

EVALUATION OF TURKISH OIL SHALES – THERMAL ANALYSIS APPROACH

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In this research, thermal characteristics of three Turkish oil shales (Himmetoğlu, Beypazarı and Hatıldağ) were studied by thermal analysis techniques (differential scanning calorimetry, thermogravimetry and pressurised differential scanning calorimetry) Two distinct exothermic peaks were identified in all experiments known as low-temperature oxidation and high-temperature oxidation reaction regions. Kinetic data were analysed by Arrhenius, and Coats and Redfern models and the results are discussed.

Introduction

Oil shale can be defined as a compact rock of sedimentary origin with ash content of more than 33 % and containing organic matter that yields oil when destructively distilled, but not appreciably when extracted with ordinary solvents. Oil shales contain organic matter mostly in the form of kerogen, which is defined as the fraction of the organic matter in a sedimentary rock insoluble in common petroleum solvents. The other, minor organic fraction called bitumen is soluble in organic solvents.

Thermal analysis (differential scanning calorimetry (DSC), thermogravimetry (TG/DTG) and pressurised differential scanning calorimetry (PDSC)) of oil shale samples has been extensively used as a means of determining the characteristics of devolatilization and kinetic parameters. Thermal methods providing information about net results of mass loss and calculation of kinetic parameters are based on simplifying assumptions, which do not correspond to the complex chemical reactions in the thermal degradation of oil shales.

Thakur and Nuttall [1] studied pyrolysis kinetics of Moroccan oil shale by the combined use of non-isothermal and isothermal thermogravimetry. It has shown that thermal decomposition of Moroccan oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow first-order kinetics. Among three models used, the Antony-Howard model yields lower deviation and thus provides a better fit of the data.

Shih and Sohn [2] used non-isothermal TG with a variety of heating rates to the determination of kinetic parameters for Green River oil shale pyrolysis. Four different methods were employed and the results appeared to be in a 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.

Lisboa and Watkinson [3] used standard thermogravimetric apparatuses for the study of chemical kinetics of oil shale pyrolysis and combustion. The thermogravimetric analysis must be carried out in conditions guaranteeing the observed reaction rate to be of the same order as the rate of chemical kinetics. They investigated the effects of key parameters which could affect this identity, such as: gas flow rate, gas purity and nature, and particle and sample sizes.

Jaber and Probert [4] studied two Jordanian oil shale samples, especially the influence of the final temperature and particle size as well as of the heating rate employed on the process of oil shale thermal degradation using a thermogravimetric analyzer. The integral method was used in the analysis of weight loss data to determine the pyrolysis and gasification kinetics. Gasification and pyrolysis of the investigated shales complied with first-order kinetics. The activation energy decreased slightly as the shale particle size was reduced.

Kök and Pamir [5] used DSC to determine combustion kinetics of oil shale samples by ASTM method. 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 to be in the range of 131.8–185.3 kJ/mol.

Berkovich *et al.* [6] presented a novel technique to thermal characterization of oil shale. This approach involves separation of unique components of oil shale, kerogen and clay minerals, using chemical and physical techniques. The heat capacity and enthalpy changes for kerogen and clay minerals were measured using non-isothermal modulated DSC from 25 to 500 °C. Enthalpy data for dehydration and pyrolysis of kerogen were also determined.

Williams and Ahmad [7] pyrolysed oil shale samples in a TG analyser in relation to heating rate and temperature using non-isothermal and isothermal analysis, respectively. The main region of weight loss corresponding to hydrocarbon oil and gas release was between 200–620 °C, and at higher temperatures significant weight loss was attributed to carbonate decomposition. Increasing of the heating rate shifted the reaction to higher temperatures. The kinetic data were analysed using Arrhenius, and Coats and Redfern methods. No clear relationship between activation energy and heating rate was found.

Kök and Pamir [8] determined thermal characteristics and kinetic parameters of oil shale pyrolysis and combustion processes by TG/DTG in non-isothermal heating conditions. A general computer program was

developed and the methods compared with regard to their accuracy and the ease of interpretation of thermal decomposition kinetics. Activation energies of the processes were determined by five different methods and the results are discussed.

Experimental

The oil shale samples studied in this research were taken from Himmetoğlu, Beypazarı and Hatıldağ oil shale fields (Fig. 1; Table 1).

Table 1. Properties of Oil Shale Samples

Sample	Calorific value, kJ/kg	Water, %	Ash, %	C, %	H, %	(O + N), %	S, %
Himmetoğlu	4540	12.9	60.5	13.6	1.5	10.48	0.99
Beypazarı	3550	2.4	65.2	8.4	1.6	4.55	0.21
Hatıldağ	3110	1.6	66.2	5.63	1.3	3.89	1.25

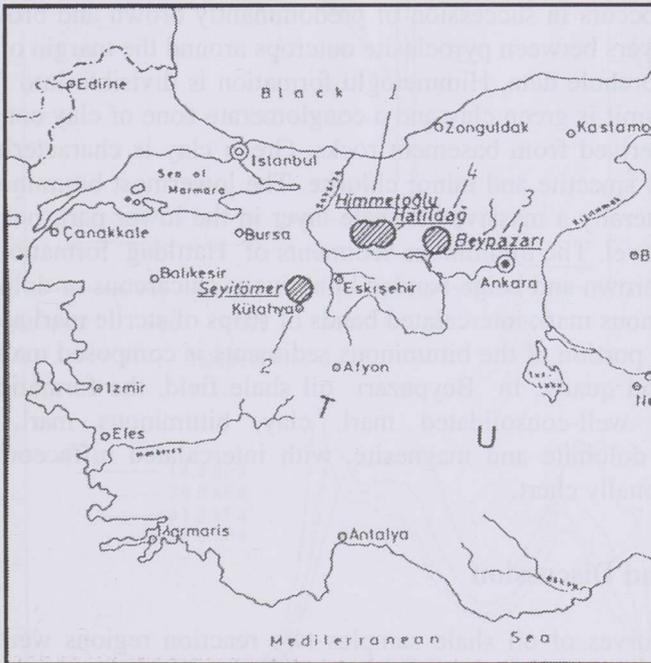


Fig. 1. Oil shale fields of Turkey

DSC and TG/DTG experiments were performed with a DuPont 9900 thermal analysis system. Sample size 10 mg, heating rate 10 °C/min, temperature range 20–600 °C and gas flow rate (air and nitrogen) 50 mL/min were used. Experiments with Himmetoğlu oil shale were also performed with a high-pressure differential scanning calorimetry (HPDSC). The oil

shale samples used had a particle size <60 mesh and were prepared according to ASTM Standards (ASTM D 2013-72). It is believed that for such small particles the effect of temperature distribution within the sample particle is eliminated. The thermal analysis system was calibrated for temperature reading with indium and calcium oxalate monohydrate. It was essential to calibrate and balance for buoyancy effects to allow quantitative estimation of weight changes. The material chosen for investigating such effect was silver having a melting point of 960.8 °C. All the experiments were performed twice in order to attest their repeatability.

Geological Information on Oil Shale Fields [9]

The oil shale deposits (see Fig. 1) in Turkey are widely distributed in middle and western Anatolia. Turkish oil shales are of Palaeocene–Eocene and middle upper Miocene age. Host rocks are marl and clays containing heterogeneously and finely dispersed organic matter. Current reserves of oil shales are approximately 1400 million tons located in the following main deposits: Himmetoğlu, Beypazarı, Hatıldağ and Seyitömer. Himmetoğlu formation occurs in succession of predominantly brown and brownish-gray oil shale layers between pyroclastic outcrops around the margin of the basin.

From borehole data, Himmetoğlu formation is divisible into four zones. The lower unit is green clay and a conglomerate zone of clay conglomerate, which is derived from basement rocks. Green clay is characterized by the presence of smectite and minor chlorite. The lowermost bituminous-banded marl is generally a massive oil shale layer in the lower part, but banded in the upper level. The bituminous sediments of Hatıldağ formation generally consist of brown and beige-banded bituminous calcareous or dolomitic marl and bituminous marl, intercalated bands of strips of sterile marl are frequent. The clastic portion of the bituminous sediments is composed mainly of clay minerals and quartz. In Beypazarı oil shale field, the formation consists mostly of well-consolidated marl, clay, bituminous marl, dolomitic limestone, dolomite and magnesite, with intercalated tuffaceous horizons and occasionally chert.

Results and Discussion

On DSC curves of oil shale samples two reaction regions were observed (Fig. 2,a). DSC analysis showed that the heat released from Himmetoğlu, Beypazarı and Hatıldağ oil shale samples is 11880, 1840 and 832 kJ/kg, respectively. The highest energy release and low on-set temperature of the Himmetoğlu oil shale shows its highest quality. High calorific value shows that the organic matter present in this shale is maturer than that in other oil shales.

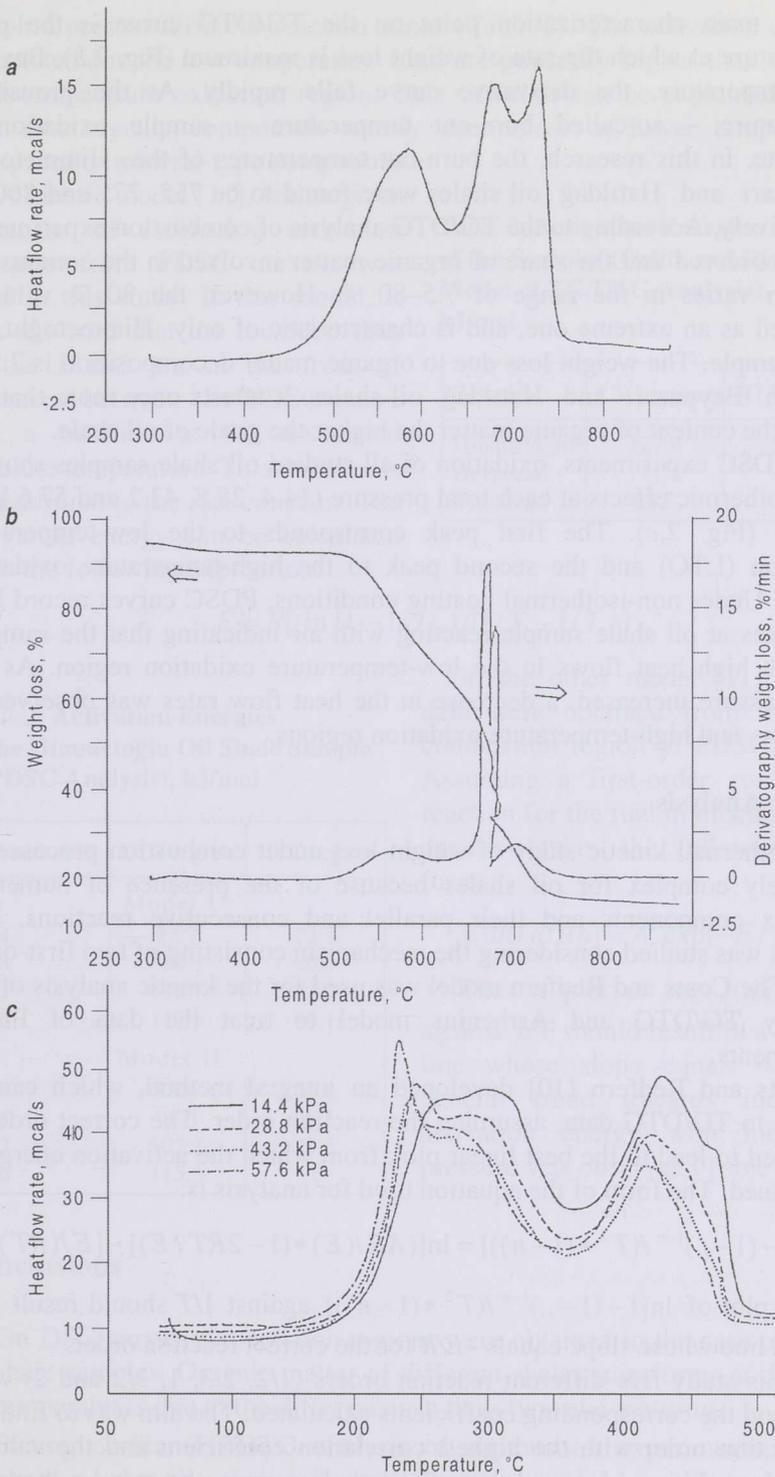


Fig. 2. DSC (a), TG/DTG (b), and PDSC (c) curves of Himmetoğlu oil shale

The main characterization point on the TG/DTG curve is the peak temperature at which the rate of weight loss is maximum (Fig. 2,b). Beyond that temperature, the derivative curve falls rapidly. At the prevailing temperature – so-called burn-out temperature – sample oxidation is complete. In this research, the burn-out temperatures of the Himmetoğlu, Beypazarı and Hatıldığ oil shales were found to be 755, 775 and 860 K, respectively. According to the TG/DTG analysis of combustion experiments, it was observed that the share of organic matter involved in the combustion reaction varies in the range of 7.5–80 %. However, the 80 % value is observed as an extreme one, and is characteristic of only Himmetoğlu oil shale sample. The weight loss due to organic matter decomposition is 7.5 % for both Beypazarı and Hatıldığ oil shales. It attests once more that the higher the content of organic matter the higher the grade of oil shale.

In PDSC experiments, oxidation of all studied oil shale samples showed two exothermic effects at each total pressure (14.4, 28.8, 43.2 and 57.6 kPa) applied (Fig. 2,c). The first peak corresponds to the low-temperature oxidation (LTO) and the second peak to the high-temperature oxidation (HTO). Under non-isothermal heating conditions, PDSC curves record heat flow rates at oil shale sample reacting with air indicating that the samples generate high heat flows in the low-temperature oxidation region. As the total pressure increased, a decrease in the heat flow rates was observed in both low- and high-temperature oxidation regions.

Kinetic Analysis

Non-isothermal kinetic study of weight loss under combustion processes is extremely complex for oil shales because of the presence of numerous complex components and their parallel and consecutive reactions. The kinetics was studied considering the mechanism consisting of two first-order steps. The Coats and Redfern model was used for the kinetic analysis of the data by TG/DTG and Arrhenius model to treat the data of PDSC experiments.

Coats and Redfern [10] developed an integral method, which can be applied to TG/DTG data, assuming the reaction order. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation used for analysis is:

$$\ln[1 - (1 - \dots)^{1-n} / (T^2 * (1 - n))] = \ln[(AR / (E) * (1 - 2RT / E)] - [E / (RT)]$$

Thus a plot of $\ln[1 - (1 - \dots)^{1-n} / (T^2 * (1 - n))]$ against $1/T$ should result in a straight line whose slope equals $-E/R$ for the correct reaction order.

In this study five different reaction orders (1/2, 2/3, 1, 3/2 and 2) were tested and the corresponding coefficients calculated. The aim was to find out the reaction order with the highest correlation coefficient and the value 1 agreed best. It was observed that all oil shale samples have more than one transmission zone, so the kinetic parameters were calculated for both peaks

which represent different reaction zones (Table 2). The activation energies calculated for the low-temperature zone are generally higher than those of high-temperature oxidation region. This situation can be explained by the fact that organic compounds mostly decompose at lower temperatures compared to mineral-type compounds.

A kinetic model [11], which gives a means of estimating activation energies from PDSC curves, was used in this study. In this model, it was assumed that the recorded data of the PDSC are in the form of distances between the PDSC curve and a baseline at the associated absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$-E = R[(\ln D_1 - \ln D_2)/(1/T_1 - 1/T_2)]$$

Table 3. Activation Energies of the Himmetoğlu Oil Shale Sample (HPDSC Analysis), kJ/mol

Pressure, kPa	LTO region	HTO region
Model I		
14.4	82.7	72.3
28.8	100.7	80.9
43.2	112.7	85.2
57.6	119.6	86.1
Model II		
14.4	78.6	69.8
28.8	98.5	75.3
43.2	107.8	79.5
57.6	115.3	.6

Table 2. Activation Energies of the Samples (Coats and Redfern Model of TG/DTG Analysis), kJ/mol

Sample	LTO region	HTO region
Himmetoğlu	127.6	24.5
Beypazarı	111.6	64.4
Hatıldağ	88.7	17.9

In the other model [11], kinetic data were obtained from the coke combustion region of PDSC curves. Assuming a first-order combustion reaction for the fuel in this region the equation takes the following final form:

$$[(dh/dt)lh] = A_r \exp(-E/RT)$$

Thus a plot of $\log [(dh/dt)lh]$ against $1/T$ should result in a straight line whose slope equals $-E/R$. A general trend towards increasing activation energy with increasing pressure was observed (Table 3).

Conclusions

1. On DSC curves two reaction regions were obtained in the case of all oil shale samples. Organic matter of different shales transforms at different temperatures due to the differences in their type and maturity.
2. Basing on the TG/DTG analysis of combustion experiments, it was observed that the share of organic matter involved in the combustion reaction varies in the range of 7.5–80 %.

3. In PDSC experiments, it was observed that as the applied total pressure is increased, activation energies of the samples also increase.
4. Throughout the kinetic analysis of the combustion experiments, it was found that low-temperature oxidation region activation energies are generally higher than those of high-temperature oxidation region, and this can be explained by the decomposition of organic matter.

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