

PYROLYSIS KINETICS OF OIL SHALES DETERMINED BY DSC AND TG/DTG

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Kinetics of oil shale pyrolysis was studied by differential scanning calorimetry and non-isothermal thermogravimetry. In nitrogen atmosphere two different mechanisms causing mass loss were observed: distillation in the region between ambient temperature and 500 K, visbreaking and cracking in the region of 500–800 K. Kinetic parameters of the sample pyrolysis are determined using different kinetic 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. Oil yield is much less when shale is extracted with ordinary solvents. The keyword is commercial amount of oil because petroleum source rocks, which often contain 1 % organic matter, can produce commercial amounts over geological times.

On the contrary, oil shales must have large fraction of organic matter to be of economic interest. The organic matter content of an oil shale should be approximately 5.5 wt.%, just to provide the calorific requirements necessary to heat the rock to 500 °C in order to produce shale oils by thermal decomposition of the organic matter. Below this amount of organic matter, the rock cannot be a source of energy, because it takes more energy to heat the rock than can be derived from the produced oil shale. A lower limit of 5 % organic matter is sometimes used to define the commercial deposit.

Differential scanning calorimetry (DSC) and differential thermogravimetry (DTG) of oil shale samples have 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 of chemical reactions occurring during thermal degradation of oil shale. The study of pyrolysis kinetics is essential for understanding the mechanisms and for mathematical modelling of

pyrolysis process, which may lead to improved techniques for oil shale conversion. In addition, as pyrolysis is directly related to the chemical composition of oil shale, the related kinetic parameters derived from thermal analysis can also be used for oil shale characterization.

Thakur and Nuttall [1] studied the pyrolysis kinetics of thermal decomposition of Moroccan oil shale by isothermal and non-isothermal TG. The combined use of these measurements has shown that thermal decomposition of oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions followed the first-order kinetics.

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

Lisboa and Watkinson [3] used standard TG apparatuses to study 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: flow rate, purity, and nature of gas, the particle and sample size.

Skala *et al.* [4] investigated the pyrolysis kinetics of oil shales under non-isothermal conditions using thermal methods. The results obtained were incorporated into the multi-step kinetic model which was adjusted according to the specific properties of particular oil shale samples and tested by comparison of the experimental and simulated TG, DTG and DSC curves.

Skala and Sokic [5] applied a kinetic expression commonly used in thermal analysis of oil shale pyrolysis. The obtained results showed that the greatest values of activation energy were determined using isothermal TG, while combined non-isothermal and isothermal TG gave the smallest ones.

Lillack and Schwochau [6] performed non-isothermal pyrolysis experiments on an immature oil shale sample. Evaluation of the experimental evolution profiles using a kinetic model yielded more kinetic parameters.

Jaber and Probert [7] studied oil shale samples by non-isothermal TG. The controlling parameters studied were the final temperature and the influence of particle size as well as the heating rate employed during the process of thermal degradation of oil shale sample. An integral method was used in the analysis of weight loss data to determine the pyrolysis and gasification kinetics. The activation energy decreased slightly as the shale-particle size was reduced.

Kök *et al.* [8–9] determined the pyrolysis and combustion kinetics of oil shale samples and 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. Two distinct peaks were identified in combustion experiments known as low-temperature oxidation and high-temperature oxidation reaction regions at different pressures.

Williams and Ahmed [10] studied oil shale pyrolysis using TG in relation to heating rate and temperature using non-isothermal and isothermal analy-

sis, respectively. It was found that for the oil shale samples analyzed increasing the heating rate shifted the reaction to higher temperatures. There was no clear relationship between activation energy and heating rate.

Experimental

In this research, differential scanning calorimetry and thermogravimetry experiments were performed with *Dupont* 9900 thermal analysis system. Three oil shale samples (Çan, Himmetoğlu and Mengen – see Table 1) studied in this research were from different deposits, prepared according to ASTM Standards (ASTM D 2013-72) and had a particle size < 60 mesh. It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated.

Table 1. Properties of Oil Shale Samples

Oil shale	Calorific value, cal/g	Water, %	Ash, %	C, %	H, %	(O + N), %	S, %
Çan	925	12.4	80.5	10.1	1.95	10.05	0.98
Himmetoğlu	1085	12.9	60.5	13.6	1.5	10.48	0.99
Mengen	850	9.5	68.4	10.05	1.9	8.8	0.85

The DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was calibrated for buoyancy effects to allow quantitative estimation of weight changes.

The resulting curves were obtained using the following conditions in both DSC and TG/DTG experiments: nitrogen atmosphere; flow rate 50 mL/min; sample mass 10 mg; heating rate 10 K/min; temperature range 295–875 K.

All the experiments were performed twice for reproducibility.

Kinetic Models

Calculation of kinetic data is based on the formal kinetic equation

$$d\alpha/dt = k\alpha^n \quad (1)$$

where α is the amount of sample undergoing reaction;

n is the reaction order;

k is the specific rate constant.

The temperature dependence of k is expressed by the Arrhenius equation

$$k = A \exp[-E/RT] \quad (2)$$

where A is the Arrhenius constant;

E is the activation energy;

R is the gas law constant.

TG/DTG data of the samples were analyzed using four different kinetic models known as Arrhenius [11], Coats & Redfern [12], Horowitz & Metzger, and Ingraham & Marrier [13] and DSC data – using a kinetic model developed by Roger & Morris [13].

Arrhenius Model

In this method, since the measured rate of mass loss accounts for gross changes in the system, the Arrhenius-type reaction model assumes that the rate of mass loss of the total sample depends only on the rate constant, the mass of sample remaining W and the temperature:

$$\log [(dW/dT)/W] = \log A - (E/RT) \quad (3)$$

In the plot of

$$\log [(dW/dT)/W] \text{ vs. } 1/T$$

there appear to be regions of marked linearity. The slope of such a linear portion is proportional to the activation energy, and the intercept to the Arrhenius constant.

Coats & Redfern Model

Coats & Redfern developed an integral method, which can be applied to TG/DTG 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 final form of the equation used for analysis is

$$\ln [1 - (1 - \alpha)^{1-n}/(T^2x(1-n))] = \ln [(AR/(\beta E) \times (1 - 2RT/E)) - [E/(RT)]] \quad (4)$$

where β is the heating rate.

Thus, a plot of

$$\ln [1 - (1 - \alpha)^{1-n}/(T^2x(1-n))] \text{ vs. } 1/T$$

should result in a straight line of slope equalling $-E/R$ for the correct value of reaction order, n .

Horowitz & Metzger Model

Horowitz and Metzger defined a reference temperature at the point of inflexion of the reaction curve and changed the variable T to θ using $\theta = T - T_m$. The value of α at the point of inflexion α determines the order of reaction:

$$\ln [-\ln (1 - \alpha)] = [(E\theta)/(RT_m^2)] \quad (5)$$

Thus, a plot of

$$\ln [-\ln (1 - \alpha)] \text{ vs. } \theta$$

should give a straight line with a slope of $E/2.303RT_m^2$.

Ingraham & Marrier Model

Ingraham and Marrier developed a simplified method for the determination of a heterogeneous reaction exhibiting linear kinetics. The temperature at any time is

$$T = \beta + \beta T$$

where β is the heating rate;

T is the initial temperature.

$$\log(dW/dT) = \log T - \log \beta + \log A - (E/2.303RT) \quad (6)$$

The activation energy is calculable from the slope of the plot:

$$\log [(dW/dT) - \log T + \log \beta] \text{ vs. } 1/T$$

Roger & Morris Model

This kinetic model gives a means of estimating activation energies from DSC curves. The recorded data are in the form of distances between the curve and the baseline at the specified absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$-E = R[(\ln D_1 - \ln D_2)/(1/T_1 - 1/T_2)] \quad (7)$$

where D_1 and D_2 are two distances from the baseline at the associated temperatures T_1 and T_2 ;

R is the gas constant (J/g mol K);

E is the activation energy (kJ/mol).

Results and Discussion

The pyrolysis process is exceedingly complex, and many competing processes contribute to thermal curves. In the initial stages of pyrolysis, distillation of low-molecular-weight species occurs, but as the temperature is raised, in addition to the increased rate of volatilization due to progressive evaporation of larger molecules, cracking of the compounds to volatile fragments may also occur.

In this research, when oil shale samples were heated in nitrogen atmosphere in DSC, it was observed that all thermal effects were endothermic and there were no exothermic regions (Fig. 1,*a*). In TG/DTG analysis, two different mechanisms causing mass loss were observed for all the oil shale samples studied (Fig. 1,*b*). In the region between ambient temperature and around 400 K distillation occurred. The second mechanism was visbreaking and cracking which was observed around 475–800 K.

The high-grade oil shale (Himmetoğlu) has lower initial temperature than poor-grade oil shales. Differences in the reaction temperature intervals and

peak temperatures (Table 2) are due to the differences in organic matter type and maturity of oil shale samples studied.

Table 2. Temperature Intervals and Peak Temperatures of Oil Shale Sample Pyrolysis Reactions, K

Indices	Oil shale		
	Çan	Himmetođlu	Mengen
D S C			
Temperature interval	490–735	475–750	505–780
Peak temperature	655	640	675
T G / D T G			
Region I:			
Temperature interval	300–400	300–395	300–385
Peak temperature	315	320	315
Region II:			
Temperature interval	520–800	475–770	500–775
Peak temperature	735	725	720

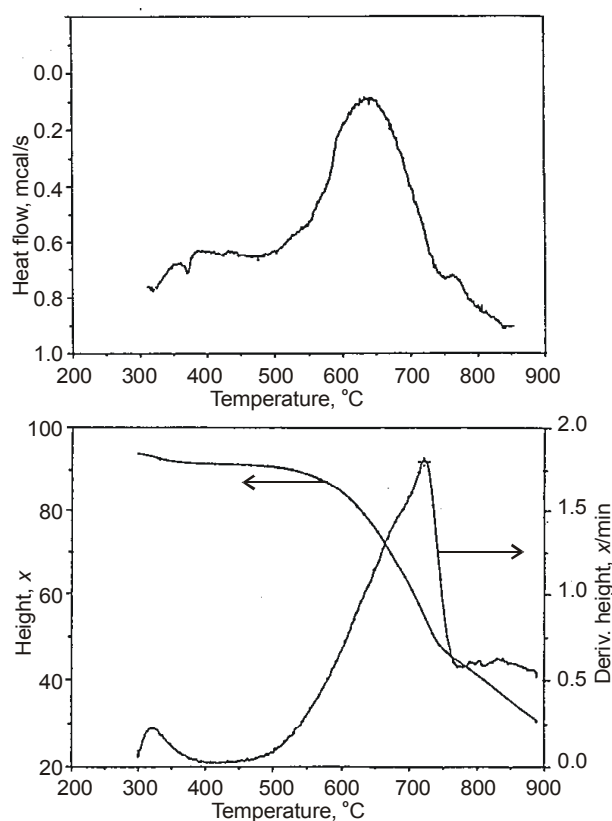


Fig. 1. DSC (a) and TG/DTG (b) curves of Himmetođlu oil shale pyrolysis

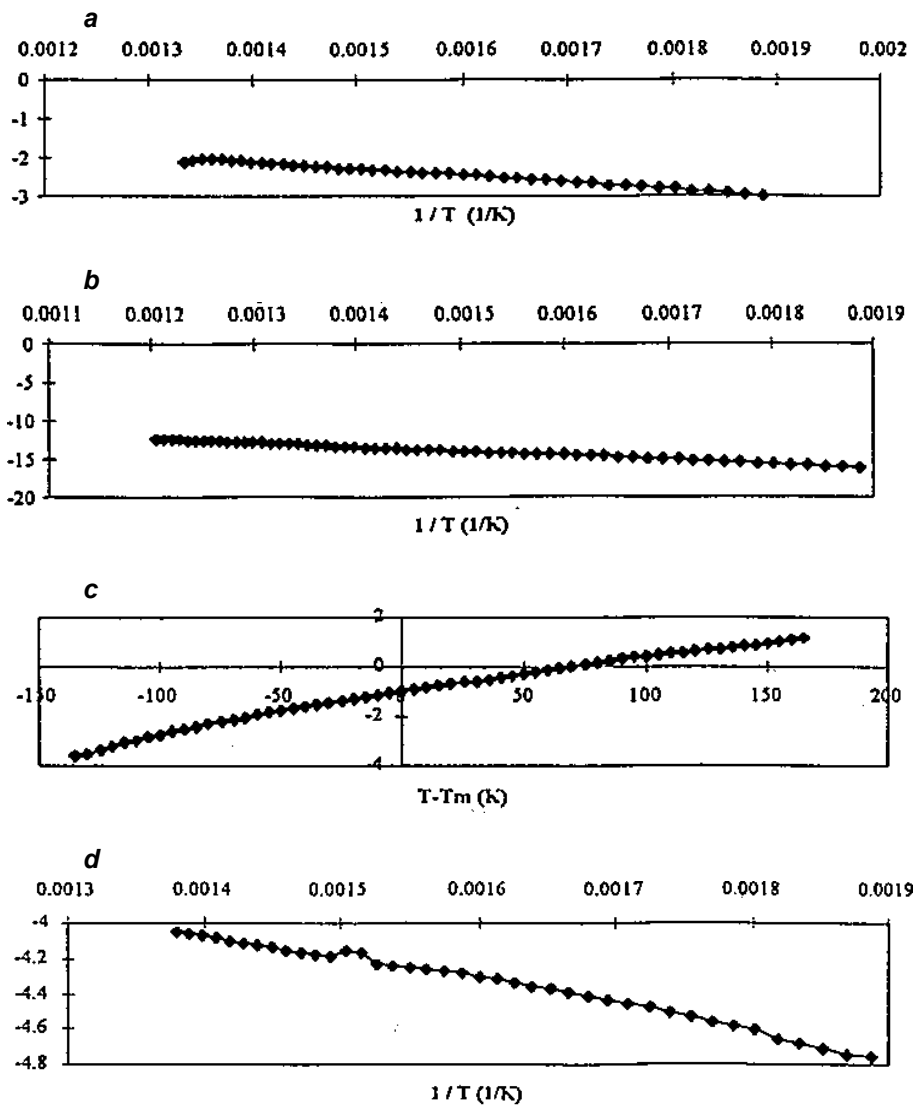


Fig. 2. Pyrolysis kinetics of Çan oil shale by different methods:
 a – Arrhenius model ($\log[(dW/dT)/W]$ vs. $1/T$);
 b – Coats & Redfern model ($\ln[1 - (1 - \alpha)^{1-n} / (T^2 x(1 - n))]$ vs. $1/T$);
 c – Horowitz & Metzger model ($\ln[-\ln(1 - \alpha)]$ vs. θ ; $\theta = T - T_m$);
 d – Ingraham & Marrier model ($\log[(dW/dT) - \log T + \log \beta]$ vs. $1/T$)

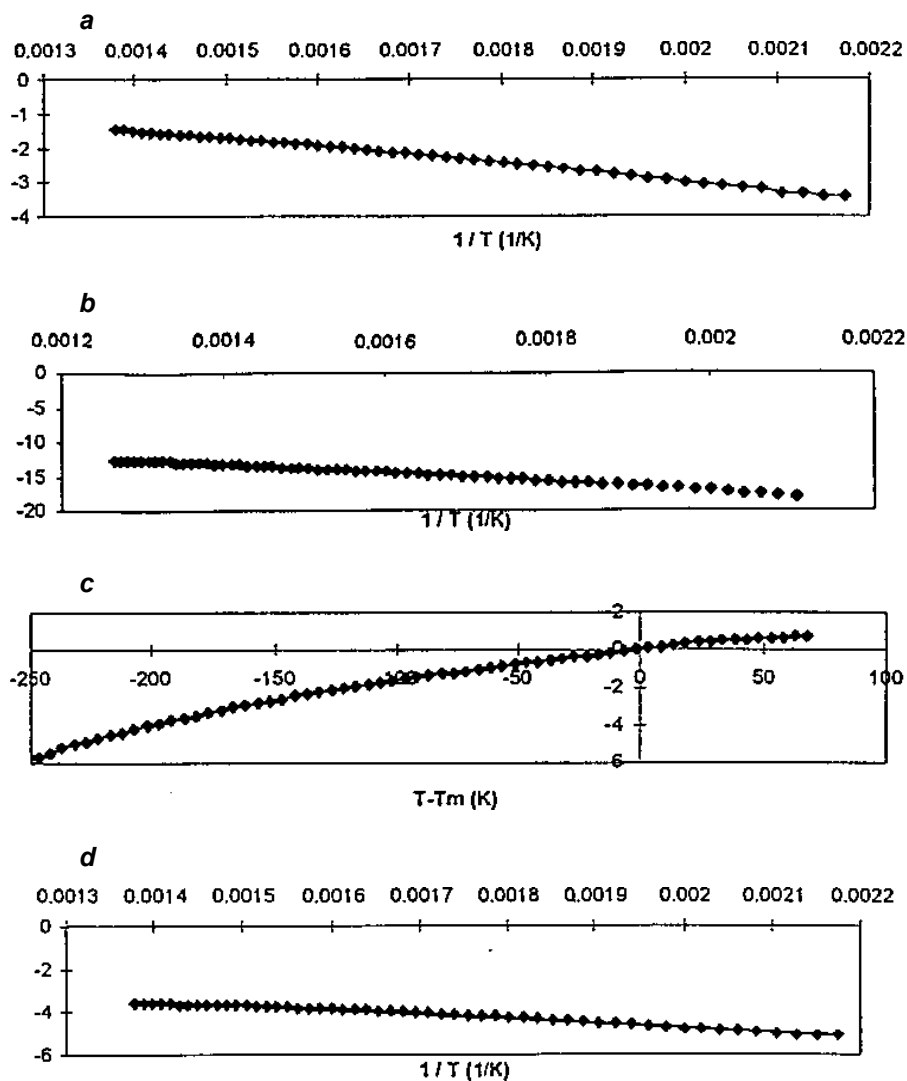


Fig. 3. Pyrolysis kinetics of Himmetođlu oil shale by different methods (for the legend, see Fig. 2)

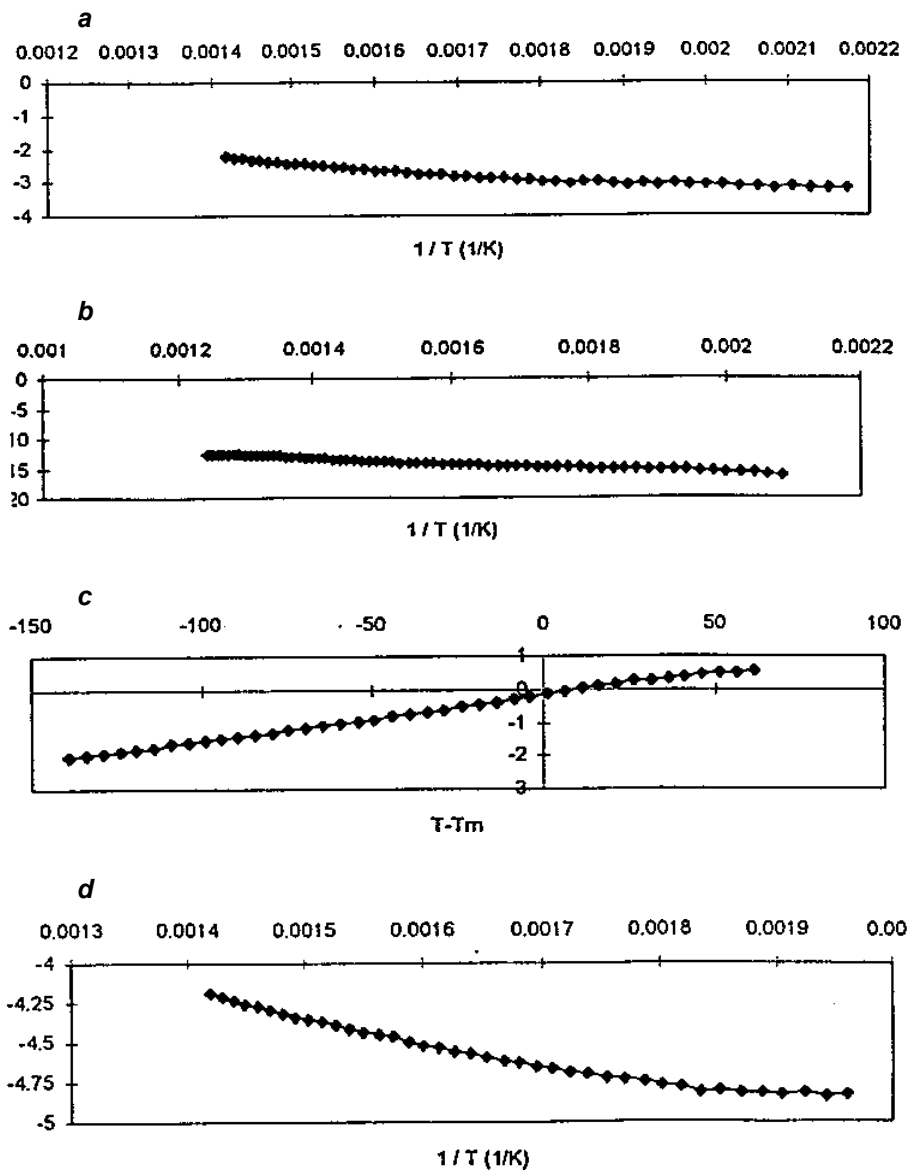


Fig. 4. Pyrolysis kinetics of Mengen oil shale by different methods (for the legend, see Fig. 2)

A general review of pyrolysis literature indicates that during pyrolysis reactions weight is lost initially at a constant rate corresponding to a zero-order process, and as temperature increases, the order usually becomes equal to unity. The nature and the yield of reaction products and kinetic parameters strongly depend on reaction conditions and sample properties. In this study, non-isothermal DSC and TG/DTG data, obtained for the pyrolysis of three oil shales, are used to derive the corresponding kinetic parameters via incorporation into a computer program, which systematically attempts to match such data with several well-known, solid-state decomposition kinetic models (Figs 2–4).

Table 3. Kinetic Parameters of Oil Shale Pyrolysis According to Various Models

Model	Sample		
	Çan	Himmetođlu	Mengen
Arrhenius	$y = -1703x + 0.265$ ($r = 0.992$)	$y = -2498x + 2.025$ ($r = 0.995$)	$y = -1267x + 0.589$ ($r = 0.936$)
Coats & Redfern	$y = -5511x + 5.697$ ($r = 0.999$)	$y = -1703x + 0.265$ ($r = 0.992$)	$y = -1703x + 0.265$ ($r = 0.992$)
Horowitz & Metzger	$y = -0.015x + 1.449$ ($r = 0.988$)	$y = -0.019x + 0.022$ ($r = 0.972$)	$y = -0.138x + 0.186$ ($r = 0.997$)
Ingraham & Marrier	$y = -1367x + 2.143$ ($r = 0.986$)	$y = -1993x + 0.733$ ($r = 0.978$)	$y = -1265x + 2.463$ ($r = 0.962$)

The values of reaction equation parameters and correlation coefficients r calculated for TG/DTG kinetic models are given in Table 3. The values of r vary between 0.93 and 0.99. The values of apparent activation energy E_a calculated by different models (Table 4) are quite similar, except for those determined by Horowitz & Metzger model. Differences in the E_a values are due to the different type of the kerogen in the oil shale sample. The values obtained by Horowitz & Metzger model are lower than the others due to high inflexion points under nitrogen atmosphere.

Table 4. Activation Energy Values E_a of Oil Shale Pyrolysis, kJ/mol

Model	Sample		
	Çan	Himmetođlu	Mengen
T G / D T G			
Arrhenius	49.5	57.5	30.7
Coats & Redfern	45.8	53.1	24.3
Horowitz & Metzger	41.1	46.6	21.8
Ingraham & Marrier	48.6	50.8	27.6
D S C			
Roger & Morris	34.3	38.1	19.9

Conclusions

- DSC experiments have shown that all thermal effects were endothermic.
- In TG/DTG experiments, two different mechanisms causing mass loss were observed for all the oil shale samples studied.
- Activation energies of oil shale sample pyrolysis are determined using five different kinetic models and their values are in the range of 19.9–57.5 kJ/mol.

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