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OXIDATION KINETICS OF TIMAHDIT AND TARFAYA MOROCCAN OIL SHALES

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Abstract

Organic matter evolution and kinetics of combustion of Tarfaya and Timahdit oil shales have been examined by thermogravimetry (TG) and by differential thermal analysis (DTA). An agreement is observed between both techniques where it was found that combustion of organic matter occurs in two steps. Kissinger's method applied on experimental results gives an activation energy of the same magnitude for the first step of both oil shales (103 kJ mol^{-1}) whereas the second is 148 kJ mol^{-1} for Timahdit and 118 kJ mol^{-1} for Tarfaya.

The changes in specific surface area during thermal combustion of Timahdit and Tarfaya oil shales have been studied by thermogravimetric gas sorption balance and correlated with experimental results obtained on TG/DTA in air. For Timahdit oil shale oxidation products, specific surface areas calculated from nitrogen adsorption data shows a slight increase during the temperature domain of 280 to 430°C and after this temperature, they increase sharply. However, data obtained with Tarfaya oil shales shows a significant increase at the temperature of maximum oxidation of the first stage of combustion of organic matter.

Keywords: kinetics analysis, surface area, Tarfaya and Timahdit oil shales, TG/DTA, thermal combustion

Introduction

Oil shales have long been recognised as a potential source of the hydrocarbon products, which are now produced from crude petroleum and natural gas.

Their thermal decomposition to produce oil is usually carried out between 200 and 500°C, temperatures where considerable degradation takes place resulting in a volatile fraction, which part of it is condensable and a residual organic carbon fraction, which remains in the solid residue.

In the methods for extracting the shale oil, heat is supplied by combustion of a portion of the oil shale residual organic matter to break down thermally and to distil

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the organic matter from oil shale [1–3]. Previous investigations were made on the thermal oxidation of the shales by using thermal analysis techniques TG, DTG [3–7] and DTA [8–10]. Lee and Sohn [3] studied the kinetics of oxidation of kerogen in Colorado oil shales by using the technique of TG. They assumed that at the relatively low temperatures at which the kinetics were measured, the oxidation reaction takes place on the surface of solid kerogen and that the decomposition of kerogen is not significant. It has been shown by technique of DTA [8–10] that combustion of kerogen is a complex multistage process indicated by broadly overlapping exotherms. This was confirmed by Earnest [4] when using TG/DTG to investigate the oxidation profiles of selected American and Australian oil shales. It was assumed that in the presence of O_2, two processes develop simultaneously: a simple thermal degradation process, and a thermochemical process combining temperature and O_2 effects [7]. Infrared emission spectroscopy has been used to monitor the chemical modifications taking place during the oxidation of kerogen and raw oil shale in the range 50–700°C. At increasing temperatures, a steady decrease in the signals due to aliphatic hydrocarbons as well as in the carbonyl/carboxyl signals and the carbonyl signal, along with an increase in the anhydride signals [11]. Changes in mass loss and in heat are accompanied during thermal decomposition by a change of physical and chemical properties of the solid [12]. Specific surface area is one of these physical properties. The reactivity of a solid material towards gases is governed, inter alia, by its active surface area. The measurements of specific surface area at various stages of reaction may provide useful information about the reactivity of a material. The nitrogen adsorption isotherm at 77 K is a widely used method for investigating surface area by using the BET equation [13].

Previous studies on surface area measurement of oil shales have been carried out by numerous authors [14–16]. Nitrogen adsorption-desorption isotherms were obtained on raw and decharred Colorado oil shales samples. The mineral constituents have an appreciable surface area, about 3 to 5 $m^2 g^{-1}$, which appears to be limited to external surface [14]. Slettevold *et al.* [15] studied the surface area and pore distribution of retorted Colorado oil shale, using nitrogen and carbon dioxide and mercury porosimetry. They combined the surface areas of decharred and retorted samples to estimate the specific surface area of the residual organic carbon (300 $m^2 g^{-1}$). The effects of retort temperature and constant heating rates of two eastern US oil shales were investigated by Schrodt and Ocampo [16]. Surface areas calculated from N_2 and CO_2 adsorption data were observed to decrease in the early, low-temperature retort stage as a result of pore mouth blockage due to the formation of a thermoplast, and then to increase markedly above the raw shales values at higher temperature. The effect of heating rate was insignificant [16]. Variation of porosity of raw and spent Turkish oil shales with retorting temperature during pyrolysis is assumed to be linear which is justified by the BET surface area measurements. These measured porosities and surface areas indicate that essentially macropores are developed during pyrolysis [17].

Kinetics and rates of oxidation will depend on the area of the shale surface and its accessibility to oxygen. The purpose of this paper was to derive kinetic parameters for the decomposition processes related to the non-isothermal oxidation of Tarfaya and Timahdit Moroccan oil shales. Also, for better understanding the thermal combustion behaviour of these shales, simultaneous TG/DTA apparatus were used and surface area measurements at various stages of oxidation reaction were obtained and correlated with TG/DTA data.

Experimental

Sample preparation

The oil shale samples used in this work was obtained from Timahdit and Tarfaya deposits (Morocco), courtesy of the 'Office National de Recherche et d'Exploitation du Pétrole (ONAREP)' and 'Ministère d'Energie et des Mines [12, 18–19]'. Table 1 gives general characteristics of both shales:

Table 1 General characteristics of oil shales

	Tarfaya	Timahdit
Density	2.20	2.02
P.C.S. kJ kg^{-1}	5133	4640
Ash/%	49.65	64.29
CO_2/%	33.00	21.80
Organic matter/%	16.25	12.83
Organic carbon/%	11.20	8.75

Particle size fraction of less than 73 μm was obtained after grinding for 20 min and sieving for 30 min for both raw oil shales.

The intermediate samples during combustion reaction were prepared in a system that was devised and consisted basically of a tube furnace, drier and nichrome wire. The procedure was as follows: firstly the sample was put inside the tube furnace and an airflow rate (34.8 cm^3 min^{-1}) and the heating rate (12°C min^{-1}) were established. Then, the sample was taken out to cold position of the glass tube by the nichrome wire from the hot zone of the furnace when the temperature reached a selected value. To prevent further oxidation of samples, air flow was turned off and nitrogen flow was established. The procedure was repeated with different samples and different temperatures using the same heating rate.

Apparatus

Thermal analysis studies were carried out on a Stanton – Redcroft STA 781 simultaneous TG/DTA unit using samples of 10 mg in flowing dry air atmospheres (dried by $MgClO_4$) and set flow rate (34.8 cm^3 min^{-1}).

Surface areas of these materials were determined by a gravimetric BET method [20], using nitrogen gas sorption balance at 77 K recorded on a vacuum microbalance, CI Microforce Mark 2B, which give µg to mg sensitivity, using sample of 250 mg.

Finally, figures were drawn in this paper by using Microsoft Excel 97 graphic's method.

Results and discussion

Effect of heating rate on the thermal analyses

Figures 1 to 4 represent the DTA and TG curves at different heating rates 5, 12, 20 and 40°C min^{-1}. The first diagram shows the variation of energy changes and the second illustrates the fractional mass loss, α, *vs.* temperature of the system Timahdit/air and Tarfaya/air. DTA results indicate that the system gives two successive exothermic reactions where the first is more exothermic than the second. This is also observed by TG, which gives a curve characterised by two stages.

Both sets of data (Figs 1 and 2) were recorded simultaneously under the same experimental conditions. The analysis of both diagrams (5°C min^{-1}) shows that the first and second DTA peaks correspond to mass losses of 2.1 and 8.9%, respectively on the TG curves, where the rates of mass loss are at their maximum.

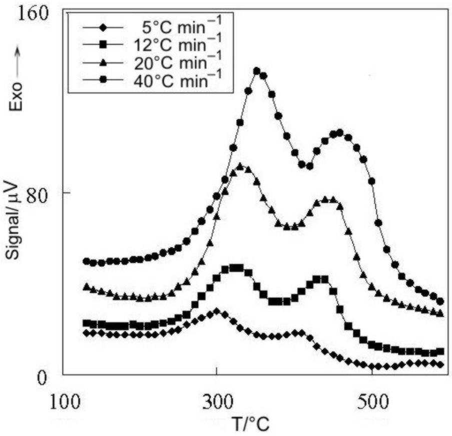

Fig. 1 DTA curves of Timahdit oil shale in dynamic air atmosphere

Therefore, the peaks are well defined and it is possible and easier in the present case to apply the Kissinger method [21] to our data. The results obtained will be compared with those obtained by applying the Coats–Redfern method to TG data.

Analogous studies by TG and DTA (Figs 3 and 4) were carried out on Tarfaya oil shales under the same experimental conditions. These show that combustion of organic matter occurs in two stages between 200 and 500°C and also, the first step is more exothermic than the second.

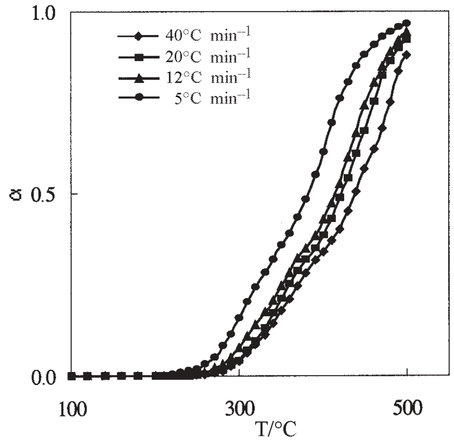

Fig. 2 Mass loss (TG) of Timahdit oil shale in dynamic air atmosphere

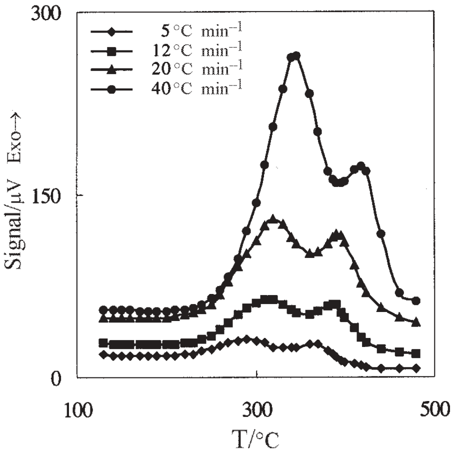

Fig. 3 DTA curves of Tarfaya oil shales in dynamic air atmosphere

The method of Kissinger

$[d(\ln(\phi/T_m^2))/d(1/T_m)=-E_A/R]$ was applied to the simultaneous DTA exotherms which were recorded at the same sensitivity, the same sample mass and at different heating rates, ϕ. Peak temperatures, T_m, were recorded and $\ln(\phi/T_m^2)$ *vs.* $1/T_m$ plotted (Fig. 5). Two straight lines were obtained with slope $-E_A/R$ for both shales, where E_A is the activation energy and R is the gas constant.

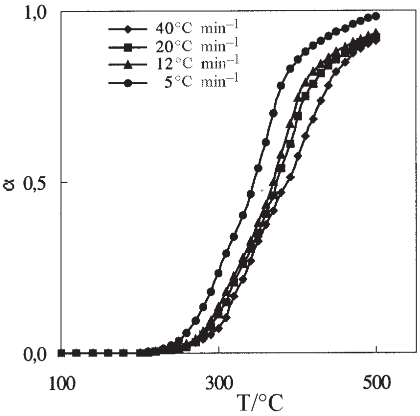

Fig. 4 Mass loss (TG) or Tarfaya oil shales in dynamic air atmosphere

The comparison between TG and DTA curves shows that, for example at 12°C min^{-1}, the temperature corresponding to the final decomposition of first kind of organic matter is 380°C. The second part of organic matter starts its decomposition after this temperature.

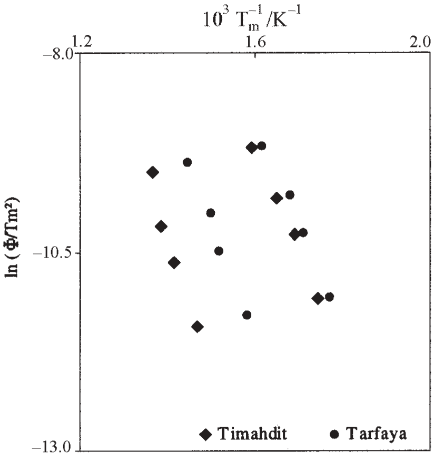

Fig. 5 Evolution of DTA picks maximum temperature of Timahdit and Tarfaya oil shales

As shown previously by numerous studies, Coats–Redfern method is applied to our data. Results obtained are shown in Fig. 6, which shows that no real straight lines were obtained. This non-linearity of the points leads us to look for another model that must fit oil shale oxidation. Future studies will look at all of the parameters accompanying oil shale decomposition to postulate a better model.

In spite of having a very high and complex heterogeneous nature, Tarfaya oil shale shares some similarities (and show some differences) compared with Timahdit oil shale.

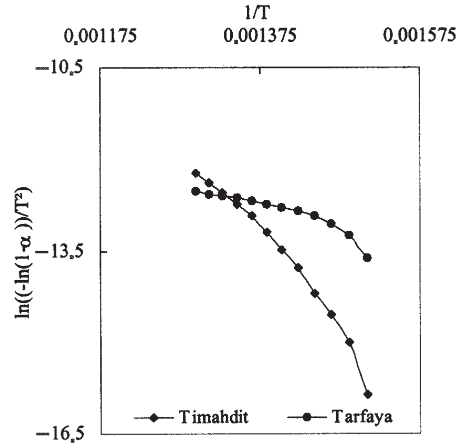

Fig. 6 Analysis of oil shale combustion by Coats–Redfern method (ln((–ln(1–α))/T^2) *vs.* 1/T)

They have practically the same activation energy (103 kJ mol^{-1}) for the first stage. Whereas, they are different in the second: 148 kJ mol^{-1} for Timahdit compared with 118 kJ mol^{-1} for Tarfaya. Thus, during combustion, Tarfaya oil shale is more reactive than Timahdit oil shale. This difference corresponds also to a drop of about 50°C in the temperature of the DTA peaks. Both exothermic peaks, where their maximums are located at about 300 and 400°C, correspond to the combustion of organic matter. This work is in a good agreement with previous researches [4–10] on oil shale oxidation, which confirmed the existence of both peaks. The first is attributed to the complete or almost complete combustion of aliphatic components to give a char containing aromatic moieties [5].

Surface area evolution during combustion

The specific surface areas of Tarfaya and Timahdit oil shale samples during combustion in air atmosphere and a heating rate of 12°C min^{-1} were obtained. Results of this investigation are summarised in Fig. 7, showing the mass of N_2 adsorbed per gram of sample *vs.* relative pressure. The adsorption isotherms are of type–II as described by the Brunauer–Emmett–Teller (BET) model indicating a predominant micro-mesopore structure. These types of isotherm were interpreted according to the BET equation:

$$p/W(p_o-p)=1/W_mC+(C-1)p/W_mCp_o$$

where C is the BET constant.

By plotting $p/W(p_o-p)$ *vs.* p/p_o, a straight line is obtained within the relative pressure range of 0.05 to 0.35. Slope and intercept give the monolayer capacity (W_m) and hence the specific surface area can be calculated. The results of this investigation are shown in Fig. 8.

One can notice in these figures, for Timahdit residual products of combustion, the surface is practically constant between 280°C (6% burn off in total organic mat-

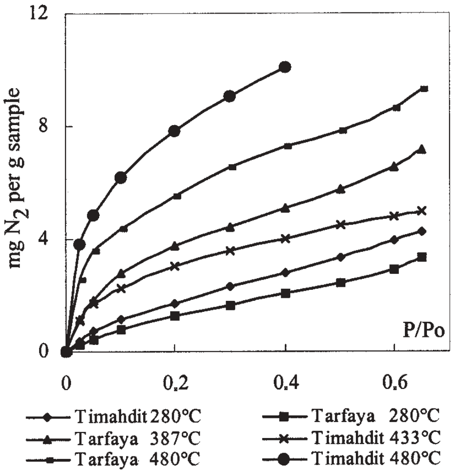

Fig. 7 The adsorption isotherm curves showing the mass of N_2 adsorbed per gram of samples heated at different temperatures *vs.* relative pressure

ter) and 430°C (47% burn off in total organic matter) and after this temperature it increases sharply.

The comparison between these surfaces with TG/DTA data of Timahdit shows that surface areas are only slightly altered during the first stage of oxidation which corresponds to the oxidation of aliphatic organic matters (first peak) and that the second accelerated variation, corresponds to the combustion of the residual organic matter and to the removal of hydrocarbons from the surface of the solid on gasification.

On the other hand, during the second stage, a noticeable increase (two to threefold increases) in surface areas is observed. Surfaces areas increase with retorting temperature indicating essentially macropores development during combustion. This

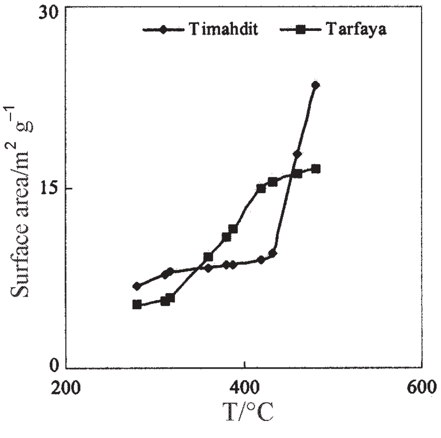

Fig. 8 Variation of specific surface area with temperature

is in good agreement with previous research on Turkish oil shales pyrolysis [17]. However, the same study was carried out on Tarfaya oil shales where the variation of specific surface area becomes significant at the temperature of maximum oxidation (312°C, 16.5% burn off) of the first stage. This difference of behaviour is related to the chemical and physical characteristics of both oil shales, involving the nature of kerogen and the structure and texture of mineral matter.

A comparison between the reactivity of both shales during the oxidation stage of organic matter, lead to the conclusion that Tarfaya oxidation products exhibit a higher reactivity, explained by the shift in the DTA peaks' maximum temperature and the TG mass losses profile to lower temperatures. Thus, the reactivity of a solid material towards gases is governed by its active surface area. On the light of both specific surface areas data, the second stage starts at about 312°C for Tarfaya whereas for Timahdit it is 420°C. This difference in temperature is more likely in relation to the lower reactivity obtained for Timahdit oil shales compared with Tarfaya during air combustion.

Conclusions

The results of this work are used to form a picture of the changes of mass and surface area during oil shale combustion with the aim of understanding better the effect of each parameter in the overall processing of oil shale and its optimisation. Our previous work shows an effect of the anisotropy of the rock on the overall process of oil shale decomposition. Good linear results were obtained by applying Kissinger method, whereas, Coats–Redfern method must be modified to fit to oil shale air oxidation reaction as shown by numerous previous studies [22]. Each stage of the reaction must be considered in the modified Coats–Redfern equation and all parameters including structural changes should be taken into account in the development of a new model for the kinetics of oil shale evolution.

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References

1 W. G. Schlinger and D. R. Jesse, I.&E.C. Proc. Des. Dev., 7 (1968) 275.
2 A. K. Burnham, Fuel, 58 (1978) 285.
3 I. C. Lee and H. Y. Sohn, Fuel, 65 (1986) 129.
4 C. M. Earnest, Thermochim. Acta, 60 (1983) 171.
5 J. H. Levy and W. I. Stuart, Thermochim. Acta, 74 (1984) 227.
6 A. Lamribah, L. Belkbir and S. A. A. Jayaweera, Qatar Univ. J., 14 (1994) 31.
7 J. P. Vantelon, C. Breillat, F. Gaboriaud and A. Alaoui-Sosse, Fuel, 69 (1990) 211.
8 K. Rajeshwar, R. Nottenburg and J. B. DuBow, J. Mater. Sci., 14 (1979) 2025.
9 K. Rajeshwar and J. B. DuBow, Fuel, 59 (1980) 790.

10 D. E. Rogers and D. M. Bibby, Thermochim. Acta, 30 (1979) 303.
11 H. R. Rose, D. R. Smith and A. M. Vassallo, Energy & Fuels, 12 (1998) 682.
12 L. Belkbir, H. Barkia and N. Gerard, Thermochim. Acta, 103 (1986) 147.
13 S. Brunauer, P. H. Emmett and E. Teller, J. Amer. Chem. Soc., 60 (1938) 309.
14 P. R. Tisot, J. Chem. Eng. Data, 7 (1962) 405.
15 C. A. Slettevold, A. H. Biermann and A. K. Burnham, L. L. N. L, Report UCRL-52619, Livermore, CA, 1978.
16 J. T. Schrodt and A. Ocampo, Fuel, 63 (1984) 1523.
17 O. M. Dogan and B. Z. Uysal, Fuel, 75 (1996) 1424.
18 H. Barkia, Doctorat d'état, Mohammed V-Agdal University, Faculty of Sciences, Rabat, Morocco, 1990.
19 H. Barkia, L. Belkbir and S. A. A. Jayaweera, Thermochim. Acta, 103 (1986) 147.
20 D. R. Glasson, J. Chem. Soc., 1956, pp. 1506-10.
21 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
22 A. K. Burnham and R. L. Braun, Energy & Fuels, 13 (1999) 1.