

Comparative combustion study of some polymers with oil shale

Yeliz Durak · Tülay Durusoy

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Abstract In this study, the combustion kinetics of Göynük oil shale, polyethylene, polyethylene glycol (PEG), polymethyl methacrylate (PMMA), polyvinyl chloride, and polymer–oil shale blends were investigated by thermogravimetric analysis. Experiments were conducted at non-isothermal conditions with a heating rate of 5 K min^{-1} in the 298–1173 K temperature interval under air atmosphere. An increase in the total conversion values with increasing mass percentage of polymers of the blends was observed. Differential thermogravimetric data were analyzed by an Arrhenius model. Effects of blending ratio of oil shale and polymer on the combustion kinetics were investigated. Kinetic parameters were determined and the results were discussed. An increase was observed in the frequency factor and activation energy values as the weight percentage of polymer in blends were increased. The minimum activation energy, 16.1 kJ mol^{-1} , was calculated for PEG/oil shale with 2/3 blending ratio.

Keywords Oil shale · Polyethylene · Polyethylene glycol · Polymethyl methacrylate · Polyvinyl chloride · Combustion · Thermogravimetry

Abbreviations

PE Polyethylene
PEG Polyethylene glycol
PMMA Polymethyl methacrylate

PVC Polyvinyl chloride
TC Total conversion (%)

List of symbols

D_p Oil shale particle size (μm)
 DTG_m Maximum decomposition rate
 E Apparent activation energy (kJ mol^{-1})
 k_0 Frequency factor (min^{-1})
 n Order of reaction
 R Ideal gas constant
 R^2 Determination coefficient
 t Time (min)
 T Absolute temperature (K)
 T_m Temperature of maximum decomposition rate (K)
 W Mass of oil shale at any time (mg)

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 means to treat this waste is thermal decomposition. Thermal decomposition process yields gaseous and liquid products as well as energy. The thermal degradation kinetics of individual polymers have been described in the previous work [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. Göynük accounting for nearly half of the total reserve ($\sim 2,500$ million tons) of Turkey [8]. Thermogravimetric analysis (TG/DTG) of oil shale samples has been extensively done as a means of determining the characterization, pyrolysis combustion behavior, and kinetic analysis. The main

Y. Durak
TÜBİTAK Marmara Research Center, Energy Institute,
41470 Gebze, Kocaeli, Turkey

T. Durusoy (✉)
Department of Chemical Engineering, University of Hacettepe,
06800 Beytepe, Ankara, Turkey
e-mail: tdurusoy@hacettepe.edu.tr

region of the sample's weight loss, arising from the conversion of organic matter into oil and gas, occurred within the temperature range 200–600 °C. The magnitude of the total weight loss was mainly dependent on the final temperature, while to a lesser extent, on the heating rate employed. Many thermogravimetric studies have been carried out under isothermal conditions. It is more accurate to use a non-isothermal method to determine the kinetic parameters of the pyrolysis process, employing a TG apparatus, where the sample is heated at a constant rate and the mass change is recorded. The mechanisms involved in the combustion of oil shale are exceedingly complex and the influence of many variables is not well understood. The TG provides only general information about the overall reaction kinetics. Products that are obtained through combustion depend on oil shale composition and conditional variables, such as temperature, time, rate of heating, pressure, and gas environment [9–21].

Recently, there has been an increase in the studies of combustion of polymers with oil shale, coal, peat, and biomass [18, 22–25]. Combined combustion of a mixture of polymers and oil shale can improve the effectiveness of oil shale processing and provide a solution to the waste problem. A method for utilization of waste rubber and plastics by means of combined pyrolysis with a solid fuel was investigated by Gersten et al. [22]. Oil shale with different kinds of waste rubber, polyethylene (PE) and polypropylene were pyrolyzed. The oil yield was 43–50 wt% from rubbers, and 93–95 wt% from thermoplastics. Gas yield was 3–6 wt%. Gersten et al. [23] investigated the thermal decomposition behavior of polypropylene, oil shale and a 1:3 mixture of the two. Experiments were conducted at three heating rates of 5, 10, and 15 K min⁻¹, in the temperature range of 30–900 °C. Obtained activation energies were 250 kJ kg⁻¹ for polypropylene, 63 kJ kg⁻¹ for the oil shale organic matter, and 242 kJ kg⁻¹ for the mixture. Değirmenci and Durusoy [24] used the thermogravimetry analysis to obtain kinetics of the pyrolysis of oil shale, polystyrene, and their blends. An increase was observed in the total conversion values of the blends with the increase in the blending ratio of polystyrene to oil shale. The main conclusion is that the polystyrene accelerated the decomposition of the organic matter in the oil shale. Yağmur and Durusoy [18] studied the pyrolysis and combustion kinetics of Göynük oil shale by thermogravimetry. Effect of the heating rate on the pyrolysis and combustion kinetics of the Göynük oil shale was investigated. The experimental results showed that the total conversion values were almost independent of heating rate during oil shale pyrolysis and combustion. It was concluded that both the temperature of maximum decomposition rate and the maximum decomposition rate were

increased with heating rate. Yağmur and Durusoy [25] investigated the combustion kinetics of Göynük oil shale, polystyrene and several polystyrene–oil shale blends by thermogravimetric analysis. It was concluded that activation energy values increased with increasing polystyrene/oil shale blending ratio for all heating rates by the Arrhenius and Coats and Redfern method. The minimum activation energy, 6.6 kJ mol⁻¹, was calculated at the heating rate value of 20 K min⁻¹ with oil shale.

Interactions between polymers and fossil fuels are not well known. In this study, degradation behavior of polyethylene (PE), polyethylene glycol (PEG), polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), Göynük oil shale, and polymer/oil shale blends were investigated under air atmosphere using a thermogravimetric analyzer to obtain an overall understanding of the interaction of oil shale and polymers. The combustion kinetic data were obtained by fitting the thermogravimetric data into an Arrhenius model. This model yields the activation energy and frequency factor of the reaction.

Experimental

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) $210 > D_p > 149 \mu\text{m}$ according to ASTM-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 the moisture content over the course of the experiments.

The following polymers (Sigma-Aldrich Ltd.) were investigated for the combined combustion with Göynük oil shale: PE, PEG, PMMA, and PVC. The physical properties of polymers are given in Table 2. The melting points of polymers were determined by using differential

Table 1 Analysis of Göynük oil shale

Elemental analyses (dry ash free)	Mass/%
Carbon	50.5
Hydrogen	4.8
Nitrogen	1.2
Sulfur	5.2
Oxygen (by difference)	38.3
Ash (dry basis)	76.2

Table 2 The physical properties of polymers

Polymer	Density/g mL ⁻¹	Melting temperature/K
PE	0.940	389
PEG	1.210	340
PMMA	1.188	513
PVC	1.385	542

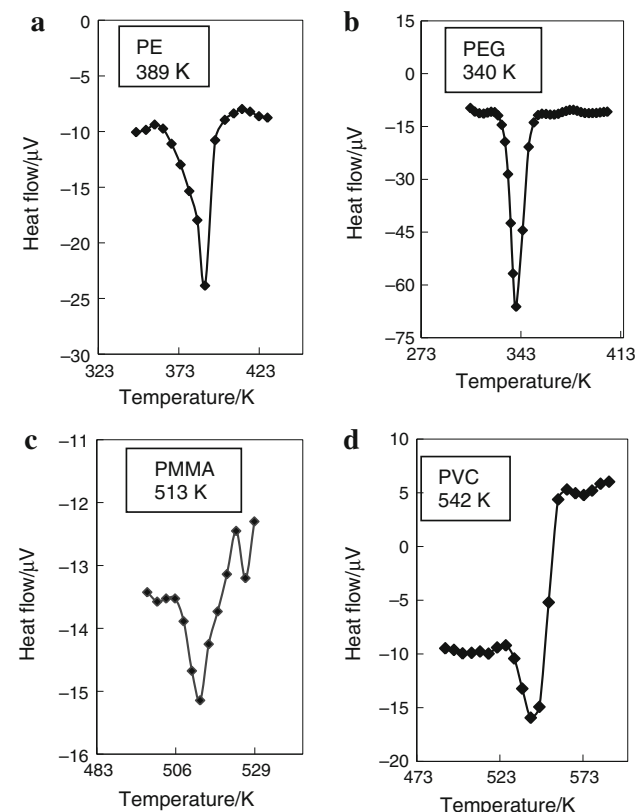


Fig. 1 The melting points of **a** PE, **b** PEG, **c** PMMA, and **d** PVC

calorimetry apparatus (Perkin Elmer Diamond DSC). The thermograms are given in Fig. 1 and are presented in Table 2. All five polymers were used in a powdered form.

The experiments were performed in a Setaram TG DTA92 thermobalance in which the sample mass loss (thermogravimetric (TG) signal) and rate of mass loss (DTG) signal as functions of time or temperature were recorded continuously under dynamic conditions. The combustion reaction was conducted under an air atmosphere. An air flow rate of 42 mL min⁻¹ was used to keep the effect of mass transfer at a minimum. Experimental conditions were as follows: interval of combustion temperature, 298–873 K, heating rate, 5 K min⁻¹, particle size: 210 > D_p > 149 μm. Experiments were performed twice for repeatability. Per cent deviation for all results were calculated and standard deviation were found to be less

Table 3 The variation in maximum decomposition rate peak (DTG_m), temperature of the maximum decomposition rate (T_m), and total conversion values (TC)

Sample	Blending ratio (polymer/oil shale)	Line zone	DTG _m /mg min ⁻¹	T _m /K	TC/%
Oil shale	0/1	First	0.2372	590	33
		Second	0.3630	813	
PE	2/3	First	1.3993	742	53
		Second	–	–	
	1/1	First	1.1752	741	58
		Second	–	–	
3/2	First	0.9914	737	66	
	Second	–	–		
1/0	First	1.0566	678	97	
	Second	–	–		
PEG	2/3	First	0.7660	500	48
		Second	–	–	
	1/1	First	0.8334	525	63
		Second	–	–	
3/2	First	0.8641	533	60	
	Second	–	–		
1/0	First	2.0426	574	99	
	Second	–	–		
PMMA	2/3	First	0.5334	597	45
		Second	1.0947	648	
	1/1	First	0.4423	551	62
		Second	0.6684	649	
3/2	First	0.5664	561	76	
	Second	0.7157	651		
1/0	First	1.7375	567	100	
	Second	1.7714	630		
PVC	2/3	First	0.8094	566	61
		Second	–	–	
	1/1	First	0.7578	564	66
		Second	–	–	
3/2	First	1.1014	560	69	
	Second	–	–		
1/0	First	1.8774	547	98	
	Second	0.3488	818		

than 1% in general. The results in Table 3 were average of at least two runs.

Results and discussion

Combustion of oil shale

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the

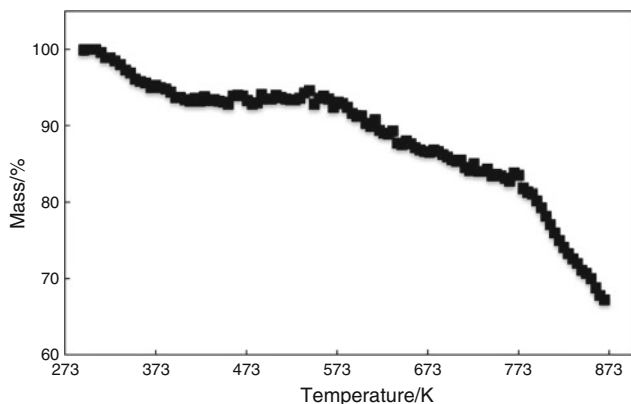


Fig. 2 Mass loss curve of combustion of Göynük oil shale at 5 K min^{-1}

temperature and composition of the fuel and oxygen supply dictate the nature of the reaction. The relative mass loss curve of the oil shale sample obtained at 5 K min^{-1} heating rate is represented in Fig. 2. There are three temperature ranges to be considered. Below 411 K, the oil shale loses its moisture; the H_2O components in the crystalline structure decomposes. Between 411 and 773 K, the organic content which is mostly kerogen and bitumen are decomposed. Temperatures exceeding 773 K the mineral constituents mostly caolinite, in the molecular structure are decomposed. The maximum decomposition rate peak, DTG_m , temperature of the maximum decomposition rate,

T_m , and total conversion, TC, values relative to the heating rate for combustion are also shown in Table 3.

Combustion of polymers

TG and DTG curves of PE, PEG, PMMA, and PVC combustion are presented for 5 K min^{-1} in Fig. 3. Examination of data clearly indicates that PE degrades in a single-stage process (Fig. 3a). The mass of the sample remained almost stable below 570 K. Above this temperature, mass loss started and increased abruptly above 570 up to 750 K. The residual mass around 750 K was about 97. The maximum decomposition rate peak, DTG_m , temperature of the maximum decomposition rate, T_m , and total conversion, TC, values relative to the heating rate for PE combustion are also shown in Table 3. The TG and DTG curves of PEG are shown in Fig. 3b. The mass of the sample remained almost stable below 500 K. Above this temperature, mass loss started and increased abruptly above 500 up to 640 K. The maximum decomposition rate peak, DTG_m , is found to be $2.0426 \text{ mg min}^{-1}$ (Table 3). PMMA degrades in a double-stage process between the temperature interval of 510–680 K (Fig. 3c). Examination of data indicates that PVC degrades in a double-stage process (Fig. 3d). The sharp mass loss is found in the first region. The maximum decomposition rate peak, DTG_m , and total conversion values are found to be $1.8774 \text{ mg min}^{-1}$ and 98%, respectively.

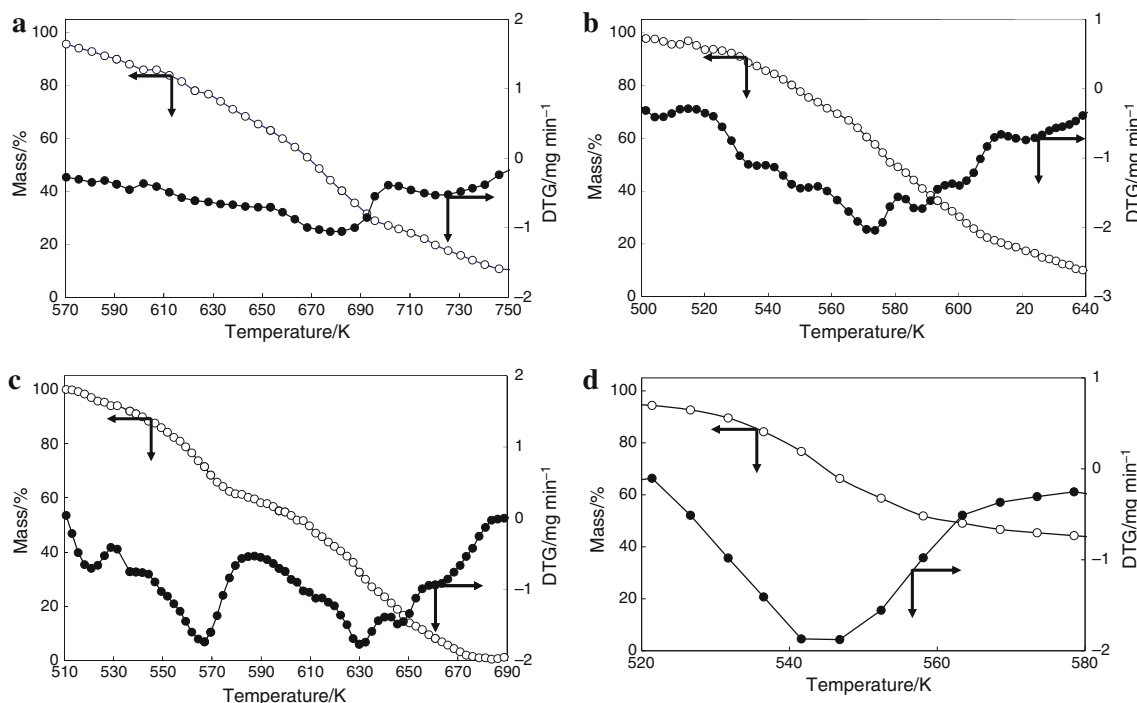


Fig. 3 TG and DTG curves of **a** PE, **b** PEG, **c** PMMA, and **d** PVC

Combustion of blends

Blends of Göynük oil shale with polymers were studied under the same combustion conditions. Blending ratios of polymers to oil shale of 2/3, 1/2, and 3/2 were performed. The TG curves of the blends at 5 K min⁻¹ are shown in Fig. 4. In order to study the catalytic effect of polymers on the degradation process of oil shale, the curves of the components and the mixture were compared. The maximum decomposition rate peak, DTG_m, temperature of the maximum decomposition rate, T_m, and total conversion, TC, values relative to the heating rate for all blends are also shown in Table 3.

Examination of data clearly indicates that PE–oil shale blends degrade in a single-stage process as PE (Fig. 4a). The mass of the sample remained almost stable below 600 K. Above this temperature mass loss started, and increased abruptly above 600 up to 750 K. It can be observed from Fig. 4a that the mass loss increases with increasing amount of polystyrene in the blends. A decrease in the values of maximum decomposition rate values with increasing percentage of PE in blends was observed (Table 3). 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 maximum peak temperature of PE is higher than that of oil shale. An increase in the maximum

peak temperature values with PE addition was observed for all blending ratios. The TG curves of PEG–oil shale blends are shown in Fig. 4b. The blends decomposition temperature interval shifted from higher temperatures to lower ones. Blends have lower DTG_m and T_m values than PEG (Table 3). Experimental data show that PMMA–oil shale blends degrade in a double-stage process. (Fig. 4c). PVC oil shale blends degrade in a single-stage process as PE and PEG oil shale blends (Fig. 4d). An increase in the total conversion values with increasing mass percentage of polymers of the blends was observed. This is an expected behavior since most of polymer in the mixture decomposes.

Kinetic model

Non-isothermal kinetic study of mass loss under combustion processes is extremely complex for oil shales because of the presence of the numerous complex components and their parallel and consecutive reactions. In the course of this research, Arrhenius kinetic theory were used for kinetic analysis of the data generated by the TG experiments. In this study, the combustion of oil shale resulted in two main reaction regions, namely primary and secondary devolatilization. Since these two volatilization sections are completely distinct, the Arrhenius kinetic model is

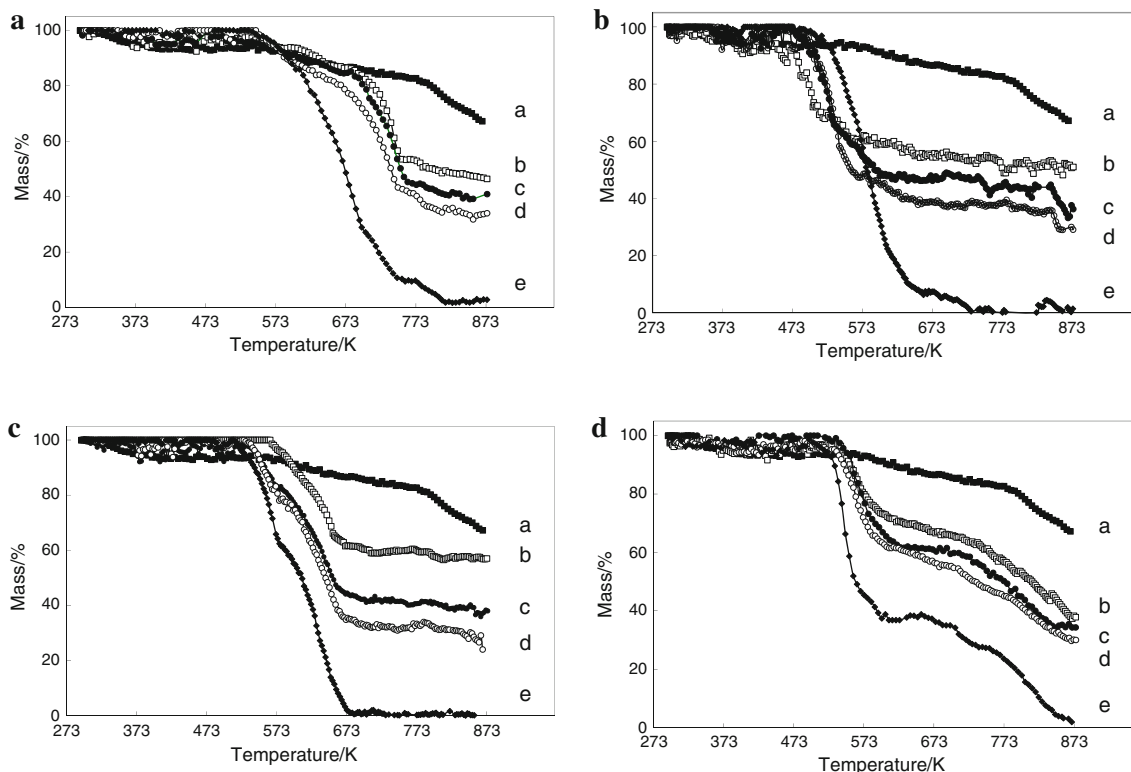


Fig. 4 TG curves of blends with different blending ratios (a 0/1, b 2/3, c 1/1, d 3/2, e 1/0) of a PE, b PEG, c PMMA, d PVC to oil shale

individually adopted to the first region to calculate the activation energies. For the application of Arrhenius kinetics, firstly the temperature values are determined from the starting and ending points of the maximum mass loss peaks for each experiment and first volatilization region in the DTG curves. A computer program was used to evaluate the model and kinetic parameters were determined. The expression of the Arrhenius model was,

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

where W is the mass of oil shale at any time in mg, k_0 is the frequency factor in $\text{mg}^{(1-n)} \text{min}^{-1}$, E is the apparent activation energy in kJ mol^{-1} , T is the absolute temperature in K, R is the gas constant, n is the total order of the whole pyrolysis process, and t is the time in minutes. The model assumes that the rate of mass loss of the total sample depends only on the rate constant, the mass of the remaining sample and the temperature, when the reaction order is assumed to be one. Therefore, the equation takes the following form:

$$\frac{-dW}{dt} = k_0 e^{-E/RT} W \quad (2)$$

Linearization of the equation yields:

$$\ln \frac{-dW}{dt} = \ln k_0 - \frac{E}{RT} + \ln W \quad (3)$$

In order to determine the combustion kinetics of oil shale, polymers and polymer/oil shale blends, Eq. 3 was applied to the mean of the measured TG and DTG data. Kinetic constants k_0 , E , and determination coefficients (R^2) were determined by multiple regression analyses and are given in Table 4. Results showed that the values of the kinetic parameters changed with the blending ratios of oil shale to polymers. The obtained activation energies were much lower than that of polymer for all blends. Besides activation energy, frequency factor is also important in determining the combustion behavior. The frequency factors of the mixtures are lower than that of polymer but higher than that of oil shale. Thermal degradation of polymer and oil shale is compensated when blended. Compensation effect occurs in cases where thermal degradation is complex and consists in two parallel competitive reactions [26, 27]. As a result of kinetic effects, the radicals formed during decomposition of the polymer will react with the organic matter of the oil shale in the mixture and accelerate its degradation. Thereby due to the increase of oil shale, the amount of complex organic content that reacts with polymer in the mixtures increases. The obtained activation energies were much higher than that of oil shale for all blends. Hence, the decomposition kinetics of the mixtures was determined by the polymer degradation. An increase

Table 4 Kinetic parameters of the samples combustion

Sample	Blending ratio (polymer/oil shale)	k_0/min^{-1}	$E/\text{kJ mol}^{-1}$	R^2
Oil shale	0/1	4.7×10^{-1}	29.1	0.965
PE	2/3	$1.3 \times 10^{+2}$	53.5	0.914
	1/1	$6.6 \times 10^{+2}$	59.6	0.894
	3/2	$2.2 \times 10^{+3}$	62.4	0.987
	1/0	$5.6 \times 10^{+3}$	63.0	0.975
PEG	2/3	5.1×10^{-1}	16.1	0.882
	1/1	9.0×10^{-1}	16.3	0.878
	3/2	$1.1 \times 10^{+1}$	23.4	0.860
PMMA	1/0	$1.1 \times 10^{+3}$	33.2	0.983
	2/3	$6.3 \times 10^{+2}$	52.1	0.937
	1/1	$1.8 \times 10^{+3}$	55.7	0.940
PVC	3/2	$1.3 \times 10^{+5}$	76.9	0.857
	1/0	$1.7 \times 10^{+8}$	101.7	0.953
	2/3	1.7×10^{-1}	36.1	0.995
	1/1	$3.7 \times 10^{+6}$	86.1	0.934
	3/2	$6.3 \times 10^{+8}$	107.9	0.975
	1/0	$2.5 \times 10^{+14}$	159.4	0.985

was observed in the frequency factor and activation energy values as the weight percentage of polymer in blends increased. The minimum activation energy, 16.1 kJ mol^{-1} , was calculated with PEG/oil shale 2/3 blending ratio.

Conclusions

Combustion of Göynük oil shale, PE, PEG, PMMA, and PVC and several polymer–oil shale blends under atmospheric pressure has been studied using a thermogravimetric apparatus. An increase was observed in the total conversion values of the blends with the increase in the blending ratio of polymer to oil shale. Total conversion values of all polymer samples were calculated to be more than 95%. Results show that the values of the maximum combustion rate and the temperature of maximum combustion rate changed with the blending ratios of polymer to oil shale. But in general, when a blend in any proportion of polymer 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 polymer content of the sample were observed. The main conclusion from this analysis is that the polymer accelerates the decomposition of the organic matter in the oil shale. Arrhenius kinetic theory was employed to study kinetic analysis of the data generated by the TG experiments. In general, the activation energies decreased with

the decrease in the weight ratio of polymer to oil shale in the blends.

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