

A STUDY ON THE KINETICS OF KEROGEN PYROLYSIS BY MEANS  
OF PRESURE DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Chemical structures of oil shales kerogens (Type I, II) sampling from Maoming, Fushun and Huangxian, and their artificial thermal-degradation samples (the final degradation temperatures are ranged from 375 to 510°C) have been investigated by means of the Pressure Differential Scanning Calorimetry (PDSC). There are two exothermic peaks in the PDSC spectrum for each kerogen under 1.5 MPa of O<sub>2</sub>. According to the integrated intensity of the peaks, the apparent aromaticity of kerogen may be determined.

A new investigation of the kinetics of kerogen pyrolysis based on the aromatic-aliphatic carbon distribution in the kerogen indicates a simplified model of kerogen pyrolysis. The preliminary results of this study show that there is little contribution in oil and gas formation from the aromatic fraction of the original kerogen; The main part of the aliphatic fraction in the original kerogen is readily converted to oil and gas but a little part of it is to the carbonaceous residue. The kinetic parameters of oil and gas generation and of carbonaceous residue formation from aliphatic fraction are studied.

## INTRODUCTION

Many previous authors have observed that there is a strong correlation between the aliphatic components and the ultimate oil yield in raw oil shales.<sup>[1,2]</sup> It have observed that the aromatic carbon content remains mainly unaffected during pyrolysis to yield a carbon rich solid residue,<sup>[3,4,5]</sup> and a quantitative relationship has been determined by Van Krevelen.<sup>[6]</sup> From the view point of oil and gas generation, Fausett and Miknis<sup>[7]</sup> proposed that only the pyrolysis kinetics of aliphatic fraction has to be studied. They simplified the rate mechanism as two parallel equations by separating kerogen into two components: aliphatic kerogen and aromatic kerogen; and reported the specific rate constant for aliphatic kerogen conversion. The goal of this paper is to study the aromatic and aliphatic carbon distribution during the kerogen pyrolysis, according to its distribution, a new kerogen pyrolysis model is suggested.

## EXPERIMENT

Samples

The oil shale kerogens (Type I, II) used in this study were taken from Maoming, Fushun and Huangxian. Their elemental analysis is listed in Table 1.

Table 1. Elemental analysis of the kerogen samples

Sample	H/C	O/C	Type
Maoming kerogen (MK)	1.38	0.084	II <sub>1</sub>
Fushun kerogen (FK)	1.47	0.078	I <sub>2</sub>
Huangxian kerogen (HK)	1.35	0.130	II

Apparatus

In order to obtain the artificial thermal-degradation samples, the TGD-3000 RH type thermogravimetric analyzer was employed. The apparent aromaticity of the samples was measured by a Du-Pont 910 Pressure Differential Scanning Calorimeter (PDSC).

### Procedure

The final thermal-degradation temperatures of the pyrolysis tests were ranged from 375 to 510°C under the N<sub>2</sub> atmosphere with a heating rate of 10°C/min. As soon as the designated final temperature was reached, the oven was air quenched to lower than 200°C and the residue was taken as the sample of PDSC. In the PDSC tests, the heating rate of 10°C/min, the O<sub>2</sub> pressure of 1.5 MPa and the final temperature of 510°C were used. In general, there are two exothermic peaks in the PDSC spectrum. According to the integrated intensity of the peaks, the apparent aromaticity of sample may be determined.

## RESULTS AND DISCUSSION

### Determination of the apparent aromaticity

W.R.Kube et al.<sup>[89]</sup> have developed a method to determine the aromaticity of lignites and peat by means of PDSC. For the partially retorted Fushun kerogens, according to the integrated intensity of the PDSC peaks as shown in Figure 1; values of the aromaticity were determined. The values of the apparent aromaticity of partially retorted Fushun kerogens determined by PDSC and Solid state C-13 NMR are summarized in Table 2. and Figure 2.

Table 2. Values of the aromaticity of partially retorted Fushun kerogens

Sample No.	Final temperature	Values obtained from NMR method	Values obtained from PDSC method
FK-0	original kerogen	0.24	0.24
FK-400	400°C	0.28	0.33
FK-430	430°C	0.47	0.45
FK-450	450°C	0.65	0.58
FK-480	480°C	0.79	0.71
FK-510	510°C	0.85	0.78

As shown in Figure 2, the values obtained from PDSC spectra look to be comparable to those from NMR method.

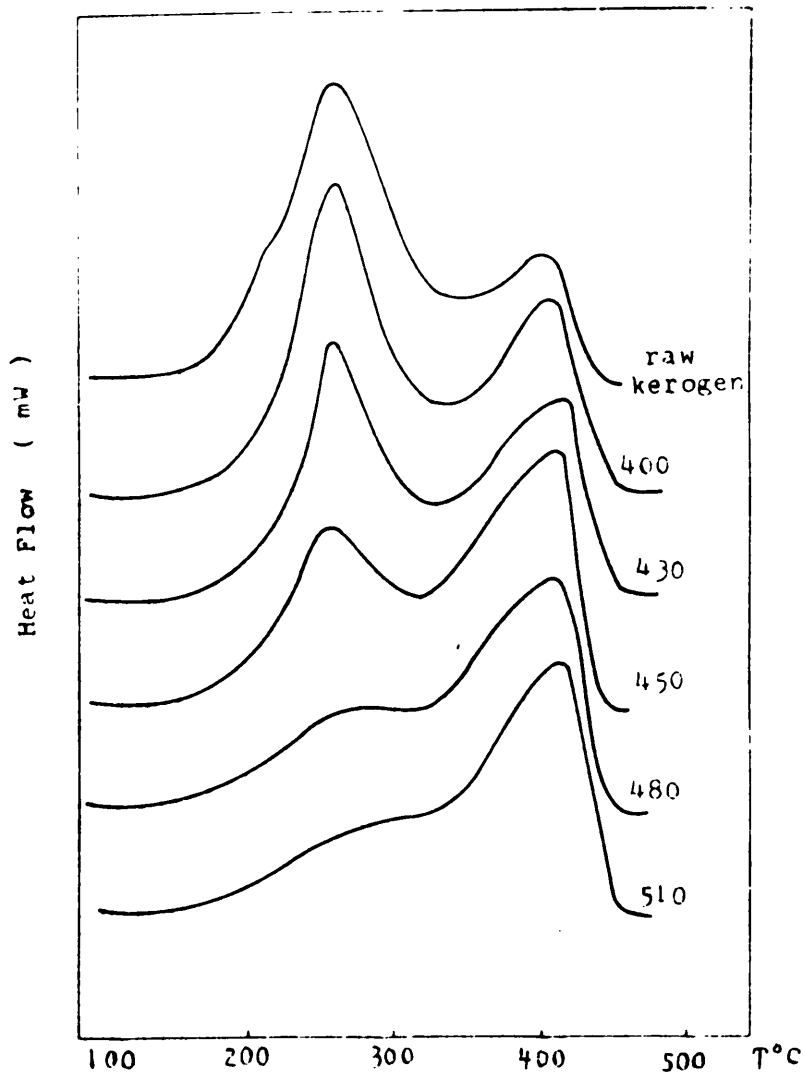


Figure 1. The PDSC spectra of partially retorted Fushun kerogen samples

### Kinetic model

The idea to be exploited for a simplified kinetic scheme of kerogen pyrolysis is that the aromatic carbon fraction remains relatively stable during retorting. It means that the main part of the carbon in the residue is accountable directly from the starting aromatic carbon without the requirement of a kinetic step for its formation. The additional carbon in the residue is produced by the coking reaction of aliphatic carbon. But the main part of the aliphatic carbon fraction in kerogen is readily converted to oil and gas. Therefore, it needs to account the disappearance of aliphatic carbon only in order to measure the pyrolysis yields. The simplified kinetic scheme of kerogen pyrolysis is shown as Figure 3.

The simplified kinetic scheme of kerogen pyrolysis is showing as follows:

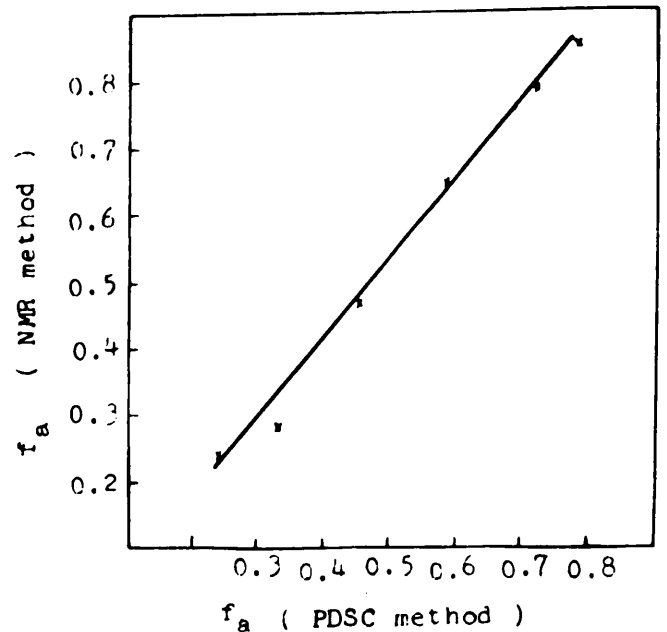


Figure 2. A comparison of the aromaticity values obtained from NMR and PDSC METHOD

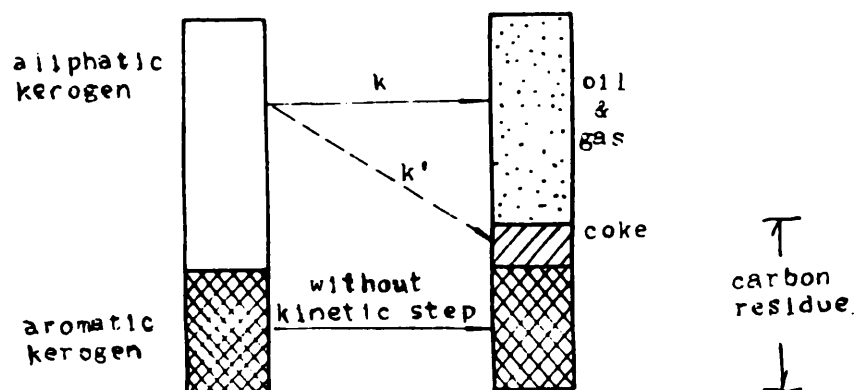


Figure 3. The simplified kinetic scheme of kerogen pyrolysis

### Kinetic parameters

PDSC spectra of the partially retorted Maoming and Huangxian oil shale kerogens are shown in Figure 4 and Figure 5 respectively.

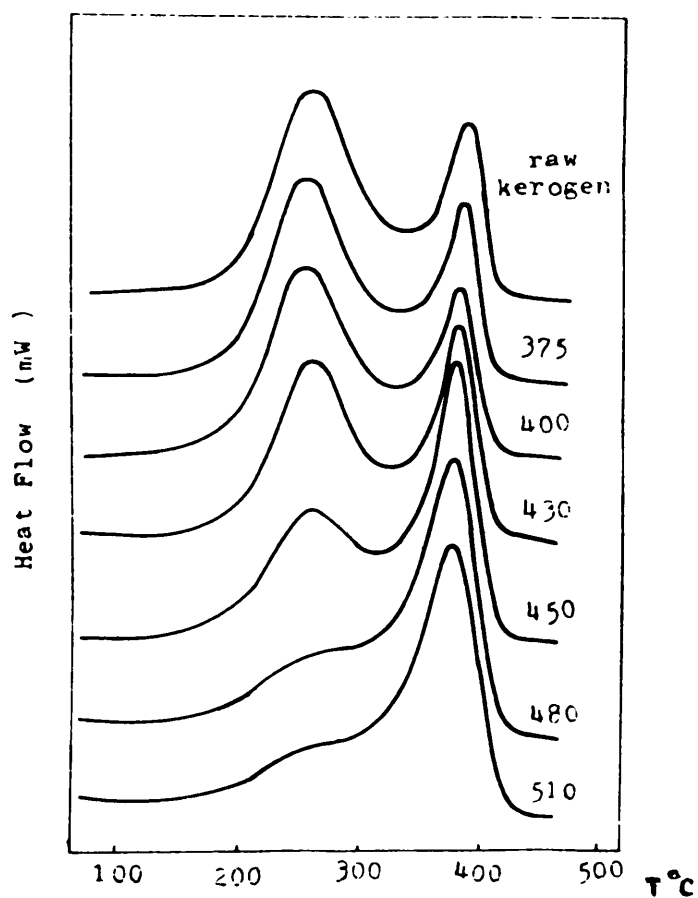


Figure 4. PDSC spectra of the partially retorted Maoming oil shale kerogen

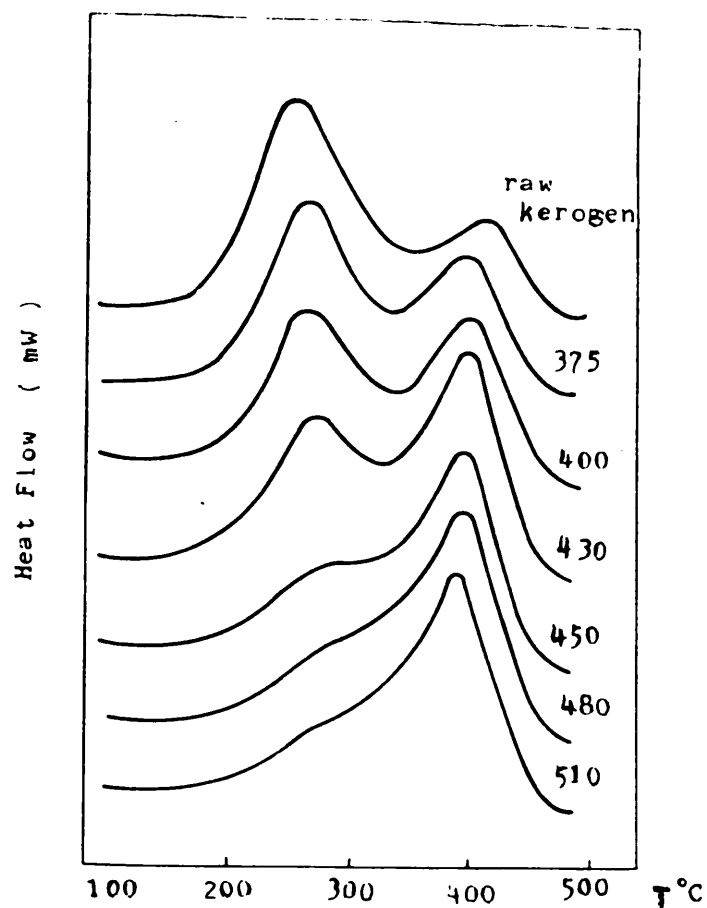


Figure 5. PDSC spectra of the partially retorted Huangxian oil shale kerogens

The experimental data for Maoming and Huangxian kerogen are summarized in Table 3 and Table 4, respectively.

As shown in Table 3 and Table 4, the amount of aromatic carbon in the kerogen is increasing while the aliphatic carbon is decreasing during the process of retorting. The additional aromatic carbon is due to the conversion of aliphatic carbon.

The integral method was employed to get the kinetic parameters. The intrinsic kinetic equations can be written as:<sup>[10]</sup>

When  $n=1$

$$-\ln(1-X) = \frac{A}{a} - \frac{RT^2}{E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right)$$

Where  $X$  -- the conversional fraction of the aliphatic carbon

$n$  -- order of reaction

$a$  -- heating rate

$T$  -- temperature

$T$  -- the value of  $T$  at  $X=0.5$

$E$  -- apparent activation energy

$A$  -- preexponential factor

Table 3. Summary of experimental data of Maoming kerogens

	partially retorted kerogen samples						
	MK-0	MK-375	MK-400	MK-430	MK-450	MK-480	MK-510
final pyrolysis temperature (°C)		375	400	430	450	480	510
sample weight $W$ (mg)		6	12	13.4	17.2	19.1	19.0
residue weight $W'$ (mg)		5.45	10.1	9.9	10.2	8.8	8.2
organic carbon content (%)	69.75	71.44	73.05	73.14	72.02	68.72	67.69
apparent aromaticity $f_a$	0.24	0.297	0.325	0.412	0.555	0.723	0.796
unconverted							
aliphatic carbon, based on 100g organic carbon (g)	76.0	65.41	59.50	45.55	27.25	12.57	8.65
aromatic carbon (g)	24.0	27.63	28.65	31.91	33.98	32.82	33.33
aliphatic carbon converted to oil & gas	0	6.96	11.85	22.54	38.77	54.61	58.11

aliphatic carbon converted to coke (g)      0      3.63      4.65      7.91      9.98      8.82      9.33

A straight-line of  $-\ln\left(\frac{-\ln(1-X)}{T^2}\right)$  vs.  $\frac{1}{T}$  will give birth to the apparent activation energy E and the preexponential factor A values.

Table 4. Summary of experimental data of Huangxian kerogens

	partially retorted kerogen samples						
	HK-0	HK-375	HK-400	HK-430	HK-450	HK-480	HK-510
final pyrolysis temperature °C	----	375	400	430	450	480	510
sample weight W(mg)		21.0	22.0	22.0	22.7	22.1	22.3
residue weight W'(mg)		17.6	16.7	14.2	12.7	11.8	10.7
organic carbon content (%)	68.99	72.39	73.91	73.50	73.91	72.15	72.16
apparent aromaticity $f_a$	0.29	0.391	0.449	0.580	0.748	0.802	0.843
unconverted aliphatic carbon, based on 100g organic carbon (g)	71.00	53.56	44.81	28.88	15.10	11.08	7.88
aromatic carbon (g)	29.00	34.39	36.51	39.88	44.83	44.77	42.31
aliphatic carbon converted to oil & gas (g)	0	12.05	18.68	31.24	40.07	44.15	49.81
aliphatic carbon converted to coke (g)	0	5.39	7.51	10.88	15.83	15.77	13.31

Figure 6. presents the plot of  $-\ln\left[-\frac{\ln(1-X)}{T^2}\right]$  versus  $\frac{1}{T}$ , in which the aliphatic fraction of Maoming kerogen was converted to oil & gas. The overall values of E and A obtained from the straight line are 79.655 KJ/mol and  $6.99 \times 10^4 \text{ min}^{-1}$  respectively.

Figure 7 presents the plot of  $-\ln\left[\frac{-\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$ , in which the aliphatic fraction of Maoming kerogen was converted to carbon residue. The overall values of E and A obtained from the straight line are 6.897 KJ/mol and  $3.69 \times 10 \text{ min}^{-1}$  respectively.

The plots of  $-\ln\left[\frac{\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$  which the aliphatic fraction of Huangxian kerogen was converted to oil & gas and to carbon residue are

shown in Figure 8 and Figure 9 respectively. The corresponding overall Values of E and A obtained are 48.018 KJ/mol, 47.36 KJ/mol and  $2.87 \cdot 10^2 \text{ min}^{-1}$ ,  $8.96 \cdot 10 \text{ min}^{-1}$  respectively.

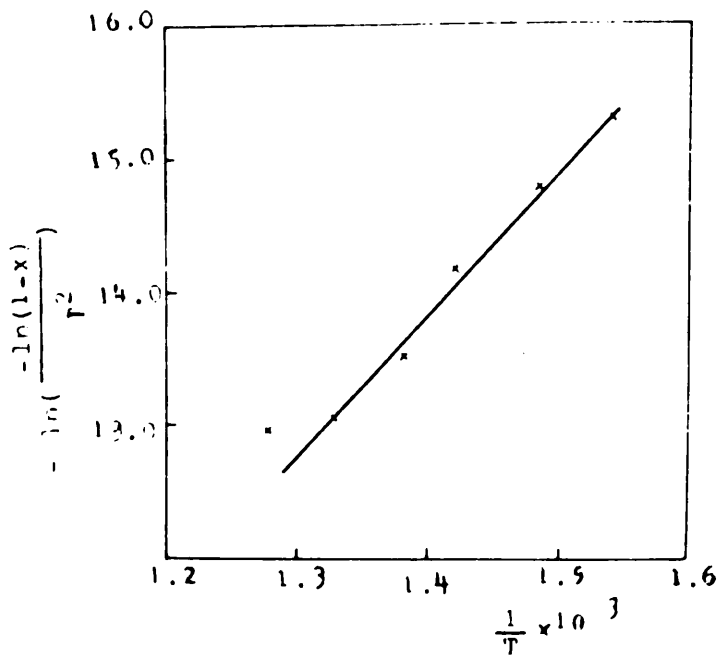


Figure 6. The plot of  $-\ln\left[-\frac{\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$ , in which the aliphatic fraction of Maoming kerogen is converted to oil & gas

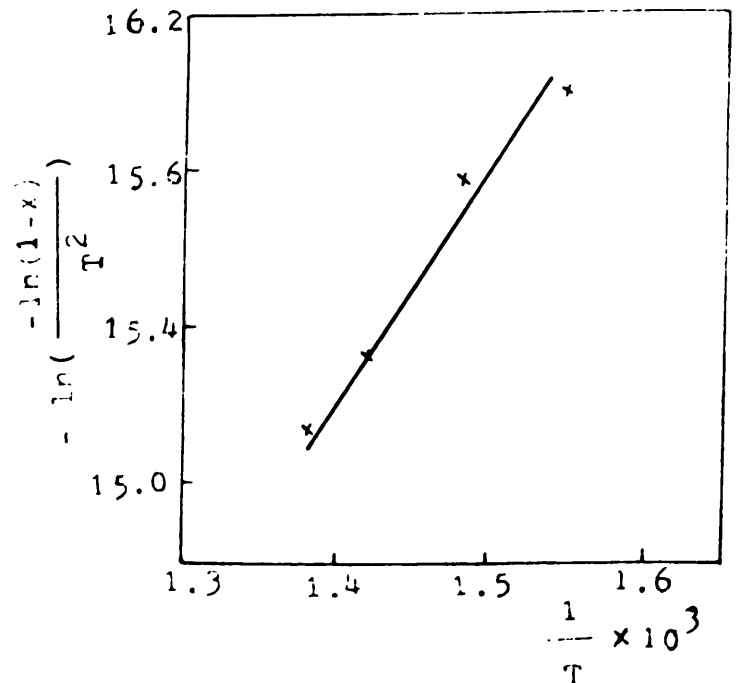


Figure 7. The plot of  $-\ln\left[-\frac{\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$ , in which the aliphatic fraction of Maoming Kerogen is converted to carbon residue

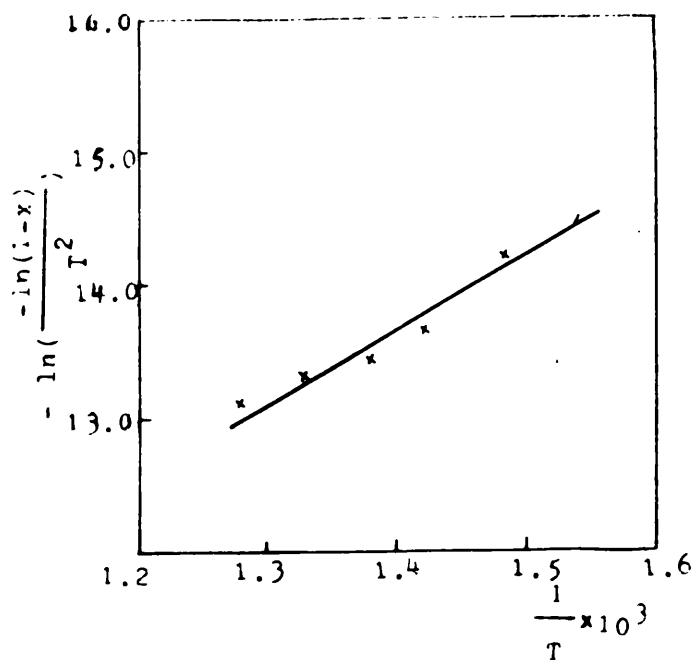


Figure 8. The plot of  $-\ln\left[-\frac{\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$ , in which the aliphatic fraction of Huangxian kerogen is converted to oil & gas.

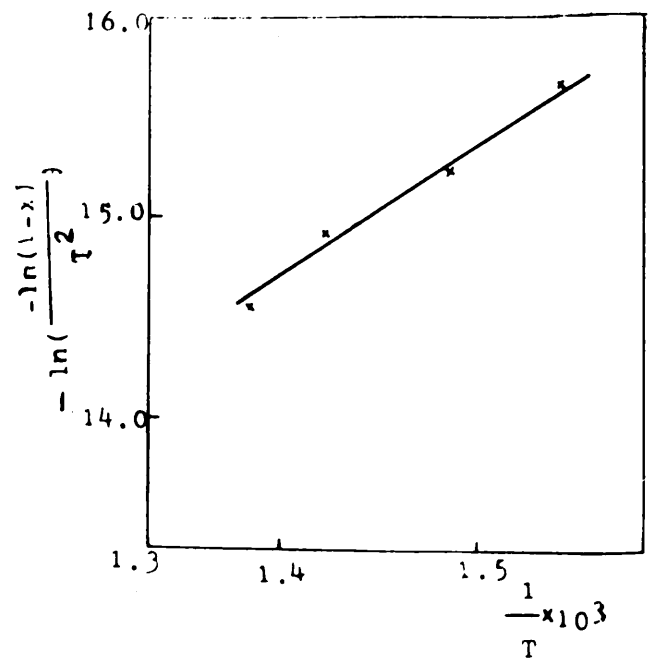


Figure 9. The plot of  $-\ln\left[-\frac{\ln(1-X)}{T^2}\right]$  vs.  $\frac{1}{T}$ , in which the aliphatic fraction of Huangxian kerogen is converted to carbon residue.



The kinetic equations of the aliphatic fraction of Maoming and Huangxian kerogen pyrolysis are shown in Table 5.

Table 5. The kinetic equations for the pyrolysis of aliphatic fraction of kerogen

<u>sample</u>	<u>k (min<sup>-1</sup>)</u>	<u>k' (min<sup>-1</sup>)</u>
Maoming	$6.99 \times 10^4 \exp \left( - \frac{79.655}{RT} \right)$	$3.69 \times 10 \exp \left( - \frac{45.376}{RT} \right)$
Huangxian	$2.87 \times 10^2 \exp \left( - \frac{48.02}{RT} \right)$	$8.96 \times 10 \exp \left( - \frac{47.36}{RT} \right)$

The characteristics of the proposed kinetic model are:

1. Molecular structural parameters of kerogen are incorporated into the model. It may be available to indicate the pyrolytic character for different types of kerogen.

2. Only the pyrolysis kinetics of aliphatic fraction of kerogen has to be studied. It is convenient to estimate the oil and gas yield for kerogen pyrolysis.

3. It may be available as a general pyrolysis scheme for fossil fuels and source rocks as well.

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