

## **NON-ISOTHERMAL KINETICS OF GASIFICATION BY CO<sub>2</sub> OF RESIDUAL CARBON FROM TIMAHDIT AND TARFAYA OIL SHALE KEROGENS**

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### **Abstract**

The gasification with carbon dioxide of residual carbons prepared from Timahdit and Tarfaya oil shale kerogens has been studied by thermal analysis techniques (TG and DTA) under heating rates varying from 5 to 48°C min<sup>-1</sup>. The reactions obey first order kinetics. Activation energies have been calculated by several methods, such as Kissinger, Chen–Nuttall and Coats–Redfern methods, and are broadly comparable with literature data for similar carbons.

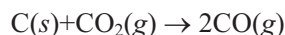
**Keywords:** Chen–Nuttall method, Coats–Redfern method, DTA, gasification, kerogen, kinetics, Kissinger method, residual carbon, Tarfaya and Timahdit oil shales, TG

### **Introduction**

As described in another paper [1], increasing interest in oil shale gasification has resulted in the need to have a better understanding of oil shale residual carbon reactivity. Numerous reactivity studies have been conducted on oil shale residual carbon and are well described in the literature. 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. The kinetics of the reactions in the systems C/O<sub>2</sub>, C/air, C/CO<sub>2</sub> and C/H<sub>2</sub>O(vapour) have been studied by numerous authors [2–15]. The first two of these (C/O<sub>2</sub> and C/air) showed that the reactions obey first order kinetics with respect to the partial pressure of oxygen and the quantity of the non-decomposed residual carbon [13–15]. The rate of gasification of the shale char can be described by a modified Langmuir–Hinshelwood expression [5]. However, the original Langmuir–Hinshelwood equation applies for gasification reactions in the systems, C/CO<sub>2</sub> and C/H<sub>2</sub>O (vapour) [6, 7].

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The reaction of carbon with CO<sub>2</sub> is an important industrial process, the Boudouard reaction in extractive metallurgy. It has been extensively studied, although there are gaps in explaining the mechanism, reaction order and activation energy. The gasification by carbon dioxide in isothermal and non-isothermal conditions



is presumed to follow the Langmuir–Hinshelwood equation [9–11]. For the isothermal reaction:

$$\text{rate} = k_1 P_{\text{CO}_2} / (1 + k_2 P_{\text{CO}} + k_3 P_{\text{CO}_2})$$

where  $k_2$  and  $k_3$  are given by:

$$k_2 = 3.3 \cdot 10^{-14} \exp(253000/RT)$$

$$k_3 = 1.74 \cdot 10^{-6} \exp(27800/RT)$$

Carbon dioxide plays the role of reactant in the above reaction, and product of gasification, combustion and other reactions of the carbon. Its reaction with carbon is important in numerous industrial operations such as the generation of water, the production of gas and the fusion of minerals [9]. Studies of reactions of carbon/oxygen system surfaces showed high affinity of the carbon towards oxygen to fix it in certain sites of its surface by chemical links. In the initial stage, the carbon dioxide is reduced to carbon monoxide at relatively low temperatures (lower than 600°C). The oxygen, lost from the dioxide, remains on the surface of the carbon and can be eliminated as monoxide [9–11, 15]. The reaction traduces a phenomenon of oxygen exchange and not a transfer phenomenon of carbon to the gaseous phase that constitutes gasification. Experimental data indicate that reactions of oxygen exchange are relatively fast compared with reactions of carbon transfer. Thomson *et al.* [6, 7] showed that the reaction of gasification by CO<sub>2</sub> is very fast for the residual carbon from Swedish oil shale [5] but distinctly slow for the one from Colorado shale [6]. Both comply with the Langmuir–Hinshelwood equation. In the case of the residual carbon, Burnham [3, 4] gave evidence for the presence of two species of carbon that react in parallel and that the reaction depends on the reactant and product partial pressures.

The aim of the work reported in this paper is to derive kinetic parameters for the decomposition processes related to the non-isothermal gasification in carbon dioxide of residual carbon obtained from kerogen of Tarfaya and Timahdit shale deposits using simultaneous non-isothermal TG/DTG/DTA technique.

## 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<sub>2</sub> atmospheres (dried using MgClO<sub>4</sub>) and gas flow rate (35 cm<sup>3</sup> min<sup>-1</sup>). Sample holders were thin-walled platinum crucibles.

### Samples

Samples of kerogen were heated up to the desired reaction temperature (773 K) at a constant heating rate of  $12^{\circ}\text{C min}^{-1}$  and in a nitrogen flowing atmosphere. The rate of heating was chosen to correspond to conditions close to those used in Fisher Assay of oil shales. When the desired temperature was attained, the sample was maintained in nitrogen ( $35\text{ cm}^3\text{ min}^{-1}$ ) for 1 h. These conditions allow obtaining a residual carbon, intermediate between coke and char. Then, dried  $\text{CO}_2$  ( $35\text{ cm}^3\text{ min}^{-1}$ ) was introduced into the system, and the mass change was monitored. The elemental analyses of the materials are given in Table 1.

**Table 1** Elemental analysis of carbon, hydrogen, nitrogen and sulfur

		C/%	H/%	N/%	S/%
Timahdit	Kerogen	65.0	5.2	1.8	10.7
	Residual carbon of kerogen	41.2	1.5	2.2	5.9
Tarfaya	Kerogen	67.7	7.4	1.8	11.1
	Residual carbon of kerogen	76.3	2.9	3.4	5.2

It is noted that the carbon and hydrogen contents of the kerogens are similar, whereas the figures are higher for the residual carbon from Tarfaya shale than from Timahdit shale.

### Results

Figures 1 to 4 represent the TG and DTA curves of the residual carbons at heating rates of 5, 12, 20, 40 and  $48^{\circ}\text{C min}^{-1}$ . For both materials, the TG curves are characterized by one reaction stage and the DTA curves show one large endotherm followed by a smaller, less significant one at higher temperatures. Increasing the heating rate shifts the gasification to higher temperatures typically, for both sets of data. The TG curves display the characteristic 'S' shape with significant decomposition above  $800^{\circ}\text{C}$  for both samples with maximum rates located in the temperature range  $800\text{--}1000^{\circ}\text{C}$ . With slower heating rates, lower minimum temperatures were obtained for the DTA peaks.

### Discussion

The analysis of non-isothermal data to deduce kinetic parameters is not so straightforward compared with manipulation of isothermal data. Several mathematical models have been proposed, involving approximations and assumptions, for deducing activation energies from DTA and non-isothermal TG results.

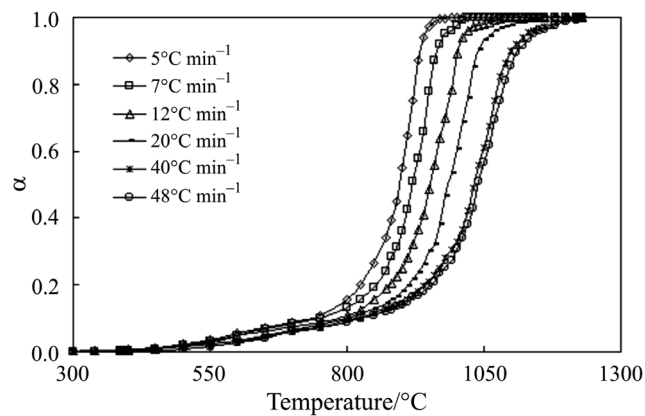


Fig. 1 Mass loss (TG) of residual carbon of Timahdit kerogen in  $\text{CO}_2$  atmosphere

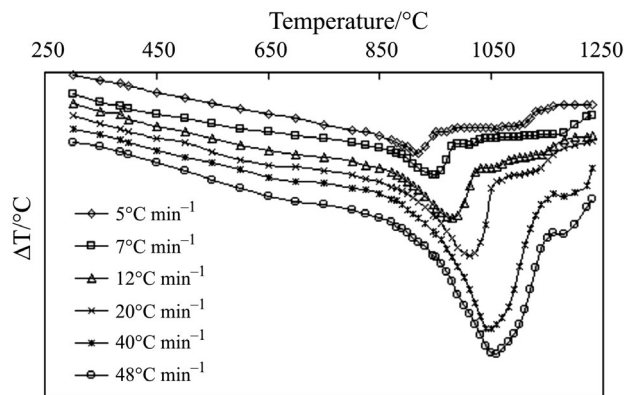


Fig. 2 DTA curves of residual carbon of Timahdit kerogen in  $\text{CO}_2$  atmosphere

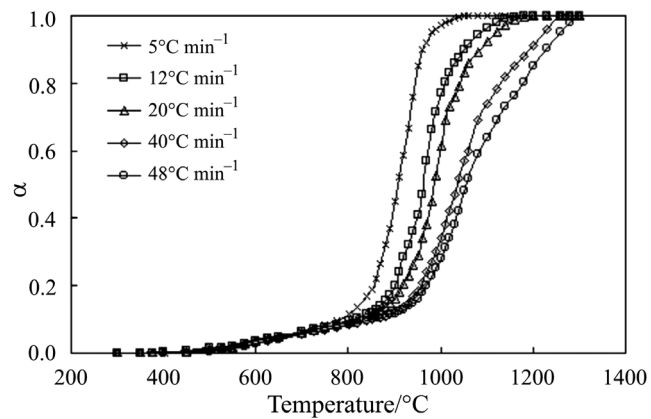


Fig. 3 Mass loss (TG) of residual carbon of Tarfaya kerogen in  $\text{CO}_2$  atmosphere

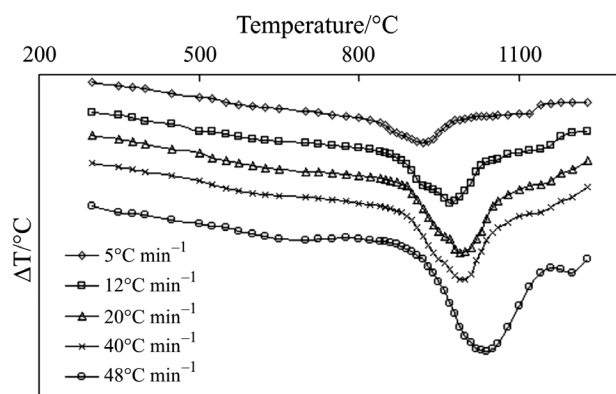


Fig. 4 DTA curves of residual carbon of Tarfaya kerogen in CO<sub>2</sub> atmosphere

#### Kissinger method

Using heat flow equations based on a second order partial differential equation, Kissinger [16] derived an equation relating the DTA peak temperature to the rate of heating

$$d(\ln(\phi/T_m^2))/d(1/T_m) = -E_a/R$$

where  $\phi$ =rate of heating,  $T_m$ =peak minimum temperature,  $E_a$ =energy of activation.

The theoretical and experimental aspects of deducing kinetic parameters from DTA data are critically reviewed by Sharp [17]. However, the Kissinger equation has been widely used to determine activation energies of reactions from DTA data. The method is based on the incorrect assumption that the DTA peak temperature corresponds to the temperature of maximum reaction rate. Nevertheless studies on metallurgical cokes and other carbons using simultaneous TG/DTG/DTA have shown that these two temperatures are very close [18].

Kissinger plots ( $\ln(\phi/T_m^2)$  vs.  $1/T_m$ ) are shown in Fig. 5. The activation energies,  $E_a$ , calculated from the gradient gave values of 182 and 216 kJ mol<sup>-1</sup> for the residual carbons from Timahdit and Tarfaya shales, respectively. The activation energy of 205 kJ mol<sup>-1</sup> reported by Burnham [2] for the gasification of residual carbon from Colorado oil shale is intermediate to the above values.

#### Chen–Nuttall method

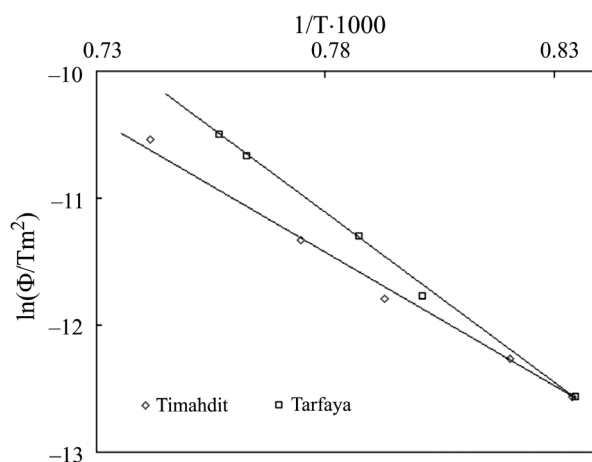
These authors developed the rate equation for a first order reaction:

$$d\alpha/dt = k(1-\alpha)$$

and applied it to a reaction of the type:



Combination with the Arrhenius equation leads to the integrated form:

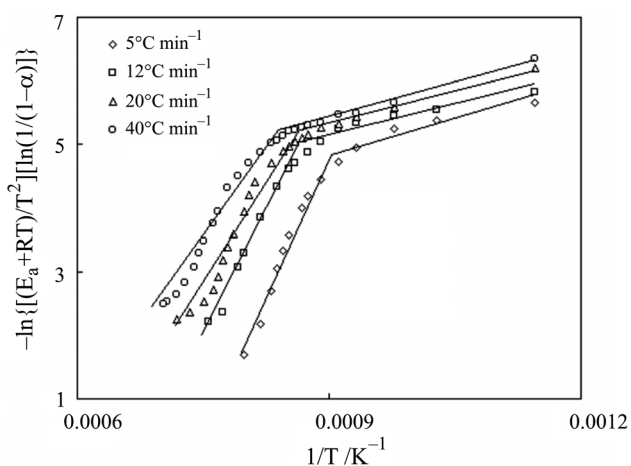


**Fig. 5** Evolution of DTA peaks minimum temperature of Tarfaya and Timahdit residual carbon kerogens during gasification  $\ln(\phi/T_m^2)$  vs.  $1/T_m$

$$\ln[(E_a + 2RT)/T^2 \times \ln(1/(1-\alpha))] = \ln(A/R) - E_a/RT$$

where  $A$  is the frequency factor and  $E_a$  and  $\phi$  are defined as above. Using a guess for the initial value of  $E_a$  and with the aid of repeated regression analysis, values for  $E_a$  and  $A$  can be calculated to the desired accuracy [19].

Figures 6 and 7 show the Chen–Nuttall plots for the gasification of residual carbons from Timahdit and Tarfaya shales at different heating rates. Results show that there is a change in the activation energy at temperatures above about 880°C and above  $\alpha$ , extent of reaction, around 0.240. Table 2 summarises the activation energies therefrom and other sources. Mean values of 168 and 207 kJ mol<sup>-1</sup> are



**Fig. 6** Analysis of Timahdit residual carbon by Chen–Nuttall method

**Table 2** Activation energies for the gasification of residual carbon from different origins

Activation energies for	5°C min <sup>-1</sup>	12°C min <sup>-1</sup>	20°C min <sup>-1</sup>	40°C min <sup>-1</sup>	Isothermal
Tarfaya					
$E_{a_1}$ /kJ mol <sup>-1</sup>	29	24	24	20	
$E_{a_2}$ /kJ mol <sup>-1</sup>	203	170	156	132	
Timahdit					
$E_{a_1}$ /kJ mol <sup>-1</sup>	38	31	30	31	
$E_{a_2}$ /kJ mol <sup>-1</sup>	247	224	188	166	184 [6]
Others					301 [5]
		205 [2]			

( $E_{a_1}$  for  $T < 880^\circ\text{C}$  and  $E_{a_2}$  for  $T > 880^\circ\text{C}$ )

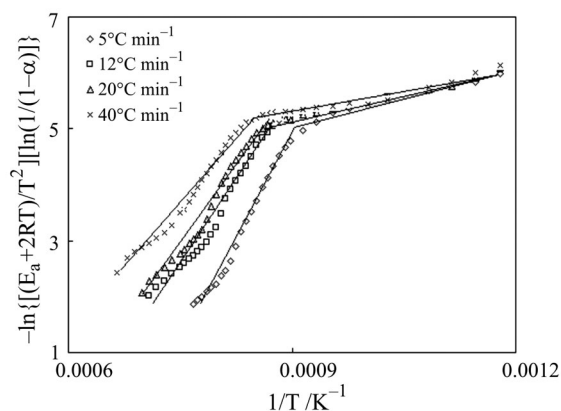


Fig. 7 Analysis of Tarfaya residual carbon by Chen–Nuttall method

obtained for the carbons from Tarfaya and Timahdit shales, respectively, using the average of the highest and lowest figures for the activation energy at higher temperatures, and mean values of 25 and 35 kJ mol<sup>-1</sup>, respectively at lower temperatures. The high temperature values show a wide variation with heating rate for carbons from both shales.

#### Coats–Redfern method

Coats and Redfern [20] developed a method for the calculation of activation energy from non-isothermal TG data at a constant heating rate. The Coats–Redfern equation for a first order reaction, based on mathematical approximations, is:

$$-\ln[-\ln(1-\alpha)]/T \approx E_a/RT + \text{constant}$$

Figures 8 and 9 show the Coats–Redfern plots for the carbons from Timahdit and Tarfaya shales, respectively. Results show that there is a change in the activation energy at temperatures above about 840°C and above  $\alpha$ , extent of reaction, around 0.180. Table 3 summarises the activation energies calculated.

**Table 3** Activation energies for the gasification of residual carbon from Timahdit and Tarfaya oil shale kerogen obtained at different heating rate with Coats–Redfern method

Activation energies for	5°C min <sup>-1</sup>	12°C min <sup>-1</sup>	20°C min <sup>-1</sup>	40°C min <sup>-1</sup>	48°C min <sup>-1</sup>
Tarfaya $E_{a_1}$ /kJ mol <sup>-1</sup>	28	23	25	21	23
Tarfaya $E_{a_2}$ /kJ mol <sup>-1</sup>	180	178	150	134	120
Timahdit $E_{a_1}$ /kJ mol <sup>-1</sup>	27	31	31	31	31
Timahdit $E_{a_2}$ /kJ mol <sup>-1</sup>	219	224	236	213	213

( $E_{a_1}$ , for  $T < 840^\circ\text{C}$  and  $E_{a_2}$  for  $T > 840^\circ\text{C}$ )



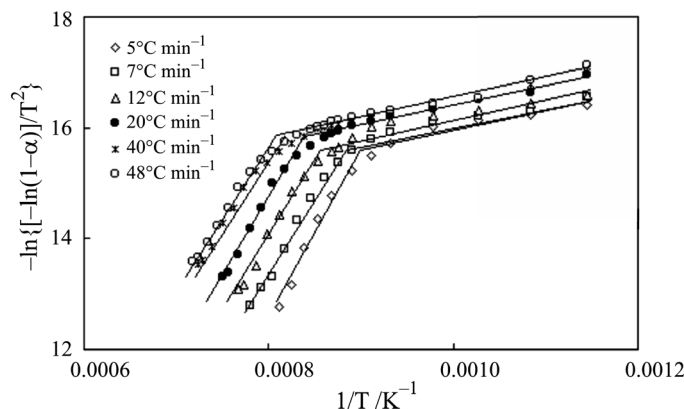


Fig. 8 Coats–Redfern plots for the reaction of residual carbon from Timahdit shale with CO<sub>2</sub>

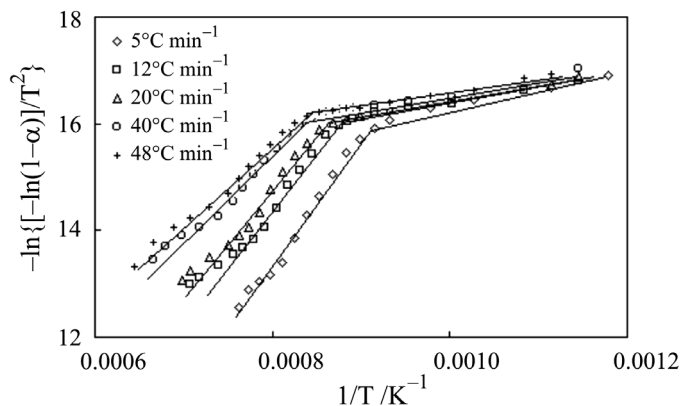


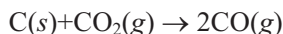
Fig. 9 Coats–Redfern plots for the reaction of residual carbon from Tarfaya shale with CO<sub>2</sub>

The activation energies calculated for the Tarfaya carbons at different heating rates at higher temperatures are less and show a wider variation than those for the corresponding Timahdit data. As in the Chen–Nuttall method, the high temperature values ( $E_{a_2}$ ) obtained for the Timahdit residual carbon by the use of Coats–Redfern method are higher than those obtained for Tarfaya carbon. This is different from the results of the Kissinger method, which gave a higher value for the Tarfaya carbon. These variations illustrate the difficulties in calculating kinetic data from non-isothermal methods, which involve mathematical approximations and assumptions.

Methods to improve the calculation of kinetic data from non-isothermal data are under consideration.

## Conclusions

Heating rate has an important effect on the non-isothermal gasification reaction of residual carbon from oil shale. Thermal analysis data show that the decomposition reaction.



follows first order kinetics with respect to the carbon. Activation energies computed using different mathematical models were found to vary somewhat, but to be generally comparable with those of reactions of other residual carbons.

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## References

- 1 H. Barkia, L. Belkbir and S. A. A. Jayaweera, *J. Therm. Anal. Cal.*, 76 (2004) 615.
- 2 A. K. Burnham, *Fuel*, 58 (1979) 285.
- 3 A. K. Burnham, *Fuel*, 58 (1979) 713.
- 4 A. K. Burnham, *Fuel*, 58 (1979) 719.
- 5 I. Bjerle, H. Eklund, M. Linné and O. Svenson, *Ind. Eng. Chem. Process Des. Dev.*, 21 (1982) 141.
- 6 W. J. Thomson, M. A. Gerber, M. A. Hatter and D. G. Oakes, *Amer. Chem. Soc. Symp. Ser.*, 163 (1981) 115.
- 7 D. E. Van Tuyl and W. J. Thomson, *Fuel*, 65 (1986) 58.
- 8 F. Hershkowitz, W. N. Olmstead, R.-P. Rhodes and K. D. Rose, in 'Geochemistry and Chemistry of oil shales', ACS. Symp. Series N° 230, Amer. Chem. Soc., Washington DC 1983, p. 301.
- 9 S. Ergun, *J. Phys. Chem.*, 60 (1965) 480.
- 10 J. Gadsby, C. N. Hinshelwood and K. W. Sykes, *Proc. Roy. Soc. (London)*, A187 (1946) 129.
- 11 M. Mentser and S. Ergun, *Carbon*, 5 (1967) 331.
- 12 D. J. McCarthy and R. C. Close, *Fuel*, 67 (1988) 1083.
- 13 H. Y. Sohn and S. K. Kim, *Ind. Eng. Chem. Process Des. Dev.*, 19 (1980) 550.
- 14 W. J. Thomson and Y. Soni, *In Situ*, 4 (1980) 61.
- 15 Y. Soni and W. J. Thomson, *Ind. Eng. Chem. Process Des. Dev.*, 18 (1979) 661.
- 16 H. E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 17 J. H. Sharp, Chapter 28 of 'Differential Thermal Analysis', (Ed. R. C. MacKenzie), Academic Press 1982.
- 18 M. A. Carter, PhD Thesis, CNAA (Plymouth Polytechnic), 1983.
- 19 W. J. Chen and H. E. Nuttall, A TG study of Colorado oil shale with a new kinetic model, 86<sup>th</sup> AIChE National Meeting, Houston, Texas 1979.
- 20 A. W. Coats and J. P. Redfern, *Nature*, 201 (1964) 68.