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RESEARCH ARTICLE

Modeling and non-linear mechanisms in heterogeneous kinetics of the non-isothermal pyrolysis or hydropyrolysis for Tarfaya oil shale (Morocco).

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Abstract

The method of analysis to reach the kinetic parameters of pyrolysis or hydropyrolysis in non-isothermal (dynamic regime) has been often discussed to try to approach the reaction mechanisms. Indeed by modifying the method one makes these kinetic parameters vary considerably. Two mechanisms have been presented to discuss these non-isothermal kinetics for pyrolysis under nitrogen and hydropyrolysis under hydrogen, we have the linear mechanism and the non-linear mechanism.The method that was adopted for this work is the Coast-Redfern approximation **(A.W.Coast and D.P.Redfern: 1964)**. We were able to achieve these kinetic parameters and design the appropriate mechanisms for the dynamic pyrolysis and hydropyrolysis of the Tarfaya oil shale (Morocco) for the Z4 layer. It turned out after discussion that it is the non-linear mechanism that fits best with pyrolysis as well as hydropyrolysis in non-isothermal mode. These two reactions are carried out by several simultaneous reactions with a fractional order for the first and an order equal to unity for the latter.

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Introduction:-

The oldest mechanism of pyrolysis dates back to 1950 and was proposed by Hubbard and Robinson (A.B. Hubbard and W.E. Robinson: 1950). These two authors determined the kinetics of oil production in the isothermal regime using a mechanism consisting of two successive stages, all of which are of the first order. Kerogen decomposes into bitumen which subsequently decomposes into oil, gas and residual carbon:

Kerogen → bitumen → oil + gas + C residual

This model is called the linear model. Another author (K.Rajeshwar: 1981) confirms the same non-isothermal regime for the thermal decomposition of the Green River shale. The kerogen decomposes to intermediate bitumen with activation energy of 62.10 KJ/mol and a frequency factor of the order of 10^6 min-1.

However, another author **(V.D.Allred: 1966)**, after examining the Hubbard and Robinson model, indicates a more complex mechanism. Similarly, in a paper, **(K. Rajeshwar and J. Dubow: 1982)** who, in reanalyzing the decomposition kinetic data of the Green River shale in order to model the reaction process, reveal that the decomposition is handled by a more complex mechanism than the first-order mechanism considered by several authors. The reactant-product interface and the effect of diffusion of product gases play a large role in this kinetics,

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and the interaction of the mineral matrix with the kerogen is likely **(B. Spiro: 1991)** to be different for different mineral compounds, oils and regenerated gases.

Authors **(D. Finucane et al: 1977, D.W. Faussett et al:1974, C.S. Wen and T.F. Yen; 1977)** after having taken up the old models, note a rather weak agreement between the calculated and measured value of the bitumen yield. They developed another procedure for calculating the rate constants in a non-linear model of the form:

kerogen $\xrightarrow{k1}$ bitumen
bitumen $\xrightarrow{k2}$ bitumen + gas
kerogen + bitumen $\xrightarrow{k3}$ bitumen + oil + gas
kerogen + bitumen $\xrightarrow{k3}$ bitumen + bitumen

This model was also adopted and verified by another author **(R. Berber: 1985)** through a developed and programmed simulation. Therefore, for the analysis of pyrolysis reactions, two models were considered, either in an isothermal regime or in a non-isothermal regime: the linear model and the non-linear model. Also, concerning the order of this reaction according to the origin of the shale, some authors take the order one and others a fractional order.

Similarly for hydropyrolysis under hydrogen three kinetic reactions are developed to arrive at the mechanism **(R.O. Koseoglu and C.R. Phillips: 1988)**:

Bitumen → gas (1)
Heavy oils → light oils → gases (2)
Asphaltenes → maltenes → gases (3)

These reactions are assumed to be of first order with respect to hydrocarbons and of zero order with respect to hydrogen and that Arrhenius' law is verified.

We will investigate by adopting a suitable mathematical modelling to approach the mechanisms of pyrolysis and hydropyrolysis of Tarfaya oil shales in non-isothermal regime.

1/Bibliographicalstudy

The method of analysis and mathematical modelling of the thermal decomposition of oil shale allows the kinetic parameters to be achieved. However, by observing for example the activation energies of decomposition which vary from 20 to 240 KJ/mol for the fifteen examples cited by the authors **(Rajeshwar et al: 1979)**, while others (Nuttal et al: 1983) find a range of 30 to 160KJ/mol for these energies which shows the dependence of the values found on the analytical methods applied **(J.M. Charlesworth: 1985).**

1) In the non-isothermal regime, several mathematical models have been put forward by authors **(A.W.Coast and D.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 their mathematical basis and according to the approximate form of its resolution, we obtain the different laws mentioned and which are attributed to their authors. The authors **(Lee and Beck: 1984)** made some developments and approximations by the integral method and which were proposed earlier by the authors **(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 the traditional one. Authors **(J.E. Cuthrell et al: 1987)** optimized differential systems into algebraic systems by a method based on finite collocation elements to algebraic equations in the residual nonlinear model knowing the factorial and additive coefficients. Similarly the authors **(Z. Smieszeki et al: 1988)** used methods for the determination of kinetic constants and noted the significant effect of the method on the estimates of the results.

In this work, one of these methods is presented in order 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.

The mechanisms previously mentioned for the pyrolysis of oil shale are the linear and non-linear models, and for hydropyrolysis we have the non-linear model, which explains that this phenomenon is carried out by several simultaneous and successive reactions (see introduction)

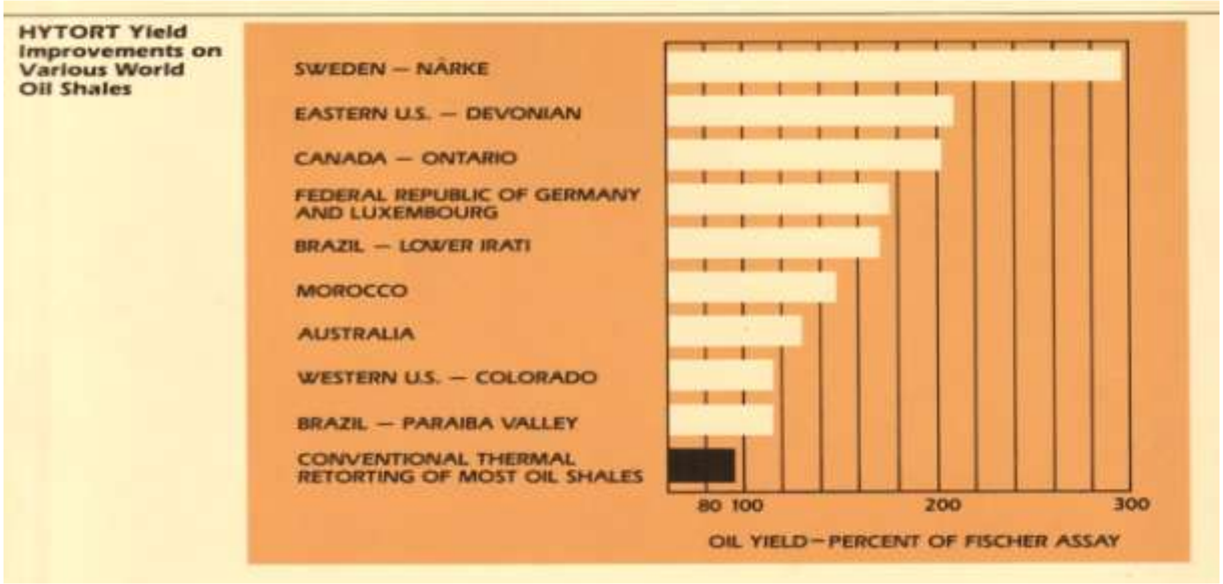
Oil shale around the world vary in their oil producing capacity and quality. For example, the Green River shale in the western United States contains a high concentration of hydrogen relative to organic carbon and yields a high yield by simple decomposition using a conventional inert gas. However, many other shale that resemble the Devonian shale in the eastern United States contain a lower concentration of hydrogen than the Green River **(J.C. Janka and R.C. Rex 1984)**. This hydrogen deficiency prevents much of the kerogen from being converted into hydrocarbons **(J.C. Janka and J.M. Dennison: 1979, R.D. Matews et al: 1981)**. The yield from conventional shale decomposition can be improved by adding more hydrogen during the decomposition process. This allows more of the kerogen to be converted to hydrocarbons rather than remaining in the ash as coke.

A process called Hytort was developed from the evolution of several organisations such as: American Gas Association, Gas Research Institute, Unated State department of Energy and some private industries **(M.J. Robert et al: 1984).** This process works, unlike the previous ones, under hydrogen pressure. However, the effect of hydrogen on shale differs according to their variety. The hydroretorting technique gives oil yields four times higher than those obtained by the old processes **(P.A. Lunch and J.C. Janta et al: 1984).**

The Hycrude cooperation, which had applied the "Hytort" process to compare shale in the eastern and western United States, has recently extended this work to the majority of the world's shale deposits. The following map (Map 1) shows the location of these deposits with their geological formation era. This map was prepared by the United States Geological Survey **(C.D. Hook et al. 1981)**. Table 1 below summarizes the percentage oil yield under the Hydroretorting test compared to the Fisher test applied to these shale. In this table, the interest of using this technique for yield multiplication is noted. If we take the case of the Timahdit shale, which gave a yield of 45.5l/tonne in the Fisher test, its yield has risen to 95.7l/tonne**(C.Rex.Jr.Raymon et al: 1983)**.

Map 1:- Oil shale tested in the Hytort process.

Table 1:- Hydroretoeting assay test results



2/ Experimental

2.1: Thermogravimetric analysis:

The technique used in this work is thermogravimetry**(A.Attaoui et al: 1992)**, it is a flail thermobalance: It consists of three main parts (figure 1).

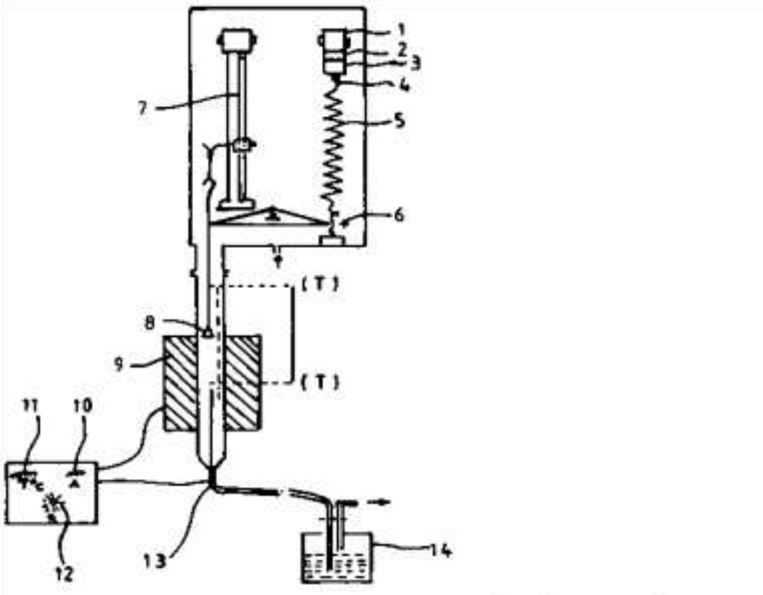


Fig. 1. Thermogravimetric apparatus: 1 electric motor, 2 potentiometer, 3 position changer, 4 axle of movement, 5 spring, 6 position detector, 7 sample holder, 8 sample, 9 furnace, 10 ammeter, 11 millivoltmeter, 12 temperature programme, 13 thermocouple, 14 flowmeter.

2.1.1: Reaction chamber

This consists of a quartz tube. The sample carrier is suspended inside this tube by means of a quartz wire, the upper end of which is connected to one end of the flail. It is made from a thin gold foil to facilitate heat exchange between the sample and the reaction medium. In addition, it has a flat surface on which the sample is spread out in a thin layer. The very small amount of sample and its distribution in a thin layer avoids the problem of diffusion through the bed and minimizes the temperature gradient in the bed.

2.1.2: Compensation element and detection system:

Using an optical method based on a light source and two phototransistors which form the position detector, the flail is held in a fixed position by a compensation system. The latter, by returning the beam to its initial position thanks to an electric motor, drives with it a potentiometer which makes it possible to translate the variation in weight into a recordable voltage.

2.1.3: Sample displacement device.

This patented device allows the sample to be moved mechanically inside the reaction chamber and isof interest in the case of thermogravimetric studies carried out in isothermal conditions.

2..2: 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 Z4 layer of Tarfaya**(A.Attaouietal:2022)**(Fig.2):
1st peak, at 2θ = 20.91; corresponds to dolomite (CaMg $(CO_3)_2$);
2nd peak, at 2θ = 23.1; corresponds to quartz (SiO_2);
3rd peak, at 2θ = 30.86; corresponds to calcite ($CaCO_3$).

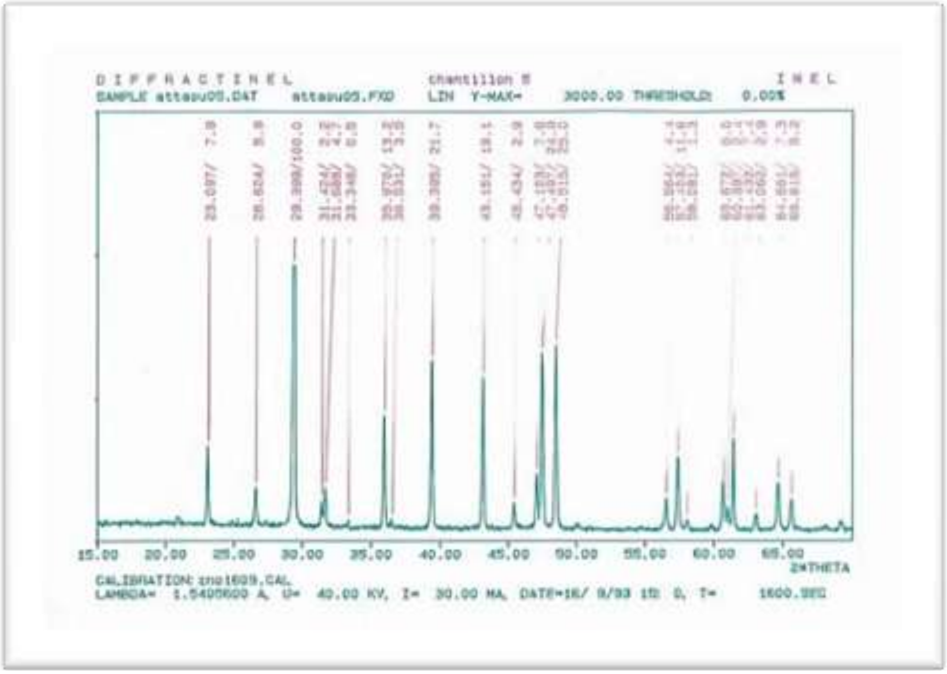


Fig 2:- X-ray spectra for Z4 layer (Tarfaya).

3/ Pyrolysis and reactivity of Tarfaya oil shale.

The pyrolysis of oil shales was carried out for the Tarfaya variety for the Z4 layer in a dynamic regime up to 750°C in a nitrogen atmosphere (PN_2= 1atm flow rate = 9 cm^3/min) on samples with a granulometry equal to 0.05 mm and a mass of between 1.4 and 2.5 mg. This mass range was determined by studying the mass effect and corresponds to the zone where this effect is no longer felt. The results obtained on the Tarfaya shale variety are shown in Figure 3. On this curve, three distinct regions of mass loss are observed:

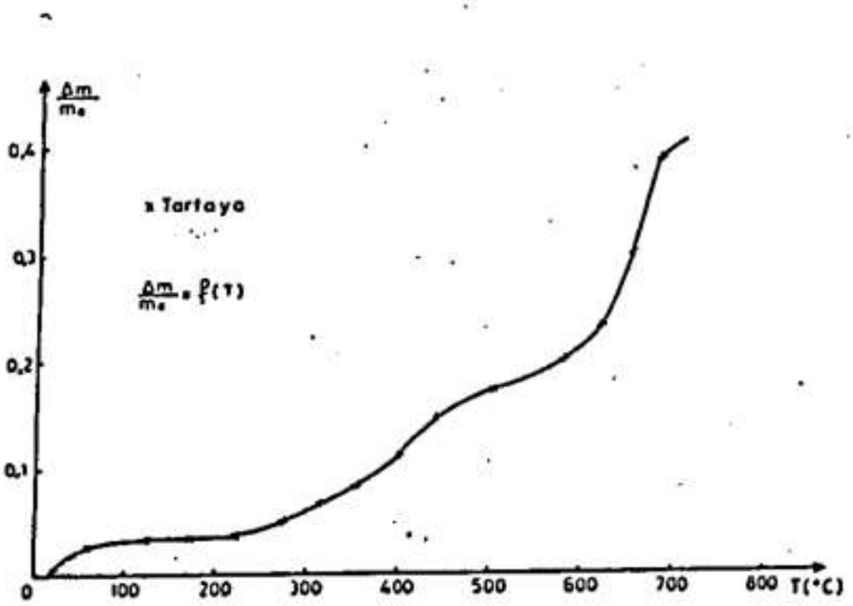


Fig 3:- Thermogram$\Delta m/m_0=f(T)$ of Tarfaya oil shale pyrolysis (Z4).

- **Ambient temperature range -250°C:**

A slight loss, which starts from ambient to 250°C is more important for the Tarfaya shale (4.1% of the total loss). This weight loss generally corresponds to the departure of water and light volatile gases.

- **Temperature range 250°C - 520°C**

After the successive losses of water, the curves show a horizontal plateau until about 250°C for Tarfaya or 300°C. After this stationary state, the curve curves to give an ascending branch corresponding to a greater loss. This loss is related to the degradation of organic matter into volatile products and that of pyrite up to 520°C

- **520 - 720°C range**

The third stage of degradation occurs up to 720°C and corresponds to a significant loss relating to the decomposition of carbonates consisting essentially of dolomite and calcite.

The decomposition in the temperature range: 250 to 520°C occurs with a loss percentage of 13.7% for the Tarfayashales. The temperature range corresponds to the oil production stage, which is usually called the primary pyrolysis stage. Figure 4: represents this stage in α which is the degree of advancement:

$$\alpha = mo - mt / mo - mf$$

mo = mass of the sample at the beginning of the decomposition step
mt = mass of the sample at time t
mf = mass of the sample at the end of the decomposition step.

Similarly, we show the instantaneous rate of this decomposition in Figure 5:

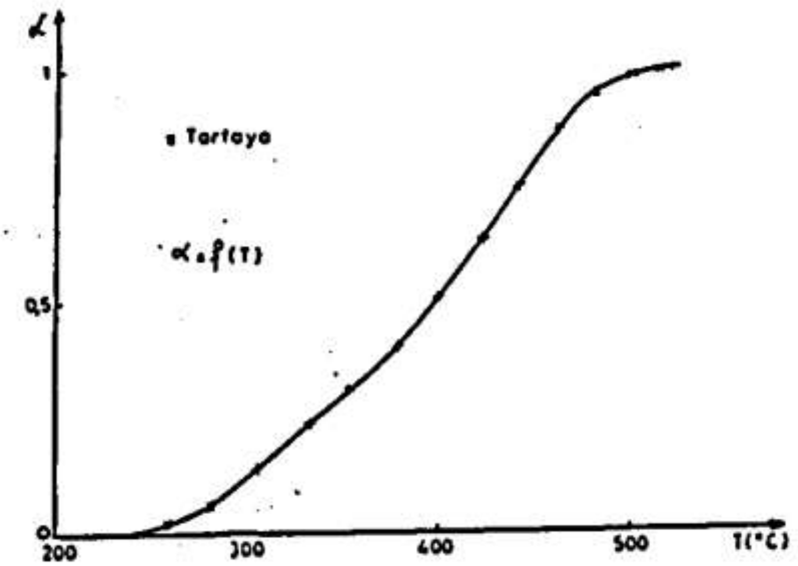


Fig 4:- Thermogram α=f(T) of the pyrolysis of organic matter in Tarfaya bituminous shale (Z4).

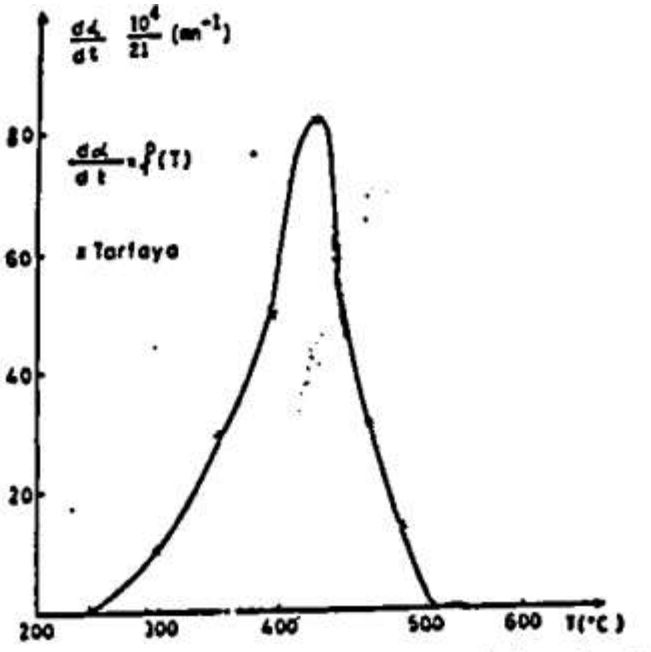


Fig 5:- Transformation rate dα=dt of organic matter pyrolysis in Tarfaya oil shale (Z4).

3.1: Kinetic study of pyrolysis.

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 method. Redfern:

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 /θ

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

F (α) = dα / (1-α) n = ko e-E/RT dT /θ (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

(5)

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

3.1.1: Approach to the pyrolysis mechanism.

When treating the experimental results in α=f (T) according to the Coats Redfern equation for an order equal to 1 by applying the first form ($\mathrm{Ln}[-\{\mathrm{Ln}(1-\alpha)\}/T^{2}] = f(1/T)$ for n = 1), we observe two lines with different slopes ((a) figure: 6). In this case we will say that the linear Hubbard-Robison mechanism is appropriate:

kerogen → bitumen → oil + gas + C residual

However, if we consider the first step of this mechanism, which consists in having bitumen from kerogen without any weight loss or gain, it is not logical because thermogravimetry is insensitive if we have no weight loss or gain.

If we apply the second form ($\mathrm{Ln}[\{1-\alpha) 1-n\}/T^{2}(1-n)] = f(1/T)$ for $n \neq 1$) for a fractional order and to fit the linearity. This order can be subject to Friedman's geometric method which consists in using several heating rates and replacing the instantaneous rate dα/dt by an average variation Δα /Δt for relatively small and equal time intervals. This method allows us to achieve the order of the average reaction of several simultaneous reactions. This ordre,whichfits the linearity, is 1,6 ((b) figure: 6):

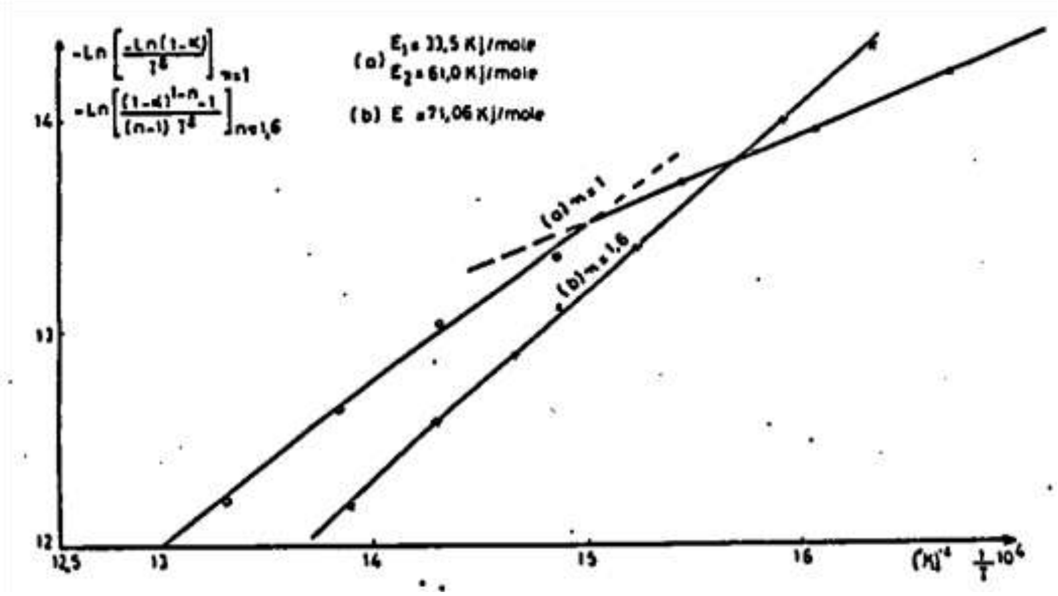


Fig 6:- Linearisation of the α=f(T) curve according to the Coats Redfern equation.
(a) for n=1 (Hubbard-Robison)
(b) For n=1,6 (n valued according to Friedman)

Finally, the appropriate mechanism for primary pyrolysis is the non-linear one which consists in considering several simultaneous reactions with an average order of n=1,6:

kerogen $\xrightarrow{k1}$ bitumen
bitumen $\xrightarrow{k2}$ bitumen + gas
kerogen + bitumen $\xrightarrow{k3}$ bitumen + oil + gas
kerogen + bitumen $\xrightarrow{k3}$ bitumen + bitumen

The average activation energy of all the simultaneous reactions is: E=71, 06 kJ/mol.

4/ Hydropyrolysis of Tarfaya oil shale

4.1: Thermal behaviour of Tarfaya oil shale during hydropyrolysis.

The thermal degradation of Tarfaya oil shales under hydrogen was carried out in a dynamic regime (21°C/min). The temperature range was from ambient to 780°C. The hydrogen pressure is one atmosphere and the gas flow rate is 9 cm^3/min. In addition, the sample was taken under the same conditions as those set for pyrolysis under inert gas: a mass between 1.4-2.5 mg and a particle size of 0.05 mm. The results of this study are shown in Figure 7 where we have the presence of the three main phenomena identical to those observed during pyrolysis under inert gas, namely dehydration, decomposition of organic matter and carbonate decompositions.

- The first loss generally corresponds to that of water and is 2.2% of the raw sample and takes place between 20 and 240°C.
- The decomposition of organic matter reacting with H2 represents 15.2% and takes place between 240 and 494°C.
- Finally, the decomposition of carbonates under H2 takes place between 500 and 780°C. These carbonates are, as noted earlier, dolomite, calcite....etc. All of these latter losses represent 33.2% of the weight of the raw sample.

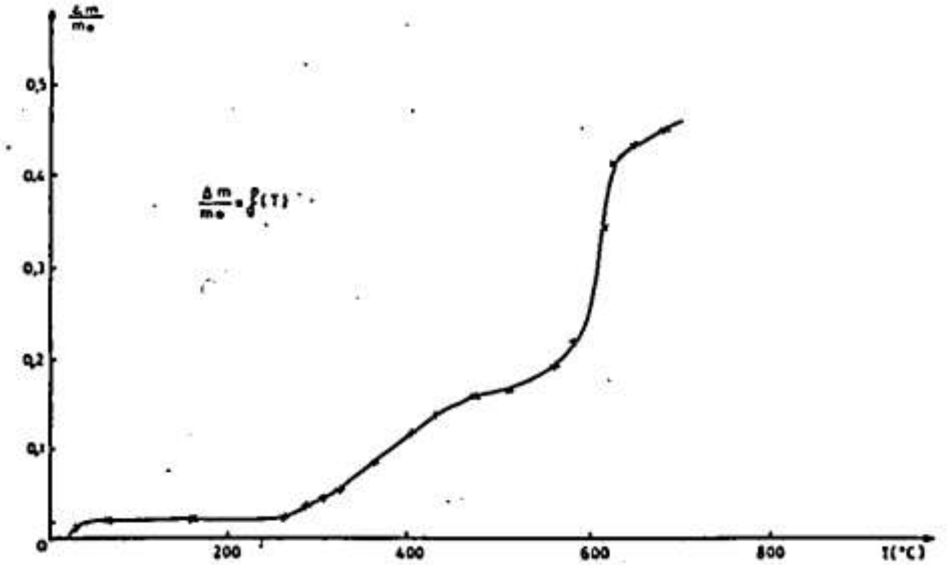


Fig 7:- Thermogram$\Delta m/m_0$=f (T) of the hydropyrolysis of Tarfaya oil shale (Z4)

In this section we will limit ourselves to the study of the reduction of organic matter and its kinetics, i.e. the stage responsible for the production of oils.

4.2: Comparative reactivity of shale under H_2 and N_2.

From the point of view of reactivity, shaleis much more reactive under hydrogen than under nitrogen (Table 2). This more sensitive reactivity under H_2 can be seen in Figure 8 where the temperature difference between the two maximum speeds is 58°C. This temperature difference represents a fairly significant energy gain when dealing with fairly high shale masses, which is generally the case.

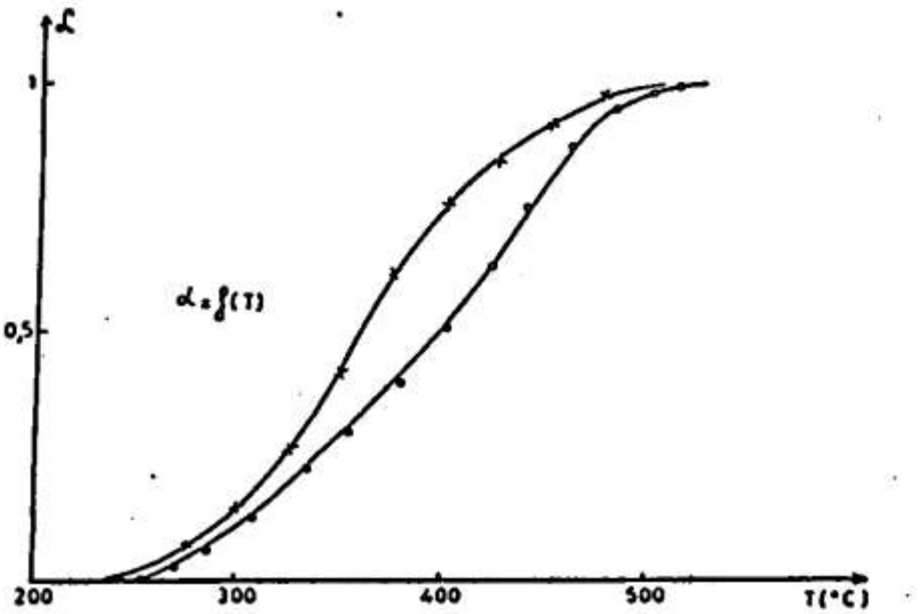


Fig 8:- Thermogram α=f(T) of pyrolysis ● and hydropyrolysis× of organic matter of Tarfayabituminous shale (Z4)

Table 2:- Physical characteristics of organic matter degradation under N_2 or H_2.

Gas (1atm)	Star temperature of reaction (°C)	Temperature at end of reaction (°C)	Percentagelos s (%)	Max speed dα/dt in mn^{-1}	Temperature of max speed (°C)
N_2	256	500	13,7	119,7 10^{-3}	425
H_2	241	494	15,2	163,8 10^{-3}	367

According to the curvature of the two curves, which is different in shape, one fits a fractional order (N_2) and the other fits the one order (H_2). We notice from this table that hydrogen increases the percentage in weight loss 11%. This translates into an improvement of the oil yield. It should be noted that this weight loss increases with hydrogen pressure **(F.S. Lan et al: 1987)**. As hydrogen is relatively expensive to produce, in industrial shale treatment processes (Hydroretorting), this gas is recycled to reduce the cost of the oil produced.

4.3: Non-isothermal kinetics of hydropyrolysis of Tarfaya oil shale.

Using the mathematical development of Coats-Redfern's law seen in detail previously to interpret the experimental results according to the three heating rates used (21°C/min), we found, after calculations and representations, a straight line (figure 9) that covers almost all the degrees of advancement with an order equal to unity. This line led us to the activation energy and the following pre-exponential factor:

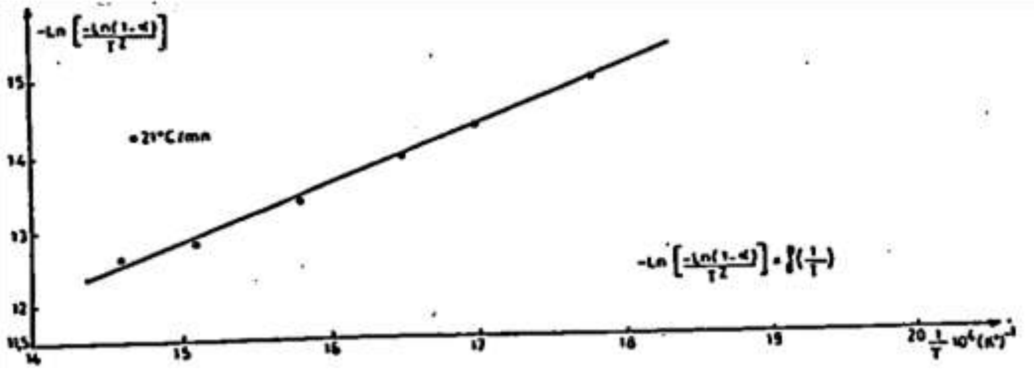


Fig 9:- Linearization of the α=f (T) curve according to the Coats -Redfern equation for order=1

Table 3:- Kinetic constants of the reduction under H_2 of Tarfaya oil shale.

Heating rate (°C/mn)	21
Activation energyKJ/mole	61,7
K_0 (mn^{-1})	96,3 10^3

From this we can say that the kinetics of hydropyrolysis of Tarfaya oil shale is simpler than pyrolysis under nitrogen since with the same order equal to one, we found one line for the hydrogen case and two lines for the nitrogen case at each heating rate.

4.4: Approach to the mechanism of hydropyrolysis.

When treating the experimental results in α=f(T) according to the Coats Redfern equation for an order equal to 1 by applying the first form (Ln [-{Ln (1 - α)}/T^2] = f (1/T) for n = 1), we observe a line.
Similarly for hydropyrolysis under hydrogen, three kinetic reactions are developed to arrive at the mechanism:
bitumen → gas (1)
Heavy oils → light oils → gases (2)
Asphaltenes → maltenes → gases (3)

Looking at the first step of both equations (1) and (2) we notice that this step for both equations is done without mass loss or gain, so this is unnoticed by thermogravimetry.

Order 1 fits for simultaneous reactions ((1), (2) and (3) in second steps.

On the same interpretation, we conclude that it is the non-linear mechanism that is appropriate and suitable to explain hydropyrolysis in the dynamic regime.

Conclusion:-

The kinetics of pyrolysis or hydropyrolysis in the non-isothermal (dynamic regime) of the oil-bearing stage (primary stage) has been frequently discussed since 1950 **(A.B. Hubbard and W.E. Robinson: 1950)**. When treating the experimental results in α=f(T) according to the Coats Redfern equation for an order equal to 1 by applying the first form (Ln [-{Ln (1 - α)}/T^2] = f (1/T) for n = 1), we observe two straight lines with different slopes ((a) figure: 6). In this case we will say that the linear Hubbard-Robison mechanism is appropriate:
Kerogen → bitumen → oil + gas + C residual

However, if we consider the first stage of this mechanism, which consists of having bitumen from kerogen without any weight loss or gain, it is not logical because thermogravimetry is insensitive if we have no weight loss or gain.

If we apply the second form (Ln [{1 - α) 1-n}/T^2 (1-n)] = f (1/T) for n ≠1) for a fractional order and to fit the linearity. This order can be subject to Friedman's geometric method which consists in using several heating rates and replacing the instantaneous rate dα/dt by an average variation Δα /Δt for relatively small and equal time intervals. This method allows us to achieve the order of the average reaction of several simultaneous reactions. This order, which fits the linearity, is 1.6 ((b) Figure: 6):

Finally, the appropriate mechanism for primary pyrolysis is the non-linear one which consists in considering several simultaneous reactions with an average order of n=1,6:

$\text{kerogen} \xrightarrow{k1} \text{bitumen}$
$\text{bitumen} \xrightarrow{k2} \text{bitumen + gas}$
$\text{kerogen + bitumen} \xrightarrow{k3} \text{bitumen + oil + gas}$
$\text{kerogen + bitumen} \xrightarrow{k3} \text{bitumen + bitumen}$

The average activation energy of all the simultaneous reactions is: E=71.06 kJ/mol.

Concerning the kinetics of hydropyrolysis, by using the mathematical development of Coats Redfern's law seen in detail previously to interpret the experimental results according to the three heating speed employed (21°C/mn), we found, after calculations and representations, a straight line (figure 9) which covers almost all the degrees of advancement with an order equal to unity. This line led us to the activation energy: E=61.7 kj/mol

When we treat the experimental results in $\alpha=f(T)$ according to the Coats Redfern equation for an order equal to 1 by applying the first form $(\mathrm{Ln}\,[-\{\mathrm{Ln}\,(1-\alpha)\}/T^2] = f\,(1/T)$ for $n = 1)$, we observe a line.
Similarly for hydropyrolysis under hydrogen, three kinetic reactions are developed to arrive at the mechanism:
Bitumen → gas
Heavy oils → light oils → gases
Asphaltenes → maltenes → gases

Looking at the first step of the last two equations we notice that this step for both is done without mass loss or gain, so this is unnoticed by thermogravimetry.

The order 1 fits for the three simultaneous reactions in the second step for the last two.

On the same interpretation, we conclude that it is the non-linear mechanism that is appropriate and suitable to explain hydropyrolysis in the dynamic regime.

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