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NON-ISOTHERMAL PYROLYSIS AND KINETICS OF OIL SHALES

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Abstract

In this research, non-isothermal pyrolysis behavior and kinetics of three oil shales were studied by thermal analysis methods. All the thermal effects were endothermic and no exothermic region was observed in DSC curves. When oil shales are heated in nitrogen atmosphere in TG/DTG, two different mechanisms causing loss of mass were observed. The region between ambient temperature and 500 K was distillation. The second mechanism was visbreaking and cracking and it was observed between the region 500 and 800 K. Kinetic parameters of all the samples are determined by Coats and Redfern method and the results are discussed with regard to their accuracy and the ease of interpretation.

Keywords: differential scanning calorimeter, kinetics, oil shale, pyrolysis, thermogravimetry

Introduction

In recent years the application of thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) to study the combustion and pyrolysis behavior of oil shales has gained a wide acceptance. Thermal methods provides information about net results of mass loss and calculation of kinetic parameters are based on simplifying assumptions which do not necessarily correspond to complex chemical reactions in the thermal degradation of oil shales. However, the data provide useful comparisons of reaction parameters such as particle grain size. Rajeshwar [1] studied the pyrolysis kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry. He reviewed the factors influencing kinetic data such as sample order geometry, heating rate and atmosphere. Earnest [2] analyzed the thermal behavior of Green River oil shale in a dynamic atmosphere with TG/DTG and compared it with that in retorting processes. Using the results of this study, the pyrolysis rate was related to the type of organic maceral components of the oil shale specimen. Thakur and Nuttall [3] studied the pyrolysis kinetics of the thermal decomposition of Moroccan oil shale by isothermal and non-isothermal thermogravimetry. Their results showed that the thermal decomposition of oil shale involves two consecutive reactions with bitumen as an intermediate. Skala *et al.* [4]

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have investigated the pyrolysis kinetics of oil shales under non-isothermal conditions by using thermal methods. The results obtained were incorporated into the multi-step kinetic model which was adjusted according to the specific properties of particular oil shale samples and tested by comparison of the experimental and simulated TG/DTG and DSC curves. Skala and Sokic [5] 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/DTG, while combined non-isothermal and isothermal TG/DTG gave the smallest value. There was an increase in the activation energy with increase content of paraffinic structures in the oil shale. Shih and Sohn [6] used non-isothermal TG/DTG with a variety of heating rates to the determination of kinetic parameters for Green River oil shale pyrolysis. Four different methods were employed for kinetic 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 in which diffusion and mass transfer effects were claimed to be unimportant. Markova and Rustchev [7] studied the changes which occur in peat and coal with different degree of carbonization when these are oxidized in the temperature range of 150–300°C, and demonstrated that interaction of the coal with atmospheric oxygen results in the formation of unstable structures.

Experimental

Experiments were performed using DuPont 990 thermal analysis system with differential scanning calorimeter (DSC) and thermogravimetry (TG/DTG) modules. DSC monitors differential heat flow of the samples whereas TG/DTG has the capability of measuring the mass loss either as a function of temperature or time in a varied but controlled atmosphere. Prior to experiments DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was also calibrated for temperature readings with calcium oxalate monohydrate. It was also essential to calibrate the balance for buoyancy effects for the quantitative estimation of mass changes. The material chosen for the investigation of such effects was silver. The oil shale samples were from Himmetoglu, Çan and Mengen fields and had a particle size <60 mesh. All the samples are prepared according to ASTM standards (ASTM D 2013-72). It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. Experiments (DSC and TG/DTG) were performed with a sample size of ~10 mg, at heating rate of 10°C min^{-1}. Nitrogen flow rate was kept constant at 50 ml min^{-1} in the temperature range of 20–600°C. Experiments were performed twice for reproducibility. Properties of these oil shales 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. The pyrolysis is exceedingly complex and many competing processes contribute to the TG curve. Initially, the predominant mechanism of mass loss may be simply evaporation, but later chemical reactions occur and in the final stages volatile matter escapes from a porous solid. In other words, in the initial stages of pyrolysis, distillation of the low molecular mass species occurs, but as the temperature is raised, in addition to the increased rate of volatilization due to progressive evaporation of larger molecules, cracking of the compounds may also occur to produce volatile fragments. During the pyrolysis of studied oil shales, all the thermal effects were endothermic and no exothermic region was observed in DSC curves (Fig. 1a). When oil shales are heated in nitrogen atmosphere in TG/DTG, two different mechanisms causing loss of mass were observed (Fig. 1b). The region between ambient temperature and 500 K was distillation. The second mechanism was visbreaking and cracking and it was observed between the region 500 and 800 K. Whilst the two stage TG/DTG process is reported for the oil

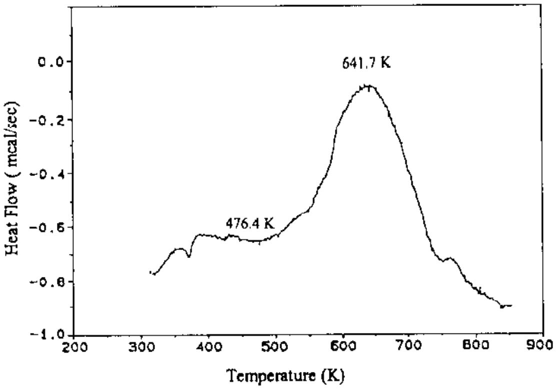

Fig. 1a DSC curve of Himmetoglu oil shale under pyrolysis

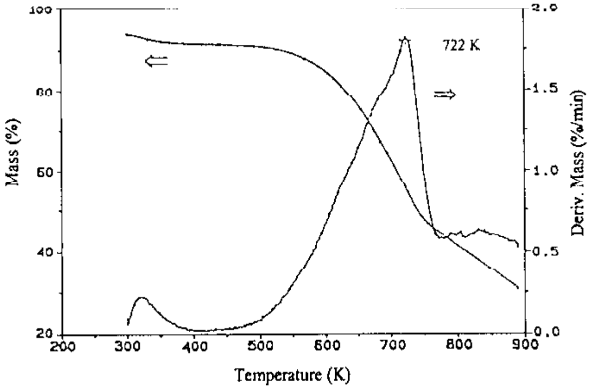

Fig 1b TG/DTG curve of Himmetoglu oil shale under pyrolysis

Table 1 Properties of oil shales

Sample	Calorif. value/cal g^{-1}	C/%	H/%	O, N/%	S/%
Çan	925	10.1	1.95	10.06	0.98
Himmetoglu	1390	13.60	1.5	10.48	0.99
Mengen	1000	10.05	1.9	8.8	0.85

shales in this research, the actual mechanism for the thermal decomposition of oil shales is a much more complex reaction involving a series of parallel reactions [8, 9]. According to Sun and Yung [10] the commencing temperature of pyrolysis of rich grade shale is lower than those of poor grade shale. This situation was also observed in this study, such that Himmetoglu oil shale, which is known to be a high grade shale in the literature, has a commencing temperature of 460 K and this is lower than those of 500 and 520 K of Mengen and Çan oil shales, respectively.

A general review of pyrolysis kinetics literature indicates that during the pyrolysis reactions mass is lost initially at a constant rate corresponding to a zero order process and as temperature increases the order usually becomes equal to unity. The nature and the yield of the reaction products and the kinetic parameters strongly depend on the reaction conditions and properties of samples. The calculation of the kinetic data is based on the formal kinetic equation;

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

where; α is the amount of sample undergoing the reaction, n is the order of reaction and k is the specific rate constant [11]. The temperature dependence of k is expressed by the Arrhenius equation;

$$k = A\exp(-E/RT) \tag{2}$$

where; A is the Arrhenius constant, E is the activation energy and R is the gas constant. There are several approaches to the kinetic analysis of TG data to determine the activation energy and Arrhenius constant for the thermal degradation of oil shale samples. In the course of this research, TG/DTG data of the samples were analyzed using Coats and Redfern method [12]. They have developed an integral method, which can be applied to TG/DTG data, assuming the order of reactions. The correct order is presumed to lead to the best linear plot, from which the activation energy is determined. The form of the equation, which is used for analysis, is,

$$\ln\left[1-(1-\alpha)^{(1-n)}/(1-n)T^2\right] = \ln[(AR/\beta E)(1-2RT/E)] - E/RT \tag{3}$$

where, β is the linear heating rate. Thus a plot of,

$$\ln\left[1-(1-\alpha)^{(1-n)}/(1-n)T^2\right]\ vs.\ 1/T$$

should result in a straight line of slope equals $-E/R$ for the corrected value of reaction order. In this study, the reaction order was assumed to be 1/2, 2/3, 1, 3/2 and 2.

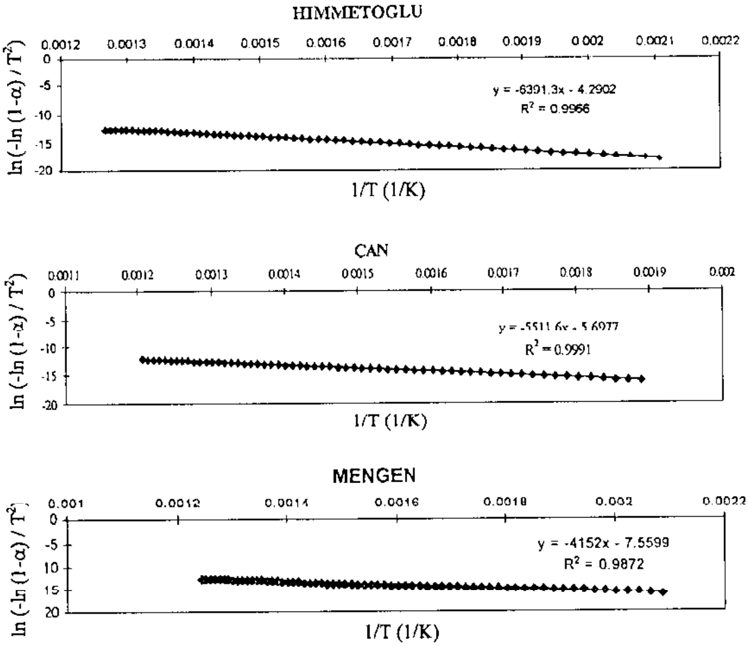

Fig. 2 Kinetic graph of oil shale samples

Coats and Redfern had wide applications in analyzing the TG/DTG data in recent years. This method provides the most reliable results due to its advantages compared with others. As mentioned above, in this study five different reaction orders were assumed and coefficient of determinations of each reaction was calculated and the highest coefficient of determination was found as 1. Within this analysis it was observed that pyrolysis analysis takes place in only one transition zone (Fig. 2). Table 2 shows the apparent activation energies, Arrhenius constants and the compensation effect of oil shale samples studied. In the course of this research, similar behavior was observed in the apparent activation values of the samples studied. Different apparent activation energy values are due to the type of kerogen in the oil shale. It was also observed that mechanisms of the thermal processes of the three samples studied

Table 2 Kinetic parameters of the samples

Sample	E/kJ mol^{-1}	A/1 min^{-1}	Comp. effect
Çan	45.8	121.5	0.9991
Himmetoglu	53.1	565.5	0.9966
Mengen	24.3	15.0	0.9872

are very similar and the small deviations from the linearity verify only the physical differences.

Conclusions

During the experiments, all the thermal effects were endothermic and no exothermic region was observed in DSC curves. When oil shales are heated in nitrogen atmosphere in TG/DTG, two different mechanisms causing loss of mass were observed. The region between ambient temperature and 500 K was distillation. The second mechanism was visbreaking and cracking and it was observed between the region 500 and 800 K. It was also found that the commencing temperature of pyrolysis of rich grade shale are lower than those of poor grade shale. Kinetic parameters of all the samples were also determined by Coats and Redfern method, which provides the most reliable results. The advantages of this method are determining the reaction order rather than assuming and considering the effect of heating rate. It was observed also that, Himmetoglu oil shale has the highest activation energy.

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