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# Thermal investigation of Seyitomer oil shale

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## Abstract

This research presents the results of experimental study on the thermal investigation of Seyitomer oil shale sample. Thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) were used to determine the thermal behaviour of the oil shale sample. From the experiments and kinetic analysis, it was observed that Seyitomer oil shale sample have more than one reaction region where the activation energies of the first region are higher. Higher heating rates resulted in higher reaction temperatures both in DSC and TG/DTG experiments.

*Keywords:* Oil shale; Thermal analysis; Thermogravimetry; Differential scanning calorimetry; Reaction kinetics

## 1. Introduction

An oil shale can be defines 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 that is insoluble in common petroleum solvents. The other fraction called bitumen is soluble in organic solvents, but represents only a small amount of the organic matter in an oil shale. The oil shale deposits in Turkey are widely distributed in middle and western Anatolian. The information on the deposits is based on borehole data and the oil shales are of Palaeocene–Eocene and middle-upper Miocene age. Current reserves of oil shales in Turkey are ~1865 million tonnes, located in Seyitomer, Himmetoğlu, Hatildağ and Beypazari oil shale fields [1].

In Seyitomer oil shale field, unstable conditions which prevailed during the formation and filling of the basin in the older Neogene. The host rocks are marl and clays in which the organic matter is heterogeneously and finely dispersed. The main mineral components of Seyitomer oil shale are quartz, dolomite, muscovite, illite and smectite [2]. The following may occur as trace amounts: feldspars; calcite; pyrite; hornblende; chlorite and aragonite (Table 1). EGOS varies considerably in thickness and quality in the lateral and vertical directions; the thickness ranges from 3 to 29.5 m, the upper calorific value from 3.14 to 4.25 MJ kg$^{-1}$ and the oil content from 4 to 5.9 wt.% (Table 2).

Thakur and Nuttall [3] studied the pyrolysis kinetics of the thermal decomposition of oil shale by isothermal and non-isothermal thermogravimetry. Their results showed that the thermal decomposition of oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow first-order kinetics. Among three models used

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Table 1
Mineral composition of oil shale deposits in Turkey[a]

| Deposit | Q | Op | F | H | Sm | mi | K | Ch | Cc | Do | Ar | Ma | Cl | Er | An | He | Ph | Py |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Seyitomer | CD | – | SD | T | CD | CD | – | A | SD | CD | A | – | – | – | – | – | – | A |

[a] Q: quartz; Op: opal-CT; F: feldspar; H: hornblende; Sm: smectite; Mi: mica-illite; K: potassium; Ch: chlorite; Cc: calcite; Do: dolomite; Ar: aragonite; Ma: magnesite; Cl: clinoptilolite; Er: erionite; An: analcite; He: heulandite; Ph: phillipsite; Py: pyrite; CD: co-dominant; SD: sub-dominant; A: accessory; T: trace.

Table 2
Characteristics of Seyitomer oil shale

| Deposit | Calorific value (MJ kg$^{-1}$) | Total organic carbon (wt.%) | Oil content (wt.%) | Total sulphur (wt.%) | Reserve (million tonnes) |
|---|---|---|---|---|---|
| Seyitomer | 3.55 | 6.9 | 5 | 0.9 | 110 |

Antony–Howard model yields lower deviation and thus provides a better fit of the data. Skala and Sokic [4] developed a kinetic expression commonly used in the thermal analysis of oil shale pyrolysis, which was derived on the basis of a simple first-order kinetic equation of kerogen decomposition. There was an increase in the activation energy with increase content of paraffinic structures in the oil shale. Rejashwar [5] studied the pyrolysis kinetics of thermal decomposition of Green River oil shale kerogene by non-isothermal thermogravimetry. He critically reviewed the factors influencing kinetic data such as sample order geometry, heating rate and atmosphere. Shih and Sohn [6] used non-isothermal thermogravimetry with a variety of heating rates to the determination of kinetic parameters for Green River oil shale pyrolysis. Four different methods were employed for kinetic analysis and the results appear to be in fair agreement. Lee et al. [7] studied the thermal behaviour of oil shale as a function of grade, gas composition and particle size. Two exothermic peaks are generated by oil shale heated in air. The first peak can be assigned to the combustion of light hydrocarbon fractions from the shale organic matter, whereas the second peak arises from the oxidation of char. Skala et al. [8] 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 purposes of particular oil shale samples and tested by comparison of the experimental and simulated thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) curves. Levy and Stuart [9] obtained TG/DTG curves of Australian oil shales and kerogen concentrates heated in a dynamic air atmosphere. It was observed that the combustion of kerogen occurs in two stages, indicated by two sharply defined peaks.

## 2. Experimental

In this research, thermal experiments were performed with Du Pont 951 TG/DTG and 910 DSC equipments. DSC monitors differential heat flow of the samples, whereas TG/DTG has the capability of measuring the mass loss either as a function of temperature or time in a varied but controlled atmosphere. Prior to experiments, DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was also calibrated for temperature readings with calcium oxalate monohydrate. It was essential to calibrate the balance for buoyancy effect for the quantitative estimation of mass changes. The material chosen for the investigation of such effect was silver. The experimental procedure involves the placing $\sim$10 mg of sample, setting the heating rate and flow rate of the purge gas (air) and then commencing the experiment. Experiments (TG/DTG and DSC) were performed at four different heating rates (5, 10, 15 and 20°C min$^{-1}$) over the temperature range 20–600°C with an air flow rate of

50 ml min$^{-1}$. The oil shale sample used in the experiments had a particle size <60 mesh and prepared according to ASTM (ASTM D 2013-72) standards. In order to assess the reproducibility, experiments were performed twice.

## 3. Results and discussion

Studies on oil shale using thermal analysis techniques have shown that combustion of indigenous organic matter is a complex multistage process. The thermal behaviour of oil shale in dynamic air atmospheres may exhibit characteristics of both the inorganic (mineral) and organic (kerogen + bitumen) components. The low temperature portion of the thermal curves may represent thermal decomposition identical to that observed in inert atmospheres, while at higher temperatures oxidative characteristics of the organic component generally predominate.

The oxidation process of Seyitomer oil shale showed an exothermic behaviour at around 310°C on DSC curves depending on the heating rate (Fig. 1). The shoulder on the high temperature side of the reaction region was attributed to the possible swelling of the sample, resulting in an impermeable mass that reduced the oxygen accessibility causing a decrease in the reaction rate. DSC analysis showed that heat released of the Seyitomer oil shale sample was around 485 cal g$^{-1}$. Higher heating rates resulted in higher peak (reaction) temperatures (Table 3).

The main characterisation point on TC/DTG curve is the peak temperature where rate of weight loss is maximum. Beyond the peak temperature, the derivative curve falls rapidly where the prevailing temperature is called burn-out temperature. Burn-out temperature represent the temperature where sample oxidation is complete.

Table 3
Peak reaction temperatures of Seyitomer oil shale (DSC)

| Sample | Heat released (cal g$^{-1}$) | Peak reaction temperature (°C) |
|---|---|---|
| Seyitomer (5°C min$^{-1}$) | 476 | 316 |
| Seyitomer (10°C min$^{-1}$) | 485 | 335 |
| Seyitomer (15°C min$^{-1}$) | 489 | 343 |
| Seyitomer (20°C min$^{-1}$) | 490 | 349 |

TG/DTG curves of Seyitomer oil shale (Fig. 2) showed the same reactivity region as DSC curves. As in DSC curves, higher heating rates resulted in higher reaction temperatures (Table 4).

### 3.1. Kinetic analysis

Non-isothermal kinetic study of weight loss under pyrolysis and combustion processes is extremely complex for oil shales because of the presence of the numerous complex components and their parallel and consecutive reactions. In this research, Coats and Redfern [10] method based on Arrhenius kinetic theory was used for kinetic analysis of the data generated by the TG/DTG experiments.

The calculation of the kinetic data is based on the formal kinetic equation

$$\frac{d\alpha}{dt} = k\alpha^n \tag{1}$$

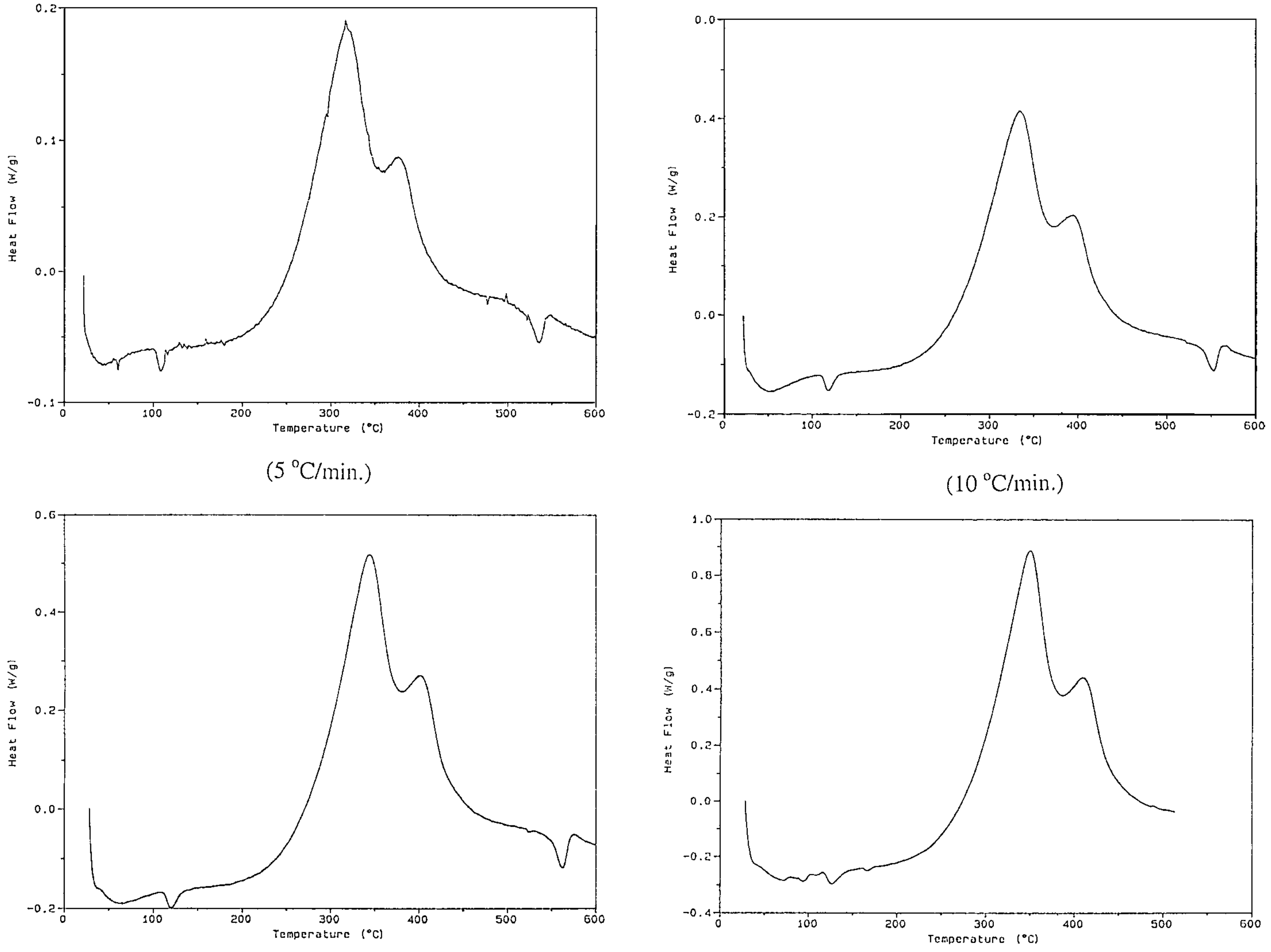
where $\alpha$ is the amount of sample undergoing the reaction, $n$ the order of reaction and $k$ the specific rate constant. The temperature dependence of $k$ is expressed by the Arrhenius equation

$$k = A \exp\left(\frac{-E}{RT}\right) \tag{2}$$

where $A$ is the Arrhenius constant, $E$ the activation energy and $R$ the gas law constant.

Table 4
Peak and burn-out temperatures of the Seyitomer oil shale

| Sample | Peak reaction temperature (°C) | | Burn-out temperature (°C) | Sample left (%) |
|---|---|---|---|---|
| | Region I | Region I | | |
| Seyitomer (5°C min$^{-1}$) | 320 | 550 | 570 | 79 |
| Seyitomer (10°C min$^{-1}$) | 340 | 565 | 585 | 79 |
| Seyitomer (15°C min$^{-1}$) | 345 | 575 | 590 | 79 |
| Seyitomer (20°C min$^{-1}$) | 350 | 585 | 595 | 79 |



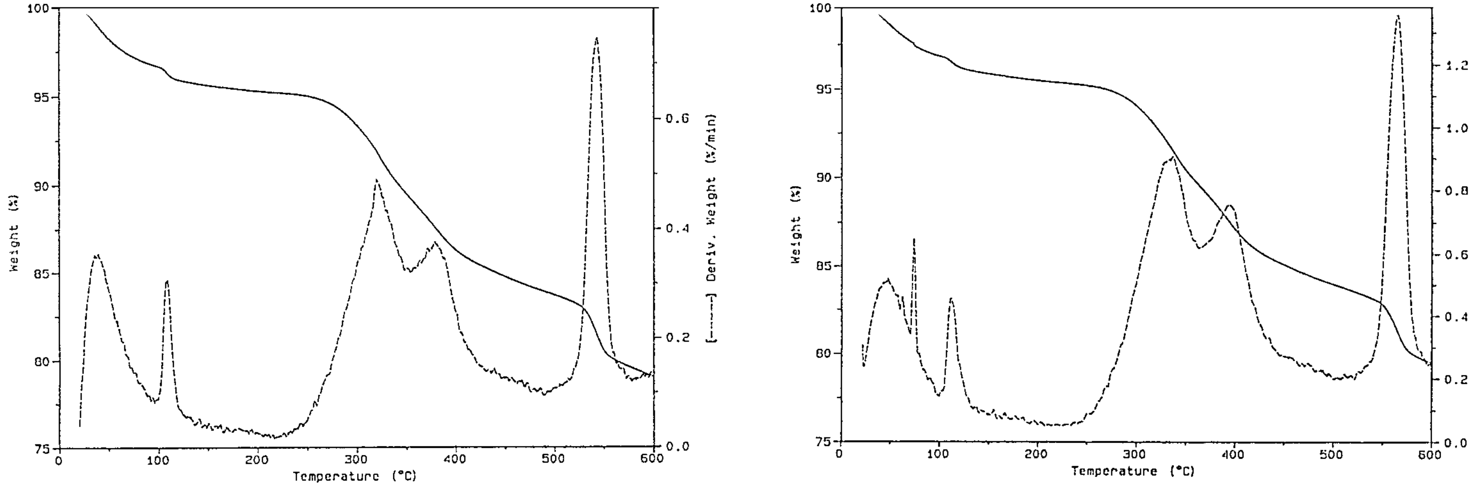
(5 °C/min.)

(10 °C/min.)

(15 °C/min.)

(20 °C/min.)

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



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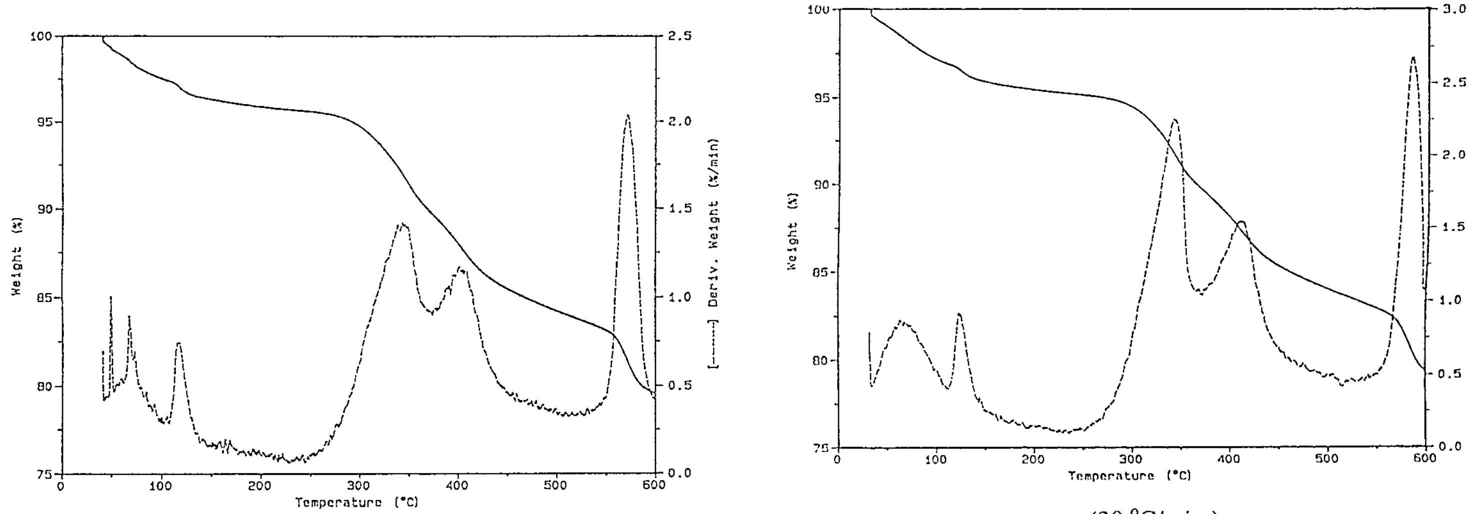


(15 °C/min.)

(20 °C/min.)

Fig. 2. TG/DTG curves of Seyitomer oil shale at different heating rates.

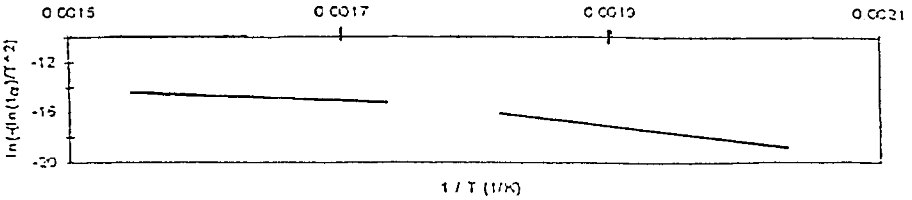
Coats and Redfern developed an integral method which can be applied to TG/DTG data assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation which is useful for analysis

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E}\frac{1-2RT}{E}\right) - \frac{E}{RT} \qquad (3)$$

where $\beta$ is the heating rate.

Thus, a plot of $\ln[(1-(1-\alpha)^{1-n})/(T^2 \times (1-n))]$ versus $1/T$ should result in a straight line (Fig. 3) of slope $-E/R$ for the correct value of reaction order ($n$). In this research, four different reaction orders (1/2, 2/3, 1 and 3/2) were assumed and coefficient of determinations of each reaction were calculated for each heating rate. Highest correlation coefficient was found at a reaction of unity for each heating rate.

Within the analysis, it was observed that Seyitomer oil shale sample have more than one transmission zone so that kinetic parameters were calculated for both peaks, such that these peaks represent different reac-



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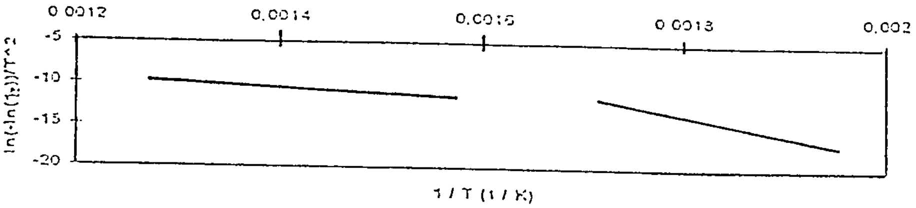

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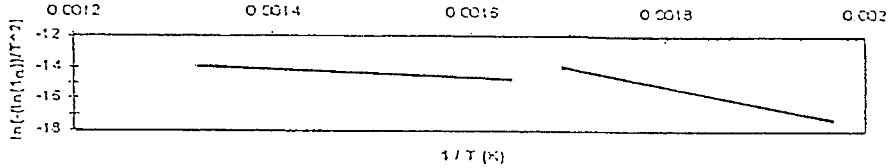

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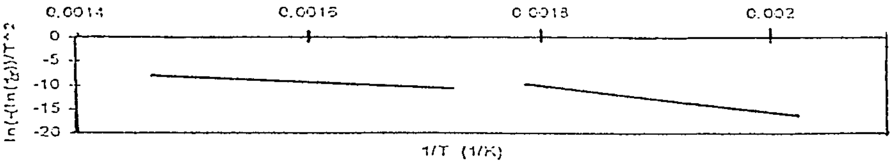

(20 °C/min.)

Fig. 3. Arrhenius plot of Seyitomer oil shale (10°C min$^{-1}$).

Table 5
Activation energy values of the Seyitomer oil shale

| Sample | Activation energy (kJ mol$^{-1}$) | |
|---|---|---|
| | Region I | Region II |
| Seyitomer (5°C min$^{-1}$) | 77.6 | 7.4 |
| Seyitomer (10°C min$^{-1}$) | 73.8 | 5.9 |
| Seyitomer (15°C min$^{-1}$) | 74.2 | 6.2 |
| Seyitomer (20°C min$^{-1}$) | 71.8 | 8.1 |

tion zones. Throughout the analysis, it was observed that first zone activation energies are higher than the second region. This situation can be explained such that organic compounds mostly decompose at lower temperatures than other mineral type compounds. Similar activation energy values were obtained at different heating rates (Table 5).

## 4. Conclusions

In this research, an experimental study on the thermal investigation of Seyitomer oil shale sample were presented. The following conclusions were derived from the research conducted:

- The oxidation process of Seyitomer oil shale showed an exothermic behaviour at around 310°C on DSC curves and a shoulder on the high temperature side of the reaction region depending on the heating rate.
- Higher heating rates resulted in higher reaction temperatures both in DSC and TG/DTG experiments.
- From the experiments and kinetic analysis, it was observed that Seyitomer oil shale sample have more than one reaction region where the activation energies of the first region is higher.

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