Journal of Thermal Analysis and Calorimetry, Vol. 89 (2007) 1, 203–209

PYROLYSIS KINETICS OF POLYPROPYLENE
Morocco oil shale and their mixture

A. Aboulkas[1], *K. El Harfi*[1*], *A. El Bouadili*[2], *M. Ben Chanâa*[1] *and A. Mokhlisse*[1]

[1]Laboratoire de Chimie Physique, Département de Chimie, Faculté des Sciences Semlalia, Université Caddi Ayyad, BP 2390, 40001 Marrakech, Maroc
[2]Laboratoire de Chimie Organique et Analytique, Departément de Chimie, Faculté des Sciences et Techniques de Béni-Mellal, Université Caddi Ayyad, BP 523, 23000 Béni-Mellal, Maroc

The pyrolysis of oil shale and plastic wastes is being presently considered as an alternative means of partial substitution of fossil fuels to generate the necessary energy to supply the increasing energy demand and as well as new technology to reduce the negative environment of plastic wastes. However, Knowledge of pyrolysis kinetics is of great imponrtance for the design and simulation of the reactor and in order to establish the optimum process conditions.

In this study, the thermal decomposition of polypropylene, oil shale and their mixture was studied by TG under a nitrogen atmosphere. Experiments were carried out for various heating rates (2, 10, 20, 50 K min^{-1}) in the temperature range 300–1273 K. The values of the obtained activation energies are 207 kJ mol^{-1} for polyethylene, 57 kJ mol^{-1} for the organic matter contained in the oil shale and 174 kJ mol^{-1} for the mixture. The results indicate that the decomposition of these materials depends on the heating rate, and that polypropylene acts as catalyst in the degradation of the oil shale in the mixture.

Keywords: *dynamic thermogravimetry, kinetics, oil shale, polypropylene, pyrolysis*

Introduction

In recent years, the plastic materials have became an important part of solid urban waste, with plastics from containers and packaging representing around 60% of this type of waste. The composition of this residue is mainly polyolefins (high and low density polyethylene, polypropylene and polystyrene), accounting for around 70% of the total plastic waste [1]. As only a small amount of waste plastic is recycled and most plastics are not biodegradable, these strong uses have led to the generation of an increased amount of plastic waste. Therefore, technical have to be implemented to reduce plastic wastes negative impact on the environment. Landfilling or incineration of plastic waste are not the right solutions, because the former has the danger of leaching and soil impregnation of its degradation products and the latter produce several pollutants (nitrous and sulphur oxides, dusts, dioxins and other toxins) that have a highly negative impact on the environment. Both processes do not allow the recovery of the organic content of plastic waste, which should be part of the organic life-cycle.

The search for new alternative fuels, together with the necessity of searching new technology to reduce the negative environment impact of plastic wastes, has led to the idea of studying co-pyrolysis of plastic wastes and oil shale.

The plastics consist of hydrocarbons-type macromolecules with a significant intrinsic energy and a very high calorific value [2, 3]. These materials are rich in hydrogen in comparison with coal [4, 5–9] and oil shale [10–15]. Oil shale, on the other hand, is considered to be the substitute for oil as a natural source of energy. However, the extraction of oil from oil shale is relatively expensive and uneconomical. Therefore, research for processes of oil shale utilization as a source of energy gains a high level of importance [16–19].

The three oil shale deposits in Morocco (Timahdit, Tanger and Tarfaya) represent about 15% of known oil shale resources in the world [20]. Extensive exploration and processing research has been conducted over the past decades [21]. These shale oil resources have been estimated to be 50 billion barrels [20]. Timahdit and Tarfaya oil shale deposits are the biggest and the most explored deposits in Morocco to have the potential to yield 17 and 23 billion barrels respectively.

The co-treatment of oil shale mixed with plastic wastes into useful energetic products or into valuable chemicals can be achieved in a thermochemical processes [10–15]. Pyrolysis has received special attention since it produces solid, liquid and gas products. With these purposes, the knowledge of the kinetics of degradation is necessary for the design of specific reactors. Thermogravimetric behaviour has been proved to be a very powerful tool for materials char-

---

[*] Author for correspondence: elharfi@ucam.ac.ma

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

acterisation and analysis, as well as for determining kinetic parameters [22, 23].

In this paper the thermal decomposition of polypropylene, oil shale and their mixture has been studied by thermogravimetric analysis. The effect of heating rate has been studied. A kinetic model has been proposed which allows a good correlation of the results obtained.

Theoretical approach

The decomposition of a solid in a non-isothermal mode can be represented by the following reaction:

$$\mathrm{A(solid)}\rightarrow\mathrm{B(solid)}+\mathrm{C(gas)}$$

The decomposition rate of a solid is generally given an equation in the form:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=K(T)F(x) \tag{1}$$

where x is the degree of advance, $F(x)$ is a function of the kinetic mechanism involved in the degradation and $K(T)$ is the rate constant which varies with temperature according to Arrhenius law

$$K(T) = A\ \exp(-\frac{E}{RT}) \tag{2}$$

where A is a pre-exponential factor, E is the activation energy, T is the absolute temperature and R is the universal gas constant.

By combining the Eqs (1) and (2), the reaction rate can be written in the form:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=A\exp(-\frac{E}{RT})F(x) \tag{3}$$

The method of Friedman [24] was adopted in this work for the kinetic analysis of the thermogravimetric curves of these materials. This method, which was widely used by several authors [25–32] for other materials, is based on the following kinetic equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t}=A\exp(-\frac{E}{RT})(1-x)^{\mathrm{n}} \tag{4}$$

Consequently, the logarithmic form of the Eq. (5) can be written:

$$\ln(\frac{\mathrm{d}x}{\mathrm{d}t}) = \ln(A)+ n\ln(1-\mathrm{x})-\frac{E}{RT} \tag{5}$$

The plot of $\ln(\frac{\mathrm{d}x}{\mathrm{d}t})$ *vs.* $\frac{1}{T}$ for a given heating rate yields a straight line of slope $-\frac{E}{RT}$, which allows determining the activation energy E. Furthermore, the plot of $\ln[(\frac{\mathrm{d}x}{\mathrm{d}t})/\exp(-\frac{E}{RT})]$ as a function of $\ln(1-x)$ yields the reaction order n and then pre-exponential factor A.

Table 1 Some average physicochemical characteristics of the oil shales of Tarfaya

Proximate analysis (mass%)	
Volatile matter	40.09
Ash	52.83
Moisture (as received)	5.15
Elemental analysis (mass%)	
C	17.60
H	1.78
N	0.70
S	0.37
Composition (mass%)	
Carbonate mineral (by HCl leaching)	70.0
Silicate mineral (by HF–HCl leaching)	10.0
Bitumen (by Soxhlet extraction with $CHCl_3$)	0.8
Pyrite (by density separation $CHCl_3$)	1.0
Kerogen	17.0

Table 2 Some characteristics of polypropylene

Proximate analysis (mass%)	
Volatile matter	99.06
Ash	0.9
Elemental analysis (mass%)	
C	85.48
H	14.44
N	–
S	0.15

Experimental

Materials

The oil shale samples used in this work originated from the underlayer R_3A_2 of Tarfaya (Morocco). The results of the analysis of these samples are gathered in Table 1.

The samples of polypropylene were provided by Plador (Marrakech, Morocco). The results of characterization of these materials are given in Table 2.

Experimental techniques

Thermogravimetric runs were performed in a Rheometrix Scientific STA 1500 TGA analyzer. The experiments for the determination of the thermal decomposition temperature were carried out with an initial sample mass between 20 and 25 mg with particle sizes in the range 0.1 to 0.2 mm and at heating rates of 2, 10, 20 and 50 K min^{-1}. The atmosphere used was nitrogen with a flow rate of around 60 mL min^{-1}.

Results and discussion

Thermogravimetric analysis

Decomposition of polypropylene

The curves of Fig. 1 are obtained for the decomposition of polypropylene at a heating rate of 10 K min^{-1}. These curves represent the total mass left, the heat flow and the instantaneous decomposition rate ($\frac{dm}{dt}$) as a function of temperature. The overall shapes of the curves obtained for the other heating rates are results to the corresponding ones in Fig. 1. However, it should be noted when the heating rate is increased the maximum decomposition rate increases and the corresponding of temperature ($T_{\max}$) shifts towards higher temperatures (Table 3).

The analysis of the results of Fig. 1 shows that the degradation of polypropylene occurs only in one step in the temperature range 300–900 K. It can also be noted that the heat flow curve represents two endothermic peaks. The first, observed between 388 and 460 K and occurring without a mass loss, is attributed to the fusion of polypropylene. The second peak, located between 675 and 756 K, corresponds primarily to the decomposition of the organic matter. The obtained mass loss percentages do not vary with the heating rate, and they are about 98%.

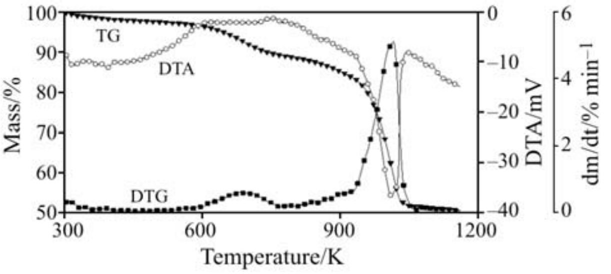

Fig. 2 TG, DTG and DTA curves of oil shale degradation (10 K min^{-1})

Decomposition of the oil shale

The total mass left, the heat flow and the decomposition rate of the oil shale are represented in Fig. 2 as a function of temperature. The analysis of these results shows that the decomposition of oil shale involves three steps:

- The first step, obtained in the temperature range (300–375 K), is attributed to the desorption of water adsorbed on material.
- The second step, obtained in the temperature range (592–776 K), is attributed to the decomposition of the organic matter. We note that this loss is approximately 9% and does not vary with the heating rate. The heat requirement for this reaction is low, as shown by the low peak in Fig. 2. The data for pyrolysis temperatures is listed in Table 3.
- The third step, obtained for temperatures between 780 and 1150 K, is attributed to the decomposition of the mineral matrix (mainly decomposition of carbonates and silicates).

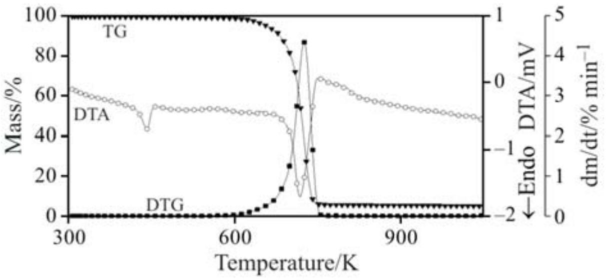

Fig. 1 TG, DTG and DTA curves of polypropylene degradation (10 K min^{-1})

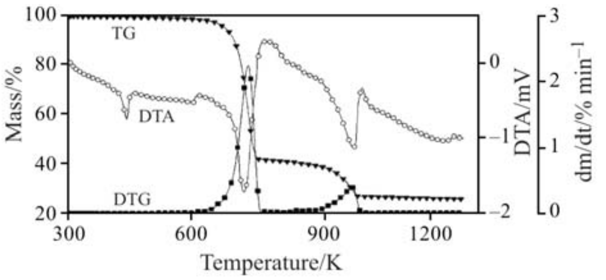

Fig. 3 TG, DTG and DTA curves of the mixture oil shale-polypropylene (1:1) degradation (10 K min^{-1})

Table 3 Maximum degradation temperature ($T_{\max}$) obtained for the polypropylene, oil shale and their mixture

Sample	2 K min^{-1}	10 K min^{-1}	20 K min^{-1}	50 K min^{-1}
Polypropylene	634	728	745	768
Oil shale	–	687	716	735
Oil shale/Polypropylene (1:1)	707	740	754	780

Table 4 Kinetic parameters of polypropylene for the four heating rates

Heating rate/K min^{-1}	Activation energy/ kJ mol^{-1}	Correlation coefficient	ln(A)	Reaction order
2	130.5	0.9937	16.52	0.85
10	145.6	0.9962	21.94	0.90
20	269.2	0.9956	43.40	1.03
50	282.7	0.9987	45.07	1.18
Average	207.0	0.9960	31.73	0.99

Decomposition of the mixture

The total mass left, the heat flow and the decomposition rate of the mixture as a function of the temperature are presented in Fig. 3. The analysis of these curves shows that the peculiarities of the decomposition of the pure materials (polypropylene and oil shale) also appear during the thermal degradation of the mixture. The dehydration of the oil shale and the fusion of polypropylene respectively appear in the temperature intervals 300–380 and 375–455 K. These peculiarities are manifested in the heat flow curves by two peaks which appear in the same temperature ranges reported above for each material separately. It can also be noticed that, independently of the heating rate used, the decomposition of the mixture involves three steps:

- The first step, obtained in the temperature range (300–380 K), is attributed to the departure of the adsorbed water from the sample.
- The second step, obtained for temperatures ranging between 640 and 768 K, is attributed to the decomposition of the organic matter contained in two materials. This loss does not depend on the heating rate and represents a total mass loss of approximately 54%. The different temperatures are listed in Table 3.
- The third step, obtained for temperatures higher than 800 K, is attributed to the decomposition of the mineral matrix of the oil shale (carbonates, silicates...). The total mass loss (14.3%) is lower than that observed in the decomposition the oil shale alone (36.4%). Similar results were observed during the pyrolysis of other oil shales mixed with polypropylene [15].

In order to study the catalytic effect of the oil shale on the decomposition of polypropylene, we compared the curves of the oil shale, polypropylene and their mixture. At the beginning of the reaction of the mixture, when the decomposition of polypropylene particles starts, that of the oil shale is already completed. Consequently, the curve of the mixture does not show that the oil shales have a catalytic effect on the decomposition of polypropylene. The analysis of the curve of the mixture shows that for temperatures between 592 K (temperature at which the decomposition begins for the oil shale at a heating rate of 10 K min^{-1}) and 654 K (temperature at which the decomposition begins for polypropylene at 10 K min^{-1}), the decomposition of polypropylene in the mixture starts to be degraded in the presence of the oil shales at a temperature lower than that of the pure material (Fig. 3).

Kinetic study of the decomposition

The kinetics of the decomposition of polypropylene

The decomposition rate is 0.51 mg min^{-1} at 687 K and reaches a maximum of around 0.92–22.48 mg min^{-1} (depending on the heating rate) at 634 to 768 K. The application of the method of Friedman to the thermogravimetric curves of polypropylene shows that the linear transforms $\frac{dx}{dt}$ as a function of $\frac{1}{T}$ yield

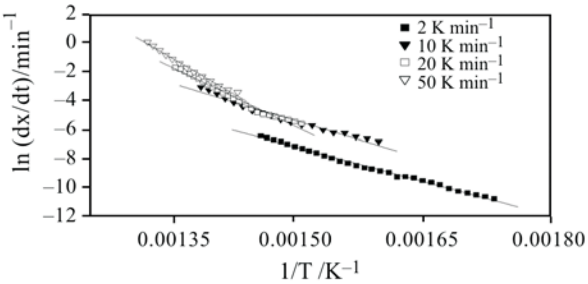

Fig. 4 $\ln(\frac{dx}{dt})$ *vs.* $\frac{1}{T}$ for polypropylene decomposition

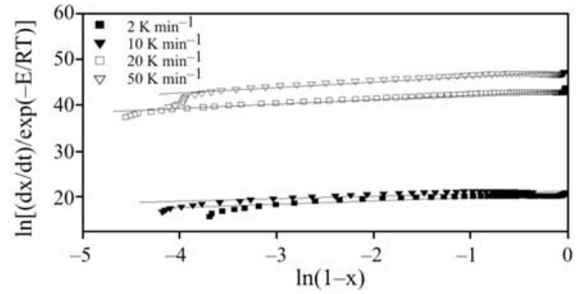

Fig. 5 Variation of $\ln[(\frac{dx}{dt})/\exp(-\frac{E}{RT})]$ with ln(1–x) for determination of reaction order and frequency factor for polypropylene degradation

Table 5 Kinetic parameters of oil shale-organic matter for the four heating rates

Heating rate/K min^{-1}	Activation energy/kJ mol^{-1}	Correlation coefficient	ln (A)	Reaction order
2	–	–	–	–
10	53.3	0.99207	6.26	0.95
20	61.5	0.99582	8.68	1.13
50	56.2	0.99789	9.63	0.99
Average	57.0	0.99526	8.19	1.023

straight lines as shown in Fig. 4. The average value of the activation energy for the four heating rates is 207 kJ mol^{-1}. The plot of $\ln[(\frac{dx}{dt})/\exp(-\frac{E}{RT})]$ as a function of $\ln(1-x)$ gives a reaction order of 0.99 in Fig. 5. The apparent activation energies reported in the literature are slightly different. Day *et al.* [33] found energies between 130 and 195 kJ mol^{-1} as function of the fractional mass loss with a first-order reaction rate, whereas Gersten *et al.* [15] obtained 250 kJ mol^{-1} also with a first-order reaction. The obtained kinetic parameters are presented in Table 4.

The kinetics of the decomposition of oil shale

At 10 K min^{-1}, decomposition begins at 593 K and reaches a maximum of 0.11 mg min^{-1} at 687 K, at 50 K min^{-1} a maximum of 1.34 mg min^{-1} at 733 K. The decomposition rate of oil shale is 13 times lower than that of polypropylene. The plot of $\ln(\frac{dx}{dt})$ as a function of $\frac{1}{T}$ for various heating rates of oil shale is given in Fig. 6. The average value of the activation energies for the decomposition of the organic matter is 57 kJ mol^{-1}. Similarly, the order of the reaction obtained from the slope of the plot of $\ln[(\frac{dx}{dt})/\exp(-\frac{E}{RT})]$ as a function of $\ln(1-x)$ in Fig. 7 is 1.02. Comparison with literature data shows that the kinetic parameters are unique to each individual case

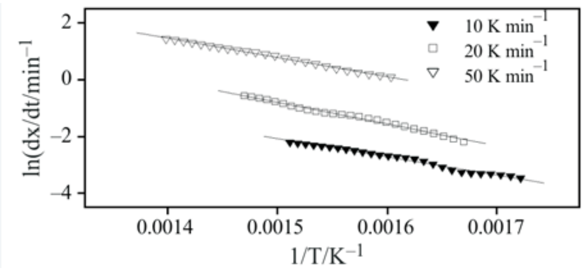

Fig. 6 $\ln(\frac{dx}{dt})$ *vs.* $\frac{1}{T}$ for decomposition of oil shale-organic matter

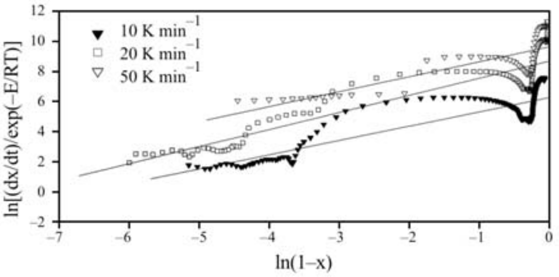

Fig. 7 Variation of $\ln[(\frac{dx}{dt})/\exp(-\frac{E}{RT})]$ with $\ln(1-x)$ for determination of reaction order and frequency factor for oil shale degradation

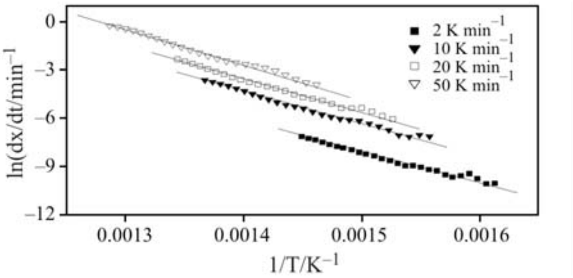

Fig. 8 $\ln\left(\frac{dx}{dt}\right)$ *vs.* $\frac{1}{T}$ for decomposition of oil shale-organic matter of mixture oil shale/polypropylene (1:1)

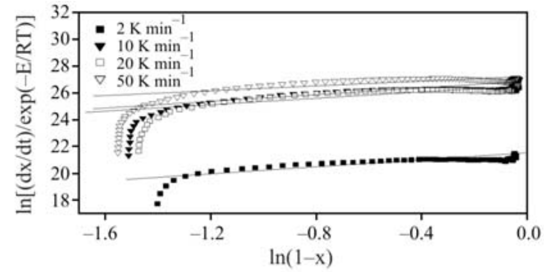

Fig. 9 Variation of $\ln[(\frac{dx}{dt})/\exp(-\frac{E}{RT})]$ with $\ln(1-x)$ for determination of reaction order and frequency factor for decomposition of the organic matter of a mixture of oil shale-polypropylene (1:1)

Table 6 Kinetic parameters of oil shale/polypropylene (1:1) mixture for the four heating rates

Heating rate/K min^{-1}	Activation energy/ kJ mol^{-1}	Correlation coefficient	ln(A)	Reaction order
2	162.3	0.9966	21.15	0.81
10	181.7	0.9948	26.58	1.13
20	176.4	0.9988	26.39	0.97
50	175.5	0.9755	27.25	1.08
Average	174.0	0.9914	25.34	0.998

of oil shale. For example, Skala *et al.* [34] investigated three deposits from oil shales Knjazevac (Yugoslavia), Northern Korea and Estonia and obtained for the organic stage, assuming a first-order reaction at 5 K min^{-1} activation energies of 55, 133 and 150 kJ mol^{-1}, respectively. This diversity is due to differences in behavior of the oil shale during pyrolysis, attribution to structural differences between the corresponding kerogens. The obtained kinetic parameters for the oil shale are presented in Table 5.

The kinetics of decomposition of the mixture

The decomposition rate of the organic material depends on temperature and the heating rate, increasing with the latter: 0.55, 2.8, 5.32 and 14.1 mg min^{-1} at 2, 10, 20 and 50 K min^{-1}, respectively.

The temperature corresponding to the maximum decomposition rate of the mixture is higher than that of oil shale by 33 to 40 K and close to that of polypropylene. The decomposition rate of the mixture is closer to that of polypropylene and much higher than that of oil shale.

The plot of $\ln(\frac{dx}{dt})$ as a function of $\frac{1}{T}$ for various heating rates is given in Fig. 8. The average value of the activation energy for the decomposition of the organic matter is 174 kJ mol^{-1}. The order of the reaction obtained from the slope of Fig. 9 is 0.998. The obtained kinetic parameters are given in Table 6. The obtained activation energy is higher than that of the oil shale (57 kJ mol^{-1}) and close to that of polypropylene (207 kJ mol^{-1}).

Conclusions

The obtained results show that:

- Polypropylene accelerates the decomposition of the organic matter of the oil shale.
- The degradation of the studied materials can be regarded as a first order reaction as shown by the method of Friedman.
- The obtained value of the activation energy for the degradation of the organic matter of the mixture (174 kJ mol^{-1}) is higher than that of the oil shale (57 kJ mol^{-1}) and close to that of polypropylene (207 kJ mol^{-1}).

References

1 D. P. Serrano, J. Aguado and M. Escola, Ind. Eng. Chem. Res., 39 (2000) 1177.
2 M. Farcasiu, Chem.Tech., 23 (1993) 22.
3 Z. Liu, J. W. Zondlo and D. B. Dadyburjor, Energy and Fuels, 8 (1994) 607.
4 F. Pinto, P. Costa, I. Gulyurtlu and I. Cabrita, J. Anal. Appl. Pyrol., 51 (1999) 399.
5 R. Sakurovs, Fuel, 82 (2003) 1911.
6 N. Horvat and T. T. Ng. Flora, Fuel, 78 (1999) 459.
7 A. Uddin, K. Koizumi, K. Murata and Y. Sakata, Polym. Degrad. S tab., 56 (1999) 37.
8 E. S. Uzumkesici, M. D. Casal-Banciella, C. McRae, C. E. Snape and D. Taylor, Fuel, 78 (1999) 1697.
9 A. M. Mastral, M. S. Callen, T. Garcia and M. V. Navarro, Fuel Process. Technol., 64 (2000) 135.
10 L. Ballice, Energy and Fuels, 15 (2001) 659.
11 L. Ballice, M. Yüksel, M. Sağlam, H. Schulz and R. Reimert, Fuel, 77 (1998) 1431.
12 H. Herbst, K. Hoffmann, R. Pfaendner and H. Zweifel, NATO ASI Series, 351 (1997) 73.
13 L. Tiikma, H. Luik and N. Pryadka, Oil Shale, 21 (2004) 75.
14 J. Gersten, V. Fainberg, A. Garber, A. Hetsroni and Y. Shindler, Fuel, 78 (1999) 987.
15 J. Gersten, V. Fainberg, G. Hetsroni and Y. Shindler, Fuel, 79 (2000) 1679.
16 K. El Harfi, A. Mokhlisse and M. Ben Chanâa, J. Anal. Appl. Pyrol., 48 (1999) 65.
17 K. El Harfi, C. Bennouna, A. Mokhlisse, M. Ben Chanâa, L. Lemée, J. Joffre and A. Ambles, J. Anal. Appl. Pyrol., 50 (1999) 163.
18 K. El Harfi, A. Mokhlisse, M. Ben Chanâa and A. Outzourhit, Fuel, 79 (2000) 733.
19 K. El Harfi, A. Mokhlisse and M. Ben Chanâa, J. Anal. Appl. Pyrol., 56 (2000) 207.
20 O. Bekri and M. Ziyad, Synthesis of oil Shale R and D Activities in Morocco, Proceedings of the 1991 Eastern Oil Shale Symposium, Lexington, Kentucky, 1991.
21 J. M. Nazzal, J. Therm. Anal. Cal., 65 (2001) 847.
22 R. López-Fonseca, I. Landa, M. A. Gutiérrez-Ortiz and J. R. González-Velasco, J. Therm Anal. Cal., 81 (2005) 65.
23 E. A. Gómez Pineda, A. D. Martins Ferrarezi, J. G. Ferrarezi and A. A. Winkler Hechenleitner, J. Therm. Anal. Cal., 79 (2005) 259.
24 H. Friedman, J. Polym. Sci., Part C 6 (1964) 183.

25 A. Marcilla and M. Beltrain, Polym. Degrad. Stab., 48 (1995) 219.
26 X. S. Wang, Xin-Gui Li and D. Yan, Polym. Degrad. Stab., 69 (2000) 361.
27 J. H. Chena, K. S. Chen and L. Y. Tong, J. Hazard. Mater., B84 (2001) 43.
28 B. J. Holland and J. N. Hay, Thermochim. Acta, 388 (2002) 253.
29 R. A. Ruseckaite and A. Jimenez, Polym. Degrad. Stab., 81 (2003) 353.
30 N. S. Vrandecic, I. Klaric and T. Kovacic, Polym. Degrad. Stab., 84 (2004) 31.
31 P. Budrugeac, E. Segalb, L. A. Perez-Maquedac and J. M. Criado, Polym. Degrad. Stab., 84 (2004) 311.
32 K. Pielichowski and K. Flejtuch, J. Anal. Appl. Pyrol., 73 (2005) 131.
33 M. Day, J. D. Cooney and M. MacKinnon, Polym. Degrad. Stab., 48 (1995) 341.
34 D. Skala, M. Kopsch, M. Sokic, H. J. Neumann and J. A. Jovanovic, Fuel, 69 (1990) 490.

Received: December 28, 2006
Accepted: January 22, 2007
OnlineFirst: April 29, 2007

DOI: 10.1007/s10973-007-7398-z