Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

ASTM KINETICS OF OIL SHALES

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Abstract

Thermal analysis is increasingly being used to obtain kinetic data relating to sample decomposition. In this research differential scanning calorimeter (DSC) was used to determine the combustion kinetics of three (Çan, Himmetoglu and Mengen) oil shale samples by ASTM and Roger & Morris methods. On DSC curves two reaction regions were observed on oil shale sample studied except Çan oil shale. In DSC experiments higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Distinguishing peaks shifted to higher temperatures with an increase in heating rate. Three different kinetic models (ASTM I–II and Rogers & Morris) were used to determine the kinetic parameters of the oil shale samples studied. Activation energies were in the range of 131.8–185.3 kJ mol^{-1} for ASTM methods and 18.5–48.8 kJ mol^{-1} for Rogers & Morris method.

Keywords: combustion, differential scanning calorimeter, kinetics, oil shale

Introduction

In recent years the application of differential scanning calorimeter and thermogravimetry to study the combustion and pyrolysis behaviour of fossil fuels has gained a wide acceptance among researchers, which are of exceptional significance for industry and for the economy. This study was performed to determine ASTM kinetics of Turkish oil shales by differential scanning calorimeter (DSC).

Oil shales contain organic matter, in the form of kerogen, which is defined as that fraction of the organic matter in a sedimentary rock that is insoluble in common petroleum solvents. The other fraction, called bitumen is soluble in organic solvents, but represents only a small amount of the organic matter in an oil shale. Oil shale reserves in Turkey are mostly grouped in Tertiary aged reserves, which are generally reported to be non-marine origin. This group is thought to accumulate in large lake basins or as smaller deposits associated with coal-bearing strata. Total oil shale reserves in Turkey are thought to be approximately

$5 \cdot 10^6$ tons, whereas oil shale reserves over the world are estimated to sum up to $39498.3 \cdot 10^6$ tons.

Rejashwar [1] studied the pyrolysis kinetics of thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry. He critically reviewed the factors influencing kinetic data such as sample order geometry, heating rate and atmosphere. He analyzed the weight loss data by direct Arrhenius, Coats & Redfern and Freeman & Carrol techniques. Earnest [2] analyzed the thermal behaviour of Green River oil shale in dynamic nitrogen atmosphere with TG and DTG and compared this with of a retorting process. Using the results of this study, the pyrolysis onset temperatures and temperatures at maximum pyrolysis rate were related to the type of organic maceral components of oil shale specimen. Skala and Sokic [3] developed a kinetic expression commonly used in the thermal analysis of oil shale pyrolysis. This kinetic expression 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 TG gave the smallest values. In all the examined samples and performed TG analysis showed that there was an increase in the activation energy with increased content of paraffinic structures in the oil shale. Shih and Sohn [4] used non-isothermal TG with a variety of heating rates to the determination of kinetics parameters for Green River oil shale pyrolysis. Four different methods were employed for kinetics analysis and the results appear to be in fair agreement. The same group has employed non-isothermal TG for studying the oxidation kinetics of oil shale char under conditions wherein diffusional and mass transfer effects were claimed to be unimportant. Levy and Stuart [5] obtained TG/DTG oxidative profiles for a number of Australian oil shales and kerogen concentrates heated in a dynamic air atmosphere. It was observed that the combustion of kerogen occurs in two stages, indicated by two sharply defined DTG peaks. The first stage involves complete or almost complete combustion of aliphatic components to give a char containing aromatics, whereas second stage involves combustion of aromatic components in the kerogen. Rajeshwar et al. [6] analyzed the kinetic data on the thermal decomposition of Green River oil shale kerogen in terms of topochemical models conventionally employed for solid-state reactions. The analyses revealed that the thermal decomposition proceeded by mechanisms that were more complex than the simple first-order rate law. Tugluhan et al. [7] studied the oxidation kinetics of a Turkish oil shale (Himmetoglu) and concluded that oxidation of oil shale is dependent upon oxygen partial pressure and organic matter content. It was also shown that the relation between reaction rate constant and temperature fits an Arrhenius type of equation.

Experimental

DSC experiments were conducted with DuPont 9900 thermal analysis system. In all cases the average initial sample mass was 10 mg while the air flow rate

kept constant at 50 ml min^{-1}. Heating rates were 2, 5, 10, 15 and 20 K min^{-1}, in the temperature range of 290–875 K. The DSC system is a plug-in module, measures temperature and heat flow associated with material transitions, providing quantitative and qualitative data on endothermic and exothermic processes. To adjust the temperature reading, indium is used as a standard with a known melting point. 10 mg of indium is placed in an aluminum sample pan, inserted a lid and crimped. Indium sample is heated from ambient to 450 K at 10 K min^{-1}. The extrapolated onset of the melting curve should be 429.7 K. If the onset temperature is not 429.7 K the difference in temperature was noted and used in further calculations. For accurate sample analysis, the temperature calibration was performed at each heating rate.

Table 1 Properties of oil shales [11]

Sample	Calorific value/ J g^{-1}	C	H	O, N	S
		%			
Çan	3867	10.1	1.95	10.06	0.98
Himmetoglu	5810	13.60	1.5	10.48	0.99
Mengen	4180	10.05	1.9	8.8	0.85

The oil shale samples (Çan, Himmetoglu and Mengen) used in all experiments had a particle size <60 mesh and were prepared according to ASTM (ASTM D 2013-72) standards. It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. All the experiments were performed twice in order to see the repeatability. It was observed that the repeatability of the experiments was excellent. Properties of the samples used in the experiments are tabulated in the Table 1.

Results and discussion

The oil shale deposits in Turkey are widely distributed in middle and western Anatolia and are of Palaeocene-Eocene and Middle Upper Miocene age. The host rocks are marl and clays, in which the organic matter is heterogeneously and finely dispersed. Smectite, calcite, mica, and dolomite are the dominant minerals in Himmetoglu oil shale. Sub-dominant minerals are mainly illite, opal, pyrite and clinoptilolite. Dolomite and quartz are the dominant minerals in Mengen oil shale, whereas magnesite, feldspar, muscovite, illite, kaolinite and pyrite are the sub-dominant minerals. Calcite and dolomite are the dominant minerals in Çan oil shale. Sub-dominant minerals are mainly smectite, quartz, kaolinite, pyrite and illite. The kerogen type of the oil shales studied is type III.

Theoretically, combustion of fuel can be initiated whenever oxygen comes in contact with oil shale. However, the temperature and composition of the oil shale

and oxygen supply dictate the nature of this reaction. On DSC curves two reaction regions were observed on oil shale samples studied except Çan oil shale. First reactions take place after 500 K and others occur about 700 K. Differences are due to the organic matter type and organic matter maturity in oil shales. In Çan oil shale, organic matter transformation occurs in only one reaction zone, which begins at 475 K and reaches maximum at 615 K (Fig. 1). For the oil shale samples studied (except Çan oil shale) a third reaction zone is observed. This reaction takes place around 800 K, due to the mineral decomposition. Endothermic behaviour and weight loss during that reaction, it can be claimed that, illite decomposition caused these reactions [8].

Table 2 Peak temperatures (K) of the samples at five different heating rates

Sample	Heating rate/K min^{-1}				
	2	5	10	15	20
Çan	601	618	628	634	640
Himmetoglu (1)	568	586	594	604	607
Himmetoglu (2)	666	679	681	694	714
Mengen (1)	568	587	600	611	614
Mengen (2)	634	654	661	673	675

(1) First reaction region
(2) Second reaction region

DSC experiments were carried out at five different heating rates (2, 5, 10, 15 and 20 K min^{-1}) and it was observed that higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Distinguishing peaks in the DSC curves shifted to the higher temperatures with an increase in heating rates (Figs 2, 3 and 4). Heat flow rates at different heating rates at maximum peak temperatures are tabulated in Table 2.

ASTM kinetics (ASTM E 698–79)

A method developed by ASTM committee [9] for chemical reactions is for determination of activation energies and Arrhenius pre-exponential factors using DSC data. In this method, the sample temperature is increased at linear heating rates (2, 5, 10, 15 and 20 K min^{-1}) and any exothermic peaks are recorded. The reciprocal of temperatures at which the reaction peaks occur are plotted as a function of the log of respective heating rates. In this method, a trial and error procedure is used and the activation energy is calculated as follows:

$$E = 2.19R\frac{d\log_{10}\beta}{d(1/T)} \tag{1}$$

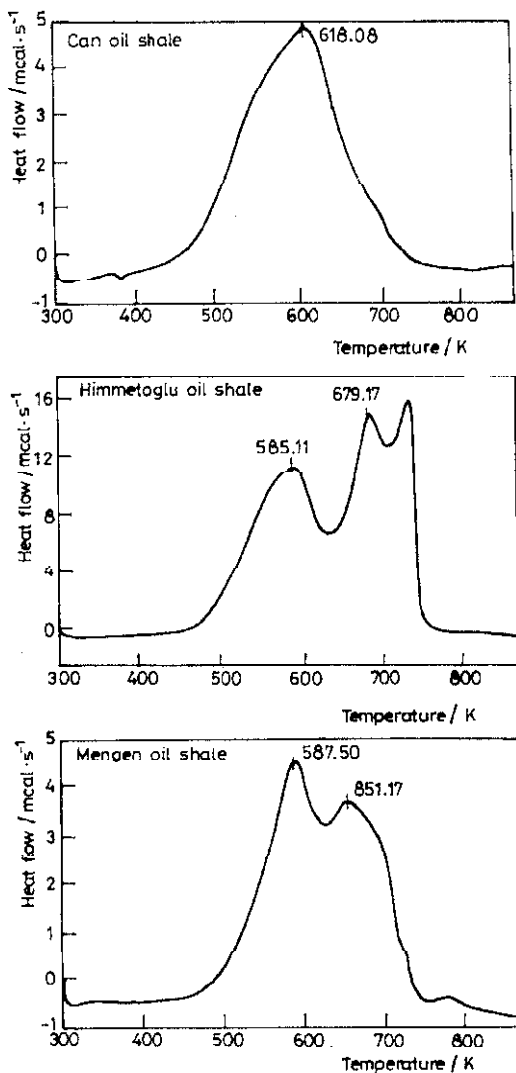**Fig. 1** DSC curves of oil shales in air at 50 ml min^{-1} (5°C min^{-1})

The Arrhenius pre-exponential factor can be calculated from the following equation:

$$A = \beta E \frac{e^{E/RT}}{RT^2}$$ (2)

where β is the heating rate from the middle of the range.
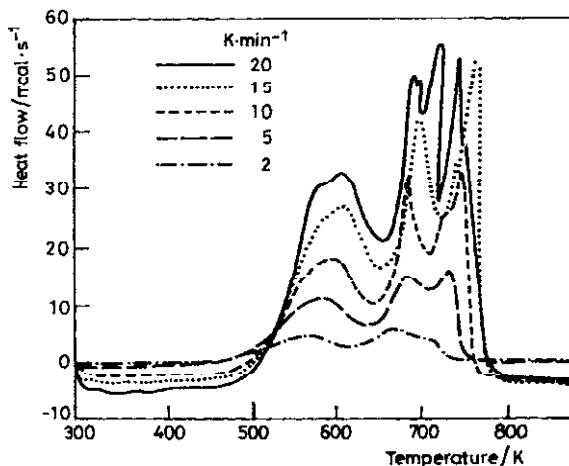
Fig. 2 DSC curves of Himmetoglu oil shales for five different heating rates in air
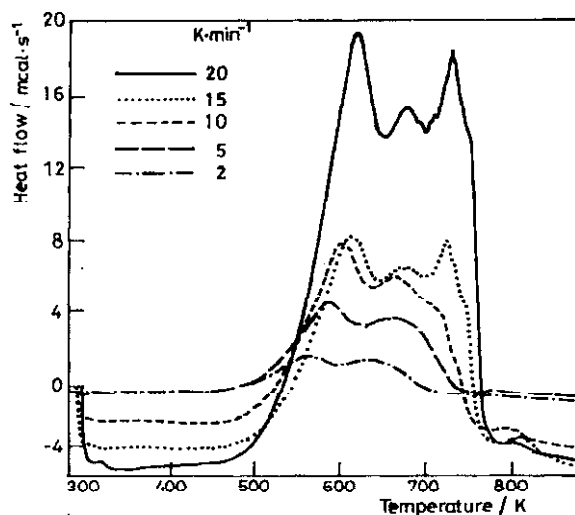

Fig. 3 DSC curves of Mengen oil shales for five different heating rates in air

An alternative method for calculating activation energy according to ASTM standard is also proposed in the course of this study. In this method, $-\ln(\beta/T^2)$ is plotted against $1/T$ and the activation energy is calculated from the slope as follows:

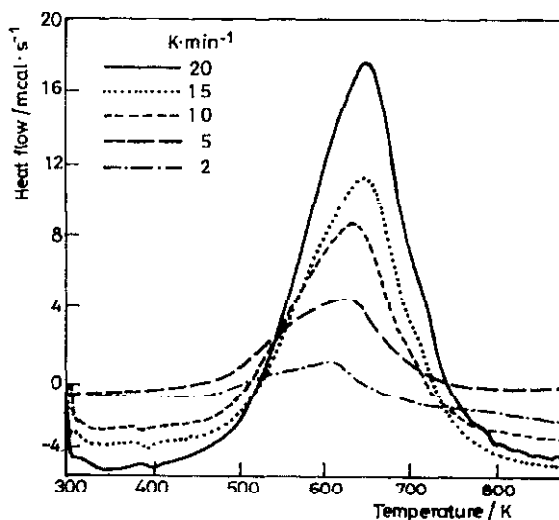$$E = R\frac{d(-\ln\beta/T^2)}{d(1/T)} \tag{3}$$

Fig. 4 DSC curves of Çan oil shales for five different heating rates in air

Applying the procedures mentioned above, activation energies and Arrhenius pre-exponential factors were determined and tabulated in the Table 3. Reaction order is assumed to be constant all over the reaction; whereas Arrhenius pre-exponential factor is believed dependent on the medium where reaction is taking place.

Table 3 Kinetic parameters of the oil shale samples using ASTM methods

Sample	Activation energy/kJ mol^{-1}		Arrhenius constant/ min^{-1}
	ASTM I	ASTM II	
Çan	182.2	182.3	7.28E+14
Himmetoglu (1)	158.7	158.4	3.96E+13
Himmetoglu (2)	172.6	172.4	4.30E+12
Mengen (1)	131.8	131.9	1.24E+11
Mengen (2)	185.3	185.3	1.65E+14

(1) First reaction region
(2) Second reaction region

In addition to ASTM methods, another method called Roger and Morris [10] was also used to determine the kinetic parameters of the samples studied. In this method somehow a graphical approach was used such that, the distance between the curve and its baseline in with respect to the corresponding temperature was obtained for each peak below the decomposition temperatures. This distance is proportional to the rate constant.

The activation energy can be calculated from the following expression. The results are given in Table 4 (DSC data of 10 K min^{-1}).

$$-E = R \frac{\ln D_1 - \ln D_2}{1/T_1 - 1/T_2} \tag{4}$$

where D_1 and D_2 are two distances from the baseline at the associated temperature T_1 and T_2 (K); R is gas constant (J mol^{-1} K^{-1}) and E is activation energy (kJ mol^{-1}).

The two methods called ASTM methods used to evaluate DSC data for the estimation of kinetic parameters involve a similar kinetic model that includes the heating rate. The calculated activation energies were therefore similar. The Roger & Morris method utilizes the distance from the baseline to the DSC curve at points below the decomposition temperature. This may be the reason for differences in activation energy values. Throughout the analysis it was observed that first zone's activation energies are usually lower than those of second one which may be due to the organic matter type and maturity in oil shales.

Table 4 Activation energy values of the oil shale samples, Roger & Morris method

Sample	Activation energy/kJ mol^{-1}
Çan	48.8
Himmetoglu (1)	58.3
Himmetoglu (2)	92.6
Mengen (1)	18.5
Mengen (2)	42.0

(1) First reaction region
(2) Second reaction region

Conclusions

Differential scanning calorimeter (DSC) was used to study the kinetics of oil shales. On DSC curves two reaction regions were observed on oil shale samples studied except Çan oil shale. In DSC experiments, higher heating rates resulted in higher reaction temperatures and higher heat of reactions. Distinguishing peaks in the DSC curves shifted to the higher temperatures with an increase in heating rates. ASTM and Roger & Morris methods were used to obtain the kinetic parameters and the results are discussed.

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