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KINETICS OF THE PYROLYSIS AND COMBUSTION OF GÖYNÜK OIL SHALE

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The pyrolysis and combustion kinetics of Göynük oil shale were investigated by thermogravimetric analysis in the present study. All experiments were conducted at non-isothermal conditions with a heating rate of 10–60 K min^{-1} in the 298–1173 K temperature interval under argon and air atmospheres for pyrolysis and combustion, respectively. Differential thermogravimetric data were analyzed by a reaction rate model assuming first order kinetics.

Keywords: *combustion, oil shale, pyrolysis, 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 pyrolysis and 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 [7–13].

The objective of this research was to investigate the pyrolysis and combustion of Göynük oil shale by thermogravimetry. Effect of heating rate on pyrolysis and combustion kinetics was examined to determine the frequency factor and apparent activation energy values.

Experimental

Göynük oil shale from the western Black Sea area of Turkey was 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) $149>D_p>88$ 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.

Table 1 Elemental analysis and ash content of the Göynük oil shale

Component (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 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 pyrolysis and combustion reactions were conducted under an argon and an air atmospheres, respectively. Gas 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 pyrolysis and combustion temperature, 298–1173 K; and range of heating rate, 10–60 K min^{-1}, particle size:

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149>D_p>88 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. The mean of the measured values were used in all subsequent k_0 and E_a calculations.

Results and discussion

Pyrolysis

Thermogravimetric analysis technique was applied to determine the pyrolysis kinetics of the Göynük oil shale. The relative mass loss (TG) and corresponding pyrolysis rate (DTG) curves of the oil shale samples obtained at different heating rates are represented in Figs 1 and 2, respectively. Figure 1 shows the mean curves obtained, referred to a starting sample mass of approximately 20 mg. There are three temperature ranges to be considered. Below 523 K, the oil shale looses its moisture. Between 523 and 823 K, the mass loss is significant for lower heating rates. The third stage, which occurred at higher temperatures exceeding 823 K, is due to the decomposition of carbonate. As indicated in Fig. 1, in the course of the pyrolysis of oil shale for all of the heating rates examined, the organic matter decomposition yield achieved (from 523 to 823 K) were ~33.6% of the total mass of the sample, the variation being linear. The difference between rapid and slow heating rates is that rapid heating may reduce the time needed to attain a specified mass loss. Under the same operating conditions it was found that the heating rate had almost no effect on the organic matter decomposition yield. The height of the DTG peaks gradually increases with the increase of the heating rate (Fig. 2). The variation in 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 pyrolysis is shown in Table 2.

Table 2 Variation in maximum decomposition rate peak, temperature of the maximum decomposition rate (T_m), and total conversion values relative to the heating rate

Process	Heating rate/ K min^{-1}	DTG_m/ mg min^{-1}	T_m/ K	TC/ %
pyrolysis	10	0.0461	705	21.8
	20	0.1681	725	21.2
	30	0.2869	729	22.2
	60	0.6518	751	22.3
combustion	10	0.1703	740	23.0
	20	0.3637	807	23.5
	30	0.3976	809	25.6
	60	0.5336	829	24.6

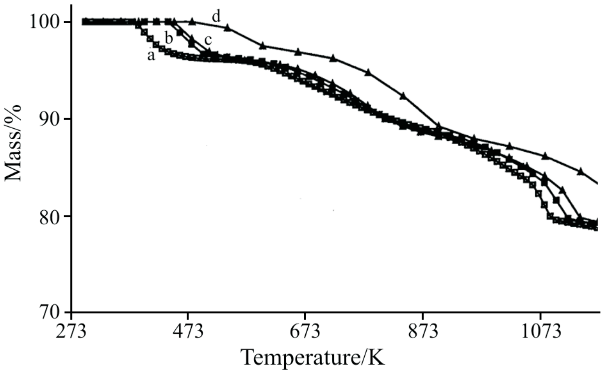

Fig. 1 TG curves of pyrolysis of Göynük oil shale at different heating rates; a – 10 K min^{-1}, b – 20 K min^{-1}, c – 30 K min^{-1}, d – 60 K min^{-1}

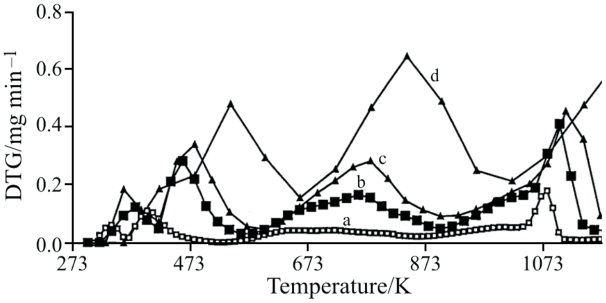

Fig. 2 DTG curves of pyrolysis of Göynük oil shale at different heating rates; a – 10 K min^{-1}, b – 20 K min^{-1}, c – 30 K min^{-1}, d – 60 K min^{-1}

Conversion values were calculated with respect to the mass of the moisture-free oil shale fed to the system. Total conversion values were almost constant at all heating rate values for pyrolysis.

Combustion

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. The relative mass loss and corresponding combustion rate curves of the oil shale samples obtained at different heating rates are represented in Figs 3 and 4, respectively. Figure 3 shows the mean curves obtained, referred to a starting sample mass of approximately 20 mg. There are three temperature ranges to be considered. Below 450 K, the oil shale losses small amounts of pyrolysis water from decomposing phenolic structures and oxides of carbon from carboxylic and carbonyl groups. At around 573 K primary carbonization starts initially with the release of carbon dioxide and hydrogen. With increase in temperature up to 1050 K methane and other aliphatics are evolved together with hydrogen, carbon monoxide and alkyl aromatics. The third stage, between 1050 and 1100 K, is due to the decomposition of mineral matter.

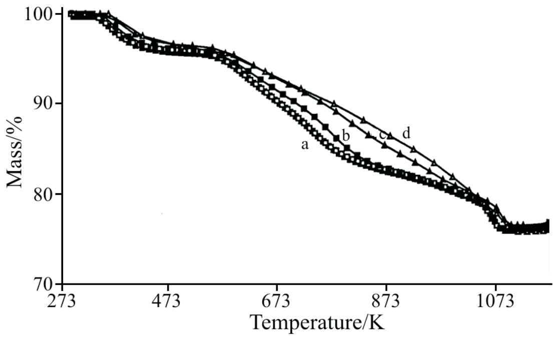

Fig. 3 TG curves of combustion of Göynük oil shale at different heating rates; a – 10 K min^{-1}, b – 20 K min^{-1}, c – 30 K min^{-1}, d – 60 K min^{-1}

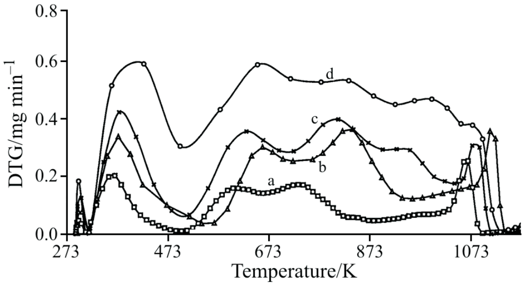

Fig. 4 DTG curves of combustion of Göynük oil shale at different heating rates; a – 10 K min^{-1}, b – 20 K min^{-1}, c – 30 K min^{-1}, d – 60 K min^{-1}

Burn-out temperatures, that represent the temperature where sample oxidation is complete, are around 1100 K and not affected by the change in heating rate.

The variation in 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 2. Total conversion values were almost constant at all heating rate values for combustion. Higher total conversion and temperature of the maximum decomposition rate values were obtained for combustion than to pyrolysis.

Kinetic model

The proposed kinetic model in this study is

$$-\frac{\mathrm{d}W}{\mathrm{d}t}=k_0\mathrm{e}^{-\mathrm{E_a}/\mathrm{RT}}W^{\mathrm{n}} \tag{1}$$

where W is the mass of oil shale at any time in mg, k_0 is the frequency factor in $mg^{(1-n)}$ min^{-1}, E_a 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

$$\ln\left(-\frac{\mathrm{d}W}{\mathrm{d}t}\right)=\ln k_0-\frac{E_\mathrm{a}}{RT}+n\ln W \tag{2}$$

Table 3 Kinetic parameters determined by the pyrolysis and combustion of Göynük oil shale

Process	Heating rate/ K min^{-1}	E_a/ kJ mol^{-1}	k_0/min^{-1}	R^2
pyrolysis	10	2.2	$3.9\cdot10^{-3}$	0.998
	20	11.4	$3.8\cdot10^{-2}$	0.988
	30	11.7	$1.5\cdot10^{-2}$	0.984
	60	15.2	$3.3\cdot10^{-1}$	0.985
combustion	10	2.5	$0.2\cdot10^{1}$	0.978
	20	2.9	$0.3\cdot10^{1}$	0.937
	30	2.3	$0.4\cdot10^{1}$	0.993
	60	2.5	$0.7\cdot10^{1}$	0.981

Table 4 Comparison of the values of the activation energy and the reaction order determined in this study with those of the literature

Reference	Process	E_a/kJ mol^{-1}	n
present study	pyrolysis	2.2	1
[2]		55.2	1
[4]		24.3	1
[15]		6.4	1
present study	combustion	2.3	1
[13]		120	1
[14]		66	1
[16]		54	1

In order to determine the pyrolysis kinetics of the oil shale, Eq. (2) was applied to the TG and DTG data. Assuming first-order kinetics (n=1), kinetic constants k_0, E_a and determination coefficients (R^2) were calculated from the multiple linear regression analysis.

In order to determine the pyrolysis and combustion kinetics of the Göynük oil shale Eq. (2) was applied to the TG data in the linear regions (523–823 K) of the TG curves. Kinetic constants k_0 and E_a were determined by the multiple linear regression analysis method and are given in Table 3. Results showed that the kinetic parameters changed with the heating rate for pyrolysis of the oil shale. A little change in activation energy values with increasing heating rate was observed for combustion of Göynük oil shale.

The minimum activation energy value obtained from the proposed reaction kinetics appears to be the lowest one when compared with those obtained from the literature (Table 4). However, it should be noted that the subject studies were not conducted under identical conditions.

Conclusions

Oil shale pyrolysis and combustion under atmospheric pressure has been studied using a thermogravimetric apparatus. The experimental results showed that the total conversion values were almost independent of heating rate during oil shale pyrolysis and combustion. Effect of the heating rate on the pyrolysis and combustion kinetics of the Göynük oil shale was investigated. It was concluded that both the temperature of maximum decomposition rate and the maximum decomposition rate increase with heating rate.

A first order reaction model of oil shale pyrolysis and combustion at atmospheric pressure for Göynük oil shale has been proposed. Activation energies and frequency factors were determined. A little change in activation energy values with increasing heating rate was observed for Göynük oil shale. The minimum activation energy, 2.2 kJ mol^{-1}, was determined at the heating rate of 10 K min^{-1}.

Nomenclature

C	carbon content of oil shale (mass% daf)
daf	dry ash free basis
db	dry basis
D_p	oil shale particle size (μm)
E_a	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	mass of oil shale at any time (mg)

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