Pyrolysis Behaviour and Kinetics of Moroccan Oil Shale with Polystyrene

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Abstract--- **Pyrolysis of oil shale/polystyrene mixture was performed in a thermogravimetric analyzer (TGA) from room temperature to 1273K, at heating rates of 2, 10, 20, 50 and 100 K/min. The global mass loss during oil shale/polystyrene pyrolysis was modelled by a combination of mass-loss events for oil shale and for polystyrene volatiles. TGA results indicate that mixture pyrolysis can be identified as three phases. The first is attributed to the drying of absorbed water; the second was dominated by the overlapping of organic matter and plastic pyrolysis, while the third was linked to the mineral matter pyrolysis, which occurred at much higher temperatures. Discrepancies between the experimental and calculated TG/DTG profiles were considered as a measurement of the extent of interactions occurring on co-pyrolysis (10% of the difference between experimental and calculated curves in the temperature range 600-900 K). The maximum degradation temperature of each component in the mixture was higher than those the individual components. The calculated residue was found to be higher than experimental. These experimental results indicate a significant synergistic effect during pyrolysis of mixture of oil shale and polystyrene. The kinetic studies were performed using Flynn-Wall-Ozawa (FWO) method. The overall activation energies were 87 kJ/mol for organic matter of oil shale, 169 kJ/mol for polystyrene and 161 kJ/mol for the mixture. Thus, it has been found that there exists an overall synergy, when two materials were pyrolysed together.**

Keywords-- **thermogravimetric; pyrolysis; kinetics; oil shale; polystyrene.**

I. Introduction

Our modern society is unimaginable without plastics. Nowadays both the consumption and production of polymers are increasing, but the increasing amount of polymer wastes from them generates further environmental problems. As only a small amount of these wastes is recycled and most of plastics are not biodegradable, these wastes need to be treated adequately to prevent environmental problems and make possible a sustainable development of modern society. Incineration with energy recovery is widely applied in some European countries. However, the generation of highly toxic chlorinated organic compounds makes this technology highly controversial and expensive to operate [1].

Mechanical recycling involves the melting and re-moulding of used thermoplastics. However, the growth potential for this technology is already limited by the low quality of the plastic produced [1-3].

Utilization of waste plastics mixed with oil shale is a more attractive way for recycling the waste plastics and generation the necessary energy to supply the increasing energy demand. The pyrolysis of the mixture of waste plastics with oil shale could play an important role in converting these solid fuels into economically valuable hydrocarbons, which can be used either as fuels or as feedstock in the petrochemical industry [4-8].

In Morocco, 90% of the energy consumed is dependent on imported oil. Thus, an intensive programme was commenced for the mobilization of indigenous energy sources, especially the local oil shales. Morocco is very rich in Upper Cretaceous oil shale deposits, the main sites are located at Timahdit (Middle Atlas Mountains) and Tarfaya (South Morocco) [9,10]. The oil shale deposits in Morocco represent about 15% of known oil shale resources in the world [11]. Oil shale deposits can be considered as interesting potential sources of carbon or of organic molecules which could be exploited diversely in the future [12,13].

Thermogravimetric analysis is an analytical method to determine the decomposition rate of reactions resulting from thermal effects and the kinetic parameters of these reactions [14-18]. The kinetic analysis in the thermal decomposition is the most important tool in the study of the complex pyrolysis mechanism [17,18]. In several publications it has been reported that weight loss occurs in relation with the temperature, and kinetic analysis is used in thermal analysis processes, such as pyrolysis of oil shale, plastic or their mixtures [16-31]. The thermal decomposition of oil shale

has been studied [19-24]. 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, polystyrene have been carried out, especially in inert atmosphere [25-28].

Knowledge of the thermal behaviour of mixtures based on fossil fuel 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 fossil fuel and polymer mixtures [16,18,29-33]. Aboulkas et al. [16] performed thermal degradation processes for a series of mixtures of oil shale/plastic using thermogravimetric analysis (TGA) at four heating rates of 2, 10, 20 and 50 K min−1 from ambient temperature to 1273 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. [30] 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 300-1173 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. L. Degirmenci and T. Durusoy [31] used the thermogravimetry analysis to obtain kinetics of the pyrolysis of oil shale, polystyrene and their mixtures. Experiments were carried out at non-isothermal decomposition conditions under argon atmosphere from 298 to 1173 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. [32].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. [33] studied the thermal decomposition of blends of coal and plastic such as high density polyethylene 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.

The goal of this paper is to examine oil shale/polystyrene mixture by thermal analysis. The pyrolysis behaviour of pure components and the mixture is measured by a thermogravimetric analyzer (TGA) and the obtained mass loss curve (TG) and its derivative (DTG) is used as a fingerprint of each component. The calculation of apparent activation energies was based on the application of the isoconversional Flynn-Wall-Ozawa method.

II. Experimental

2.1. 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 [11]. 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 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 [34,35].

The samples of polystyrene were provided by Plador, Marrakech, Morocco (particle size of 0.1-0.2 mm). 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/ polystyrene 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 from 0.1 and 0.2 mm were placed in the platinum crucible of a thermobalance.

2.2. Experimental Techniques

Raw oil shale, polystyrene and their mixture samples were subjected to thermogravimetric analysis (TGA) in an inert atmosphere of nitrogen. Rheometrix Scientific STA 1500 TGA 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 K and 1273 K. Nitrogen gas was used as an inert purge gas to

Proximate analysis (wt %)	
Volatile matter	40.09
Ash	52 .83
Moisture (as received)	5.15
Fixed carbon	01.10
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

Table 2
Some characteristics of polystyrene

Proximate analysis(wt %)			Elemental analysis(wt.% dry ash free)	
Volatiles	F.C	Ash	C	H
99.6	0.4	0.00	91.5	8.5

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 at 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 experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out two or three times.

III. 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

Table 1
Some average physicochemical characteristics of the Tarfaya oil shales

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

(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:

$$\frac{dx}{dt} = K(T) f(x)$$

(2)

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

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

(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 $\beta = dT/dt$, Eq. (2) is modified as follows:

$$\beta \frac{dx}{dT} = A \exp\left(-\frac{E}{RT}\right) f(x)$$

(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:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \equiv \frac{AE}{\beta R} p\left(\frac{E}{RT}\right)$$

(5)

where T0 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 an analytical solution. If T0 is low, it may be reasonably assumed that T0 → 0, so that the lower limit of the integral on the right-hand side of Eq (5), T0, can be approximated to be zero.
The isoconversional integral method suggested independently by Flynn and Wall [36] and Ozawa [37] uses Doyle's approximation [38] for the temperature integral:

$$\ln p\left(\frac{E}{RT}\right) = -5.331 - 1.052 \frac{E}{RT}$$

(6)

Relations (5) and (6) lead to

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

(7)

Thus, for x = const., the plot ln β vs. (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.

IV. **Results and Discussion**

4.1. Thermogravimetric analysis of oil shale

4.1.1. Thermal degradation of oil shale

TG 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 loss of 7-9 % (depending on the heating rate) due to the degradation of the organic matter content of the oil shale. The last step, which begins at 800-930 K (depending on the heating rate), presents a mass loss of 36 % due to the transformation of the mineral matter in the oil shale (calcite, quartz, kaolinite and pyrite). The characteristic temperatures are listed in Table 3.
As the heating rate is increased, Table 3 shows that there was a lateral shift to higher temperatures at wich the peak rate of mass loss (T_{max}). The lateral shift is also illustrated in Fig. 1. The rate of weight

Table 3

Characteristic temperatures of the pyrolysis of oil shale, polystyrene 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
Polystyrene	587-701	682	621-745	708	642-759	718	682-806	736	710-826	769
Oil shale/ polystyrene	617-719	688	646-748	716	658-766	729	675-792	748	704-828	775

* Temperature at wich the peak rate of mass loss (-dm/dt) occurs.
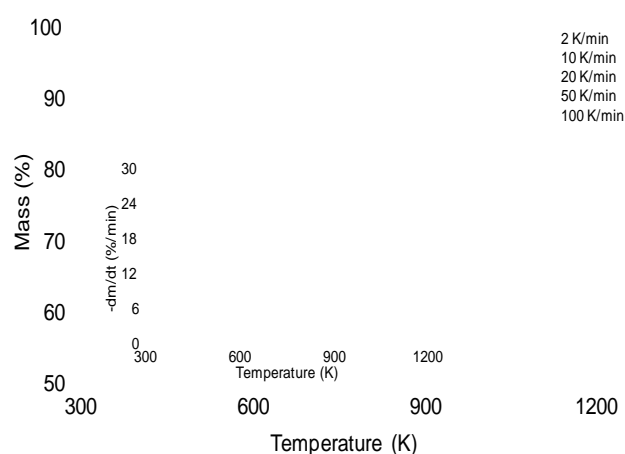

Fig. 1 TG curves of Oil Shale at different heating rates. Inset: corresponding DTG curves.

loss also reflects the lateral shift with an increase in the rate as the heating rate was increased from 2 K/min to 100 K/min. The residual weight seemed to reach some constant values after 1200 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 loss rate has also been observed by other workers using TGA to investigate the pyrolysis of oil shales. For example, Gersten et al. [30] showed a shift in the temperatures of maximum mass loss rate of 38 ℃ towards higher temperatures as the heating rate was increased from 5 to 15 K/min for Israel oil shale. Williams and Nasir [39] and Jaber and Probert [23] also showed a lateral shift in the maximum rate of weight loss for the TGA of oil-shale samples. Williams and Nasir [24] 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.

4.1.2. Kinetic study of oil shale

Applying Eq. (7) on the TGA data, a plot of $\ln \beta \ vs \ 1/T$ for oil shale was obtained (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 4 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 [40] obtained activation energy of 167 kJ/mol for non-isothermal TGA of Puertollano (Spain) oil shale. Sonibare et al [41] performed non-isothermal TGA on Lokpanta oil shales (Nigeria) and found the activation energies vary from 73.2 to 75 kJ/mol. Dogan and Uysal [42], 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. The difference between the results determined by our study and literary data is
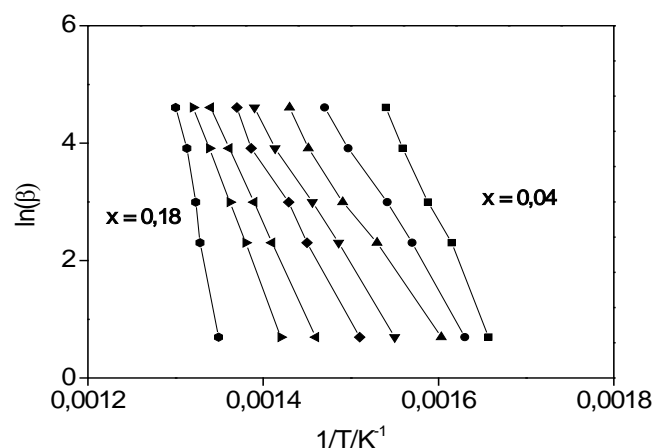
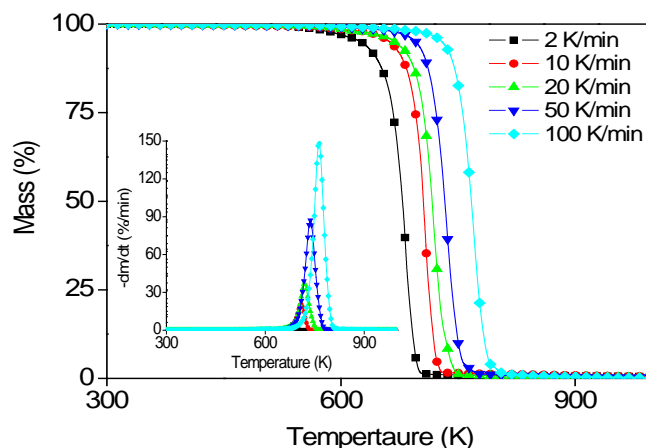Fig. 2 Ozawa-Flynn-Wall plots for Oil Shale thermal degradation

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

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

Oil shale		Polystyrene		Oil shale/ Polystyrene	
x	E (kJ/mol)	x	E (kJ/mol)	x	E (kJ/mol)
0.04	104	0.1	158	0.15	147
0.06	72	0.2	159	0.20	153
0.08	69	0.3	163	0.25	155
0.10	77	0.4	169	0.30	158
0.12	87	0.5	173	0.35	159
0.14	92	0.6	176	0.40	161
0.16	89	0.7	176	0.45	165
0.18	109	0.8	175	0.50	168
		0.9	172	0.55	169
				0.60	167
				0.65	166
				0.70	164
Mean	**87**	*Mean*	**169**	*Mean*	**161**

probably due to the influence of process parameters, such as heating rate and particle size. In addition, oil shale, especially its kerogen, is characterized by a complex heterogeneous nature; hence, it would be difficult to obtain the same experimental results even for nominally the same sample. Therefore, the same experimental technique, including sample preparation procedure, analysis method adopted, and the kinetic model for the analysis, should be employed in order to enable a reasonable comparison to be achieved.

4.2. Thermogravimetric analysis of polystyrene

4.2.1. Thermal degradation of polystyrene

TG and DTG curves of thermal decomposition of polystyrene at four heating rates are represented in Fig. 3. It can be seen that the shape of the mass curves does not change with variations in heating rate, but the peak mass loss temperatures show an increase at higher heating rates. The mass loss shows that degradation occurs almost totally in one step as can be concluded by the presence of only one peak in DTG.

The TG curves show that the polystyrene thermal degradation starts at 550 K and is almost complete at approximately 820 K. At higher heating rates the maximum degradation rate shifted from 682 K at 2 K min^{-1} to 769 K at 100 K min^{-1}. The maximum degradation rate also increased from 4.4 % min^{-1} at 2 K min^{-1} to 150 % min^{-1} at 100 K min^{-1}. The TG/DTG curves were displaced to higher temperature due to the rate of heat transfer increasing with increasing heating rate. The characteristic temperatures are summarized in Table 3.

4.2.2. Kinetic study of polystyrene

A similar kinetic study was carried out for polystyrene (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 polystyrene. It was found that the mean value of activation energy was 169 kJ/mol. The calculated apparent activation energies reported in
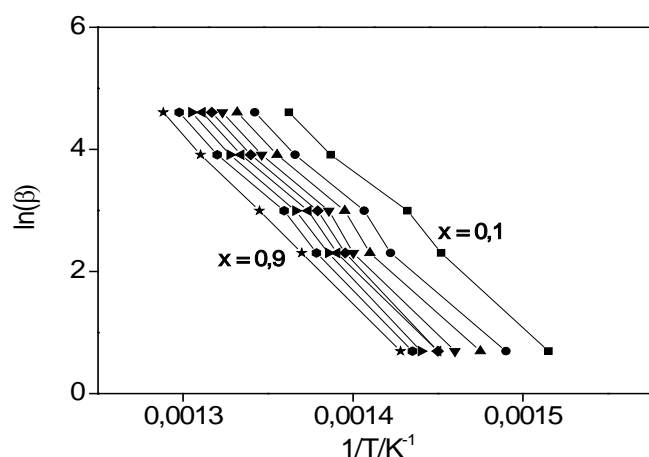
Fig. 4 Ozawa-Flynn-Wall plots for polystyrene thermal degradation

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

the literature for polystyrene varyed over a wide range. Similar results were obtained by Wu et al. [28] on the pyrolysis of plastic mixtures of municipal solid waste (MSW), the apparent activation energy of polystyrene degradation was found of 172 kJ/mol. Whereas Encinar and Gonzalez [26] found for polystyrene degradation an activation energy of 137 kJ/mol. Aguado et al. [43] reported the activation energy of polystyrene degradation of 123 kJ/mol, and Sorum et al. [27] found for polystyrene degradation an activation energy of 312 kJ/mol.

4.3. Thermogravimetric analysis of oil shale/ polystyrene mixture

4.3.1. Thermal degradation of oil shale/ polystyrene mixture

TG/DTG curves of thermal degradation of oil shale/polystyrene 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 polystyrene exists. 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 of peak temperature toward higher values (Table 3). It should be added that the residue yield of the mixtures is lower than that of oil shale alone.
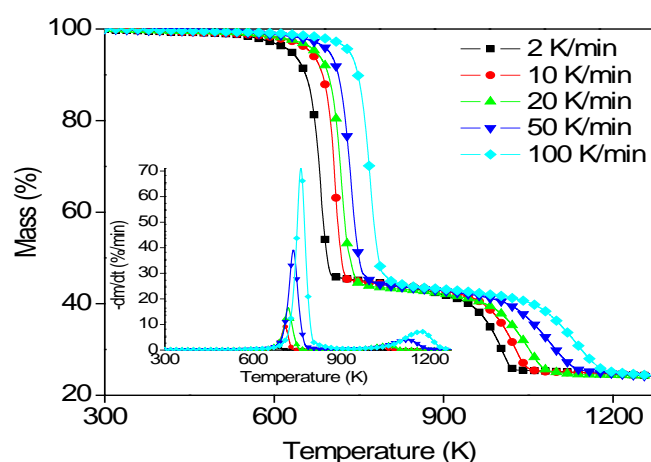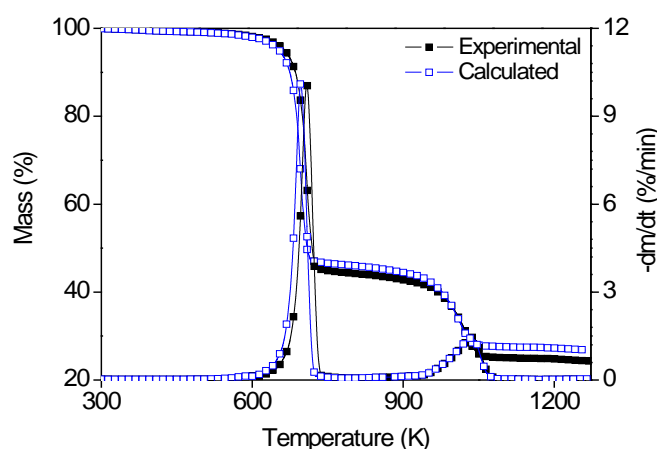

Fig. 6 Comparison between experimental and calculated TG/DTG values for the oil shale/polystyrene mixture at 10 K/min

TG/DTG curves show that the degradation proceeds through three steps. The first step, obtained in the temperature range (300 - 430 K), is attributed to the departure of the adsorbed water from the sample. The second step occurs between 617 and 828 K and exhibit a total mass loss of 57.4-58.2 % (depending on the heating rate), which corresponds to the overlapping of the organic matter of the oil shale and polystyrene degradations. The third step between 870 and 1250 K with 18.3-18.9 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. Polystyrene significantly increases its temperature at the maximum rate of mass loss (6-12 °C), while the variations for organic matter of oil shale are more pronounced (5-29 °C).

As in the case of oil shale and polystyrene, 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.

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

$$m_{sum} = x_1 m_{oilshale} + x_2 m_{polystyrene}$$

where $m_{oil\ shale}$ and $m_{polystyrene}$ are mass loss as of the materials in the same operational condition, and x_1 and x_2 are the mass fractions of oil shale and polystyrene in the mixture. The calculated and experimental curves for oil shale/ polystyrene mixture at 10 K/min are illustrated in Fig. 6. We can note that an interaction is observed between organic matter of oil shale and polystyrene at 570-840 K, while the degradation of mineral matter of oil shale is not affected. However, the temperature of the DTG maximum of oil shale and polystyrene shifted to higher temperatures in the mixture. The maximum temperature increased by 5-29 °C for oil shale and 6-12 °C for polystyrene. Comparing the TG/DTG curves, discrepancies between experimental and calculated curves are observed (10% of the difference between experimental and calculated curves in the temperature range 600-900 K). The presence of polystyrene resulted in the increase of weight loss of mixture organic matter. Again, the residue obtained was found to be lower than the calculated value. Hence, there may be synergistic interaction between oil shale and polystyrene, when they are co-pyrolyzed. This synergistic interaction is due probably to that the products formed during polystyrene degradation participate in reactions of the oil shale degradation. These results are in good agreement with those of Gersten et al. [30] and Degirmenci et al. [31], who concluded that plastics accelerate the decomposition of the organic matter of oil shale. Cai et al. [32] found that the reaction of hydrogen transferring from a polyolefinic chain to coal radicals will stabilize the primary products from coal thermal degradation. This would result in higher weight loss and lower yield of char.

4.3.2. Kinetic study of oil shale/polystyrene mixture

Flynn-Wall-Ozawa method was also applied to the study of the mixture of oil shale with
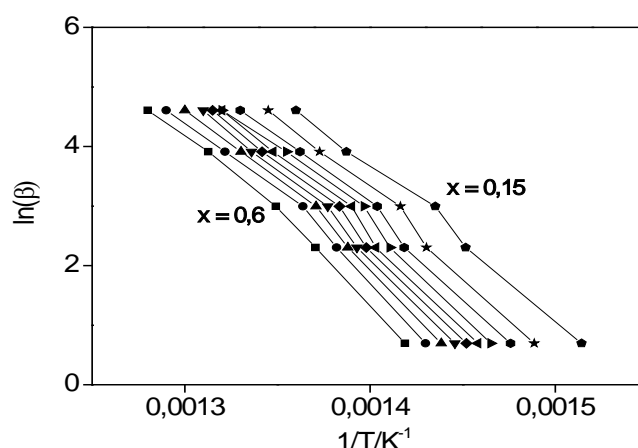

Fig. 7 Ozawa-Flynn-Wall plots for Oil shale/polystyrene mixture thermal degradation

polystyrene (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 remains relatively constant between 15 and 75 % conversion (between 147 and 169 kJ/mol). The average value of activation energy of oil shale/polystyrene process is 161 kJ/mol.

The obtained activation energy for the overlap of organic matter of oil shale and polystyrene decomposition in the mixture (161 kJ/mol) is higher than that of the oil shale (87 kJ/mol) and close to that of polystyrene (169 kJ/mol). When comparing these results with those of the thermal decomposition of the pure materials, it is noteworthy that the activation energy of polystyrene in the mixture was lower than the activation energy of polystyrene and the activation energy of the organic matter of oil shale in the mixture is higher than for the oil shale. It is possible to think that polystyrene acted as a catalysts in the pyrolysis of oil shale in the mixture while the mineral matter of oil shale acted as inhibitor in the pyrolysis of polystyrene in the mixture [16,30,31]. The mechanism of the synergistic effect between oil shale and polystyrene 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 [44-47]. It is reasonable to explain the influence of oil shale on the thermal degradation of polystyrene in the framework of the well-known mechanism of polystyrene decomposition [44]. 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.

V. Conclusions

A thermogravimetric study revealed that three stages of weight loss are involved during oil shale/polystyrene decomposition. The first step, obtained in the temperature range (300 -430 K), is attributed to the departure of the adsorbed water from the sample. The second step occurs between 570 and 840 K, which corresponds to the overlapping of the organic matter of the oil shale and plastic degradations. The third step between 870 and 1250 K was attributed to the degradation of mineral matter of oil shale content in the mixture (carbonate and silicate).

Comparing the TG/DTG curves, discrepancies between experimental and calculated curves are observed (10% of the difference between experimental and calculated curves in the temperature range 600-900 K). Both co-components increase its T_{max} toward higher values. The presence of polystyrene resulted in the increase of weight loss of mixture organic matter. Furthermore, the residue obtained (24 %) was found to be lower than the calculated value (27.7 %). Hence there may be synergistic interaction between oil shale and polystyrene, when they are co-pyrolyzed.

The obtained activation energy of overlap organic matter of oil shale and polystyrene decomposition in the mixture (161 kJ/mol) is higher than that of the oil shale (87 kJ/mol) and close to that of polystyrene (169 kJ/mol). The overlapping degradation temperature of oil shale and polystyrene in TG/DTG curves of the mixture may provide an opportunity for free radicals from oil shale pyrolysis to participate in reactions of polystyrene decomposition.

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