

GEOLOGICAL CONSIDERATIONS FOR THE ECONOMIC EVALUATION OF TURKISH OIL SHALE DEPOSITS AND THEIR COMBUSTION – PYROLYSIS BEHAVIOR (REVIEW)

Mustafa Versan KOK

Dept. of Petroleum and Natural Gas Engineering,
Middle East Tech. Univ., 06531, Ankara-Turkey
Email: Kok@metu.edu.tr

ABSTRACT

The oil shale deposits in Turkey are widely distributed in middle and western Anatolia. Turkish oil shales are of Palaeocene-Eocene and middle upper Miocene age. Current reserves of oil shales are approximately 2220 million tones (total reserve) and mainly located in Himmetoğlu, Seyitömer, Beypazarı and Hatıldığ deposits. Some petrological, geochemical, Fisher Assay and fluidized combustion test are performed for these oil shale fields and it was concluded that Himmetoğlu oil shale is the most appropriate for domestic and industrial utilization. On the other hand, Differential scanning calorimetry-pressurized- (DSC-PDSC) and thermogravimetry (TG/DTG) experiments were performed with these oil shale samples. In pyrolysis experiments, oil shale samples showed one exothermic effect at each total pressure studied. A general trend to decreasing in activation energy with increasing pressure in pyrolysis, and increasing in activation energy with increasing pressure was observed in combustion experiments.

1. 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.

Oil shales are broadly defined as petroleum source rocks containing sufficiently high contents of organic matter to make utilization a possibility. Like coal, the world's reserves of oil shales are vast, being many times larger than those proven for crude oil. Oil shale utilization has attracted renewed attention as a source of transport fuels and chemical feed stocks due to the long-term uncertainties over crude oil supplies. Indeed the last twenty years has seen the development of a number of innovative process concepts, such as fluid-bed pyrolysis, combustion and hydro-retorting, that has enabled considerably higher oil yields to be obtained than by the classic retorting procedures.

The need for energy is a critical concern for Turkey. The energy consumption of Turkey was recorded to increase from 53 to 77 Mtoe (million tons of oil equivalents) from 1990 to 2001, corresponding to a rise of around 50%. The oil and natural gas reserves in Turkey are minor; solid fossil fuels are the primary potential energy resources. These resources include a wide variety of bituminous coal, lignite, oil shale, asphaltite, and peat deposits and vary in reserve quality and physical characteristics. 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 500 to 4500 kcal/kg in calorific value, revealing that each deposit requires a detailed study regarding its possible use (Güleç and Önen, 1992).

2. OIL SHALE POTENTIAL IN TURKEY

The oil shale resources of Turkey are distributed mainly in middle and western Anatolia. Presence of authigenic zeolites and preservation of the organic matter reveal the influence of hypersaline conditions during formation in closed basins during the Paleocene-Eocene and Upper Miocene Epochs. Generally, marl, clay and carbonates are the host rocks and organic matter is found in disseminated form (Şener et.al, 1995). The main oil shale deposits in Turkey with the amounts of their geological (proved) and possible reserve is given in Table-1. Among the potential resources, Beypazarı, Seyitömer, Himmetoğlu and Hatıldığ deposits are of major importance in terms of quality, amount and exploitability which constitute around 50% of the total oil shale potential of Turkey. Other potentially important resources are in Mengen, Ulukışla, Bahçecik, Burhaniye, Beydili, Dodurga and Demirci (Figure-1).

Table 1. Main oil shale reserves in Turkey.

Name of the Deposit	Geological reserve ($\times 10^6$ tones)	Possible reserve ($\times 10^6$ tones)	Total reserve ($\times 10^6$ tones)
Beypazarı	327.68	-	327.68
Seyitömer	83.32	38.85	122.17
Himmetoğlu	65.97	-	65.97
Hatıldığ	78.37	389.20	467.57
Mengen	-	50.00	50.00
Ulukışla	-	130.00	130.00
Bahçecik	-	42.00	42.00
Burhaniye	-	15.60	15.60
Beydili	-	300.00	300.00
Dodurga	-	138.00	138.00
Demirci	-	172.00	172.00
Sarıcakaya	-	300.00	300.00
Çeltik	-	90.00	90.00
Total :	555.34	1665.65	2220.99

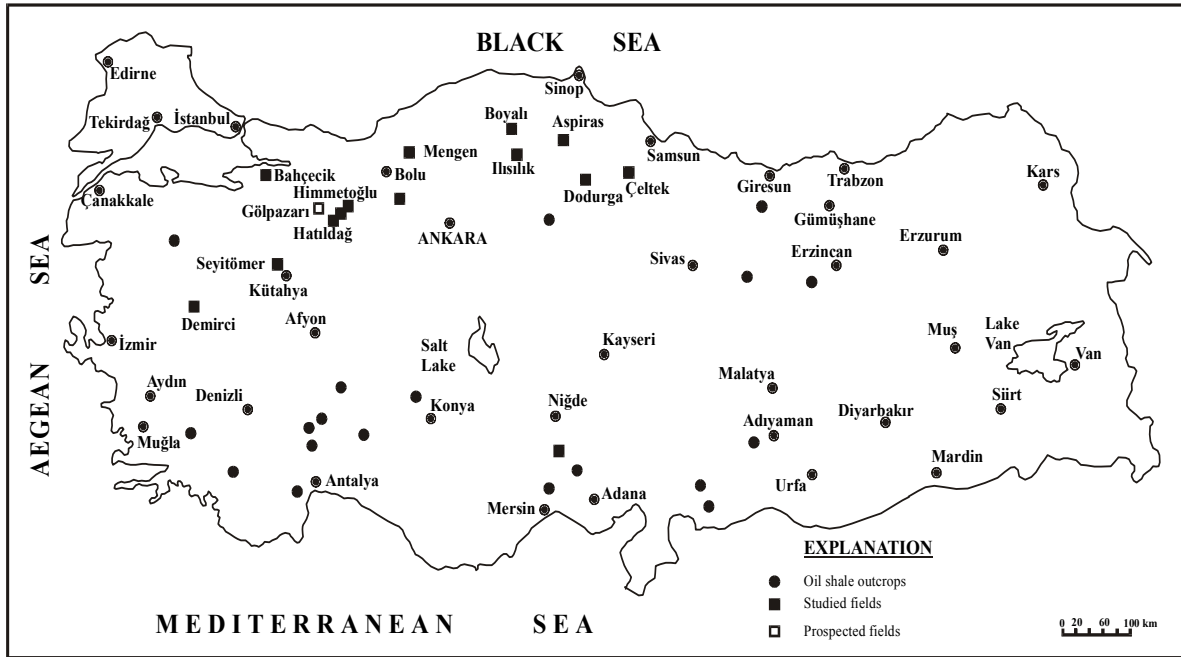


Figure-1 Location of Major Oil Shale Deposits in Turkey (Şener et.al. 1995)

2.1 Beypazarı Oil Shale Field

The Beypazarı oil shale deposit is located at the northwestern part of Ankara, in the neighborhood of the Beypazarı-Çayırhan lignite field. The stratigraphic units occurring in the Beypazarı oil shale area is given in Figure-2. The Hırka formation consist mostly of well consolidated marl, clay, bituminous marl, dolomitic limestone, dolomite and magnesite, with intercalated tuffaceous horizons and occasionally chert. The stratigraphic data revealed that well consolidated marl and clays occur as host rocks. Carbonates (dolomite, calcite) and quartz occur in significant quantities as the main inorganic constituents. Localized occurrences of trona are also found. Si, Mg and Ca occur as major elemental constituents but trace elements are rare (Şener et.al, 1995). The cumulative (drilled) thickness of the economic grade oil shale (EGOS), which is persistent and is distributed over a relatively wide area, varies from 5 to 22 m, the upper calorific value from 3150 to 3890 kJ/kg. Characteristics of the Beypazarı oil shale deposit is given in Table-2. The Beypazarı oil shale is on average of low quality, and owing to the tectonic situation, low-cost opencast mining is inappropriate. Therefore industrial utilization under the present conditions is low.

2.2 Seyitömer Oil Shale Field

The Seyitömer oil shale deposit is found in the northwestern part of province of Kütahya. The deposit overlies the Seyitömer lignite basin, which supplies a 300 MW thermal power plant at the mine site. The rock units occurring in this field is given in Figure-2. The unstable conditions which prevailed during the formation and the filling of the basin in the older Neogene the morphological differentiation of the basin floor by island-like elevations, lateral facies changes, tectonic movements and partial

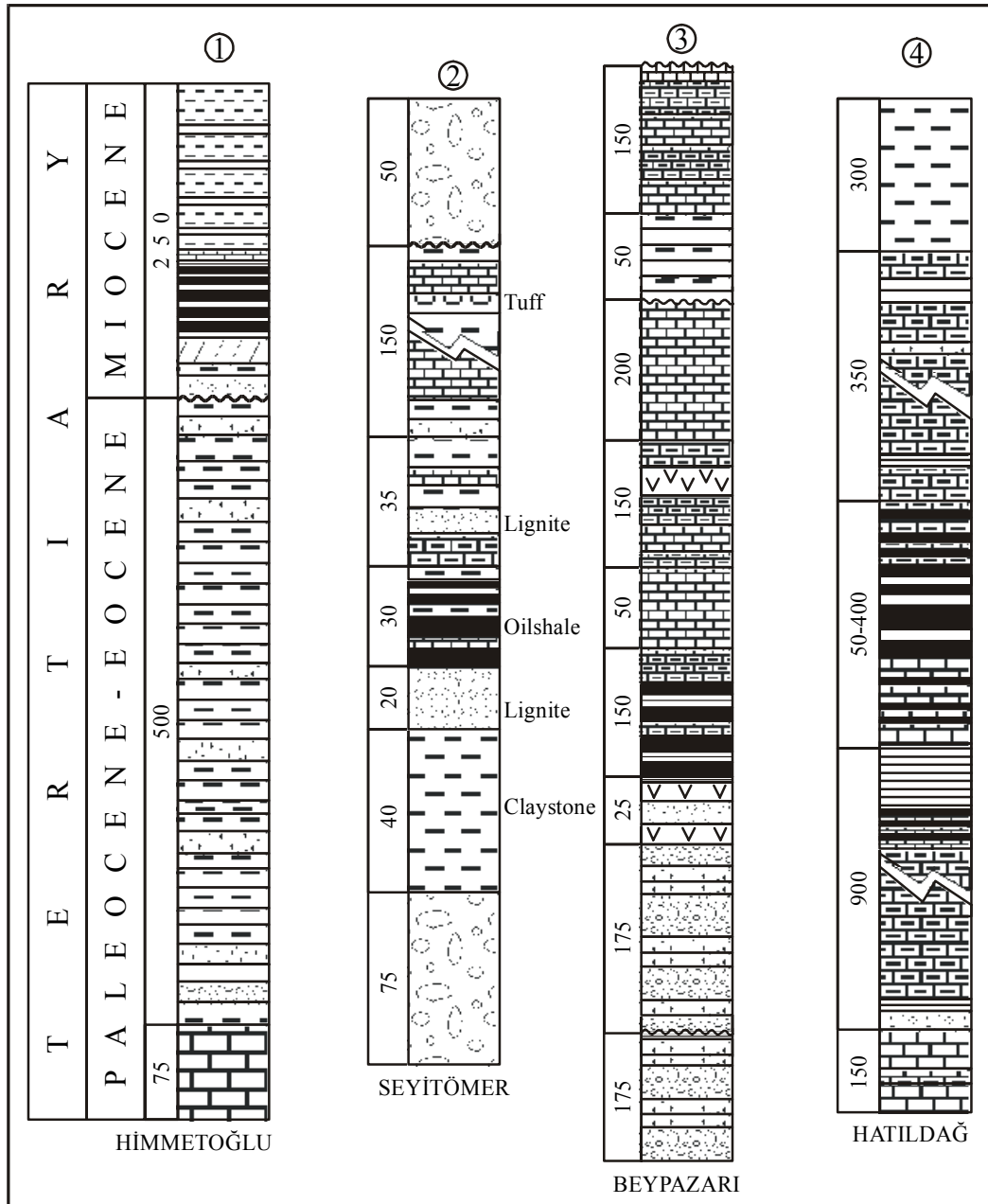


Figure-2 Diagrammatic columnar sections showing oil shales in four basins (Şener et. al.1995)

erosion has affected the sediments. Bituminous marl unit crops out around Seyitömer and has been penetrated by many drill holes for lignite prospecting. The main mineral components of Seyitömer oil shale are quartz, dolomite, muscovite-illite and smectite. The main maceral components of Seyitömer oil shale are laminated algae pollen, and planktonic algae (Şener et.al, 1995). EGOS vary 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 3140 to 4250 kJ/kg. Characteristics of the Seyitömer oil shale deposit is given in Table-2. High grade oil shale has a tendency to spontaneous in-situ combustion, as a result of which, extensive areas of burnt bituminous beds have originated. The EGOS reserves situated in the mining area are estimated to amount to 110 million tones. Because of the low quality, efficient utilization on a large scale would be direct combustion for the generation of electricity by the circulating

fluidized bed process. The suitability of the EGOS for this advanced, almost pollution-free technology has been proved by *Vereinigte Kesselwerke* (VKW) in Germany by a pilot plant test with 100 tone of sample. The best result was achieved when the oil shale was blended with 20 % of Seyitömer lignite (Hufnagel, 1991).

2.3 Himmetoğlu Oil Shale Field

The Himmetoğlu oil shale deposit is located in the southwestern part of province of Bolu, in the neighborhood of the Beypazarı, Hatıldağ and Mengen oil shale deposits. The Himmetoğlu oil shale basin is of Neogene age, and volcanism and tectonic activity have considerable influence on the environmental conditions during the deposition period (Şener et. al, 1995). The drill hole data shows three main zones from top to bottom: bituminous marl (BLM), bituminous banded marl (BBM) and the major oil shale formation of the Himmetoğlu (HOS) seam (Figure-2). The Himmetoğlu oil shale strata overlie a lignite zone and extend throughout the deposit. The Himmetoğlu oil shale seam consists of more than 50% liptinite, 20–50% huminite and 0–20% inertinite maceral groups and is characterized by its high organic content (Hufnagel, 1991). The origin of the organic matter is mainly algae and land plants. The major inorganic constituents in the organic-rich zones are calcite, dolomite, silica, and considerable amounts of pyrite. The average calorific value of the EGOS zone is around 4900 kcal/kg. The in-place shale oil content of the Himmetoğlu oil shale is 43% by weight or approximately 482 l/ton of shale. However, the average total sulphur content is high (2.5%) due to considerable pyrite (Table-2). The Himmetoğlu oil shale is the highest quality oil shale in Turkey. The Himmetoğlu oil shale zone is being excavated (2005) to exploit an underlying high-quality lignite seam utilized for domestic heating. On account of its high thermal quality, the Himmetoğlu oil shale is an attractive alternative for power generation in Turkey. Himmetoğlu oil shale is occasionally used for domestic purposes; however industrial utilization of the EGOS would best be offered by fluidized bed combustion for the generation of electricity. The suitability of the oil shale for this process has been demonstrated by a pilot plant test by *Vereinigte Kesselwerke* (VKW) in Germany. The best result, with very low air pollutant emissions were obtained with mixtures of oil shale and up to 40 % of lignite (Hufnagel, 1991).

2.4 Hatıldağ Oil Shale Field

The Hatıldağ oil shale deposit is located in the Hatıldağ-Bolu lacustrine basin at the south-eastern part of Göynük in Bolu province. The deposit, of Paleocene- Eocene age, is in a 50 to 75-thick limic series of calcareous bituminous rocks. The series consists of two zones, an economic grade oil shale and bituminous marl (Figure-2). It contains around 80% liptinite, 5–10% bituminite and 5–10% huminite. The high liptinitic content shows that the organic matter originated mainly from hydrogen-rich organic remains of algae and pollen. Calcite, dolomite, quartz and smectite are the major inorganic constituents. Analcime, feldspar, chlorite and mica-illite are found in lesser amounts (Şener et. al, 1995). The economic grade oil shale zone is in the lower part of the bituminous sequence. The upper calorific value from 3160 to 3310 kJ/kg The Hatıldağ oil shale is characterized as a poor quality deposit with a shale oil yield of 5.3%, which is similar to the Beypazarı and Seyitömer deposits (Table-2). In the current economic situation, the economic utilization of this oil shale is quite impossible. At best, utilization might be possible together with the oil shale and lignite from Himmetoğlu if a fluidized bed plant for the generation of electricity could be realized at this site.

Table 2. Characteristics of oil shale deposits

Name of the Deposit	Total Organic Carbon (wt%, average)	Oil content (wt%, average)	Total sulfur (wt%, average)
Beypazarı	4.8	5.4	1.4
Seyitömer	6.9	5.0	0.9
Himmetoğlu	3.2	4.6	0.9
Hatıldağ	5.6	5.3	1.3

2.5 Other potential reserves

The other potential oil shale deposits at Mengen, Ulukışla, Bahçecik, Burhaniye, Beydili, Dodurga, Demirci, Sarıcakaya and Çeltik have not yet been investigated in detail. The information about these deposits is derived from preliminary geological borehole data and analysis. Among these deposits, Beydili and Sarıcakaya are distinguished by their huge resources. The Mengen deposit is of Eocene age and is located near the Hatıldağ and Himmetoğlu deposits. The Mengen deposit overlies a lignite seam and is 24 m thick. The Bahçecik oil shale bed lies between two tuffs and the average thickness of the oil shale is 4.30 m. and the shale yield ranges between 2 and 19%. The Ulukışla oil shale deposit underlies conglomeratic rocks and the average thickness of the oil shale bed is 13 m. The calorific value and oil content of the deposit averages 2790 kcal/kg and 13.7%, respectively. The Demirci oil shale field is of Miocene age. The thickness of the oil shale bed ranges between 3 and 15.60 meter.

3. PYROLYSIS AND COMBUSTION BEHAVIOR OF BEYPAZARI, SEYİTÖMER, HİMMETOĞLU AND HATILDAĞ OIL SHALES

In recent years, an increase in the scientific investigation and characterization of oil shales and other source of organic content of ant level can be seen. The main thermal analysis techniques applicable to solid hydrocarbon fuels are thermogravimetry (TG/DTG), differential thermal analysis (DTA), differential scanning calorimeter (DSC) and evolved gas analysis (EGA). The requirement of only a small amount of material coupled with the comparatively fast and easy performance of experiments makes the techniques attractive. In recent years, the application of DSC and TG/DTG to study the combustion and pyrolysis behavior of oil shales has gained a wide acceptance.

The mechanisms involved in the decomposition 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 a wide range of minerals. The thermal degradation of oil shale is too complex to be described by an individual chemical reaction. The TGA provides only general information about the overall reaction kinetics. Products that are obtained through pyrolysis depend on oil shale composition and conditional variables, such as temperature, time, rate of heating, pressure, and gas environment (Değirmenci and Durusoy 2002, Kök and Pamir 1998, Kök et. al. 1999). On the other hand, the factors influencing kinetic data, such as sample order geometry, heating rate and atmosphere, of oil shales has been studied under non-isothermal conditions (Kök and Pamir 1999, Doğan and Uysal 1996, Abu-Qudais et. al. 2005, Jaber and Probert 1999).

Standard thermogravimetric apparatuses offer highly desirable conditions for the study of the chemical kinetics of oil shale combustion, such as controlled temperature and simultaneous weighing of the sample. The thermogravimetric analyses carried out in such conditions that the observed reaction rate is identical to the rate of the chemical kinetics. effects of key parameters which could affect this identity, such as: the gas flow rate and

purity, heating rate, the particle and sample sizes has been studied under air atmosphere and the effect of different kinetic models are discussed (Kök and Pamir 2000, Lisboa and Watkinson 1999, Kök 2001, Torrente and Galan 2001, Kök et. al. 2001, Karayıldırım et.al. 2004)

3.1 Experimental Equipment

In this research, differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) experiments were carried out in the temperature range of 20-900 °C, a sample size of ~10 mg., gas flow rate (nitrogen and air) of ~50 ml/min. and heating rate of 5-25 °C/min. The oil shale samples used in all experiments had a particle size of <60 mesh and prepared according to ASTM standards (ASTM D 2013-72). It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. The TG/DTG system as calibrated for temperature reading with calcium oxalate monohydrate and DSC with indium. It was essential to calibrate and balance for buoyancy effects to allow quantitative estimation of weight changes. All the experiments were performed twice in order to see the repeatability. The properties of oil shale samples are given in Table-3.

Table 3. Properties of oil shale samples

Oil shale	Calorific Value (J/gr.)	Water (%)	Ash (%)	C (%)	H (%)	O,N (%)	S (%)
Beypazarı	3555	2.40	65.20	8.40	1.60	4.55	0.21
Seyitömer	4205	2.80	70.90	8.58	1.40	4.39	0.19
Himmetoğlu	4540	12.90	60.50	13.60	1.50	10.48	0.99
Hatıldağ	3235	1.60	66.20	5.63	1.30	3.89	1.25

3.2 Pyrolysis Experiments

Many hydrocarbon compounds undergo a permanent change when subjected to extreme heat. The extent of this change depends on the complexity of the molecular structure and the reaction environment. The pyrolysis process is exceedingly complex and many competing processes contribute to the DSC and TG/DTG curves. Initially, the predominant mechanism of mass loss may be simply evaporation, but later chemical reactions occur and in the final stage volatile matter escapes from a porous solid. In other words, in the initial stages of pyrolysis, distillation of low molecular mass species occurs, but as the temperature is raised, in addition to the increased rate of volatilization due to the progressive evaporation of larger molecules, cracking of the compounds may also occur to produce volatile fragments. During the pyrolysis of oil shale samples studied, all the thermal effects were endothermic and no exothermic region was observed in DSC curves.

On the other hand, when oil shales are heated in nitrogen atmosphere in TG/DTG, two different mechanisms causing loss of mass were observed (Figure-3). The region between ambient and ~230 °C was distillation. The second mechanism was visbreaking and cracking occurred between 270 and 525 °C. Whilst the two stage TG/DTG process is reported for the oil shales in this research, the actual mechanism for the thermal decomposition of oil shales is a much more complex reaction involving a series of parallel reactions. It was mentioned that the commencing temperature of pyrolysis of rich grade oil shale is lower than those of poor oil shale. (Burnham et. al. 1983). This situation was also observed in this study, such that

Himmetoğlu oil shale, which is known to be a high grade shale in the literature, has a commencing temperature of 190 °C and this is lower than those of other oil shales.

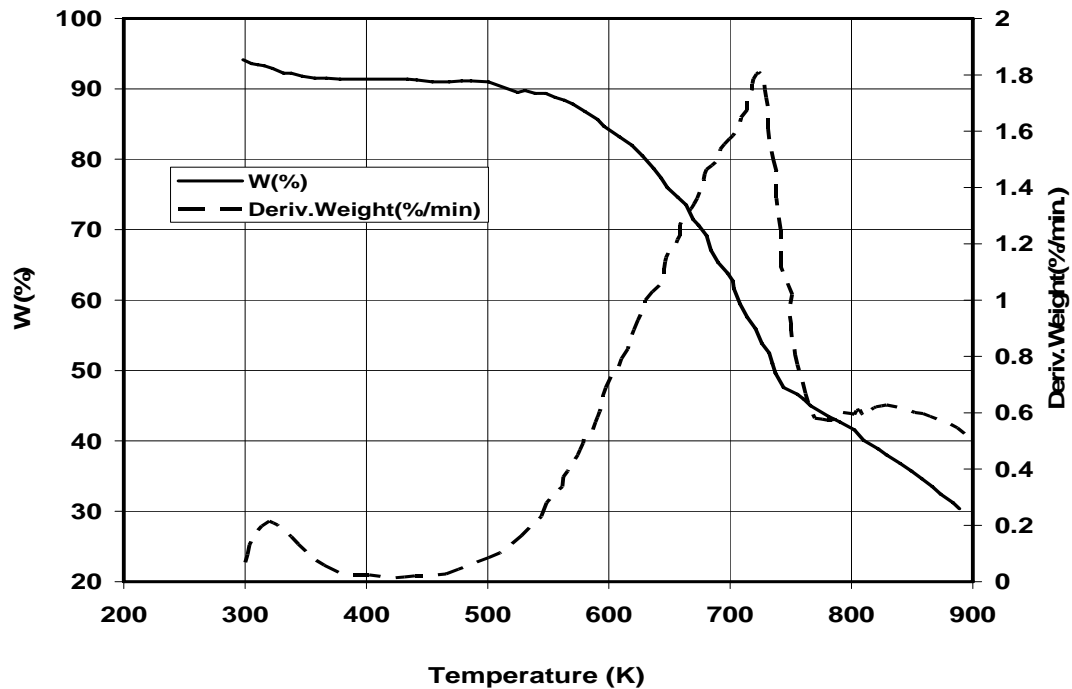


Figure-3 TG/DTG Curve of Himmetoglu Oil Shale -Pyrolysis-

3.3 Combustion Experiments

Studies on oil shale using thermal analysis techniques have shown that combustion of indigenous organic matter is a complex multi-stage process. The thermal behavior 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 atmosphere, while at higher temperatures oxidative characteristics of the organic component generally predominate. 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. On DSC combustion curves of oil shale samples two reaction regions were observed. The highest energy release and low onset 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 in other oil shales. The main characterization point on the TG/DTG curve is the peak temperature at which the rate of weight loss is maximum. Beyond that temperature the derivative curve falls rapidly. At the prevailing temperature -burn out temperature- sample oxidation is complete (Figure-4). According to TG/DTG analysis of the combustion experiments, it was observed that the share of organic matter varies in the range of 7.5 – 80 %. However, the 80 % value is observed as an extreme one, and is characteristics of only Himmetoğlu oil shale. It attest once more that the higher the content of organic matter, the higher the grade of oil shale. The peak and burn-out temperatures of oil shale samples (TG/DTG) are given in Table-4.

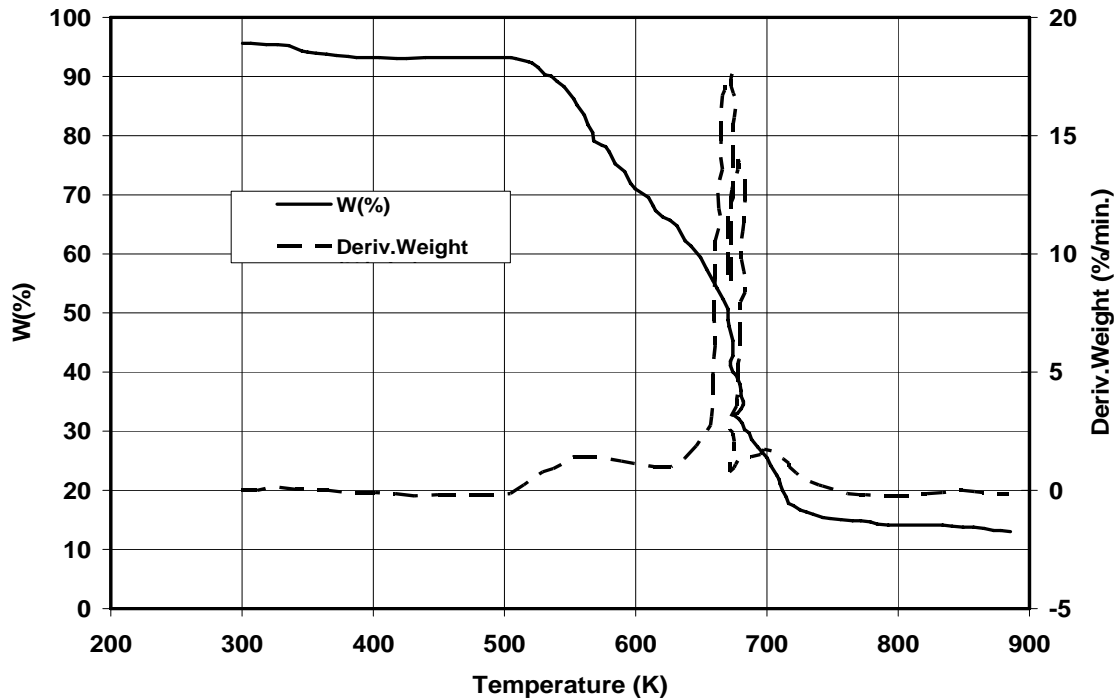


Figure-4 TG/DTG Curve of Himmetoglu Oil Shale –Combustion-

Table 4. Peak and burn-out temperatures of oil shale samples, (TG/DTG)

Oil shale	Peak temp. (LTO), °C	Peak temp. (HTO), °C	Burn-out temp. °C
Beypazarı	347	392	502
Seyitömer	320	380	577
Himmetoğlu	292	401	482
Hatıldağ	323	446	587

In pressurized differential scanning calorimetry (PDSC) experiments, oil shale samples exhibit two exothermic effects at each total pressure applied (100,200,300 and 400 psi) known as low temperature oxidation (LTO) and high temperature oxidation (HTO). Under non-isothermal heating conditions, PDSC curves record heat flow rates of 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 (Table-5)

Table 5. Heat Values of Himmetoğlu oil shale, (PDSC)

Pressure (psi)	LTO region (J/gr)	HTO region (J/gr)
100	11740	8220
200	11465	6445
300	11275	6315
400	10750	5440

3.4 Kinetic Analysis

Non-isothermal kinetic study of weight loss under pyrolysis and combustion process is extremely complex for oil shales, because of the presence of the numerous components and their parallel and consecutive reactions. The Coats and Redfern (1964) model was used for

the kinetic analysis of the data by TG/DTG and Arrhenius model (Kök, 1993) to treat the data of PDSC experiments. Coats and Redfern 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 final form of the equation is as follows:

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

Thus a plot of $\ln [1-(1-\alpha)^{1-n} / (T^2 (1-n))]$ vs. $1/T$ should result in a straight line whose slope equals $-E/R$ for the correct reaction order (Figure-5a,b).

Kinetic parameters were calculated for both peaks which represents different reaction zones (LTO and HTO). The activation energies calculated for the low temperature oxidation region are generally higher than those of high temperature oxidation region (Table-6). This situation can be explained by the fact that organic compounds mostly decompose at lower temperatures compared to mineral-type compounds.

Table 6. Activation energies of oil shale samples (TG/DTG)

Oil Shale	LTO region (kJ/mol)	HTO region (kJ/mol)
Beypazarı	111.6	64.4
Seyitömer	93.6	28.8
Himmetoğlu	127.6	24.5
Hatıldag	88.7	17.9

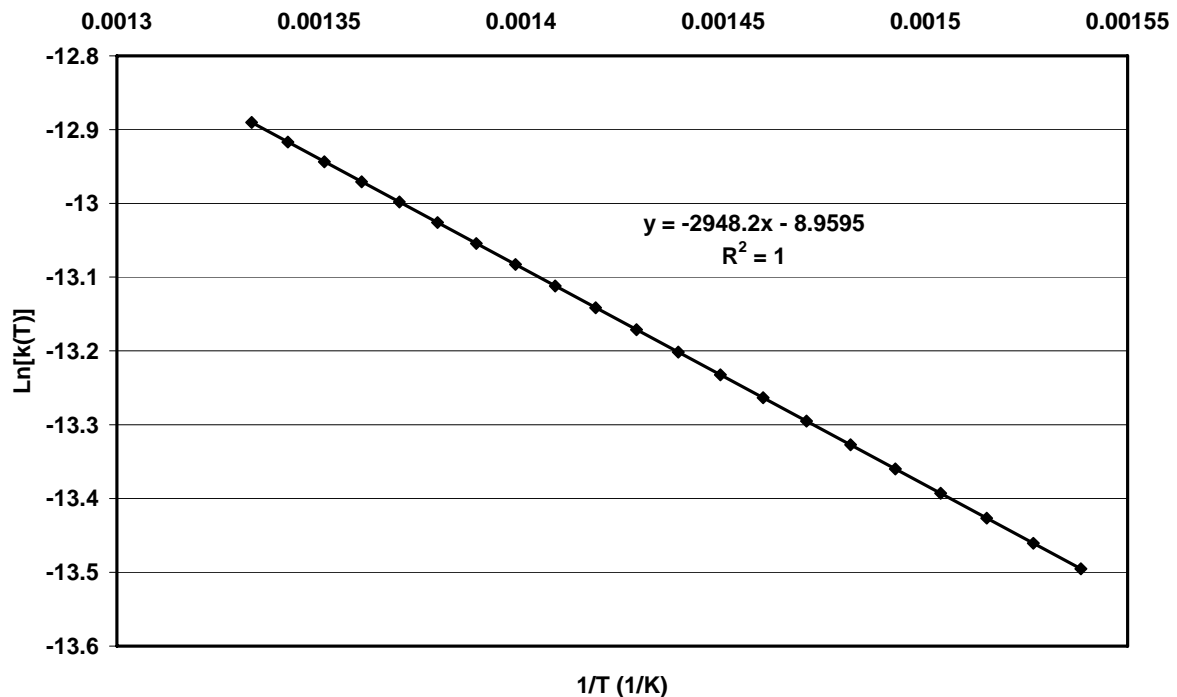


Figure-5a HTO plot for Himmetoglu Oil Shale –Combustion-

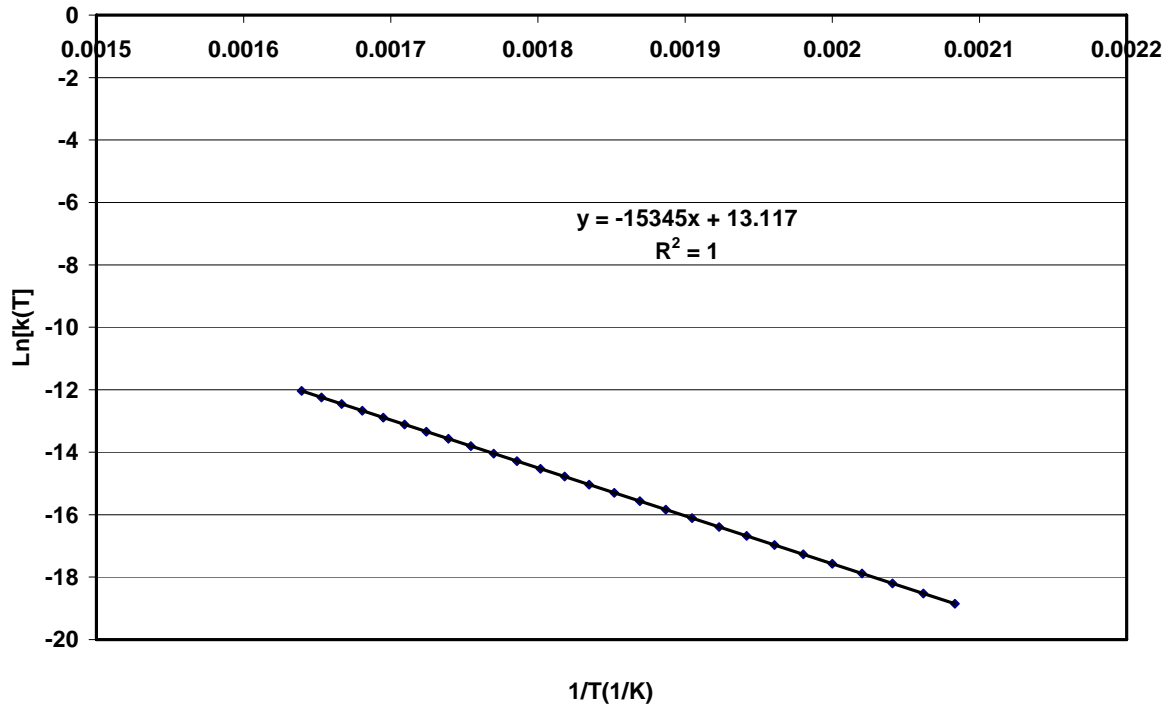


Figure-5b LTO plot for Himmetoglu Oil Shale –Combustion-

A kinetic model which gives a means of estimating activation energies from PDSC curves was used in this research. It was assumed that the recorded data of the PSC 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.

$$-E = R [\ln D_1 - \ln D_2] / (1/T_1 - 1/T_2) \quad (2)$$

As the total pressure is increased, activation energies of the samples are also increased (Kok et.al. 1999). A decrease in peak temperatures were obtained as the total pressure is increases in both low and high temperature oxidation regions (Table-7).

Table 7. Activation energies of Himmetoğlu oil shale (PDSC)

Pressure (psi)	LTO region (kJ/mol)	HTO region (kJ/mol)
100	82.7	72.3
200	100.7	80.9
300	112.7	85.2
400	119.6	86.1

4. CONCLUSIONS

During the pyrolysis of oil shale samples studied, no exothermic region was observed in DSC curves, whereas, when oil shales are heated in nitrogen atmosphere in TG/DTG, two different mechanisms causing loss of mass were observed.

On combustion DSC and TG/DTG 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.

Throughout the kinetic analysis of the combustion experiments, it was observed that the 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.

In PDSC experiments, it was observed that, as the total pressure is increased, activation energies of the samples also increased. A decrease in peak temperatures were obtained as the total pressure is increases in both low and high temperature oxidation regions.

5. NOMENCLATURE

D_1 - D_2	distance from baseline, cm
E	activation energy, kJ/mol
R	gas constant, J/mol K
T	absolute temperature, K
T_1 - T_2	associated temperatures, K
n	reaction order, dimensionless
α	reaction mechanism

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