

OXIDATION STUDIES ON ŞIRNAK ASPHALTITES. DETERMINATION OF KINETIC PARAMETERS

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Oxidation of Şırnak asphaltite samples was investigated under isothermal conditions using a fixed-bed reactor in various temperature modes. Combustion profiles were obtained by using a continuous gas analyzer. The rate data were analyzed based on the assumptions that oxidation reaction takes place on the surface of solid asphaltite particles and decomposition of organic structures is not significant. Oxidation rates were determined and constant overall order of reaction (1.7 ± 0.3) was established. The effect of heating rate on reaching final isothermal temperatures was investigated and kinetic parameters of the overall oxidation reaction for each heating rate determined.

Introduction

Generally asphaltic materials are formed by migration of petroleum into cracks during tectonic movements. During and after migration, petroleum loses its light components and undergoes a series of complex chemical and physical changes. Turkey has large sources of asphaltic materials and asphaltite, especially in the southeastern region, around Siirt, Şırnak, and Hakkari [1]. The amount of asphaltite reserves there is approximately 77.5 million tonnes [1, 2].

Oxidation of asphaltite attracts our attention for two main reasons: first, as for consumption of asphaltite in Turkey, it is almost completely consumed for domestic heating [3] and second, though numerous studies have been made to understand the mechanism and kinetics of coal and oil shale oxidation [4–7], asphaltite has not been investigated in this respect. Isothermal studies have some advantages compared to non-isothermal ones as isothermal measurements are less influenced by heat transfer limitations and the sample thickness has less impact on the overall kinetics.

In this study, kinetics of oxidation of Şırnak asphaltite (ASP) was investigated under isothermal conditions using a fixed-bed reactor in various

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temperature modes. The effects of different heating rates and final temperatures on kinetics of ASP oxidation were studied to obtain a better understanding of this process.

Theoretical

As this study represents a continuation of the research on oxidation of Turkish oil shale [8], analogous rate equations and mathematical procedures were used to interpret experimental data. The rate of ASP 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 designated final temperature as a function of time. Degressive kinetic rate expression was used to treat the data obtained during the experiments [9, 10].

The equation used to evaluate rate coefficient k and reaction order n has the form

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

Experimental conversion level is calculated as

$$\alpha = \frac{W_o - W_t}{W_o} \quad (2)$$

where W_o is the amount of organic carbon charged initially, mg;

W_t is the amount of organic carbon in sample at any time, mg.

The difference between W_o and W_t gives the amount of carbon released as CO and CO₂ during processing.

Conversion of organic matter during oxidation reactions at final temperatures is presented in Fig. 1. The values of reaction orders and rate constants were calculated for each isothermal temperature using conversion data in Fig. 1. Conversion of organic carbon into CO was extremely low because of O₂ excess in the reaction space. Thus, the mass of carbon in CO was added to the mass of carbon in CO₂, and the total conversion of organic carbon into combustion gases was considered in calculations.

The aim of this work was to examine the oxidation behavior of ASP at temperatures up to 823 K in the flow of depleted air. The values of kinetic parameters of ASP oxidation were determined with the help of combustion profiles for each sample. For that a direct search method was applied. According to it, a plot of $[(1 - \alpha(t))^{1-n} - 1]/n - 1$ versus t should result in a straight line whose slope determines the rate coefficient $k(T)$ for each temperature at a constant heating rate. Assuming an Arrhenius-like temperature dependency $k(T) = A \exp(-E_a/RT)$, the energy of activation E_a and the pre-exponential factor A are obtained by linear regression of $-\ln k$ versus $1/T$.

Experimental

Samples

Asphaltite samples taken from the deposit in Şırnak province were investigated. Data of their analyses are as follows. Ultimate analysis, wt.% (dry basis): C: total 40.2, organic 39.0, inorganic 1.2; H 3.2, N 0.5, total S 4.8. Proximate analysis, wt.% (as received): moisture 1.4, ash 38.4, volatile matter 35.1, fixed carbon 25.1.

Oxidation Procedure

The experiment protocol and analysis technique are also given in the paper [8]. 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 Duran-glass reactor tube (10 mm i.d.). The ASP samples (100 mg) were mixed with 5 ml quartz sand (particle size 0.1–0.25 mm) and transferred to the reactor tube fitted into the stainless steel reactor shell. The latter was enclosed in a temperature-programmable furnace by a three-zone electric heater. The same equipment was used for Turkish oil shale pyrolysis and co-pyrolysis with low-density polyethylene [11–14].

Oxidation was carried out in the flow of depleted air (100 mL min⁻¹, 10 vol.% O₂, 90 vol.% N₂). ASP samples were heated in an oxidative atmosphere at 723, 773 and 823 K during 60 min. CO and CO₂ concentrations were recorded each five minutes at the final isothermal temperature. The effect of heating rate (20, 30 and 40 K/min) to reach 723, 773 and 823 K was also investigated.

After sweeping out of the reactor the cooled and dried effluent gas was continuously analyzed on CO and CO₂, and excess O₂. The amount of organic carbon recovered as CO and CO₂ was determined by combustion curves for each final temperature as a function of time. Numerical integration of these curves for each isothermal temperature made it possible to account the mass of organic carbon obtained in the CO and CO₂ form. Total conversion of organic carbon into oxidation products was calculated according to Eq. (2).

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 ASP organic matter during oxidation reactions at 723, 773, 823 K as a function of time is presented in Fig. 1.

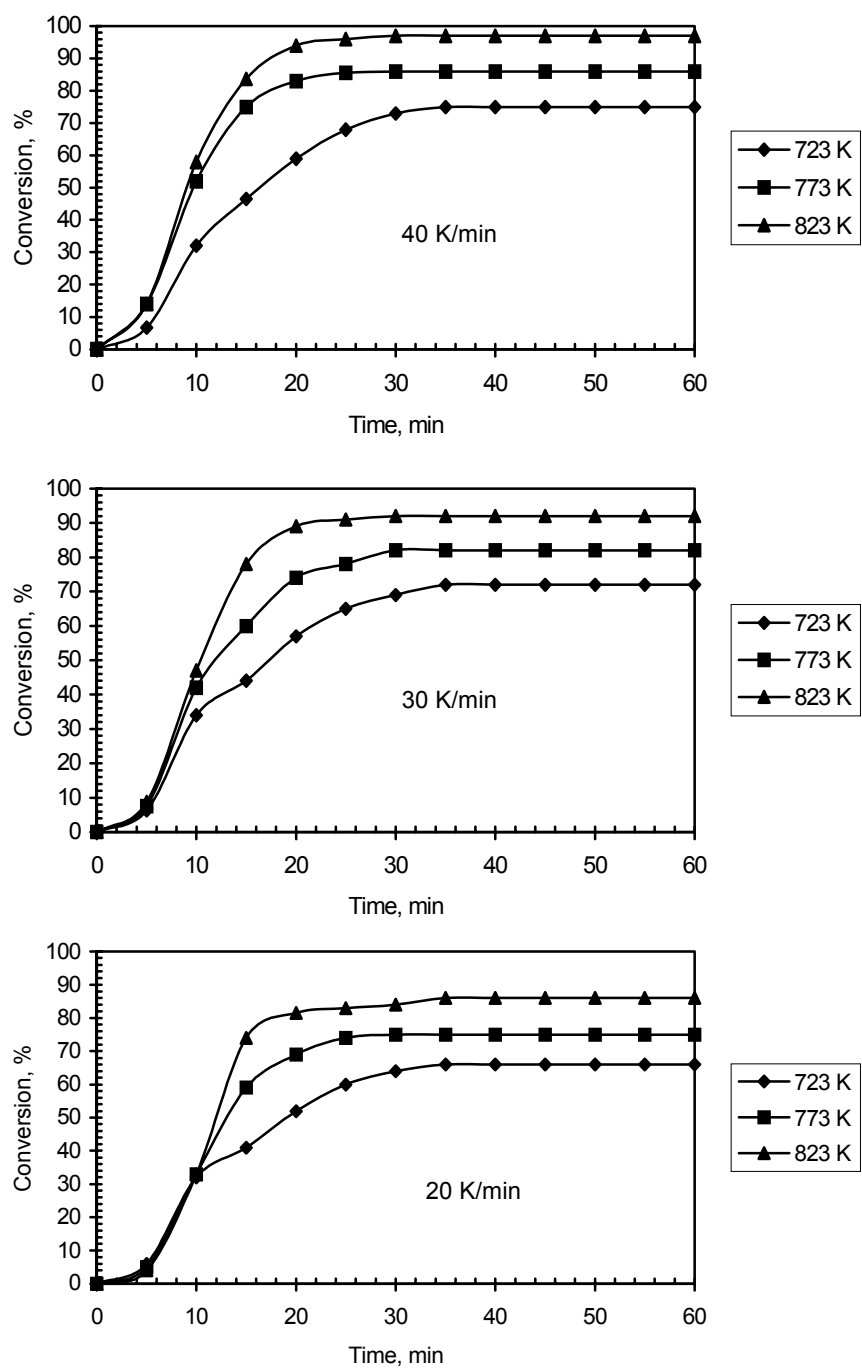


Fig. 1. Conversion of organic carbon into combustion products ($\text{CO} + \text{CO}_2$) at various heating rates

Final conversion values shown in Table 1 are averages of three replications for each. Increasing temperature and higher heating rates both increased the conversion of organic matter in all of the samples (Fig. 2).

Table 1. Conversion Values, Reaction Rate Coefficients $-lnk$, and Reaction Order n of ASP Oxidation

T, K	Conversion values		$-lnk$	n
	Final, %	Standard deviation σ		
Heating rate, 20 K/min				
823	86.0	0.5	1.61	2.0
773	75.0	0.7	2.40	1.7
723	66.0		2.92	1.8
Heating rate, 30 K/min				
823	92.0	0.7	1.47	1.7
773	82.0	0.6	2.03	1.8
723	72.0	0.7	2.53	2.0
Heating rate, 40 K/min				
823	97.0	0.7	1.45	1.4
773	86.0	0.5	1.67	1.8
723	75.0	0.6	2.44	1.9

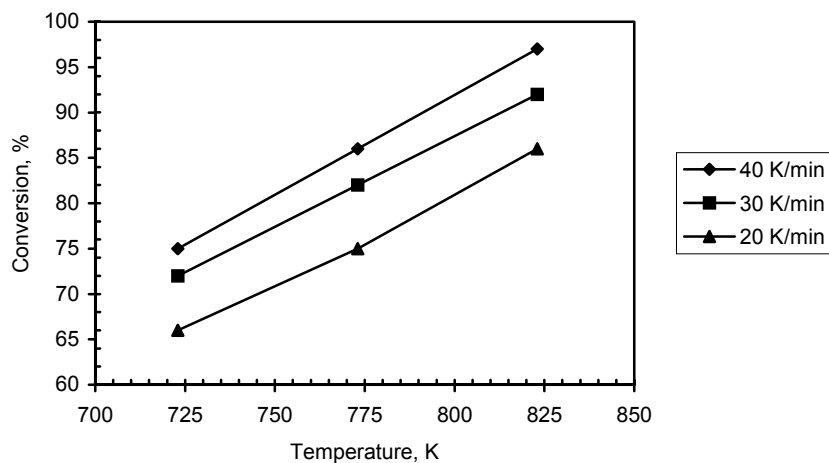


Fig. 2. Effect of temperature and heating rate on ASP oxidation

It can be assumed that at high combustion temperatures the emission of unburned volatile hydrocarbons will be minimal. However, with such a high oxygen excess the competition between oxidation and condensation reactions will be reduced and oxidation favored. One can also assume that

generation of radicals will be constant due to the constant-temperature combustion, and competition between oxidation of radicals (high excess of oxygen) and their condensation reactions will be minimal and constant. The same assumptions were also made by Mastral *et al.* [14]. They studied PAH emissions with the airflow during coal combustion and concluded that the interaction between radicals depends on their residence time in the reactor.

The values of ASP conversion measured at final temperatures after 60 min were 86, 92 and 97%. In all experiments, the calculated overall reaction order was 1.7 ± 0.3 (see Table 1).

The rate coefficients are summarized in the Arrhenius plot (Fig. 3). From that activation energy of ASP oxidation was calculated (Table 2). The energy E_a needed to activate oxidation decreases when higher heating rates are used. The order of activation energies was found to be E_a (20 K/min) $>$ E_a (30 K/min) $>$ E_a (40 K/min).

Table 2. Activation Energies E_a , and Pre-Exponential Factors A of ASP Oxidation Reaction

Heating rate, K/min	Activation energy E_a , kJ/mol	Pre-exponential A , min ⁻¹
20	63.8	2042.5
30	51.9	431.2
40	48.9	313.1

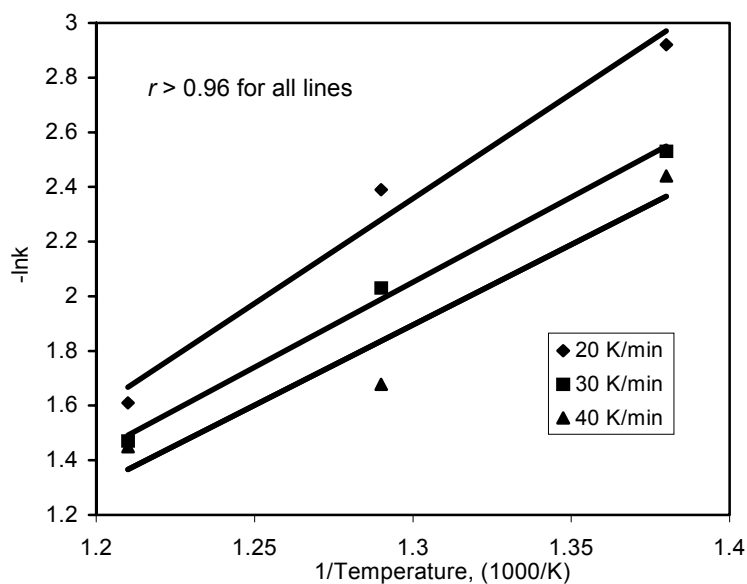


Fig. 3. Rate coefficients in an Arrhenius plot for ASP oxidation

With increasing heating rate, the transport of volatile hydrocarbons and pyrolysis products by diffusion to the surface of the particle also increased, thus the 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 [15]. Karabakan *et al.* also found a lower activation energy value for oxidation of oil shale with increasing heating rate. They indicated that at higher heating rates the oil shale particles disintegrated into smaller ones, thus allowing easier contact of oxygen with organic material and higher rate of oxidation reactions [10].

As seen from Table 2, activation energies of oxidation of ASP samples are much higher when compared with coal whose activation energy was found to vary between 9–29 kJ/mol [16–20]. These results show how difficult it is to initiate the combustion of asphaltite.

The effects of particle size and heating rate on the combustion properties of Silopi asphaltite were investigated by Altun *et al.* [21]. Non-isothermal oxidation studies' results showed that the activation energy varied between 45.8 to 48.6 kJ/mol depending on particle size and heating rate used. They stated that asphaltite as a heating agent has some disadvantages compared to coal. The values of activation energy of ASP oxidation E_a are in rough agreement with the results stated in [21].

The rate of oxidation reaction depends on the rate of gas transport into the zone of reaction influenced by diffusion. Diffusion of oxygen into the organic matrix is the major resistance controlling the rate of oxidation reactions. Inclusion of organic matter into mineral matrix has been probably more intensive in the case of ASP than that in Silopi asphaltite because of different mineral content of these materials. That may be the reason for higher activation energies for ASP. A direct comparison of the activation energy values for asphaltites from different regions may not be a good approach regardless of their similar proximate analysis data.

Conclusions

Thermal oxidation of ASP was investigated under isothermal conditions in a fixed-bed reactor. Kinetic parameters of oxidation were determined.

Heating rate has a significant effect on combustion reactions, influencing not only the combustion efficiency but also the activation energy for combustion. Higher heating rates increase combustion efficiency and decrease activation energy.

It can be assumed that at higher heating rates the emission of unburned volatile hydrocarbons would be minimal and because of higher kinetic energies of the samples initiation of the combustion process would be easier, too.

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