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# THERMAL DEGRADATION KINETICS OF GÖYNÜK OIL SHALE WITH POLYSTYRENE

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Göynük oil shale, polystyrene and several polystyrene-oil shale blends were degraded in a thermobalance apparatus at atmospheric pressure. Experiments were carried out dynamically by increasing the temperature from 298 to 1173 K with heating rates of 10 and 60 K $\text{min}^{-1}$ under an argon atmosphere. Derivative thermogravimetric data were analyzed by a reaction rate model assuming first order kinetics. Effects of blending ratio of oil shale and polystyrene and heating rate on the thermal degradation kinetics were investigated. Kinetic parameters were determined and the results were discussed.

***Keywords:*** *oil shale, polystyrene, thermogravimetry*

## Introduction

Plastics at present make up approximately 10% by mass of the total waste stream. These are not biologically degradable and create problems of disposal. One of the ways to treat this waste is thermal decomposition. Thermal decomposition process yields both energy and gaseous and liquid products, which can be used in various ways. The thermal degradation kinetics of individual polymers have been described in [1–7].

Oil shale is one of the most promising sources of energy in the world with large deposits situated in almost all the continents. The oil shale deposits in Turkey are widely distributed in middle and western Anatolia, the deposits of Göynük–Bolu accounting for nearly half of the total reserve (~2500 million tons) [8]. This resource is of poor quality: a low organic matter content and oil yield. Thermogravimetric analysis (TG/DTG) of oil shale samples has been extensively used as a means of determining the characteristic of decomposition and kinetic parameters [9–12]. Many thermogravimetric studies have been carried out under isothermal conditions; nevertheless it is more accurate to use a non-isothermal method to determine the kinetic parameters of the pyrolysis process, employing a TG apparatus, with the sample heated at a constant rate and recording its mass change. Using a non-isothermal method decreases experimental time and eliminates the difficulties associated with the isothermal method due to the initial heat up period. Considering the simulation of the conditions expected in commercial scale oil shale retorting systems, non-isothermal method is more reasonable [10, 12–15].

The mechanisms involved in the thermal decomposition of oil shale are exceedingly complex, and the influence of many variables is not well understood. Oil shale is a complex mixture of kerogen and wide range of minerals. The thermal degradation of oil shale is too complex to be described by an individual chemical reaction. The TG provides only general information about the overall reaction kinetics. Products that are obtained through pyrolysis depend on oil shale composition and conditional variables, such as temperature, time, rate of heating, pressure and gas environment [16–19].

Combined thermal degradation of a mixture of polymers and oil shale can improve the effectiveness of oil shale processing and provide a solution to the waste problem [20, 21]. The objective of this research was to investigate the thermal degradation kinetics of an oil shale, a polymer, and their blends.

## Experimental

Polystyrene (particle size of 2 μm) and Göynük oil shale from the western Black Sea area of Turkey were used in this study. The elemental analysis and ash content of Göynük oil shale are given in Table 1. Original oil shale, grounded in a ball mill, was sized to the particle size ($D_p$) 177>$D_p$>149 μm according to A.S.T.M.-E11-61. Carbon, hydrogen, nitrogen and sulfur contents were determined by LECO CHNS-932 instrument and oxygen was determined from the difference. The oil shale was stored in sealed containers at room temperature and there was no measurable change in its moisture content over the course of the experiments.

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**Table 1** Analysis of the Göynük oil shale

| Elemental analyses (daf) | |
|---|---|
| Carbon | 47.8 |
| Hydrogen | 6.0 |
| Nitrogen | 1.2 |
| Sulfur | 4.0 |
| Oxygen (by difference) | 41.0 |
| Ash (db) | 74.9 |

The experiments were performed in a Setaram TG DTA92 thermobalance with which the sample mass loss (thermogravimetric (TG) signal) and rate of mass loss (derivative thermogravimetric (DTG) signal) as functions of time or temperature were recorded continuously under dynamic conditions. The pyrolysis reaction was conducted under an argon atmosphere. An argon flow rate of 42 mL min$^{-1}$ was used to keep the effect of mass transfer at a minimum. All thermal degradation experiments were conducted at atmospheric pressure. The other experimental conditions were as follows: Thermal degradation temperature interval, 298–1173 K; heating rates 10 and 60 K min$^{-1}$, particle size: $177>D_p>149$ µm. Experiments were performed twice for repeatability.

## Results and discussion

### *Degradation of oil shale*

TG analysis was applied to determine the pyrolysis kinetics of oil shale. The TG and DTG curves of the Göynük oil shale for 10 and 60 K min$^{-1}$ are shown in Fig. 1. There are three temperature ranges to be considered. Below 523 K, the oil shale loses its moisture. Between 523 and 823 K, the mass loss is significant because of hydrocarbon material release. The third stage, which occurred at higher temperatures exceeding 823 K, is due to the decomposition of the mineral matter in the oil shale. Maximum thermal degradation rate peak (DTG$_m$) was observed as 0.0809 and 0.3818 mg min$^{-1}$ at a temperature of 717 and 706 K for 10 and 60 K min$^{-1}$, respectively. There is an increase in DTG curve with the increase in heating rate as seen from the figure. It is thought that thermal degradation of oil shale at higher heating rates proceeds faster. There is no net change in the TG curve with heating rate which supports the validity of this observation. Effect of heating rate on thermal degradation was also shown in Table 2. The rate of maximum decomposition (DTG$_m$) increases with increasing heating rate as seen from the table. The slight decrease in the temperature of maximum decomposition rate ($T_m$) and total conversion values are observed with increasing heating rate.

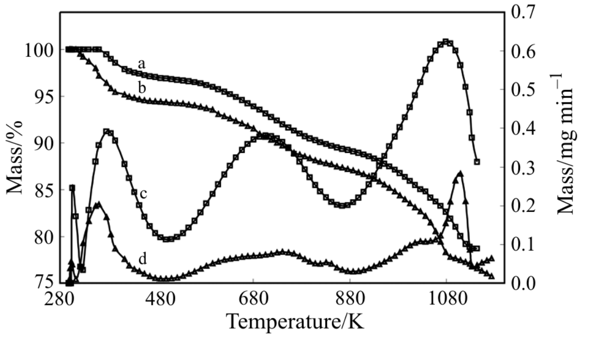

**Fig. 1** TG and DTG curves of Göynük oil shale; a – TG 60 K min$^{-1}$, b – TG 10 K min$^{-1}$, c – DTG 60 mg min$^{-1}$ and d – DTG 10 mg min$^{-1}$

### *Degradation of polystyrene*

Mass loss and derivative mass loss curves of polystyrene degradation are presented for 10 and 60 K min$^{-1}$ in Fig. 2. Examination of the data clearly indicates that polystyrene degrades in a single-stage process. The mass of the sample remained almost stable below 650 K. Above this temperature mass loss started, and increased abruptly above 650 up to 750 K. The residual mass around 750 K was about 93 and 82% for 10 and 60 K min$^{-1}$, respectively. There is an increase in DTG curve which imply that the reaction be accelerated with the increase in heating rate. However TG curve decreases for the same situation and examining the results in Table 2, it is seen that the onset of polystyrene degradation increases with increasing heating rate and total conversion value decreases. It is thought that effect of heating rate on polystyrene degradation is not the same as in oil shale and the reaction is not completed when heating rate is increased.

### *Degradation of blends*

Blends of Göynük oil shale with polystyrene were studied under the same thermal degradation conditions. Blending ratios of polystyrene to oil shale of 20:80, 40:60, 60:40 and 80:20 were performed. The

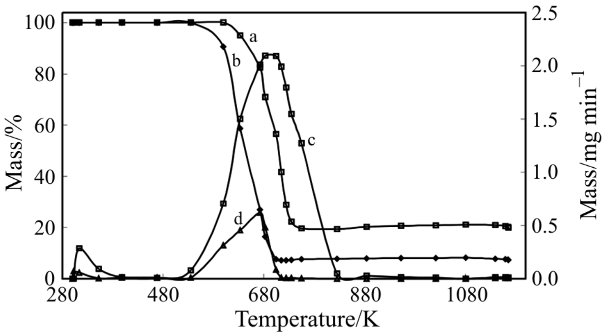

**Fig. 2** TG and DTG curves of polystyrene; a – TG 60 K min$^{-1}$, b – TG 10 K min$^{-1}$, c – DTG 60 mg min$^{-1}$ and d – DTG 10 mg min$^{-1}$

**Table 2** The variation in maximum decomposition rate peak, onset temperature, temperature of maximum decomposition rate, and total conversion values relative to the blending ratio, at different heating rates

| Heating rate/ $K\ min^{-1}$ | | Polystyrene/oil shale (mass basis) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0/100 | 20/80 | 40/60 | 60/40 | 80/20 | 100/0 |
| 10 | $DTG_{m,1}$/mg $min^{-1}$ | 0.0809 | 0.5331 | 1.3811 | 1.3048 | 1.8730 | 0.6406 |
| | $DTG_{m,2}$/mg $min^{-1}$ | 0.0809 | 0.5005 | 1.3795 | 1.3266 | 1.8696 | 0.6500 |
| | $DTG_{m,m}$/mg $min^{-1}$ | 0.0809 | 0.5168 | 1.3803 | 1.3157 | 1.8713 | 0.6453 |
| | Onset $temp_1$/K | 555.0 | 662.8 | 660.0 | 637.0 | 649.7 | 567.6 |
| | Onset $temp_2$/K | 563.0 | 663.4 | 663.8 | 645.0 | 651.9 | 567.0 |
| | Onset $temp_m$/K | 559.0 | 663.1 | 661.9 | 641.0 | 650.8 | 567.3 |
| | $T_{m,1}$/K | 710.0 | 685.0 | 700.5 | 695.0 | 690.0 | 661.0 |
| | $T_{m,2}$/K | 724.0 | 691.0 | 707.5 | 703.0 | 694.0 | 663.0 |
| | $T_{m,m}$/K | 717.0 | 688.0 | 704.0 | 699.0 | 692.0 | 662.0 |
| | $Conversion_1$/% | 25.6 | 34.0 | 45.0 | 60.3 | 78.0 | 94.0 |
| | $Conversion_2$/% | 25.2 | 38.0 | 49.0 | 61.5 | 75.6 | 92.0 |
| | $Conversion_m$/% | 25.4 | 36.0 | 47.0 | 60.9 | 76.8 | 93.0 |
| 60 | $DTG_{m,1}$/mg $min^{-1}$ | 0.3835 | 2.1996 | 2.2143 | 3.6332 | 4.5897 | 2.0965 |
| | $DTG_{m,2}$/mg $min^{-1}$ | 0.3801 | 2.1988 | 2.2117 | 3.6312 | 4.5921 | 2.0941 |
| | $DTG_{m,m}$/mg $min^{-1}$ | 0.3818 | 2.1992 | 2.2130 | 3.6322 | 4.5909 | 2.0953 |
| | Onset $temp_1$/K | 522.0 | 668.0 | 706.5 | 701.0 | 667.0 | 648.0 |
| | Onset $temp_2$/K | 524.0 | 664.0 | 707.5 | 701.0 | 665.0 | 652.0 |
| | Onset $temp_m$/K | 523.0 | 666.0 | 707.0 | 701.0 | 666.0 | 650.0 |
| | $T_{m,1}$/K | 708.0 | 737.5 | 737.0 | 723.0 | 717.5 | 689.0 |
| | $T_{m,2}$/K | 704.0 | 738.5 | 741.0 | 727.0 | 718.5 | 685.0 |
| | $T_{m,m}$/K | 706.0 | 738.0 | 739.0 | 725.0 | 718.0 | 687.0 |
| | $Conversion_1$/% | 22.0 | 36.1 | 45.0 | 59.8 | 71.0 | 81.6 |
| | $Conversion_2$/% | 22.2 | 36.1 | 45.4 | 59.4 | 71.2 | 82.0 |
| | $Conversion_m$/% | 22.1 | 36.1 | 45.2 | 59.6 | 71.1 | 81.8 |

$^1$first experiment; $^2$second experiment; $^m$calculated mean value

TG and DTG curves of the blends at 60 K $min^{-1}$ are shown in Fig. 3. In order to study the catalytic effect of polystyrene on the degradation process of oil shale we had to compare the curves of the components and the mixture. It can be observed from Fig. 3b that the height of the DTG peaks gradually increase with increasing amount of polystyrene in the blends.

The variation in maximum decomposition rate peak ($DTG_m$), the onset temperature, temperature of the maximum decomposition rate ($T_m$), total conversion (*TC*) values relative to the blending ratio for different heating rates are shown in Table 2. The variation in $DTG_m$ values with the polystyrene content in the blends for 10 and 60 K $min^{-1}$ is shown in Fig. 4. An increase in the values of the maximum decomposition rate up to the blending ratios of polystyrene to oil shale of 80:20 is observed when compared with the corresponding value obtained for the Göynük oil shale. The main characterization point in the TG/DTG curve is the peak temperature ($T_m$), where the rate of mass loss is at maximum. The change of the temperature of maximum decomposition rate with polystyrene content of the blends for 10 and 60 K $min^{-1}$ is shown in Fig. 5. The maximum peak temperature of oil shale is higher than that of polystyrene. A decrease in the maximum peak temperature values with increasing percentage of polystyrene in blends was observed. The onset temperatures of the blends for 60 K $min^{-1}$ were between 666–707 K for the mixtures, indicating a 16–57 K increase on the onset of polystyrene degradation and 143–184 K increase on the onset of oil shale degradation. The cause of the shift on the onset values of the mixtures can be explained by compensation effect. Compensation effect occurs in cases where thermal degradation is complex and consists in two parallel competitive reactions [22, 23]. Thermal degradation of polystyrene and oil shale is compensated when blended. In the mixtures it is believed that the radicals formed during the decomposition of polystyrene to its monomers reacted with the organic content of oil shale, which accelerated its degradation. Due to the decrease

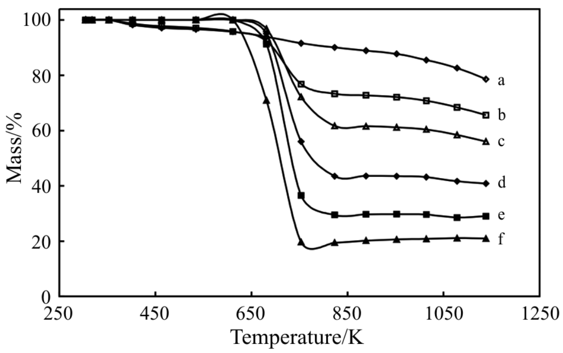

**Fig. 3a** TG curves of blends with different blending ratios of polystyrene to oil shale at 60 K $min^{-1}$; a – 0/100, b – 20/80, c – 40/60, d – 60/40, e – 80/20 and f –100/0

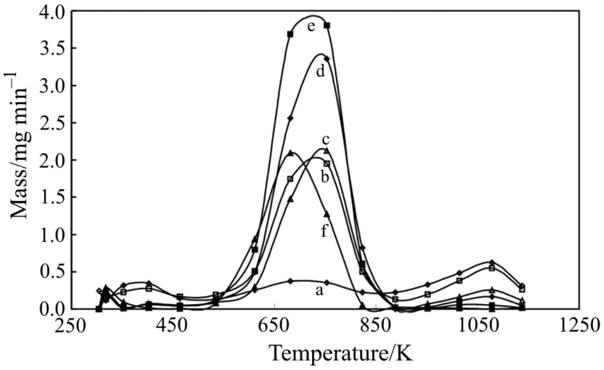

**Fig. 3b** DTG curves of blends with different blending ratios of polystyrene to oil shale at 60 K $min^{-1}$; a – 0/100, b – 20/80, c – 40/60, d – 60/40, e – 80/20 and f – 100/0

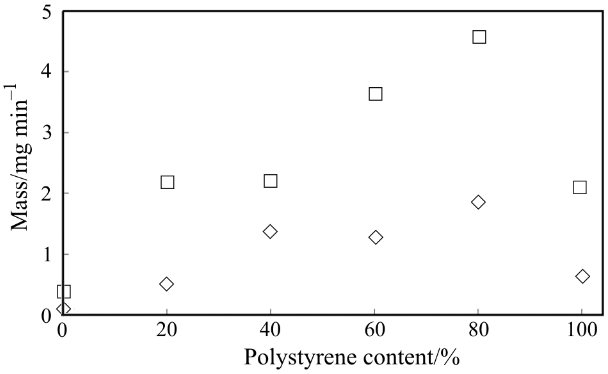

**Fig. 4** Change of decomposition rate with polystyrene content of blends; ◇ – 10 K $min^{-1}$, □ – 60 K $min^{-1}$

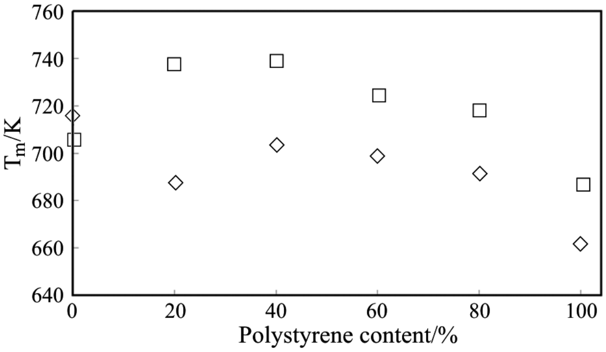

**Fig. 5** Change of temperature of maximum decomposition rate with polystyrene content of blends; ◇ – 10 K $min^{-1}$, □ – 60 K $min^{-1}$

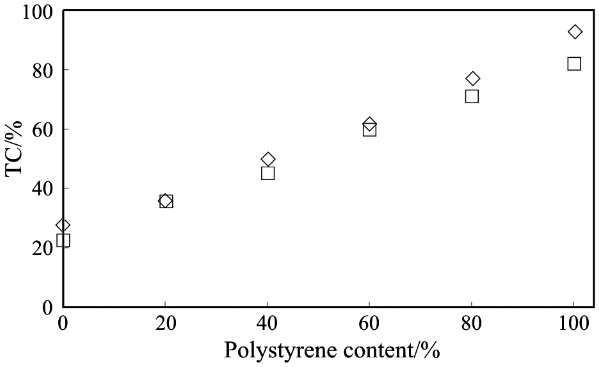

**Fig. 6** Change of total conversion percentage with polystyrene content of blends; ◇ – 10 K $min^{-1}$, □ – 60 K $min^{-1}$

of oil shale, thereby the amount of complex organic content that reacts with polystyrene in the mixtures decreases (Fig. 5). In other words, the radicals formed as a result of polystyrene degradation has increased which has a decreasing effect on the temperature values. Total conversion values of the blends were calculated based on the mass of the moisture-free blends fed to the system. Figure 6 shows the change of total conversion values with the polystyrene mass percentage of the blends for 10 and 60 K $min^{-1}$. An increase in the conversion with increasing percentage of polystyrene was observed. This is an expected situation since most of polystyrene in the mixture decomposes.

### *Kinetic model*

The proposed thermal degradation kinetics model in this study is

$$-\frac{dW}{dt}=k_0 e^{-E/\mathrm{RT}}W^{\mathrm{n}} \qquad (1)$$

where $W$ is the mass of sample at any time in mg, $k_0$ is the frequency factor in $mg^{1-n}$ $min^{-1}$, $E$ is the apparent activation energy in kJ $mol^{-1}$, $T$ is the absolute temperature in K, $n$ is the total order of the whole pyrolysis process and $t$ is the time in min.

The logarithmic expression of Eq. (1) yields

$$\ln\left(-\frac{dW}{dt}\right)=\ln k_0-\frac{E}{RT}+n\ln W \qquad (2)$$

In order to determine the pyrolysis kinetics of oil shale, Eq. (2) was applied to the mean of the measured

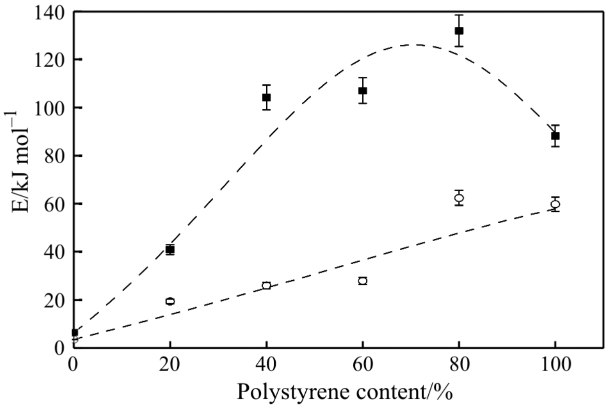

**Fig. 7** Change of activation energy with polystyrene content; ■ – 10 K min$^{-1}$, ○ – 60 K min$^{-1}$

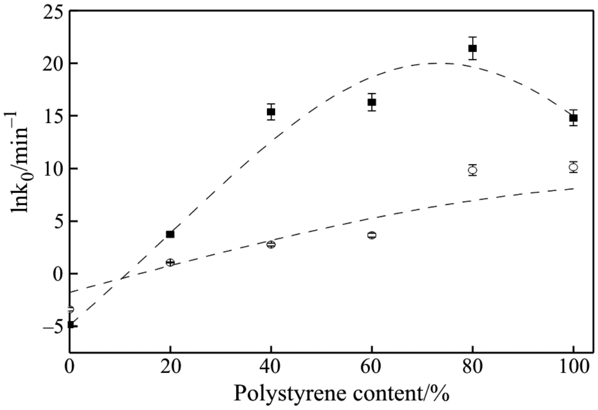

**Fig. 8** Change of frequency factor with polystyrene content; ■ – 10 K min$^{-1}$, ○ – 60 K min$^{-1}$

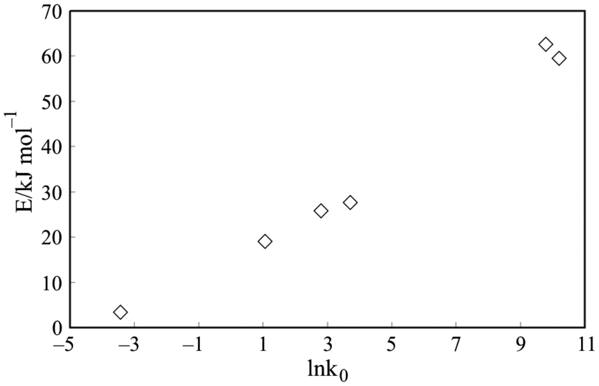

**Fig. 9** Linear correlation between activation energy and frequency factor at 60 K min$^{-1}$

TG and DTG data. Assuming first-order kinetics ($n$=1), kinetic constants $k_0$ and $E$ were calculated from the multiple linear regression analysis and results were given as activation energy *vs*. polystyrene/oil shale blend for 10 and 60 K min$^{-1}$ in Fig. 7. Activation energies in the figure are not exact values and are given with 5% accuracy. The mechanisms involved in the thermal decomposition of solid fossil fuels are exceedingly complex and the influence of the variables is not well understood. The complexity of the thermal degradation phenomena has handicapped the development of models for design and scale-up. Simplistic models that correlate the data reasonably well have been advanced. It is thought that kinetic models do not give the exact results but give an idea about general reaction pathway. Results showed that the values of the kinetic parameters changed with the blending ratios of oil shale to polystyrene. The obtained activation energies were much higher than that of oil shale for all blends. Hence, the decomposition kinetics of the mixtures were determined by the polystyrene degradation. Besides activation energy, frequency factor is also important in determining the thermal degradation behavior (Fig. 8). The frequency factors of the mixtures are lower than that of polystyrene but higher than that of oil shale. As a result of kinetic effects, the radicals formed during decomposition of the polystyrene will react with the organic matter of the oil shale in the mixture and accelerate its degradation. An increase was observed in the frequency factor and activation energy values as the mass percentage of polystyrene in blends increased. Activation energy and frequency factors for 10 K min$^{-1}$ is higher than the values obtained with 60 K min$^{-1}$, which imply that the reaction be not completed at higher heating rates. There is a good linear correlation between $\ln k_0$ and $E$, which was formulated according to the equation

$$E=4.429\ln k_0+15.363\ (R^2=0.986) \tag{4}$$

for 60 K min$^{-1}$ and shown in Fig. 9. It is believed that the relationship between $\ln k_0$ and $E$ corresponded to a compensation effect [22].

**Table 3** Comparison of activation energy values for 10 K min$^{-1}$ with those obtained from literature

| Reference | Sample | $E$/kJ mol$^{-1}$ |
|---|---|---|
| Present study | Oil shale | 6.4 |
| Jaber and Probert (2000) | Oil shale | 7.0 |
| Skala *et al*. (1990) | Oil shale | 55.2 |
| Present study | Polystyrene | 88.2 |
| Budrugeac (2000) | Polystyrene | 85.7 |
| Nishizaki (1980) | Polystyrene | 244.0 |
| Present study | Polystyrene/oil shale | 40.9 |
| Gersten *et al*. (2000) | Polypropylene/oil shale | 242.0 |

The minimum activation energy value obtained from the proposed reaction kinetics appears to be the lowest one when compared to those obtained from the literature (Table 3). However, it should be noted that the subject studies were not conducted under identical conditions.

## Conclusions

Thermal degradation of Göynük oil shale and polystyrene was investigated by thermogravimetry. 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 $\text{min}^{-1}$. Blends of oil shale and polystyrene were also degraded. 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.

A first-order kinetic model was proposed to describe the main decomposition processes for both the individual feedstocks and their blends and activation energies and frequency factors were determined. The activation energies and frequency factors both increased with the increase in the mass ratio of polystyrene to oil shale in the blends.

The main conclusion from this analysis is that the polystyrene accelerates the decomposition of the organic matter in the oil shale.

## Acknowledgements

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## Nomenclature

| | |
|---|---|
| DTG | rate of mass loss |
| daf | dry ash free basis |
| db | dry basis |
| $D_p$ | oil shale particle size/μm |
| $\text{DTG}_m$ | maximum decomposition rate /mg $\text{min}^{-1}$ |
| $E$ | apparent activation energy/kJ $\text{mol}^{-1}$) |
| $k_0$ | frequency factor ($\text{min}^{-1}$) |
| $n$ | order of reaction |
| $R^2$ | determination coefficient |
| $T$ | temperature/K |
| $TC$ | total conversion/% |
| TG | mass loss/% |
| $t$ | time/min |
| $T_m$ | temperature of maximum decomposition rate/K |
| $W$ | mass of oil shale at any time/mg |

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