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THERMAL ANALYSIS STUDIES OF OIL SHALE RESIDUAL CARBON

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Abstract

Thermal analysis has been used to determine the impact of heating on the decomposition reaction of two Moroccan oil shales between ambient temperature and 500°C. During pyrolysis of raw oil shale, the residual organic matter (residual carbon) obtained for both shales depends on the heating rate (5 to 40°C min^{-1}). Three stages characterize the overall process: the concentration of carbonaceous residue decreases with increase of heating rate, become stable around 12°C min^{-1} and continue to decrease at higher heating rates.

Activation energies were determined using the Coats–Redfern method. Results show a change in the reaction mechanism at around 350°C. Below this temperature, the activation energy was 41.3 kJ mol^{-1} for the decomposition of Timahdit, and 40.5 kJ mol^{-1} for Tarfaya shale. Above this temperature the respective values are 64.3 and 61.3 kJ mol^{-1}.

The reactivity of Timahdit and Tarfaya oil shale residual carbon prepared at 12°C min^{-1} was subject to a dynamic air atmosphere to determine their thermal behaviour. Residual carbon obtained from Tarfaya oil shale is shown to be more reactive than that obtained from Timahdit oil shale.

Keywords: carbon, combustion, gasification, kinetic, oil shale, pyrolysis, thermogravimetry

Introduction

The supply of energy has become a worldwide problem during recent decades. Many countries have attempted to diversify their potential energy sources in order to cope with oil price increases and their effect on the economy. The mobilisation of national energy resources became a vital task for many countries for economic development and social progress.

In Morocco, 90% of the energy consumed is dependent on imported oil. Thus, an intensive programme was commenced for the mobilization of indigenous energy sources, especially the local oil shales. Morocco has more than 15% of world reserves of oil shales. Exploitation of this resource enables Morocco to produce oil and gas by

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pyrolysis of the shales, and electricity by direct combustion. The resulting ash is a potential material for the cement and road construction industries. Attention was focused at the most important deposits of Moroccan oil shales at Timahdit and Tarfaya [1, 2].

An important difference between oil shales when compared with coals and tar sands is their mineral matter content. Oil shales have mineral matter content of 33% or more, significantly higher than for coals and tars [3].

Extensive studies have been carried out on the physical and chemical characteristics of Timahdit and Tarfaya oil shales in order to exploit these deposits commercially [4–17].

Oil shales are highly heterogeneous in their chemical composition and physical properties. Thus, during their thermal decomposition, a complex set of parallel and sequential reactions occur, for example, evolution of water vapour, conversion of kerogen to bitumen and its dissociation into low-volatile and high-volatile hydrocarbons (gas and oil), oxidation of residual carbon, etc. In the processing of oil shales, pyrolysis leads to condensable products and a solid residue, whereas combustion results in fully oxidized products. The former occurs in the presence of limited supply of oxygen (air); the latter requires excess oxygen.

Crawford *et al*. have reported the enthalpies of combustion for samples of raw and spent oil shales [18]. Docter [19] reports that shales having an oil content of more than 83 dm^3 ton^{-1} produce sufficient coke, complete combustion of which can produce sufficient energy for retorting the shale. Thus the residual carbon content of a shale is an important parameter in its commercial exploitation. This is dependent on, inter alia, the rate of reaction [20]. At fast heating rates, about 20% of the original carbon in a shale remains as residual carbon, usually called char [21, 22]. At lower heating rates, the residual carbon is called coke, the production of which results from oil degradation [21, 23].

Interest in oil shale gasification has brought about the need to have a better understanding of the reactivity of residual carbon of shales. Numerous reactivity studies have been conducted on oil shale residual carbon and well reported in [24–32]. The reactivity of the residual carbon during its oxidation depends on conditions of pyrolysis of the raw shale, namely, the heating rate and the final temperature. However, there is little on measurement of kinetic parameters on residual carbon from Moroccan oil shales. The present work is a part of a larger programme of thermal analysis studies on the decomposition reactions of Moroccan oil shales.

Experimental

Apparatus

All experiments were conducted at atmospheric pressure on a Stanton–Redcroft STA 781 Thermal Analyser, capable of simultaneous TG/DTG/DTA, using samples of 10 mg in flowing dry N_2 and air atmospheres (dried using $MgClO_4$) and gas flow rate (35 cm^3 min^{-1}).

Samples

The oil shale samples used in this work was obtained from Timahdit and Tarfaya deposits (Morocco). Table 1 gives the general characteristics of both shales:

Table 1 General characteristics of oil shales [4, 16]

Characteristics	Tarfaya	Timahdit
Density/g cm^{-3}	02.20	02.02
Humidity/%	01.10	01.00
Low and high-volatile hydrocarbons/%	12.90	09.90
Residual carbon/%	03.35	02.93
Total organic matter/%	16.25	12.83
Ash/%	49.65	64.29
CO_2/%	33.00	21.80
Organic carbon/%	11.20	08.75
Mineral carbon/%	09.00	05.95
H/%	01.50	01.30
N/%	00.40	00.40
S/%	09.00	00.80
Calorific value/kJ kg^{-1}	5133	4640

Residual carbon preparation and combustion

The samples were heated up to the desired reaction temperature (773 K) at a constant heating rate of 12°C min^{-1} and in nitrogen flowing atmosphere. When the desired temperature was attained, the sample was maintained in nitrogen (35 cm^3 min^{-1}) for 1 h. Then, air was introduced into the system, and the mass change was measured to determine the quantity and the reactivity of residual carbon.

Results and discussion

Figure 1 shows the extent of reaction, α, *vs*. temperature for raw oil shale from Timahdit and Tarfaya at four heating rates ranging from 5 to 40°C min^{-1}. For both shales, thermal decomposition started at 200°C and reached a maximum rate at around 420°C for the slowest heating rate, moving to higher temperatures with increasing heating rate.

The total organic matter (low-and high-volatile hydrocarbons plus residual carbon) in the shale for each heating rate was determined after heating all samples in nitrogen flowing atmosphere (35 cm^3 min^{-1}) to 500°C and keeping for 1 h at this temperature. Air was then introduced to obtain the quantity of organic carbon remaining in the shale.

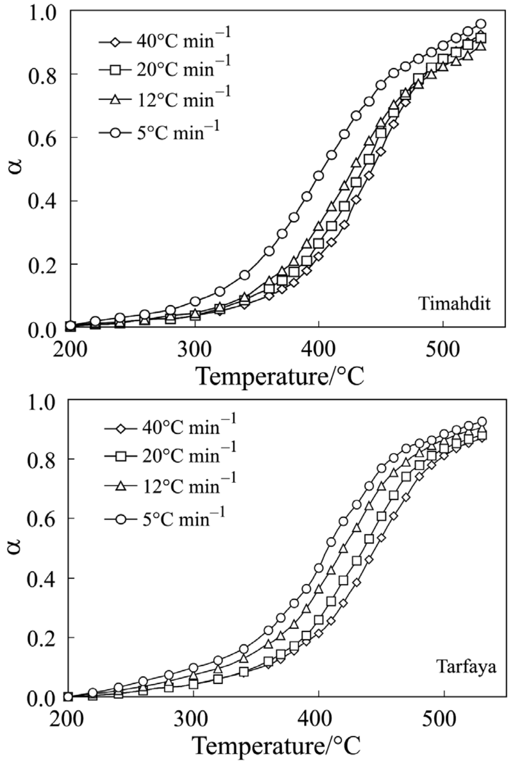

Fig. 1 Thermal decomposition of Tarfaya and Timahdit oil shale in nitrogen atmosphere realised at different heating rates (α *vs.* *T*)

It was found that the residual carbon (2 to 5%) for both shales depends on the heating rate used during the pyrolysis of raw oil shale (Fig. 2). Three stages characterize the overall process under pyrolysis (decomposition of organic matter to produce volatile hydrocarbons and its degradation into mineral support to give residual carbon): the concentration of residual carbon decreased with increasing of heating rate, became stable around 12°C min^{-1} and continued to decrease for higher heating rates. There are two types of very distinguishable residual organic carbons: those whose mass changes with low heating rate of its preparation (<12°C min^{-1}), and those in which the mass remained was stable (at heating rate >12°C min^{-1}). This difference of behaviour can be explained by coking and cracking phenomena which accompany the degradation of hydrocarbon molecules within the shale.

The total organic matter determined for each shale was 13.05% for Timahdit and 16.60% for Tarfaya. According to Mckay *et al.* [33], the total organic matter in the shale is linked to the amount of organic carbon in the raw oil shale and in kerogen. This method leads to 13.46% for Timahdit and 16.54% for Tarfaya.

As done in numerous studies previously, the Coats–Redfern method was applied to our data. Results obtained are shown in Fig. 3 for samples heated at 12°C min^{-1}. This shows two straight lines with the gradient changing at around 350°C, indicating that organic matter decomposition undergoes a change. It is explained in terms of the presence of two successive steps in temperature range 250–500°C, namely, the decomposition of kerogen to bitumen, which itself then decomposes to give oil, gas and residual carbon. The first occurs at low temperatures with an activation energy of 41.3 kJ mol^{-1} for Timahdit and 40.5 kJ mol^{-1} for Tarfaya shale, whereas the second occurs at high temperatures with an activation energy 64.3 kJ mol^{-1} for Timahdit and 61.3 kJ mol^{-1} for Tarfaya shale. These values are lower than those obtained for Green River oil shale [34] but slightly higher than for Jordanian oil shale [35, 36].

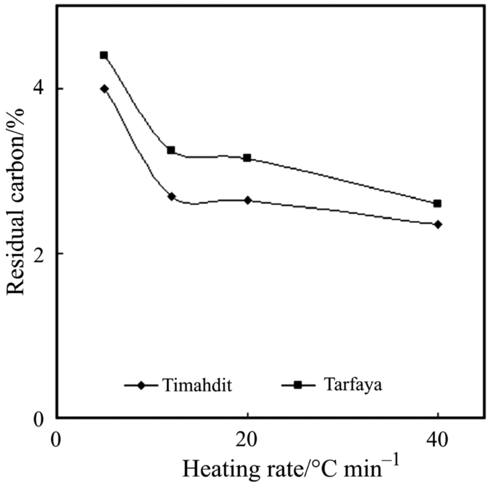

Fig. 2 Percentage of residual carbon in Moroccan oil shale

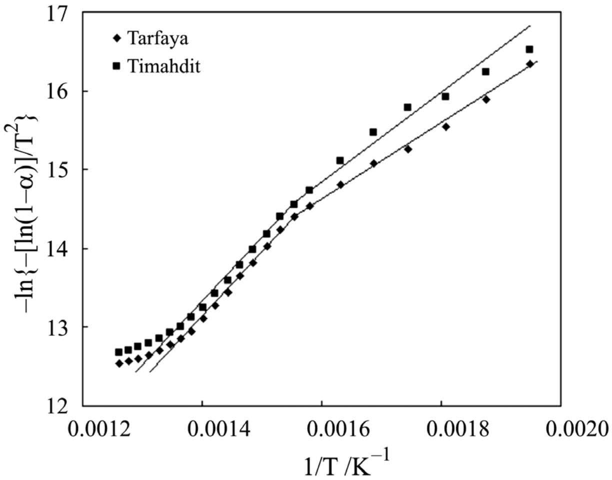

Fig. 3 Analysis of oil shale pyrolysis by Coats–Redfern method ($-\ln((-\ln(1-\alpha))/T^2)$ *vs.* $1/T$)

The reactivity of Timahdit and Tarfaya oil shale residual carbon (obtained at 12°C $\min^{-1}$) has been studied by isothermal thermogravimetry in air (35 cm^3 $\min^{-1}$) at atmospheric pressure. The residual carbon was prepared under the same experimental conditions as shown before. Figure 4 shows the extent of reaction *vs.* time at T=773 K where residual carbon of Tarfaya oil shale is more reactive in air than that of Timahdit oil shale. As shown in Fig. 5, kinetic interpretation of data shows that thermal oxidation of both residual carbons obey a first order reaction ($-\ln(1-\alpha)=kt$) for 90% of the reaction for Tarfaya and 80% for Timahdit if the induction period is not taken into account. This is related to the replacement of nitrogen by air atmospheres (replacement of nitrogen by air in the reactor tube takes half a minute to establish from zero time). The method yields linear plots under constant experimental conditions which lead to the value of the rate constant, k.

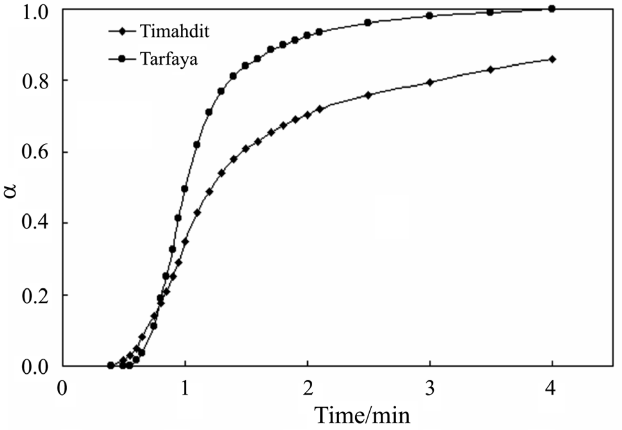

Fig. 4 Oil shale residual carbon oxidation (T=773 K) in dynamic air atmosphere

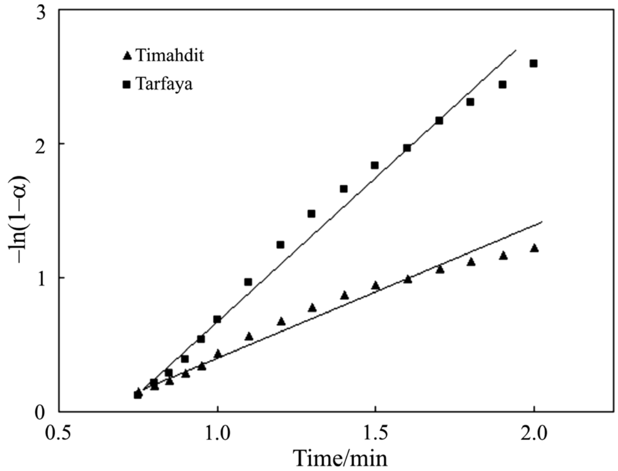

Fig. 5 Plot of the function $-\ln(1-\alpha)$ *vs.* time for oil shales residual carbon combustion in air

Thus, a value of 1.88 min^{-1} for k is obtained for Tarfaya and 0.90 min^{-1} for Timahdit residual carbon.

Conclusions

The heating rate has an important effect on the pyrolysis of oil shale and the amount of residual carbon obtained therefrom. Kinetic studies show that the pyrolysis takes place in two stages. Oxidation of the residual carbon follows first order kinetics.

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References

1 M. Belhaj, Energy Policy, 30 (2002) 1163.
2 O. Bekri, Possibilities for oil shale Development in Morocco, CAER – University of Kentucky, Center for applied Energy Research, Vol. 3, No. 5, 1992.
3 R. D. Noble, W. F. Tucker and H. G. Harris, Fuel, 61 (1982) 482.
4 H. Barkia, L. Belkbir and S. A. A. Jayaweera, J. Therm. Anal. Cal., 71 (2003) 97.
5 N. Salhi, C. Bennouna, H. Bitar, M. Sergent and R. T. L. Phan, Fuel, 75 (1996) 633.
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 H. Barkia, L. Belkbir, S. A. A. Jayaweera, J. H. Moss and M. W. Thwaites, Thermochim. Acta, 152 (1989) 175.
9 H. Barkia, L. Belkbir, N. Gerard and S. A. A. Jayaweera, Thermochim. Acta, 152 (1989) 197.
10 T. Berraja, H. Barkia, L. Belkbir and S. A. A. Jayaweera, Thermal analysis studies of the combustion of Tarfaya oil shale, Proceeding of an International Conference on Carbon, Carbon'88, Eds B. McEnnaney and T. J. Mays, Univ. Newcastle Upon Tyne, UK, 18–23 Sept. 1988.
11 L. Belkbir, H. Barkia and N. Gerard, Thermochim. Acta, 103 (1986) 147.
12 M. Ziyad, J.-P. P. Garnier and M. Halim, Fuel, 65 (1986) 715.
13 O. Bekri, A. Benlahcen and R. Brochu, Analysis, 8 (1980) 80.
14 A. Attaoui, Doctorat d'état Thesis, Mohammed V-Agdal University, Faculty of Sciences, Rabat, Morocco 1999.
15 M. Halim, Doctorat d'état Thesis, Mohammed V-Agdal University, Faculty of Sciences, Rabat, Morocco 1994.
16 H. Barkia, Doctorat d'état Thesis, Mohammed V-Agdal University, Faculty of Sciences, Rabat, Morocco 1990.
17 A. Saoiabi, Doctorat d'état Thesis, Mohammed V-Agdal University, Faculty of Sciences, Rabat, Morocco 1988.
18 P. C. Crawford, D. L. Ornellas, R. C. Lum and P. G. Johnson, Thermochim. Acta, 34 (1979) 239.
19 L. Dockter, AIChE Symp. Ser., 72 (1976) 24.
20 H. Y. Sohn and S. K. Kim, Ind. Eng. Chem. Process Des. Dev., 19 (1980) 550.
21 J. H. Campell, G. H. Koskinas, N. D. Stout and T. T. Coburn, In Situ, 2 (1978) 1.

22 A. K. Burnham, P. C. Crawford and J. F. Carley, Ind. Eng. Chem. Process Des. Dev., 21 (1982) 485.
23 N. D. Stout, G. H. Koskinas, J. H. Raley, S. D. Santor, R. J. Opila and A. J. Rothman, Pyrolysis of oil shale: The effect of thermal hystory on oil yield, LLL, UCRL-77831, 1976.
24 D. J. McCarthy and R. C. Close, Fuel, 67 (1988) 1083.
25 I. Bjerle, H. Eklund, M. Linné and O. Svenson, Ind. Eng. Chem. Process Des. Dev., 21 (1982) 141.
26 B. G. Charlton, Fuel, 67 (1988) 1365.
27 S. C. Mraw and C. F. Keweshan, Ind. Eng. Chem. Res., 26 (1982) 1713.
28 A. K. Burnham, Fuel, 58 (1979) 285.
29 A. K. Burnham, Fuel, 58 (1979) 713.
30 A. K. Burnham, Fuel, 58 (1979) 719.
31 W. J. Thomson and Y. Soni, In Situ, 4 (1980) 61.
32 Y. Soni and W. J. Thomson, Ind. Eng. Chem. Process Des. Dev., 18 (1979) 661.
33 J. F. Mackay, S.-L.Chong and G. W. Gardner, Liq. Fuels Technol., 1 (1983) 259.
34 K. Rajeshwar, Thermochim. Acta, 45 (1981) 253.
35 R. A. Haddadin and K. M. Tawarah, Fuel, 59 (1980) 539.
36 R. A. Haddadin and F. A. Mizyed, Ind. Eng. Chem. Process Des. Dev., 13 (1974) 332.