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Study on the pyrolysis of Moroccan oil shale with poly (ethylene terephthalate)

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Abstract Investigations into the pyrolytic behaviours of oil shale, poly (ethylene terephthalate) (PET) and their mixture have been conducted using a thermogravimetric analyzer. Experiments were carried out dynamically by increasing the temperature from 298 to 1,273 K with heating rates of 2–100 K/min under a nitrogen atmosphere. Discrepancies between the experimental and calculated TG/DTG profiles were considered as a measurement of the extent of interactions occurring on co-pyrolysis. The maximum degradation temperature of each component in the mixture was higher than those the individual components; thus an increase in thermal stability was expected. The kinetic processing of thermogravimetric data was carried out using Flynn–Wall–Ozawa (FWO) method.

Keywords Pyrolysis · Oil shale · Poly (ethylene terephthalate) · Kinetics

Introduction

An increase in the usage and consumption of plastics such as polyethylene, polystyrene, polypropylene, and poly (ethylene terephthalate) is considered to be inevitable, because of their versatility, their myriad of uses, and the relatively small amount of energy required for their production (compared to that of other materials). At the same time, plastic wastes are becoming a serious environmental problem worldwide, because of their quantity, complexity (in terms of having multiple polymers and mineral additives), and inherent stability. Landfilling has long been the most widely used waste disposal method. Inert plastics will not degrade over thousands of years in a landfill; however, the additives and plasticizers, which contain lead, chlorine, and other toxic compounds, have aroused the growing concern of the public. Recycling is one of the more acceptable methods of the disposal of plastic waste. However, conventional plastic recycling is facing many problems, such as the existence of 100 classes of plastic polymer with 1,000 specifications. Therefore, an advanced technology is required for sorting and separating post-consumer waste plastic for high-quality recycling [1, 2].

Another option for plastic waste disposal is incineration. Although incineration facilities are equipped with air pollution control devices, such as electrostatic precipitators, fabric filters for particulate control, and dry or wet scrubbers for acid gas removal, there is still substantial public concern over environmental issues regarding incineration. Such concerns not only add to the high cost of pollution control but also result in significant uncertainty with regard to the construction and future operation of these facilities.

Recently, there has been an increased interest in the co-pyrolysis of waste plastics with oil shale, coal and biomass. Oil shale is one of the most promising sources of energy in the world with large deposits situated in almost all the continents. Morocco is very rich in Upper Cretaceous oil shale deposits, the main sites are located at Timahdit (Middle Atlas Mountains) and Tarfaya (South Morocco) [3, 4]. The oil shale deposits in Morocco represent about

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15% of known oil shale resources in the world [5]. Oil shale deposits can be considered as interesting potential sources of carbon or of organic molecules which could be exploited diversely in the future [6, 7].

Thermogravimetric analysis (TG) is one of the commonly used techniques to study thermal events during the pyrolysis process of fuel [8–15]. The thermal decomposition of oil shale has been studied [13–20]. Two or three peaks that appear in thermogravimetric curves are due to organic and mineral matter. Numerous studies on the thermal decomposition of polyolefin and, in particular, poly (ethylene terephthalate) have been carried out, especially in inert atmosphere [21–24]. Under pyrolysis conditions, the material decomposition starts at approximately 580 K and progresses very rapidly up to 660–760 K with producing solid residue that could be used as combustible for supplying energy to the global process. Consequently, knowledge of the thermal behaviour of mixtures based on solid materials and polymers is of great importance from the processing point of view. In this sense, many reports in literature were devoted to the analysis of the effect of co-pyrolysis of oil shale or coal and synthetic polymer mixtures [25–30]. Aboulkas et al. [25, 26] performed thermal degradation processes for a series of mixtures of oil shale/plastic using TG at four heating rates of 2, 10, 20 and 50 K min^{-1} from ambient temperature to 1,273 K. High density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) were selected as plastic samples. The overlapping degradation temperature of oil shale and plastic in TG/DTG curves of the mixture may provide an opportunity for free radicals from oil shale pyrolysis to participate in reactions of plastic decomposition. Gersten et al. [27] investigated the thermal decomposition behaviour of polypropylene, oil shale and a 1:3 mixture of the two in a TG/DTG reaction system in an argon atmosphere. Experiments were conducted at three heating rates in the temperature range of 300–1,173 K. The results indicated that the characteristics of the process depend on the heating rate, and the polypropylene acts as a catalyst in the degradation of oil shale in the mixture. Degirmenci and Durusoy [28] used the thermogravimetry analysis to obtain kinetics of the pyrolysis of oil shale, polystyrene and theirs mixtures. Experiments were carried out at non-isothermal decomposition conditions under argon atmosphere from 298 to 1,173 K at heating rate values of 10 and 60 K min^{-1}. An increase was observed in the total conversion values of the blends with the increase in the blending ratio of polystyrene to oil shale. When a blend in any proportion of polystyrene to oil shale was degraded, an increase in maximum decomposition rate and a decrease in the temperature of maximum decomposition rate with the increase in polystyrene content of the sample were observed. The main conclusion is that the polystyrene accelerates the decomposition of the organic matter in the oil shale. Thermogravimetric analysis and kinetics of coal/plastic blends during co-pyrolysis in nitrogen atmosphere were investigated by Cai et al. [29].The results indicated that plastic was decomposed in the temperature range 711–794 K, while the thermal degradation temperature of coal was 444–983 K. The overlapping degradation temperature interval between coal and plastic was favourable for hydrogen transfer from plastic to coal. The difference of weight loss between experimental and theoretical ones, calculated as an algebraic sum of those from each separated component, was 2.0–2.7% at 823–923 K. These experimental results indicated a synergistic effect during plastic and coal co-pyrolysis at the high temperature region. The overlapping degradation temperature of coal and plastic in TG/DTG curves of the mixture may provide an opportunity for free radicals from coal pyrolysis to participate in reactions of plastic decomposition. Vivero et al. [30] studied the thermal decomposition of blends of coal and plastic such as HDPE and polypropylene using the thermogravimetric method. It was shown that plastic wastes have a strong influence on the thermoplastic properties of coal as well as the structure and thermal behaviour of the semicokes.

In the present study, thermal behaviours of oil shale/PET mixture were investigated under inert atmosphere using a thermogravimetric analyzer to obtain an overall understanding of the interaction of oil shale and PET. The thermal events taking place during pyrolysis of oil shale/PET were identified and the kinetic data were obtained to fit thermogavimetric data by using the Flynn–Wall–Ozawa method.

Experimental

Materials

The oil shale used in this work was from the Tarfaya deposit located in the south of Morocco. This deposit consists of several layers that are in turn subdivided in sub-layers, each having a different amount of organic matter. The samples were obtained from the R3 sub-layer, characterized by its high content of organic matter [5]. The results of the analysis of these samples are given in Table 1.

A sample from Tarfaya oil shale was obtained from the Moroccan “Office National de Recherche et d’Exploitation Pétrolière (ONAREP)”. The organic matter belongs to Type II kerogen and covers a relatively wide range of maturity with $R_0 = 0.32 \pm 0.04\%$ (vitrinite reflectance). The kerogen was prepared by the following procedure: the dried oil shales were treated with chloroform to extract the

Table 1 Some average physicochemical characteristics of the Tarfaya oil shales

Proximate analysis/wt%	
Volatile matter	40.09
Ash	52 .83
Moisture (as received)	5.15
Elemental analysis/wt%	
C	17.60
H	1.78
N	0.70
S	0.37
Composition/wt%	
Carbonate mineral (Calcite)	70.0
Silicate mineral (Quartz, Kaolinite)	10.0
Bitumen	0.8
Pyrite	1.0
Kerogen	17.0

bitumen. The solution was then filtered and the solvent eliminated in a rotary apparatus at reduced pressure. Pre-extracted samples were treated with diluted HCl, HF and HCl successively to eliminate carbonates and silicates. The isolated solid was washed with distilled hot water until the silver nitrate test for chlorides was negative. The pyrite was removed by the method of density difference. The H/C and O/C atomic ratios (1.62 and 0.14, respectively) correspond to a low maturity type II kerogen [31, 32].

The samples of poly (ethylene terephthalate) were provided by Plador (Marrakech, Morocco). The results of characterization of these materials are given in Table 2. Raw oil shale samples were ground and sieved to give particle size of 0.1 mm. Oil shale/poly (ethylene terephthalate) mixture (1:1 in mass) were blended by tumbling for 30 min in order to achieve homogeneity. In all experiments, samples of around 20 mg with particle sizes ranging approximately from 0.1 to 0.2 mm were placed in the platinum crucible of a thermobalance.

Experimental techniques

Raw oil shale, poly (ethylene terephthalate) and their mixture samples were subjected to TG in an inert atmosphere of nitrogen. Rheometrix Scientific STA 1500 TG analyzer was used to measure and record the sample mass change with temperature over the course of the pyrolysis reaction. Thermogravimetric curves were obtained at four different heating rates (2, 10, 20, 50 and 100 K min^{-1}) between 300 and 1,273 K. Nitrogen gas was used as an inert purge gas to displace air in the pyrolysis zone, thus avoiding unwanted oxidation of the sample. A flow rate of around 60 mL min^{-1} was fed to the system from a point below the sample and a purge time of 60 min (to be sure the air was eliminated from the system and the atmosphere is inert). The balance can hold a maximum of 45 mg; therefore, all sample amounts used in this study averaged approximately 20 mg. The reproducibility of the experiments is acceptable and the experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out two or three times.

Table 2 Some characteristics of PET

Proximate analysis/wt%			Elemental analysis (wt% dry ash free)		
Volatiles	FC	Ash	C	H	O
87.4	12.6	0.04	62.6	4.3	33.1

Kinetic modeling

Non-isothermal kinetic study of weight loss under pyrolysis of carbonaceous materials is an extremely complex task because of the presence of numerous complex components and their parallel and consecutive reactions.

The extent of conversion or the fraction of pyrolysed material, x, is defined by the expression

$$x = \frac{m_0 - m}{m_0 - m_f} \tag{1}$$

where m is the mass of the sample at a given time t; m_0 and m_f refer to values at the beginning and the end of the mass event of interest.

The rate of the kinetic process can be described by Eq. 2:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K(T)f(x) \tag{2}$$

where $K(T)$ is a temperature-dependent reaction rate constant and $f(\alpha)$ is a dependent kinetic model function. There is an Arrhenius type dependency between $K(T)$ and temperature according to Eq. 3

$$K(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

where A is the pre-exponential factor (usually assumed to be independent of temperature), E the apparent activation energy, T the absolute temperature and R is the gas constant.

For non-isothermal conditions, when the temperature varies with time with a constant heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. 2 is modified as follows:

$$\beta\frac{\mathrm{d}x}{\mathrm{d}T} = A\exp\left(-\frac{E}{RT}\right)f(x) \tag{4}$$

The use of Eq. 4 supposes that a kinetic triplet (E, A, $f(x)$) describes the time evolution of a physical or chemical change.

Upon integration Eq. 4 gives:

$$g(x)=\int_{0}^{x}\frac{dx}{f(x)}=\frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T\equiv\frac{AE}{\beta R}p\left(\frac{E}{RT}\right) \tag{5}$$

where T_0 is the initial temperature, $g(x)$ the integral form of the reaction model and $p(E/RT)$ is the temperature integral, which does not have analytical solution. If T_0 is low, it may be reasonably assumed that $T_0 \rightarrow 0$, so that the lower limit of the integral on the right-hand side of Eq. 5, T_0, can be approximated to be zero.

The isoconversional integral method suggested independently by Flynn and Wall [33] and Ozawa [34] uses Doyle's approximation [35]. This method is based on the equation:

$$\ln\beta=\ln\frac{AE}{Rg(x)}-5.331-1.052\frac{E}{RT} \tag{6}$$

Thus, for $x = \text{const.}$, the plot $\ln\beta$ versus $(1/T)$, obtained from thermograms recorded at several heating rates, should be a straight line whose slope can be used to evaluate the apparent activation energy.

Results and discussion

Thermogravimetric analysis of oil shale

Thermal degradation of oil shale

Thermogravimetric analysis and DTG curves at different heating rates for thermal degradation of Oil shale are shown in Fig. 1. The oil shale degradation occurs in three steps. The first step is from 300 to 430 K corresponds to drying of the oil shale. The second step, at about 566–915 K, has mass of 7–9% (depending on the heating rate) due to the degradation of the organic matter content of the oil shale. The last mass, which begins at 800–930 K (depending on the heating rate), presents a mass of 36% due to the degradation of the mineral matter in the oil shale (calcite, quartz, kaolinite and pyrite). The characteristic temperatures are listed in Table 3.

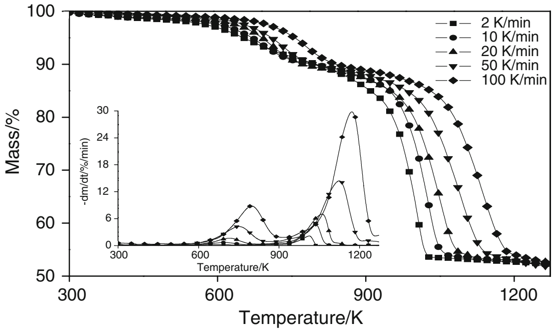

Fig. 1 TG curves of oil shale at different heating rates. *Inset*: corresponding DTG curves

As the heating rate is increased, Table 3 shows that there was a lateral shift to higher temperatures. The lateral shift is also illustrated in Fig. 1. The rate of weight loss also reflects the lateral shift with an increase in the rate as the heating rate was increased from 2 to 100 K/min. The residual weight seemed to reach some constant values after 1,200 K. The values of residual mass were calculated to be about 52.9%. The lateral shift to higher temperatures for the maximum region of mass has also been observed by other workers using TG to investigate the pyrolysis of oil shales. For example, Gersten et al. [27] showed a shift in the temperatures of maximum mass loss rate of 311 K towards higher temperatures as the heating rate was increased from 5 to 15 K/min for Israel oil shale. Williams and Nasir [18] and Jaber and Probert [19] also showed a lateral shift in the maximum rate of weight loss for the TG of oil-shale samples. Williams and Nasir [20] suggested that the shift to higher temperatures of degradation represented differences in the rate of heat-transfer to the sample as the heating rate was varied.

Kinetic study of oil shale

Applying Eq. 6 on the TG data, plots of $\ln\beta$ vs. $1/T$ for oil shale are shown in Fig. 2. The values of activation energy were determined from the best-fit lines as explained above (0.99 correlation coefficient). The activation energies determined from the slope of $\ln\beta$ vs. $1/T$ plots from 6 to 18% conversion for degradation of organic matter of oil shale are listed in Table 4. It was found that the activation energies remain relatively constant between 6 and 16% conversion, which reveal that there is one dominant kinetic process. The mean value of the activation energies was 87 kJ/mol. Comparison with literature data shows that the kinetic parameters are unique to each individual case of oil shale. Torrente and Galan [36] obtained activation energy of 167 kJ/mol for non-isothermal TG of Puertollano (Spain) oil shale. Sonibare et al. [37] performed non-isothermal TG on Lokpanta oil shales (Nigeria) and found the activation energies vary from 73.2 to 75 kJ/mol. Dogan and Uysal [38], however, reported results for Turkish oil-shale, of approximately 25 kJ/mol for the lower temperature decomposition and up to 43 kJ/mol for the main stage of decomposition.

Thermogravimetric analysis of PET

Thermal degradation of PET

Thermogravimetric analysis and DTG curves of thermal decomposition of PET at four heating rates are represented

Table 3 Maximum degradation temperature (T_{max}) of the oil shale, PET and their mixture

	2 K min^{-1}		10 K min^{-1}		20 K min^{-1}		50 K min^{-1}		100 K min^{-1}	
	Pyrolysis range/K	Peak temperatures/K	Pyrolysis range/K	Peak temperatures/K	Pyrolysis range/K	Peak temperatures/K	Pyrolysis range/K	Peak temperatures/K	Pyrolysis range/K	Peak temperatures/K
Oil shale	537–740	664	580–780	687	602–800	716	626–848	733	660–900	770
PET	596–710	690	630–760	716	650–762	724	692–802	746	718–835	778
Oil shale/PET	630–728	699	651–755	722	660–768	730	675–809	750	715–842	782

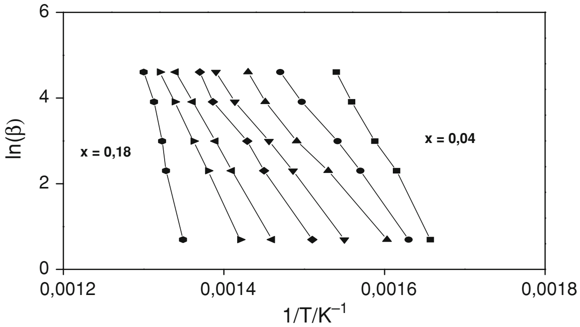

Fig. 2 Ozawa–Flynn–Wall plots for oil shale thermal degradation

Table 4 Kinetic parameters for pyrolysis of the oil shale, PET and their mixture

Oil shale		PET		Oil shale/PET	
x	E_a/kJ mol^{-1}	x	E_a/kJ mol^{-1}	x	E_a/kJ mol^{-1}
0.04	104	0.1	163	0.15	154
0.06	72	0.2	164	0.20	160
0.08	69	0.3	168	0.25	165
0.10	77	0.4	174	0.30	166
0.12	87	0.5	178	0.35	168
0.14	92	0.6	181	0.40	172
0.16	89	0.7	181	0.45	175
0.18	109	0.8	180	0.50	176
		0.9	177	0.55	173
				0.60	171
Mean	87 ± 20	Mean	174 ± 8	Mean	168 ± 11

in Fig. 3. It can be seen that the shape of the mass curves does not change with variations in heating rate, but mass loss temperatures show an increase at higher heating rates. The mass loss shows that degradation occurs in one step as can be concluded by the presence of only one peak in DTG with 11.7% for the mass of the final solid residue.

The TG curves show that the PET thermal degradation starts at 560 K and is almost complete at approximately 820 K. At higher heating rate the maximum degradation rate shifted from 690 K at 2 K min^{-1} to 778 K at 100 K min^{-1}. The maximum degradation rate also increased from 5.4% min^{-1} at 2 K min^{-1} to 210% min^{-1} at 100 K min^{-1}. The TG/DTG curves were displaced to higher temperature due to the heat transfer large with increasing heating rate. The characteristic temperatures are summarized in Table 3.

Kinetic study of PET

A similar kinetic study was carried out for PET (Fig. 4). The value of activation energy of degradation of these samples from 10 to 90% conversion is cited in Table 4. These values also remain relatively constant after 10% conversion, which reveal that there is one dominant kinetic process of PET. It was found that the mean value of activation energy was 174 kJ/mol. The calculated apparent activation energies reported in the literature for PET varied over a wide range. Senneca et al. [39] reported activation energy of PET degradation of 217 kJ/mol, Saha and Ghoshal [24] found for PET degradation activation energy between 162 and 210 kJ/mol by application of ASTM E698 technique.

Thermogravimetric analysis of oil shale/PET mixture

Thermal degradation of oil shale/PET mixture

TG/DTG curves of thermal degradation of oil shale/PET mixture are represented in Fig. 5. In general, we can note that the domains of degradation of both components are well overlapped. It can be seen that no separation of the DTG peaks of organic matter of oil shale and PET. It should be added that the characteristic temperatures for the mixtures change in comparison with those for each component (Table 3). Both co-components increase their thermal stability as can be concluded from the shift to T_{max} toward higher values (Table 3). It should be added that the residue yield of the mixtures is lower than that of oil shale alone.

TG/DTG curves show that the degradation proceeds through three steps. The first step, obtained in the

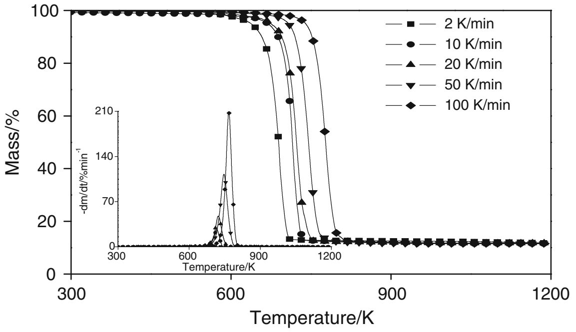

Fig. 3 TG curves of PET at different heating rates. *Inset*: corresponding DTG curves

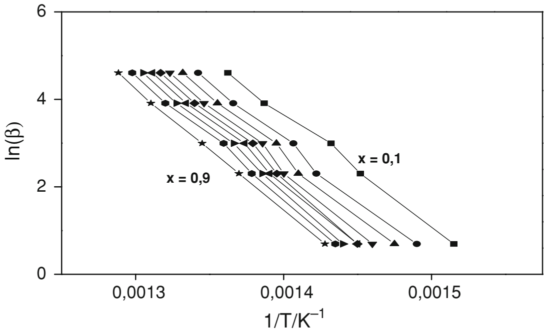

Fig. 4 Ozawa–Flynn–Wall plots for PET thermal degradation

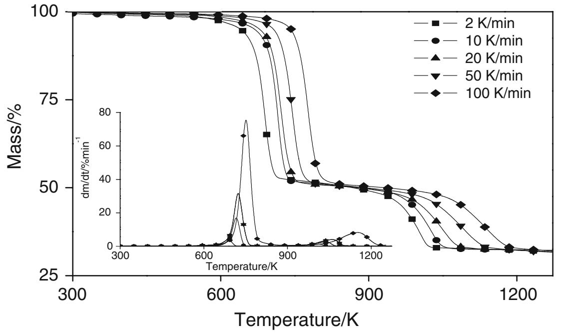

Fig. 5 TG curves of Oil shale/PET mixture at different heating rates. *Inset*: corresponding DTG curves

temperature range (300–430 K), is attributed to the departure of the adsorbed water from the sample. The second step occurs between 615 and 820 K and exhibit a total mass loss of 51.4–52% (depending on the heating rate), which corresponds to the overlapping of the organic matter of the oil shale and PET degradations. The third step between 850 and 1,220 K with 17.1–17.9 wt% (depending on the heating rate) mass loss was attributed to the degradation of mineral matter of oil shale content in the mixture. Some differences in such temperatures are observed when compared to those of pure materials. PET significantly increases its maximum temperature (4–9 °C), while the variations for organic matter of oil shale are more pronounced (12–37 °C), but both materials increase their thermal stability.

As in the case of oil shale and PET, the characteristic temperatures of the process depend on the heating rate (Table 3). A higher heating rate shifted the TG/DTG curves rightward to the higher temperature range. The values of residue yields were calculated to be about 31.2–31.9%.

To investigate whether interactions existed between the oil shale and PET, a theoretical TG/DTG curves was calculated. This curve represented the sum of individual components behaviour in the mixture:

$$m_{\mathrm{sum}} = x_1 m_{\mathrm{oil\,shale}} + x_2 m_{\mathrm{PET}}$$

where $m_{\mathrm{oil\ shale}}$, m_{PET} are mass loss of each material in the same operational condition and x_1, x_2 are the mass fraction of oil shale and PET in the mixture. The calculated and experimental curves for oil shale/PET mixture at 10 K/min are illustrated in Fig. 6.

In Fig. 6, co-components show a different behaviour from that of the pure materials. A significant interaction is observed in the second stage of degradation at 615–820 K, while the third stage of degradation is not affected. However, the interactions in the second stage have no significant impact on the degradation of mineral matter at higher temperatures. Although thermal degradation of organic matter of the oil shale overlaps with PET, the decomposition curves of both co-components in the mixture are overlapped, as can be seen in Fig. 6. Comparing the TG/DTG curves, some discrepancies between experimental and calculated curves are observed: both co-components increase the thermal stability, as can be concluded from the shift in $T_{\max}$ toward higher values. These experimental results indicate a significant synergistic effect during pyrolysis of oil shale mixed with PET.

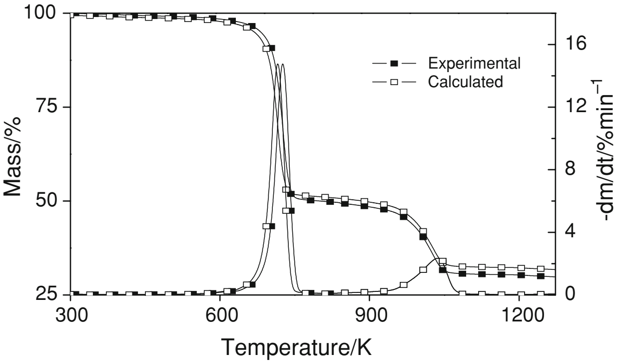

Fig. 6 Comparison between experimental and calculated TG/DTG values for the oil shale/PET mixture at 10 K/min

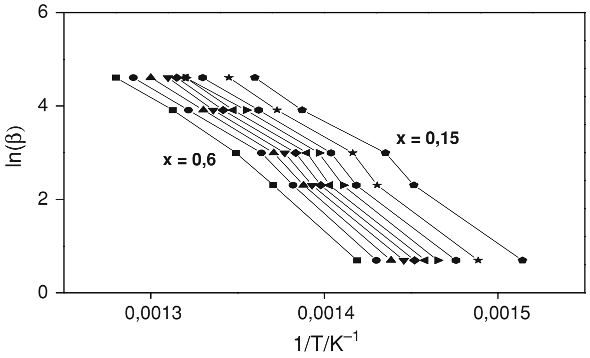

Fig. 7 Ozawa–Flynn–Wall plots for oil shale/PET mixture thermal degradation

Kinetic study of oil shale/PET mixture

Flynn–Wall–Ozawa method was also applied to the study of mixture of oil shale with PET (Fig. 7). The relationship between the activation energy and the conversion are shown in Table 4. It is interesting to note that the activation energy remain relatively constant between 15 and 60% conversion. The average value of activation energy of oil shale/PET process is 168 kJ/mol.

From Table 4, the obtained activation energy of overlap organic matter of oil shale and PET decomposition in the mixture (168 kJ/mol) is higher than that of the oil shale (87 kJ/mol) and close to that of PET (174 kJ/mol). When comparing these results with those of the thermal decomposition of the pure materials, it is noteworthy that the activation energy of PET in the mixture were lower than the activation energies of PET pure and the activation energy of organic matter of oil shale in the mixture are higher than the oil shale pure. It is possible to think that PET acted as catalysts in the pyrolysis of oil shale in the mixture while the mineral matter of oil shale acted as inhibitor in the pyrolysis of PET in the mixture [25, 27]. The mechanism of the synergistic effect between oil shale and PET during co-pyrolysis is not very clear. According to the common views, the thermal degradation of polyolefins proceeds as a radical chain process, including the steps of radical initiation, chain propagation and radical termination. The mechanisms of this process and composition of formed products were studied in a number of articles [40–43]. It is reasonable to explain the influence of oil shale on the thermal degradation of PET in the framework of well-known mechanism of PET decomposition. In the first stage of the co-pyrolysis process, oil shale components can start the radical formation initiating the scission of the synthetic polymer chain. Then the reaction of hydrogen transferring from a polyolefinic chain to oil shale-derived radicals will probably stabilize the primary products from oil shale thermal degradation. This would result in higher weight loss and lower yield of char, as observed in our experiments.

Conclusions

The following conclusions can be made from this study:

- The TG/DTG curves show clearly two major steps. The first step, obtained in the temperature range (615–820 K), is attributed to the overlapping of the organic matter of the oil shale and PET degradations. The second step occurs between 850 and 1,220 K, which corresponds to the degradation of mineral matter of oil shale content in the mixture (carbonate and silicate).
- Comparing the TG/DTG curves, some discrepancies between experimental and calculated curves are observed: both co-components increase the thermal stability, as can be concluded from the shift in $T_{\max}$ toward higher values. These experimental results indicate a significant synergistic effect during pyrolysis of oil shale mixed with PET.
- The obtained activation energy of overlap organic matter of oil shale and PET decomposition in the mixture (168 kJ/mol) is higher than that of the oil shale (87 kJ/mol) and close to that of PET (174 kJ/mol). The overlapping degradation temperature of oil shale and PET in TG/DTG curves of the mixture may provide an opportunity for free radicals from oil shale pyrolysis to participate in reactions of PET decomposition.

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