

HEATING RATE EFFECT ON THE DSC KINETICS OF OIL SHALES

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This research was aimed to investigate the combustion and kinetics of oil shale samples (Mengen and Himmetoğlu) by differential scanning calorimetry (DSC). Experiments were performed in air atmosphere up to 600°C at five different heating rates. The DSC curves clearly demonstrate distinct reaction regions in the oil shale samples studied. Reaction intervals, peak and burn-out temperatures of the oil shale samples are also determined. Arrhenius kinetic method was used to analyze the DSC data and it was observed that the activation energies of the samples are varied in the range of 22.4–127.3 kJ mol⁻¹ depending on the oil shale type and heating rate.

Keywords: activation energy, DSC, heating rates, oil shale, reaction kinetics, thermal analysis

Introduction

Energy production is one of the most important concerns of the world. The inevitable dependence of the industrialized world on energy requires the sustainable development of energy. To develop an energy policy that can both ensure current needs and meet future expectations, a number of aspects have to be considered. These aspects include new techniques for efficient source utilization, exploration of new deposits and evaluation of potential alternatives. The common point of all these aspects is the suitability for all existing and prospective sources from the view of feasibility and environmental concerns [1]. Oil shale comprises the second largest potential fossil fuel in Turkey. The main oil shale resources are located in middle and western regions of Anatolia. The amount of proved explored reserves is around 2.22 billion tons while the total reserves are predicted to be 3 to 5 billion tons. Despite this vast potential, the stated amount cannot be accepted as the amount of commercial reserves. The deposits vary from 2100 to 18900 kJ kg⁻¹ in calorific value, revealing that each deposit requires a detailed study regarding its possible use [2].

Shih and Sohn [3] used non-isothermal TG with a variety of heating rates to determine kinetic parameters for Green River oil shale pyrolysis. Four different methods were employed for kinetics analysis and the results appear to be in fair agreement. The same group has employed non-isothermal TG for studying the oxidation kinetics of oil shale char under conditions in which diffusion and mass transfer effects were claimed to be unimportant. Thakur and Nuttall [4] studied the kinetics of the thermal decomposition of Moroccan oil

shale by isothermal and non-isothermal thermogravimetry. The combined use of non-isothermal and isothermal TG measurements has shown that the thermal decomposition of Moroccan oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow first-order kinetics. Kök and Pamir [5–8] used differential scanning calorimetry (DSC) to determine the combustion kinetics of oil shale samples by ASTM method. It was observed that higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Distinguishing peaks shifted to higher temperatures with an increase in heating rate. Activation energy values were found in the range of 131.8–185.3 kJ mol⁻¹. They also determined the thermal characteristics and kinetic parameters of oil shale samples by thermogravimetry (TG/DTG) at non-isothermal heating conditions both for pyrolysis and combustion processes. A general computer program was developed and the methods are compared with regard to their accuracy and the ease of interpretation of the kinetics of thermal decomposition. Activation energies of the oil shale samples were determined by five different methods and the results are discussed. Lisboa and Watkinson [9] used standard thermogravimetric apparatuses for the study of the chemical kinetics of oil shale pyrolysis and combustion, such as controlled temperature and simultaneous weighing of the sample. This study investigated the effects of key parameters, which could affect this identity, such as: the gas flow rate, the gas purity, the gas nature, the particle sizes and sample sizes. Jaber and Probert [10] studied two oil shale samples non-isothermally using a thermogravimetric analyser. The controlling parameters studied were the final temperature and influence of

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particle size as well as the heating rate employed during the process of thermal degradation of the oil shale sample. The integral method was used in the analysis of mass loss data to determine the pyrolysis and gasification kinetics. The activation energy decreased slightly as the shale-particle size reduced. Torrente and Galan [11] studied the kinetics of thermal decomposition of oil shale using thermogravimetry (TG/DTG). It was observed that the thermal decomposition of oil shale can be suitably described by overall first-order kinetics. No mass and heat transfer resistance was observed for the different particle sizes studied. Kök [12–14] studied the thermal characteristics of oil shale samples by thermal analysis techniques (TG-DTG, DSC and PDSC). Two distinct exothermic peaks were identified in all experiments known as low temperature oxidation and high temperature oxidation reaction regions. The pyrolysis process of all oil shale samples showed one exothermic effect on each total pressure studied. Kinetic data were analyzed by different methods and the results are discussed. He also reviewed the application of thermal analysis techniques on oil shale pyrolysis and combustion. Kök *et al.* [15] studied the thermal and organic geochemical investigation of Seyitömer oil shale. DSC and TG/DTG were used to determine the thermal behavior of oil shale sample. On the other hand, organic carbon content, pyrolysis and gas and liquid chromatograph experiments were conducted to determine the geochemical properties of oil shale sample. Han *et al.* [16] conducted combustion and pyrolysis experiments using thermogravimetric analyzer. The effect of various factors on combustion of oil shale was studied. Increase of heating rate can result in ignition temperature, burn-out temperature and maximum rate of combustion mass loss increasing. Homogeneous ignition mechanism of oil shale is ascertained using a hot stage microscope. Results show that activation energy will increase with heating rate. Kök and Acar [17] investigated the thermal characterization and kinetics of Karakus crude oil in the presence of limestone matrix. In combustion with air, three distinct reaction regions were identified known as low temperature oxidation (LTO), fuel deposition (FD) and high temperature oxidation (HTO). Five different kinetic methods used to analyze the TG/DTG data to identify reaction parameters. On the other hand, different $f(\alpha)$ models from literature were also applied to make comparison. Kök [18] investigated the role of clay on the combustion and kinetic behav-

ior of crude oils in limestone matrix. For this purpose, simultaneous TG (thermogravimetry) and DTA (differential thermal analysis) experiments were performed at three different heating rates at 10, 15 and 20°C min⁻¹, respectively. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clay's surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process.

Experimental

In this research, oil shale combustion experiments were performed with DuPont 9900 thermal analysis system with differential scanning calorimetry (DSC) module. DSC monitors differential heat flow of the samples either as a function of temperature or time in a varied but controlled atmosphere. Prior to the experiments, DSC system was calibrated for temperature readings using indium as reference standard. The oil shale samples (Mengen and Himmetoğlu) used in this research had a particle size <60 mesh and prepared according to the ASTM Standards (D 2013-72). DSC experiments were performed with a sample size of ~10 mg, at five different heating rates (2, 5, 10, 15 and 20°C min⁻¹). Air flow rate through the sample pan was kept constant at 50 mL min⁻¹, in the temperature range of 20–600°C. For repeatability, experiments were performed twice. The properties of the oil shale samples are given in Table 1.

Results and discussion

Differential scanning calorimetry (DSC) and thermogravimetry (TG-DTG) of oil shale samples has been used extensively as a means of determining the characteristics of devolatilization and kinetic parameters. Within the analysis of DSC data at different heating rates, it was observed that Mengen and Himmetoğlu oil shales has more than one reaction zone (Figs 1–2). First reaction region is known as low temperature oxidation (LTO) and the second one is the high temperature oxidation (HTO) zone. Low-temperature oxidation region occurs between 177 and 377°C depending on the heating rate and oil shale type. It has been established that the low temperature oxidation

Table 1 Properties of oil shale samples

Sample	Calc. value/J g ⁻¹	Water/%	Ash/%	C/%	H/%	O.N./%	S/%
Mengen	3555	9.50	68.40	10.05	1.90	8.80	0.85
Himmetoğlu	4540	12.90	60.5	13.60	1.50	10.48	0.99

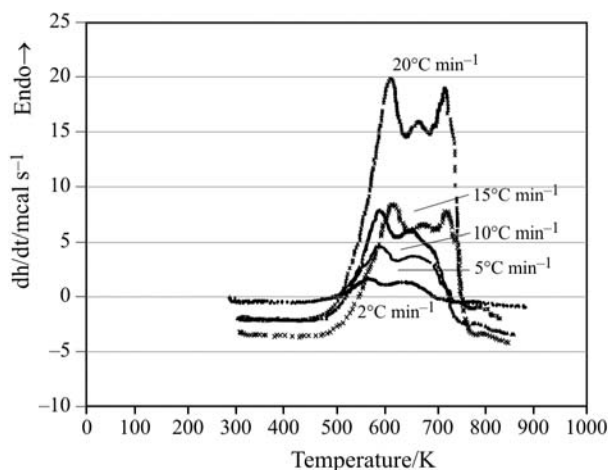


Fig. 1 DSC curves of Mengen oil shale at different heating rates

leads to the reduction of the H/C ratio, and an increase in the yield of CO₂ and H₂O, which is explained by the formation of oxygen bonds. On the other hand, high temperature oxidation region occurs between 337 and 512°C depending on the heating rate and oil shale type. From the experiments, it was also observed that the reaction intervals, peak and burn-out temperatures of the oil shale samples increased as the heating rate increased (Table 2).

Kinetic analysis

Kinetic data were obtained from the differential scanning calorimetry (DSC) curves, assuming first

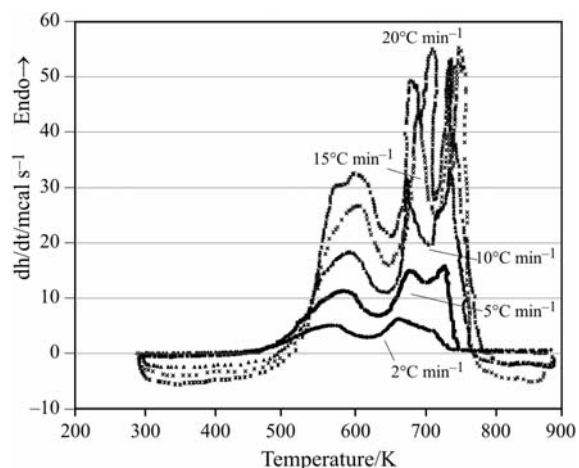


Fig. 2 DSC curves of Himmetoğlu oil shale at different heating rates

order combustion reaction for the fuel laid down in this region.

$$dh/dt = kh^n \tag{1}$$

The temperature dependence of *k* is expressed by the following Arrhenius equation:

$$k = A_r \exp(-E/RT) \tag{2}$$

Assuming first-order kinetics,

$$dh/dt = A_r \exp(-E/RT)h \tag{3}$$

$$[(dh/dt)1/h] = A_r \exp(-E/RT) \tag{4}$$

taking the logarithm of both sides,

$$\log[(dh/dt)1/h] = \log A_r - E/2.303RT \tag{5}$$

Table 2a Reaction intervals, peak and burn-out temperatures of Mengen oil shale (LTO)

Heating rate/ °C min ⁻¹	Reaction interval/°C	Peak temperature/ °C	Burn-out temperature/ °C
2	177–307	295	307
5	200–340	315	340
10	220–360	320	360
15	250–360	330	365
20	255–370	335	370

Table 2c Reaction intervals, peak and burn-out temperatures of Himmetoğlu oil shale (LTO)

Heating rate/ °C min ⁻¹	Reaction interval/°C	Peak temperature/ °C	Burn-out temperature/ °C
2	177–348	295	348
5	187–357	311	357
10	223–362	321	362
15	233–367	331	367
20	252–377	333	377

Table 2b Reaction intervals, peak and burn-out temperatures of Mengen oil shale (HTO)

Heating rate/ °C min ⁻¹	Reaction interval/°C	Peak temperature/ °C	Burn-out temperature/ °C
2	337–457	361	457
5	350–460	381	470
10	380–480	385	480
15	430–490	450	490
20	440–500	455	500

Table 2d Reaction intervals, peak and burn-out temperatures of Himmetoğlu oil shale (HTO)

Heating rate/ °C min ⁻¹	Reaction interval/°C	Peak temperature/ °C	Burn-out temperature/ °C
2	337–447	393	447
5	367–452	404	452
10	387–457	407	457
15	382–462	421	460
20	389–512	440	512

where h is the fraction of the enthalpy yet to be released, E is the activation energy, T is the temperature, A_r is Arrhenius constant, n is the reaction order and k is the rate constant expressed in terms of usual Arrhenius relation. When $\log[(dh/dt)/h]$ is plotted vs. $1/T$ a straight line is obtained which will have a slope equal to $-E/2.303R$.

In general, DSC kinetic study under combustion process is extremely complex for oil shales. As mentioned, oil shale samples have more than one

reaction region so the activation energy values were calculated for both reaction regions (Table 3). Throughout the kinetic analysis of Mengen and Himmetoğlu oil shales, it was observed that the activation energy values in low temperature oxidation region are generally higher than those of the activation energy values in high temperature oxidation region. This is probably due to the fact that the organic compounds mostly decompose at lower temperatures, which can be easily identified at low heating rates. As

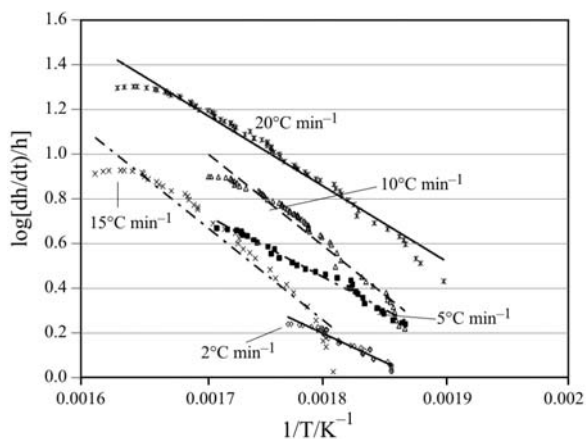


Fig. 3 Arrhenius plot of Mengen oil shale at different heating rates (LTO)

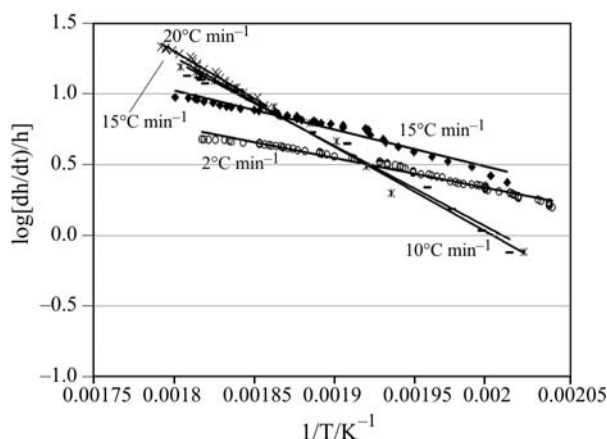


Fig. 5 Arrhenius plot of Himmetoğlu oil shale at different heating rates (LTO)

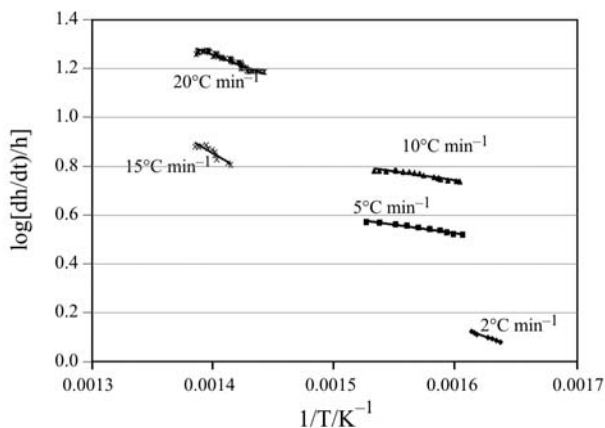


Fig. 4 Arrhenius plot of Mengen oil shale at different heating rates (HTO)

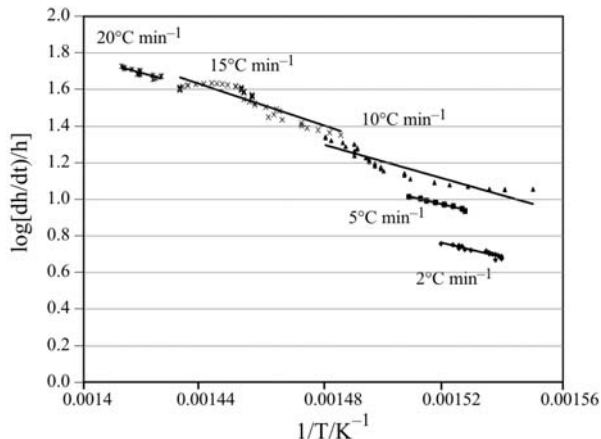


Fig. 6 Arrhenius plot of Himmetoğlu oil shale at different heating rates (HTO)

Table 3 Activation energies of oil shale samples (kJ mol^{-1})

Heating rate/ $^{\circ}\text{C min}^{-1}$	Mengen oil shale (LTO)	Mengen oil shale (HTO)	Himmetoğlu oil shale (LTO)	Himmetoğlu oil shale (HTO)
2	48.5	32.5	42.6	74.9
5	54.9	23.2	52.9	75.6
10	83.1	22.4	115.3	89.6
15	83.5	55.1	121.3	105.5
20	63.6	35.2	127.3	86.5

LTO–low temperature oxidation, HTO–high temperature oxidation

mentioned by Jiang *et al.* [19], there is no clear relationship between activation energy and heating rate. They concluded that the discrepancies in the activation energy for oil shale are not surprising, in that variations will occur depending on the type of oil shale.

Conclusions

In this research, differential scanning calorimetry (DSC) has been used to obtain combustion characteristics and kinetics of oil shales of different origin. The results showed that:

- Mengen and Himmetoğlu oil shales has more than one reaction zone known as low temperature and high temperature oxidation regions.
- The activation energies of the samples are varied in the range of 22.4–127.3 kJ mol⁻¹ depending on the oil shale type and heating rate.
- There is a general trend that the activation energy values in low temperature oxidation region is higher than those of the activation energy values in high temperature oxidation region.

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