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RESEARCH ARTICLE

Decomposition of volatile gases and water from Tarfayaoil shale (Morocco) under hydrogen.Behavior in heterogeneous kinetics

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Abstract

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Volatile gases and oil shale water are the first constituents to decompose during hydropyrolysis (H2) in the dynamic regime. In this study we investigated the kinetics of this reaction for these compounds. In addition to TG (thermogravimetry), the Red-Croft (microthermobalance) also provides information on DTG (thermogravimetric derivative).By adopting the resolution of the Coast-Redfern approximation, we have given an approach to the activation energies for volatile gases (Ea_1) and for water (Ea_2). The bituminous layers chosen are the Z2 layer, which formed in the Cretaceous in a cold climate, and the Z3 layer (Cretaceous, Turonin), which formed in the warm climate**(A.Attaoui et al: 2022).**At a heating rate of 21°C/min, we noted for the Z2 layer:Ea (volatile gases)=27.31 kj/mole and Ea (water)=34 kj/mole and for Z3 we noted:Ea (volatile gases) = 27.34 kj/mol and Ea (water) = 32.9 kj/mol.

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Introduction:-

In previous work, we established energy balances for the last two decomposition stages during hydropyrolysis (H_2), i.e. the decomposition of organic matter **(A.Attaoui: 2023**) and that of mineral matter **(A.Attaoui: 2022).**

Methane, butane, propane, etc. are the volatile gases that decompose first at low temperatures, while water evaporates at around 100°C. Normally, volatile gases are detected by gas chromatography.

Four reaction modes have been tested, either for the purpose of studying or exploiting oil shale: pyrolysis, hydropyrolysis, oxidation and gasification. The aim of these techniques is to carry out comparative studies, such as pyrolysis (Fisher test) and hydropyrolysis (Hydroretorting test), or to use them, such as combustion (air oxidation) to produce energy in the form of electricity.

Hydropyrolysis is a technique based on the thermal treatment of shale in the presence of hydrogen, the aim being to improve the extracted oils or to crack organic matter in order to produce gas.

In this work we will focus on the first stage, i.e. the decomposition of volatile gases and water under hydrogen, and follow the kinetics of this reaction to access the activation energies.

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1/ Literature Review:-

The volatile products were the subject of gas chromatographic tests in the case of Timahdit and on a Porapak Q column at 40°C **(M. Ferhat and A. Saoiabi: 1983, A. Saoiabi: 1982).** The gases detected by this technique correspond to the departure of the following gases and in the order indicated: O2, CH_4, C_2H_4, H_2S, H_2O and C_2H_2. The heaviest gases were analysed on a SE 30 silicone column at 20°C and the gases detected were CH_4, C_2H_2, C_2H_4 and C_6H_6. A C_3 peak containing propene was also noted. Among the gases detected was H_2S, which comes from the decomposition of complex organic matter and pyrite (FeS_2) contained in the shale. The latter was the subject of a study by Eugène R. Bissel**(E.R. Bissell: 1983**) using a method based on the reduction of sulphide derivatives by hydrogen in the presence of molybdenum sulphide as a catalyst.

The rate of the methanation reaction and its order indicate that the entire surface of the catalyst is not saturated by CO,unliketheobservationsconcerning conventionalCOhydrogenation.Theestimandanalysisoftheparameters enable the rate of the methanation stage to be determined. The proposed catalytic cycle allows not only themeasurementofmethaneandheavy hydrocarbonsbutalsothedimethyl ether producedfirst.Theabsorptionofhydrogen can be explainedbythemixedgas theory **(D.P.Yalenzuelaetal:1985)** which is extendedtotheheterogeneous energetic reactionsHIAS;thelattercausesegregationinthecompositionoftheabsorbedphasewhich allowstheproductionofaconcentrationgradientandthus facilitatesthediffusionofhydrogen.

Asmentionedearlier,oilshalearoundtheworldvaries accordingtotheiroilproductioncapacityandquality.TheGreenRiver shale in the western United States, for example, contains a high concentration of hydrogen in relation toorganiccarbonandyieldsahighyieldsimplybydecomposingitusingtheconventionalprocedureinvolvingtheuseofaninertgas. However, muchother shale thatresembles the Devonian shale in the eastern United States contains a lowerconcentrationofhydrogenthantheGreenRivershale**(J.C.JankaandR.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 decompositioncanbeimprovedbyaddingextrahydrogenduringthedegradationprocess.Thisallowsmoreofthekerogentobeconvertedintohydrocarbonsratherthanremainingintheashascoke.

Theeffectsofhydrogenhavebeenstudiedpreviouslybyauthors**(LarsenandWen:1967)**whohaveshownthatdegradationunderhydrogenpressurereducestheH/Cratiointheresidue.Otherauthors **(SchlingesandJess:1981)** have shownthatusinghydrogencanimprove the Fisher test. The samebeneficialeffects of hydrotreatmenthavebeenreported 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 underhydrogenconditions, and foundthat the presence of thesemetalsdid not affect the kineticorder of kerogendecomposition, butdidreducetheactivationenergy.

In the non-isothermal regime, several mathematical models have been putforwardbyauthors**(A.W.Coast and D.P.Redfern: 1964,Z.S.Freemanand B. Carroll:1952, D.B.Anthonyand J.B.Howard: 1976,H.L.Friedman:1965,S.M.ShinandH.Y.Sohn;1980,M.Suzikietal:1980)**aswellastheextensionofArrhenius'law,for theevaluationofkineticparameters.Letusrecall thatall thesemodelshavetheArrheniuslawastheir mathematicalbasisandaccordingtotheapproximateform ofitsresolution,weobtain the different law mentioned and which are attributed to their authors. The authors **(Lee and Beck: 1984)** made some developmentsandapproximationsby the integral method and which were proposed earlier by the authors**(V.M.Gorbachev:1976,R.K.Agrawaletal:1987)**madeinthesamevisionbytheirapproximations,theauthors**(S.V.Vyazovkinetal: 1987)**madeamethodofapproach,theynotedthatthe nontraditional lmethodgivesgreatinformationthat the traditional one.Authors**(J.E.Cuthrelletal:1987)**optimizeddifferential systemsintoalgebraicsystemsbyamethodbasedon finite collocation elements to algebraic equations in the residual nonlinear model knowingthe factorial and additive coefficients .Similarly the authors **(Z.Smieszeki et al: 1988)** used methods for the determination of kinetic constants and noted the significanteffectof the methodon the estimates of the results.

2/ Experimental techniques

2.1: Thermogravimetry

The thermal analysis technique of thermogravimetry (TG) is one in which the change in mass of the sample (loss of mass or grain) 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 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.

2.2: Morphology layers (Z2, Z3) before and after hydrotreating(550°C).

The photos shown below have been made by the scanning electron microscope (SEM) in the raw state and after having carried out the hydrogen treatment, i.e. hydropyrolysis in a dynamic regime (21°C/min) under a pressure of one atmosphere.

Scanning electron microscopy (SEM) is a technique based on the analysis of electron-matter interactions. The surface of the sample is subjected to a bombardment of electrons. Some radiation (backscattered electrons, secondary electrons and X-rays) is emitted as a result of the multiple collisions between the electrons that scan the surface and the atoms of the material under test. This radiation is analyzed by different detectors to build an image of the surface and to observe the presence of elements in the analyzed area.

Both samples were examined under the scanning electron microscope. Figures 1 and 3shows the photos of the Z2 and Z3 layers before and figures 2 and 4 after hydrotreating**.**

Fig 1:- Raw Z2 layer.

Fig 2: Z2 layer after hydrotreating. .

Fig 3:- Raw Z3 layer.

Fig 4:- Z3 layer after hydrotreating.

We note the volume contractionforthe hydrotreated Z2 and Z3 sampleswhichbecomesincreasingly apparentas thetemperatureincreasestill 550°C.

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 (PH_2 = 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 2 and 3 of the Tarfaya deposit are shown in figures 5, expressed in Δm/mo = f(T) for each heating rate. Figure 6 also shows the degradation under hydrogen for samples Z2 and Z3, expressed as

Δm /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 volatile gases and water,**

*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.

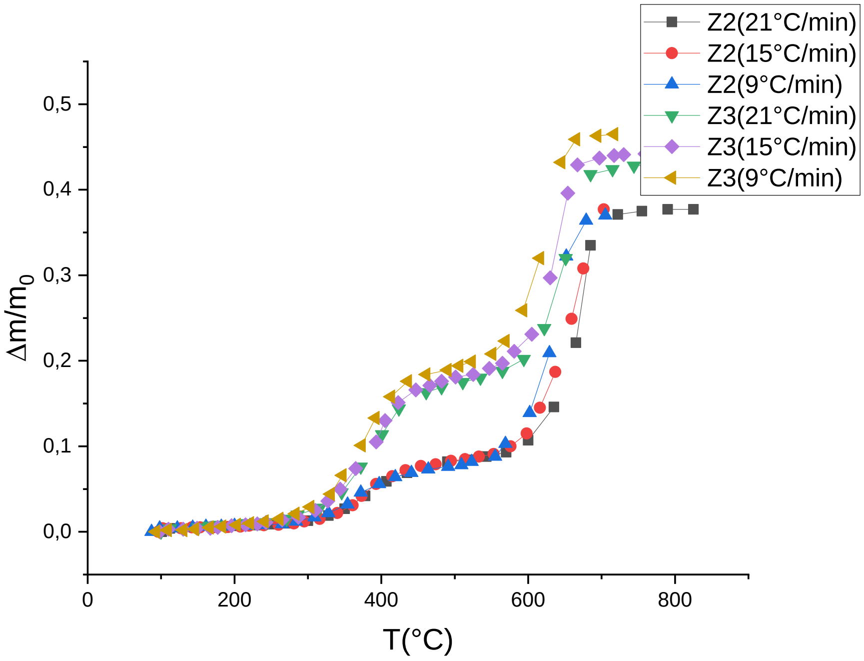

Fig 5:- Decomposition of oil shale in $\Delta m/m_0$=f (T) into hydrogen carrier gas of Z2 and Z3 layers of Tarfaya at different heat rate (ϴ=21°C/min, ϴ=15°C/min and ϴ=9°C/min).

The following table shows the percentages of mass loss for gas volatiles and water during hydrogen degradation and the temperatures of the tow DTG peaks for each sample and for the three heating rates indicated.

Table 1:- Percentage loss of gas volatiles and water likewise the tow DTG peak temperatures for thehydrotreating reaction.

Heating rate (°C/min)	**Characteristics**	**Samples**	
	Origin	Tarfaya	
	Zone	Z_2	Z_3
21	Percentage loss	0,9	1,1
	First peak DTG (°C)	56	58

	Second peak DTG (°C)	113	105
15	Percentage loss	0,96	0,7
	First peak DTG (°C)	45	43
	Second peak DTG (°C)	97	97
09	Percentage loss	0,71	1
	First peak DTG (°C)	36	32
	Second peak DTG (°C)	93	90

Note that the first peak corresponds to volatile gases and the second peak to water.

Figure 6 below shows the first decomposition domain corresponding to the departure of volatile gases and water. It is represented in α = f(T) for the Z2 layer at the three heating rates.

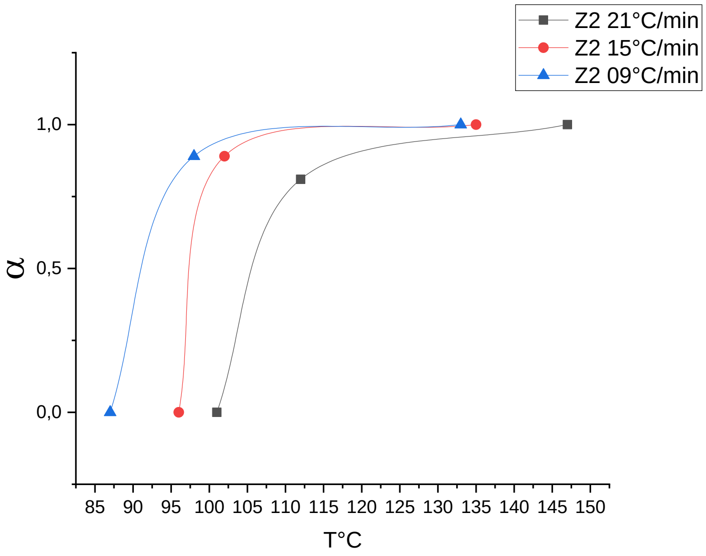

Fig6:-Thermogramsinαofthehydropyrolysisfor theZ2layeratthethreeheatingrates.

Similarly, Figure 7 below shows the first decomposition domain corresponding to the departure of volatile gases and water, represented as α = f(T) for the Z3 layer at the three heating rates.

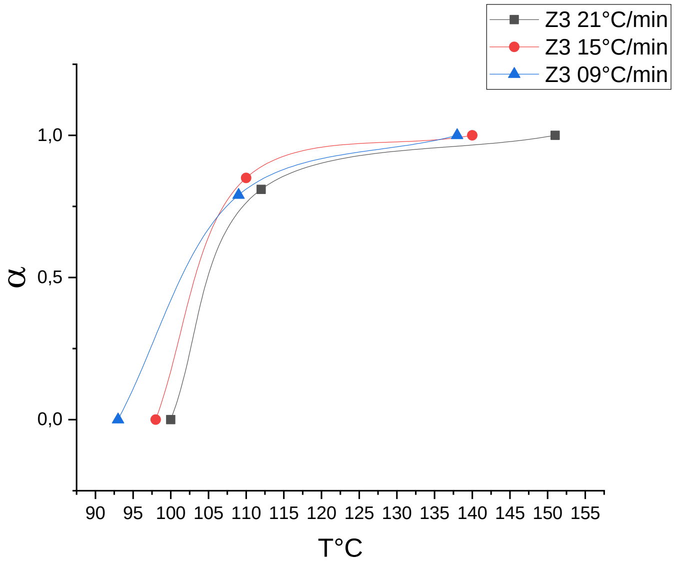

Fig7:-Thermogramsinαofthe hydropyrolysisfor theZ3layeratthethreeheatingrates.

Aslightoffset isfeltduetotheheatingrate.

2.4: AnalysisofthermogramsforZ2andZ3intermsofdegreeofadvancementα(Θ=21°C/min)

The followingtwo tables show the degree of advancement α of hydropyrolysis of volatiles gas and water as a function of temperature:

Z2Z3

α	T°C
0	101
0,77	110
0,91	127
0,95	135
1	147

α	T°C
0	100
0,78	110
0,92	127
0,96	135
1	151

Thefollowingcurverepresentsthesethermogramsofhydropyrolysisinα=f(T)

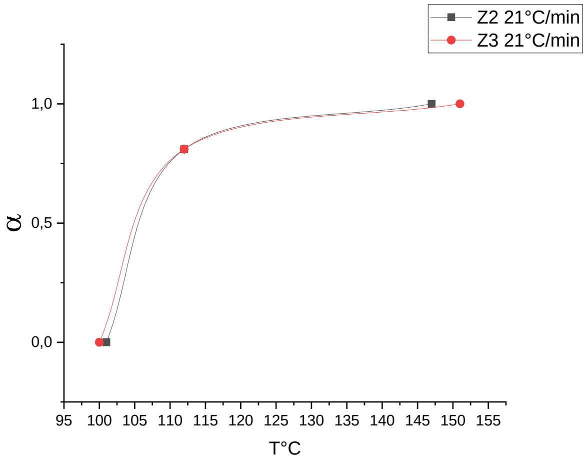

Fig8:-ThermogramsinαofthehydropyrolysisoftheZ2andZ3layersatheatingrateΘ=21°C/min.

2.5: Coast-Redfern method:

In this work,as the last article **(A.Attaoui: 2023)**, 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

$d\alpha/dT = ko\,(1-\alpha)^{n}\, e\text{-}E/RT /\theta$

The total variation of α as a function of temperature will be:

$F(\alpha) = d\alpha / (1-\alpha)\, n = ko\, e\text{-}E/RT\, dT / \theta$ (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).

$1-(1-\alpha)^{1-n}/ 1-n = k_{o}RT^{2}\,(1-2RT/E)\, \exp(-E/RT)/\theta E$ pour $n \neq 1$

(4)

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

It is therefore possible to determine the value of the apparent activation energy from the slope of the line by plotting:

$\mathrm{Ln}\,[-\mathrm{Ln}\,(1-\alpha)/T^{2}] = f\,(1/T)$ pour n = 1

or (5)

$\mathrm{Ln}\,[1-(1-\alpha)^{1-n}/T^{2}(1-n)] = f\,(1/T) = f\,(1/T)$ pour $n \neq 1$

To arrive at the activation energies we use order 1 **(A.Attaoui: 2023)** and adopt the first equation:

$\mathrm{Ln}\,[-\mathrm{Ln}\,(1-\alpha)/T^{2}] = f\,(1/T)$ pour n = 1

2.6: Activation energies for the decomposition of water under hydrogen in non-isothermal (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 and of Z2 and Z3 layers for **volatiles gas and water** can be found in the following tables:

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

$(1-\alpha)$	$1/T$	$1/T^{2}$	$-\frac{\ln(1-\alpha)}{T^{2}}$	$-\ln\left(\frac{-\ln(1-\alpha)}{T^{2}}\right)$
0,23	$2{,}610^{-3}$	$6{,}76\ 10^{-6}$	$9{,}94\ 10^{-6}$	11,52
0,09	$2{,}5\ 10^{-3}$	$6{,}25\ 10^{-6}$	$15{,}05\ 10^{-6}$	11,1
0,05	$2{,}45\ 10^{-3}$	$6{,}0\ 10^{-6}$	$17{,}97\ 10^{-6}$	10,92

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

$(1-\alpha)$	$1/T$	$1/T^{2}$	$-\frac{\ln(1-\alpha)}{T^{2}}$	$-\ln\left(\frac{-\ln(1-\alpha)}{T^{2}}\right)$
0,23	$2{,}610^{-3}$	$6{,}76\ 10^{-6}$	$10{,}23\ 10^{-6}$	11,49
0,09	$2{,}5\ 10^{-3}$	$6{,}25\ 10^{-6}$	$15{,}79\ 10^{-6,}$	11,06
0,05	$2{,}45\ 10^{-3}$	$6{,}0\ 10^{-6}$	$19{,}21\ 10^{-6}$	10,85

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

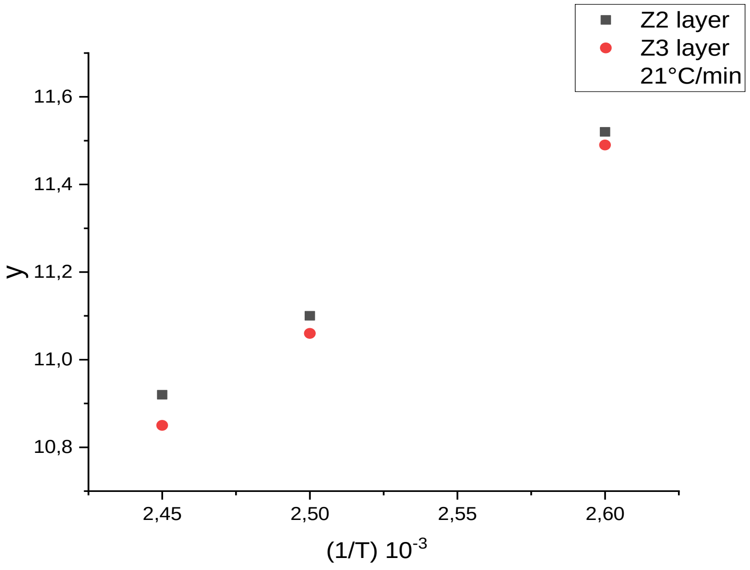

Fig 9:- Linearization according to Coast-Redfern for an order n=1 of the two layers Z2 and Z3for hydropyrolysis of volatiles gas and water.

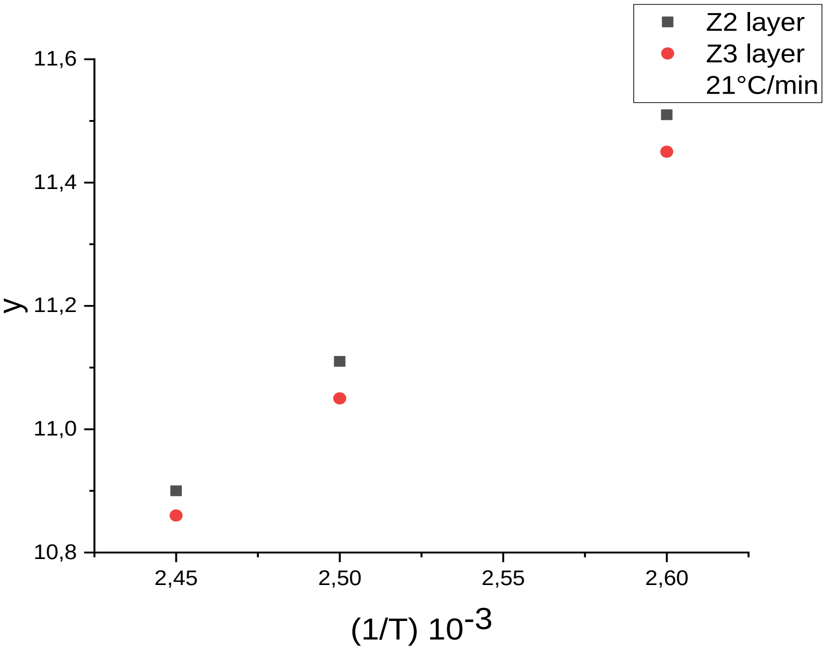

Fig 10:- Linearization according to Coast-Redfern after simulation for an order n=1 of the two layers Z2 and Z3for hydropyrolysis of volatile gases and water.

Taking the equation $y= -\ln\left(\frac{-\ln(1-\alpha)}{T^2}\right) = f(1/T)$ 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:

Samples	Ea (kj/mole)
Z2	34,0
Z3	32,9

By observing the temperature ranges and defining the variation in α as a value greater than 0.77, we can logically assume that these energies correspond to the decomposition of the hydrogenated water contained in the bituminous shale

2.7: Modeling for the extension of the activation energies for volatiles gas and water of the two layers Z2 and Z3 at different heating rates.

Activation energy is an extensive quantity and the Coast-Redfern equation can be applied using several approximations. For order n=1 we have:

$-\mathrm{Ln}\,(1-\alpha) = k_oRT^2\,(1-2RT/E)\,\exp(-E/RT) / \Theta E$ for n=1

We go to -Ln and this becomes:

$-\mathrm{Ln}\,(-\mathrm{Ln}\,((1-\alpha) / T^2)) = -\mathrm{Ln}\,(k_oR\,(1-2RT/E) / \Theta E) + E/RT$ so it is a straight line of the form

$y = px + k$

$y= -\mathrm{Ln}\,(-\mathrm{Ln}\,((1-\alpha) / T^2))$

$p= E/R$

$x= 1/T$ and

$k=-\mathrm{Ln}\,(k_oR\,(1-2RT/E) / \Theta E)$

Coast-Redfern considers that the term $k=-\mathrm{Ln}\,(k_oR\,(1-2RT/E) / \Theta E)$ is a constant even though it depends on T.

As energy is an extensive quantity, and as 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 :

$E_{1/2} =RT(DTG)(-\mathrm{Ln}\,(-\mathrm{Ln}\,((1-0.5) / T^2\,(DTG)) - k)$

At the DTG peak, the constant k is assumed to be negligible:

$E_{1/2} =RT(DTG)\,(-\mathrm{Ln}\,((1-0.5) / T^2\,(DTG)).$

We'll do the calculation for the Z2 layer (21°C/min).
According to Table 1: T (DTG) = 113°C= 386°K
$E_{1/2}$ = (0.3665 + 11,91) × 4.18 × 2 × 386 =39,58kj/mole
Now, when we look for the activation energy of the Z2 layer (Θ=21°C/min) using the slope, we find (previous paragraph)
E_{total} =34,0kj/mole which is an energy lower than $E_{1/2}$
So in this case for organic matter we will assume that
$E_{total} = E_{1/2} - E_S$
E_S is the energy that must be subtracted and is due to the model adopted.
E_S=39,58 – 34,0 = 5,58kj/mole
This energy E_S will be subtracted when we are in a cold climate.
The same reasoning will be used for tick Z3 (21°C/min).
According to Table 1: T(DTG) = 105°C= 378°K
$E_{1/2}$ = (0.3665 + 11,87) × 4.18 × 2 × 378 =38,67kj/mole
Now, when we look for the activation energy of the Z3 layer (Θ=21°C/min) using the slope, we find (previous paragraph)
E_{tota}l =32,9kj/mole which is an energy lower than $E_{1/2}$
So in this case, in the same way as for organic matter, we will assume that
$E_{total} = E_{1/2} - E_S$
E_S is the energy that must be subtracted and is due to the model adopted.
E_S=38,67 -32,9 = 5.77kj/mole
This E_S energy will be subtracted when we are in a warm climate.
For a cold climate Z2
E_{Total} = ($E_{1/2}$ – 5,58)kj/mole
For a warm climate Z3
E_{Total}= ($E_{1/2}$ - 5.77) kj/mole

2.8: Activation energies for the decomposition of oil shale water under hydrogen in the non-isothermal Z2 and Z3 layers according to the chosen model.

The activation energy for the decomposition of oil shale water under hydrogen for the Z2 layer is:
E_{Total}= ($E_{1/2}$ - 5.58)kj/mol for the heating rate of 21°C/min, and we know the temperatures of the DTG peaks, so we can calculate $E_{1/2}$ each time.
For Z3 we have E_{Total}= ($E_{1/2}$ - 5.77) kj/mol. Using all this data, we calculate the activation energy for the waters in Z2 and Z3 at different heating rates:
The expression for $E_{1/2}$ is: $E_{1/2}$ =RT(DTG) (-Ln (-Ln ((1-0.5) / T2 (DTG)) - k)
Similarly, the temperatures T(DTG) are given in Table 1.
For example, for Z2 at 21°C/min we have T(DTG) = 386°K so:
$E_{1/2}$ = (0.3665 + 11.91) × 4.18 × 2 × 386 =39.58 kj/mol
ES =5.58kj/mol
E_{Total}= 39.58 -5.58=34.0kj/mol
According to Table 1, we calculate the activation energies and combine them in the following table:

Heating rate (°C/min)	**Characteristics**	**Samples**	
	Origin	Tarfaya	
	Zone	Z_2	Z_3
21	Percentage loss	0,9	1,1
	Second peak DTG (°C)	113	105
	Activation energy (kj/mole)	34,0	32,9
15	Percentage loss	0,96	0,7
	Second peak DTG (°C)	97	97
	Activation energy (kj/mole)	32,15	31,96
09	Percentage loss	0,71	1
	Second peak DTG (°C)	93	90
	Activation energy (kj/mole)	31,65	31,12

2.9:Activation energies for the decomposition of oil shale water under hydrogen in the non-isothermal Z2 and Z3 layers according to the chosen model.

The range of variation of α for volatile gases and waters coincides in thermogravimetry while the DTG peaks of the two constituents are clearly discernible, so we can always arrive at the activation energies for the decomposition of volatile gases under hydrogen by adopting the same approximation model:

$E_{Total} = E_{1/2} - E_S$

Where E_S differs according to climate.

Heating rate (°C/min)	**Characteristics**	**Samples**	
	Origin	Tarfaya	
	Zone	Z_2	Z_3
21	Percentage loss	0,9	1,1
	First peak DTG (°C)	56	58
	Activation energy (kj/mole)	27,31	27,34
15	Percentage loss	0,96	0,7
	First peak DTG (°C)	45	43
	Activation energy (kj/mole)	26,02	26,6
09	Percentage loss	0,71	1
	First peak DTG (°C)	36	32
	Activation energy (kj/mole)	25,0	24,33

2.10: Activation energies for the decomposition of volatile oil shale gases under hydrogen in the non-isothermal Z2 and Z3 layers according to the chosen model.

The Z3 layer was formed in the Turonian (Upper Cretaceous), which has a warm climate, whereas the climate of the Z2 layer is cold. We would expect to have lower activation energies for the Z3 layer, but this is not the case, which can be explained by the high concentration of organic matter in Z3, which is more than double that of Z2 **(H. Ouajih and A. Attaoui:2022).**

The following figure shows the activation energies of the first two oil shale constituents in the hydrogen decomposition reaction (hydropyrolysis).

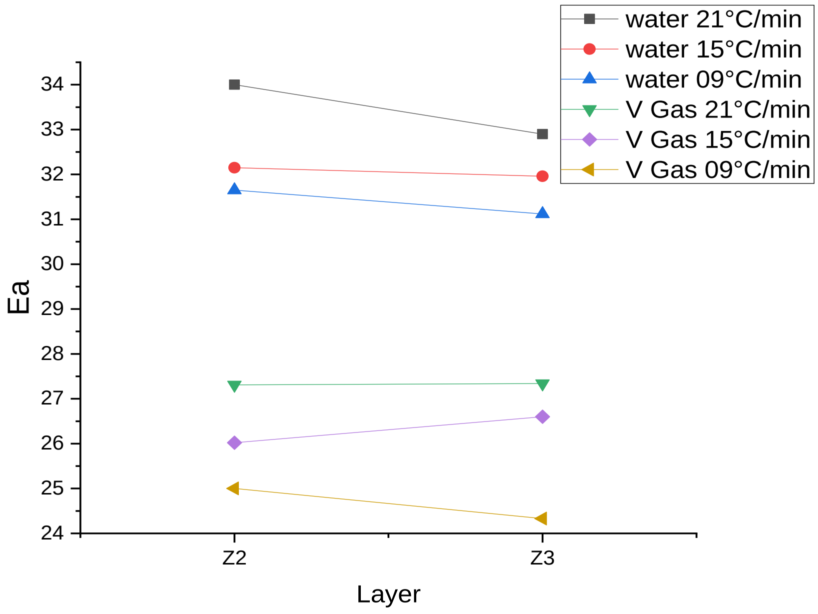

Fig 11:- Activation energies of water and volatiles gas from oil shale in hydropyrolysis reaction at different heating rate.

Conclusion:-

Volatile gases and oil shale water are the first constituents to decompose during hydropyrolysis (H2) in the dynamic regime. In this study we investigated the kinetics of this reaction for these compounds.
Methane, butane, propane, etc., are the volatile gases that decompose first at low temperatures, while the waters then evaporate at around 100°C. Volatile gases are normally detected by gas chromatography.

Discerning these first two constituents of oil shale, i.e. volatile gases and water, is not possible by thermogravimetry using the Red-Croft thermobalance in the temperature range under consideration [ambient-150°C]. Fortunately, the DTG peaks are detectable by the equipment:

By adopting the resolution of the Coast-Redfern approximation, we have given an approach to the activation energies for water (Ea_1) and for volatile gases (Ea_2). The bituminous layers chosen are the Z2 layer, which formed in the Cretaceous in a cold climate, and the Z3 layer (Cretaceous), which formed in the warm climate known as the Turonian.
Energy is an extensive characteristic and the adapted approximation model using the DTG peak temperatures and also combining the Coast-Redfern resolution in the dynamic regime led us to the following equalities:
For a cold climate Z2
$E_{Total} = (E_{1/2} - 5.58)$kj/mol
For a warm climate Z3
$E_{Total} = (E_{1/2} - 5.77)$ kj/mole.

The following table shows the activation energies for the decomposition of volatile gases and water under hydrogen under dynamic conditions.

Heating rate	Activation energy	Z2	Z3
21°C/min	V Gas activation energy (kj/mole) Water activation energy (kj/mole)	27,31 34,0	27,34 32,9
15°C/min	V Gas activation energy (kj/mole) Water activation energy (kj/mole)	26,02 32,15	26,6 31,96
09°C/min	V Gas activation energy (kj/mole) Water activation energy (kj/mole)	25,0 31,65	24,33 31,12

The evolution of these activation energies leads us to the following remarks:
For volatile gases, it is the concentration of organic matter that defines reactivity (21°C/min and 15°C/min).

The Z3 layer, formed during the Turonian period in a warm climate, is the most reactive for the three heating rates.

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