

ISOTHERMAL PYROLYSIS GAS CHROMATOGRAPHY FOR STUDY OF
HYDROCARBON FORMATION KINETICS FROM KEROGENS

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ABSTRACT

Four Chinese immature kerogens of different types from Fushun (FK), Maoming (MK), Huangxian (HSK) oil shales and Huangxian lignite (HLK) were selected as samples in the study of hydrocarbon formation kinetics by using the sequential isothermal pyrolysis gas chromatography technique. The kinetic parameters of light hydrocarbons C_1 - C_7 , paraffinic monomers and toluene generated from these four kerogens have been determined.

The relations between these kinetics parameters and the kerogen structure viewed by FTIR are also discussed. It provides a new standpoint for the study of pyrolysis mechanism of kerogen.

INTRODUCTION

Many studies of the thermal decomposition kinetics of oil shale and its kerogen have been conducted by different investigators,^[1-4] however, little information has been reported in literature on the kinetics of various individual constituents of products generated from the kerogen pyrolysis. In this paper, we introduce a new experimental method named sequential isothermal pyrolysis gas chromatography, by which the hydrocarbon monomer formation kinetic parameters in the kerogen pyrolysis products can be determined. Since the method is based on the principle of isothermal pyrolysis, a very high heating and cooling rate of the pyrolyzer have to be achieved. It is realized by a special designed operation procedure using a micro-scale flash pyrolyzer connected with a gas chromatograph.

EXPERIMENTAL

Samples

Four typical kerogens from Fushun (FK), Maoming (MK), Huangxian(HSK) oil shales and Huangxian lignite (HLK) were selected as the samples. The kerogen concentrates were obtained by treating the raw oil shale and lignite with hydrochloric acid and hydrofluoric acid at 70°C. Their main properties are listed in Table 1. It is evident that these kerogens are all immature in nature, but are different in type.

Table 1. The main properties of kerogen concentrates

Sample	Ultimate analysis					Atomic ratio		Kerogen type	Reflectance of Vitrinite	
	C	H	N	S	O	H/C	O/C		R ₀	%
FK	78.3	9.6	2.4	1.5	8.2	1.47	0.079	1	0.33	
MK	76.6	8.8	1.4	4.7	8.5	1.38	0.083	2	0.32	
HSK	72.3	8.2	1.5	3.4	14.6	1.35	0.15	2	0.36	
HLK	65.9	5.4	1.2	1.0	26.5	0.98	0.30	3	0.42	

Instruments

The main instruments used are:

- (1) CDS-120 flash pyrolyzer, with a platinum coil pyroprobe and a 0.17 i.d. x 24.2 mm quartz tube for packing samples.
- (2) SP-3700 Varian gas chromatograph, with a 0.25x25m OV-101 capillary column and a flame ion detector (FID).
- (3) SP-4270 integrator.

The schematic diagram is shown as Figure 1.

Sample---Injector---Interface---Capillary column---FID---SP-4270
(CDS-120 flash pyrolyzer)(SP-3700 gas chromatograph) (Integrator)

Figure 1. The schematic diagram of experimental instruments

Operation conditions

The pyrolysis temperature indicator of the automatic controller was recalibrated in the range of 300-1000°C. The heating rate was kept at 0.5°C per milli-second, the final temperature was held in different time intervals, ranging from 5 to 20 seconds. The temperature of the interface was maintained at 200°C.

The initial temperature of capillary column kept constant for 5 min

at 50°C, the program heating rate was 6°C/min and the final temperature kept at 280°C for 20 minutes. The FID temperature was 300°C. The gas flow rates were: 300 ml/min for air, 30 ml/min for hydrogen and 18 cm/sec for the carrier gas nitrogen.

Each sequential pyrolysis of one sample involved a series of interrupted flash pyrolyses. The sample was exposed to the same temperature but for different retention time in each pyrolysis series. The number of pyrolysis needed for one designated temperature depended upon the time required for decomposition of the sample, that was indicated by the GC spectrum as the peaks of liquid hydrocarbons diminished gradually.

Kerogen sample 1-2 mg was weighted to 0.01 mg for each test. Since the accumulation of heating time and amount of pyrolysis products may bring error to the calculation of kinetic parameters, a preliminary experiment for examination was conducted under 480°C with two parallel tests. The retention time of the first pyrolysis test was 20 seconds, and that of the second test was 10 seconds twice. The result showed that these two tests gave a relative error 2.1%, which is generally acceptable for the kinetics calculation.

The measured heating and cooling time required to across the pyrolysis temperature interval for each test was less than 1 second, consequently, the results of the pyrolysis tests may be treated as isothermal tests. In general, the experiments presented good repeatability and dependability for the purpose of kinetics studies.

RESULTS AND DISCUSSION

Pyrolysis model and kinetics equation

Low maturity kerogens produce gases, liquids and solids in a pyrolysis test. The pyrolysis products can be detected by gas chromatograph are limited for the gases and volatile matters. Under the conditions used in our Py-GC tests, the corresponding molecules larger than carbon 6 and smaller than carbon 30 n-paraffin can be separated and measured clearly in the GC spectra. The gaseous products C-1 to C-6 are treated as one component.

The pyrolysis model viewed by Py-GC may be written as follows:

Kerogen --- $\left\{ \begin{array}{l} \text{-Volatile matters, } B_1+B_2+B_3+B_4+\dots\dots+B_i+\dots \\ \text{-Nonvolatile matters (heavy liquids+solids)} \end{array} \right.$

The general kinetics equation of kerogen pyrolysis is (1)

$$dx/dt = k(1-x)^n$$

where $x = C_A / C_{A0}$; C_A is the integration area of GC peaks of the products generated at the moment t ; and C_{A0} is the total amount of products generated as the experiment is finished.

Assuming that kerogen pyrolysis is a first order reaction, we have

$$-\ln(1-x) = kt \quad (2)$$

where k is the constant of reaction rate and t is the pyrolysis time.

According to the Arrhenius equation,

$$k = A \exp(-E/RT),$$

$$-\ln k = E/RT - \ln A,$$

where A is the apparent pre-exponential factor, sec^{-1} ; R is the universal gas constant, 8.314 KJ/mol; T is the temperature of pyrolysis, K; and E is the apparent activation energy, KJ/mol. The kinetics parameters were determined by the least square method.

Kinetics parameters

The kinetics parameters of FK, MK, HSK and HLK measured by sequential pyrolysis for different hydrocarbons are listed in Table 2. The products generated from HLK was too complex, only the kinetics constants of $<C_7$ and the toluene were listed.

Taking account of the influence of heating rate ($0.5^\circ\text{C}/\text{msec}$), in order to minimize the error of kinetics calculation, the data of conversion percentage smaller than 80% were used.^[5] As an example, the Arrhenius plot of the generation rate for $<C_7$ hydrocarbons at temperature $430\text{-}500^\circ\text{C}$ is shown in Figure 2, 3 and 4.

Significance of kinetics parameters to the kerogen structure and mechanism of pyrolysis

The kinetics parameters of different volatile constituents listed in Table 2 were calculated according to the equation of first order reaction. The high correlation coefficients suggest that the generation of these hydrocarbons are mainly due to the primary decomposition reactions of kerogen, but not the secondary reactions between the primary reaction

products.

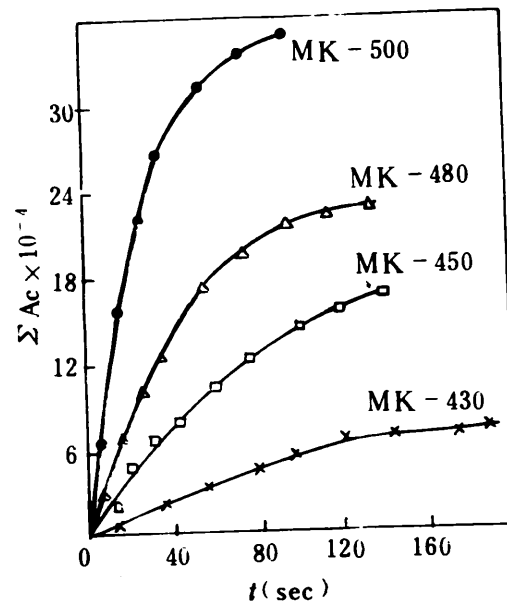


Figure 2.

The plot of integrated peak area of $\langle C_7 \rangle$ hydrocarbons versus retention time under different pyrolysis temperatures (MK)

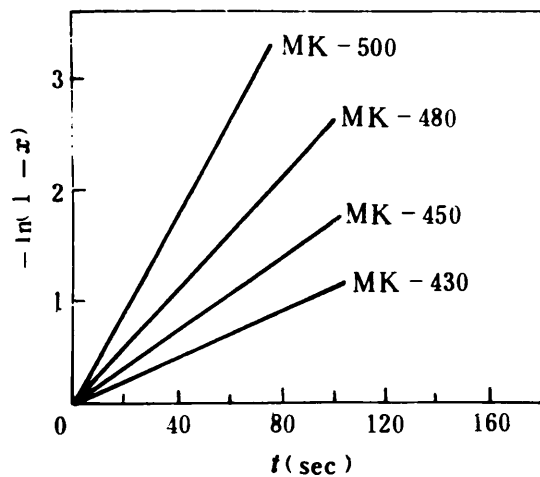


Figure 3.

The plot of $-\ln(1-x)$ of $\langle C_7 \rangle$ hydrocarbons versus retention time under different pyrolysis temperatures (MK)

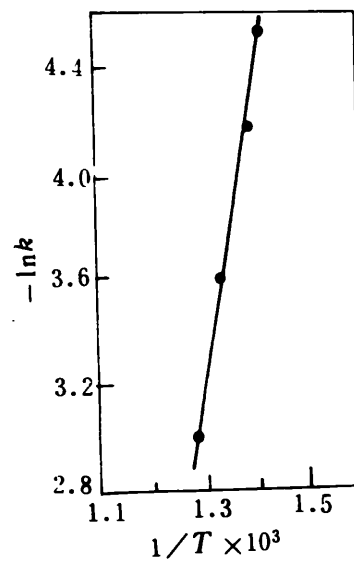


Figure 4.

The relationship between $-\ln k$ and $1/T$ for $\langle C_7 \rangle$ hydrocarbons of MK

Table 2. The hydrocarbon formation kinetics parameters from pyrolysis of oilshale kerogen

Constituent	Apparent activation energy, E(KJ/mol)				Apparent per-exponential factor, A(1/sec)				Correlation coefficient							
	FK	MK	MSK	MLK	FK	MLK	MSK	MLK	FK	MLK	MSK	MLK	FK	MLK	MSK	MLK
<C ₇	107.17	95.47	98.73	57.78	7.59x10 ⁵	1.27x10 ⁵	1.23x10 ⁵	3.92x10 ²	0.981	0.994	0.980	0.989	0.981	0.994	0.980	0.989
$\sum_{i=7} (C_i^0 + C_i^-)$	80.66	72.69	84.46	---	1.63x10 ⁴	4.36x10 ³	1.93x10 ⁴	-----	0.993	0.992	0.988	---	0.993	0.992	0.988	---
$\sum_{i=7} C_i^0$	79.48	70.47	84.02	---	9.66x10 ³	2.93x10 ³	1.78x10 ⁴	-----	0.994	0.991	0.985	---	0.994	0.991	0.985	---
$\sum_{i=7} C_i$	79.46	74.31	85.33	---	1.03x10 ⁴	5.88x10 ³	2.27x10 ⁴	-----	0.991	0.987	0.988	---	0.991	0.987	0.988	---
Toluene	52.08	32.47	51.63	57.43	1.85x10 ²	9.56x10 ⁰	1.38x10 ²	3.20x10 ²	0.987	0.990	0.987	0.998	0.987	0.990	0.987	0.998
C ₉	84.84	50.85	102.56	---	4.82x10 ⁴	1.05x10 ²	3.55x10 ⁵	-----	0.995	0.994	0.985	---	0.995	0.994	0.985	---
C ₁₁	81.29	71.14	100.00	---	1.32x10 ⁴	3.16x10 ³	2.37x10 ⁵	-----	0.991	0.980	0.985	---	0.991	0.980	0.985	---
C ₁₃	80.81	68.80	100.17	---	1.23x10 ⁴	2.17x10 ³	2.49x10 ⁵	-----	0.993	0.991	0.985	---	0.993	0.991	0.985	---
C ₁₆	86.34	69.26	97.15	---	3.12x10 ⁴	2.43x10 ³	1.64x10 ⁵	-----	0.997	0.984	0.987	---	0.997	0.984	0.987	---
C ₁₈	83.30	67.89	96.12	---	1.93x10 ⁴	1.96x10 ³	1.39x10 ⁵	-----	0.996	0.989	0.981	---	0.996	0.989	0.981	---
C ₂₀	89.84	74.81	97.65	---	5.56x10 ⁴	6.46x10 ³	1.89x10 ⁵	-----	0.991	0.970	0.980	---	0.991	0.970	0.980	---
C ₂₂	103.00	85.92	81.64	---	4.97x10 ⁵	3.08x10 ⁴	1.26x10 ⁴	-----	0.995	0.971	0.985	---	0.995	0.971	0.985	---

As shown in Table 2, the kinetics parameters of a same constituent from different types of kerogen may be quite different. In general, the apparent activation energy E and pre-exponential coefficient A of FK and HSK are somewhat higher than that of MK, it means the chemical structure of the later is relatively unstable than the formers.

For these three oil shale kerogens, it is found that the formation of simple aromatic constituents such as toluene has much lower E and A values than the aliphatic monomers, while the light hydrocarbons ($<C_7$) has the higher values of E and A . It implies that these products may be broken down from different structural linkages in the kerogen. For example, the rupture of ether linkaged aromatic structures with weaker bond energies may generates simple aromatics readily; the beta-scission of the alkyl substituents produces the aliphatic monomers; the cracking of normal C-C aliphatic structures having stronger bond energies may be the main reactions of light hydrocarbons formation.

But for the kerogen of type 3, HLK, the E and A values of light hydrocarbons formation are as low as that of simple aromatics, it shows that the kerogen structure of the lignite is different to the oil shale kerogens. In the light of knowledge of coal structure^[6], the methoxyl groups and the methylene linkages between the aromatic structures of one or two rings are the matrix of the gaseous hydrocarbons.

For the pyrolysis reaction of an oil shale kerogen, the kinetics parameters of the formation of a normal alkane and alkene are very similar in magnitude. As an instance, the E of the formation of C_7 alkane from FK is 79,48 KJ/mol, and it is 79,46 KJ/mol for the C_7 alkene. In addition, it yields nearly equal quantities of n-alkane and n-alkene molecules of alpha-1 with the same carbon number. This may be explained by the free radicals mechanism of kerogen pyrolysis. The free radicals generated from the kerogen matrix such as $CH_3(CH_2)_nCH_2CH_2\cdot$ were rearranged to produce $CH_3(CH_2)_nCH=CH_2$ and $CH_3(CH_2)_nCH_2CH_3$, the alkene-1 and alkane of the same molecular ratio.

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