Thermal Analysis of Huadian Oil Shale with Isoconversional Method

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Introduction

Thermal analysis is a useful means to provide necessary information on the reactivity of samples, and thus widely applied. Apparent activation energy, Frequency factor and reaction mechanisms are the three key parameters to characterize a pyrolysis process. Three oil shale samples from Huadian deposits have been performed in a TGA under non-isothermal conditions to determine their pyrolysis characteristics. The Friedman method, a typical isoconversional method. Furthermore, was used to analysis their kinetic parameters and the reaction mechanism.

Experimental

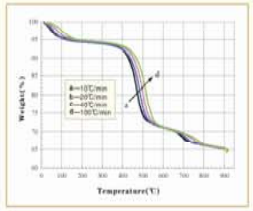
The thermal decomposition of Huadian oil shale samples was studied on the thermogravimetric analysis (TG, DTG) at different heating rates (i.e., 10, 20, 40, 100℃/min) under the nitrogen environment using Perkin Elmer Pyris 1 Thermal Analyser. The initial sample mass was ~10 mg, and the particle size was ~ 0.2mm prepared according to the ASTM standards.

The investigations were performed on three oil shale samples taken from the 4th、5th and 7th layer of Gonghe mines in Huadian, China. The samples were denoted by OS1、OS2 and OS3, respectively.

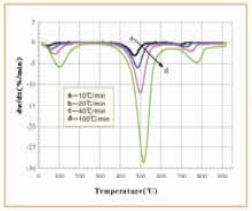
Proximate and Ultimate analysis of Huadian oil shales

	Proximate analysis (%)					Ultimate analysis (%)				
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	$Q_{net,ar}$(J/g)	C_{ad}	H_{ad}	N_{ad}	O_{ad}	S_{ad}
OS1	5.31	29.76	60.27	4.66	8817	23.68	3.96	0.59	5.36	0.83
OS2	5.52	26.96	65.45	2.07	5923	17.69	2.48	0.39	7.89	0.58
OS3	5.51	24.21	69.95	0.33	4095	14.01	2.91	0.39	5.94	1.29

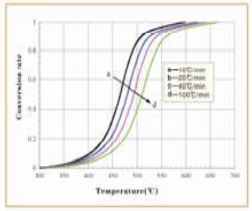
Results



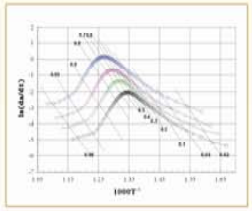
TG curves for OS1 at various heating rates



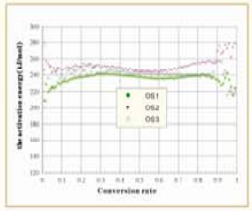
DTG curves for OS1 at various heating rates



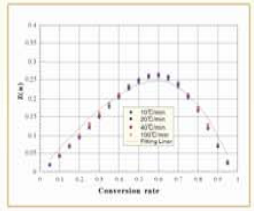
The α–T curves for OS1 at various heating rates



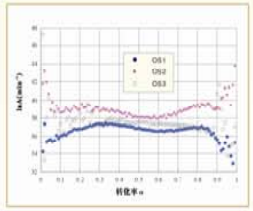
Friedman analysis for the pyrolysis of Os1



The curves of E–α for oil shale pyrolysis



Fitting liner for the pyrolysis reaction mechanism of Os1



The frequency factor of oil shale samples

Conclusions

1. The decomposition process involves three stages and the second stage (200~600℃) is the main weight loss stage, which attributed to the decomposition of hydrocarbon material.
2. The apparent activation energy of the Huadian oil shale pyrolysis was calculated by the Friedman method and the results show that the activation energy of oil shale pyrolysis is not a constant throughout the reaction process. But in the range of 0.1-0.9 for the conversion rate,the activation energy changes slightly, which the mean values of three samples are 237.6kJ • mol^{-1}、249.61 kJ • mol^{-1} and 242.67 kJ • mol^{-1} respectively.
3. The Sestak's complex mechanism was used to fit liner for the pyrolysis reaction mechanism of oil shale. The results show that oil shale pyrolysis is not a simple first order reaction and its pyrolytic mechanisms are complex and mainly attribute to the nuclear mechanism.