Mineral matter hydropyrolysis of Tarfaya oil shale and influence of sedimentation edge

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Abstract. In hydrotreating the reactivity of the mineral matter of the oil shale from the five layers of the Tarfaya deposit and the M layer of the Timahdit deposit, both located in Morocco, is different. This reactivity is a function of the climates of the geological eras: Z0 (Tertiary era: cold climate), Z1 (Maestrichtian: hot climate), Z2 (Senonian: cold climate), Z3 (Turonian: warm climate) and Z4 (Cenomanian: warm climate). This explains why the Z3 and Z4 layers are the most reactive, also due to the location of the low peak temperatures as established by derivative thermogravimetry (DTG) for these two layers. There was also a disproportion between the DTG peak area values and the reactivity of the mineral material. The composition of dolomite $CaMg(CO_3)_2$ in the Z1 layer is responsible for the low reactivity observed for this layer.

Oil shale is a sedimentary rock which is composed of a complex mixture of organic and mineral matter. It is a natural mineral resource, and constitutes a richness of Morocco, with the most important deposits being Tarfaya of marine origin and Timahdit of lacustrine origin.

A comparison was made between the reactivity of the mineral matter of layers Z1, Z2, Z3, Z4 (deposit of Tarfaya) and M (deposit of Timahdit) by using the thermogravimetric analysis (TGA) coupled with its derivative. This is a technique of analysis consisting in following the loss in mass of a compound according to the temperature in dynamic regime at three speeds of heating: 9 °C/min, 15 °C/min and 21 °C/min. This analysis was carried out for the hydrotreating reaction (hydrogen carrier gas) for the 5 layers of Tarfaya: Z0, Z1, Z2, Z3, Z4 and the M layer of Timahdit.

The influence of the climate of the sedimentation geological stage of the different layers of the Tarfaya deposit was discussed in order to understand the corresponding reactivity.

Keywords: hydropyrolysis, Moroccan oil shale, mineral matter, thermogravimetric analysis, reactivity, X-ray diffraction.

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1. Introduction

As the main supplementary and alternative non-fossil fuel, oil shale occupies an extraordinary place in the energy development and utilization agenda of many countries. Oil shale is a complex mixture of organic and inorganic materials. The inorganic part consists mainly of silicates, carbonates and pyrite minerals, in addition to trace elements Ti, Ni, Zn, B, Mo, etc. The organic materials kerogen and bitumen [1], which can be converted into shale oil at about 350–600 °C, are heterogeneous and finely dispersed in the complex mineral matrix.

Morocco has significant mineral resources. Among these natural resources, oil shale is a sedimentary rock containing organic substance kerogen in sufficient quantity to provide oil and gas fuel. This organic material is trapped in the mineral matrix consisting largely of silica and clay. Most researchers have focused attention on the major oil shale deposits in Morocco, namely those of Timahdit and Tarfaya [2]. However, the oil shale of the Rif region, northern Morocco is not well valorized due to its low organic matter content. The Timahdit oil shale deposit, located in the Middle Atlas Mountains, is divided into four layers – T, Y, X and M with a thickness varying from 100 to 150 m and variable organic matter content in the environment of basalt, limestone and marl. The organic matter in this deposit is of lacustrine or marine origin depending on the depth of the deposit. The Tarfaya deposit is located in the southern provinces and covers an area of about 2500 km^2 bordering the Atlantic Ocean. This deposit is made up of marl of organic matter dating from the Middle and Upper Cretaceous. A large part of the Upper Cretaceous series consists of oil shale with variable organic matter contents. This deposit has been divided into five layers: Z0, Z1, Z2, Z3 and Z4. The reserves in layer Z are 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 80 billion tons of rocks, for the deposit of Tangier the chemical composition differs from those of Timahdit and Tarfaya by the content of organic and mineral matter. The Timahdit and Tarfaya oil shales are mainly constituted of carbonates, quartz and clays associated with organic matter (Table 1) [3]. These constituents are found in compatible proportions in the Timahdit oil shale. The clays are composed of kaolinite and illite and the Tarfaya shale also contains montmorillonite. Studies have shown that there is a good correlation between carbonate content and oil content.

Over the past decade, a number of approaches have been tested for the eastern United States (US eastern) oil shale pyrolysis, including pyrolysis in pressurized hydrogen fluidized (PFH) bed and autoclaves. The results of these studies show that the highest oil yields are obtained for this shale in the presence of hydrogen at high pressures [4]. The US eastern oil shale affords better oil quality when processed in a hydrogen atmosphere [5]. The evaluation showed that processing this oil shale in autoclaves produced less

Table 1. Mineral matrix composition [3]

Composition	Timahdit deposit, %	Tarfaya deposit, %
Calcite	21.9	63.7
Dolomite	15.9	3.5
Quartz	19.1	6.5
Pyrite	1.0	<1.0
Clays and other minerals	24.0	10.0
Kerogen	17.7	15.9

oil than using the fluidized bed [6]. The PFH process has several advantages over moving-bed hydrotreating. The moving-bed reactive hydrogen transport requires feed shale size of 0.3 to 2.5 cm. Mining and crushing operations reduce production by 20% when using moving-bed vessels [7]. The PFH process uses shale sizes smaller than 0.3 cm. Thus, the entire shale resource can be used in the PFH process. In addition to full resource utilization, the PFH process produces higher oil yields than moving-bed hydro reactors, because the oil yield decreases with grain size above 0.3 cm [8]. Efforts to improve the economics of hydrotreating have led to the development of a second-generation hydropyrolysis system; the PFH has been used by the researchers at the Institute of Gas Technology (IGT). As a result, the development of an advanced hydrotreating process has created a database for laboratory, batch and continuous shale processing [9]. A block diagram of the main integrated PFH processes is shown in Figure 1. The exact factors that make up the integrated fluidized bed PFH process offer the possibility of higher oil yields and selectivity depending on hydrogen consumption, shale residence time and improved shale throughput. The smaller shale particles used in the PFH process improve the selectivity of carbon to oil. Hydrogen consumption is reduced as it takes about half the hydrogen to make oil (CH_4) as it does to make gas (CH_3). Compared to moving-bed hydrotreating, the PFH process is expected to have a shorter shale residence time. The use of a fluidized bed and the smaller shale particles will result in large increases in mass and heat transfer rates of New Albany shale [10, 11]. Shorter residence times in a fluidized bed mean that PFH reactors can be smaller and less expensive than moving-bed hydrotreating reactors. PFH studies have been conducted for six shale samples using a laboratory-scale batch unit in Indiana.
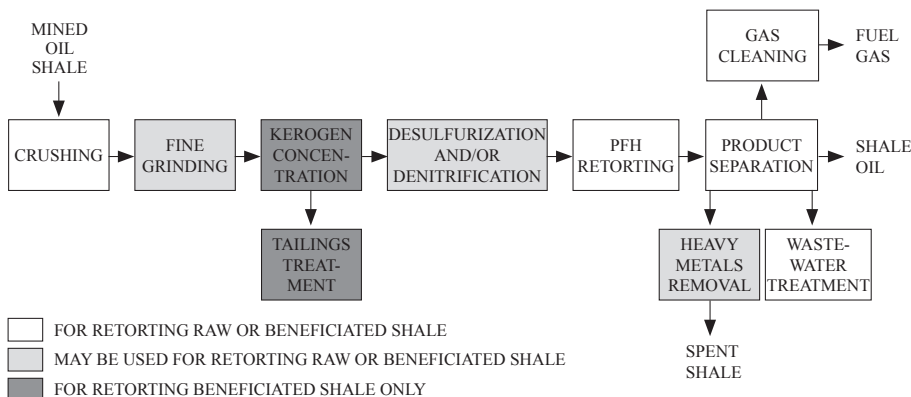
Fig. 1. Main components of the integrated PFH process.

The results in Table 2 show that hydrotreating increased the overall carbon conversion rate for the Alabama shale from 64.5 to 72.9%. The fraction of feed carbon appearing in the oil increased from 44.0 to 58.1%. The Indiana shale conversions were similar to those of the Alabama shale at 7.0 MPa pressure. The enriched Indiana shale gave more carbon-forming oil and less carbon-forming gas and its overall carbon conversion was 80.8%.

Table 2. The results of hydrotreating

		Alabama	Indiana	Beneficiated Indiana
Ultimate analysis, wt%	Moisture, wt%	0.94	1.56	1.88
	Organic carbon	15.94	12.95	28.05
	Mineral carbon	0.07	0.08	0.05
	Hydrogen	1.57	1.48	2.81
	Oxygen	2.90	3.16	5.41
	Nitrogen	0.49	0.35	0.74
	Sulphur	9.05	2.93	2.71
	Ash	73.59	80.25	61.11
Gross calorific value	MJ/kg	7.60	5.81	12.52
	Btu Ib^{-1}	3266	2497	5385
Fisher assay	l/t	53	54	108
	Gallon/t	12.7	12.9	25.9

The treatment of oil shale with hydrogen, either to improve the products of oil shale (gas, oil and solid fuel) or in the particular sense to get rid of some undesirable elements that have harmful effects on the operation of the materials, such as the phenomenon of corrosion, requires some documentation in this area. One example is hydrodesulphurization (HDS), a reaction which is used to remove sulphur. Studies of HDS reactions of sulphur model compounds on US eastern and western oil shale minerals have been conducted to provide a fundamental understanding of the heterogeneous catalytic behavior of minerals in oil shale pyrolysis [12]. The products obtained from the reaction of thiophene with eastern low-temperature ashed (LTA) shale are C_1–C_4 hydrocarbons, whereas those obtained with western LTA shale contain higher hydrocarbons, such as C_5 and C_6 unsaturated cyclic compounds, as well as a wide variety of alkyl benzenes. The HDS reactions of thiophene with dolomite, siderite, illite, calcite and a mixture of these minerals have also been studied. The HDS activity of burnt waste shale will be discussed.

One of the objectives of oil shale researchers is to develop mechanistic models that provide a reliable predictive capability for efficient and acceptable conversion. The development of a predictive model requires a fundamental but detailed understanding of primary and secondary chemical reactions, including the role of minerals during oil shale pyrolysis. In the course of the decomposition process, shale oil vapors pass over and come into contact with mineral surfaces, particularly in hot-solid recycling processes. The minerals are known to catalyze both primary and secondary reactions during autoclaving [13].

Products formed from the decomposition of kerogen during autoclaving can react both within the shale particles and subsequently on the surface of the shale particles, leading to side reactions that alter the yield and composition of oil. To understand the effect of minerals in oil shale retorts and their influence on oil yield and composition, it is necessary to know which constituents of oil shale are catalytically active. This information is not only interesting from a theoretical point of view; it should also be of help in the design and scale-up of improved autoclave processes.

A comparison of oil shale pyrolysis with that of kerogen has shown that the mineral material in oil shale provides surfaces capable of cracking high molecular weight products by thermal or catalytic mechanism [14]. This study indicates that reactions involving the cleavage of carbon-carbon bonds and carbon-hydrogen bonds on mineral surfaces have been documented to some extent. In addition, a study by Regtop et al. [15] demonstrated that the carbonized residue in spent shale can increase the magnitude of secondary reactions. The findings of the researchers were based on the examination of the pyrolysis of model compounds under oil shale retorting conditions on spent shale, mineral and charcoal.

From the pertinent literature on the catalytic effects of minerals, Regtop et al. [15] reported that the reactions which led to heteroatom displacement were the same. The motivation for investigating the possibility of removing sulphur, nitrogen and oxygen in oil shale retorts includes firstly the production

of oil acceptable for conventional oil refining operations and secondly the ability to store the oil without insoluble sediments as a result of heteroatom compounds.

A research by Shamsi et al. [16] investigates the effects of US eastern and western shale minerals on the HDS reactions of thiophene. The first part of the study shows that shale minerals are capable of desulphurating theophany to hydrogen sulphide and hydrocarbons and that they promote desulphurization, isomerization and polymerization reactions under autoclave conditions. The current work is focused on understanding the catalytic effect of mineral and burnt waste shale for the removal of sulphur from theophany.

Both the US eastern and western LTA shales were active in HDS and hydrodenitrogenation (HDN) reactions. The present study is a continuation of previous work and aims to identify the mineral(s) responsible for the catalytic behavior and to determine the influence of time and temperature on the selectivity and conversion of the product, in order to improve sulphur removal and minimize side reactions that may contribute to the cracking of higher hydrocarbons into gas.

The elemental compositions of high ash shale of these minerals were determined using X-ray fluorescence (XRF) spectrometry. Each of shale minerals, a mixture of minerals (MIXM), Colorado LTA shale and Colorado combusted spent shale showed HDS activity at the reaction conditions (400–600 °V). The elemental analyses are reported in Table 3 as oxide by weight percentage [16].

Table 3. XRF analysis of minerals of high-temperature ashed (HTA) oil shale (as weight oxide)

	Siderite	Illite	Colorado dolomite	Calcite	MIXM	Colorado Mahogany LTA
CaO	0.70	0.60	34.22	51.41	26.00	26.90
K_2O		5.10			1.40	1.80
P_2O_5	0.21	0.31	0.06	0.20	0.72	0.88
SiO_2	8.80	52.80	6.01		48.60	42.50
Al_2O_3	7.70	22.00			11.60	12.70
Fe_2O_3	60.40	8.90	0.69	0.05	2.50	1.80
TiO_2		0.71	0.05	0.03	0.14	0.21
MgO	5.50	1.70	1.54	0.54	3.20	8.60
S		0.69	0.08	0.06	0.24	0.05
MnO	1.25	0.02	0.14	0.01	0.08	0.04
ZnO	0.03	0.01	0.01		0.02	0.02
SrO		0.04		0.12	0.07	0.11

2. Experimental

2.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a classical method widely used in materials and energy sciences and geology to determine the weight variations of materials. It graphically observes mineral decomposition or reactions through peaks or valleys. The purpose of this analysis is to characterize materials by directly measuring mass loss as a function of temperature and/ or time. It measures the change in mass of a sample when it is subjected to a temperature program, under a controlled atmosphere. This change can be a mass loss (vapor emission) or a gain (gas fixation, oxidation). Experiments can be performed in an oxidizing or inert atmosphere.

The thermo-microbalance is the Redcroft 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 heating rates: 21 °C/min, 15 °C/min and 9 °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 of 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. 2).
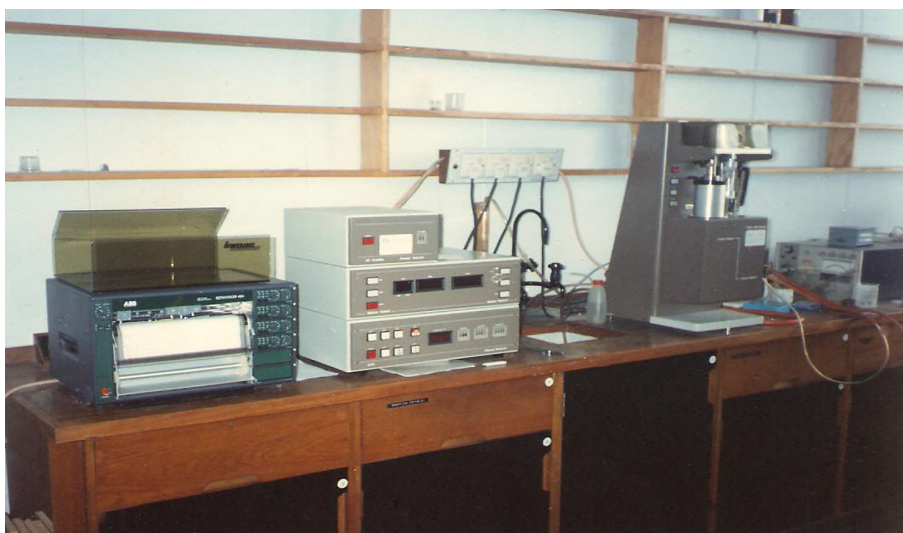

Fig. 2. Photo of thermobalance Redcroft.

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 (XRD) with a copper anticathode of a wavelength of 1.54051 Å. The following X-ray spectra correspond to the M layer of Timahdit (Fig. 3) 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 six samples in slightly different quantities.
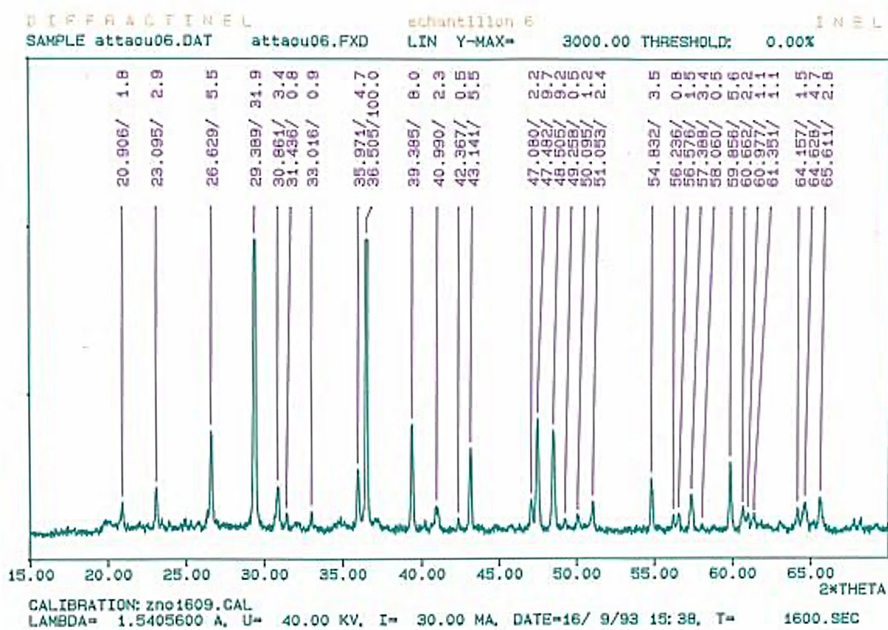
Fig. 3. X-ray spectra for M layer (Timahdit).

We notice that the X-rays corresponding to dolomite are more accentuated in the Timahdit deposit than in the Tarfaya deposit, which shows that this mineral is strongly present in Timahdit.

Similarly the following spectra represent the X-ray diffraction (XRD) of the first three layers of the Tarfaya deposit, which are classified from bottom to top respectively Z0, Z1, Z2 and Z3 (Fig. 5).
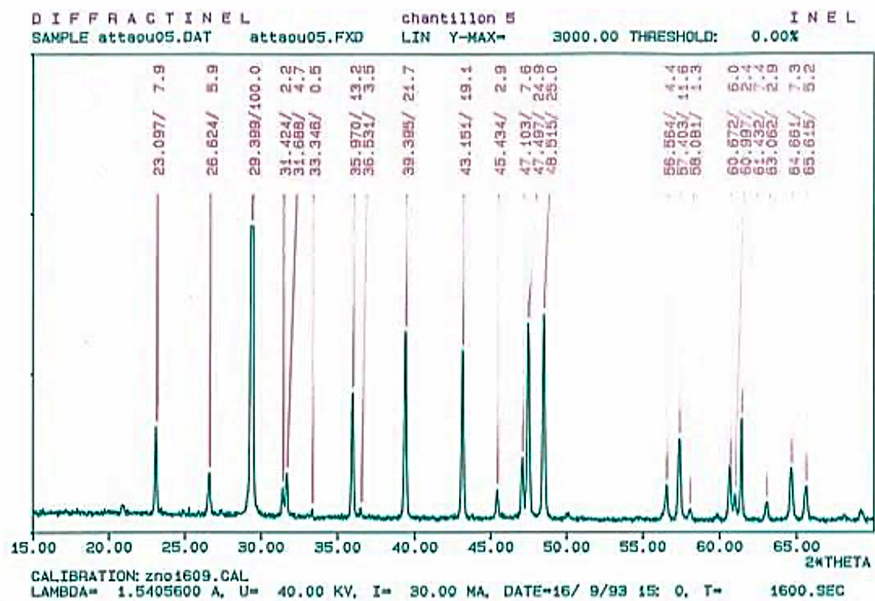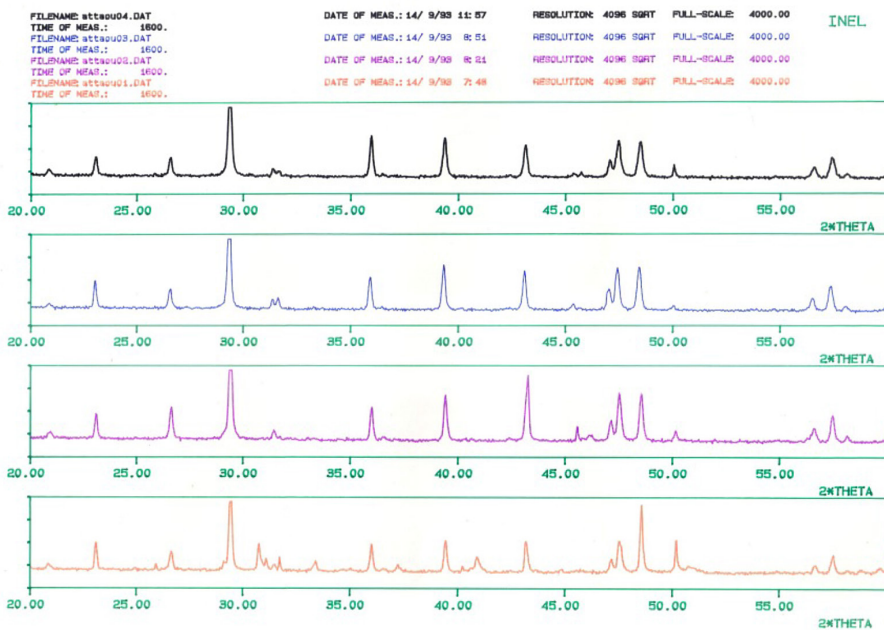
Fig. 4. X-ray spectra for Z4 layer (Tarfaya).

Fig. 5. X-ray spectra classified from bottom to top of the Z0, Z1, Z2 and Z3 layers of Tarfaya oil shale.

2.3. Thermogravimetric results for mineral matter

Thermogravimetric tests were carried out by hydrotreating (H_2 flow rate = 20 cc/min) for the five Tarfaya layers: Z0, Z1, Z2, Z3, Z4, and the M layer of Timahdit in dynamic regime at three heating speeds: 9 °C/min, 15 °C/min, 21 °C/min. The decomposition of mineral matter takes place after the departure of water, volatile gases and organic matter [17]. The stage we are interested in is the third one, the stage of decomposition of the mineral matter; Figures 6–11 represent these thermograms in Δm (mg) = f (T), the initial mass is 15 mg.
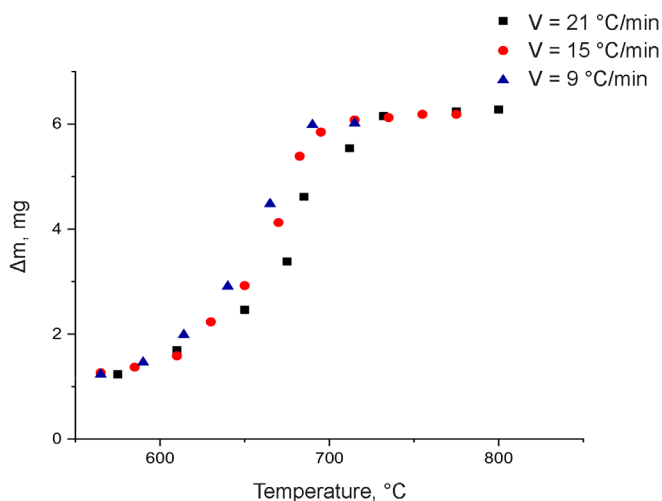
Fig. 6. Decomposition of mineral material Δm = f (T) into hydrogen carrier gas of the Z0 layer of Tarfaya.
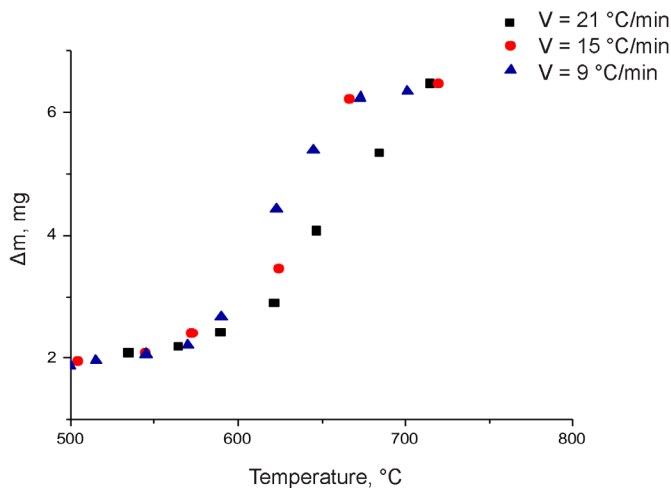

Fig. 7. Decomposition of mineral material Δm = f (T) into hydrogen carrier gas of the Z1 layer of Tarfaya.
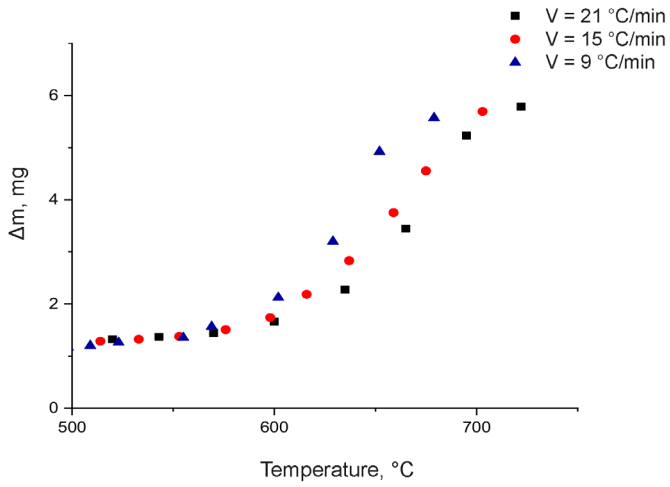
Fig. 8. Decomposition of mineral material $\Delta m = f(T)$ into hydrogen carrier gas of the Z2 layer of Tarfaya.
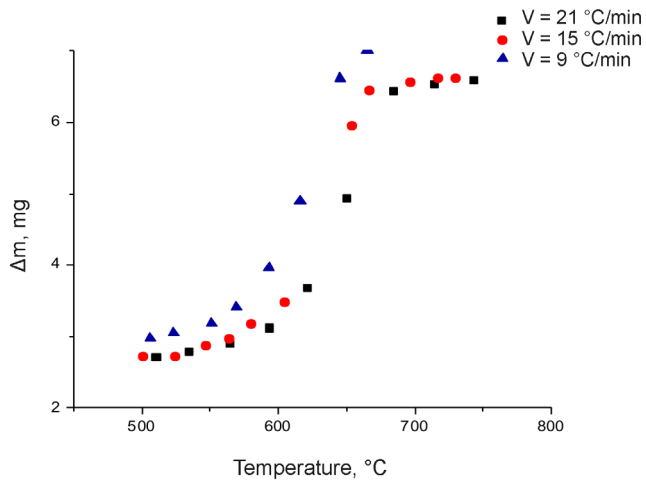

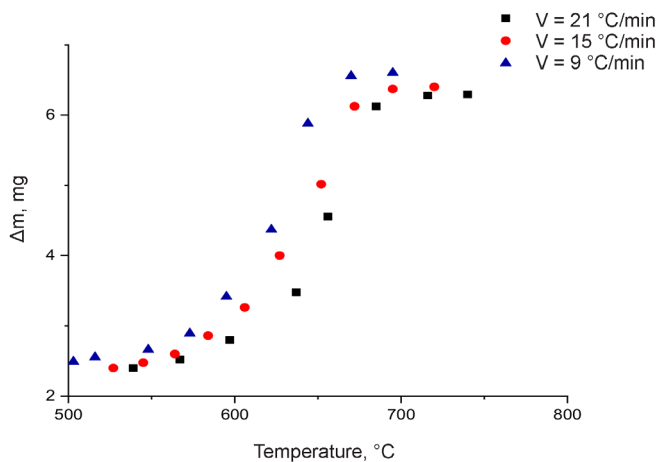Fig. 9. Decomposition of mineral material $\Delta m = f(T)$ into hydrogen carrier gas of the Z3 layer of Tarfaya.

Fig. 10. Decomposition of mineral material Δm = f (T) into hydrogen carrier gas of the Z4 layer of Tarfaya.

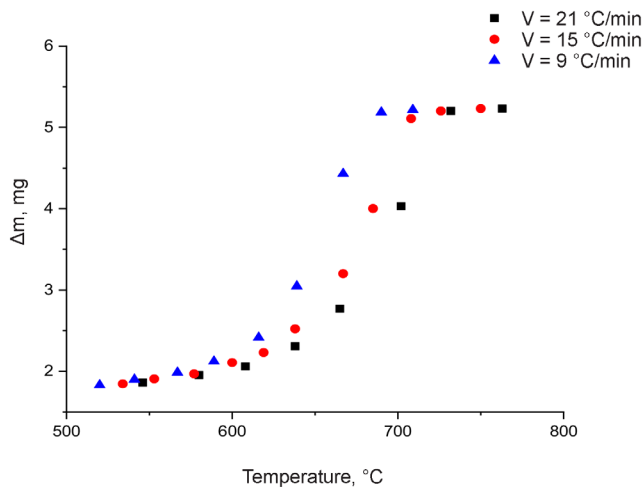Fig. 11. Decomposition of mineral material Δm = f (T) into hydrogen carrier gas of the M layer of Timahdit.

These thermograms given by the apparatus are accompanied by the derivative thermogravimetry (DTG) peak.

We collected the percentage losses of this reaction for each sample for the decomposition step of the mineral material under hydrogen as a carrier gas in Table 4, this table presents the DTG peak temperatures at different heating rates.

Table 4. Percentage loss and temperature of the DTG peak for each sample during the reaction

Heating rate, °C/min	Characteristics	Sample					
	Origin	Tarfaya					Timahdit
	Zone	Z0	Z1	Z2	Z3	Z4	M
21	Percentage loss	33	29.4	28.7	25.3	25.1	22.1
	DTG peak temperature	–	717	704	677	669	712
15	Percentage loss	33.6	30.6	29.2	26	26	22.4
	DTG peak temperature	–	680	673	657	663	687
09	Percentage loss	31.7	29.1	28.8	27.1	26.5	22.1
	DTG peak temperature	–	666	651	642	647	664

2.4. Morphology layers (Z4, M) before and after hydrotreating

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 12, 13, 14 and 15 show the photos of the Z4 and M layers before and after hydrotreating.
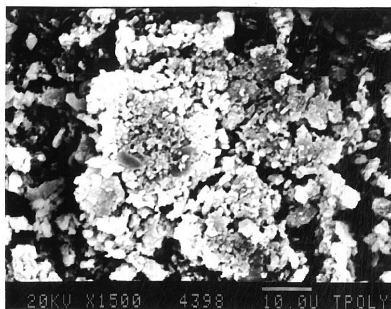

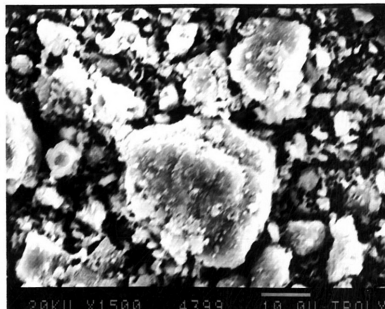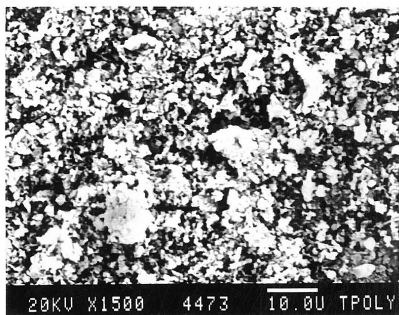Fig.12. Raw Z4 layer.   Fig. 13. Raw M layer.
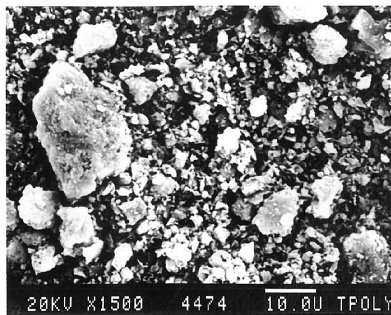
Fig. 14. Z4 layer after hydrotreating.

Fig. 15. M layer after hydrotreating.

We can clearly see the shrinkage of the grains in the Z4 layer, which is much more reactive than the M layer.

2.5. Derivative thermogravimetry

The Redcroft thermobalance is equipped with the DTG technique. We collected the temperature maxima of the DTG peak (°C) for all samples at three heating rates (see Fig. 16).
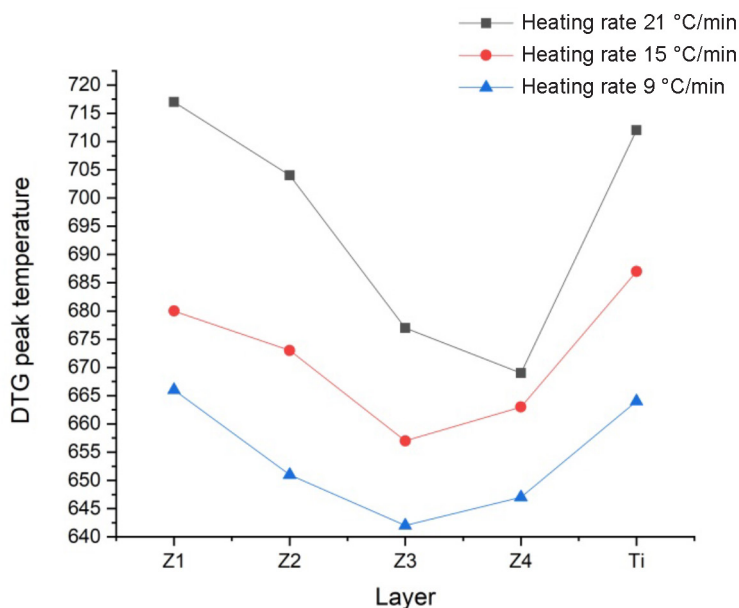

Fig. 16. Maximum temperatures of the DTG peak for different layers at different heating rates.

In the Upper Secondary the Cenomanian (Z4) and Turonian (Z3) geological strata are considered the hottest strata [18], the in situ pyrolysis occurred first in the Cenomanian and later in the Turonian [19]. These two layers, given the location of the low DTG peak temperatures, are the most reactive.

This order of pyrolysis occurrence is quite obvious for the first two heating rates (9 °C/min and 15 °C/min). But at the 21 °C/min heating rate there is a competition between the deactivation of the heating rate increase and the mass effect (59.3% for Z3 and 54.9% for Z4) [20], this is why Z4 is the most reactive sample after Z3.

Concerning the Z1 layer (Maestrichtian: warm climate) and the Z2 layer (Senonian: cold climate) their reactivity is a function of the quality of the mineral material. The high concentration of dolomite for the Z1 layer (6%) compared to the Z2 layer (1%) can be noted [9], which delimits the deactivation in spite of the climate factor.

Concerning the lake deposit of Timahdit, the low dimensions of DTG peaks observed prove the activity of the lake deposit, as well as the position of temperature of the peaks being superior to the others except Z1, which has changes of activity of Ti and Z1. This can be explained only by the high dolomite percentage of this mineral material [21].

2.6. DTG peak areas – elements of reactivity comparison

We calculated the DTG peak area for each sample at three heating rates; the results are given in Table 5.

Table 5. DTG peak areas

Heating rate, °C/min	DTG peak area, mg				
	Tarfaya				Timahdit
	Z1	Z2	Z3	Z4	M
21	4.59	5.06	3.96	4.75	3.64
15	4.75	4.90	3.96	4.11	3.8
9	4.11	3.96	4.11	5.06	5.06

Considering similar or neighboring sedimentation climates, the reactivity is a function of the composition of the mineral matter. A statistically observed rule is that when the surface area of the DTG peak decreases, the reactivity of this mineral matter increases, which is opposite for organic matter.

Two by two the layers respect this hypothesis, namely Z2 and Z3, Z2 and Z4, Z4 and Z3, at the end Z1 and Z3. This means that when the surface area decreases, the reactivity conversely increases.

Two special cases have arisen: layers Z1 and Z2 and Z1 (v = 9 °C/min), according to their mineral matter composition, are largely concentrated in dolomite $MgCa(CO_3)_2$, but the decomposition range of this compound increases with increasing temperature, which makes the layers less reactive.

3. Conclusions

In this work, the reactivity of the mineral material of the five layers of the Tarfaya deposit and the M layer of the Timahdit deposit was shown to be different. A comparison of this reactivity was made using thermogravimetric analysis coupled with its derivative in dynamic regime at heating rates of 9 °C/min, 15 °C/min and 21 °C/min. The analysis was carried out for the hydrotreating reaction (hydrogen carrier gas) for the five Tarfaya layers (Z0, Z1, Z2, Z3 and Z4) and the M layer of Timahdit, for comparison.

The influence of the climate of the geological sedimentation stage of the different layers of the Tarfaya deposit was discussed in order to understand the corresponding reactivity. In the Upper Secondary (Cretaceous), the Cenomanian (Z4) and Turonian (Z3) geological layers are considered the hottest, first the Cenomanian and later the Turonian where the in situ pyrolysis occurred. These two layers, given the location of the low derivative thermogravimetry peak temperatures, are the most reactive.

The experimental results and observations clearly show that the reactivity of the mineral material can be influenced by the mass effect and the increase of the heating rate, as was observed in the case of two layers, Z3 and Z4, at the heating rate of 21 °C/min where the order of reactivity between the two samples was reversed by the action of the mass effect (49.7% for Z3 and 40.7% for Z4) and the increase of the heating rate. However, despite the climate factor of the Z1 (Maestrichtian: hot climate) and Z2 (Senonian: cold climate) layers, in this analysis the reactivity was reduced by the high concentration of dolomite $CaMg(CO_3)_2$ for the Z1 layer (9.3%) compared to the Z2 layer (6.6%), which explains the low reactivity of the mineral material in Z1.

For the Timahdit lake deposit the low reactivity is shown by the size of the low DTG peaks and the temperature position of these peaks, which are always higher than those of the other layers. The reversal of the reactivity order observed between the Z2 layer and the Z1 layer is due to the quality of this material, namely the high dolomite percentage in Z1. It was also noticed that in similar or neighboring sedimentation climates the reactivity is a function of the composition of the mineral material.

A relationship of disproportionality was established between the surface area of the DTG peak and the reactivity of the mineral matter of these layers. Statistically it is that when the surface area of the DTG peak decreases, the reactivity increases, inversely for the organic matter. Two by two the layers respect this hypothesis, which are Z2 and Z3, Z2 and Z4, Z4 and Z3, at the

end Z1 and Z3. This means that when the surface area decreases, the reactivity inversely increases. Two special cases have arisen: Z1 and Z2 and Z1 (Ө = 9 °C/min). The Z1 layer, due to its mineral matter composition, is largely concentrated in dolomite $MgCa(CO_3)_2$, but the decomposition range of this compound increases with increasing temperature, which makes the layer less reactive. Due to the low percentage of material in this stage, the low peak area for the Timahdit deposit can be observed.

Acknowledgment

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