

## SUPERCRITICAL EXTRACTION OF CHINESE OIL SHALES

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### ABSTRACT

On a semi-continuous installation, eight Chinese oil shales were extracted in nonisothermal experiments with toluene. The relationship between the conversion degree and extract yield in process and volatile matter content and kerogen content of oil shale used was obtained. On the basis of experiments, kinetic treatment of extraction process was made and the relationship between kinetic parameters and volatile matter and kerogen content of oil shale used was also obtained.

### 1. INTRODUCTION

The reserves of oil shale in China are abundant. A great variety of oil shale is widely dispersed over the country. Some oil shales are the overburden of coal, e.g. Fushun and Maoming oil shale, and some are intergrowth of coal, e.g. Huangxian oil shale. As the coal being mined, the oil shale is mined too. There is a pressing need to find means of making use of these oil shales rationally. In this paper, eight Chinese oil shales were investigated using supercritical extraction technique. This can provide scientific basis for developing new technology to make use of oil shale.

## 2. EXPERIMENTAL<sup>(1)</sup>

The experiment was carried out on a semi-continuous installation (see Fig.1). Under the constant heating rate, The solvent, toluene, continuously passed through oil shale sample in a fixed bed where oil shale was extracted. The extraction condition were: pressure, 10 MPa; toluene flowrate, 2dm<sup>3</sup> /h; heating rate, 3K/min; particle size, 1.2-2.5mm; temperature, from room temperature to 550°C. Oil shale samples studied are from 4 different deposits, which are Huangxian, Huadian, Fushun and Maoming. The analyses of oil shale samples is shown in Table 1.

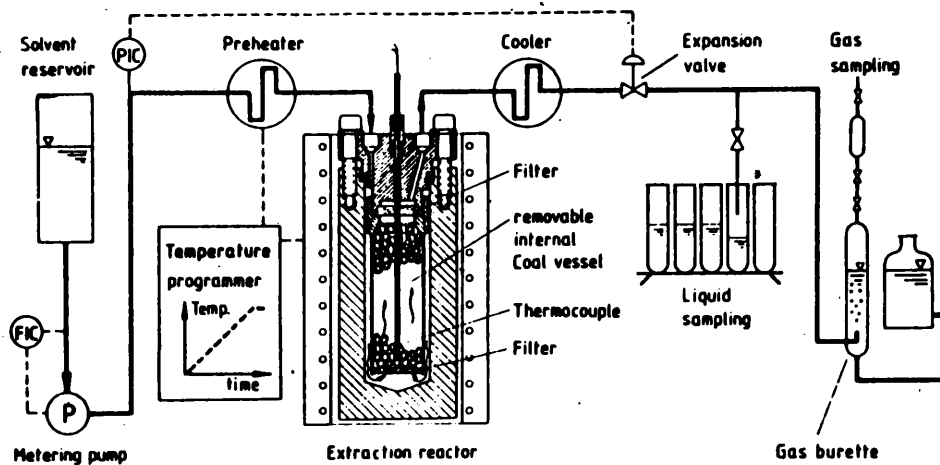


Fig.1: Scheme of the experimental setup

TABLE 1: Analyses of oil shale samples

Sample*	Moisture wt.% raw	Ash wt.% m.f.	Volatile matter wt.% m.f.	Kerogen** wt.% m.f.	Fischer assay wt.% m.f.			Ultimate Analysis wt.% m.f.			
					Oil	Residue	Gas + loss	C	H	S	N
EL1	12.57	15.93	56.53	84.1	31.7	53.5	10.4	63.55	5.14	0.93	1.71
EL2	6.41	41.00	42.46	51.7	24.5	63.1	8.9	38.42	4.32	1.61	0.97
EH4	7.91	57.00	33.48	38.5	19.8	70.6	7.2	28.65	3.10	0.89	0.62
EH6	9.67	65.10	29.24	32.7	15.9	75.6	5.8	23.42	2.42	1.22	0.59
EF1	2.93	72.90	22.00	24.8	12.6	82.3	4.1	16.58	2.16	0.75	1.04
EF3	2.61	79.00	15.87	17.2	7.6	86.9	4.7	10.31	1.43	0.50	0.88
EM1	5.18	65.00	27.32	35.0	10.9	80.9	4.4	21.14	2.43	1.75	0.82
EM2	8.38	73.30	22.40	23.7	10.6	83.6	4.1	16.38	1.66	0.90	0.60

\* sample code: EL = Huang Xian (Lung Kou), EH = Huading, EF = Fushun, EM = Maoming

\*\* kerogen content is defined as: kerogen (m.f.) = 100 - ash (m.f.) - CO<sub>2</sub> (m.f.), whereby CO<sub>2</sub> is determined by treatment with hydrochloric acid

During the experiment, liquid samples at different time and different temperature were collected. By analyses of extract content in liquid samples, extract formation rate (EFR(t)) and extract yield (EY(t)) at different temperature could be calculated.

### 3. EXPERIMENTAL RESULTS

#### 3.1. Effect of some main process parameters on extraction results<sup>(2,3)</sup>

To obtain optimum extraction condition under which the high conversion degrees of kerogen and high yields of liquid products could be obtained, experiments were made by a systematic variation of the extraction parameters: particle size, pressure, final extraction temperature, solvent flowrate, and H-donor content in the solvent. The results indicated that, for oil shale, the appropriate extraction condition were: particle size of less than 4mm, pressure of 10-15 MPa, temperature of 400-450°C. With toluene/donor-solvent mixtures, the kerogen could be extracted completely, the higher kerogen content of oil shale, the larger effect on the result.

#### 3.2. Extraction of different oil shale samples

Under experiment condition, eight oil shales were extracted. Fig.2.1 and Fig.2.2 showed the relationship between conversion degree and extract yield and volatile matter and kerogen content of oil shale used. Fig.3.1 and Fig.3.2 showed the effect of temperature on the extract formation rate and extract yield. Fig.4.1 and Fig.4.2 showed the relationship of main temperature range\* with volatile matter and kerogen content of oil shale used.

From Fig.2.1, conversion degree and extract yield were related with volatile matter, following formulas were obtained:

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 \*Main temperature range: temperature range of  $EFR(t) > 2 \cdot 10^{-5} g_E \cdot (g_K \cdot s)^{-1}$ ,  
 $g_E$  is the g of extract,  $g_K$  is the g of kerogen

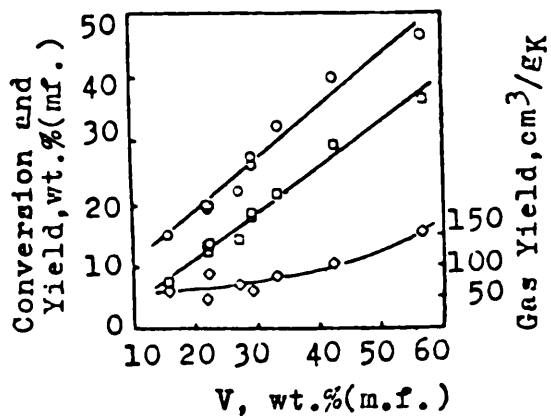


Fig. 2.1: Conversion and Yield vs V

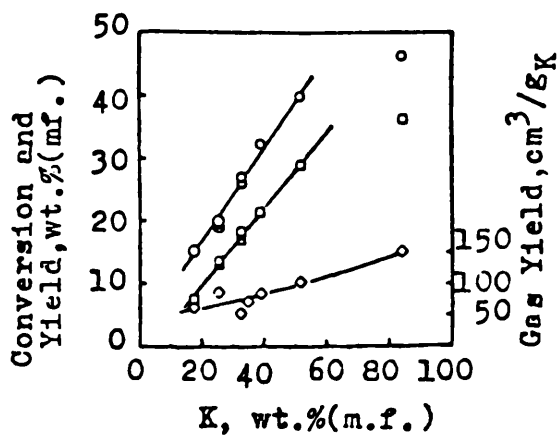


Fig. 2.2: Conversion and Yield vs K

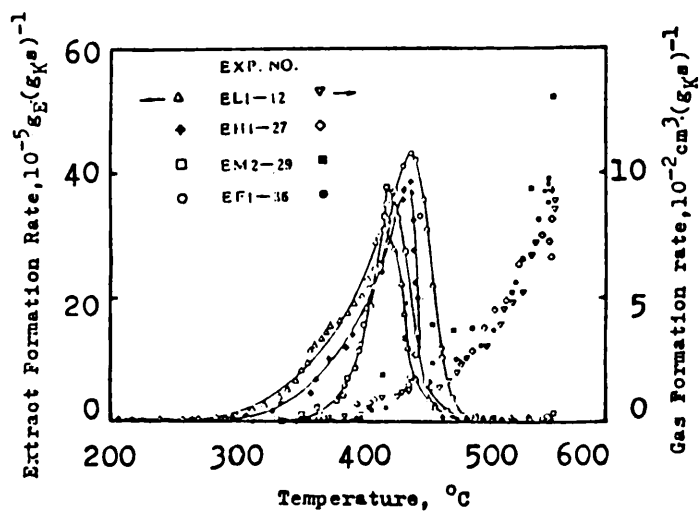


Fig. 3.1: EFR vs T

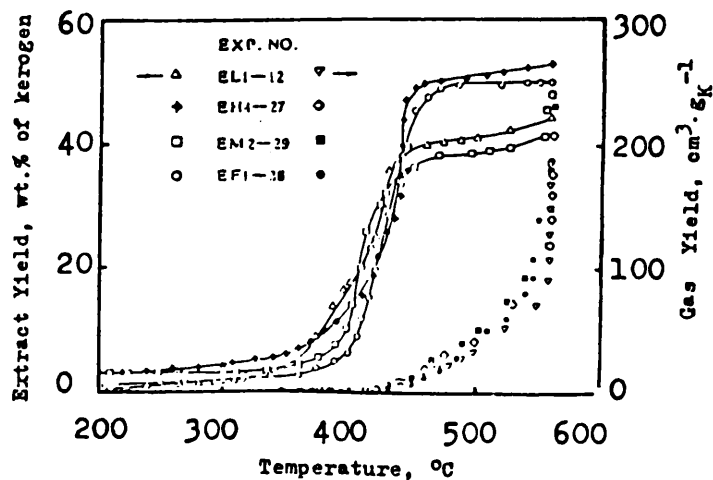


Fig. 3.2: EY vs T

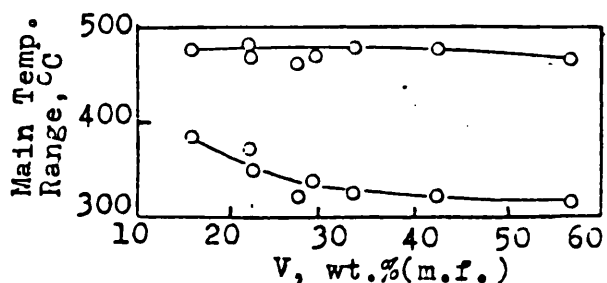


Fig. 4.1: Main Temp. Range vs V

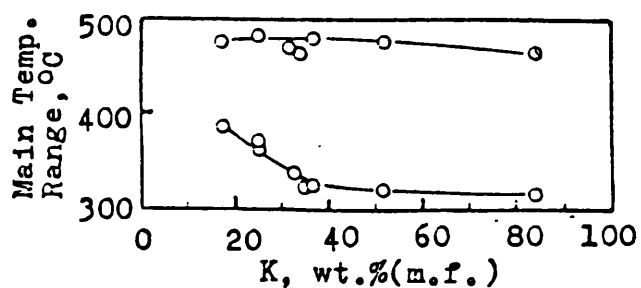


Fig. 4.2: Main Temp. Range vs K

$$C=0.81V+2.88 \quad (1)$$

$$E=0.71V-2.96 \quad (2)$$

From Fig2.2, conversion degree and extract yield were related with kerogen content(except EL1), following formulas were also obtained:

$$C=0.75K+1.51 \quad (3)$$

$$E=0.62K-2.93 \quad (4)$$

where C,E is the conversion degree and extract yield of oil shale, V,K is volatile matter and kerogen content of sample respectively (all in m.f.basis).

From these results, it can be seen that the conversion degree and extract yield increase linearly with volatile matter or kerogen content, the temperature at which the effective extraction\* started increases with volatile matter or kerogen content and the temperature at which the effective extraction ended changed little as the volatile matter or kerogen content increased, the whole result is that the main temperature range increase with the volatile matter or kerogen content of oil shale. These results indicated that the higher the volatile matter or kerogen content of oil shale is, the more the amount which can be extracted, the longer the time of effective extraction, the higher the extract yield. Therefore, to obtain high shale oil from unit weight of oil shale, it is suitable to use oil shale which has higher volatile matter or kerogen content.

#### 4. KINETIC OF SUPERCRITICAL EXTRACTION

Under the experiment condition, the dominating step of extraction process is the pyrolysis reaction of kerogen<sup>(4)</sup>. The supercritical extraction process of oil shale can be described by a simple first order reaction kinetic equation which is shown as following:

$$\frac{dn_E}{n_K dt} = k_0 \cdot \exp(-E_A / RT) (EY(t_e) - EY(t)) \quad (5)$$

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\*Effective extraction of  $EFR(t) > 2 \cdot 10^{-5} \text{ g}_E \cdot (\text{g}_K \cdot \text{s})^{-1}$

where  $m_E$ ,  $EY(t)$  is the extract weight and extract yield respectively at the time  $t$ ,  $EY(t_e)$  is the final extract yield at the end of the experiment,  $m_K$  is the initial mass of kerogen in the reactor, all in m.a.f. basis.

By treatment appropriately, following formula can be obtained from formula 5.

$$\ln(-\ln(1-EY(t)/EY(t_e))/T^2) = \ln\left(\frac{k_0 \cdot R}{H \cdot E_A} \cdot \left(1 - \frac{2RT}{E_A}\right)\right) - \frac{E_A}{RT} \quad (6)$$

where  $H = dT/dt$ , is the heating rate of process.

Generally,  $E_A \gg RT$ , so the first row of right hand side may be regarded as constant. The kinetic data of extraction can be determined from the slope and intercept of Equation 6, if the left hand side is plotted against  $1/T^2$ .

Table 2 shows the kinetic parameters of supercritical extraction of eight oil shales. From Table 2, it can be seen that, the extraction of oil shale can be divided into two stages. The first stage, taking place below about  $400^\circ\text{C}$ , is the depolymerization of kerogen and dissolution of some depolymerization products. This stage has a lower activation energy (45-90kJ/mol), because the cleavage of side chains and bridges are dominating factor. The second stage, taking place above about  $400^\circ\text{C}$ , is the further decomposition of the depolymerized kerogen (bitumen) and the dissolution of a large amount of products. This stage has higher activation energy (130-190kJ/mol) because of the rupture of covalent bonds and more liquid and gas product were produced.

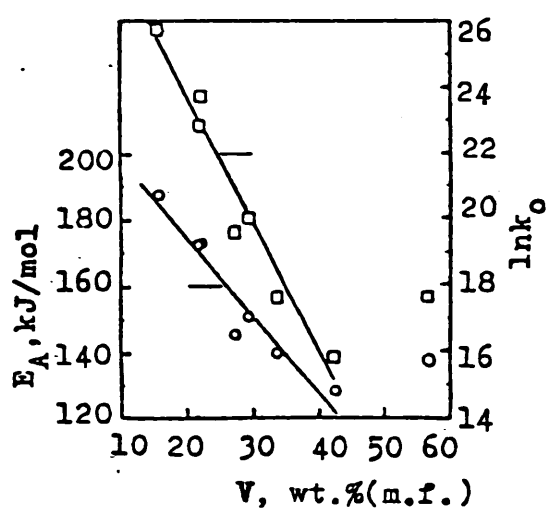
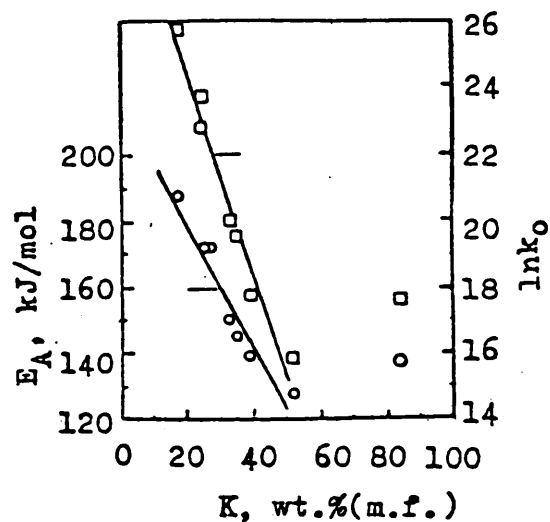
Fig.5.1 and Fig.5.2 shows the relationship of the kinetic parameters in main extraction stage (about  $400-450^\circ\text{C}$ ) and the volatile matter and kerogen content of oil shale respectively. Except for EL1, the kinetic parameters of other seven oil shales were related with volatile matter and kerogen content of samples, following formulas were obtained:

$$E_A = -2.34V + 220.9 \quad (7)$$

$$\ln k_0 = -0.39V + 31.6 \quad (8)$$

Table 2: Kinetic parameters of supercritical oil shale extraction

Sample		EL1	EL2	EH4	EH6	EF1	EF3	EML	EM2
region A	Temp.interval (°C)	320-410	340-390	360-410	340-390	340-390	—	340-395	340-390
	$E_A$ (kJ/mol)	75.2	70.5	88.7	58.0	44.9	—	85.4	65.5
	$k_0$ (1/s)	$4.7 \cdot 10^2$	$1.2 \cdot 10^2$	$4.4 \cdot 10^3$	$1.1 \cdot 10^1$	$2.6 \cdot 10^{-1}$	—	$3.9 \cdot 10^3$	$3.4 \cdot 10^1$
region B	Temp.interval (°C)	410-470	390-465	410-470	390-460	390-485	380-465	395-430	390-460
	$E_A$ (kJ/mol)	137.2	128.1	139.4	150.4	172.1	187.7	145.2	172.1
	$k_0$ (1/s)	$4.7 \cdot 10^7$	$7.5 \cdot 10^6$	$4.7 \cdot 10^7$	$5.1 \cdot 10^8$	$8.2 \cdot 10^9$	$1.5 \cdot 10^{11}$	$3.2 \cdot 10^8$	$2.0 \cdot 10^{10}$

Fig.5.1:  $E_A$  ( $\ln k_0$ ) vs VFig.5.2:  $E_A$  ( $\ln k_0$ ) vs K

or

$$E_A = -1.85K + 216.2 \quad (9)$$

$$\ln k_0 = -0.31K + 30.7 \quad (10)$$

besides this, there is a relation between the activation energy and the preexponential factor:

$$E_A = 6.05 \ln k_0 + 30.7 \quad (11)$$

where  $E_A$  in kJ/mol,  $k_0$  in 1/s, V, K is the volatile matter and kerogen content of oil shale respectively, all in m.f.basis.

## 5. CONCLUSIONS

- (1). The conversion degree and extract yield of supercritical extraction of oil shale increase linearly with the volatile matter or kerogen content of the oil shale tested.
- (2). The kinetic process of supercritical extraction of oil shale can be described by a simple first-order reaction equation. The kinetic parameters have close relation with the properties of oil shale.

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