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# Combustion performance and kinetics of oil shales

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## ABSTRACT

In this research, combustion performance and kinetics of two Turkish oil shales were investigated using differential scanning calorimetry (DSC), thermogravimetry (TGA/DTG), and thermogravimetry–mass spectrophotometry (TG–MS) techniques at three different heating rates (10, 30, and 50°C/min). The combustion reaction occurred in two different regions and the corresponding mass loss of oil shales was calculated. Activation energies of oil shale samples are calculated using three different methods and the results are discussed from the viewpoint of the origin and grade of the samples.

## KEYWORDS

Combustion; differential scanning calorimetry; kinetics; oil shale; thermogravimetry

## 1. Introduction

The idea of utilization of new or alternative energy sources to meet increasing energy demand is gaining popularity. There are alternative fossil fuels; such as, oil shale, oil sand, tar, asphaltite, shale gas, etc.; which can be utilized to play a part in the energy supply issue. Oil shale is one of the promising energy sources among the group and can be utilized in the pyrolysis method to obtain shale oil or in direct combustion in thermal power plants to generate electricity.

A large number of lab scale research studies have been reported in the literature concerning the pyrolysis and combustion of oil shales. Pyrolysis and combustion kinetics of oil shales were studied using a thermogravimetric analyzer (TGA) at 5°C/min heating rate, and it was observed that the maturity and structure of oil shales influence the behavior of pyrolysis and combustion. It was also observed that the rate control mechanism was the chemical kinetics in the first reaction region due to lighter compounds while diffusion was the rate controlling in the last stage of the reaction due to heavier compounds (Kok and Pamir, 2000, 2003). In another research, combustion behavior of oil shales was studied using both differential scanning calorimetry (DSC) and thermogravimetry (TGA) at high heating rates. They observed that the combustion of some oil shales can be problematic due to high ash content and biomass fuels producing much volatile matter and containing less cellulose are good candidates for co-firing with oil shales (Ozgur et al., 2012). In other research, pyrolysis experiments of oil shales were studied in TGA at different heating rates and three different reaction stages were observed involving: evaporation of water and volatiles, conversion of kerogen to bitumen and ash decomposition (Jaber and Probert, 2000). Pyrolysis of different oil shale samples using TGA at different heating rates was also studied. It was concluded that there is one major pyrolysis peak in the TGA curve and the loss of hydrocarbon materials took place during that major stage between 200 and 550°C. It was also observed that as the heating rate was increased, a shift occurs in the reaction temperature range, due to temperature gradient, however, the heating rate has no effect on the final mass loss (Abu-qudais et al., 2005). Oxidizing tests on oil shale samples were also studied using different thermal analysis techniques at different heating rates and they observed thermo-oxidative decomposition of oil shales in three stages: thermo-oxidation of volatile organic compounds,

thermo-oxidation of heavier parts of kerogen and fixed carbon, and finally decomposition of ash content (Kaljuvee et al., 2011).

In this research, combustion performance and kinetics of two oil shale samples were studied using non-isothermal DSC and TG-DTG at different heating rates. At the same time, the aim was to assess the variations in the combustion behavior of oil shale samples and kinetics, as the heating rate was changed.

## 2. Experimental procedure

In this research, two oil shale samples from different oil shale fields in Turkey (Ulukışla and Himmetoğlu) were studied. The oil shale samples are prepared according to American Society for Testing and Materials (ASTM) Standards (ASTM D 2013-72) and had a particle size of <60 mesh. It is believed that for such a small particle size, the effect of temperature distribution within the sample particle is relatively eliminated.

Non-isothermal DSC and TGA-DTG experiments were conducted at three different heating rates of 10, 30, and 50°C min<sup>-1</sup>, in the temperature range of 20–600°C (DSC) and 20–800°C (TGA-DTG), respectively, and the air flow rate during the experiments was kept constant at 50 ml min<sup>-1</sup>. On the other hand, TGA-MS experiments are performed at 10°C min<sup>-1</sup>, in the temperature range of 20–1000°C. The combustion environment was O<sub>2</sub>/Ar (20–80 in volume), and the flow rate of gas was 100 ml/min. The system was kept isothermal at 105°C for 5 min to remove moisture.

Prior to experiments, the DSC system was calibrated for temperature readings using indium as reference standard. On the other hand, the TG-DTG system was calibrated for buoyancy effects to allow quantitative estimation of weight changes. For repeatability, all the experiments were performed twice to ensure repeatability (standard errors ±1°C, within a confidence interval of 95%).

## 3. Results and discussion

Prior to thermal analysis experiments, the proximate and ultimate analysis of oil shale samples is determined (Table 1). Based on the proximate-ultimate analysis (**Ulukışla**: moisture: 7.0%; volatile matter: 8.4%; fixed carbon: 0.1%, ash: 84.5%; C: 3.75%; H: 1.05%; N: 0.22%, and O + S: 10.48%; **Himmetoğlu**: moisture: 5.0%; volatile matter: 63%; fixed carbon: 13.5%, ash: 18.5%; C: 53.3%; H: 6.13%; N: 1.73%, and O + S: 20.54%), it was observed that the Ulukışla oil shale sample has high ash

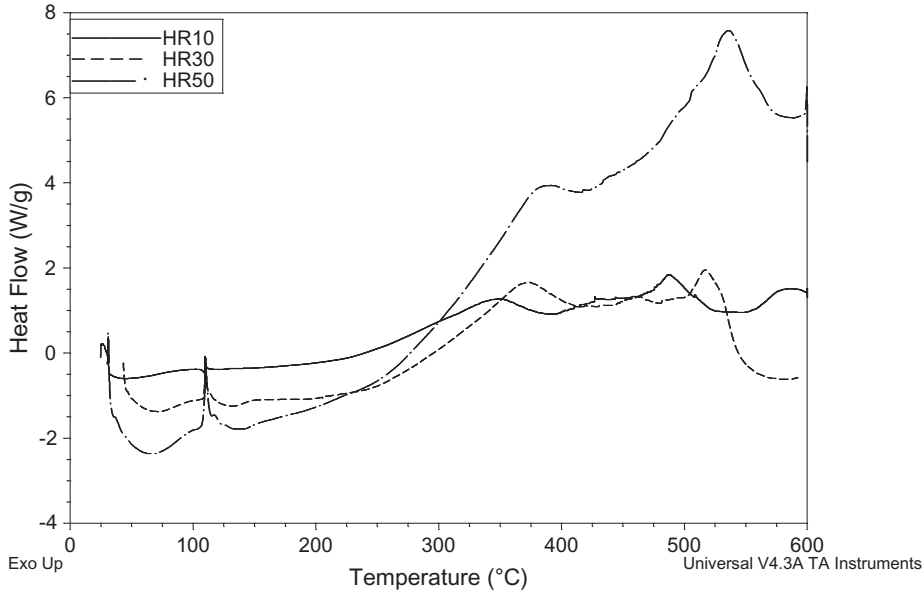
**Table 1.** Properties oil shale samples during combustion (DSC).

Ulukışla oil shale	10°C min <sup>-1</sup>	30°C min <sup>-1</sup>	50°C min <sup>-1</sup>
Region-I	25–244	25–296	25–302
Region-II	244–400	296–425	302–425
Region-III	400–550	425–550	425–600
Peak Temp.-Region- III (°C)	487	517	535
Heat value (kJ kg <sup>-1</sup> )	1001	983	932
Ignition temperature (°C)	244	296	302
<i>Kinetic parameters</i>	ASTM-I	ASTM-II	-
Activation Energy (kJ/mol)	128.7	122.1	
<b>Himmetoğlu oil shale</b>	10°C min <sup>-1</sup>	30°C min <sup>-1</sup>	50°C min <sup>-1</sup>
Region-I	25–197	25–224	25–232
Region-II	197–375	224–410	232–425
Region-III	375–600	410–600	425–600
Peak Temp.-Region- III (°C)	488	519	536
Heat value (kJ kg <sup>-1</sup> )	14084	13910	10763
Ignition temperature (°C)	197	224	231
<i>Kinetic parameters</i>	ASTM-I	ASTM-II	-
Activation energy (kJ/mol)	105.4	102.1	

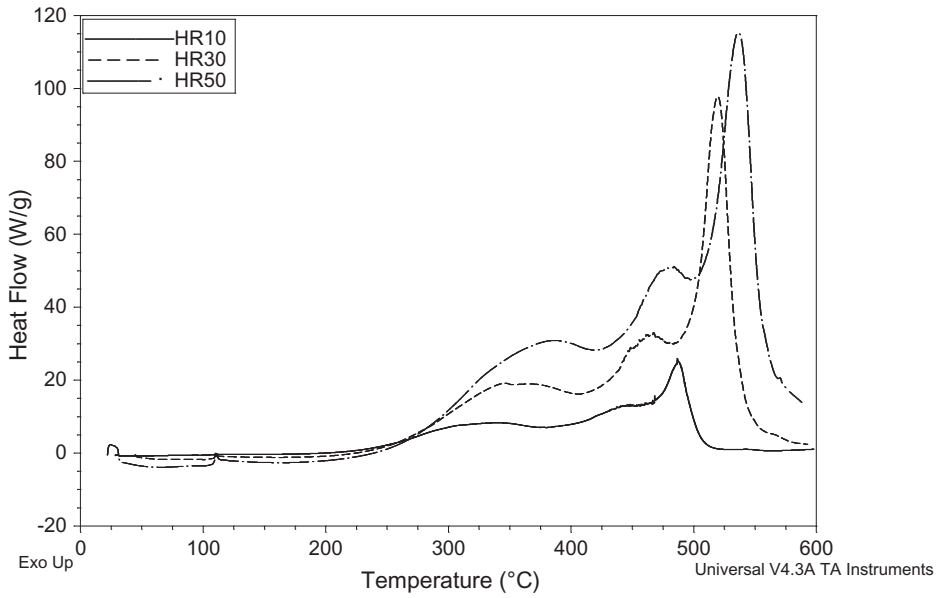
**Region-I:** Vaporization of moisture and devolatilization of volatile matter.

**Region-II:** Combustion of light compounds.

**Region-III:** Combustion of heavy compounds.



a-Ulukışla



b-Himmetoğlu

**Figure 1.** DSC curves of oil shale samples at different heating rates.

contents and can be characterized as low-grade oil shales. It is clear that the Himmetoğlu oil shale sample has high volatile matter and carbon content.

### 3.1. Combustion characterization of oil shale samples (DSC)

In general, oil shale combustion is a complex process and involves a series of parallel reactions. In the oil shale samples studied, a two-step process was observed (Figure 1). In the first process, it is believed that combustion of light hydrocarbon fractions (bitumen) from the shale organic matter

takes place; combustion of the heavy hydrocarbon fractions (kerogen) is known as the second process. In the oil shale samples studied, two reaction regions were identified at different temperature intervals depending on the heating rate. It was observed that the second peak of the Himmetoğlu oil shale is much larger than the Ulukışla oil shale sample, because of higher kerogen and fixed carbon content of this oil shale. The formation of the two peaks in the second reaction region is due to the combustion of different types of kerogens (Table 1). The differences between reaction regions of oil shales are due to their different carbon and volatile matter contents. However, the reaction regions cannot be clearly separated in DSC figures because of the mixing of reaction regions. Also, the isothermal part at 105°C leads to deviation in the DSC peak which shouldn't be linked to any reactions.

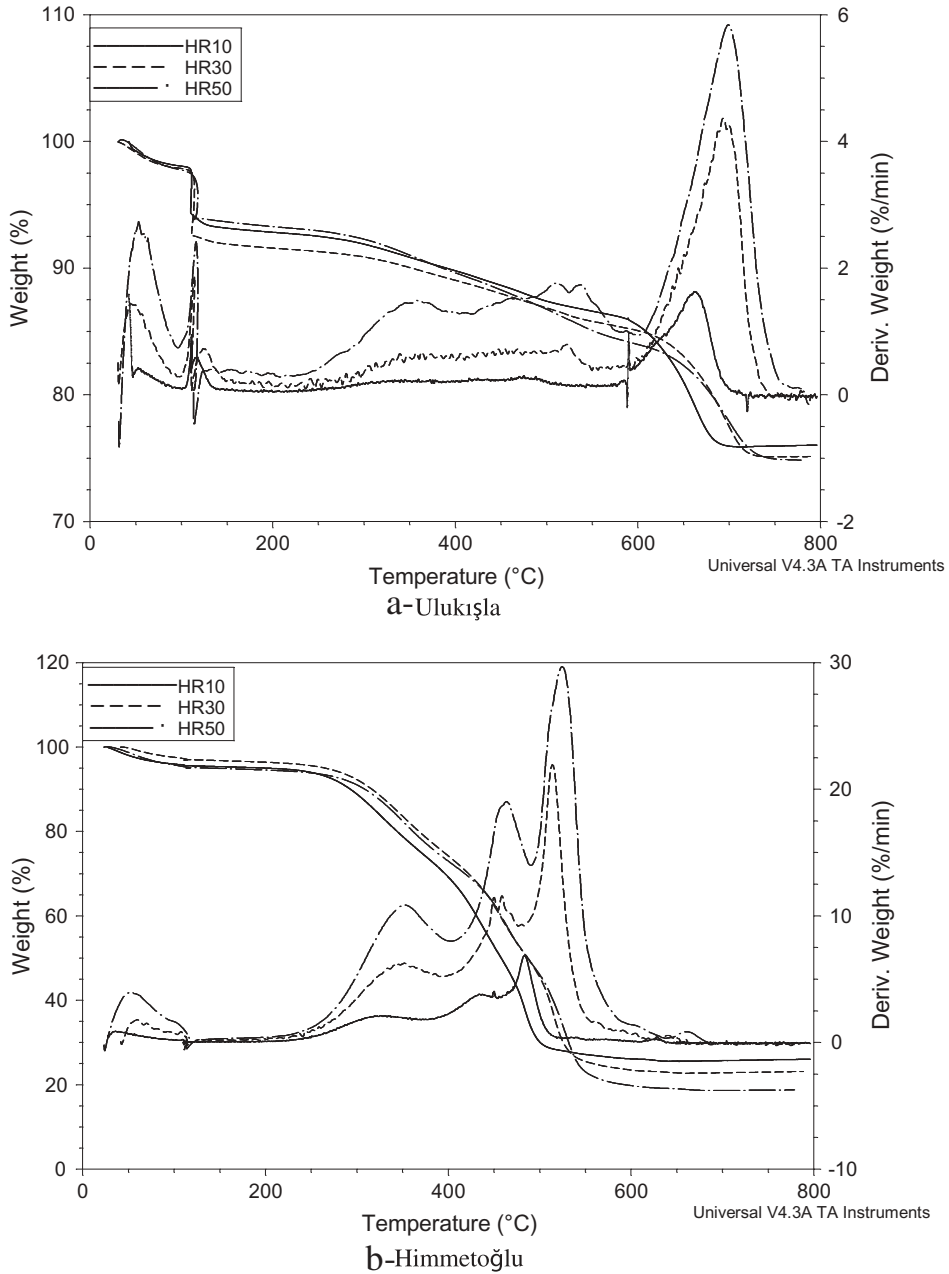
On the other hand, it can be concluded that the combustion of the Himmetoğlu oil shale is more exothermic (more energetic) compared to Ulukışla oil shale combustion. This fact can be verified by semi-quantitative analysis based on the peak heat flow values in DSC curves; 120 W/g for Himmetoğlu and 8 W/g for the Ulukışla oil shale, respectively. It can also be verified by the heat liberated values during reactions (Table 1). It was observed that as the heating decreases, there is a tendency that heat liberated from reaction increases due to the long exposure time of samples to heater so that bonds are cracked easily.

### **3.2. Ignition temperature determination of oil shale samples (DSC)**

The ignition temperature is the lowest temperature at which combustion occurs. However, the ignition temperature of solid fuels cannot be given in exact terms since it depends upon several conditions. The heating rate and particle size have a significant influence on ignition temperature. Ignition temperature is directly proportional to the oxidative stability of a sample. Lower ignition temperature means lower oxidative stability. Solid fuel combustion is primarily governed by its ignition temperature. Ignition temperature is not only an important parameter for the characterization of the solid fuel but also crucial for the design of the boiler equipment of thermal power plants. In this study, DSC curves are preferred for ignition temperature determination, because DSC equipment has high sensitivity and eliminates high errors which are common with the extrapolation method. To obtain the ignition temperatures from DSC, the temperatures were based on the first deviation from the baseline. It was observed that, as the heating rate increased, the ignition temperature values of oil shale samples were also increased. This was due to the shorter residence times for fuels at higher heating rates (Table 1).

### **3.3. Combustion characterization of oil shale samples (TGA-DTG)**

The similar observations can be verified by TG-DTG curves; however, separation of bitumen and kerogen for Ulukışla oil shales was difficult because of low amounts of bitumen and kerogen (Figure 2). From the combustion profile of the Ulukışla oil shale, it was clear that as the heating rate was increased the rate of DTG was also increased in the specific interval. This was the result of high heating leading to a higher mass loss rate. At 110°C, a sharp loss in mass can be observed because moisture is evolved at this point. Similar to the DSC profiles of the Ulukışla oil shale, two reaction regions were identified at different temperature intervals depending on the heating rate. The first reaction represents the combustion of bitumen while the second identifies combustion of kerogen. From the TG-DTG profile of the Himmetoğlu oil shale, it was observed that the combustion is more exothermic compared to the Ulukışla oil shale. The DTG peak of the Himmetoğlu oil shale was much higher than that of the Ulukışla oil shale (Table 2). The TGA profile of the Himmetoğlu oil shale showed three main peaks. The first peak was probably due to the combustion of light volatiles like bitumen. The other two peaks in the reaction region were clear and possibly due to the combustion of different types of kerogens. In TG-DTG curves, at around 600°C, the



**Figure 2.** TGA–DTG curves of oil shale samples at different heating rates

destruction of the ash compound begins (mineral decomposition) which is apparent for oil shales with high ash contents.

It was observed that, during the combustion process, the mass loss amounts was higher for the Himmetoğlu oil shale due to its high volatile matter and high fixed carbon lower ash contents. The total mass loss during the combustion of each oil shale was almost the same for each heating rate so that no relationship was observed connected with the heating rate due to the partial mixing of reaction regions at higher heating rates. It can be concluded that the Himmetoğlu oil

**Table 2.** Properties oil shale samples during combustion (TGA-DTG).

<i>Ulukışla oil shale</i>	10°C min <sup>-1</sup>	30°C min <sup>-1</sup>	50°C min <sup>-1</sup>
Region-I	25–245	25–300	25–300
Region-II	245–400	300–425	300–425
Region-III	400–550	425–550	425–600
Peak Temp.-Region- III (°C)	473	522	538
Average mass loss (%)	4.5	5.0	5.3
Ignition temperature (°C)			
<i>Kinetic parameters</i>	<b>OFW Method</b>	<b>KAS Method</b>	-
Activaiton energy (kJ/mol)	156.1	137.0	
<i>Himmetoğlu oil shale</i>	10°C min <sup>-1</sup>	30°C min <sup>-1</sup>	50°C min <sup>-1</sup>
Region-I	25–200	25–225	25–230
Region-II	200–375	225–410	232–425
Region-III	375–600	410–600	425–600
Peak Temp.-Region- III (°C)	483	514	525
Average mass loss (%)	24.6	25.4	26.6
<i>Kinetic parameters</i>	<b>OFW Method</b>	<b>KAS Method</b>	-
Activaiton energy (kJ/mol)	101.3	113.0	

**Region-I:** Vaporization of moisture and devolatilization of volatile matter.

**Region-II:** Combustion of light compounds.

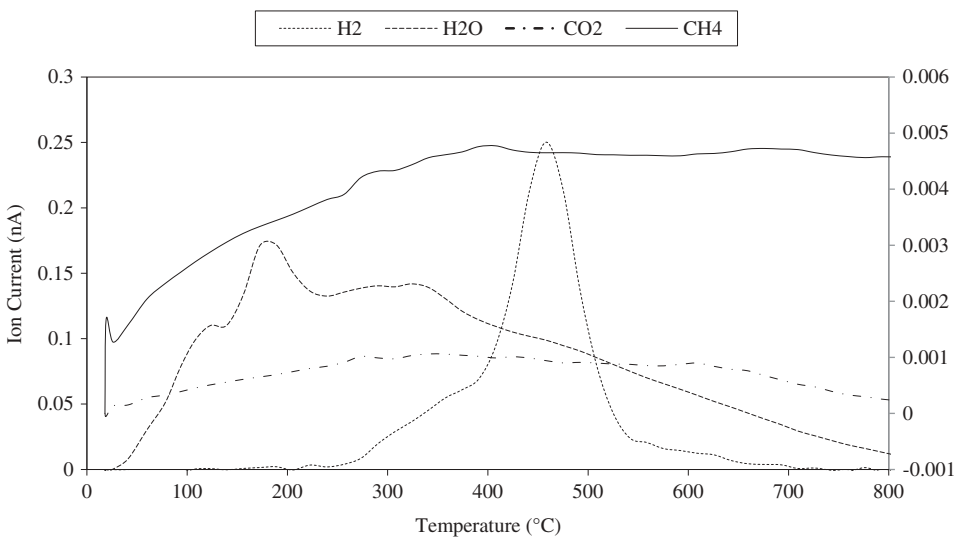
**Region-III:** Combustion of heavy compounds.

shale has the highest energy content due to higher fixed carbon and volatile matter. It was also observed that as the heating rate was increased, the corresponding peak temperatures of the oil shale samples, the reaction region intervals, and peak temperatures of all the oil shale samples were increased (Table 2).

### 3.4. Combustion characterization of oil shale samples (TGA–MS)

In this study, a comparison of the intensity peak areas of the Ulukışla oil shale sample was performed using TGA–MS technique. The shape and the characteristics temperatures of the peaks were compared. Hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), water vapor (H<sub>2</sub>O), and carbon dioxide (CO<sub>2</sub>) were monitored, among the emitted gases.

In complete combustion, water vapor and carbon dioxide are the only products, though in practice it is almost impossible to achieve. During combustion, most of the intermediate products



**Figure 3.** TGA–MS curves of the Ulukışla oil shale for different gas emissions.

are burnt and some – such as hydrogen and methane – escape as emissions without burning. Methane and hydrogen are formed and released due to devolatilization; reforming; and/or charring reactions during combustion (Figure 3). It was observed that a hydrogen and methane emission of the Ulukışla oil shale sample was low due to the volatile content. Between 110 and 150°C, first water loss was observed due to physical adsorption (physic-sorption). The second water loss region was observed at around 180°C for the Ulukışla oil shale sample. The water in this region is due to reaction water and chemisorption which is characterized by a strong interaction between an adsorbate and a substrate surface, compared to physisorption which is controlled by weak Van der Waals forces. Carbon dioxide in the emissions is a primary product of the combustion process as an O<sub>2</sub>/Ar environment is used for TGA–MS experiments. Higher carbon dioxide emissions mean better energy content in the fuel in the combustion interval. Side reactions (cracking, polymerization, reforming, etc.) – different from combustion reactions – may also partially lead to the formation of carbon dioxide in the reaction interval, as well. The carbon dioxide emission was low for Ulukışla oil shale sample because of its lower exothermic behavior.

### 3.5. Kinetic analysis

The non-isothermal kinetic study during the combustion process of oil shales is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions. To perform a kinetic analysis based on TGA and DSC output data; there are different kinetic methods available in the thermal analysis literature. In this research, three different kinetic methods were used known as; Ozawa–Flynn–Wall (OFW), Kissinger–Akahira–Sunose (KAS), and ASTM methods. Due to its large instability, the value of the frequency factors does not provide meaningful interpretations. Therefore, values of activation energies were treated as superior parameters for the interpretations. Also, the conversion intervals were selected between the beginning of the first reaction regions and the end of the second reaction regions for the simplicity of the processes and comparisons. The weight in the kinetic methods is considered as the organic material burnt in the reaction regions.

#### 3.5.1. Ozawa–Flynn–Wall (OFW) method

In the Ozawa–Flynn–Wall (OFW) method (Ozawa, 1965), TG–DTG curves are used simultaneously to determine the activation energy values at the same conversion levels, using the following relationship which is from the P function of Doyle's approximate expression.

$$[d(\log\beta)/d(1/T)] = 0.4565 (E/R). \quad (1)$$

In this method, activation energies generated for the combustion region for oil shale samples was 156.1 kJ mol<sup>-1</sup> for the Ulukışla oil shale and 101.3 kJ mol<sup>-1</sup> for the Himmetoğlu oil shale, respectively (Table 2).

#### 3.5.2. Kissinger–Akahira–Sunose (KAS) method

In the Kissinger–Akahira–Sunose (KAS) method (Akahira and Sunose, 1971), the apparent activation energy is obtained from a plot of  $\ln(\beta_i/T_{ai}^2)$  vs.  $1,000/T_{ai}$  for a given value of conversion,  $\alpha$ , where the slope is equal to  $-E_\alpha/R$ . The final form of the equation which is used to determine the apparent activation energy is given below.

$$\ln(\beta_i/T_{ai}^2) = \ln[(A_\alpha R)/(E_\alpha g(\alpha))] - (E_\alpha/RT_{ai}). \quad (2)$$

In this method, it was observed that the activation energy values were close to each other on each conversion levels and the mean activation energy was 137 kJ mol<sup>-1</sup> for the Ulukışla oil shale and 113 kJ mol<sup>-1</sup> for the Himmetoğlu oil shale, respectively. Therefore, it can be concluded that the reaction mechanism is the same for all the oil shale samples studied and is not dependent on conversion levels (Table 2).



### 3.5.3. ASTM methods

A well-known approach for DSC kinetics is the ASTM E-698 methods (ASTM E 698, 1979; Altun et al., 2003; Kok, 2008). In these methods (ASTM I and II), the sample temperature is increased at linear heating rates and any exothermic peaks are recorded. In ASTM-I, a trial and error procedure was used and the activation energy is calculated approximately from the following equations respectively.

$$E = [(-2.303R/D) \times (d(\log\beta)/d(1/T))], \quad (3)$$

$$A = \beta E e^{E/RT} / RT^2. \quad (4)$$

In the ASTM-2 method, the activation energy is calculated using the following equation.

$$E = [-R \times d(\ln\beta/T^2)/d(1/T)]. \quad (5)$$

In two different applications of ASTM methods, the activation energies generated for the combustion region for oil shale samples were in the range of 122.1–128.7 kJ mol<sup>-1</sup> for the Ulukışla oil shale and 102.1–105.4 kJ mol<sup>-1</sup> for the Himmetoğlu oil shale, respectively (Table 1).

Throughout the study, it was observed that the activation energy (the energy that must be overcome in order for a chemical reaction to occur or the minimum energy required in order to start a chemical reaction) values of the oil shale samples was close to each other for all the methods studied; however there are differences in results of kinetic methods due to different equation parameters and assumptions (Ozbas et al., 2000; Kok and Iscan, 2001; Kok, 2003; Ozgur et al., 2012). Finally, it can be concluded that the reactivity of the Himmetoğlu oil shale is higher, because of the lower activation energy. In the same trend, the Ulukışla oil shale has lower reactivity due to its higher activation energy. It was also observed that the kinetic results are close to the other research findings in the literature from the viewpoint of oil shale combustion.

## Conclusions

In the study, combustion performance and kinetics of two oil shale samples are determined using DSC, TGA–DTG, and TG–MS techniques at different heating rates. From this study, the following conclusions were derived.

- In a low grade oil shale, two stages are observed at different temperature intervals depending on the heating rate known as bitumen and kerogen combustion. In contrast, a high grade oil shale showed three stages of combustion possibly due to the combustion of different types of kerogen.
- It was observed that the intervals of reaction regions during the combustion process depend on the heating rate and the grade of the oil shales studied. On the other hand, the heating rate has no significant effect on the mass loss of the oil shale samples studied.
- TGA–MS measurements perceive the evolution of the main gas products during the combustion of oil shale samples. This technique is the only one to simultaneously measure in real time gas product release of the samples.

3-Differences in activation energy values of different kinetic methods are due to different equation parameters and assumptions.

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