

## KINETIC ANALYSIS OF CENTRAL ANATOLIA OIL SHALE BY COMBUSTION CELL EXPERIMENTS

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In this study, four oil-shale samples (Niğde-Ulukışla) excavated from Central Anatolia Turkey were analyzed where this region is believed to have a high potential of oil in its shale rich outcrops. The samples (~40 g) were combusted at 50 psi gas injection pressure, at an air injection rate of 1.5 L min<sup>-1</sup> in a combustion-reaction cell. All the experiments were conducted up to 600°C. The percentages of oxygen consumption and carbon monoxide and carbon dioxide production were obtained instantaneously with respect to time. The combustion periods and relative reaction rates were determined by examining the effluent gas concentration peaks. Activation energies of the samples were determined using Weijdema's approach. It was observed that the activation energies of the samples are varied between 22–103 kJ mol<sup>-1</sup>.

**Keywords:** activation energy, combustion cell, oil shale, reaction kinetics

### Introduction

Thermal analysis techniques – thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), and differential thermal analysis (DTA) – are popular and convenient tools in studying combustion reactions of fossil fuels. The requirement of only a small amount of material coupled with the comparatively fast and easy performance of experiments makes the technique attractive. Thermal analytical instruments monitor the changes in properties caused by different processes. Much of the work on thermal analysis of oil shale samples was directed towards on characterization, pyrolysis-combustion kinetic analysis.

Earnest [1] analyzed the thermal behaviour of Green River oil shale in a dynamic nitrogen atmosphere with TG and DTG and compared it with that in retorting processes. Using the results of this study, the pyrolysis onset temperatures and the temperatures at the maximum pyrolysis rate were related to the type of organic maceral components of the oil shale specimen. Skala and Sokic [2] developed a kinetic expression commonly used in the thermal analysis of oil shale pyrolysis. This was derived on the basis of a simple first-order kinetic equation of kerogen decomposition. The obtained results show that the largest activation energies were detected by using isothermal TG, while combined non-isothermal and isothermal. Lisboa and Watkinson [3] used standard thermogravimetric apparatuses for the study of the chemical kinetics of oil shale pyrolysis and combustion, such as controlled temperature and

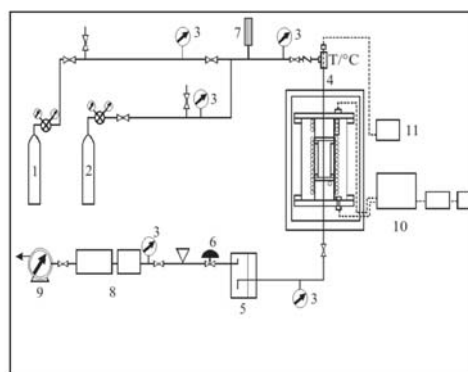
simultaneous weighing of the sample. This study investigated the effects of key parameters, which could affect this identity, such as: the gas flow rate, the gas purity, the gas nature, the particle sizes and sample sizes. Karabakan and Yürüm [4] investigated the effect of mineral matrix of oil shales and air diffusion on the conversion of organic material in oxidation reactions. The overall reaction orders from the kinetic analysis were found to be pseudo first order. It was found that the rate of reaction depends on the rate of transport of the gas into the zone of reaction by diffusion. It was also observed that the diffusion of oxygen into the organic matrix was the major resistance controlling the rate of oxidation reactions. Kök [5, 6] studied the thermal characteristics of four oil shale samples by thermal analysis techniques. Two distinct exothermic peaks were identified in all experiments known as low temperature oxidation and high temperature oxidation reaction regions. Kinetic data were analyzed by different methods and the results are discussed. Değirmenci and Durusoy [7] studied the combustion and pyrolysis kinetics of oil shales. They analyzed their thermogravimetric data by a first order kinetic model. The aim of their research is to investigate the pyrolysis and combustion of Göynük oil shale by thermogravimetry. They concluded that the total conversion values are independent of heating rate during pyrolysis and combustion. They stated that maximum deposition rate increases with heating temperature. Kök and Pamir [8–12] determined the thermal characteristics and kinetic parameters of oil

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shale samples by thermogravimetry (TG/DTG) at non-isothermal heating conditions both for pyrolysis and combustion processes. A general computer program was developed and the methods are compared with regard to their accuracy and the ease of interpretation of the kinetics of thermal decomposition. Activation energies of the oil shale samples were determined by five different methods and the results are discussed. Kök [13] investigated the role of clay on the combustion and kinetic behavior of crude oils in limestone matrix. For this purpose, simultaneous TG-DTA experiments were performed at three different heating rates as 10–15 and 20°C min<sup>-1</sup>, respectively. A uniform trend of decreasing activation energies was observed with the addition of clay. It was concluded that clays surface area affects the values of Arrhenius constant, while it is the catalytic properties of clay, which lower the activation energies of all the reactions, involved in the combustion process. Kök [14] used differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) to obtain information on the temperature-controlled combustion characteristics of seventeen coals of different origin. The DSC/TG curves clearly demonstrate distinct transitional stages in the entire coal samples studied. Reaction intervals, peak and burn-out temperatures of the coal samples are also determined. Two different kinetic methods known as, Arrhenius and Coats–Redfern, were used to analyze the kinetic data and the results are discussed.

## Experimental

The oil shale samples (from four different locations of Niğde-Ulukışla oil shale field) used throughout the research was from Central Anatolia region (Table 1). In this research, a reaction kinetic cell was used to conduct the experiments. The reaction kinetic cell is constructed from stainless steel tube and two iron-constantan thermocouples are inserted into the reaction kinetics cell, one of them is used to measure the temperatures at the center of the reaction cell. Another thermocouple is used to control and measure the temperature of the heater. The cell was equipped with furnace, temperature programmer, air and nitrogen flow rate controller, digital temperature indicator, pressure gauges and continuous gas analysis equipment (Fig. 1). Variable temperature program was applied to the reaction kinetics cell



**Fig. 1** Experimental set-up; 1 – high pressure air cylinder, 2 – high pressure nitrogen cylinder, 3 – pressure gauge, 4 – thermocouple and reaction kinetic cell, 5 – kinetic cell outlet, 6 – ball valve, 7 – rotameter, 8 – continuous gas analyzer, 9 – wet test meter, 10 – temperature controller programmer unit, 11 – digital temperature readout

with increase at a constant heating rate, in order to determine reaction rate data. 40 g of oil shale was packed in reaction kinetics cell. During the experiments, initial temperature of the reaction cell was set around 20°C, then the cell temperature was raised to 100°C in 5°C min<sup>-1</sup> rate and retained for a half hour at 100°C in order to reach thermal equilibrium in the reaction cell. Then the reaction cell temperature was increased at a constant rate of 1°C min<sup>-1</sup> after this point throughout the heating of the cell and air (21% oxygen, 79% nitrogen) was injected into the cell at a constant rate of 1.5 L min<sup>-1</sup>. The cell was continuously heated to 600 with 1°C min<sup>-1</sup> heating rate. During the experiments, centre temperatures in the cell and O<sub>2</sub>, CO<sub>2</sub> and CO gases were analyzed and recorded from continuous gas analyzer. This recording procedure continued until no carbon oxide gases were observed in the produced gas from the reaction kinetics cell. To check the reproducibility, experiments were performed twice.

## Results and discussion

A total of eight combustion reaction kinetic runs were performed using four different oil shale samples (from four different locations of Niğde-Ulukışla oil shale field) of the same region (Central Anatolia). Produced CO<sub>2</sub>, CO and consumed oxygen and the temperature of the sample (y-2) as a function of time from the beginning of air injection are given in Fig. 2. Two apparent

**Table 1** Properties of oil shale sample

Calorific value/cal g <sup>-1</sup>	Total organic carbon/mass%	Oil content/mass%	Total sulphur/mass%	Reserve/ton
851	4.8	5.2	0.8	130·10 <sup>6</sup>

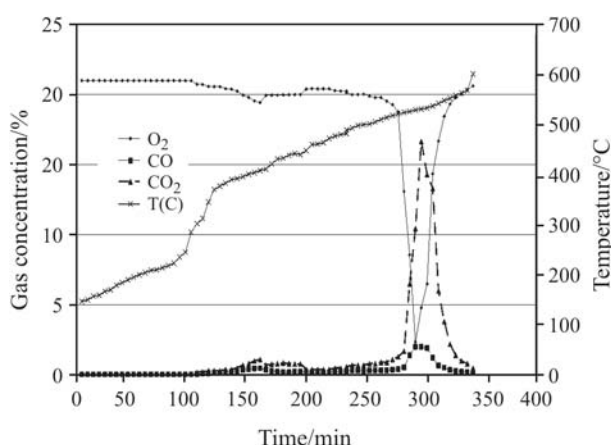


Fig. 2 Gas composition and temperature as a function of time

peaks existed for consumed oxygen, CO<sub>2</sub> and CO at different temperature intervals known as low temperature oxidation and fuel combustion. It was observed that at high temperatures almost all of the oxygen is consumed to produce CO<sub>2</sub> and CO, which indicates complete combustion. The atomic H/C ratio of the reacting sample was calculated for each combustion reaction. The atomic H/C ratio of the fuel consumed was calculated from the analysis of produced gases for each run, as a function of temperature [15]. These calculations were based on the assumption that all the oxygen not observed in the exit gas was reacted to form water. A general decrease in the atomic H/C ratio with an increase in temperature was observed (Fig. 3). On the other hand, addition of a solvent to a highly oil prone oil shale sample expedited the reaction and resulted in higher H/C ratio.

### Kinetic analysis

A kinetic model developed by Weijdema [16] and adapted to reaction kinetics studies by Fassihi *et al.* [17] was used for analysis of non-isothermal runs of

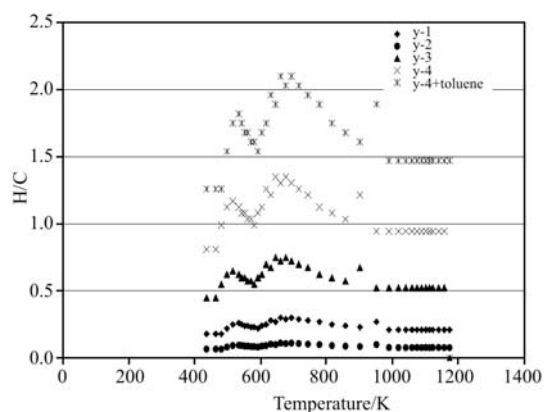


Fig. 3 H/C ratios as a function of temperature

this study. The rate of oxygen consumption per unit volume is:

$$q\Delta\gamma/AL = ArP_{O_2}^m C_f^n \exp(-E/RT) \quad (1)$$

This is also equal to the rate of decrease of oil saturations:

$$q\Delta\gamma/AL = -\alpha dC_f/dt \quad (2)$$

where  $\alpha$  is the proportionality factor, equal to the amount of oxygen in moles that reacts with 1 g of the oil. The rate of oxygen consumption at any time can be obtained by combining Eqs (1) and (2):

$$q\Delta\gamma/AL = ArP_{O_2}^m C_f^n \exp(-E/RT) = -\alpha dC_f/dt \quad (3)$$

Integration between  $t=t$  and  $t=\infty$  yields:

$$\alpha C_f(t) = \int_t^\infty (q\Delta\gamma/AL) dt' \quad (4)$$

where  $C_f=0$  at  $t=\infty$ . From Eq. (3):

$$C_f^n(t) = (q\Delta\gamma/AL) / (ArP_{O_2}^m) C_f^n \exp(-E/RT) \quad (5)$$

If we substitute Eq. (5) in Eq. (4) we obtain:

$$\Delta\gamma / \left[ \int_t^\infty \Delta\gamma dt' \right]^n = \beta' \exp(-E/RT) \quad (6)$$

where

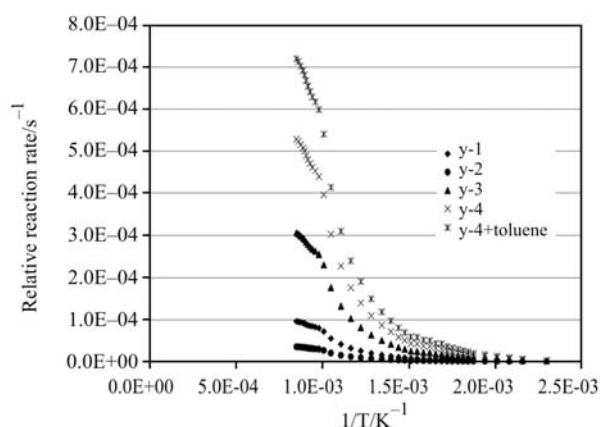
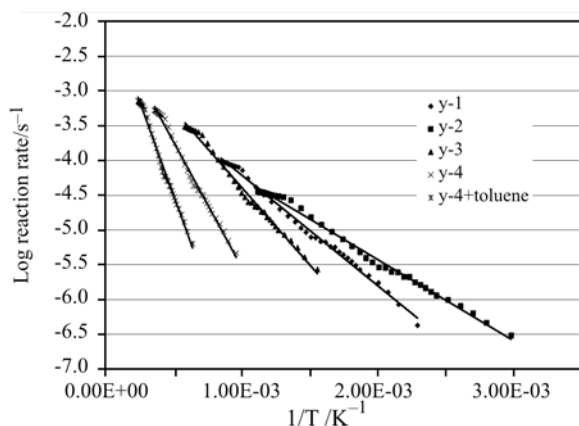
$$\beta' = (q/AL)^{n-1} ArP_{O_2}^m / \alpha^n \quad (7)$$

Values for the left hand side of Eq. (6) can be found by graphical integration of the curve  $\Delta\gamma=f(t)$ . Then the logarithm of the left hand side of Eq. (6) can be graphed vs.  $1/T$  to obtain  $(-E/2.303R)$  as the slope, and  $\log\beta'$  as the intercept. In order to find the values of the left hand side of Eq. (6), the graphical integration can be applied to the curve  $W=f(t)$ . The trapezoidal rule was applied to the area under this curve to calculate the relative reaction rate.

In this model, the temperature linearly increases with time, and by proper graphing of the variables, a semi-logarithmic straight line should result. The relative reaction rate was calculated and graphed (Fig. 4). On the other hand, straight lines of the same slope were drawn in the Arrhenius plots (Fig. 5). From this figure, a straight line was obtained for the fuel combustion region, where the activation energies of the samples were determined from the slope of the line (Table 2). It was observed that the calculated activation energies vary between 22–103 kJ mol<sup>-1</sup>. The slopes of the linear plots indicated that toluene addition increases the activation energy of the sample. Linear intercepts values increased as the activation energy increased.

**Table 2** Activation energy ( $\text{kJ mol}^{-1}$ ) and  $\beta'$  values of oil shale samples – combustion

Sample	Activation energy/ $\text{kJ mol}^{-1}$	$\beta'$
y-1	30.5	0.0025
y-2	22.3	0.0008
y-3	42.6	0.0071
y-4	69.0	0.0121
y-4 with toluene	103.0	0.0165

**Fig. 4** Relative reaction rates vs. inverse temperature**Fig. 5** Arrhenius plot vs. inverse temperature;  
 $y_1 = -1590x - 2.61$ ,  $y_2 = -1167x - 3.08$ ,  $y_3 = -2224x - 2.15$ ,  
 $y_4 = -3600x - 1.916$ ,  $y_{4+\text{toluene}} = -5401x - 1.78$ 

## Conclusions

A total of eight experiments were performed, as well as a reaction kinetic analysis of four oil shale samples from Central Anatolia region. The following results were obtained:

- In all the experiments the combustion of the oil shales started at around  $530^\circ\text{C}$ . The oxygen consumption during combustion was around 18.4%.
- H/C ratio increased as the activation energy increased.
- Maximum activation energy was obtained with the solvent mixing process. Addition of toluene enhanced the combustion characteristic of the oil shale sample y-4 by 50% from 69 to  $103 \text{ kJ mol}^{-1}$ .

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DOI: 10.1007/s10973-006-8026-z