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OIL SHALE KINETICS BY DIFFERENTIAL METHODS

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In this research, pyrolysis and combustion behavior of three different oil shale samples from Turkey were characterized using thermal analysis techniques (TG/DTG). In pyrolysis experiments, two different mechanisms causing mass loss were observed as distillation and cracking. In combustion experiments, two distinct exothermic peaks were identified known low and high temperature oxidation. On the other hand, determination of activation energies are required for the estimation of oil extraction conditions from the oil shales. Differential methods are used to determine the activation energies of the samples where various $f(\alpha)$ models are applied from the literature. It was observed that the activation energies of the all oil shale samples are varied between 13.1–215.4 kJ mol^{-1} in pyrolysis and 13.1–408.4 kJ mol^{-1} in combustion experiments which are consistent with other kinetic results.

Keywords: *activation energy, combustion, kinetics, oil shale, pyrolysis, thermal analysis*

Introduction

Thermal analysis is a popular and convenient tool in studying combustion reactions of fossil fuels Differential Scanning Calorimetry (DSC) and thermogravimetry (TG/DTG) of oil shale samples has been extensively used as a means of determining the 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 chemical reactions in the thermal degradation of the oil shale. The study of kinetics is essential for the understanding of the mechanisms and mathematical modeling of process, which may lead to improved techniques for oil shale conversion.

Thakur and Nuttall [1] studied the pyrolysis kinetics of thermal decomposition of oil shale by isothermal and non-isothermal thermogravimetry. The combined use of isothermal and isothermal TG measurements showed that thermal decomposition of oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions followed first order kinetics. Karabakan and Yurum [2] 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. The magnitude of the activation energies of oxidation reactions at equal heating rates changed. Berkovich *et al.* [3] presented a novel technique to the thermal characterization of oil shale. This approach involves the separation of the unique components of oil shale, the kerogen and the clay minerals, using chemical and physical techniques. Enthalpy data for dehydration and pyrolysis of kerogen were also determined. Jaber and Probert [4] studied oil shale samples using a thermogravimetric analyzer. The controlling parameters studied were the final pyrolysis temperature and the influence of the heating rate as well as type of purge gas employed on the process of thermal degradation of the shale sample. The integral method was used in the analysis of TG data in order to determine the pyrolysis kinetics. It was observed that the magnitude of the total mass loss was mainly dependent on the final temperature, as well as, to a lesser extent, on the heating rate employed. Williams and Ahmad [5] studied oil shale samples in a thermogravimetric analyzer in relation to heating rate and temperature using non-isothermal and isothermal analysis respectively. The main region of mass loss corresponding to hydrocarbon oil and gas release was between 200–620°C and at higher temperatures significant mass loss was attributed to carbonate decomposition. The kinetic data were analyzed using different methods. There was no clear relationship between activation energy and heating rate. Kok and Pamir [6–10] determined the thermal characteristics and kinetic parameters of oil shale samples by TG and 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. Torrent and Galen [11] studied the kinetics of thermal decomposition of oil shale using thermogravimetry. It was

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observed that the rate of thermal decomposition of oil shale can be suitably described by overall first-order kinetics. No mass and heat transfer resistance was observed for the different particle sizes studied. Jaber and Moshe [12] investigated the drying kinetics of two oil shales from different deposits over a temperature range of 70–150°C in thermogravimetry under direct insulation. The mass loss and drying rates of the samples were determined gravimetrically. It has been observed that drying rate falls off at a critical temperature and approaches zero beyond this temperature. Kok [13, 14] 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. Kok *et al.* [15] studied the thermal and organic geochemical investigation of Seyitömer oil shale. DSC and TG/DTG is used to determine the thermal behavior of oil shale sample. On the other hand, organic carbon content, rock-eval pyrolysis and gas and liquid chromatograph experiments were conducted to determine the geochemical properties of oil shale sample. Barkia *et al.* [16] conducted studies on thermal analysis studies about residual carbon in oil shales. They aimed to observe the effect of heating rate on oil shales between ambient temperature and 500°C. They concluded that pyrolysis of this oil shale took place in two stages whereas, oxidation of residual carbon had a first order kinetic behavior. Han *et al.* [17] investigated the thermal analysis on combustion mechanisms of oil shales. They applied combustion and pyrolysis tests on oil shale. They analyzed effects of various parameters such as particle size, oxygen amount and heating rate. They found out that particle size has less effect on combustion characteristics. However, starting temperature of combustion decreases with increasing oxygen concentration. They concluded that activation energy and ignition temperature will increase as the heating rate increases.

Experimental

In this research, experiments were performed with DuPont 9900 thermal analysis system with thermogravimetry module. Thermogravimetry (TG/DTG) has the capability of measuring the mass loss either as a function of temperature or time in a varied but controlled atmosphere and calibrated with calcium oxalate monohydrate for temperature readings and silver was used in order to correct for buoyancy effects. The oil shale samples used in this research had a particle size <60 mesh and prepared according to the ASTM Standards (D 2013-72). Air flow rate through the sample pan was kept constant at 50 mL min^{-1}, and all the experiments were conducted in the temperature range of 20–600°C at 5°C min^{-1} heating rate. For repeatability, experiments were performed twice. Properties of oil shale samples are given in Table 1.

Results and discussion

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. Non-isothermal TG/DTG study of mass loss under pyrolysis and combustion process is extremely complex for oil shales, because of the presence of the numerous complex components and their parallel and consecutive reactions. As it is mentioned before, combustion and pyrolysis experiment were performed using three different oil shale samples known as Çan, Mengen and Himmetoğlu (Figs 1 and 2). In combustion experiments two reaction regions, known as low temperature oxidation (LTO) and high temperature oxidation (HTO), were obtained for Himmetoğlu and Mengen oil shales and one reaction region for Çan oil shale. On the other hand, only one reaction region was seen in pyrolysis experiments for all the oil shale samples studied. The reaction intervals and peak temperatures of the oil shale samples for pyrolysis and combustion are given in Table 2.

In the kinetic analysis part of this study, the obtained combustion and pyrolysis experimental data were analyzed by differential alpha approach (Figs 3 and 4). The significance of this approach is plotting alpha (α) *vs.* time graphs and determining the equation of alpha (α) as a function of time [18, 19].

The most commonly used equation to describe the reaction rate is in the differential form:

Table 1 Properties of oil shale samples

Oil shale	Calorific value/J g^{-1}	Water/ %	Ash/ %	C/ %	H/ %	O, N/ %	S/ %
Çan	3865	12.40	80.50	10.10	1.95	10.06	0.98
Mengen	3555	9.50	68.40	10.05	1.90	8.80	0.85
Himmetoğlu	4540	12.90	60.50	13.60	1.50	10.48	0.99

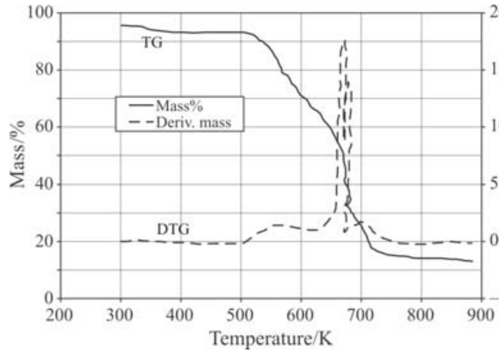

Fig. 1 TG/DTG curve of Himmetoğlu oil shale –Combustion

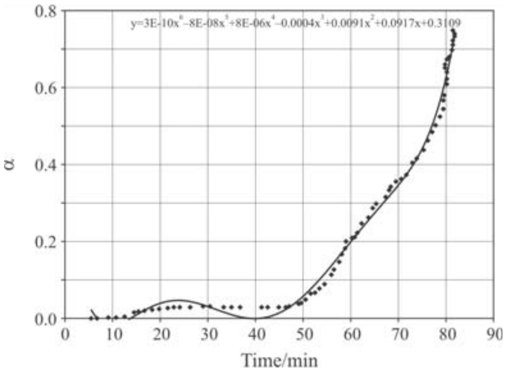

Fig. 3 α *vs.* time of Himmetoğlu oil shale –Combustion–

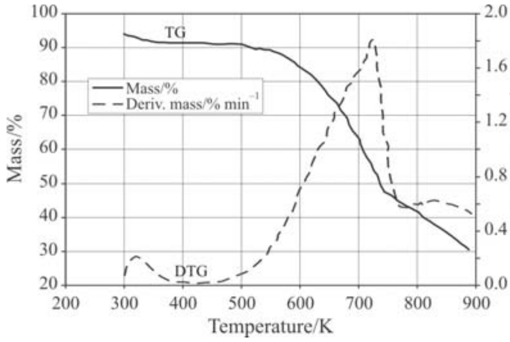

Fig. 2 TG/DTG curve of Himmetoğlu oil shale –Pyrolysis–

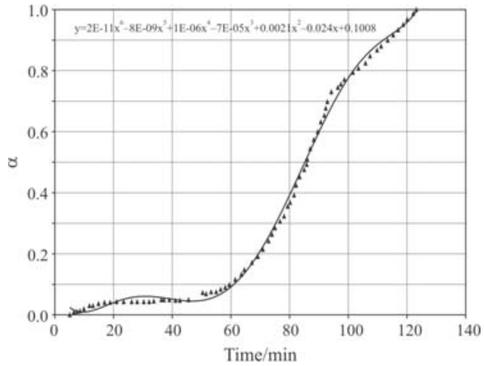

Fig. 4 α *vs.* time of Himmetoğlu oil shale –Pyrolysis–

$$d\alpha/dt=f(\alpha)k(T) \tag{1}$$

where $f(\alpha)$ is the function of α which represents the reaction mechanism (Table 3), $k(T)$ is the rate constant at the temperature T, and α is equal to:

$$\alpha=(W_i-W)/(W_i-W_f) \tag{2}$$

where W is the mass or the mass% of the sample at a certain time. W_i and W_f are the initial and final values of the reaction and generally takes the Arrhenius equation form:

$$k(T)=A\exp(-E/RT) \tag{3}$$

where A is the frequency factor, E is the activation energy, R is the gas constant and T is the absolute temperature.

In this application, the idea is representing alpha (α) as a function of time. Otherwise, it would be rather difficult to determine the derivative function. It was seen that all of the alpha (α) *vs.* time graphs were in 's' shape. The correlations of alpha (α) and time were obtained by curve fitting. The derivative of the alpha (α) function was taken with respect to time. After having known all those function values, the values of the $k(T)$ for different temperatures were calculated. Taking the natural logarithm of both hand sides of the above Eq. (3)

$$\ln k(T)=-E/(RT)+\ln A \tag{4}$$

Plots of $\ln k(T)$ *vs.* $1/T$ gave out the slopes as $-E/(RT)$ and the activation energies were calculated from the slope of the equations.

As it is mentioned above, the activation energies of the oil shale samples, both for pyrolysis and combustion, were determined by introducing eight different alpha (α) calculations (Tables 4, 5). The following equations of n^th^ order polynomials and differentiable with respect to time fits the alpha (α) *vs.* time data very well.

$$\alpha=3\text{E-}10t^6-8\text{E-}08t^5+8\text{E-}06t^4$$
$$-0.0004t^3+0.0091t^2-0.0917t+0.3109 \tag{5}$$

Table 2 Reaction intervals and peak temperatures of oil shale samples

Oil shale	Reaction int./K Pyrolysis	Peak temp./K Pyrolysis	Reaction int./K LTO Combustion	Peak temp./K LTO Combustion	Reaction int./K HTO Combustion	Peak temp./K HTO Combustion
Çan	426–720	641	480–720	618	–	–
Mengen	504–808	720	520–600	587	600–725	654
Himmetoğlu	550–720	650	525–630	586	642–735	679

Table 3 Common forms of $f(\alpha)$

Mechanism	$f(\alpha)$	Identification
S shaped α-t curve	$1.5(1-\alpha)(-\ln(1-\alpha))^{1/3}$	α–1
	$2(1-\alpha)(-\ln(1-\alpha))^{1/2}$	α–2
	$3(1-\alpha)(-\ln(1-\alpha))^{2/3}$	α–3
	$4(1-\alpha)(-\ln(1-\alpha))^{3/4}$	α–4
	$\alpha/(1-\alpha)$	α–5
	$0.5(1-\alpha)(-\ln(1-\alpha))^{-1}$	α–6
	$1/3(1-\alpha)(-\ln(1-\alpha))^{-2}$	α–7
	$1/3(1-\alpha)(-\ln(1-\alpha))^{-3}$	α–8

$$\alpha=2\text{E-}11t^6-8\text{E-}09t^5+1\text{E-}06t^4 \\ -7\text{E-}05t^3+0.0021t^2-0.024t+0.1008 \qquad (6)$$

The slopes of the linear plots with eight different $f(\alpha)$ calculations were obtained for both combustion and pyrolysis. The combustion slopes were almost on top of each other with the first four alpha function definitions. The fifth function indicated a different profile with a positive slope while the other functions all gave out negative slopes. However it was seen that as the slopes decreased, the coefficients of the alpha function – $f(\alpha)$ – increased within the first four functions and the slopes increased with the reduction of the function coefficients in alpha functions six to eight (Figs 5, 6). The equations of linear plots and their regression coefficients (R^2) values are all very close unity. The pyrolysis analysis of the oil shales depicted similar trends as the combustion lines (Fig. 7). In general, the different alpha functions – $f(\alpha)$ – are generally of the similar form. However, the equation constants and powers vary significantly. Even though all of the linearization plots had similar trends, the slopes and consequently the activation en-

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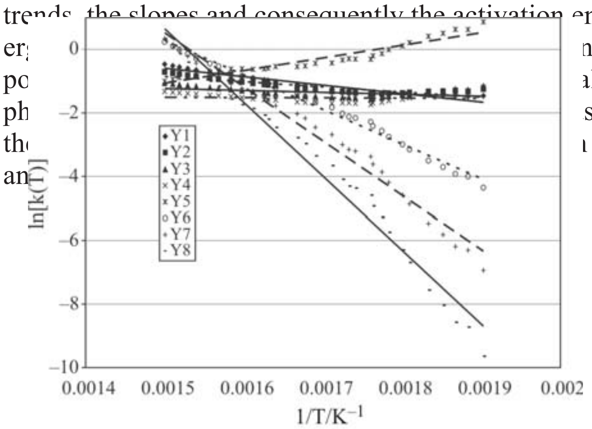

Fig. 5 ln$k(T)$ *vs.* $1/T$ of Himmetoğlu oil shale with different α Functions –LTO–Combustion, $y_1=-2662+3.398$ $R_1^2=0.9395$, $y_2=-6627.4x+1.5974$ $R_2^2=0.8731$, $y_3=-9105x-0.3211$ $R_3^2=0.9132$, $y_4=-3788x-1.3653$ $R_4^2=0.9414$, $y_5=6663x-7.0238$ $R_5^2=0.9091$, $y_6=-10878x+16.601$ $R_6^2=0.9895$, $y_7=-17040x+26.1$ $R_7^2=0.9802$, $y_8=-23202x+35.45$ $R_8^2=0.9748$

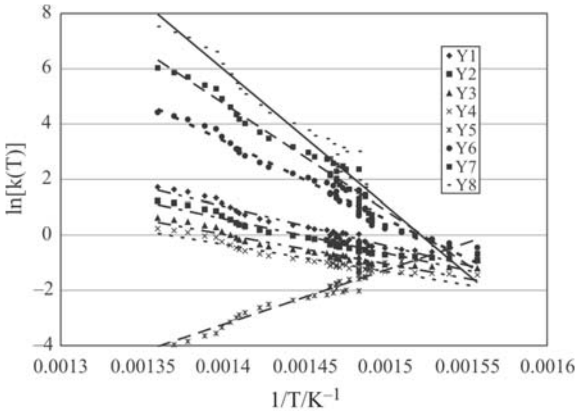

Fig. 6 ln$k(T)$ *vs.* $1/T$ of Himmetoğlu Oil Shale with Different α Functions –HTO–Combustion– $y_1=-14155x+20.859$ $R_1^2=0.9533$, $y_2=-12406x+17.965$ $R_2^2=0.9437$, $y_3=-10657x+14.953$ $R_3^2=0.9273$, $y_4=-9783.1x+13.362$ $R_4^2=0.9151$, $y_5=19680x-30.795$ $R_5^2=0.9532$, $y_6=-28144x+42.808$ $R_6^2=0.9669$, $y_7=-38636x+58.8$ $R_7^2=0.9648$, $y_8=-49128x+7$ $R_8^2=0.9625$

Table 4 Activation energy values (kJ mol^{-1}) of oil shale samples –Combustion

α	Himmetoglu oil shale, LTO	Himmetoglu oil shale, HTO	Mengen oil shale, LTO	Mengen oil shale, HTO	Çan oil shale, HTO
α–1	24.6	117.6	22.3	86.9	19.3
α–2	55.1	103.1	31.2	79.1	17.5
α–3	75.7	88.6	15.7	71.3	14.3
α–4	31.5	81.3	25.2	67.4	13.1
α–5	53.4	163.6	27.4	40.3	18.3
α–6	90.4	233.9	17.3	149.5	39.4
α–7	141.6	321.2	24.9	193.3	54.4
α–8	192.9	408.4	40.3	243.4	69.5

Table 5 Activation energy values (kJ mol^{-1}) of oil shale samples –Pyrolysis

α	Himmetoğlu oil shale	Mengen oil shale	Çan oil shale
α–1	77.6	42.1	71.4
α–2	70.7	35.6	78.6
α–3	63.8	28.9	85.9
α–4	60.4	22.9	89.4
α–5	41.8	66.1	169.7
α–6	132.7	93.2	13.1
α–7	174.1	128.9	29.7
α–8	215.4	141.3	73.1

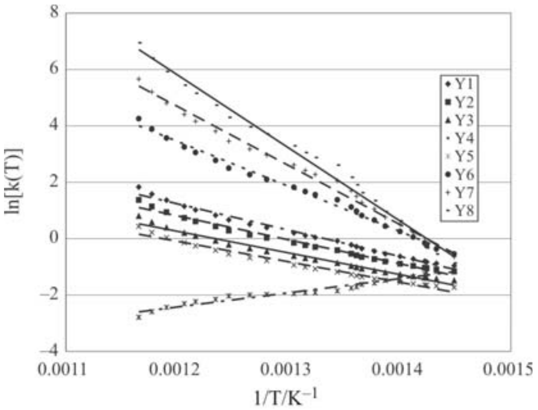

Fig. 7 ln*k*(*T*) *vs.* 1/*T* of Himmetoğlu oil shale with different α functions –Pyrolysis; y_1= –9328.9x+12.4 R_1^2=0.9888, y_2= –8500x+11.1 R_2^2=0.9855, y_3= –7671.4x+9.4 R_3^2=0.9803, y_4= –7257xx+8.6 R_4^2=0.9766, y_5=5027.4x–8.4 R_5^2=0.96, y_6= –15969x+22.6 R_6^2=0.9933, y_7=–20931x+29.8 R_7^2=0.9912, y_8= –25903x+36.9 R_8^2=0.9891

and 1 decrease with the increasing powers. The activation energies were calculated for all of the reaction regions available for combustion applications and it was observed that the values are varied between 22.3–192.9 kJ mol^{-1} in low temperature oxidation (LTO) region and 40.3–408.4 kJ mol^{-1} in high temperature oxidation (HTO) region. The pyrolysis activation energy interval is 13.1–69.5 kJ mol^{-1}. These values are in consistent with the values which were calculated by some other kinetic methods [6, 7]. The differences are because of the variations in linearization of the first order reaction equations and due to the consideration of different alpha equations.

Conclusions

In this research, pyrolysis and combustion behavior of three different Turkish oil shale samples were characterized with eight different alpha (α) approaches. The activation energies were calculated with eight different alpha functions was in the range of (LTO: 24.6–192.9 kJ mol^{-1}; HTO: 81.3–408.4 kJ mol^{-1}) for combustion of Himmetoğlu oil shale and in the range of (LTO: 15.7–40.3 kJ mol^{-1}; HTO: 40.3–243.4 kJ mol^{-1}) for combustion of Mengen oil shale. For pyrolysis the activation energies was in the range of 41.8–215.4 kJ mol^{-1} for Himmetoğlu oil shale and 22.9–141.3 kJ mol^{-1} for Mengen oil shale. On the other hand, the activation energies of Çan oil shale were found in the range of (13.1–69.5 kJ mol^{-1}) and (13.1–169.7 kJ mol^{-1}) for combustion and pyrolysis, respectively. This variation range is due to the variant coefficients and powers of the alpha equations. As the coefficients and powers of alpha functions increased the activation energies decreased. Proposing nth order polynomial equations for correlating alpha and time is very convenient and easy to apply for differential thermal analysis techniques.

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