

CHARACTERIZATION OF OIL SHALES BY HIGH PRESSURE DSC

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Abstract

Pressurised differential scanning calorimeter (PDSC) has been used to obtain information on the pyrolysis and combustion characteristics of oil shales. Two distinct exothermic peaks were identified in combustion experiments known as low temperature oxidation (LTO) and high temperature oxidation (HTO) reaction regions. The pyrolysis process of all studied oil shale samples showed one exothermic effect at each total pressure studied. Kinetic data were analysed by Roger & Morris and Arrhenius methods and the results are discussed.

Keywords: combustion, high pressure DSC, kinetics, oil shale, pyrolysis

Introduction

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. Current reserves of oil shales in Turkey are ~1865 million tons, located in the following deposits: Seyitömer, Himmetoglu, Hatildag, Çan, Mengen and Reyazari [1].

Recent years an increase in the scientific investigation and characterisation of oil shales and other source of organic content of any level can be seen. The thermal analysis techniques applicable to solid hydrocarbon fuels are thermogravimetry, (TG/DTG) differential thermal analysis (DTA) and differential scanning calorimeter (DSC), evolved gas analysis (EGA), thermomagnetometry (TM), and variable temperature and atmosphere X-ray diffraction. In the field of coal and oil shale research, characterisation, development and utilisation, the work indicates that important contributions can be made with variable atmosphere DSC, DTA and TG/DTG. In recent years the application of DSC and TG/DTG to study the combustion and pyrolysis behaviour of oil shales has gained a wide acceptance. Rejashwar [2] studied the pyrolysis kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry. He critically reviewed the factors influencing kinetic data such as sample geometry, heating rate and atmosphere. Earnest [3] analysed the thermal behaviour of Green River oil shale in a dynamic nitrogen atmosphere with

TG/DTG and compared it with that in retorting processes. Using the results of this study, the pyrolysis onset temperatures and the temperatures at the maximum pyrolysis rate were related to the type of organic maceral components of the oil shale specimen. Skala *et al.* [4] has investigated the pyrolysis kinetics of oil shales under non-isothermal conditions using thermal methods. The results obtained were incorporated into the multistep kinetic model which was adjusted according to the specific properties of particular oil shale samples and tested by comparison of the experimental and simulated DSC and TG/DTG curves. Shih and Sohn [5] used non-isothermal TG with a variety of heating rates to the determination of kinetic parameters for Green River oil shale. Four different methods were employed for kinetic analysis and the results seem to be in fair agreement. Elder [6] developed a procedure for the automatic proximate analysis of solid fuels and related matter. The procedure is tested with coals of varying rank, biomass samples and Devonian oil shales. The simplicity of the technique suggests that it may complement the classical ASTM method and could be used. Thakur and Nuttall [7] studied the pyrolysis kinetics of the thermal decomposition of 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 intermediate. Skala and Sokic [8] developed a kinetic expression commonly used in the thermal analysis of oil shale pyrolysis. The obtained results showed an increase in the activation energy with increase content of paraffinic structures in the oil shale.

Experimental

All experiments were conducted using DuPont 990 Thermal Analyser with a high pressure DSC Cell module that is capable of calorimetric measurements up to elevated pressures of 1000 psi. In this technique the material was subjected to a linear temperature programme and the rate of heat flow into the material was continuously measured at elevated pressures. In this research all experiments were performed with three different oil shale samples (Mengen, Çan and Himmetoglu) which is prepared according to ASTM standards (<60 mesh size). Properties of the oil shales are given in Table I. The experimental procedure involves placing ~10 mg of sample in a pan, setting the desired pressure and heating rate then commencing the experiment. All experiments were performed at a linear heating rate of $10^{\circ}\text{C min}^{-1}$ over the temperature range of 25–600°C. Air and argon flow rates kept constant for combustion and pyrolysis experiments. The high-pressure DSC cell was pressurised and controlled at a reselected pressure within the range of 100 to 400 psi at 100 psi intervals. Prior to experiments high pressure DSC system was calibrated for temperature readings using indium as a reference standard. In order to assess the repeatability, experiments were performed twice.

Results and discussion

Any kind of minerals, which contain organic substances in large quantities, may be characterised as oil shale regardless of their mineralogical structure. Studies on oil shale using thermal analysis techniques have shown that combustion of indige-

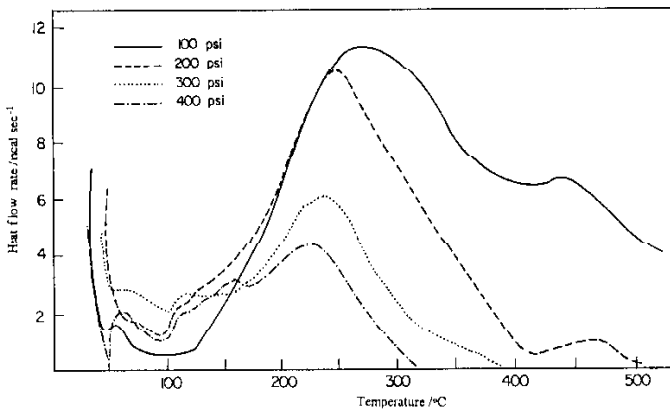
Table 1 Properties of oil shales

Properties	Mengen	Çan	Himmetoglu
C/%	10.05	10.10	13.60
H/%	1.90	1.95	1.50
C-N/%	7.80	10.06	10.48
S/%	0.85	0.98	0.99
Calor. value (cal/g)	850	925	1046

ious organic matter is a complex multistage process. The thermal behaviour of oil shales in dynamic air atmospheres may exhibit characteristics of both the inorganic (mineral) and organic (kerogen + bitumen) components. The low temperature portion of the thermal curves may represent thermal decomposition identical to that observed in inert atmospheres while at higher temperatures oxidative characteristics of the organic component generally predominate. Thermal events, which may also appear in this region, although generally to a much less extent, include dehydroxylation of clay mineral components.

Pyrolysis experiments

Many hydrocarbon compounds undergo permanent changes when subjected to extreme heat. The extent of this change depends on the complexity of the molecular structure and the reaction environment. This class of reactions is generally termed as pyrolysis reactions. The pyrolysis process of all studied oil shale samples showed one exothermic effect at each total pressure studied (Fig. 1). Reaction intervals of the oil shales and corresponding peak temperatures are given in Table 2.

**Fig. 1** PDSC curves of Himmetoglu oil shale (Pyrolysis)

Combustion experiments

The oxidation process of all studied oil shale samples showed two exothermic effects at each total pressure applied (Fig. 2). The first peak is the low temperature oxidation (LTO), which occurs between 150 and 370°C depending on the oil shale type. It has been established that the low temperature oxidation leads to the reduction of the H/C atomic ratio, and an increase in the yield of CO₂ and H₂O, which is explained by the formation of oxygen bonds, or reduction of aliphatic hydrogen in oil shale. The second, high temperature oxidation (HTO) peak occurs between 370 and 520°C. In dynamic air, resolution was vastly improved, but the peak area in HTO region reduced to about half. This was probably because some of the volatilised organic matter was swept away from the sample by the flowing gas, before it had burned completely. A decrease in peak temperatures was observed as the total pressure is increased in both low and high temperature oxidation regions. Same effect

Table 2 Reaction intervals and peak temperature of oil shale samples (°C)-Pyrolysis

Oil shale	Press/MPa	Press/psi	Reac. int./°C	Peak temp./°C
Mengen	0.78	100	175-415	285
	1.46	200	175-420	280
	2.14	300	170-415	275
	2.82	400	175-420	270
Çan	0.78	100	150-510	275
	1.46	200	150-515	270
	2.14	300	150-515	265
	2.82	400	150-510	260
Himmetoglu	0.78	100	100-420	255
	1.46	200	100-415	250
	2.14	300	100-420	245
	2.82	400	100-415	240

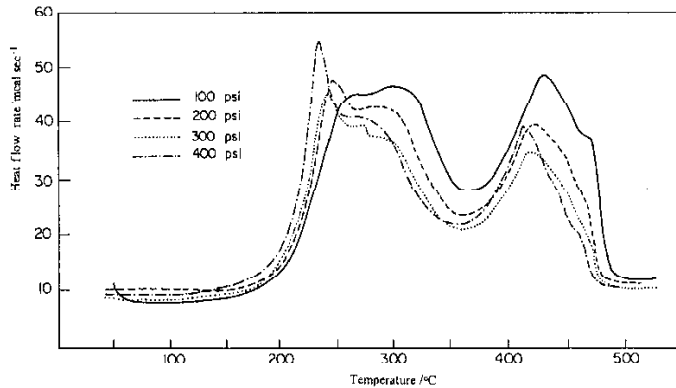


Fig. 2 PDSC curves of Himmetoglu oil shale (Combustion)

Table 3 Reaction intervals and peak temperatures of oil shales ($^{\circ}\text{C}$)-Combustion

Oil shale	Press./MPa	Press./psi	Peak temp.		Reac.(LTO)	Reac.(HTO)
			(LTO)	(HTO)		
Mengen	0.78	100	295	395	150-355	355-500
	1.46	200	290	390	150-350	350-490
	2.14	300	285	385	150-345	345-485
	2.28	400	280	385	150-340	340-475
Çan	0.78	100	290	365	150-330	330-520
	1.46	200	280	365	150-330	330-510
	2.14	300	270	360	150-325	325-500
	2.82	400	265	360	150-325	325-490
Himmetoglu	0.78	100	250	430	150-370	370-495
	1.46	200	250	425	150-365	365-485
	2.14	300	245	420	150-365	365-480
	2.82	400	240	415	150-355	355-475

Table 4 Heat values of the oil shales/ J g^{-1}

Oil shale	Press./MPa	Press./psi	$\Delta H(\text{LTO})$	$\Delta H(\text{HTO})$	$\Delta H(\text{Total})$
Mengen	0.78	100	6720	4220	10940
	1.46	200	6140	3300	9440
	2.14	300	5810	2740	8550
	2.82	400	5700	2565	8265
Çan	0.78	100	7025	4465	11490
	1.46	200	6965	4440	11405
	2.14	300	6880	3755	10635
	2.82	400	6855	3555	10410
Himmetoglu	0.78	100	11740	8220	19960
	1.46	200	11465	6445	17910
	2.14	300	11275	6315	17590
	2.82	400	10750	5440	16190

was also observed in reaction intervals (Table 3). Under non-isothermal heating conditions PDSC curves giving heat flow rates as the oil shale sample reacted with air, indicated that oil shale samples were generating high heat flows in the low temperature oxidation region. As the total pressure increased, a decrease in heat flow rates were observed in low and high temperature oxidation regions (Table 4).

Kinetic analysis

The kinetics of kerogen in oil shale, which is the precursor of oil, has been studied by a number of investigators. The complex nature of kerogen and its decomposition reaction has complicated the interpretation of data and led to various postulates for the decomposition mechanisms. Investigators treated the kinetics using a mechanism consisting of two first order steps for the decomposition of kerogen to bitumen

which subsequently decomposes to oil, gas and carbon residue. Also it was found that the kinetics to be a diffusion-limited first order reaction complicated by the possibility of bond-breaking steps [5].

Table 5 Activation energies (kJ mol⁻¹) and Arrhenius const. (1 min⁻¹) of oil shales-Pyrolysis-(model-1)

Oil shale	Press/MPa	Press./psi	E_a	Arrh. const.
Mengen	0.78	100	46	4.9E-01
	1.46	200	42	9.8E-02
	2.14	300	39	1.6E-02
	2.82	400	32	5.9E-02
Çan	0.78	100	56	5.6E-04
	1.46	200	52	1.1E-03
	2.14	300	45	4.3E-03
	2.82	400	42	3.2E-03
Himmetoglu	0.78	100	25	1.9E-01
	1.46	200	24	2.2E-01
	2.14	300	20	4.4E-01
	2.82	400	18	6.2E-01

A kinetic model [9] which gives a means of estimating activation energies from PDSC curves was used in this study (model-1). In this model, it was assumed that the recorded data of the PDSC are in the form of distances between the PDSC curve and a baseline at the associated absolute temperature. This distance is proportional to the rate constant. The activation energy can be calculated from the following expression:

$$E=R[(\ln D_1 - \ln D_2)/(1/T_1 - 1/T_2)] \quad (1)$$

A method of estimating the Arrhenius constant from PDSC curves requires that the decomposition be first-order in the reactant. The deflection of PDSC curve from the baseline is given by the following expression:

$$b = -\alpha dm/dt \quad (2)$$

If the sample decomposes according to the first-order rate law, then:

$$b = \alpha m A c^{-E/RT} \quad (3)$$

Differentiating with respect to time:

$$db/dt = \alpha dm/dt A c^{-E/RT} + \alpha m A c^{-E/RT} E/RT^2 dT/dt \quad (4)$$

The maximum in the PDSC curves occurs when $db/dt=0$, so:

$$A_T = [(BEc^{-1/RT})/(RT_{max}^2)] \quad (5)$$

Table 6 Activation energies (kJ mol^{-1}) of oil shales-Combustion-(model-1)

Oil shale	Press./MPa	Press./psi	E_a (I)	E_a (II)	Arrh. const. (I)	Arrh. const. (II)
Mengen	0.78	100	37.1	29.7	3.1E-03	1.2E-01
	1.46	200	43.2	34.5	4.2E-03	2.5E-01
	2.14	300	49.3	36.5	4.9E-03	8.4E-01
	2.82	400	67.1	48.1	6.7E-04	1.3E-02
Çan	0.78	100	49.9	25.5	4.7E-03	2.0E-01
	1.46	200	55.7	29.7	6.6E-04	3.9E-01
	2.14	300	62.1	43.1	1.5E-04	2.3E-02
	2.82	400	62.4	43.4	1.2E-04	2.1E-02
Himmetoglu	0.78	100	82.7	72.3	1.1E-06	5.2E-05
	1.46	200	100.7	80.9	2.0E-08	5.6E-05
	2.14	300	112.7	85.2	1.1E-09	1.2E-06
	2.82	400	119.6	86.1	1.8E-10	2.3E-06

Table 7 Activation energies (kJ mol^{-1}) of oil shales-Combustion- (model-2)

Oil shale	Press./MPa	Press./psi	E_a (I)	E_a (II)	Arrh. const. (I)	Arrh. const. (II)
Mengen	0.78	100	46.3	21.5	2.7E-03	2.5E-01
	1.46	200	51.6	26.3	3.5E-03	3.4E-01
	2.14	300	53.8	29.6	8.7E-03	1.4E-02
	2.82	400	62.8	37.3	3.6E-04	6.4E-02
Çan	0.78	100	43.5	21.2	2.5E-03	3.9E-01
	1.46	200	51.7	23.2	3.8E-03	4.4E-01
	2.14	300	58.7	32.5	1.5E-04	2.7E-02
	2.82	400	68.1	36.5	9.2E-04	3.2E-02
Himmetoglu	0.78	100	78.6	69.8	2.3E-06	4.7E-05
	1.46	200	98.5	75.3	1.8E-08	9.2E-05
	2.14	300	107.8	79.5	2.3E-09	3.2E-06
	2.82	400	115.3	83.6	3.4E-10	8.6E-06

In the second model, kinetic data were obtained from the coke combustion region of pressurized differential scanning calorimeter (PDSC) curves. Assuming a first-order combustion reaction for the fuel lay down in this region [10].

$$dh/dt = kh^n \quad (6)$$

$$k = A_1 \exp(-E/RT) \quad (7)$$

Assuming first order kinetics,

$$dh/dt = A_1 \exp(-E/RT) h \quad (8)$$

$$[(dh/dt)/h] = A_1 \exp(-E/RT) \quad (9)$$

taking the logarithm of both sides and assuming $n=1$,

$$\log[(dh/dt)/h] = \log A_r - E/2.303RT \quad (10)$$

where; dh/dt is the rate of enthalpy change of the reacting material, h is the fraction of the enthalpy yet to be released, R is the gas constant ($\text{J g}^{-1} \text{mol}^{-1} \text{K}^{-1}$), E is the activation energy (kJ mol^{-1}), A_r the Arrhenius constant (l min^{-1}), T is the temperature (K) and n the reaction order.

Pyrolysis kinetic data were obtained from the PDSC curves are apparent due to the assumptions made in (model-1). There is a general trend to decreasing in activation energy with increasing pressure in pyrolysis experiments (Table 5). A general trend to increasing in activation energy with increasing pressure was observed in combustion experiments (Tables 6 and 7).

Conclusions

PDSC techniques have yielded much useful information regarding to oil shale characterisation. In this research pyrolysis and combustion characteristics of oil shales were analysed. The combustion process of all studied oil shale samples showed two exothermic effects at each total pressure applied. The first peak is the low temperature oxidation (LTO), which occurs between 150 and 370°C depending on the oil shale type. The second, high temperature oxidation (HTO) peak occurs between 370 and 520°C. A decrease in peak temperatures was observed as the total pressure is increased in both low and high temperature oxidation regions. Under non-isothermal heating conditions PDSC curves giving heat flow rates as the oil shale sample reacted with air, indicated that oil shale samples were generating high heat flows in the low temperature oxidation region. As the total pressure increased, a decrease in heat flow rates was observed in low and high temperature oxidation regions. The pyrolysis process of all studied oil shale samples showed one exothermic effect at each total pressure studied. There is a general trend to decreasing in activation energy with increasing pressure in pyrolysis experiments whereas in combustion experiments increasing in activation energy with increasing pressure was observed.

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