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OXIDATION STUDIES OF TURKISH OIL SHALES AND DETERMINATION OF THEIR KINETIC PARAMETERS

L. BALLICE*

University of Ege, Faculty of Engineering,
Department of Chemical Engineering
35100 Bornova, Izmir, Turkey

Kinetics of oxidation of oil shales of Göynük (kerogen type I) and Beypazari (kerogen type II) deposits was investigated under isothermal conditions using a fixed-bed reactor in various temperature modes. Combustion profiles were obtained using a continuous gas analyzer. Rate data were analyzed basing on the assumption that oxidation takes place on the surface of solid oil-shale particles and decomposition of kerogen is not significant. Oxidation rates were determined and constant overall-orders of reaction from the kinetic analysis within investigated heating rates were found. Effect of heating rates on reaching final isothermal temperatures was investigated, and kinetic parameters of the overall oxidation reaction for each heating rate determined.

Introduction

Oxidation of oil shale attracts the attention of researchers for two main reasons: this enables, first, to obtain information on oil shale structure and, second, to convert oil shale into volatile hydrocarbons via *in-situ* retorting. Auto-ignition, a problem encountered at storage and transportation of coal [1], should also be a reason to investigate oxidation of oil shales being a combustible substance as well. Differences in chemical and physical properties of oil shale organic and inorganic matter are reflected in their combustion behaviour. Oil shale combustion profiles depend on oil shale characteristics, especially the maturation level of its organic matter, mineral composition, and experimental conditions [2].

Oil shale is a complex heterogeneous material generally considered to have a cross-linked macromolecular structure. The heterogeneity of oil shale can be seen at the microscopic level as distributions of maceral groups. Vitrinites are generally the most reactive macerals, and inertinites, due to

* e-mail: ballice@eng.ege.edu.tr; fax: 00 90 232 388 76 00.

their more aromatic nature, the least reactive ones [3]. The liptinite sporinite has a low ignition temperature due to its greater yield of volatile matter, but the remaining char behaves more like inertinite [3]. Vitrinite and inertinite macerals are generally minor components of oil shale and these components can be referred to by the names of maceral groups as defined for coal [4]. Liptinite macerals are the major components of oil shale organic matter, and the intensity of liptinite oxidizability depends on several parameters such as origin of organic matter and its maturity.

Oxidation studies of oil shales using thermal analysis techniques indicated that high-temperature oxidation of kerogen is a complex two-stage phenomenon [5–7]. The first step completes at about 400 °C, and the solid product of this stage represents a char with aromatic structure [5, 7].

Numerous attempts have been made to understand the mechanism and kinetics of the process occurring during oil shale oxidation. Non-isothermal and isothermal methods of investigation often reveal inconsistent results, but isothermal measurements are less influenced by heat transfer limitations than non-isothermal ones. In the case of isothermal measurements, the sample thickness has less impact on the overall kinetics. In our investigation, we used the apparatus described in the previous papers [8–10].

The rate of oil shale oxidation is equivalent to the rate of evolution of oxidation products. The amount of carbon recovered as CO and CO₂ can be determined by combustion profiles for each desired final temperature as a function of time. Mathematical procedure used in the analysis of oxidation data for determination of kinetic parameters corresponds to degressive kinetic rate expression

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad (1)$$

where $k(T)$ is the rate constant;

n is the reaction order of the overall oxidation reaction.

The conversion level for isothermal degradation obtained by integration of Equation (1) valid for $n \neq 1$ is

$$\alpha(t) = 1 - (k(T)t(n-1) + 1)^{\frac{1}{1-n}} \quad (2)$$

Rearranging of Equation (2) gives

$$\left[\frac{(1 - \alpha(t))^{1-n} - 1}{n - 1} \right] = k(T)t \quad (3)$$

This equation was used to evaluate the rate coefficient k and reaction order n . The conversion level given in Equation (3) is fitted by means of least square method to the experimental conversion level given by Equation (4) by variation of n in Eq. (3):

$$\alpha = \frac{W_o - W_t}{W_o} \quad (4)$$

where W_o is amount of organic carbon charged initially (C, mg);

W_t is amount of organic carbon in sample at any time (C, mg).

The difference between W_o and W_t gives the amount of carbon released as CO and CO₂ during processing. The amount of carbon present in CO and CO₂ is proportional to the integral of CO and CO₂ generation rate dm/dt from $t = 0$ to the desired t value, where m is amount of carbon in CO and CO₂ (C, mg) and t is time (min).

Table 1. Elemental Analysis and Fisher Assay of Göynük (GOS) and Beypazari (BOS) Oil Shales, wt. % [11]

Indices	GOS	BOS
Ultimate analysis		
Moisture (as received)	3.8	0.6
C (total, dry basis)	47.2	12.9
C (organic, dry basis)	46.3	7.7
C (inorganic, dry basis)	0.9	5.2
CO ₂	3.3	19.0
H (dry basis)	5.8	1.3
N (dry basis)	1.3	0.3
S (dry basis)	2.2	1.5
Fisher assay		
Shale oil	31.8	6.4
Gas	9.6	1.1
Decomposition water	3.6	0.7
Residue	51.2	91.2
Composition of gaseous product		
H ₂	1.5	2.7
CO	10.0	5.4
CO ₂	39.1	52.7
CH ₄	15.3	4.0
C ₂ -C ₇	34.1	35.2
Elemental analysis of shale oil		
C	76.1	79.6
H	11.3	11.4
N	1.1	1.3
S	1.5	1.3
Elemental analysis of residue		
C	37.9	8.5
H	1.7	0.3
N	1.5	0.03
S	0.8	0.3

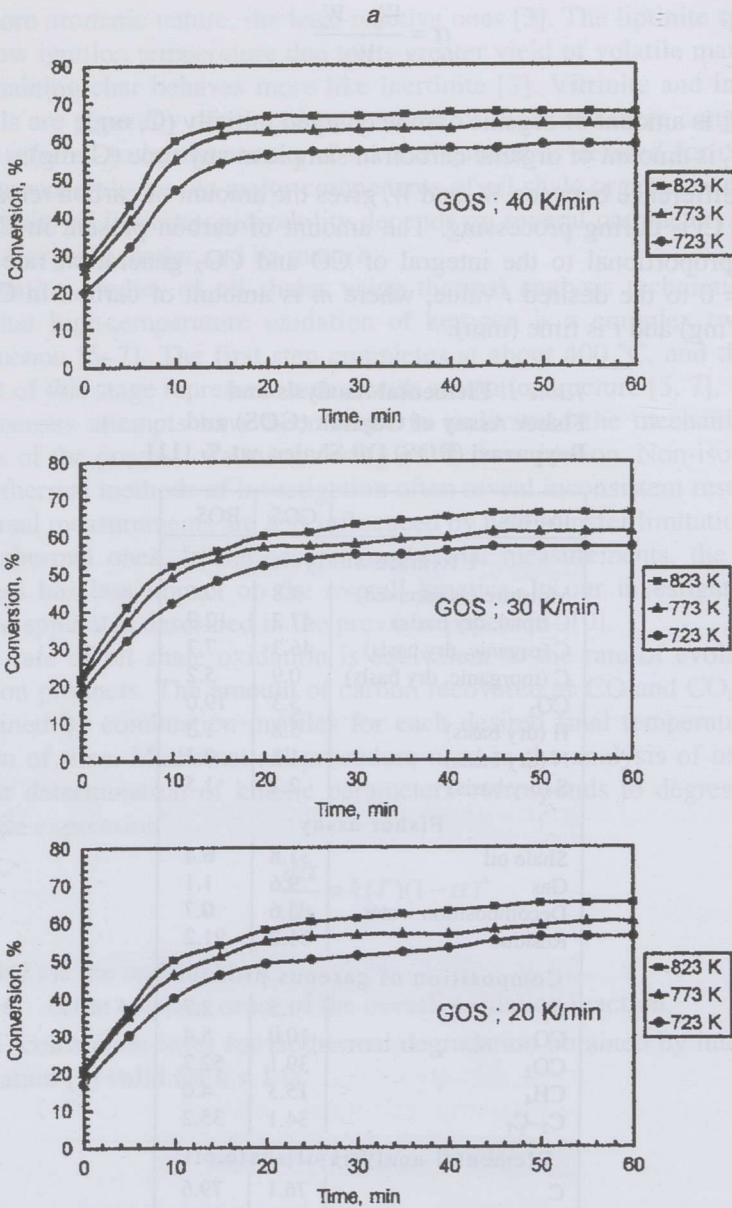
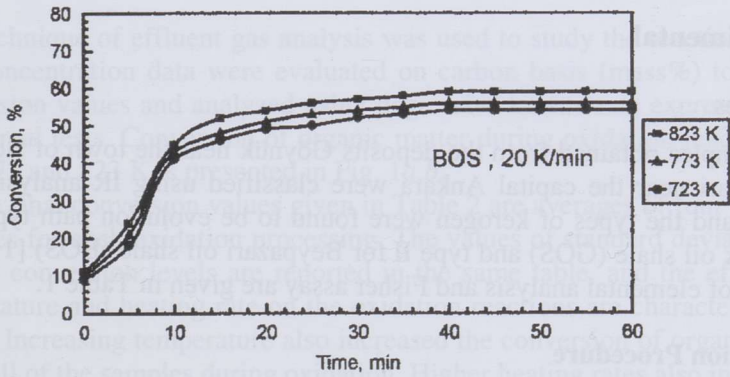
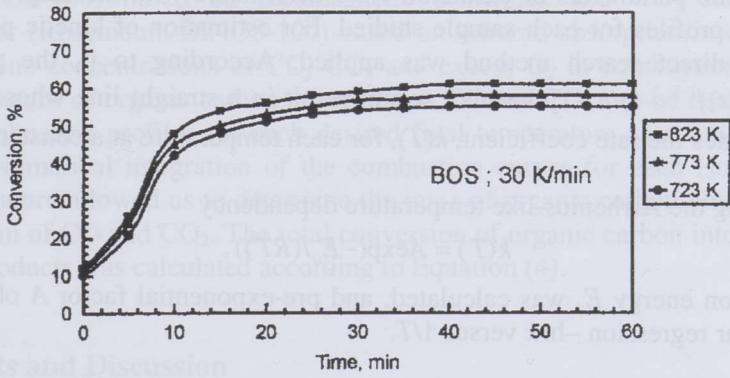
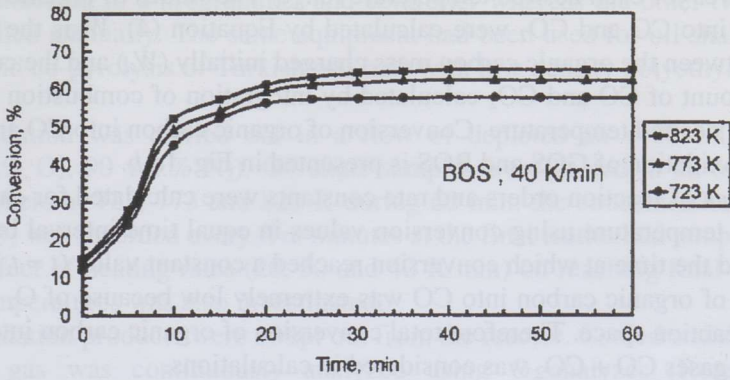


Fig. 1. Conversion of organic carbon into combustion products ($\text{CO} + \text{CO}_2$)

b



during oxidation reactions of (a) GOS and (b) BOS at 723, 773 and 823 K

These values were determined by numerical integration of the combustion curves for each desired temperature range. The values of organic C conversion into CO and CO₂ were calculated by Equation (4). W_t is the difference between the organic carbon mass charged initially (W_0) and the cumulative amount of CO and CO₂ calculated by integration of combustion curves for each desired temperature. Conversion of organic carbon into CO and CO₂ during oxidation of GOS and BOS is presented in Fig. 1a,b.

Values of reaction orders and rate constants were calculated for each isothermal temperature using conversion values in equal time interval between $t = 0$ and the time at which conversion reached a constant value ($t = t_c$). Conversion of organic carbon into CO was extremely low because of O₂ excess in the reaction space. Therefore total conversion of organic carbon into combustion gases CO + CO₂ was considered in calculations.

Kinetic parameters of oxidation were determined with the help of combustion profiles for each sample studied. For estimation of kinetic parameters, a direct search method was applied. According to it, the plot of $[(1 - \alpha(t))^{1-n} - 1]/n - 1$ versus t would result in a straight line whose slope determines the rate coefficient, $k(T)$, for each temperature at a constant heating rate.

Using the Arrhenius-like temperature dependency

$$k(T) = A \exp(-E_a/RT),$$

activation energy E_a was calculated, and pre-exponential factor A obtained by linear regression $-\ln k$ versus $1/T$.

Experimental

Samples

The samples obtained from the deposits Göynük near the town of Bolu and Beypazari near the capital Ankara were classified using IR analysis technique, and the types of kerogen were found to be evolution path type I for Göynük oil shale (GOS) and type II for Beypazari oil shale (BOS) [11]. The results of elemental analysis and Fisher assay are given in Table 1.

Oxidation Procedure

Oxidation was carried out in an electrically-heated fixed-bed reactor consisting of a stainless-steel reactor shell (400 mm long, 15 mm i.d.) and a Duranglass reactor tube (10 mm i.d.). Oil shale samples (100 mg of GOS and 200 mg of BOS) were mixed with 5 mL of quartz sand (particle size 0.1–0.25 mm) and transferred to the reactor tube. A thermocouple was inserted in the middle of sample bed, and the reactor tube was fitted into the reactor shell. Three thermocouples were fitted to its outer side and connected to a temperature controller. The reactor shell was enclosed in a temperature-

programmable furnace with a three-zone electric heater. The middle zone was connected to a programmer and controller whereas the other two were controlled manually. The same equipment had been used for oil shale pyrolysis and co-pyrolysis of Turkish oil shale with low-density polyethylene [8–10].

Oxidation was carried out in a flow of depleted air (100 mL min^{-1} , 10 vol.% O_2 , 90 vol.% N_2). Oil shale samples were heated in an oxidative atmosphere at 723, 773 and 823 K during 60 min; the concentration of CO and CO_2 was recorded every five minutes at the final isothermal temperature. The effect of heating rates (20, 30 and 40 K/min) on reaching final isothermal temperatures was also investigated.

Oxidation products were swept out from the reactor. Cooled and dried effluent gas was continuously analyzed using O_2 -analyzer (Rosemount-OXYNOS-100) based on paramagnetic principles and CO- and CO_2 -analyzer (Rosemount-BINOS-100) based on infrared absorption in order to determine concentrations of CO, CO_2 and excess O_2 in combustion gases. The amount of organic carbon recovered as CO and CO_2 can be determined by combustion profiles for each desired final temperature as a function of time. Numerical integration of the combustion curves for each isothermal temperature allowed us to determine the mass of organic carbon obtained in the form of CO and CO_2 . The total conversion of organic carbon into oxidation products was calculated according to Equation (4).

Results and Discussion

The technique of effluent gas analysis was used to study the reaction kinetics. Concentration data were evaluated on carbon basis (mass%) to obtain conversion values and analyzed using degressive kinetic rate expression for isothermal tests. Conversion of organic matter during oxidation reactions at 723, 773 and 823 K is presented in Fig. 1a,b.

The final conversion values given in Table 2 are averages of four parallel analyses for each oxidation processing. The values of standard deviation, σ , for the conversion levels are reported in the same table, and the effects of temperature and heating rate on the oxidation reactions are characterized in Fig. 2. Increasing temperature also increased the conversion of organic matter in all of the samples during oxidation. Higher heating rates also increased the conversion of oil shales.

It can be assumed that at high combustion temperatures the emission of unburned volatile hydrocarbons would be minimal. However, with such a high oxygen excess competition between oxidation reactions and condensation reactions will be reduced and oxidation favoured. It can also be assumed that generation of radicals will be constant due to the constant combustion temperature, and competition between radical oxidation (high excess of oxygen) and radical condensation reactions would be minimal and constant. The

same assumptions were also made by Mastral *et al.* [12]. They studied PAH emissions of the airflow during coal combustion and concluded that interaction of radicals depends on their residence time in the reactor, i.e. on the flow rate.

Table 2. Conversion of Göynük (GOS) and Beypazari (BOS) Oil Shales in Oxidation Reaction, %

T, K	GOS		BOS	
	Conversion values	Standard deviation σ	Conversion values	Standard deviation σ
Heating rate 20 K/min				
823	65.0	0.6	59.0	0.5
773	60.0	0.8	56.0	0.4
723	56.0	0.5	54.0	0.6
Heating rate 30 K/min				
823	66.0	0.7	61.0	0.4
773	61.0	0.6	58.0	0.3
723	57.0	0.7	55.0	0.5
Heating rate 40 K/min				
823	67.4	0.6	65.0	0.4
773	64.2	0.5	62.2	0.5
723	58.8	0.5	57.5	0.5

Conversion level of GOS organic matter was higher than that of BOS (at 823 K after 60 min 67.4 and 65 %, respectively). Silicates present in BOS probably inhibited oxidation reactions of its organic matter. Cations of earth alkali metals such as calcium and magnesium can promote oxidation of oil shale but the inhibiting effect of silicate minerals originally present in shales seemed to be greater than the catalytic action of carbonates present in BOS.

According to our earlier non-isothermal thermogravimetric analysis of GOS and BOS [11], mineral content of the latter essentially exceeds that of GOS and the weight loss due to decomposition of carbonates present in it exceeds that of GOS as well. High silicate content of BOS was established also by IR spectra of original and de-mineralized samples of both oil shales.

Karabakan *et al.* [6] have carried out a series of experiments on oxidation of Turkish oil shales using original and de-mineralized oil shales. Maximum conversion of organic matter was observed for HF-washed and original oil shale and the lowest one for HCl-washed oil shale. These results indicate that carbonate and magnesium present in the original oil shale washed with HCl have a mild promoting effect on oxidation of organic matter, whereas silicate minerals present in the oil shale treated with HF have a negative effect. It was observed that after the removal of silicates conversion of organic matter in oxidation reactions increased.

The effects of oil shale inorganic matrix on kerogen oxidation were also investigated by Yürüm *et al.* [7]. Kerogen was isolated by successive treatment with HCl, HF and LiAlH₄, and oxidation products were analyzed by Fourier-transform infra-red spectroscopy. It was found that calcium minerals increased the reactivity of the organic matter aromatic part during oxidation reactions whereas silicate and pyrites had no effect.

Table 3 presents rate coefficients and reaction orders calculated for GOS and BOS. In all experiments performed, the overall reaction orders were found to equal approximately 3. Rate coefficients are summarized in the Arrhenius plot in Fig. 3. Values of E_a of GOS and BOS oxidation determined from this plot are given in Table 4. In all of the experiments increase in the heating rate from 20 to 40 K/min decreased the value of E_a . Activation energies are ranged as follows: $E_a(20 \text{ K/min}) > E_a(30 \text{ K/min}) > E_a(40 \text{ K/min})$. With increasing heating rate, transport of volatile hydrocarbons and pyrolysis products by diffusion to the particle surface also increased, thus oxidation reactions occurred easily. The effect of mass transfer processes was established when determining the amount and composition of volatiles obtained during rapid pyrolysis of coals [13].

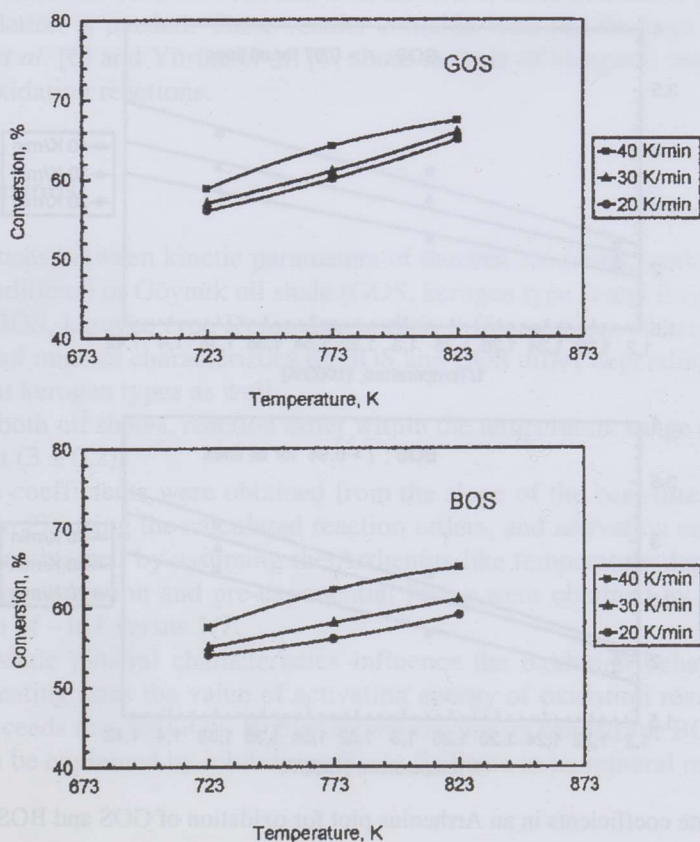


Fig. 2. Effect of temperatures and heating rates on oxidation of GOS and BOS

Table 3. Reaction Rate Coefficients, $-\ln k$, and Reaction Order, n , for the Göynük (GOS) and Beypazari (BOS) Oil Shales in Oxidation Reaction

T, K	$-\ln k$		n	
	GOS	BOS	GOS	BOS
Heating rate 20 K/min				
823	2.20	2.15	3.2	2.9
773	2.80	2.70	3.1	2.9
723	3.10	3.15	3.2	3.0
Heating rate 30 K/min				
823	2.10	2.08	3.2	2.9
773	2.57	2.70	3.1	3.0
723	2.82	2.90	3.1	3.1
Heating rate 40 K/min				
823	2.01	1.92	3.0	3.1
773	2.21	2.22	3.1	3.2
723	2.64	2.70	3.0	3.0

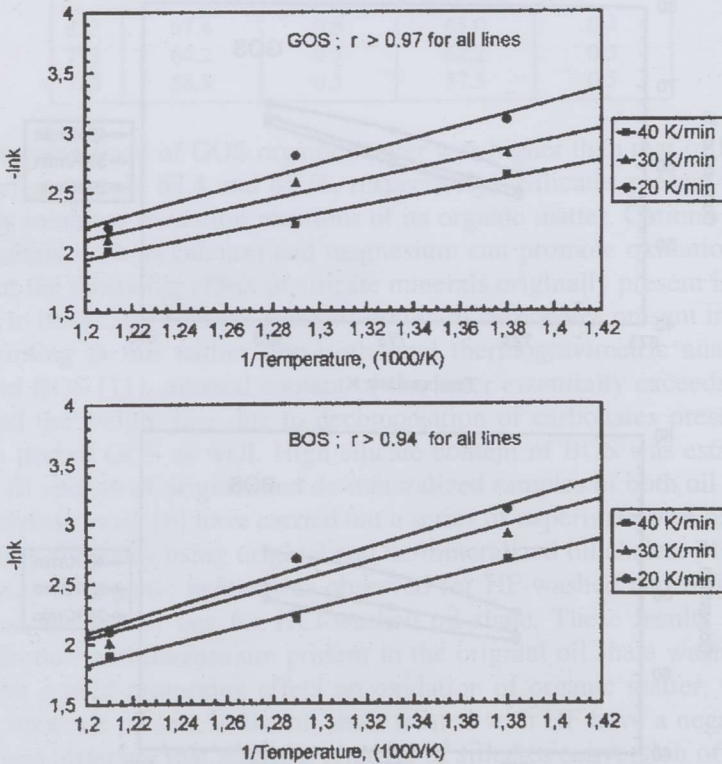


Fig. 3. Rate coefficients in an Arrhenius plot for oxidation of GOS and BOS

Table 4. Activation Energies E_a , kJ/mol, and Pre-Exponential Factors A , min^{-1} , of Göynük (GOS) and Beypazari (BOS) Oil Shales

Heating rate, K/min	E_a		A	
	GOS	BOS	GOS	BOS
20	43.7 ± 0.3	49.2 ± 0.2	59.5 ± 1.1	149.9 ± 2.2
30	35.0 ± 0.4	43.7 ± 0.3	18.9 ± 0.6	70.8 ± 0.3
40	31.0 ± 0.4	39.3 ± 0.4	12.4 ± 0.2	46.5 ± 0.3

Karabakan with co-authors also found the activation energy of oil shale oxidation to decrease with increasing heating rate. At higher heating rates oil shale particles disintegrate into smaller ones, thus allowing easier contact of oxygen with organic matter and, consequently, easier run of oxidation reactions [6].

At equal heating rates, the value of activation energy of GOS oxidation is lower than that of BOS. This result coincides with the data for their conversion values. High silica content of BOS inhibited oxidation reactions, slightly decreased the reaction rate and, therefore, more activation energy for its oxidation is needed. These results coincide with the findings by Karabakan *et al.* [6] and Yürüm *et al.* [7] about the role of inorganic matter in oil shale oxidation reactions.

Conclusions

Differences between kinetic parameters of thermal oxidation (under isothermal conditions) of Göynük oil shale (GOS, kerogen type I) and Beypazari oil shale (BOS, kerogen type II) are due to their different types of kerogen. Organic and mineral characteristics of GOS and BOS differ depending on their different kerogen types as well.

For both oil shales, reaction order within the temperature range studied is constant (3 ± 0.2).

Rate coefficients were obtained from the slope of the best-fitted line for Equation (3) using the calculated reaction orders, and activation energy values were obtained by assuming the Arrhenius-like temperature dependency, energy of activation and pre-exponential factor were obtained by linear regression of $-\ln k$ versus $1/T$.

Oil shale mineral characteristics influence the oxidation behaviour. At equal heating rates the value of activation energy of oxidation reactions for BOS exceeds that for GOS. Higher activation energy needed for BOS oxidation can be explained by inhibiting effect of silicate in its mineral matrix.

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