

KINETICS OF COMBUSTION OF OIL SHALE WITH POLYSTYRENE

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The combustion kinetics of Göynük oil shale, polystyrene and several polystyrene–oil shale blends were investigated by thermogravimetric analysis in the present study. Experiments were conducted at non-isothermal conditions with a heating rate of 5, 10 and 20 K min⁻¹ in the 298–1173 K temperature interval under an air atmosphere. Differential thermogravimetric data were analyzed by two different models. Effects of blending ratio of oil shale and polystyrene and heating rate on the combustion kinetics were investigated. Kinetic parameters were determined and the results were discussed.

Keywords: combustion, oil shale, polystyrene, thermogravimetry

Introduction

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. Current reserves of oil shales in Turkey are ~5300 million tons, located in the following deposits: Göynük–Bolu, Beypazarı–Ankara, Seyitömer–Kütahya; the deposits of Göynük accounting for nearly half of the total reserve (~2500 million tons) [1]. Thermogravimetric analysis (TG/DTG) of oil shale samples has been extensively used as a means of determining the characteristic of decomposition and kinetic parameters [2–5]. 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, with the sample heated at a constant rate and recording its mass change [6].

The mechanisms involved in the combustion 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 and combustion depend on oil shale composition and conditional variables, such as temperature, time, rate of heating, pressure and gas environment [7–19].

The objective of this research was to investigate the combustion 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) $210 > D_p > 149$ μm 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 its moisture content over the course of the experiments.

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

Table 1 Analysis of the Göynük oil shale

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

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as follows: interval of combustion temperature, 298–1173 K; and range of heating rate, 5–20 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 than 1% in general. The results in Table 2 were average of at least two runs.

Results and discussion

Combustion of polystyrene

TG and DTG curves of polystyrene combustion are presented for 5, 10 and 20 K min⁻¹ in Fig. 1. Examination of data clearly indicates that polystyrene degrades in a single-stage process. The mass of the sample remained almost stable below 580 K. Above this temperature mass loss started, and increased abruptly above 580 up to 710 K. The residual mass around 710 K was about 97 for all heating rates. There is an increase in DTG curve which imply that the reaction be accelerated with the increase in heating rate. How-

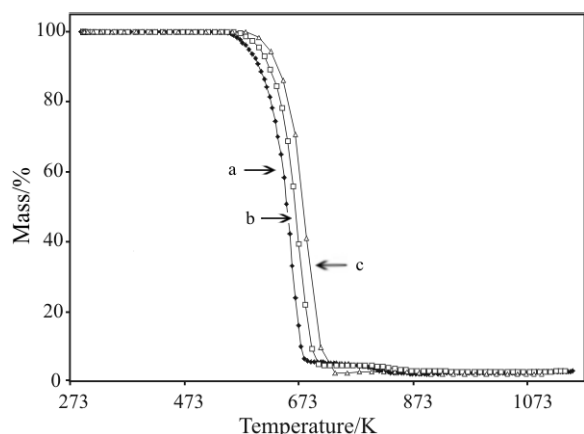


Fig. 1a TG curves of combustion of polystyrene at different heating rates a – 5, b – 10, c – 20 K min⁻¹

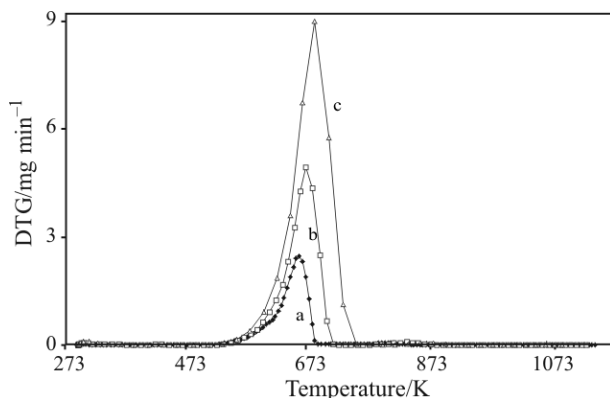


Fig. 1b DTG curves of combustion of polystyrene at different heating rates a – 5, b – 10, c – 20 K min⁻¹

ever TG curve decreases for the same situation and examining the results in Table 2, it is seen that the onset of polystyrene combustion increases with increasing heating rate.

Combustion of oil shale

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with fuel. However, the temperature and composition of the fuel and oxygen supply dictate the nature of the reaction. As an example the relative mass loss and corresponding combustion rate curves of the oil shale sample obtained at 20 K min⁻¹ heating rate are represented in Fig. 2. There are 3 temperature ranges to be considered. Below 500 K, the oil shale loses its moisture; the H₂O components in the crystalline structure decomposes. Between 500–850 K the organic content mostly the kerogen and bitumen are decomposed. Temperatures exceeding 850 K the mineral constituents (caolinite mostly) in the molecular structure are decomposed.

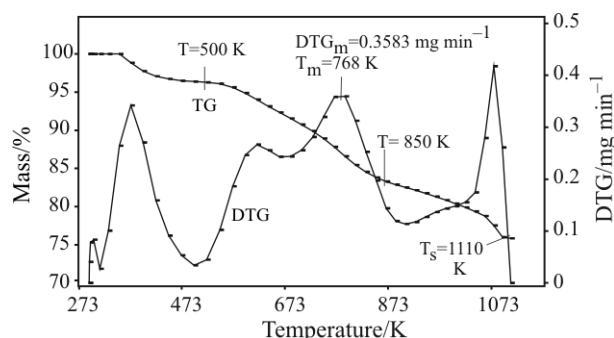


Fig. 2 TG and DTG curves of Göynük oil shale at 20 K min⁻¹

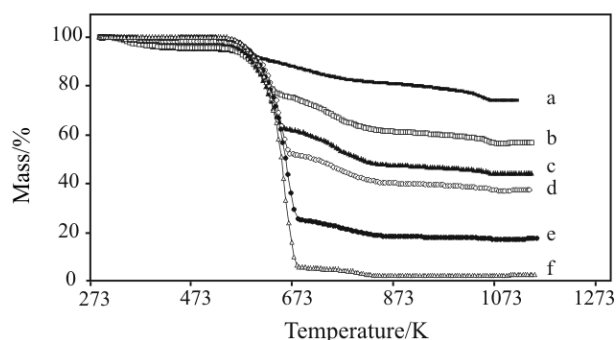
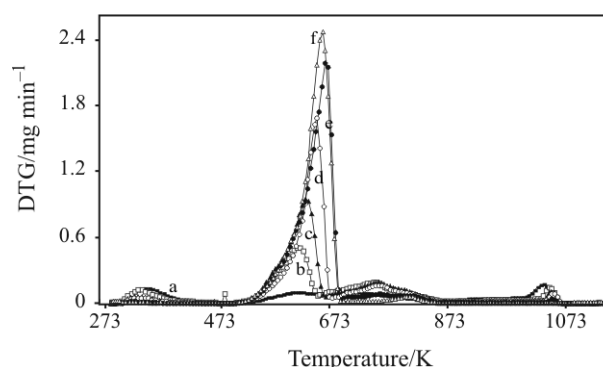
The variation in maximum decomposition rate peak, DTG_m, temperature of the maximum decomposition rate, T_m, burn-out temperature T_f, and total conversion, TC, values relative to the heating rate for combustion are also shown in Table 2. Total conversion values were almost constant at all heating rate values for combustion.

Combustion of blends

Blends of Göynük oil shale with polystyrene were studied under the same combustion conditions. Blending ratios of polystyrene to oil shale of 1:4, 2:3, 3.2 and 4:1 were performed. The TG and DTG curves of the blends at 5 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

Table 2 The variation in maximum decomposition rate peak (DTG_m), temperature of the maximum decomposition rate (T_m), burn-out temperature (T_f), and total conversion values relative to the blending ratios at different heating rates

Blending ratio polystyrene/oil shale	Heating rate/ K min ⁻¹	DTG _m / mg min ⁻¹	T _m /K	T _f /K	TD/%
0/1	5	0.0888	727	1056	25.6
	10	0.1825	735	1085	24.6
	20	0.3583	768	1110	24.2
1/4	5	0.5063	623	1076	43.3
	10	0.7185	648	1090	37.1
	20	1.2744	673	1074	34.6
2/3	5	0.9454	631	1070	55.8
	10	1.3813	656	1089	47.9
	20	3.2178	692	1078	50.0
3/2	5	1.6856	652	1085	62.7
	10	2.6170	666	1098	60.9
	20	4.2643	690	1092	60.7
4/1	5	2.1895	665	1069	82.5
	10	3.6081	684	1084	80.6
	20	6.6139	710	1074	78.3
1/0	5	2.4733	661	842	97.6
	10	4.9395	673	900	96.9
	20	9.0097	687	904	97.7

**Fig. 3a** TG curves of blends with different blending ratios of polystyrene to oil shale at 5 K min⁻¹ a – 0/1, b – 1/4, c – 2/3, d – 3/2, e – 4/1 and f – 1/0**Fig. 3b** DTG curves of blends with different blending ratios of polystyrene to oil shale at 5 K min⁻¹ a – 0/1, b – 1/4, c – 2/3, d – 3/2, e – 4/1 and f – 1/0

polystyrene in the blends. An increase in the values of maximum decomposition rate values with increasing percentage of polystyrene in blends was observed for all heating rates (Table 2). 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 oil shale is higher than that of polystyrene. An increase in the maximum peak temperature values with increasing percentage of polystyrene in blends was observed. Burn-out temperatures indicating the end of sample oxidation were affected by the change in the heating rate and blending ratios. The highest burn-out temperatures of different blending ratios was measured for

3/2 polystyrene/oil shale ratio for all heating rate values. Lower burn-out temperatures also indicates that the sample oxidation is completed in a shorter time (Table 2). An increase in the total conversion values with increasing mass percentage of polystyrene of the blends was observed. This is an expected situation since most of polystyrene 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, two different models (Arrhenius and Coats and Redfern) all based on 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 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 simply made by the formula:

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

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:

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

kinetic constants k_0 , E , and determination coefficients (R^2) were determined by multiple regression analyses using Eq. (3).

Coats and Redfern [20] developed an integral method, which can be applied to TG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation, which is used for analysis, is

$$\log \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \log \left(\frac{AR}{\beta E} \left(1 - \frac{2RT}{E} \right) \right) - \left(\frac{E}{2.303RT} \right) \quad (4)$$

where α is the mass fraction and β is the linear heating rate. Thus a plot of $\log k$ vs. $1/T$, where

$$k = \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \quad (5)$$

Table 3 Kinetic parameters of the samples combustion

Heating rate/ K min ⁻¹	Blending ratio polystyrene/oil shale	Activation energy, $E=\text{kJ mol}^{-1}$		Reaction order for Coats and Redfern method
		Arrhenius method	Coats and Redfern method	
5	0/1	7.3	13.4	1/2
	1/4	39.7	31.0	1
	2/3	61.1	53.5	3/2
	3/2	69.6	69.0	3/2
	4/1	104.7	115.7	2
	1/0	165.5	133.0	2
	0/1	7.0	15.4	1/2
10	1/4	9.5	23.0	2/3
	2/3	21.5	52.2	3/2
	3/2	42.0	88.6	2
	4/1	124.6	120.0	2
	1/0	137.7	137.4	2
	0/1	6.6	13.5	1/2
	1/4	42.9	46.4	3/2
20	2/3	100.9	96.7	2
	3/2	138.9	90.7	2
	4/1	150.5	134.3	2
	1/0	162.5	145.6	3/2

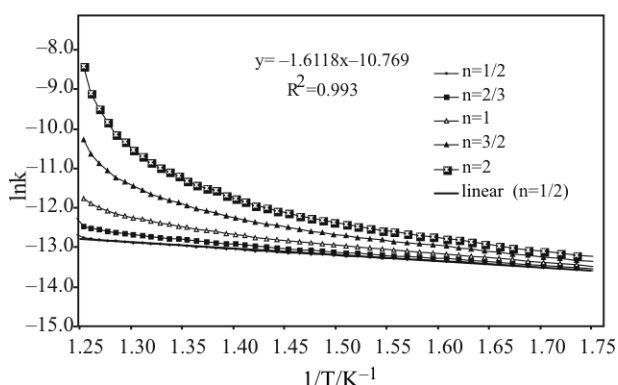


Fig. 4 Coats and Redfern method result of $(-210+149) \mu\text{m}$ particle size sample with a heating rate of 5 K min^{-1}

should result in a straight line of slope equals $-E/2.303R$ for the corrected value of reaction order. In this study, reaction order was assumed to be $1/2$, $2/3$, 1 , $3/2$ and 2 . Coefficient of determinations of each reaction was calculated and the highest coefficient of determination was found as $1/2$ for oil shale. As an example the TG and DTG curves kinetic graph of $(-210+149) \mu\text{m}$ particle size sample with a heating rate of 5 K min^{-1} was chosen to explain the kinetic behaviour of oil shale (Fig. 4).

Through the kinetic analysis it was observed that higher activation energies were obtained by the Coats and Redfern method (Table 3) with oil shale. It was concluded that activation energy values had 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.

Conclusions

Göynük oil shale, polystyrene and several polystyrene–oil shale blends combustion 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 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 from this analysis is that the polystyrene accelerates the decomposition of the organic matter in the oil shale. The highest burn-out temperatures of different blending ratios was measured for $3/2$ polystyrene/oil shale ratio for all heating rate values.

Two different models (Arrhenius and Coats and Redfern) all based on Arrhenius kinetic theory were used for kinetic analysis of the data generated by the TG experiments. Through the kinetic analysis it was observed that higher activation energies were obtained by the Coats and Redfern method with oil shale. It was concluded that activation energy values had increased with increasing polystyrene/oil shale blending ratio for all heating rates by the Arrhenius and Coats and Redfern method. The activation energies decreased with the decrease in the mass ratio of polystyrene to oil shale in the blends.

Nomenclature

C	carbon content of oil shale (mass% daf)
daf	dry ash free basis
d	dry basis
D_p	oil shale particle size (μm)
E	apparent activation energy (kJ mol^{-1})
H	hydrogen content of oil shale (mass% daf)
k_0	frequency factor (min^{-1})
N	nitrogen content of oil shale (mass% daf)
n	order of reaction
O	oxygen content of oil shale (mass% daf)
R^2	determination coefficient
S	total sulfur content of oil shale (mass% daf)
T	temperature (K)
t	time (min)
T_m	temperature of maximum decomposition rate (K)
W	weight of oil shale at any time (mg)

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