

# Pyrolysis and reactivity of Timahdit and Tarfaya (Morocco) oil shales

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## Abstract

In the course of this work, essentially carried out using dynamic thermogravimetry, certain properties of oil shales were determined. A comparative study of the thermal behaviour of two Moroccan oil shale varieties (Tarfaya and Timahdit) showed that the Tarfaya oil shales were more reactive than the Timahdit shales. This reactivity is explained by a difference in temperature of 60 K between the maximum rate of pyrolysis and weak activation energies for the Tarfaya oil shale in comparison with the Timahdit oil shale.

## 1. Introduction

Several studies of kerogens isolated from their mineral matrices [1–4] have shown that it is possible to classify the different types of kerogen and to follow the physico chemical transformations undergone during the course of their deposition. van Krevelen [5] compared oil shale lignites using a diagram presenting the atomic composition of the kerogen in the form of ratios of the three principal elements  $[H]/[C]$  and  $[O]/[C]$ . He found that samples of the same type of organic deposit were grouped on a curve called an “evolution way”. Thus we can distinguish several of these evolution ways which correspond to differences in organic matter. Wen and Yen [6] compared the thermal behaviour and properties of two varieties of oil shale (Devonian and Green River) using two analysis methods, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

They found that the activation energy and kerogen concentration are of more interest for Devonian than for Green River shales. Earnest [7] studied three oil shale varieties (Australian, Glen Davis and Green River) and affirmed that the starting temperatures and temperatures of maximum rates were influenced by the composition of organic matter. To contribute to a better knowledge of the physical and chemical phenomena of Moroccan oil shales, a comparative study of the reactivity of the two principal deposits (Tarfaya and Timahdit) was carried out.

## 2. Experimental technique and starting matter

The main technique used in this work was TGA, along with X-ray diffraction. The thermogravimetric apparatus (Fig. 1), built in the laboratory, [8] has a

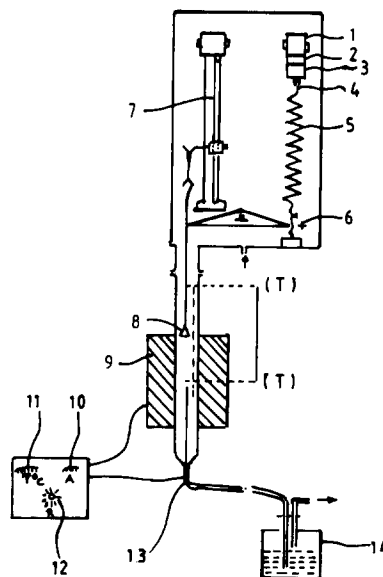


Fig. 1. Thermogravimetric apparatus: 1 electric motor, 2 potentiometer, 3 position changer, 4 axle of movement, 5 spring, 6 position detector, 7 sample holder, 8 sample, 9 furnace, 10 ammeter, 11 millivoltmeter, 12 temperature programme, 13 thermocouple, 14 flowmeter.

thermobalance with a sensitivity of  $10 \mu\text{g}$ . It has three principal sections: a reaction vessel comprising a quartz tube and gold sample holder, the element of compensation and the detection system, and the apparatus for placing the sample in the reaction tube.

The starting matter was provided by two different deposits, Tarfaya and Timahdit. The first is located in the south of Morocco, and the second in the north (Middle Atlas). In Table 1, we have gathered some characteristics of two typical samples from the two deposits [9].

TABLE 1. Physico chemical characteristics of average samples from the two deposits (Tarfaya and Timahdit)

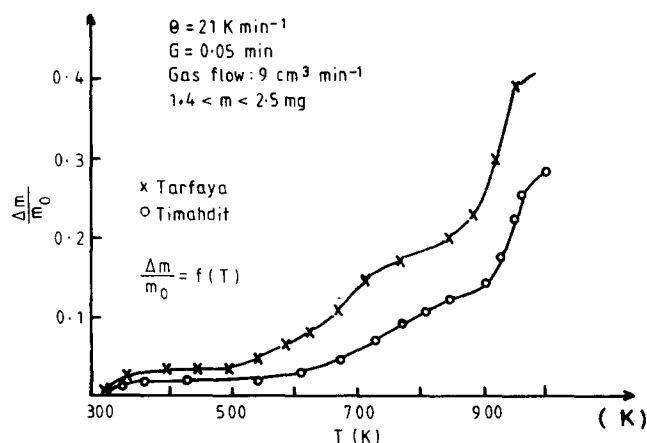
Characteristic	Deposit	
	Timahdit	Tarfaya
Density	2.21	2.24
P.C.S (kcal kg <sup>-1</sup> )	1340	1228
Ash (%)	64	59.46
CO <sub>2</sub>	20.4	26.7
Organic matter	15.8	14.47
Total carbon (%)	18.34	17.74
Mineral carbon (%)	5.57	7.72
Organic carbon (%)	12.77	10.62
Total sulphur (%)	2.26	1.92
Organic sulphur (%)	1.54	1.6
Pyritic sulphur (%)	0.60	0.31
S <sub>sul</sub> (%)	0.12	—

Table 2 shows the mineralogical compositions of the rock from Tarfaya [10], Timahdit [11] and Colorado [12] for comparison. We note that the Tarfaya oil shales contain less dolomite and more clay than those of Timahdit and Colorado.

### 3. Results and discussions

#### 3.1. Thermal behaviour of the two varieties of oil shale (Tarfaya and Timahdit)

After determining the operation conditions corresponding to a purely chemical regime (regime controlling pyrolysis) and by studying the parameters that influence the reaction such as mass effect, granulometry, gas flow and heating rate, experiments were carried out on the two oil shales in the dynamic thermal range up to 1023 K and under a nitrogen atmosphere ( $P_{N_2} = 1$  atm, gas flow  $9 \text{ cm}^3 \text{ min}^{-1}$ ) on samples with granulometry equal to 0.05 mm and a mass between 1.4 and 2.5 mg (optimal region for the mass effect). All the experiments used a heating rate of  $21 \text{ K min}^{-1}$ . The

Fig. 2. Thermograms  $\Delta m/m_0 = f(T)$  for pyrolysis of the two oil shale varieties.

results obtained for the two varieties of oil shale are presented in Fig. 2. We notice three distinct regions of loss of mass.

##### 3.1.1. Ambient temperature to 523 K

A slight loss of mass, beginning at ambient temperature to 393 K, is more significant for the oil shales of Tarfaya (4.1% of the total loss) than for the Timahdit shale (2% of the total loss). Generally, this weight loss corresponds to the departure of water and volatile gas. In a previous study realized in the laboratory [13], it was shown that the water found in oil shales is of two types: the first is water of hydration, and the second is associated with clay.

##### 3.1.2. 523–793 K

After the continuous loss of water, the curves show a horizontal region up to approximately 523 K for the Tarfaya shale and 573 K for the Timahdit shale. After this stationary phase the curves turn to give an ascending branch corresponding to a more significant loss of mass. This loss is related to degradation of the organic matter in volatile products and pyrites up to 793 K.

TABLE 2. Mineralogical composition of rock for the Tarfaya, Timahdit and Colorado oil shales

Constituent (%)	Deposit		
	Tarfaya	Timahdit	Colorado
Dolomite ( $\text{CaMg}(\text{CO}_3)_2$ )	4.1	15.9	32
Calcite ( $\text{CaCO}_3$ )	59.2	41.5	16
Quartz ( $\text{SiO}_2$ )	—	19.2	15
Clay (illite-kaolinite)	28.4	13.4	0
Pyrite ( $\text{FeS}_2$ )	2.4	1.8	1
$\text{FeCO}_3 + \text{Fe}_2\text{O}_3$	—	1.8	—
$\text{TiO}_2 + \text{phosphate}$	1.2	2.4	—
Other elements	4.7	3.7	—

These products have been the objects of many chromatography tests [14, 15]. The gases detected by this technique correspond to  $O_2$ ,  $CH_4$ ,  $C_2$ ,  $H_4$ ,  $H_2S$ ,  $H_2O$  and  $C_2H_2$ . The heaviest gases were analysed using a silicon column SE30 at 293 K and the gases detected were  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ . A  $C_3$  peak containing propene was also noted. We deduce that  $H_2S$  is formed by the decomposition of the complex organic matter and of the pyrite  $FeS_2$  [16].

### 3.1.3. 793–993 K

The third stage which continues up to 993 K also shows a significant loss of mass with respect to carbonate decomposition, constituted essentially of dolomite and pyrite.

To conclude this descriptive study, we can say that the Tarfaya oil shales are richer in water, organic matter, and pyrite. They are also richer in carbonates and calcite in comparison with the Timahdit shales.

The general interest in these rocks concerns whether it is possible either to extract the oils (pyrolysis) or to use them directly as solid fuel (combustion). The next section is mainly a kinetic study of the stage responsible for oil production which we normally call primary pyrolysis.

### 3.2. Pyrolysis under nitrogen of the Timahdit and Tarfaya oil shales (primary pyrolysis), 523–793 K

The results of pyrolysis of the two oil shale varieties are presented in Fig. 3, and the instantaneous rates are shown in Fig. 4. Comparison of the instantaneous rates of the two oil shales in terms of temperature shows that the Tarfaya oil shales are more reactive than the Timahdit shales. In fact a temperature difference of about 60 K separates the maximum rate of loss of the Tarfaya and Timahdit shales. It has been noted that the

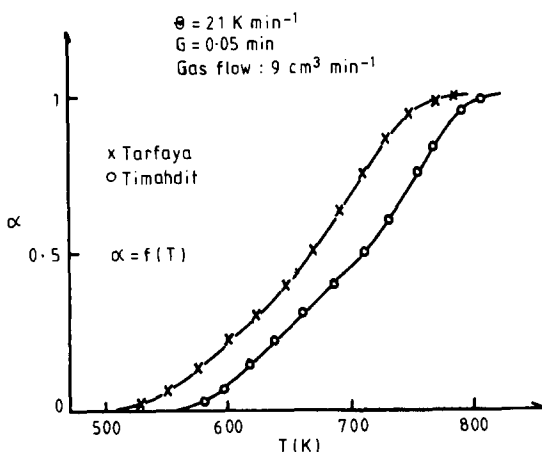


Fig. 3. Thermograms  $\alpha = f(T)$  of pyrolysis of organic matter of the two oil shale varieties.

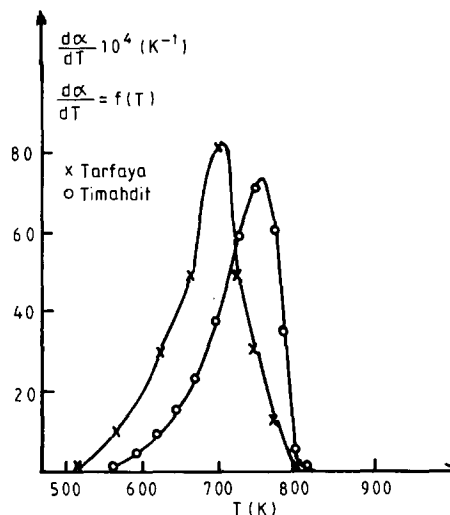


Fig. 4. Transformation rate  $d\alpha/dT = f(T)$  of pyrolysis of organic matter of the two oil shale varieties.

thermal behaviour and the physicochemical properties vary over a large range according to the type of shale.

To evaluate the activation energies, we used the Coats–Redfern [17] mathematical method in a dynamic regime. The rate of solid–gas reaction and the thermogravimetric analysis is written as follows:

$$\frac{d\alpha}{dt} = K_0(1 - \alpha)^n \exp(-E/RT) \quad (1)$$

where  $\alpha$  is the degree of advancement,  $K_0$  is the frequency factor,  $n$  is the order of the chemical reaction,  $E$  is the activation energy, and  $R$  is the gas constant, or

$$\frac{d\alpha}{dt} = \frac{K_0}{\theta} (1 - \alpha)^n \exp(-E/RT) \quad (2)$$

with  $\theta = dT/dt$  the heating rate.

To solve this equation the Coats–Redfern method gives a form based on asymptotic development which is easy to use. This development gives two forms according to the value of  $n$ :

$$\ln[-\{\ln(1 - \alpha)\}/T^2] = f\left(\frac{1}{T}\right) \quad \text{for } n = 1$$

$$\ln[-\{1 - (1 - \alpha)^{1-n}\}/T^2(1 - n)] = f\left(\frac{1}{T}\right) \quad \text{for } n \neq 1$$

Using Hubbard and Robinson's [18] hypothesis, which was also used by Rajeshwar for two successive reactions, both of first order (for primary pyrolysis) [19], we have

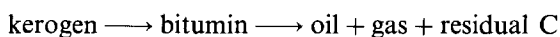


Figure 5 shows a linear plot of  $\ln[-\ln(1 - \alpha)/T^2]$  vs.  $1/T$ , assuming  $n = 1$ , for the two oil shales. For each variety we obtain two straight portions which give the kinetic parameters of the oil shales (Table 3).

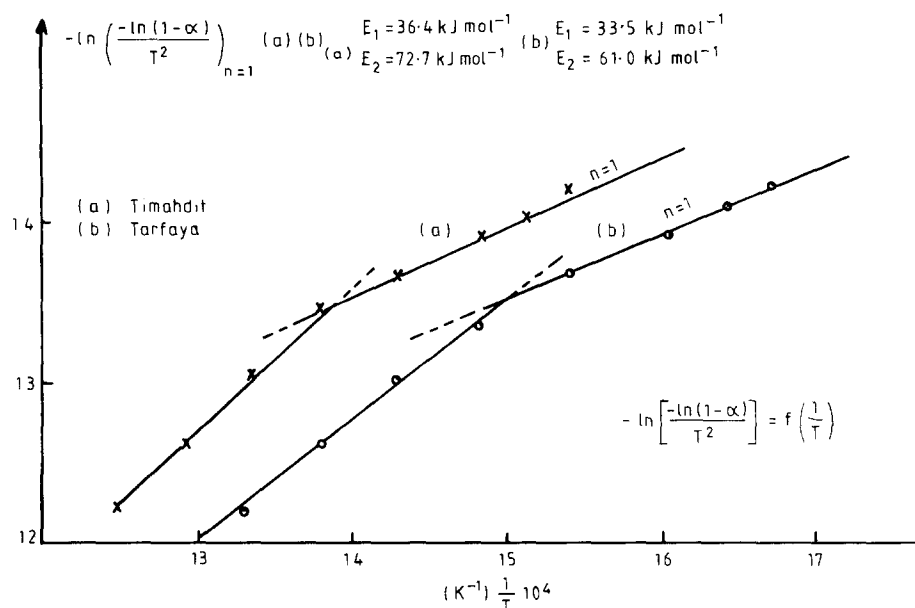


Fig. 5. Linearity of curves  $\alpha = f(T)$  according to the Coats-Redfern model for  $n = 1$  (Hubbard-Robinson hypothesis) for the two oil shales.

TABLE 3. Kinetic characteristics of pyrolysis of the Tarfaya and Timahdit oil shales

Oil shale	$E_1$ (kJ mol <sup>-1</sup> )	$E_2$ (kJ mol <sup>-1</sup> )	$K_{01}$ (min <sup>-1</sup> )	$K_{02}$ (min <sup>-1</sup> )
Timahdit	36.4	72.7	54.56	$50 \times 10^3$
Tarfaya	33.5	61	36	$12.3 \times 10^3$

The values of the activation energies  $E_1$  and  $E_2$  are slightly less for the Tarfaya shale than for the Timahdit shale.

#### 4. Conclusion

The oil shales of Tarfaya are kinetically more reactive than those of Timahdit. This reactivity is explained by a lower temperature of pyrolysis and by a relatively weak activation energy. This reactivity can be attributed to the nature of the organic matter, and could be a result of the interaction between organic and mineral matter. The mineralogical compositions of the oil shales are not the same (see Tables 1 and 2).

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