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NONISOTHERMAL THERMOGRAVIMETRY OF SPANISH FOSSIL FUELS

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Low-rank coals from Mequinenza (type III-S) and Utrillas (type III) basins, characterized by high sulfur content, as well as type I-S oil shales from Ribesalbes were analyzed by thermogravimetry. Process kinetics was studied using the Friedman equation to interpret one point data – temperature of maximum generation of oil and gas (maximum on several experimental and simulated TG curves recorded at heating rates 5, 15 and 25 K·min^{-1}*,* T_{max}*). These results are contrasted with those obtained by a method based on NLS (nonlinear least-squares) algorithms which derives kinetic parameters from a single TG curve recorded within a temperature interval nearby* T_{max}*.*

The final conclusion is that the reliability of kinetic parameters obtained from one point (T_{max}*) at several heating rates is low. On the other hand, the Friedman isoconversional method was used to elucidate the kinetic scheme which is derived from dependencies of apparent activation energy (E) on conversion level (*α*). Analysis of kinetic data of pyrolysis of Mequinenza coal shows that in this case the dependence of activation energy on conversion level is characteristic of a reversible reaction followed by an irreversible one, whereas in the case of pyrolysis of Utrillas coal and Ribesalbes oil shales such dependence is characteristic of a reversible reaction.*

Introduction

Most hydrocarbons in crude oils are formed through partial decomposition of kerogen due to thermal stress during subsurface burial in a sedimentary basin [1]. Knowing the kinetics of this process allows to determine the extent and temporal course of hydrocarbon generation during crude oil formation. Kinetic controls on hydrocarbon generation require pyrolysis experiments to be conducted at higher temperatures (300 to 650 °C) than those experienced in sedimentary basins (70 to 200 °C). During diagenesis, the carbon skeleton

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of the kerogen network is not severely altered, as the temperature is low (<50 °C). As sediment burial increases, petroleum is progressively generated by cracking the bonds C-C, C-O or C-S in the kerogen network. Finally, during metagenesis with more severe thermal alteration, hydrocarbon gases are produced, either due to secondary cracking of hydrocarbons already produced at lower temperatures [2] or due to the cracking of kerogen itself [3].

Sulfur is also believed to be a critical variable in the time-temperature requirements for oil generation, so kerogens rich in organic sulfur are thought to generate petroleum at a lower level of thermal stress than sulfur-lean kerogens [4]. The mechanism of initial generation is supposed to be due to the cleavage of the weakest polysulfide and sulfur-carbon linkages, instead of ether or ester oxygen bridges and aliphatic C-C bonds [5, 6].

Most kinetic models are based on a first-order reaction by estimating quantitatively hydrocarbon evolution as a function of burial time [7, 8]. Modeling of hydrocarbon generation kinetics assumes that transformation of organic matter during thermal treatment can be described by a series of parallel reactions involving kerogen cracking. Calculation of activation energy allows the kinetic evolution of organic matter to be described. However, the use of these kinetic parameters is questionable because there is no definitive proof that decomposition of kerogen follows the first-order reaction [9]. Maximum temperature ($T_{\max}$) from kinetic predictions is mainly ascribed to the main stage of hydrocarbon generation [8, 10]. Extrapolation of laboratory-derived kinetic parameters to geological conditions is a matter of debate, especially when the non-uniqueness of kinetic parameters (compensation effect) is taken into account [11–13]. Determination of kinetic parameters of hydrocarbon generation is a process consisting of artificial maturation experiments followed by fitting of kinetic parameters with the laboratory data. One of the artificial maturation techniques performed in the laboratory is thermogravimetry (TG) [2, 14] and that is revealed as a useful technique in fossil fuel research [15]. Kök et al. [16–19] have determined thermal characteristics and kinetic parameters of pyrolysis of oil shales by thermal analysis methods.

Generally in thermogravimetry (TG) heterogeneous reactions under non-isothermal conditions may be studied by using two types of approximations: model and homogeneous approximations [20]. By using the first approach, kinetic equations are derived taking into account the physical processes of formation, growth and diffusion of nuclei of the decomposition product. The second approach of homogeneous kinetics is applied by considering that reaction rate, defined by means of conversion level (α), might be given as the product of Arrhenius equation and a certain conversion function. Such equation is a temperature-dependent relationship. The conversion function is presumed to be a n-th order homogeneous reaction. The product is

$$d\alpha \Big/ dT = A\frac{1}{\beta}\exp(E/RT)(1-\alpha)^{n} \tag{1}$$

According to Eq. 1, from the kinetic point of view, heterogeneous reactions may be characterized by means of three parameters – *A* (pre-exponential factor, min^{-1}), *E* (activation energy; kJ·mol^{-1}) and *n* (reaction order).

Various methods have been developed for the treatment of nonisothermal thermoanalytical data in order to obtain the kinetic parameters that could reproduce the experimental data and to predict the behaviour of the system in different conditions [20, 21]. Nonlinear least-squares (NLS) algorithms have been proved to be the most reliable method to calculate kinetic parameters from a single TG curve [22]. From the mathematical point of view, all these methods mean the use of a variational method by choosing the function (1), containing 3 variational parameters (*E*, *A* and *n*) and by determining the parameter values ensuring the minimum deviation of experimental points from theoretical curves. Consequently, the so-called kinetic parameters *A*, *E* and *n* have no clear meaning and they do not characterize the chemical reaction itself, but the whole complexity of processes occurring during pyrolysis experiments. Hence, they are designated as apparent values. However, it is well known that these apparent kinetic data (activation energies, *E*, and their corresponding frequency factors, *A*) give reasonable extrapolations for petroleum formation in sedimentary basins and show geologically significant variations in the temporal course and thermal-stress levels for petroleum formation [8]. For this reason, high quality kinetic analysis (and derived activation energy values) is essential for these models because of the need to extrapolate fast heating rates and high temperatures applied in the laboratory measurements to very slow heating and relatively low temperatures typical of geological conditions.

In this paper an equation defined by Friedman [23] and a method based on NLS (nonlinear least-squares) algorithms have been applied in order to determine the variability in kinetic parameters as a consequence of the compensation effect in the temperature of maximum oil generation for Spanish fossil fuels. Furthermore, the isoconversional Friedman method has been applied to establish the *kinetic scheme* occurring under nonisothermal linear heating of these Spanish fossil fuels.

Thus, the main objectives of the present work are

(1) to make a more accurate approach to determination of kinetic parameters in the interval related to oil and gas generation in order to obtain more approximate results in geochemical extrapolations. General assumptions made frequently in the most kinetic models, as supposing the first-order reaction at the maximum temperature of oil generation, could cause erroneous extrapolations in future predictions of oil and gas generation,

(2) to use an isoconversional method to establishing the *kinetic scheme* of thermally induced reactions in Spanish fossil fuels. *Kinetic scheme* of thermal decomposition of polymers has been worked out basing on actual data, but little is known about this issue in fossil fuels.

Material and methods

Methods used for kinetic analysis

Friedman method [23]

This method allows the calculation of apparent activation energy (*E*) from one point data (maximum on the DTG curve) at several heating rates (*ß*) according to Eq. 2. The plot of the left-hand side vs. $1/T_{\max}$ allows to derive the kinetic parameters, *n* ensures the best linearity of the plot, *E* is obtained from the slope of straight line and ln*A* from the ordinate intercept.

$$\ln\left[\beta.\left(\frac{d\alpha}{dT}\right)_{\max}\left(1-\alpha_m\right)^{-n}\right]=\ln A-\frac{E}{RT\max} \qquad (2)$$

Friedman equation (Eq. 2) assumes that the inflection point of the experimental curve ($\alpha_{\max}$, $T_{\max}$) is constant for any heating rate. However, experimentally, kinetic parameters can vary due to different systematic errors in the temperature measurement as compensation effect [24, 25].

NLS (nonlinear least-squares) algorithms

This method allows to calculate kinetic parameters from a single TG curve within a temperature interval. NLS analyses presented in this paper are based on the *n*-order rate (Eq. 1) written as

$$\alpha=1-\left[\frac{d\alpha}{dT}.\frac{\beta}{A}.\frac{1}{e^{-m/T}}\right]^{1/n}, \qquad (3)$$

where $\alpha = [1-(m(\mathrm{t})-m_f)/(m_0-m_f)]$, $m(\mathrm{t})$ is the time-dependent sample mass, m_0 the initial, dry sample mass, m_f the final sample mass; *A* is the pre-exponential factor; *β* is the heating rate; $m = E/R$ where *E* is apparent activation energy, *R* gas constant; and *T* sample temperature. We used nonlinear least-squares (NLS) algorithms which identified variable parameters (*A*, *m* and *n*) that minimized the values of the objective function χ^2 given below (Eq. 4).

$$\chi^2=\frac{\sum_{j=1}^{N}\left[\left(\alpha_j^{\exp}-\alpha_j^{calc}\right)^2\right]}{N-n}, \qquad (4)$$

where $(\alpha)^{\exp}$ is the experimental TG mass measurement, and $(\alpha)^{\mathrm{cal}}$ is the calculated mass value obtained by numerical solution of the *n*-order rate equation with the given set of parameters. Subscript *j* denotes discrete values of *m*; n is the number of free parameters (*A*, *m*, *n*); N is the number of data points used in the least-squares assessment. The function χ^2 was evaluated within an interval that was defined relative to the value of the differential thermogravimetric (DTG) peak temperature (T_{max}). The ending and the starting points of the interval to calculate the kinetic parameters were considered at T_{max} ±40 °C respectively. The Microcal Origin Program 3.0 was used for NLS analysis.

Simnon program [26] was used to simulate Eq. 3 at heating rates 5, 15 and 25 $\mathrm{K \cdot min^{-1}}$. Simnon program is a special language for solving ordinary differential (specified as a continuous system) and difference equations (specified as a discrete system) and for simulating dynamic systems. According to the Simnon language, Eq. 3 can be expressed as a continuous time system described in Table 1. The system description has two parts, a declaration and a body. There are three types of declarations. A time variable may be declared for simulation of time varying differential equations. This is done by the keyword TIME (corresponds to temperature in nonisothermal experiments) followed by an identifier. The state variables and their derivatives are declared by the keywords STATE and DER, followed by a list of the state variables and the derivatives. The body system description specifies the derivatives of the state variables in terms of state variables and parameters. The body also contains assignment of parameters and initial values.

Table 1. **Simulation of Eq. (3) for Mequinenza coal at 25 $\mathrm{K \cdot min^{-1}}$ by using the Simnon program**

Continuous system Mequinenza	
state x	*Conversion*
der dx	Derivative of the conversion
time te	*Temperature*
dx =(1/b)*g*g1*A*exp(-m/te)	*Differential eq.(1)*
g = (1-x)*(1-x)*(1-x)	$f(\alpha)= (1-\alpha)^3$ *function*
b: 25	*Heating rate*
x: 0.23	*Initial conversion*
a: 4.64029E11	*Preexponential factor*
m: 19843.03	*E/R*

Isoconversional method: Friedman method [23]

This method foresees a constant conversion level; one has to draw parallel lines α_m = constant, α_n = constant, etc. which intersect the N curves corresponding to N heating rates. For each line, α_m = constant, and a set of pairs $(T_{m1}, \beta_1)\ldots.(T_{mN}, \beta_N)$ is obtained [21].

The plot

$$\left\{ \; k(T) \quad vs \quad \beta.\frac{d\alpha}{dT} \; \right\}$$

will be a straight line passing through the origin of the axes only for a proper choice of the analytical form of $k(T)$.

Eq. 1 can be put in the following form:

$$\ln\left[\beta\cdot\frac{d\alpha}{dT}\right]=\frac{-E}{RT}+\ln\left[A\cdot(1-\alpha)^{\mathrm{n}}\right], \tag{5}$$

and the plot

$$\left\{\ \ln\left[\beta.\frac{d\alpha}{dT}\right]\ \ vs-1/T\ \right\}$$

allows to compute the value of apparent activation energy, E. Additionally, from the intercept, the value of the apparent pre-exponential factor, A, may be also calculated.

It is important to emphasize the different meaning of the concepts of *kinetic mechanism* and *kinetic scheme*. The first one is habitually used to designate a sequence of elementary steps involved in the process. Such a comprehensive information cannot be obtained from thermal analysis data. The latter may be defined as a sequence of those steps which affect a change in a physical property being measured by a thermal analysis technique. Isoconversional methods reveal the dependence of E on α which is a source of kinetic information [27, 28]. Subsequently it was shown that this dependence helps not only to disclose the complexity of a process, but also to identify its *kinetic scheme* as well [29]. Such a scheme establishes a relationship between the overall kinetics of the process and its current mechanism. Pyrolysis under non-isothermal conditions using thermal methods has been successfully applied to study kinetics of thermal decomposition of polymers [30], solid organic substances [31], wood [32] and oil shale [33, 34].

In this paper, the isoconversional method based on Eq. 5 has been used to study the dependencies of activation energy on conversion level and consequently to establish the *kinetic scheme* in Spanish coals and oil shales.

Experimental

Designation, origin and kerogen type of different low-maturity (vitrinite reflectance <0.4) fossil fuels are shown in Table 2. The samples studied were two coals from Mequinenza and Utrillas basins and two oil shales from the Ribesalbes basin. Ribesalbes oil shales were previously decarbonated using 5N hydrochloric acid. Elemental analysis of carbon and hydrogen were carried out using a Fisons 1106, and the total sulfur was determined in an elementary analyzer Fisons 1108.

The Mequinenza (8-Me) coal-bearing sequence is included in Los Monegros Lacustrine System (SE Ebre basin) and it was deposited during late Oligocene (ca. 30 Ma). Evaporitic facies were developed mainly in the marginal lacustrine zones while carbonate and lignite deposits were dominant in inner lacustrine area [35]. Utrillas subbituminous coal (Cañizara) was taken from the Maestrazgo basin, which is located in the Iberian Range linking zone with the southernmost sector of the Catalan coastal range, deposited during middle Albian (late Lower Cretaceous, ca. 105 Ma) [36]. Ribesalbes oil shales are taken from a basin located in the southern part of the Iberian chain, which belongs to the Miocene lacustrine system (ca. 10 Ma) [37]. The other main characteristics of these fossil fuels can be found elsewhere [38, 39].

Table 2. **C, H and S percentages, on dry ash free basis (d.a.f.), of Mequinenza and Utrillas coals, as well as of dry oil shales from Ribesalbes. Kerogen type of each sample in this study**

Samples	Basin	C	H	S	Kerogen type
8-Me	Mequinenza	60.6	5.3	13.4	III-S
Cañizara	Utrillas	73.2	5.8	5.4	III
Rib-3	Ribesalbes	10.7	1.8	1.9	I-S
Rib-7	Ribesalbes	10.3	2.4	0.4	I-S

All experiments were performed with a CAHN thermobalance TG-151 attached to an analytical thermal system. The specifications of the equipment are: balance capacity 100 g, sensitivity 10 μg, maximum temperature 1100 °C, maximum heating rate 25 $K\cdot min^{-1}$, quartz crucible (CAHN). Thermal experiments were conducted in the temperature range 25–850 °C with samples weighing between 26 and 27 mg. The analyses were carried out at three constant heating rates (5, 15 and 25 $K\cdot min^{-1}$) with a nitrogen purge flow of 200 $ml\cdot min^{-1}$. For each sample, two reproducible experiments were carried out. The lower rate (5 $K\cdot min^{-1}$) was chosen to minimize systematic errors in temperature measurement due to thermal lag during pyrolysis. TG/DTG curves recorded during pyrolysis of Mequinenza and Cañizara coals and Ribesalbes oil shale at heating rate 15 $K\cdot min^{-1}$ are shown in Fig. 1.

Figure 2 shows TG/DTG curves at several heating rates for Cañizara coal.

The program used in order to treat the experimental data was Micro-Cal Origin 3.0. Determinations of the distribution of organic sulfur forms in these coals and oil shales and of their evolution during pyrolysis experiments were carried out previously [40, 41].

Thus, it is known that the maximum weight loss is attributed to the formation of hydrocarbon gases [40, 42].

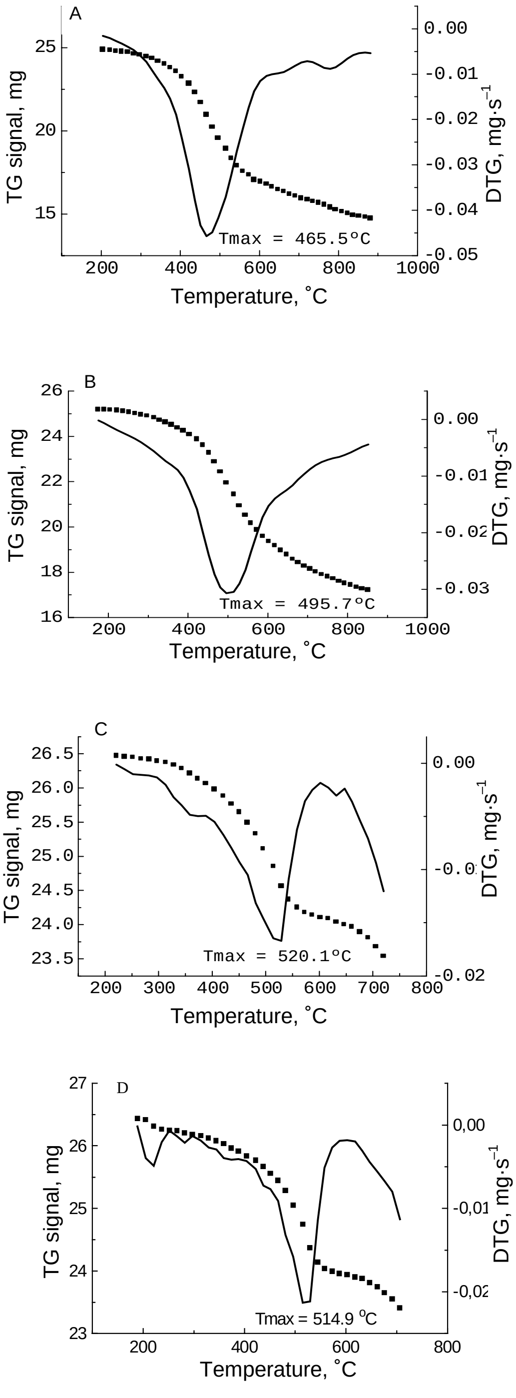

Fig. 1. TG (−) / DTG (■) curves of A) Mequinenza (8-Me) coal, B) Utrillas (Cañizara) coal, C) Ribesalbes (Rib-3) oil shale, D) Ribesalbes (Rib-7) oil shale at heating rate 15 K·min^{-1}

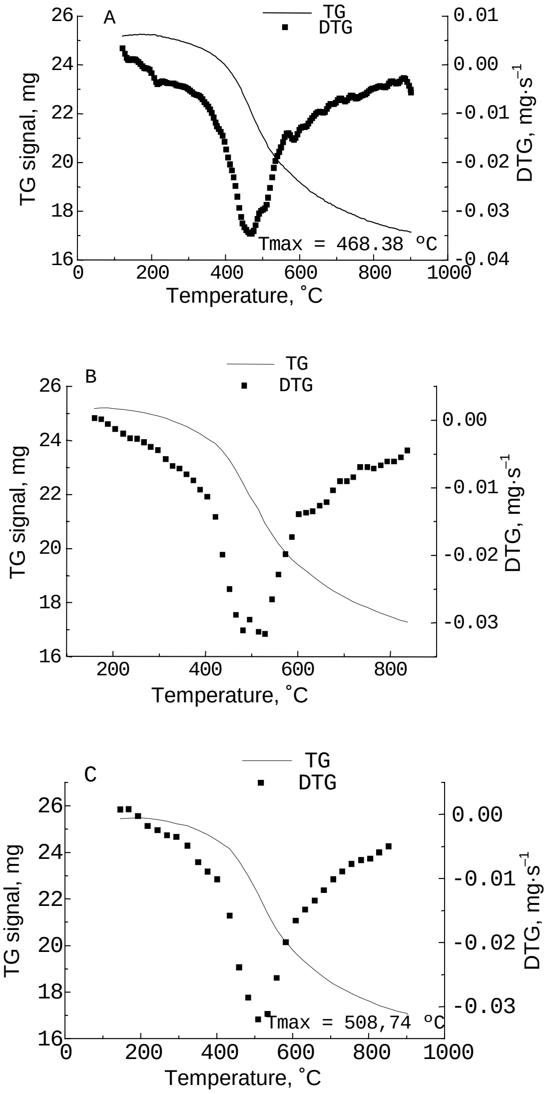

Fig. 2. TG/DTG curves for Utrillas (Cañizara) coal at heating rate A) 5 K·min^{-1}, B) 15 K·min^{-1}, C) 25 K·min^{-1}

Results and discussion

Analysis of TG/DTG data at T_{max}

Kinetic parameters calculated by Friedman equation (Eq. 2) and NLS algorithms from experimental curves are shown in Table 3. It has been deduced from this table that the values of apparent activation energies and pre-exponential factors obtained for 8-Me and Cañizara coals by Friedman equation (Eq. 2) do not differ markedly from those obtained by NLS analysis, whereas the reaction orders are considerably different (n = 1 using Friedman equation; $n \geq 3$ for NLS analysis). Although good correlation coefficients have been obtained ($R^2 > 0.92$) (Table 3a) using Friedman equation, the kinetic parameters could not be representative of pyrolysis process in the maximum point. This fact is tested by supposing the non-existence of the compensation effect which means to keep constant the kinetic parameters with an increase in the heating rate. The kinetic parameters calculated at 5 $K \cdot min^{-1}$ using NLS algorithms were chosen to be constant at heating rates 15 and 25 $K \cdot min^{-1}$, and then the curves at 5, 15 and 25 $K \cdot min^{-1}$ were simulated by using Simnon program. From these simulated curves the kinetic parameters have been calculated using the Friedman method (Table 3b). As shown in Table 3c, the apparent activation energies and pre-exponential factors obtained without taking into account the compensation effect are similar to those calculated by the NLS algorithms from an experimental curve (Table 3a) indicating that more than a kinetic behavior, the first-order reaction could reflect a good correlation of kinetic parameters with the heating rate mainly due to the compensation effect. A familiar manifestation of the compensation effect is the decrease in the values of both *E* and ln*A* at higher heating rates.

Table 3. **Kinetic parameters: a) obtained by the Friedman equation derived from TG/DTG experimental curves, b) obtained by the Friedman equation derived from TG/DTG simulated curves using the Simnon program, c) NLS algorithms based on a single curve**

Samples	**a) Friedman eq.***				**b) Friedman eq. simulated***				**c) NLS algorithms****			
	ln*A* A, min^{-1}	*E*, $kJ \cdot mol^{-1}$	n	R^2	ln*A* A, min^{-1}	*E*, $kJ \cdot mol^{-1}$	n	R^2	ln*A* A, min^{-1}	*E*, $kJ \cdot mol^{-1}$	n	χ^2 $(\cdot 10^{-6})$
8-Me	23.6	158.3	1	0.99	23.1	161.2	3	0.99	26.9	165.0	3	8.2
Cañizara	27.6	191.5	1	1	31.8	197.7	4	1	32.5	200.4	4	3.2
Rib-3	16.7	131.2	1	0.92	30.3	220.3	6	0.99	32.8	211.5	6	0.4
Rib-7	15.7	124.5	1	0.99	28.3	190.3	7	0.99	27.0	186.4	7	0.4

* heating rates 5, 15 and 25 $K \cdot min^{-1}$

** heating rate 5 $K \cdot min^{-1}$

Worth of attention is also the fact that the values of *E* are good correlated ($R^2 > 0.98$) with ln*A* at heating rates 5, 15 and 25 $K \cdot min^{-1}$ in the samples selected for this study [38] showing that kinetic parameters are good correlated with heating rates due to the compensation effect. Both, this decrease in *E* and ln*A* and the related compensation effect can result from increased thermal lag at higher heating rates [22, 43]. Thus, the linearity between pre-exponential factors and activation energies when increasing the heating rate has been also reported by Mianowski and Radko [44] in the case of coals. The simulated curves based on kinetic parameters obtained at heating rate 5 K·min^{-1} by NLS analysis show a good fit (see Fig. 3 for 8-Me coal) with experimental data in all samples tested by the low χ^2 values obtained ($<8.2 \cdot 10^{-6}$, Table 3c). The conversion level used in Fig. 3 is between 0 and 1. Additionally, high reaction orders have been obtained by NLS analysis of Ribesalbes oil shales. According to many authors [43, 45] high reaction orders can give some indication of simultaneous multiple reactions that take place probably due to the heterogeneity of the solid or variable values of activation energy typical of a reaction and also of the considerable influence of mass diffusion effects [46]. By supposing first-order reaction as a fix parameter, the kinetic parameters obtained by NLS analysis from a single TG curve for all samples are unrealistic (negative ln*A*, apparent activation energy too low) [38]. This also shows that the first-order reaction and consequently *E* and *A* obtained using Friedman method are unreliable. Hence, to suppose a first-order reaction at the maximum temperature of hydrocarbon generation can induce erroneous results in future predictions of oil and gas generation. However, it does not mean that pyrolysis kinetics of fossil fuels cannot follow first-order reactions [33].

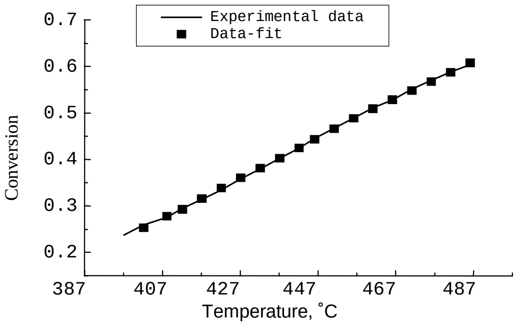

Fig. 3. Experimental data and the best-fitting curve by NLS analysis for 8-Me coal at 5 K.min^{-1}

Study of the kinetic scheme

In order to understand better the complexity of these coals we have applied the isoconversional method based on Eq. 5 to Mequinenza and Utrillas coals and Ribesalbes oil shales in order to establish the dependence of *E* on α which is a source of information about the *kinetic scheme* of these fossil fuels.

As it is shown in Fig. 4*A*, the dependence of apparent activation energy on conversion level in the case of Mequinenza coal is decreasing and has a concave shape, up to the conversion value of about 0.4. At higher conversions the dependence becomes convex. It has been shown [28] that the decreasing dependence of *E* on conversion corresponds to the *kinetic scheme* of an endothermic reversible reaction followed by an irreversible one. The maximum apparent activation energy value for all processes is about 1035 kJ/mol, which approximately equals the sum of the apparent activation energy of the irreversible reaction and the enthalpy of the reversible reaction. The minimum value is about 318 kJ/mol and should be interpreted as an estimation of the apparent activation energy of the irreversible reaction.

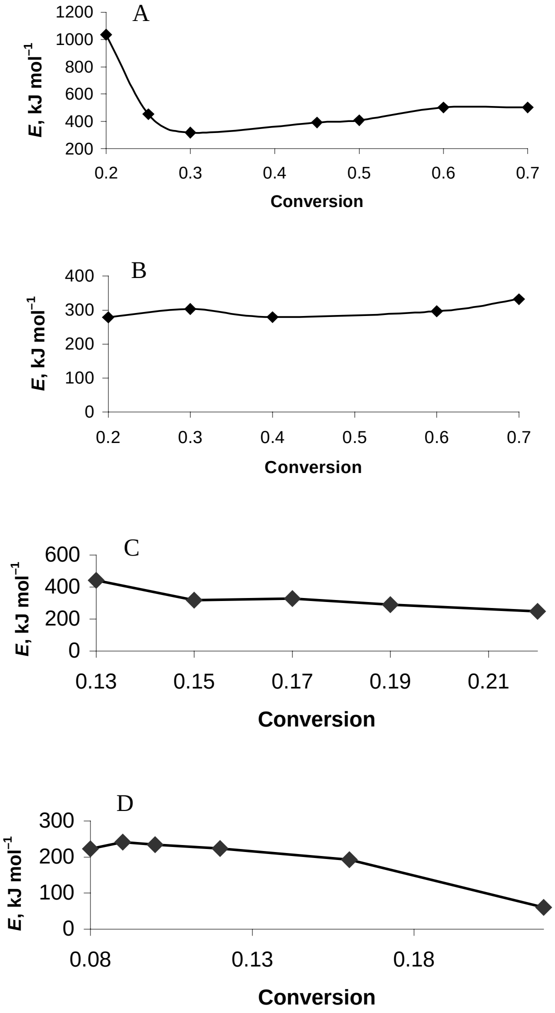

Fig. 4. The dependence of apparent activation energy (*E*) on conversion level: A) a reversible reaction followed by an irreversible one in the case of Mequinenza coal (8-Me), B) a reversible reaction in Utrillas coal, C) a reversible reaction in Ribesalbes oil shale (Rib-3), D) a reversible reaction in Ribesalbes oil shale (Rib-7)

The *kinetic scheme* of Utrillas coal is characterized by the almost independence of apparent activation energy on conversion level (Fig. 4B). This shape has been found also for a reversible reaction [47]. On the other hand, pyrolysis of Ribesalbes oil shales (Fig. 4C and Fig. 4D) is a reversible process, because the dependence of apparent activation energy on conversion level is of decreasing shape.

Although a further research is necessary to fully understand the complex kinetics of these fossil fuels, this approach carried out under nonisothermal experiments inform us about the *kinetic scheme* which represents a starting point to elucidate the *kinetic mechanism*.

Conclusions

On the basis of the above results it is deduced that kinetic parameters obtained at around $T_{\max}$ using NLS algorithms show an excellent agreement with the experimental data testing the reliability of the kinetic values obtained. In contrast, the kinetic values calculated by the Friedman equation from one point at several heating rates are affected by the compensation effect and therefore erroneous values are obtained. Finally, an isoconversional method is used to study the characteristic dependencies of apparent activation energy on conversion level by showing two different *kinetic schemes*: a reversible reaction followed by an irreversible reaction characteristic for Mequinenza coal and a reversible reaction characteristic for Utrillas coal and Ribesalbes oil shales.

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