

KINETIC ASPECT OF THERMAL DECOMPOSITION OF NATURAL PHOSPHATE AND ITS KEROGEN

Influence of heating rate and mineral matter

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Abstract

The natural phosphate and its demineralization products from Moroccan deposit were pyrolysed in a thermogravimetric analyser (TG) to examine the influence of the heating rate and mineral matter on their thermal decomposition. The heating rates investigated in the TG were 5–100°C min⁻¹ to final temperature of 1200°C. The integral method was used in the analysis of the TG to determine the kinetic parameters. It has been found that for the natural phosphate and corresponding kerogen analysed in the TG, the increase of the heating rate shifts the maximum rate loss to higher temperature. A first order reaction was found to be adequate for pyrolysis in the range 150–600°C which was attributed to kerogen decomposition. In addition, the results indicate that the removal of mineral matter affected the kinetic parameters found for kerogen in the natural phosphate.

Keywords: kerogen, kinetic parameters, natural phosphate, thermogravimetry

Introduction

Kerogen pyrolysis has been subjected to much research in recent years with the incorporation of laboratory pyrolysis methods such as Rock-Eval, hydrous, pyromat pyrolysis and more recently, thermogravimetric analysis (TG) which provides a rapid quantitative method to examine the overall pyrolysis process and enables to estimate the effective kinetic parameters of overall decomposition reactions. Therefore, this technique has been widely used in recent years for the investigation of pyrolysis, combustion and structural characteristics of the fossil fuel such as coals oil shales and tar sands [1–8].

Numerous attempts addressing the mechanistic and kinetic points of view have made the processes occurring during pyrolysis understood. However, several methods are available for the evaluation of TG data for kinetic purposes, but generally two

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main approaches have been used [8–13]. In the first one, a single first-order reaction assumption was used for the representation of pyrolysis. In the second one, the multiple parallel first-order reactions or the combined parallel and consecutive reactions model with a statistical distribution of activation energies was used for the description of the pyrolysis process [8, 11, 14–17]. This approach was later represented by n^{th} order reaction model for overall process and widely used to investigate oil shales and coals pyrolysis.

In the present work, the non-isothermal TG and DTG data from natural phosphate and its demineralized products have been gathered and a preliminary global kinetic analysis has been carried out.

Our objective was to obtain some basic information on the non-isothermal decomposition of natural phosphate or demineralized products and to discuss the effect of the heating rate and the acid treatments on the thermal decomposition characteristics. Basically, TG and DTG data have been used for the estimation of the effective parameters of the process.

Mathematical procedure for the determination of thermogravimetrically derived kinetics

The kinetic analysis of non-isothermal pyrolysis is generally based on the following three equations [9]:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

$$T = T_0 + \beta t \quad (3)$$

where α is the fraction decomposed, $f(\alpha)$ is a function of the degree of the reaction, t is the reaction time, k the rate constant, T is absolute temperature (K), E and A are the activation energy and pre-exponential factor, respectively, R is the gas constant, β is the heating rate ($^{\circ}\text{C min}^{-1}$) and T_0 the initial temperature. By combining Eqs (1), (2) and (3), the decomposition rate may be expressed as:

$$\frac{d\alpha}{dT} = f(\alpha) \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (4)$$

In the analysis of TG data, several definitions have been used for the fraction mass loss, α , but in this work, this is defined as:

$$\alpha = \frac{1-w_t}{1-w_{\infty}} \quad (5)$$

where w_t and w_∞ are the instantaneous and the final values of the mass fraction, respectively. A graph of α vs. temperature gives a modified TG plot, which can be used for kinetic analysis.

Based on recent calculation, $f(\alpha)$ is defined as $f(\alpha)=(1-\alpha)^n$ (n is the overall reaction order) with singular E and A values [15, 16]. Taking into account Eq. (4), we obtain:

$$\frac{\left(\frac{d\alpha}{dT}\right)}{(1-\alpha)^n} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) \quad (6)$$

The order of reaction n can be determined by taking logarithm of this equation and then plotting $\ln(d\alpha/dT)/(1-\alpha)^n$ vs. $1/T$. A rectilinear plot may be obtained with a correct value for n . Coats and Redfern [18] integrated Eq. (6) by expanding it into series with the limit conditions of $\alpha=0$ for $T=T_0$ and $\alpha=\alpha$ for $T=T$. For $n \neq 1$, they obtained the following equation by ignoring the higher order terms of the series,

$$\frac{(1-(1-\alpha)^{1-n})}{(1-n)T^2} = \left(\frac{AR}{\beta E}\right) \left(\frac{1-2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Equation (7) may be further simplified if we assume $2RT \ll E$. Based on these assumptions, the following equation may be used to estimate the kinetic parameters from TG data

$$\ln\left[\frac{(1-(1-\alpha)^{1-n})}{(1-n)T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (8)$$

With some assumptions as given before, the integration of Eq. (6) for the first order reaction ($n=1$) gives:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (9)$$

By using α values, a plot of the left side of Eqs (8) or (9) vs. $1/T$, should give straight lines for a correct value of n with a slope of $-E/R$ which can be used to evaluate the activation energy.

Experimental

Sample

Phosphate samples were obtained from a mine located at Youssoufia (Morocco). Rock phosphates in this site cover an area of about 700 km², which extends over 50 km in length. The phosphate bed has a maximum depth of 15 m and is divided into layers II–III and I deposited during the Montien and Maestrichien period, respectively. Our samples are from layer I where the organic matter is trapped in the frame-

work of the rocks. Favourable physical conditions allowed the conversion of this matter to bituminous compounds, responsible for the grey colour of the phosphate. The origin and composition of this matter are probably similar to those of all fossil fuels, which have not undergone complete decay [19]. The total organic matter constitutes around 5% of the rock dry mass. In the case of phosphates, and contrary to other sediments such as bituminous shales, this value indicates that the rock is relatively rich in organic matter [20].

Preparation of kerogen

The phosphate sample was demineralized by a modified version of the methods used for the isolation of kerogen natural phosphate [21]. 100 g of dried natural phosphate were treated with chloroform to extract the bitumens until the solvent in the soxhlet arm becomes colourless. The bitumen-free (BF) phosphate was then dried and weighed. It is subsequently attacked with HCl until no further carbon dioxide evolved. The residue was washed with hot distilled water until the silver nitrate test for chlorides was negative. The hydrochloric attack was repeated twice to eliminate all calcium products. The decarbonated phosphate was dried, washed with concentrated HCl and treated with concentrated HF (5 mL g⁻¹ decarbonated phosphate) at 60°C under a nitrogen atmosphere for 8 h. The silicate-free phosphate obtained in this step was then washed with hot distilled water and HF treatment step was repeated. After drying SF phosphate, a saturated boric acid solution was added and the sample was stirred for 30 min. Finally, the remaining brown solid was treated with 6 N HCl and the kerogen was washed with hot distilled water to remove chlorides and dried overnight at 60°C. It should be noted that pyrite is known to be the major mineral component remaining after HCl/HF treatment [22]. The yields of the demineralization procedure of the natural phosphate are presented in Table 1.

Table 1 The composition of natural phosphate

Component	Mass/%
Bitumen	0.40±0.03
Apatite, carbonates ^a	86.6±0.2
Silicates	7.9±0.1
Pyrite	0.30±0.01
Kerogen	4.8±0.1

^aIncludes sulphides, sulphates, oxides and hydroxides

TG-DTG

The thermogravimetric data were obtained in a Shimadzu Model-50 Series TG analyzer. The sample was heated to 1200°C at 5, 20, 50 and 100°C min⁻¹ rate with nitrogen as the purge gas. The TG apparatus provides the continuous measurement of

sample mass as a function of temperature and provision is made for an electronic differentiation of the mass signal to give the rate of mass loss (DTG).

Results and discussion

TG-DTG analysis

TG and DTG traces of natural phosphate and its demineralized products, for a heating rate of $5^{\circ}\text{C min}^{-1}$ in inert atmosphere are represented in Fig. 1. The figure indicated that natural phosphate exhibited distinct steps of thermal decomposition as the temperature was increased.

Lower temperature thermal decomposition, up to about 200°C produced mass loss, which was attributed to the loss of moisture, Haddadin and Mizyed [23] also attributed the lower temperature mass loss to the physical change in the kerogen, molecular rearrangement accompanied by the gas release. The main part of mass loss $200\text{--}500^{\circ}\text{C}$ was because the loss of hydrocarbon material and the evolution of gases and oil vapour, with the maximum rate at about 400°C (T_{max1}). Mass loss of this part represents about 3% of the total natural phosphate mass. The decomposition at higher temperatures observed between approximately $600\text{--}900^{\circ}\text{C}$ was attributed to the decomposition of carbonate minerals such as calcite and dolomite present in natural phosphate, with the maximum rate at about 760°C (T_{max2}). This caused a mass loss of about 16% of the total natural phosphate mass. At temperature above 800°C , a second mass loss is observed in the kerogen experiment Fig. 1c, which is accompanied with a 10% mass change (Fig. 1c). This could be a consequence of the secondary pyrolysis (coking) of heavy fractions produced during kerogen degradation. It is clear that the observed effect could not be related to the decomposition of mineral phosphates, because the same effect did not appear with an increase of the heating rate during the pyrolysis concentrated kerogen (Fig. 2).

Table 2 presents the analysis of the DTG data in relation to heating rate in terms of the temperature at which the maximum devolatilisation, initial temperature of kerogen decomposition (T_{onset}) and the maximum rates of mass loss in the temperature range of $140\text{--}1200^{\circ}\text{C}$ are obtained.

With an increase in the heating rate there was a lateral shift to higher temperature for T_{onset} , T_{max1} and T_{max2} for both samples as the heating rate was increased (Table 2). The rate loss also reflects the lateral shift with an increase in the rate as the heating rate was increased from 5 to 100°C . The lateral shift to higher temperatures for the maximum region of mass loss was observed by other workers using TG to investigate the pyrolysis of oil shale. For example, Drescher *et al.* [24] reported a lateral increase in the maximum rate of mass loss of about 60°C as the heating rate was increased from 0.66 to $50^{\circ}\text{C min}^{-1}$ for Green River oil shale. Data in Table 2 also indicate that T_{onset} of demineralized phosphate are approximately 40°C inferior to those of natural phosphate.

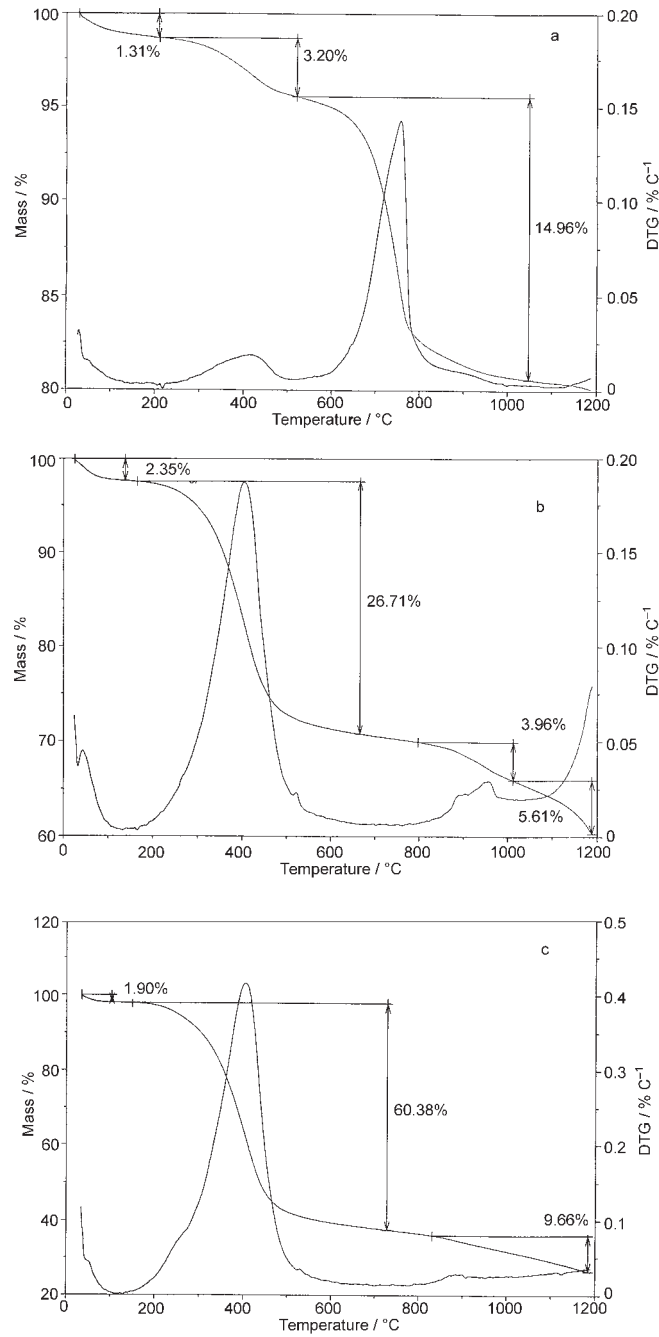


Fig. 1 Non-isothermal TG-DTG curves at heating rate of $5^{\circ}\text{C min}^{-1}$ for a – natural phosphate, b – decarbonated phosphate and c – kerogen

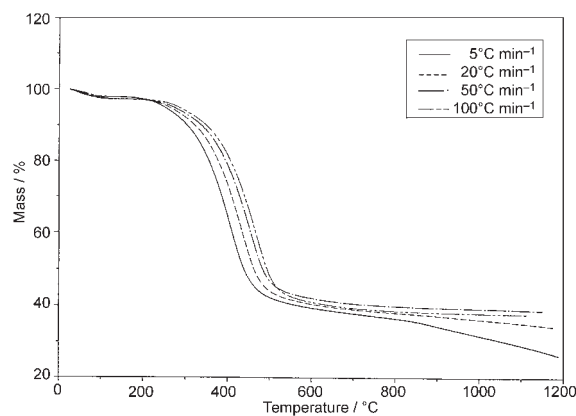


Fig. 2 Non-isothermal DTG curves for kerogen at various heating rates

Table 2 Comparison of thermogravimetric data in relation to heating rate and phosphate products

Samples	$\beta/^\circ\text{C min}^{-1}$	Temperature/ $^\circ\text{C}$			Rate of mass loss/ $\text{mass}\% \text{ min}^{-1}$	
		T_{onset}	T_{max1}	T_{max2}	R_{max1}	R_{max2}
Natural phosphate	5	200	417	758	0.10	0.72
	20	227	423	808	0.29	3.58
	50	234	457	842	0.54	6.14
	100	297	475	870	1.92	10.48
Decarbonated phosphate	5	160	400	—	0.94	—
Kerogen	5	150	408	—	2.08	—
	20	166	426	—	8.10	—
	50	183	451	—	19.61	—
	100	200	474	—	39.47	—

Kinetic analysis

The mathematical procedure used in the analysis of TG data to determine the pyrolysis kinetics corresponds to the integral method used by many other investigators [25–27]. Assuming first-order for the rate of mass loss during pyrolysis in TG experiments, the plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. $1/T$ corresponds to a straight line with a slope of $-E/R$ can be used to evaluate the activation energy. The pre-exponential factor can be determined from the intercept.

Figures 3a, 3b and 3c. show that the first-order reaction model generally gives straight line with higher correlation coefficients for each heating rate. Therefore, the assumption related to the first-order is valid for the temperature region below 600°C . The variation in heating rate did not alter the slopes of these lines.

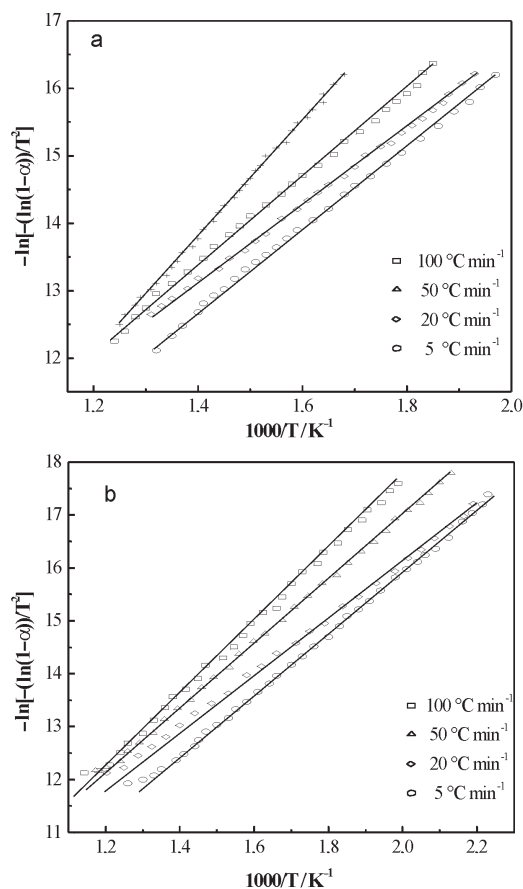


Fig. 3 Determination of kinetic parameters from TG data for different heating rates for: a – natural phosphate and b – kerogen

TG-derived kinetic parameters in relation to heating rate for natural phosphate and its demineralized products are given in Table 3. According to the data, the removal of the carbonates resulted in a decrease in the activation energies of the pyrolysis reaction of the phosphate. It is probable that the diffusion of the organic matter throughout the carbonate matrix required a higher temperature and relatively more energy. This is in accordance with greater T_{onset} observed for original phosphate (Table 2). Activation energies calculated for the pyrolysis reaction of HF washed phosphate (kerogen) were much lower than those of the original phosphate. This result indicated that the silicate minerals originally present in the phosphate had a similar effect to that of carbonate minerals. In this respect, the values reported here are similar to those given in literature for oil shale [8, 25, 28]. Dembicki [29] examined the effect of various minerals on the determination of source rock kinetic parameters, by pyrolyzing mixtures of sedimentary minerals with varying concentration of a kerogen

isolated from Kimmridgian black shale. The kinetic parameters derived indicated that added mineral matter such as quartz, calcite and dolomite shifted the activation energy to higher values than those of observed for the isolated kerogen.

The mineral matter content is not the only factor of low activation energies. However, the decrease in the activation energy may be a consequence of the physical

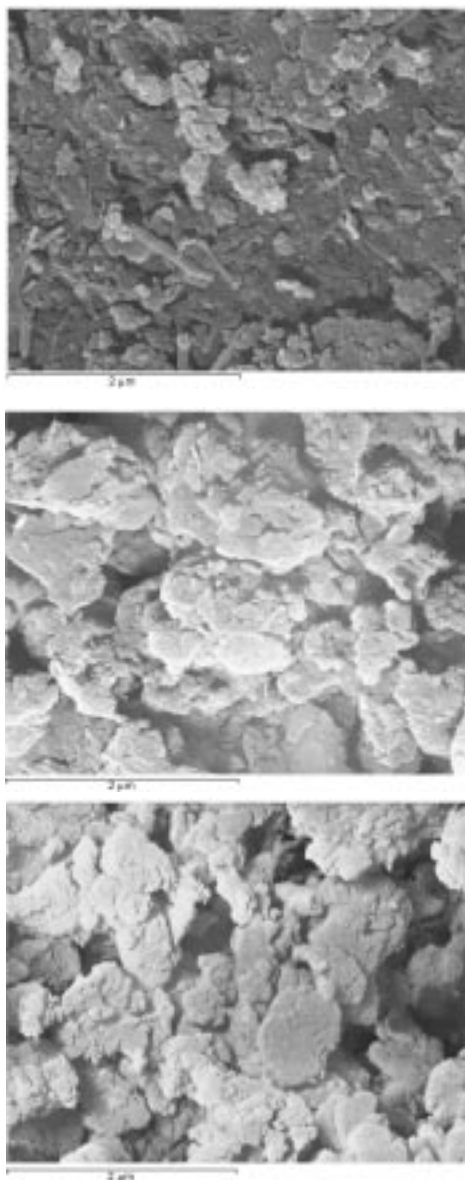


Fig. 4 The grain morphology of a – natural phosphate, b – decarbonated phosphate and c – kerogen

structure of the solid during the demineralization process. The grains morphology of the natural phosphate and its demineralised products has been analysed using scanning electron microscopy (Fig. 4). After acid treatments, porosity, and total surface area increased as almost all of the inorganic matter of original phosphate is removed. Similar results are reported by other authors [4, 5, 30, 31]. Ceylan *et al.* [26] suggested that structural changes might affect the activation energies if the pyrolysis process is diffusion controlled.

In addition, the effect of the heating rate on the kinetic parameters can also be seen in Table 3, the activation energy decreases when the heating rate is above $20^{\circ}\text{C min}^{-1}$, in accordance with the data in literature [8, 27, 32–36]. When the heating rate is higher than $20^{\circ}\text{C min}^{-1}$, there is no dependence on kinetic parameters. This difference is due to a shorter exposure time to a particular temperature at faster heating rates and causing transport limitations due to heat transfer. In fact, the energies estimated from thermogravimetric analyses are essentially the effective energies for the sum of different reactions occurring simultaneously. The real activation energies for several reactions may be much higher.

Table 3 TG-derived kinetic parameters

	Natural phosphate				Decarbonated phosphate		Kerogen			
	$\beta/^{\circ}\text{C min}^{-1}$	5	20	50	100	5	5	20	50	100
$E/\text{kJ mol}^{-1}$	50.41	47.44	53.50	71.63	47.38	45.34	42.43	49.83	56.06	
$A/10^{-6} \text{ s}^{-1}$	2.13	19.68	25.67	4.86	2.83	2.35	36.49	43.56	45.33	

Conclusions

Thermogravimetric analysis of natural phosphate and its demineralized products in relation to heating rate showed that the maximum range of mass loss due to hydrocarbon formation occurred between 150 and 600°C . At higher temperatures there was a significant mass loss because of mineral carbonate composition. The increase of the heating rate shifts the maximum rate loss to higher temperature.

The non-isothermal TG measurements indicated that the thermal decomposition of natural phosphate and its demineralized products can be described by a first-order reaction. Furthermore, the obtained results showed that the removal of the mineral matter decreased the kinetic parameters found for kerogen in the natural phosphate. As the heating rates were increased above $20^{\circ}\text{C min}^{-1}$, the activation energy increased in pyrolysis reaction of original phosphate and corresponding kerogen.

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