A STUDY OF THE THERMAL PROPERTIES OF CHINESE OIL SHALES

1. the measurements of the heat of pyrolytic reaction and the specific heats of oil shale, char and burned shale.

Tingfen Wang   Shaoxin Lu
Beijing Graduate School of East-China Petroleum Institute
P.O. Box 902, (URIACCE-SINOPEC),
Beijing, P.R.China.

ABSTRACT

The study of properties of oil shale is of primary importance, since the process of converting the organic matter in oil shale into a liquid product is accomplished readily by application of heat. A differential scanning calorimeter (DSC) has been used in this study. The heats of pyrolytic reaction and the specific heats of Chinese oil shales have been determined. The results show that the heats of pyrolytic reaction of oil shales obtained from the same place are increased with the oil shale grade. The relationships between H (the heat of pyrolytic reaction) and X% (Fischer Assay oil yield) for Fushun oil Shale and Maoming oil shale have been obtained. The specific heats of six Chinses oil shales, four chars and two spent shales are presented in this paper. In either case, the specific heat results tend to increase with increase in temperature.

INTRODUCTION

Thermal properties are of primary importance in the study of oil hales processing. Since the process of converting organic matter in the oil shale into a liquid product is accomplished most readily by the application of heat. A knowledge of the thermal behavior of oil shales is therefore relevant to the design and optimization of recovery procedures.

In order to know the over-all heat requirements for retorting oil shale, we have to measure the heat of pyrolytic reaction of oil shale and the specific heat of oil shale.

D.B.Jones et al. have reported that the C_p values of Green River oil shale (28 L/t) and Kentucky shale (52 L/t) are in the range 0.2 - 0.3 cal g^{-1} $^{o}C^{-1}$, 0.23 - 0.32 cal g^{-1} $^{o}C^{-1}$ for temperatures ranging from 100 to 300 ^{o}C, respectively. K. Rajeshwar et al. have reported that the specific heats of Devonian shales are in the range 0.2 - 0.3 cal g^{-1} $^{o}C^{-1}$, and increase with increasing temperature.(1-4) But unfortunately the literature has been found to have not such data of Chinese oil shales.(5) Thus, it is necessary to work on these data for developing Chinese oil shale industry.

The research carried out in this field includes the heats of pyrolytic reaction of Fushun, Maoming and Huadian oil shales, the specific heats of Fushun, Maoming oil shales, as well as shale char and burned shale.

EXPERIMENT

1. Calibration and running experiments

A differential scanning calorimeter (model CDR-1 made in China) was used in the study. In DSC the differential power required to maintain this "null balance" condition is given by the distance written by the recorder-pen from the base line. This is read out directly in millicalories per second. The area under thermogram peak gives the heat of the transition directly in calories.

High purity nitrogen (99.999%) whose flow rate is 30 ml/min was used as the sweep gas throughout the experiment for the determination of the heats of pyrolytic reaction of oil shales. The experimenting conditions are given as follows:

Heat rate	10 C/min
Paper rate	5 mm/min
DSC measure rang	± 5 mcal/sec
Reference material	burned shale
Sample	about 5 mg (- 200 mesh)

The heats of pyrolytic reaction of oil shales can be obtained from the formula:

$$H = \frac{K \cdot A \cdot R}{W \cdot S \cdot b} \quad mcal/mg \qquad (1)$$

where: K = Apparatus constant

A = DSC curve area	mm^2
W = Sample weight	mg
S = Paper rate	mm/sec
b = Paper width	mm
R = DSC measure rang	mcal/sec

The apparatus constant K is given from

$$K = \frac{H_{stan} \cdot W \cdot S \cdot b}{A \cdot R} \qquad (2)$$

or

$$K_o = \frac{K \cdot R}{S \cdot b} = \frac{H_{stan} \cdot W}{A} \qquad (3)$$

where, H_{stan} = The enthalpy of standard materials mcal/mg.

The Zn (99.999%) and Na_2WO_4 were used as standard materials to get the apparatus constant K.

In order to measure the specific heats of oil shales, a sample of known specific heat, synthetic sapphire, was used to calibrate the ordinate displacement of the Model CDR-1. The baseline can be adjusted by running weighted empty sample pans in the sample and reference holder and making appropriate electronic adjustments. Typical experimental data are given in Figure 1. At the temperature of interest the specific heats of the sample, therefore, are obtained by applying to the formula:

$$C_{p,sam} = \frac{W_{saph}}{W_{sam}} \cdot \frac{D_{sam}}{D_{saph}} \cdot C_{p,saph} \qquad (4)$$

where, $C_{p,sam}$=Specfic heat of sample

$C_{p,saph}$=Specific heat of sapphire

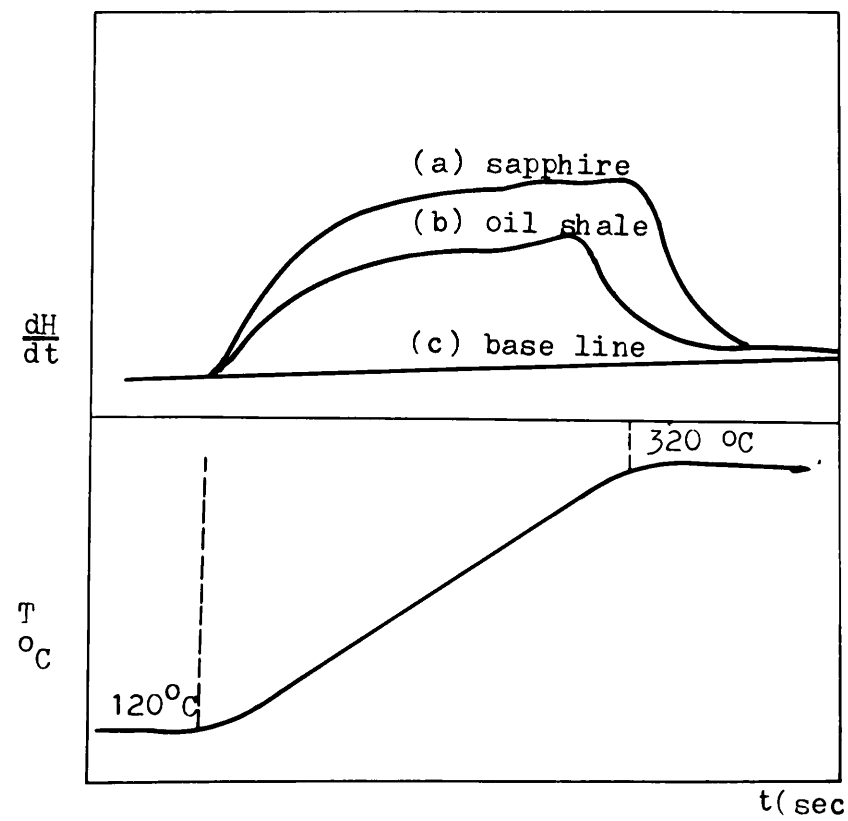

Figure 1. Typical DSC curves of sapphire standard and oil shale

W_{sam} = Weight of sample
W_{saph} = Weight of sapphire
D_{sam} = Sample ordinate displacement
D_{saph} = Sapphire ordinate displacement

2. Sample preparation

The oil shales used were obtained from Fushun, Maoming and Huadian oil shales of different grades (oil yield in x% (wt)) which were confirmed by the standard Fischer Assay. The raw shales were finely grounded to -200 mesh. The shale char was obtained by Fischer retorting and the sample of burned shale was prepared by combustion of the raw shale in air in the Muffle furnace at 800 °C for 2 hours.

RESULTS and DISCUSSION

1. Effect of the oil shale grade on the heat of pyrolysis reaction.

Three different grades Fushun oil shales, three different grades Maoming oil shales and a high grade Huadian oil shale were used in this study. The experiment data are shown in Table 1.

Table 1. The heats of pyrolytic reaction of oil shales

place	sample No.	Fischer Assay oil yield x% (wt)	heat of pyrolysis reaction H (kcal/kg)
Fushun	F 821	5.9	69.08
	F 832	6.8	71.13
	F 812	9.8	78.37
Maoming	M 821	7.7	43.37
	M 811	8.8	54.09
	M-II	13.13	77.83
Huadian	HD 831	19.17	32.79

It can be seen from Table 1. that:

(1) The heats of pyrolytic reaction of oil shales obtaned from the same place are increased with the oil shale grade (i.e. Fischer assay oil yield). Their relationships are shown in Figure 2.

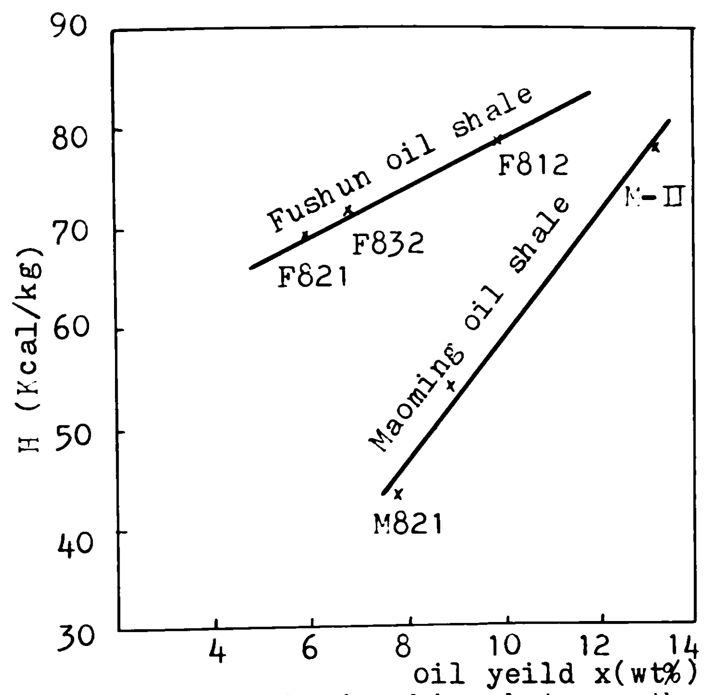

Figure 2. The relationships between the heats of pyrolysis reaction and oil shale grade for Fushun and Maoming oil shale

There is a straight line relationship for Fushun and Maoming oil shale. This result is nearly the same as that of Stanfield(6). The correlation equations are as follows:

for Fushun oil shale:

$$H=2.39x+54.94 \text{ (kcal/kg)} \quad (5)$$

$$(r = 0.9999)$$

for Maoming oil shale:

$$H=6.10x-1.84 \text{ (kcal/kg)} \quad (6)$$

$$(r = 0.9933)$$

where: H=the heat of pyrolysis of oil shale
x=oil shale grade (Fischer assay oil yield (wt)%)

(2). Among Fushun, Maoming and Huadian oil shales there is no relationship between the heat of pyrolysis and oil-shale grade. For example, the heat of pyrolysis for the high grade Huadian oil shale (oil yield 19.6%) is only 32.8 kcal/kg while that of Fushun oil shale (oil yield 5.9%) is 69.8 kcal/kg, and Maoming oil shale (oil yield 7.7%) 43.37 kcal/kg. The reason is probably

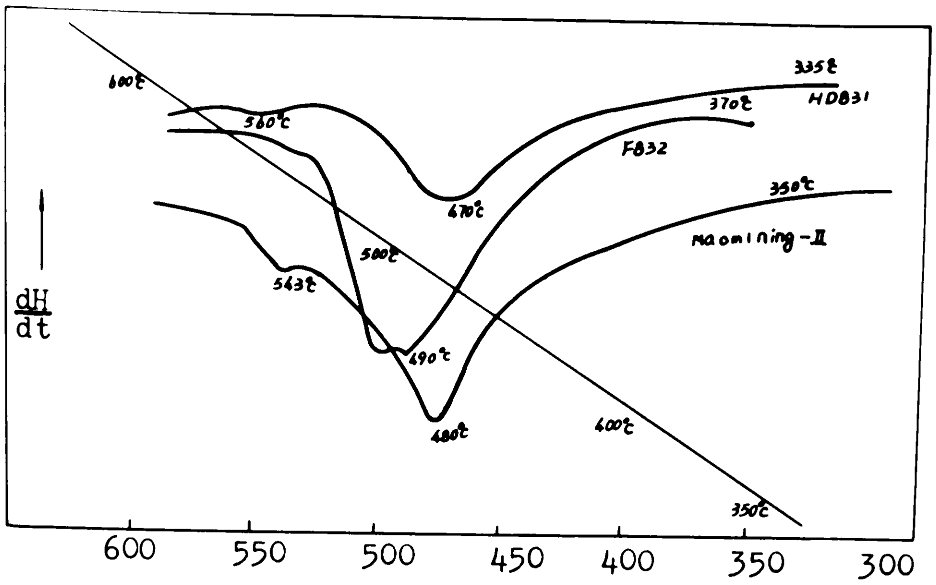

Figure 3. DSC curves for Fushun, Macming and HD oil shale.

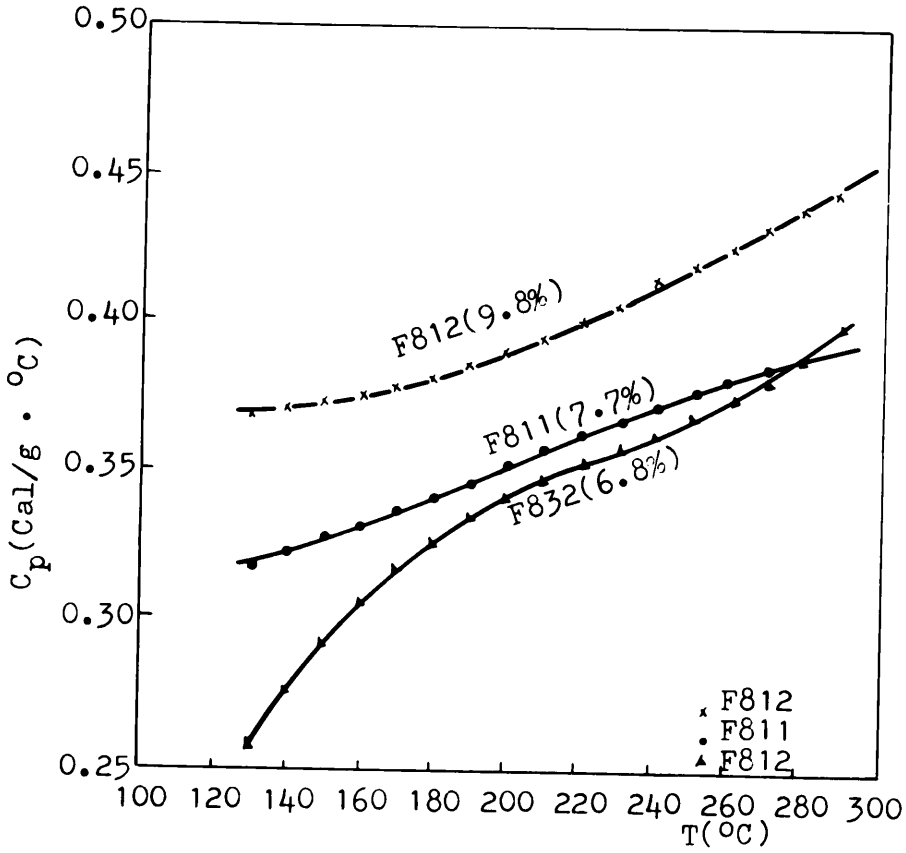

Figure 4. The specific heats of Fushun oil shales

that the kerogen structure in Fushun, Maoming and Huadian oil shales is not the same. It can be seen from Figure 3. that the initial pyrolytic temperature for Huadian oil shale was about 350 °C. It is lower than that of Fushun oil shale (360°C-380 °C), and the final pyrolytic temperature for Huadian oil shale is lower than that of Fushun oil shale too. It is evident that Huadian oil shale is easier to be pyrolyzed.

2. Comparison of the specific heats of kerogen oil shale, shale char and burned shale.

Figure 4 and Figure 5 show that the variation of specific heat (C_p) with temperature for Fushun, Maoming and Huangxian oil shale. The shale grade is shown as the parameter. Data are presented for shales with Fischer assay oil yield ranging from 6.8% to 17.7%.

It can be seen from Figure 4 and Figure 5 that the specific heats of oil shales in temperature ranging from 373 k to 573 k increase with the Fischer assay oil yield. A possible reason for this behavior is that the specific heat of kerogen in oil shale is larger than that of the minerals of the oil shale. Figure 6 tells us that the specific heats of kerogen

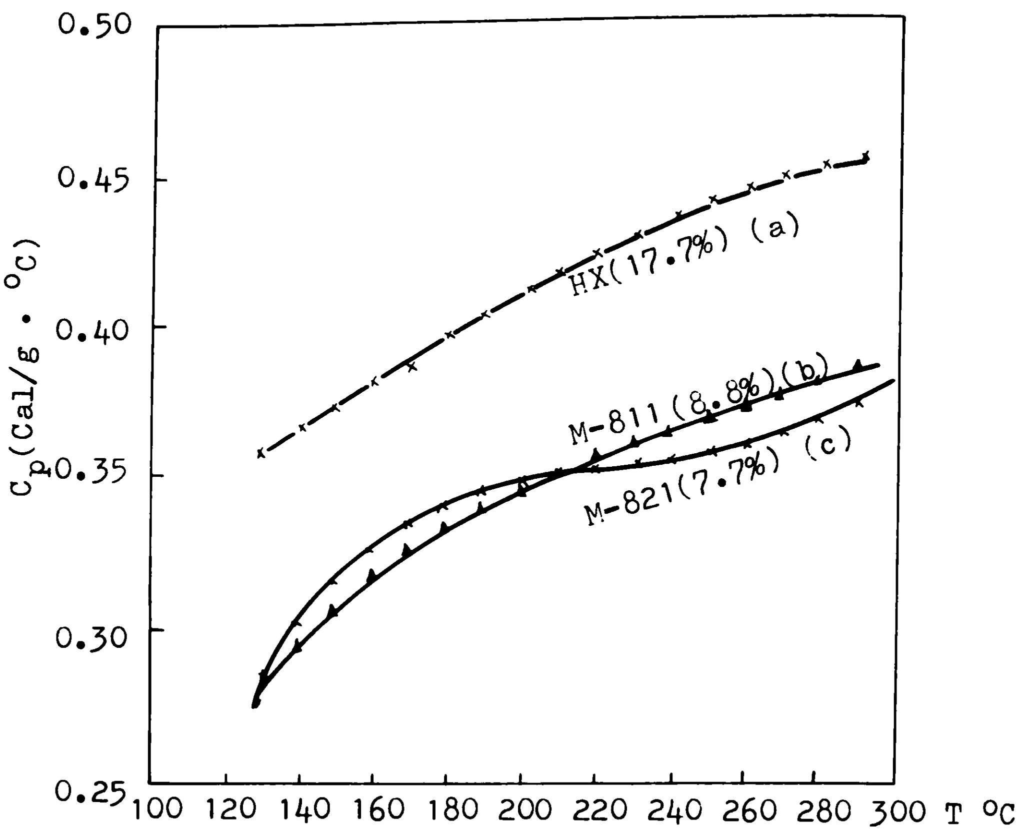

Figure 5. The specific heats of Maoming and HX oil shales

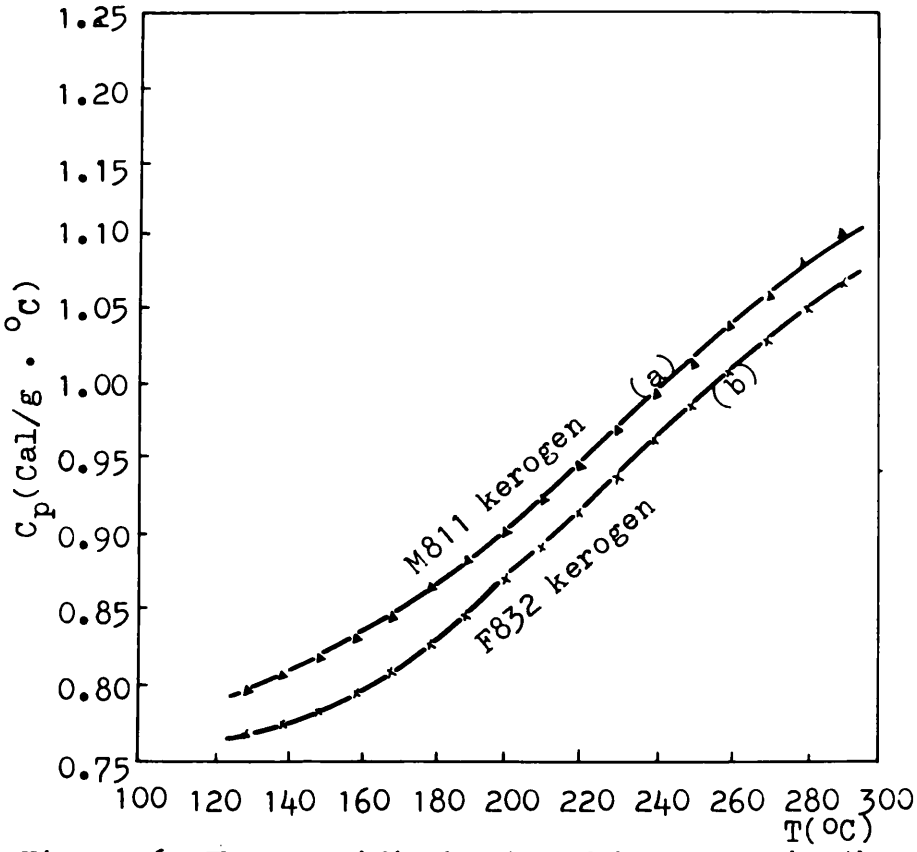

Figure 6. The specific heats of kerogens in the Fushun and Maoming oil shales.

in Fushun and Maoming are much larger than those of Fushun and Maoming oil shales. The specific heat of kerogen is nearly 0.8 - 1.0 cal/°Cg, while the heats of Fushun and Maoming oil shales are nearly 0.25 - 0.4 cal/°C g.

Standard linear regression techniques were used to develop, from the experimental data, predicative equations relating C_p values to temperature (T). The obtained equations are as follows:

$$C_p=a_1 + b_1T + c_1T^2 + d_1T^3 + e_1T^4 + f_1T^5 \qquad (373k \quad T \quad 573k) \qquad (7)$$

Table 2. Values of coefficients in Eq.7 for raw shales and kerogen

sample	Fischer assay oil yield (wt%)	a_1	b_1	$c_1 \cdot 10^5$	$d_1 \cdot 10^8$	$e_1 \cdot 10^{10}$	$f_1 \cdot 10^{13}$
F - 832	6.8	-5.552	0.027	-1.360	-1.060	1.870	-0.860
F - 811	7.7	0.360	-0.00104	0.3247	-0.2296	0	0
F - 812	9.8	-4.594	0.033	-5.466	-7.189	2.780	-2.014
M - 821	7.7	-8.970	0.049	-4.385	-16.40	3.651	-2.060
M - 811	8.8	2.146	$-8.199 \cdot 10^{-3}$	0.147	3.812	-0.516	0.147
Huang-xian	17.7	0.585	$-3.087 \cdot 10^{-3}$	0.923	-0.737	0	0
M - 811 Kerogen		5.508	-0.0309	6.464	-4.192	0	0
F - 832 Kerogen		8.967	-0.0528	11.010	-7.313	0	0

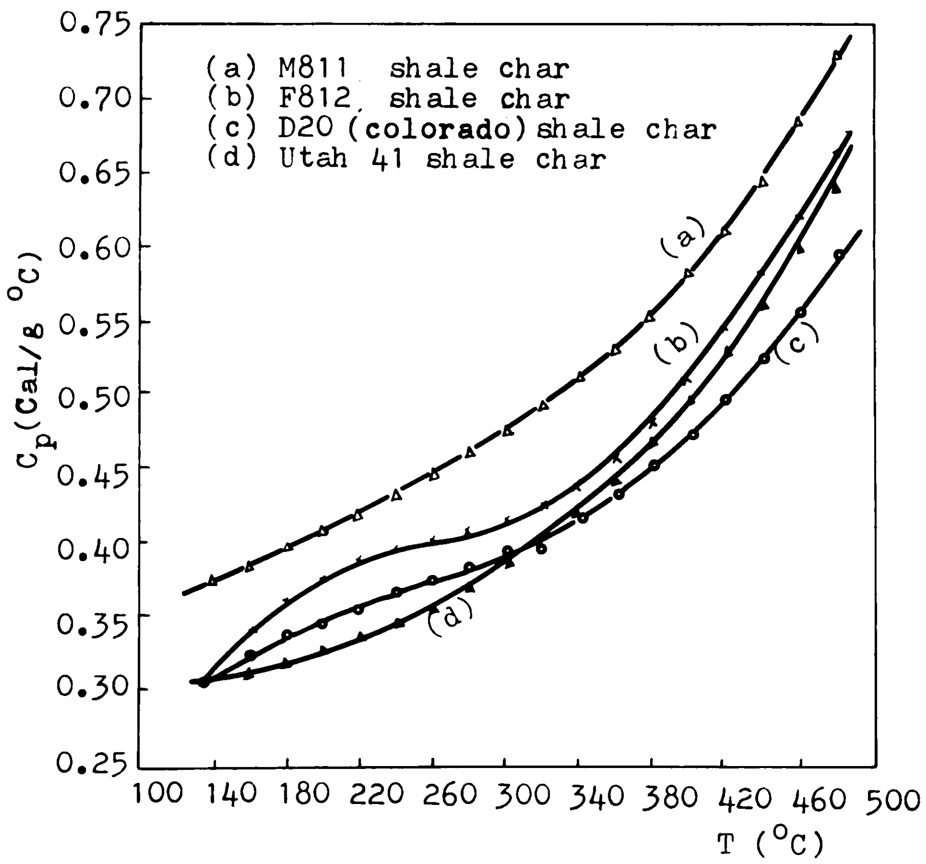

Figure 7. The specific heat of shale char

where: a, b, c, d, e, and f are empirical constants. The values of these constants are listed in Table 2.

Figure 7 shows the specific heat varying with the temperature for shale char samples of different levels of organic carbon content. The temperature variation of C_p for shale char can be described by a third-order equation:

$$C_p = a_2 + b_2T + c_2T^2 + d_2T^3 \qquad (8)$$

$$(373\ ^oK \quad T \quad 573\ ^oK)$$

Values of coefficients in the above equation are listed in Table 3.

Table 3. Values of coefficients in Eq. 8 for shale char

Shale char	organic carbon content (wt%)	a_2	$b_2 \cdot 10^3$	$c_2 \cdot 10^6$	$d_2 \cdot 10^7$
M-811C	8.51	-0.819	6.472	-12.070	8.243
F-812C	7.06	-3.303	19.790	-35.770	21.960
Utah-41C	5.02	-0.879	6.836	-13.580	9.635
D-20C	2.26	0.075	0.994	- 1.953	2.020

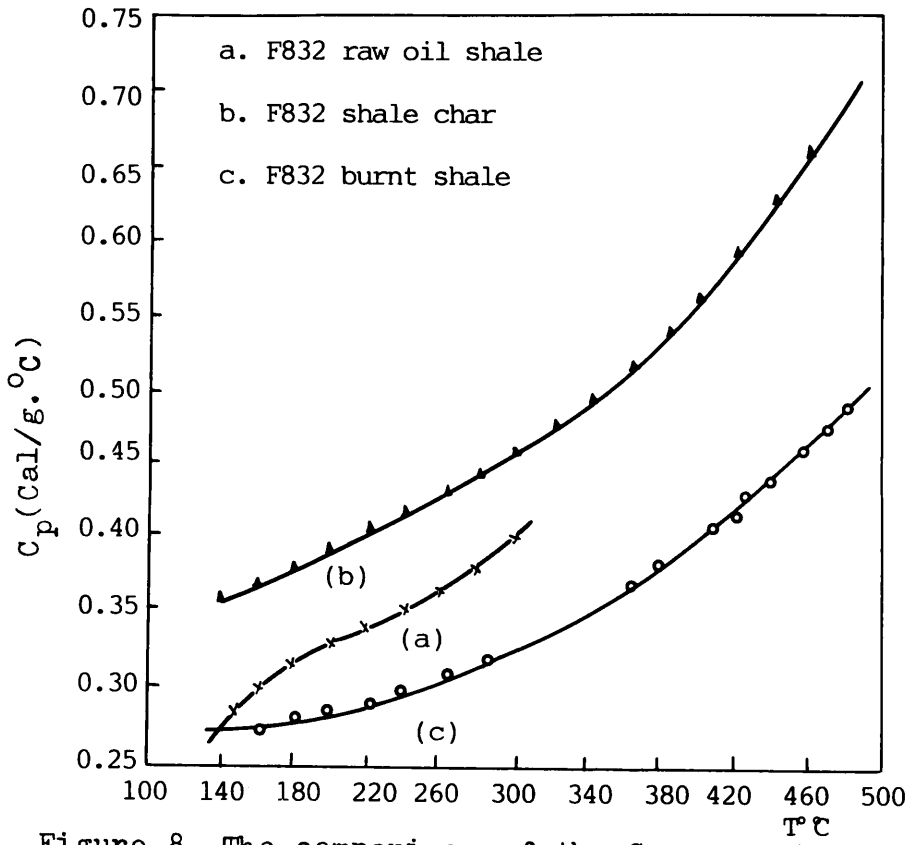

Figure 8. The comparison of the C_p vs. T behavior for the Fushun oil shale, char and burnt shale

Figure 8 shows a comparison of the C_p vs. T behavior for the Fushun oil shale (F-832), char and burnt shale, while Figure 9 shows that of the Maoming oil shale (M-811), char and burnt shale. It can be seen from Figure 8 and 9 that the specific heat of shale char is larger than that of raw shale. The temperature depending on C_p for the burnt shale is also described by a third-order equation.

$$C_p=a_3+b_3T+c_3T^2+d_3T^3 \qquad (9)$$

$$(373\ ^{o}K \quad T \quad 773\ ^{o}K)$$

Values of the coefficients in Eq.(9) for Fushun and Maoming burnt shale are shown in Table 4.

3. Effect of the final retorting temperature on the specific heat of shale char.

In order to understand the effect of

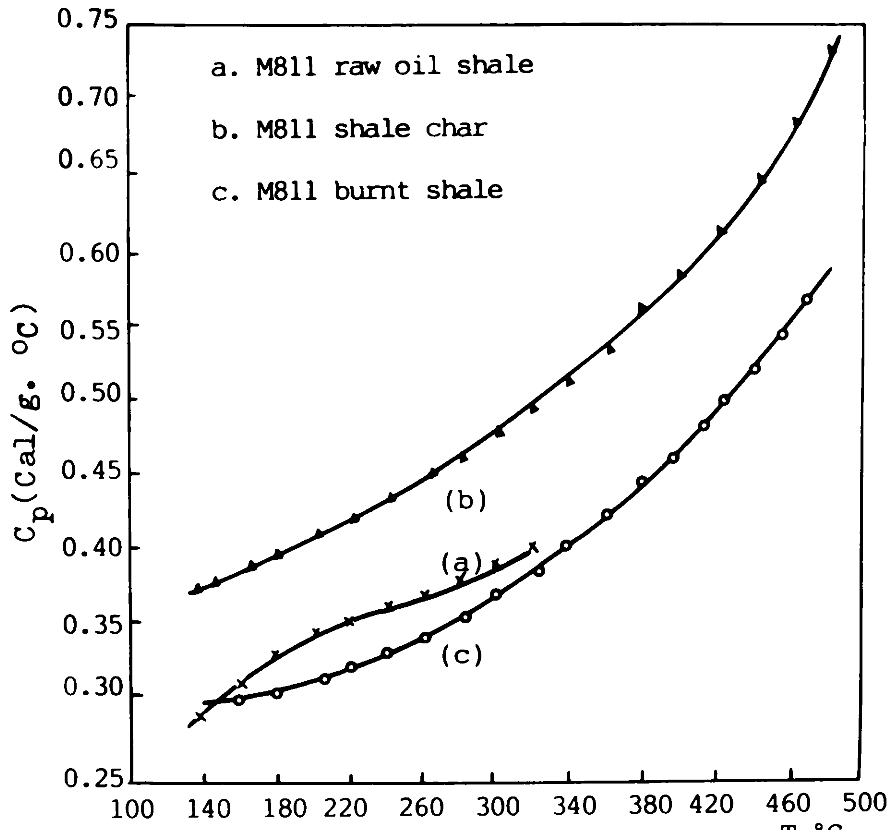

Figure 9. The comparison of the C_p vs. T behavior for Maoming oil shale, char and burnt shale.

Table 4. Values of coefficients in Eq.(9) for Fushun and Maoming burnt shale

burnt shale	initial Fischer Assay oil yield of raw shale (wt%)	a_3	$c_3\ 10^6$	$b_3\ 10^4$	$d_3\ 10^9$
F-832	6.8	0.239	2.518	-1.04	1.508
M-811	8.8	-0.0238	17.95	-3.864	3.398

the final retorting temperature on the specific heat of shale char, four shale char obtained from the Fischer ratort with different final retorting temperatures 380 °C, 430 °C, 470 °C, 530 °C were used in this study. Figure 10 shows the specific heat varying with the temperature for Fushun shale char, the final retorting temperature being used as the parameter. It can be seen from Figure 10 that all the specific heat of Fushun shale char is higher than that of Fushun raw shale.

Acknowledgment:

The authors are grateful to Prof. Qian Jialin for enthusiastic help in the experiments reported here. Thanks are due to Ms. Wang Jianqiu who has participated in part of the present work.

LITERATURE CITED

1. H.W.Sohn, et al., Ind. Eng. Chem. 1951, 43, 31.
2. D.B.Jones, K.Rajeshwar and J.B.Dubow, Ind. Eng. Chem. Pro. Des. Dev. 1980, 19, 125.
3. K. Rajeshwar, D.B.Jones and J.B.Dubow, Fuel, 1982, 61, 237.
4. K. Rajeshwar, and J.B.Dubow, Fuel, 1980, 59, 790.
5. "Chinese Oil Shale Industry" Petroleum Industry Press, 1984.

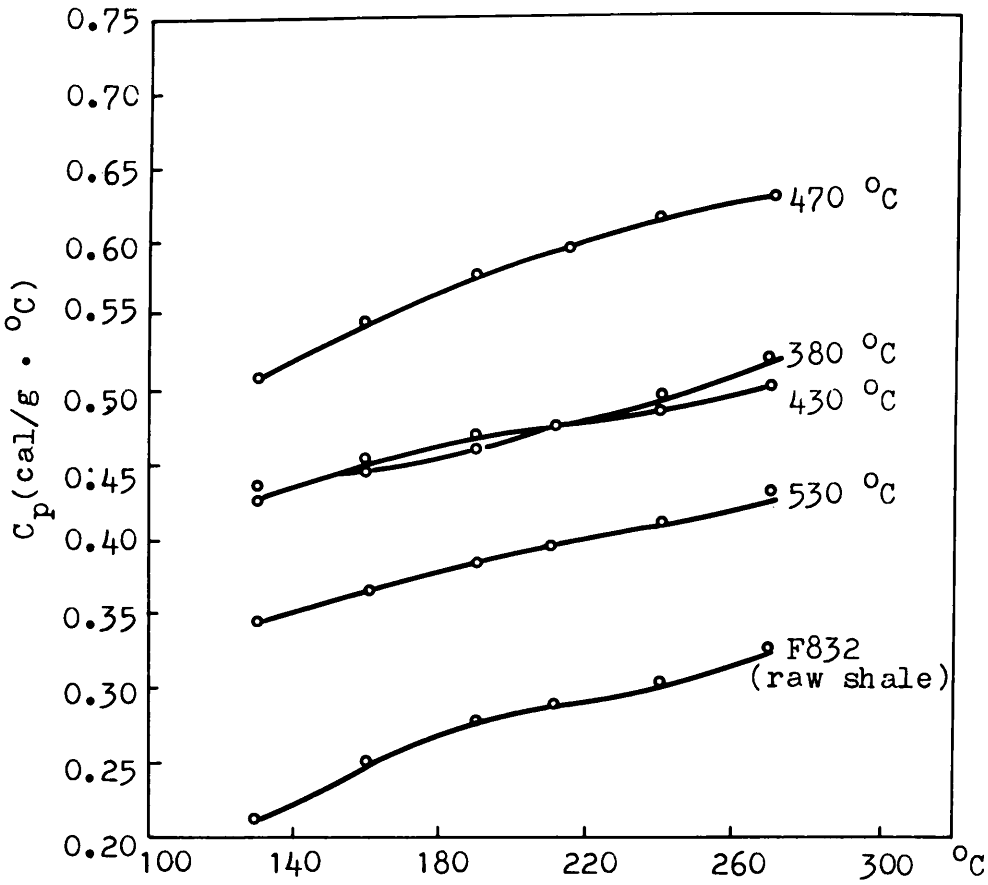

Figure 10. The specific heats of shale char which were obtained from Fischer assay at different retorting temperature

6. K.E.Stanfield, I.C.Frast, W.S.Meautey, H.N.Smith, U.S.B.M. Report of Invest, 1951, p.4825.