern United States contain a lower concentration of hydrogenthan the Green River shale **(J.C. Janka and R.C. Rex: 1984)**.

This hydrogendeficiencypreventsmuch of the kerogenfrombeingconvertedintohydrocarbons**(J.C. Janka and J.M. Dennison: 1979, R.D. Matews et al: 1981)**. The yieldobtained by conventional shale decompositioncanbeimproved by adding extra hydrogenduring the degradationprocess. This allows more of the kerogen to beconvertedintohydrocarbonsratherthanremaining in the ash as coke.

The effects of hydrogen have been studiedpreviously by authors**(Larsen and Wen: 1967)**who have shownthatdegradationunderhydrogen pressure reduces the H/C ratio in the residue. Otherauthors**(Schlinges and Jess: 1981)** have shownthatusinghydrogencanimprove the Fisher test. The samebeneficialeffects of hydrotreatment have been reported by otherauthors**, (Huntington: 1966), (Tarman et al: 1977), (Weil et al: 1976). (Toreis et al: 1986)** studied the effect of a number of transition metals (Mo, Rn, Pd, Co, Ni, CoMo) on oil shale underhydrogen conditions, and foundthat the presence of thesemetalsdid not affect the kineticorder of kerogendecomposition, but didreduce the activation energy.

Hydrogenreactswith carbonates, and mainlywith calcite, in the decomposition range of organicmatter to form the hydrolite CaH2. Othermineral compounds are alsoattacked by hydrogendepending on their respective thermal decomposition range. These ranges go from 300 to 750°C. **(M. Nadif and A. Attaoui : 2022)**.

- With calcite

$$Ca\,CO_3 Ca\,H_2 + CO2 + 6H_2O \xrightarrow{2} 500 < T < 750°C$$

Hydrolith

- With dolomite

H_2

$Ca (Mg) (CO_3)_2Ca\ H_2 + \xrightarrow{MgH_2} CO2 + 6H_2O$ 500 < T < 750°C

- With kaolinite:

$2Al_2Si_2O_5 (OH)_4 \xrightarrow{H_2}$ [4 $+ 2Al_2Si_2O_7 + Al_2O_3 + 4H_2O$ 300 < T <750°C
onosilane

- With pyrite:

H_2FeS_2 $FeS + \xrightarrow{H_2}$ < T < 600°C

- With magnétite

$Fe_3O_4 + 3H_2S \xrightarrow{H_2} 3FeS + 4H_2O$ 550 < T < 750°C

- With char
  $C (char) + H_2 \rightarrow CH_4$ 550°C< T < 750°C

2/ Experimental study:

2.1:Thermogravimetricanalysis:

Thermogravimetry is the main technique used in this study, preceded by X-ray diffraction. The microthermobalance is called the Red-Croft and is of British origin. It gives thermogravimetry (TG), the thermogravimetric derivative (DTG) and the amplified calorimetric difference (DCA).

The thermo-microbalance is the Red-croft which is a setaram used for thermogravimetric (TG) measurements related to degradation in dynamic regime. It has a resolution of 0.1 µg. In our conditions, it operates between room temperature and 750°C, with different hating rate: 21°C/min, 15°C/min and 09°C/min.

This top-loading thermobalance is easy and safe to use, having no hanging wires or exposed fragile parts. The following picture shows a thermobalance from the Setaram series called Redcroft, which is a flail thermobalance with a compensation system based on a photoelectric source to keep the sample at the same position in the furnace, thus avoiding the temperature gradient due to sample movement in the furnace (Fig.1).

Fig 1:- Photo of thermobalance Red-croft**X-ray diffraction.**

In this study, the phase identification of the shale mineral material was carried out on powder by using a C.G.R (Theta 60) X-ray diffractometer with a copper anticathode of wavelength of 1.54051Å.

The following X-ray spectra correspond to the M layer of Timahdit (Fig.2) and the Z4 layer of Tarfaya (Fig.4):
1st peak, at $2\theta = 20.91$; corresponds to dolomite ($CaMg (CO_3)_2$);
2nd peak, at $2\theta = 23.1$; corresponds to quartz (SiO_2);
3rd peak, at $2\theta = 30.86$; corresponds to calcite ($CaCO_3$).

The main mineral compounds are therefore dolomite, quartz and calcite, which are found in the five samples in slightly different quantities

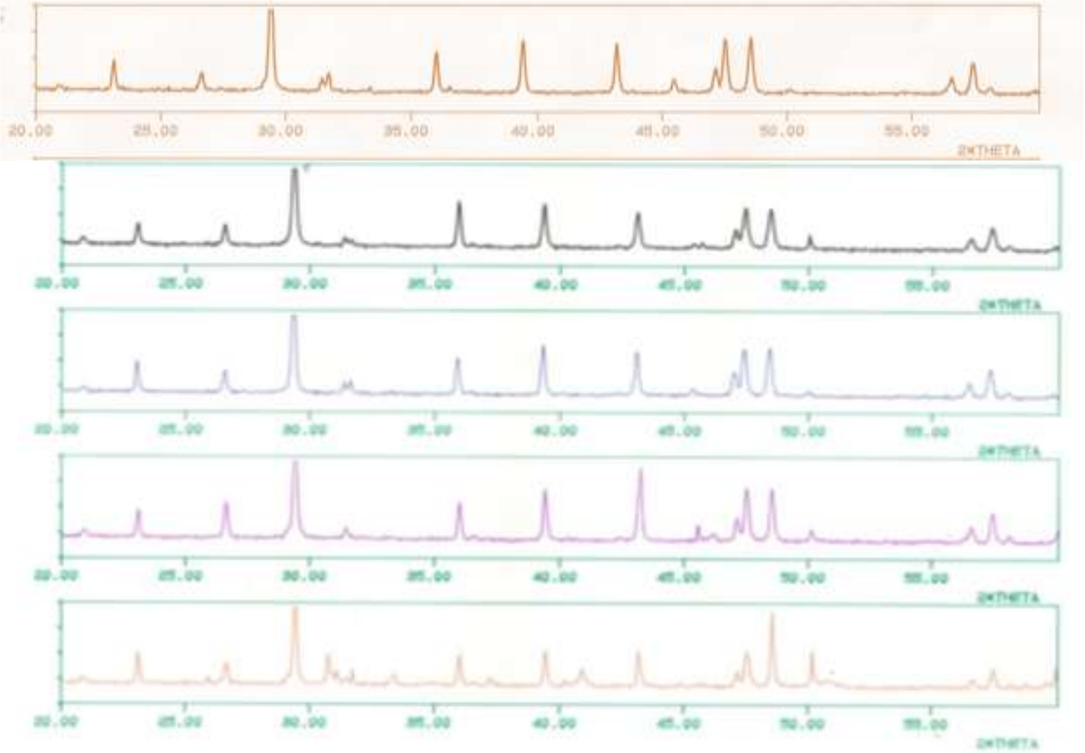

Fig. 2:- X-ray spectra classified from bottom to top of the Z0, Z1, Z2, Z3 and Z4 layers of Tarfaya oil shale.

2.3: Thermogravimetric results.

The following experiments were carried out in a dynamic thermal regime at three heating rates of 9, 15 and 21°C/min up to 750°C in a hydrogen atmosphere (PH2 = 1atm, flow rate = 20 cm^3/min) on samples with a particle size of 0.25 mm and a mass of approximately 15 mg. The thermograms obtained for samples from zones 0, 1, 2, 3 and 4 of the Tarfaya deposit are shown in figures 3, 4 and 5, expressed in $\Delta m/mo = f(T)$ for each heating rate. Figure 6 also shows the degradation under hydrogen for samples Z2 and Z3, expressed as

$\Delta m /mo = f (T)$ at each heating rate. In all the figures we observe three distinct regions of mass loss, as in the case of pyrolysis:
*a first slight loss related to the departure of water and volatile gases,
*a second loss relating to the degradation of organic matter (a stage known as primary hydropyrolysis)
***and then a third loss relating to the decomposition of carbonates.**

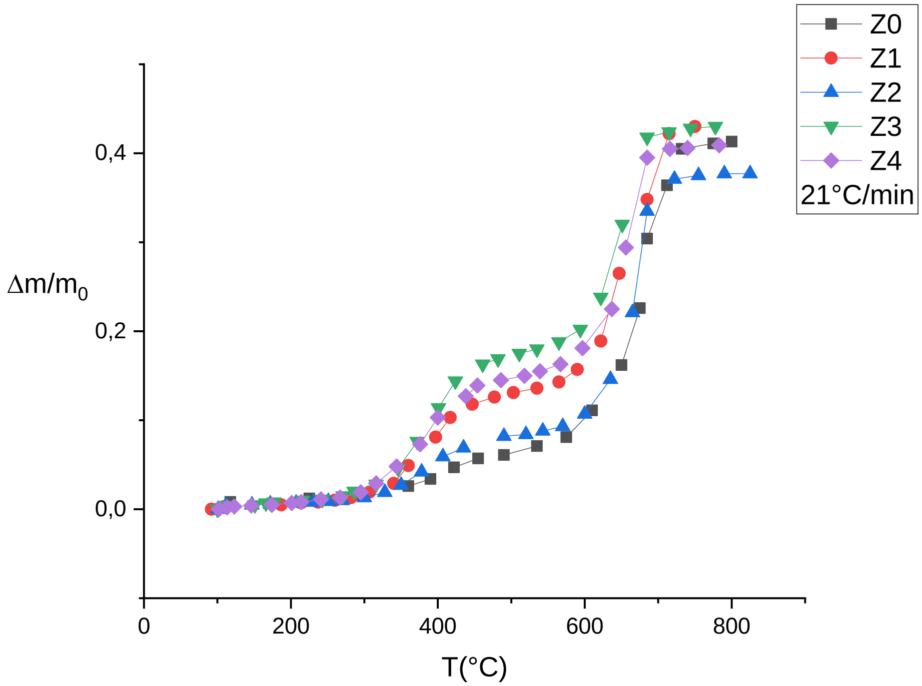

Fig 3:- Decomposition of oil shale in $\Delta m/m_0$=f (T) into hydrogen carrier gas of the different layer of Tarfaya (Θ=21°C/min).

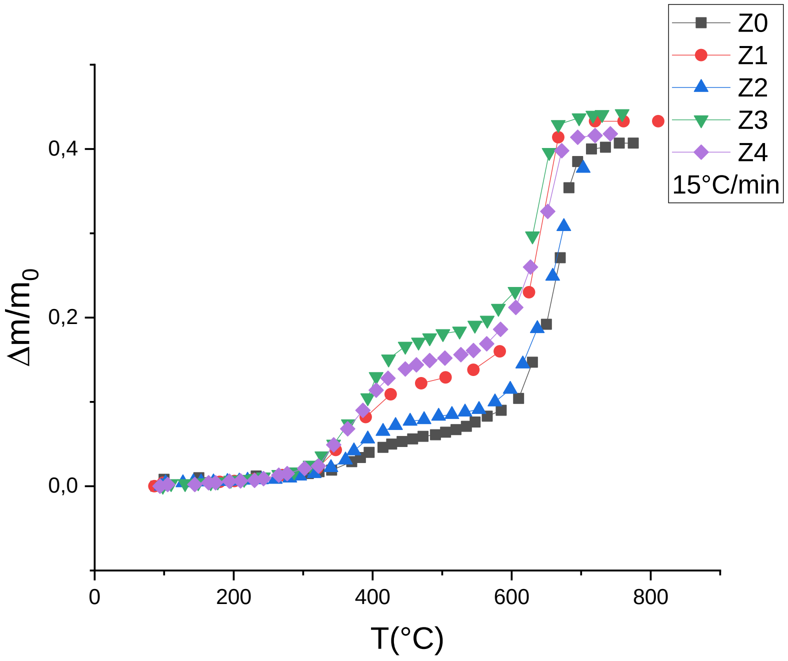

Fig 4:- Decomposition of oil shale in $\Delta m/m_0$=f (T) into hydrogen carrier gas of the different layer of Tarfaya (Θ=15°C/min).

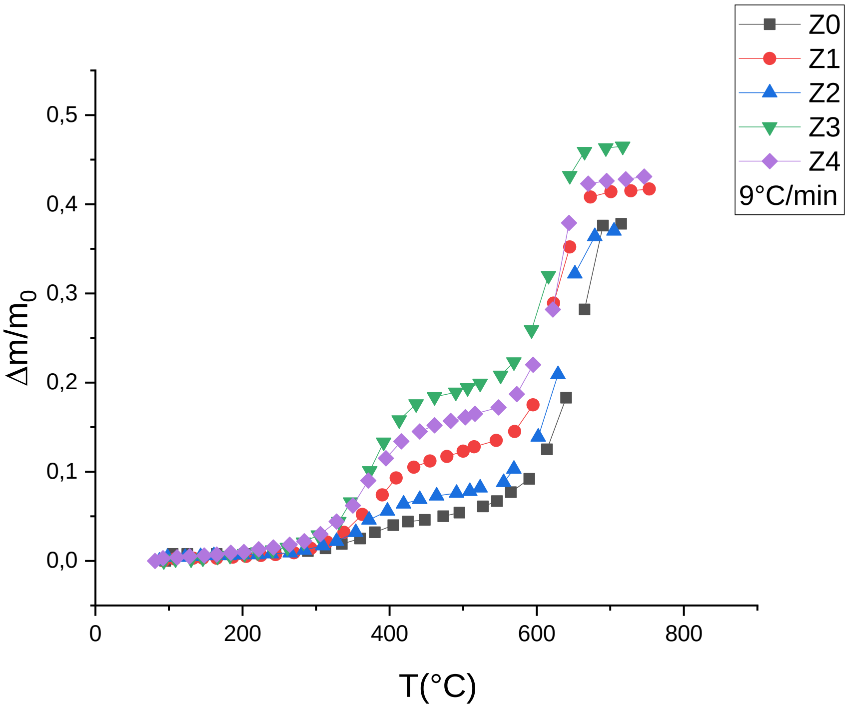

Fig 5:- Decomposition of oil shale in $\Delta m/m_0$=f (T) into hydrogen carrier gas of the different layer of Tarfaya (ϴ=21°C/min).

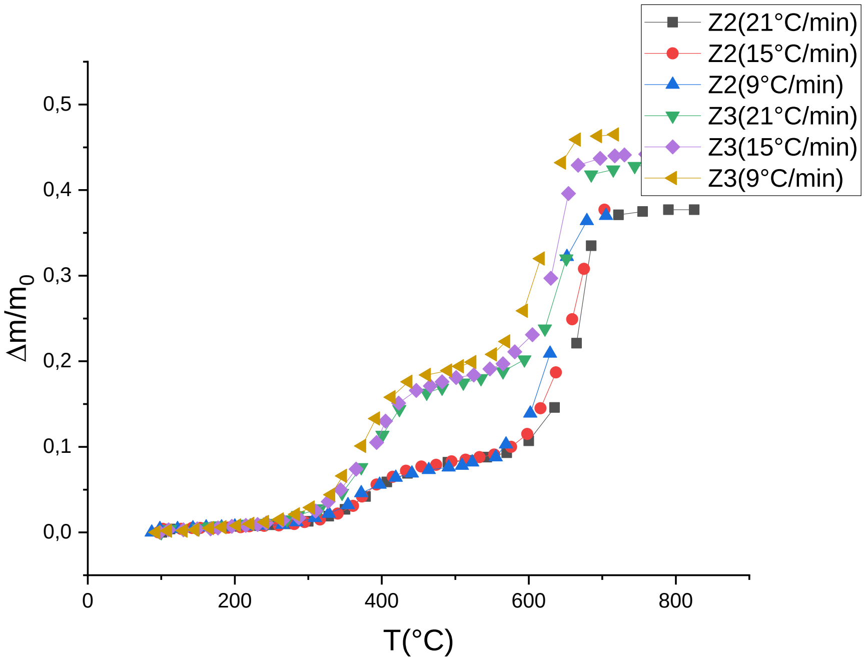

Fig 6:-Decomposition of oil shale in $\Delta m/m_0$=f (T) into hydrogen carrier gas of Z2 and Z3 layers of Tarfaya at different heat rate (ϴ=21°C/min, ϴ=15°C/min and ϴ=9°C/min)

In the following table we present the remarkable characteristics given by thermogravimetry:

Table1:- Percentage loss and temperature of the DTG peak for each sample during the reaction.

Heating rate (°C/min)	**Characteristics**	**Samples**				
	origin	Tarfaya				
	Zone	Z_0	Z_1	Z_2	Z_3	Z_4
21	Percentageloss	33	29,4	28,7	25,3	25,1
	DTG peaktemperature (°C)	-	717	704	677	669
15	Percentageloss	33,6	30,6	29,2	26	26
	DTG peaktemperature (°C)	-	680	673	657	663
09	Percentageloss	31,7	29,1	28,8	27,1	26,5
	DTG peaktemperature (°C)	-	666	651	642	647

In Figure 7 below, we represent the part concerning the decomposition of the mineral matter, with α the degree of progress of the reaction

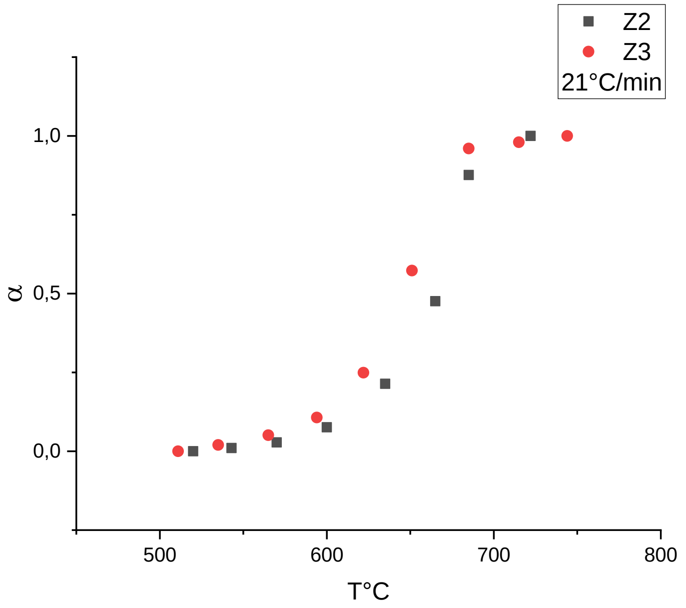

Fig 7:-Decomposition of oil shale in α=f (T) into hydrogen carrier gas of Z2 and Z3 layers of Tarfaya at heat rate ϴ=21°C/min.

By analyzing we obtain the values of α=f (T) of the mineral part for Z2 and Z3 at the heating rate of 21°C/min.

Z2

α	T (°C)
0	525
0,04	550
0,11	575
0,18	600
0,38	625
0,76	650
0,95	675
1	700

Z3

α	T (°C)
0	525
0,05	550
0,12	575
0,31	600
0,53	625
0,88	650
0,99	675
1	700

2.4: Coast-Redfermethod:

In this work, a mathematical method is presented to arrive at kinetic constants and to choose the mechanism that best fits with the experimental results and that will take into account the physical and chemical reality of the system studied. This method is the Coats-Redfern method:

The rate equation for the decomposition reaction is expressed as:
$d\alpha /dt = ko\ (1-\alpha)^{n}\ e^{-E/RT}$(1) with $Koe^{-E/RT}$ the Arrhenius constant
or
$d\alpha/dT = ko\ (1- \alpha)^{n}\ e^{-E/RT} /\theta$
The total variation of α as a function of temperature will be:
$F (\alpha) = d\alpha / (1-\alpha)\ n = ko\ e^{-E/RT}dT /\theta$(2)
If x= E/RT, the integration of the second member of equation (2) gives the exponential integral function
$p(x) = \int_{x}^{\infty} e^{-x}/x^{2}dx$. This integral can be calculated for each value of x. However, to avoid the long calculations that this would cause, many authors have given approximate forms of this function. Coats-Redfern gave a form that is based on the asymptotic expansion of p(x) and is easier to use. This series expansion gives:
$\int^{\infty}e^{-x}\ x^{-b}\ dx \sim x^{1-b}\ e^{-x}\sum\ (-1)^{n}\ (b)^{n}/x^{n+1}$ (3)
The latter leads to expression (4) by integrating the first member of equation (2).
$1-(1- \alpha)^{1-n}/ 1-n\ = k_{0}RT^{2}\ (1-2RT/E)\ \exp (-E/RT)/\theta E$ pour $n \neq 1$
or (4)
$-Ln (1- \alpha) = koRT^{2}(1-2RT/E)\ \exp(-E/RT) /\theta E$ pour n=1
It is therefore possible to determine the value of the apparent activation energy from the slope of the line by plotting:
$Ln [-Ln (1 - \alpha)/T^{2}] = f (1/T)$ pour n = 1
or (5)
$Ln [1-(1 - \alpha)^{1-n}/T^{2}(1-n)] = f (1/T) = f (1/T)$ pour $n \neq 1$
To arrive at the activation energies we use order 1 **(A.Attaoui: 2023)** and adopt the first equation:
$Ln [-Ln (1 - \alpha)/T^{2}] = f (1/T)$ pour n = 1

2.5: Activation energies for the decomposition of mineral matter under H_2 in non-isotherm (ϴ=21°C/min)

The calculations to be made using the Coast-Redfern equation for n=1 and for a heating rate of 21°C/min can be found in the following tables:

Table 2:- Calculs by Coast- Redfern for Z2 layer.

$(1-\alpha)$	1/T	$1/T^2$	$\frac{-\ln(1-\alpha)}{T^2}$	$-\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$
0,96	1,22 10^{-3}	1,48 10^{-6}	0,0604 10^{-6}	16,6
0,89	1,18 10^{-3}	1,39 10^{-6}	0,162 10^{-6}	15,6
0,82	1,15 10^{-3}	1,31 10^{-6}	O,26 10^{-6}	15,2
0,62	1,11 10^{-3}	1,24 10^{-6}	0, 593 10^{-6}	14,3
0,24	1,08 10^{-3}	1,17 10^{-6}	1,67 10^{-6}	13,3
0,05	1,05 10^{-3}	1,11 10^{-6}	3,325 10^{-6}	12,6

Table 3:- Calculs by Coast- Redfern for Z3 layer.

$(1-\alpha)$	1/T	$1/T^2$	$\frac{-\ln(1-\alpha)}{T^2}$	$-\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right)$
0,95	1,22 10^{-3}	1,48 10^{-6}	0,076 10^{-6}	16,4
0,88	1,18 10^{-3}	1,39 10^{-6}	0,178 10^{-6}	15,5
0,69	1,15 10^{-3}	1,31 10^{-6}	0,486 10^{-6}	14,5
0,47	1,11 10^{-3}	1,24 10^{-6}	0,936 10^{-6}	13,9
0,12	1,08 10^{-3}	1,17 10^{-6}	2,48 10^{-6}	12,9
0,01	1,05 10^{-3}	1,11 10^{-6}	5,117 10^{-6}	12,2

We show the figures $y = -\ln\frac{(-\ln(1-\alpha))}{T^2} = f(1/T)$ for the two layers

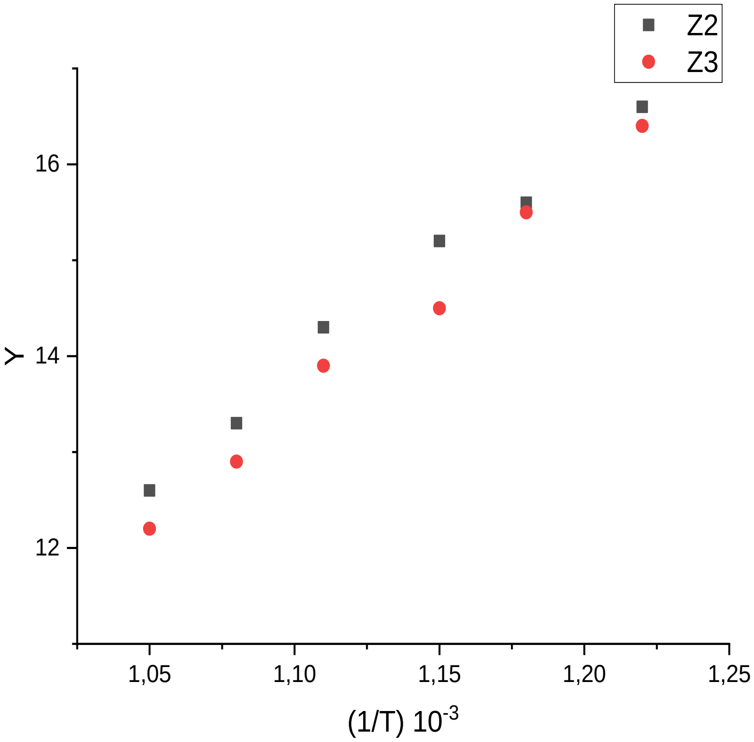

Fig 8:- Linearization according to Coast-Redfern for an order n=1 for the two layers Z2 and Z3.

A simulation of the experimental values was carried out to obtain the activation energies

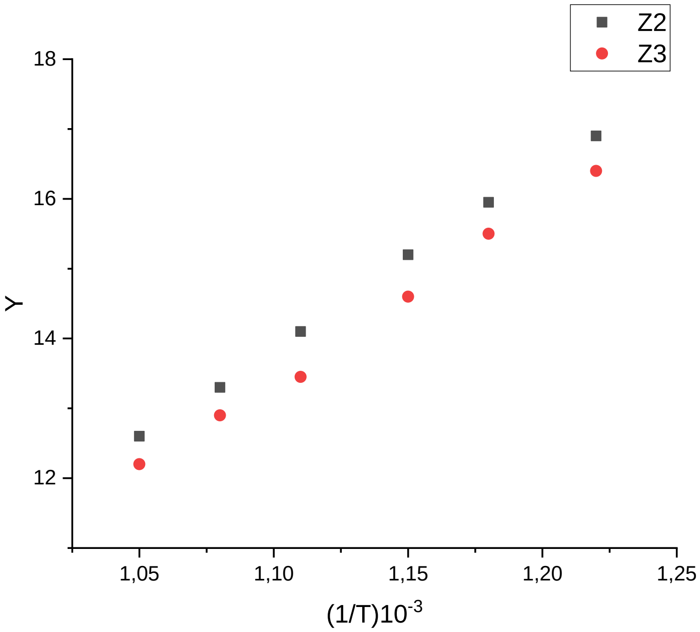

Fig 9:- Linearisation according to Coast-Redfern after simulation for an order n=1 for the two layers Z2 and Z3.

Taking the equation $y= -\ln(\frac{-\ln(1-\alpha)}{T^2}) = f(1/T)$ according to Coast-Redfern approximations for n =1. The slope is equal to E/R and the intersection with the ordinate axis is: -ln (koR (1-2RT/E)) assuming again that this value is a constant according to Coast-Redfern despite containing temperature as a value. We end up with activation energies as follows:

Sample	Ea (kj/mole)
Z2	211,46
Z3	196,19

A certain reactivity for the Z3 layer relative to Z2 is noted, this is quite obvious since the Z3 layer was formed at the geological stage with a warm climate which is the Turonian whereas the Z2 was formed at the geological stage Senonian whose climate was cold **(Ahmed Malal, Doha Lahmadi and bdeljabbar.Attaoui : 2022)**.

2.6: Modelling to obtain the activation energies for the other layers and at the three heating rates.

The Coast-Redfern equation can be applied using several approximations. For order n=1 we have :
$-\text{Ln}(1-\alpha) = k_oRT^2 (1-2RT/E) \exp(-E/RT) / \Theta E$ for n=1
We go to -Ln and this becomes:
$-\text{Ln}(-\text{Ln}((1-\alpha) / T^2)) = -\text{Ln}(k_oR(1-2RT/E) / \Theta E) + E/RT$ so it is a straight line of the form
$y = px + k$
with :
$y= -\text{Ln}(-\text{Ln}((1-\alpha) / T^2))$
$p= E/R$
$x= 1/T$ and
$k=-\text{Ln}(k_oR(1-2RT/E) / \Theta E)$
Coast-Redfern consider that the term $k=-\text{Ln}(k_oR(1-2RT/E) / \Theta E)$ is a constant even though it depends on T.
Since energy is an extensive quantity, and since the second term of the Coast-Redfern equation is a constant, we will look for the quantity of energy at maximum velocity, i.e. at the temperature of the DTG peak, which we will call $E_{1/2}$ since α at this temperature (DTG) is equal to 1/2, so :
$E_{Total} = E_{1/2} + E_S$
$-\text{Ln}(-\text{Ln}((1-0,5) / T^2_{(DTG)}) =-\text{Ln}(k_oR(1-2RT/E) / \theta E) + E1_{/2} /RT_{(DTG)}$
or
$-\text{Ln}(-\text{Ln}((1-0,5) / T^2_{(DTG)}) = E_{1/2} /RT_{(DTG)} + k$
$E_{1/2} =RT_{(DTG)}(-\text{Ln}(-\text{Ln}((1-0,5) / T^2_{(DTG)}) - k)$
At the DTG peak, the constant k is assumed to be negligible:
$E_{1/2} =RT_{(DTG)} (-\text{Ln}(-\text{Ln}((1-0,5) / T^2_{(DTG)})$
We will calculate $E_{1/2}$ and knowing the total energy given by the slope according to the Coast-Redfernlinearisation

We'll do the calculation for the Z2 layer (21°C/min)
$E_{Total} =211,46$ kj/mole
$E_{1/2}= (-\text{Ln}-\text{Ln}(0,5) + \text{Ln}\, T^2_{(DTG)})\ RT_{(DTG)}$
In table 1:$T_{(DTG)} = 704$ °C= 977°K
$E_{1/2} = (0,3665 + 13,76) \times 4,18 \times 2 \times 977 =115,38$ kj/mole
$E_{Total} = E_{1/2} + E_S$
hence
$E_S = 211, 46 – 115, 38 =96, 08$kj/mole

We'll do the same calculation for the Z3 layer (21°C/min)
$E_{Totale} = 196,19$ kj/mole
$E_{1/2}= (-\text{Ln}-\text{Ln}(0,5) + \text{Ln}\, T^2_{(DTG)})\ RT_{(DTG)}$
At le table 1 : $T_{(DTG)} = 677$ °C= 950°K
$E_{1/2}= (0,3665 + 13,71) \times 4,18 \times 2 \times 950 =111,8$ kj/mole
$E_{Totale} = E_{1/2} + E_S$
Where
$E_S = 196,19 – 111,8 =84,34$kj/mole
We will use this energy depending on whether we have a cold climate (Z0 and Z2)

E_S = 96.08 kj/mol
Similarly, we will use this energy in hot climates (Z1, Z3 and Z4)
E_S = 84,39kj/mole

For a cold climate (Z0 and Z2)
Total E = ($E_{1/2}$ + 96.08)kj/mol
For a warm climate (Z1, Z3 and Z4)
Total E = ($E_{1/2}$ + 84,39) kj/mol
In the following table, we have calculated the total activation energies for the layers at different heating rates (except for the Z0 layer where the thermobalance did not indicate the temperature $T_{(DTG)}$), by applying the form $E_{1/2}$=(-Ln-Ln (0.5) + Ln $T^2_{(DTG)}$) $RT_{(DTG),}$ given the temperature values in Table1.

Table 4:- Activation energy for different layers at different heating rate.

Heating rate (°C/min)	**Characteristics**	**Samples**				
	origin	Tarfaya				
	Zone	Z_0	Z_1	Z_2	Z_3	Z_4
21	DTG peaktemperature °C	-	717	704	677	669
	Activation energy (kj/mole)	-	201,64	211,46	196,19	195,11
15	DTG peak temperature °C	-	680	673	657	663
	Activation energy (kj/mole)	-	196,62	207,33	193,52	194,33
09	DTG peak temperature °C	-	666	651	642	647
	Activation energy (kj/mole)	-	194,81	204,43	191,48	192,22

Figure 10 below shows these activation energies as a function of the layers in the deposit. Note that the Z0 layer is not shown because there are no DTG peaks in this layer:

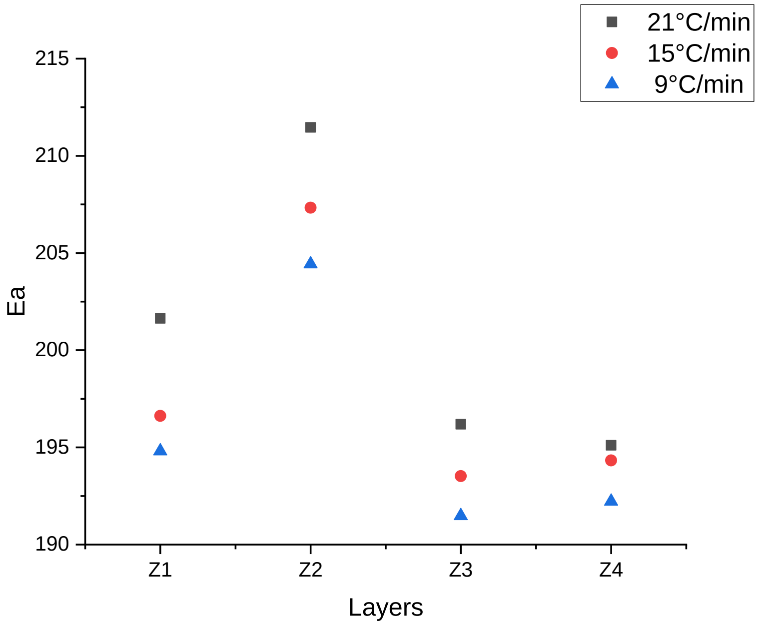

Fig 10:- Activation energies in function of different layers for Tafaya deposit at different heating rate.

We note the high reactivity of the Z3 and Z4 layers, which were formed in the Turonian and Cenomanian geological stages, with their warm Upper Cretaceous climates.

These layers were subjected to pyrolysis in situ **(Ahmed Malal, Doha Lahmadi and bdeljabbar.Attaoui: 2022)**.

Conclusion:-

The hydropyrolysis stage of the decomposition of inorganic matter is as important as the primary hydropyrolysis (decomposition of organic matter under hydrogen) since during the former many fuels are formed in the form of hydrides in the presence of hydrogen.

Accessing the activation energies for this reaction requires us to choose suitable approach equations. In true thermogravimetry (also called thermogravimetry in dynamic regime or in isothermal name) several models are presented, we chose the equations of Coast-Redfern.

The order of this reaction was studied in a previous article **(A.Attaoui : 2023)** it is of the order of one, the representative equation for this model being :

$-\text{Ln}\,(1-\alpha) = koRT^2(1-2RT/E)\,\exp(-E/RT)\,/\theta E$ pour n=1

To get the energy, all we have to do is log this equation by moving T^2 to the first term:

$-\text{Ln}\,(-\text{Ln}\,(1-\alpha)/T^2) = -\text{Ln}\,(koR(1-2RT/E)/\theta E) + E/RT$

So it's a straight line y = f (1/T) with slope E/R

As an approximation, Coast-Redfern considers the term $-\text{Ln}\,(koR\,(1-2RT/E)/\theta E)$ to be a constant, even though it is temperature-dependent.

We used this model to obtain the energies for the Z2 and Z3 layers at a heating rate of 21°C/min. These energies are 211.46 kj/mole for Z2 and 196.19 kj/mole for Z3.

In order to access the other energies, we applied a model based on the extensivity of the energy. To do this, we assumed that the total energy is the sum of an energy E1/2 when the temperature is that of the DTG peak (maximum transformation rate) and an additional energy E_S: $E_{Total} = E_{1/2} + E_S$

So: at peak DTG energy $E_{1/2} = RT_{(DTG)}\,(-\text{Ln}\,(-\text{Ln}\,((1-0{,}5)/T^2_{(DTG)})$ with the proviso that at this position the Cast-Redfern constant is negligible. We looked for the ES energies for each case (Z2 as a cold climate and Z3 as a hot climate) and found the total energies: E_S = 96.08 kj/mol for Z2 and ES = 84,39kj/mol for Z3.

Using this simple method, given that energy is an extensive quantity, we calculated the other energies:

ϴ (°C/min)	Ea	Z1	Z2	Z3	Z4
21	Activation energy (kj/mole)	201,64	211,46	196,19	195,11
15	Activation energy (kj/mole)	196,62	207,33	193,52	194,33
9	Activation energy (kj/mole)	194,81	204,43	191,48	192,22

Layers Z3 and Z4 were formed during the Upper Cretaceous at the Turonian and Cenomanian geological stages respectively, and were subject to in situ pyrolysis.

The climate of these two stages is a warm climate, more precisely the Turonian climate was the warmest, which shows their high relativities.

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