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THERMOGRAVIMETRY AND INFRARED SPECTROSCOPY OF MOROCCAN OIL SHALES IN AN OXIDATIVE DYNAMIC ATMOSPHERE

By

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التحليل الوزني الحراري وطيف الأشعة تحت الحمراء للزيت الأحفوري المغربي في جو مؤكسد متحرك

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أجريت التحاليل الوزنية الحرارية لزيت خام التيماديت (المغربي) ونواتج تحلله في وسط مؤكسد . وقد فصل الكيروچين بمعالجة الخام بحمض الهيدروكلوريك وحمض الهيدروفلوريك بشكل متتابع أثناء استخدام طريقة التعويم (Float-Sink) للفصل . وقد تم أكسدة الخام والمواد الناتجة من تحلله ، كل على حده ، في المحلل الوزني الحراري في جو متحرك من الهواء .

وقد استخدمت قياسات طيف الأشعة تحت الحمراء (FTIR) لتتبع تفاعلات الأكسدة وكذلك التغيرات الوزنية الحرارية الحادثة للمواد العضوية .

وقد ثبت من المخطط الوزني الحراري (TG) والمخطط الوزني الحراري التفاضلي (DTG) أن عملية حرق المركبات العضوية في زيت خام التيماديت تحدث في خطوتين منفصلتين . تتضمن الخطوة الأولى من الأكسدة حرق الأجزاء الأليفاتية ومجموعات الكربونيل ، بينما تختص الخطوة الثانية من الأكسدة بالتركيبات الأروماتية ومجموعات الكربوكسيل .

Key Words: Thermogravimetry, Infrared spectroscopy, Analysis of Moroccan oil shales.

ABSTRACT

Thermogravimetric analyses were carried out on raw Timahdit (Morocco) oil shales and its demineralisation products in an oxidative atmosphere. The kerogen was isolated by successive HCl, HF and float-sink separation treatments. raw shale and each product of every demineralisation step were oxidised in a thermal analyser system in dynamic air atmosphere.

Solid-state FTIR spectroscopy was issued to follow the oxidation reactions and thermochemical changes occured in the organics.

TG and DTG oxidative profiles of Timahdit oil shale indicated that the combustion of the organics occurred in two separate phases. The first oxidation stage involves the combustion of aliphatic moieties and carbonyl groups while the second one is related to the oxidation of aromatic structures and carboxylic groups.

INTRODUCTION

Anticipating a future shortage of petroleum and since the onset of the energy crisis a few year ago has caused an increased world interest in the extraction of liquid fuels from oil shale. This interest is evidence by the exploration for new deposits, new research studies of oil shale conversion and the development of new retorts and retorting technology. Oil shale contains no oil, but rather kerogen, a solid organic, substance which is insoluble in typical petroleum solvents, which is bound within the shale inorganic matrix.

Oil shale can burn directly in the furnace to produce steam and electricity. In addition, when oil shale is pyrolysed to produce shale oil, gas and residual carbon. The residual carbon is a potential energy source, which can react with air to supply heat energy for the retorting process. Efficient utilisation of technologically important materials like oil shale requires a good characterisation of their thermophysical behaviour and the knowledge of their combustion properties.

Thermogravimetric analysis has come into use in the last decades for studying the pyrolysis and oxidation of oil shale. Studies using thermal analysis technique have shown that the combustion of selected American and Australian raw oil shales is a complex multistage process [1]. Recently, it was found that the oxidation of kerogen occurred in two stages [2-10]. Several authors [2, 6] indicated that the first stage involved the oxidation of aliphatic material while the second one involved the combustion of aromatic moieties and may be elemental carbon.

In the present study, solid-state IR spectroscopy and non isothermal thermogravimetric analysis are employed to study the oxidation of Timahdit raw oil shale and its demineralisation products.

EXPERIMENTAL

Large chunks of raw Timahdit oil shale deposit (Morocco) were ground, sieved and stored until their usage. The kerogen concentrate was isolated by successive HCl and HF demineralisation procedures [6, 7, 11] and float-sink separations [7]. It was found that hydrochloric acid and hydrofluoric acid treatment did not destroy the thermophysical properties and did not alter the chemical composition of the shale organics [6, 7].

Thermogravimetric data were obtained using a Stanton Redcroft STA 781 Thermal Analyser. All TG and DTG thermal curves presented in this work were obtained using a heating rate of 20°C min^{-1} and a dynamic air purge of 40 $\mathrm{cm}^3\ \mathrm{min}^{-1}$.

Solid-state IR spectra for Timahdit raw oil shale, its demineralisation products and kerogen residue were obtained using the pressed KBr disc technique. These spectra were measured using the Perkin Elmer 1600 series FTIR Spectrophotometer.

RESULTS and DISCUSSION

The average weight loss which occurred with each one of the isolation steps is presented in Figure 1. From these data, we can calculate that Timahdit oil shale contains 3.89% bitumen, 36.04% carbonates, 39.79% silicates, 15.5% organic matter, 1.4% pyrite and about 3.36 ash.

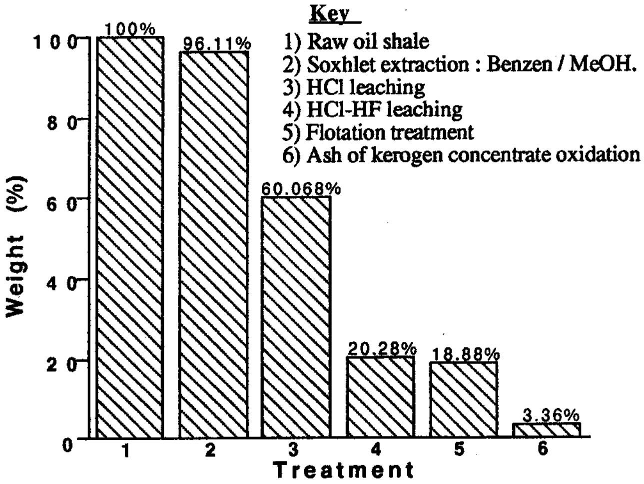

Fig. 1: Weight loss on Timahdit kerogen isolation.

Timahdit oil shale yielded kerogen concentrate containing 15-18% mineral matter which gives 2.8 to 3.4% of ash, with pyrite as a major mineral component. The persistence of ash in the isolated kerogen supports the model of oil shale in which the organics are the continuous phase which bind together a discrete mineral phase. This model suggests that kerogen could completely shield some mineral particles preventing complete removal of the minerals by HCl and HF.

TG and DTG oxidative profiles of Timahdit and its demineralisation products are given in Figures 2 and 3 respectively. TG oxidative curve of raw Timahdit oil shale presented in Figure 2D shows two weight losses between the ambient and 900°C. The first weight loss in the temperature range 200-600°C corresponds to the oxidation of the organics in the shale and represents about 16% of the hole shale.

Table 1
DTG Characteristics of Timahdit oil shale in dynamic air atmosphere

Material	Oxidation Temperature			The amount of kerogen oxidised (%):	
	Peak Temperatures(°C)		Valley Temp.(°C)	First stage	Second stage
	t1	t2			
Raw Shale	410	510	446	37.5	62.5
Carbonates free shale	385	500	420	30.30	69.7
Silicates free shale	318	385	350	25.0	75.0
kerogen	325	400	375	30.35	69.64

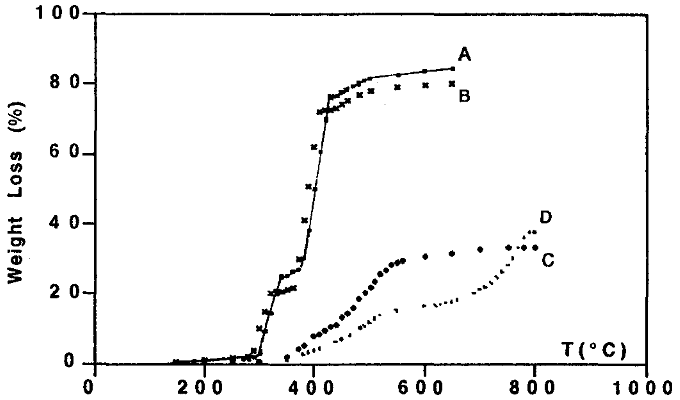

Fig. 2: TG curves for Timahdit shale and its demineralisation products heated at 20°C/min in air. A) kerogen concentrate; B) silicates free shale; C) carbonates free shale D) raw oil shale.

The second weight loss is due to the carbonate decomposition and constitute about 22% of the shale. Although, the TG oxidative curve of organic components in the 200-600°C region is one step in nature, in the sense it is a single weight loss, DTG oxidative profile of Timahdit row oil shale shows that the combustion of organic matter occurs in two separate phases.

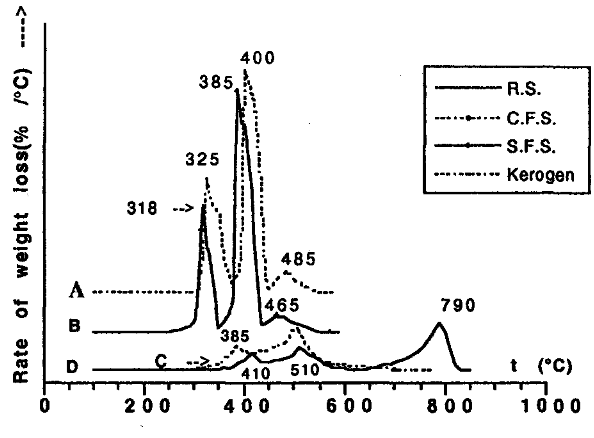

Fig. 3: DTG curves for Timahdit oil shale and its demineralisation products heated at 20(C/min in air. A) Kerogen concentrates, B) Silicates free shale, C) Carbonates free shale and D) Raw shale.

TG oxidative curves of the shale demineralisation products Fig. (2) , kerogen concentrate (A), silicates free shale (B) and carbonates free shale (C) show first, that as the severity of the treatment for demineralisation increased, temperature at which the oxidation reaction start decreased steadily which confirm the multistage nature of the combustion of kerogen in air. Second, the kerogen oxidation exhibits a major weight loss during the second stage and the amount of organic matter oxidised during this stage increased from raw to silicates free shale. Finally, it must be noted that the removable of pyrite by flotation, affected the amount of the organic matter oxidised during both stages and shifted the oxidation of kerogen towards higher temperature (Table 1). This is due to the catalytic effect of the inorganic matrix upon to the oxidation of the organic material.

Derivative thermogravimetric DTG oxidative profiles of the shale demineralisation products show two sharp peaks related to the combustion of the kerogen. The removal of the inorganic matrix shifted towards lower temperatures the position of the DTG oxidation peaks. While the float-sink separation treatments, to minimize pyrite content in the organics shifted the two peaks towards higher temperatures.

Fourier transform infrared (FTIR) spectroscopy was used in order to follow the oxidation reactions of the organics and thermochemical changes occurred in the kerogen. Figure 4 compares the FTIR spectra of Timahdit raw shale, its demineralisation products and he kerogen remaining material from experiments run until the end of the first oxidation stage. Table 2 lists the principal organic and inorganic frequencies, together with their assignments observed in the shales and in their demineralisation products.

Timahdit shale displays an intense bands at 1425, 875 and 712 cm-1, due to the calcium carbonate (calcite) and a band at 1035 cm-1 related to the silicate. The kerogen concentrate FTIR spectrum shows a substantially intense bands of alkanes at 2930, 2852, 1453 and at 1383 cm-1 and the O-H stretching band at 3424 cm-1, together with a relatively intense aromatic band at 1636 cm-1. There are, however fewer carbonyl groups, as indicated by lower relative intensities of the C=O stretching band at. 1700 cm-1. Timahdit kerogen also displays a large band at 618 cm-1 due probably to the pyrite content in the shale.

Table 2

Principle inorganic and organic frequencies encountered in oil shale

Wave number cm-1	Assignment
1425,875,711	Calcium carbonates (calcite)
1100-900,550-450	Silicates [12]
3700-3600	Kaolinite [12]
425-350 (618-635 for Timahdit shale)	Pyrite [13]
3424	O-H stretching
2923	Asymmetric CH stretch. of methylene groups
2852	Symmetric CH stretch. of methylene groups
1700	C=O stretching
1636	Aromatic ring stretching
1457	Asym. CH_2 and CH_3 bending
1378-1636	Asym. CH_3 bending

FTIR spectra of the residual matter of oxidised kerogen concentrate which was obtained in experiments run until the end of the first oxidation stage contains diminished organic groups absorption bands. It can be seen that alkane bands are no longer evident, and are drastically reduced bands arising from O-H, C=O and aromatic vibration. These results show that the first oxidation stage involved the combustion of aliphatic content and carbonyl groups.

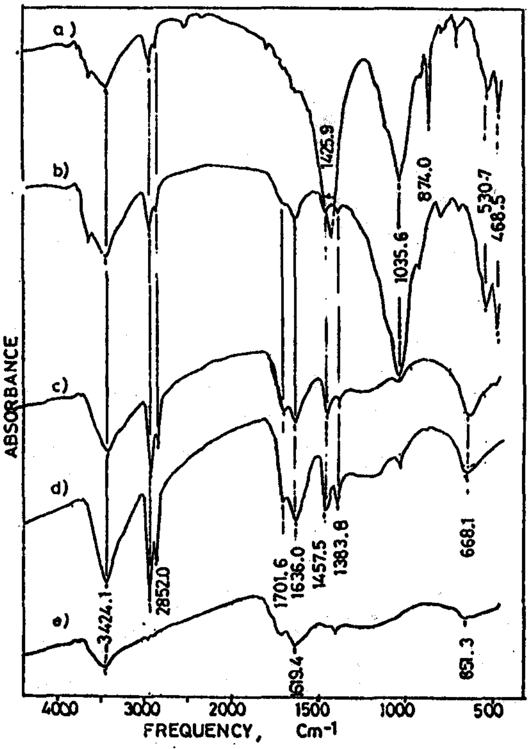

Fig. 4: FTIR spectra of: a) Timahdit raw oil shale, b) carbonates free shale, c) Silicates free shale, d) Kerogen concentrate and e) The remaining material of the oxidation of kerogen up to the end of the first oxidation stage.

CONCLUSION

DTG oxidative profiles of Timahdit kerogen concentrate shows two sharp peaks at about 325°C and 400°C. In addition of these peaks, this concentrate displays a third peak at about 485°C which is probably due to the oxidation of the carbonaceous material.

The shift of the two oxidation stages towards lower temperatures was due to the removal of inorganic material which prevented the proper contact of oxygen and kerogen. Therefore, upon the removal of inorganic matrix, the organics became more susceptible for oxidation reactions which probably started at lower temperatures.

Solid-state FTIR spectra of the oxidised material up to the end of the first stage, indicated that the first oxidation stage involved the combustion of aliphatic contents and carbonyl groups. Whereas the second stage involved the oxidation of aromatic structures and carboxylic groups.

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