INVESTIGATION ON PYROLYSIS OF HUANGXIAN OIL SHALE BETWEEN 550°--750°C

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ABSTRACT

A comprehensive investigation of the second weight loss step for Huangxian (HX) oil shale was carried out by comparison of IR spectra of shale semicoke obtained in various end temperature of pyrolysis and shale sample treated with HCl and in combination with kinetic parameters of the second pyrolysis and other evidences. From these results, it was verified that the second weight loss step is mainly decomposition of dolomite and calcite in the shale. Thermogravimetric data of the second weight loss step were fitted satisfactorily by the first-order kinetic model. Apparent activation energy E and preexponential factor A determined in this study agreed considerably with those of decomposition of dolomite in Colorado oil shale and calcite, which cited from reference.

INTRODUCTION

The distinct characteristics of pyrolysis for HX oil shale, compared with Fushun and Maoming oil shale, are that it has two clear pyrolysis processes below about 750°C and shows two weight loss steps in thermogravimetric curve. It is determined now that the first weight loss step is basically pyrolysis of organic matters in shale(1). From a point of view of use or research for HX oil shale, it is necessary to demonstrate the property of the second pyrolysis. In this paper, it was investigated comprehensively by comparing of IR spectra of semicoke obtained in various end temperature of pyrolysis and shale sample treated with HCl and in combination with kinetic parameters of the second pyrolysis and other evidences.

EXPERIMENTAL

Thermogravimetric Analysis

Thermogravimetric analyses were run by using a modified stanton thermobalance. The main operating conditions are described as follows: linear heating rate 6.62 K/min, flowrate of inert gas (nitrogen) 100 ml/min, particle size of shale 0.076 mm and sample weight 45 $\pm$ 1 mg. Details of the apparatus and operating were reported in reference[2].

Infrared (IR) Spectroscopy

IR spectra of shale sample and semicoke were measured by using a Hitachi 260-50 grating spectrophotometer. The samples were prepared as KBr pellets for shale and its semicoke. Range of wavenumbers is 4000-250 cm^{-1}.

Acid treatment of oil shale

Sample was treated by 12.3%(wt.) HCl and washed by distilled water till the wash water became neutral, then dried in 90^{o}C up to its weight being constant.

Oil shale sample

The sample is same as reported in reference [1].

RESULTS AND DISCUSSION

1. IR spectra of HX oil shale

IR spectra of HX oil shale are shown in Fig.1. According to the references [3,4], signification of the major peaks in Fig.1 has been

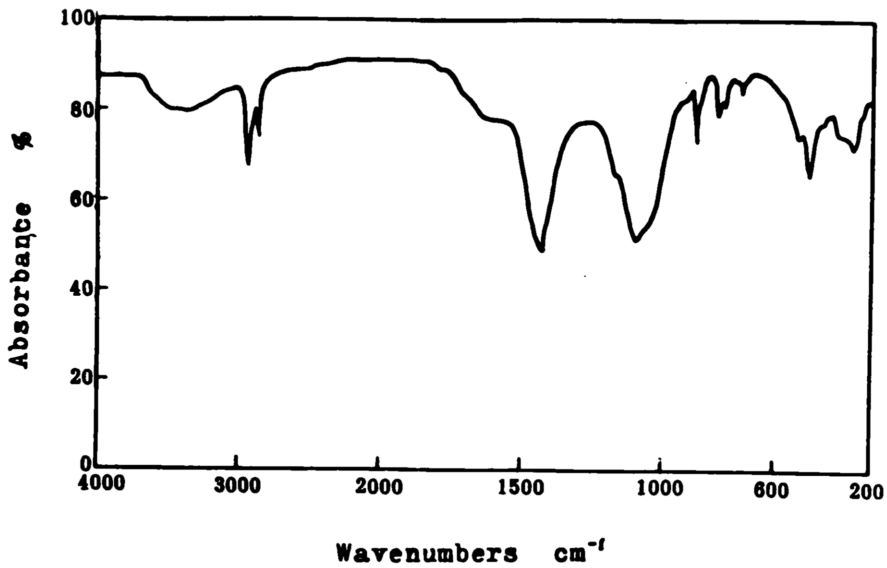

Fig.1 IR spectra of HX oil shale

clear. From comparing to IR spectra of Fushun and Maoming oil shale in the reference[4], it can be found that besides sharp peaks characterizing organic matters near 2900 cm^{-1}, an important difference is that there exists a strong peak of dolomite and calcite near 1400 cm^{-1} in HX oil shale.

2. Basic features of the second weight loss step for HX oil shale

A typical thermogravimetric curve of HX oil shale (a) in Fig. 2 shows that the first weight loss step begins at 221°C and finishes below about 550°C. As the pyrolysis temperature rises to 586°C, the second weight loss step starts. The temperature range of intense pyrolysis is between 650°-710°C. Above 750°C pyrolysis tends to end gradully.

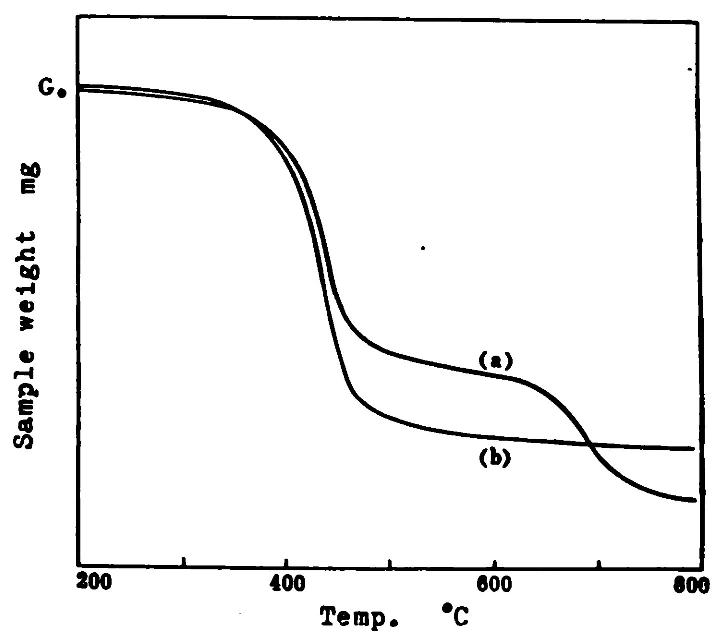

Fig. 2 Typical thermogravimetric curves of HX oil shale (a) and sample treated with HCl (b)

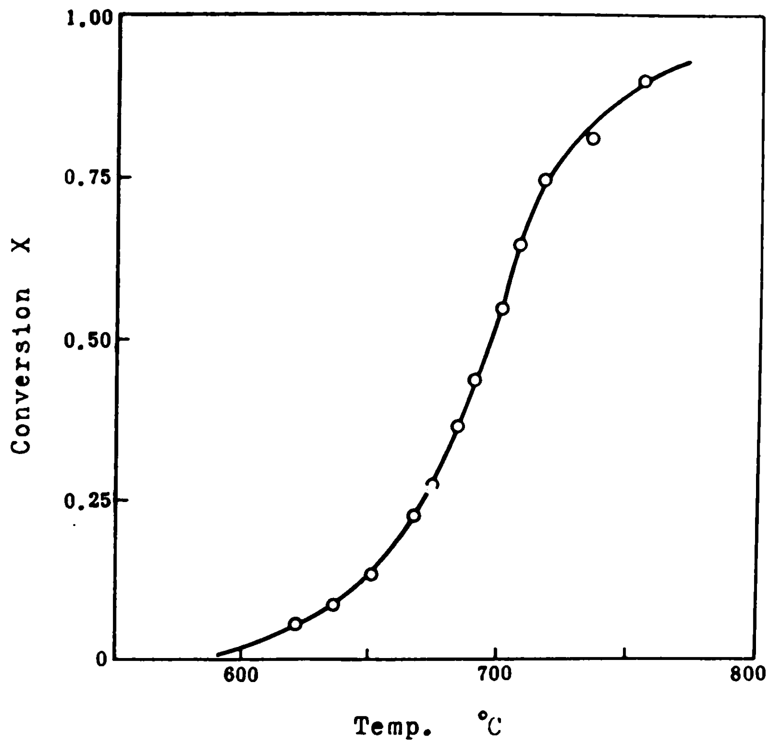

Fig. 3 Conversion VS. temperature curve during the second pyrolysis of HX oil shale

Conversion VS. temperature curve of the second pyrolysis for HX oil shale is shown in Fig.3.

3. Characterization of the second weight loss step for HX oil shale

(1) Characterization based on IR spectra of semicoke in various end temperature of pyrolysis

In order to investigate the properties of two weight loss steps for HX oil shale, the semicokes in end of the first and second pyrolysis were obtained by cooling with nitrogen respectively. Then their IR spectras were measured. Results indicate that the aliphatic peaks of 2930 cm^{-1} and 2860 cm^{-1}, as a major sign of organic matters in shale, has disappeared in IR spectra of semicoke obtained in pyrolysis temperature 586°C (see Fig.4) and the weaker broad peak between 3700-3100 cm^{-1} has also tended to disappear, and others have not changed basically. Here, it can be determined that the first weight loss step below 586°C is mainly pyrolysis of organic matters and formation of shale oil. However, in IR spectra of semicoke obtained in 750°C and undergone two weight loss steps (see Fig.5), not only peaks of 2930 cm^{-1} and 2860 cm^{-1} and but also the strong peaks of dolomite and calcite, 1430 cm^{-1}, 883 cm^{-1} and 720 cm^{-1}, have disappeared, and broad peak of sulfurous iron ore near 320 cm^{-1} tends to disappear too. Other peaks of minerals in shale have still remained. It is obvious that the

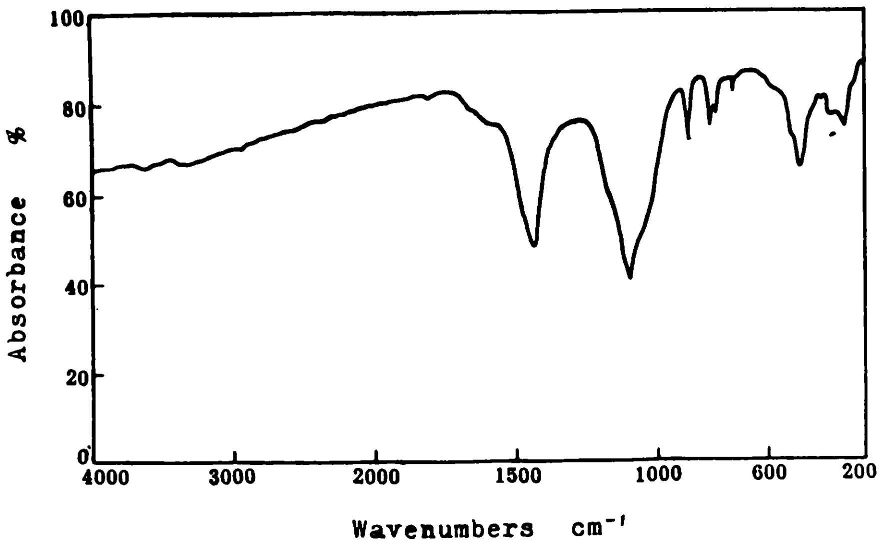

Fig. 4 IR spectra of semi-coke obtained in end temperature of pyrolysis 586°C

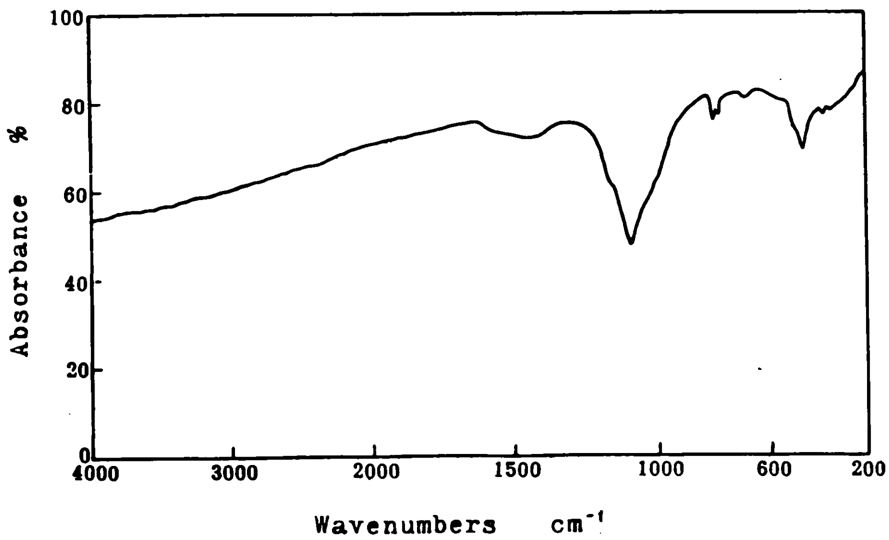

Fig. 5 IR spectra of semi-coke obtained in end temperature of pyrolysis 750°C

second weight loss step occured above 586°C is mainly decomposition of dolomite, calcite etc. and in company with decomposition of sulfurous iron ore in shale.

(2) Characterization based on IR spectra of shale sample treated with HCl

If there exist dolomite, calcite etc. in shale, their characteristic peak, 1430 cm^{-1} and 883 cm^{-1}, should disappear after occuring following reactions with HCl:

$$CaMg(CO_3)_2 + 4HCl \longrightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$$
$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

From IR spectra of sample treated with HCl (see Fig.6), it is verified that this prediction agrees with the fact.

Morever, decomposition of dolomite and calcite results in appearance of the second weight loss step. Figure 2 indicates that indeed only one obvious weight loss step appears in thermogravimetric curve of sample

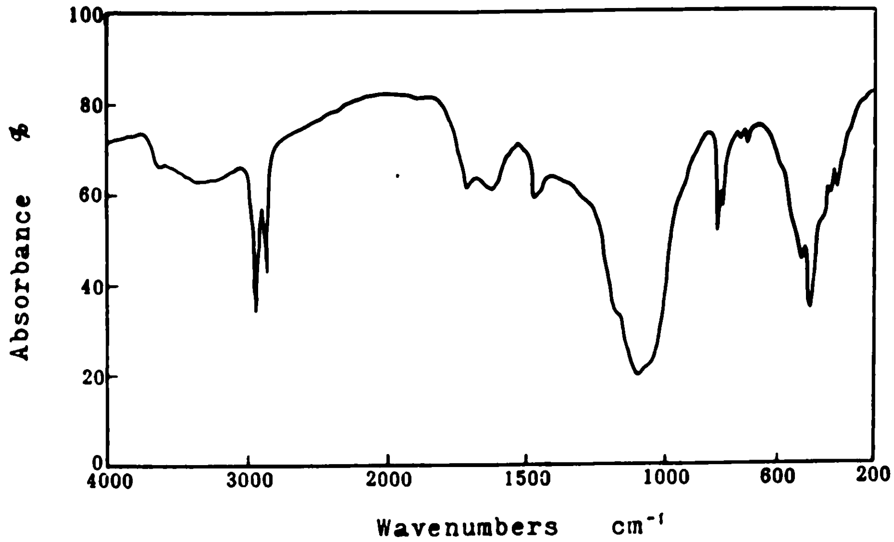

Fig. 6 IR spectra of sample treated with HCl

treated with HCl. Thus, there is enough evidence to prove the property of the second pyrolysis.

(3) Characterization based on kinetic parameters of pyrolysis

For decomposition of carbonates in shale,

$$MCO_3 \longrightarrow MO + CO_2$$

the reaction can be seen as first-order reaction, and M as Ca and Mg etc.. Based on the previous work[2,5], the thermogravimetric data of the second pyrolysis for HX oil shale were related by followingequation:

$$\mathrm{Ln}\left[-\frac{\mathrm{Ln}(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HrE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

Figure 7 is kinetic curve obtained by plotting $\mathrm{Ln}(-\mathrm{Ln}(1-x)/T^2)$ VS. 1/T.

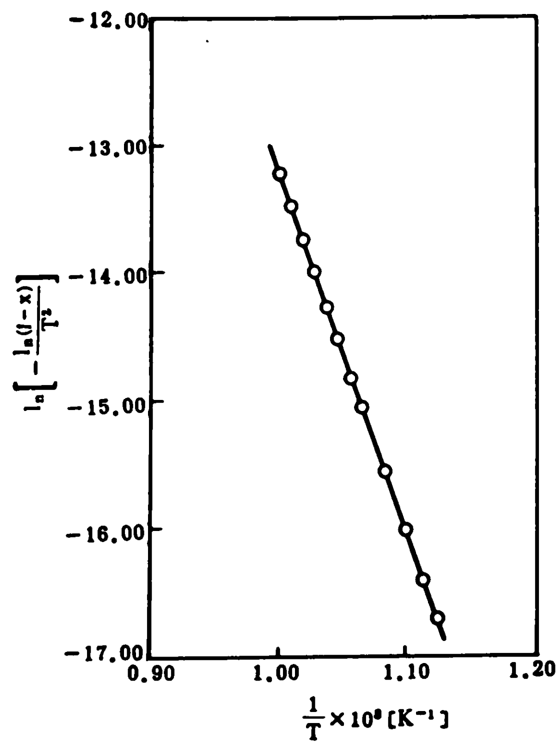

Fig. 7 Kinetic curve of the second pyrolysis for HX oil shale

A good linear relation of data in Fig.7 shows that it is reasonable to fit the data of the second pyrolysis by the equation as mentioned above. Apparent activation energy E and preexponential factor A were calculated respectively by linear regression and were shown together with data from reference[6] in table 1.

From table 1 it can be found that the values of kinetic parameters of the second pyrolysis for HX oil shale agree well with those of dolomite (ankerite) in Colorado oil shale and of calcite. Thus, it is confirmed that the second pyrolysis of HX oil shale is conformable to decomposition of dolomite and calcite in kinetics.

Table 1. Kinetic parameters of the second pyrolysis for HX oil shale and comparison with data from reference

Kinetic parameters	Data of this study	Data from the reference(6)	
	The second pyrolysis of HX oil shale	Dolomite-ankerite (in Colorado shale)	Calcite (pure)
Reaction order n	1	1	1
Apparent activation energy E kJ/mol	241	242	230
Preexponential factor A S^{-1}	4.3×10^{10}	1.7×10^{10}	1.3×10^{10}
Relative coefficient	-0.9983		

(4) Other evidences

As mentioned above, the second pyrolysis of HX oil shale start at 586°C, and its temperature range of intense pyrolysis is about between 650°-710°C. This agrees basically with temperature range of decomposition of dolomite and calcite, 600°-750°C, which cited from reference[6].

Morever, proximate analysis of HX oil shale indicates that its CO_2 yield is up to 11.2% and far more than that of Maoming 1.4% and Fushun oil shale 2.9%[1]. This fact is a obvious evidence that there exists a considerable quantity of carbonate in HX oil shale.

CONCLUSIONS

1. From IR spectra of semicoke and sample treated with HCl and kinetic parameters and other evidences, it is verified that for HX oil shale the existence of the second pyrolysis is mainly due to decomposition of dolomite, calcite etc. in shale.

2. Thermogravimetric data of the second pyrolysis for HX oil shale were fitted satisfactorily by the first-order kinetic model. The following reaction rate constant expression was obtained:

$$K = 4.3 \times 10^{10} \exp(28940/T) \quad S^{-1}$$

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