

## A STUDY OF OXIDATION TECHNIQUE OF OIL SHALE

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## ABSTRACT

Owing to high chemical activity, Huangxian (Shandong province) oil shale and Maoming (Guangdong province) oil shale can be directly oxidized by air for producing organic acids, without being treated and concentrated. The effective conversion ratio of organic carbon could reach more than 50% with operation pressure 8 kg/cm<sup>2</sup> and temperature 155 °C.

The kinetics and mechanism of oxidation reaction of Huangxian oil shale were investigated. The activation energy of oxidation of cross-link bonds in the kerogen was 43 KJ/mole within 115-155°C. The mechanism was also confirmed by IR of residues. The IR of products indicated that water-insoluble acids of Huangxian black oil shale were mainly aromatics, while for Maoming oil shale mainly aliphatics. The composition of Huangxian water-insoluble acid was further verified by NMR.

## INTRODUCTION

With rising consumption and diminishing reserve of crude oil, it is imperative to find alternative hydrocarbon resources for petro-chemical raw material. Because of abundant reserve and similar composition, fossil fuel, especially oil shale, becomes one of the most hopeful.

Until present, there is no direct chemical utilization of oil shale in commercial scale yet. Only some research work was conducted in Soviet Union in the 60's and 70's. What they have done was to oxidize concen-

trated kerogen from oil shale with nitric acid or with 40 atm air at 175°C in water-alkali solution to produce carboxylic acids, predominantly C<sub>4</sub>-C<sub>10</sub> carboxylic acids. They developed the application of C<sub>4</sub>-C<sub>10</sub> dicarboxylic acids in synthesis of polyamide and polyester and the use of macromolecular acids as plant growth stimulator.<sup>[1]</sup>

In China, some exploratory work in direct chemical utilization of oil shale was conducted. Yang Qiushui and others tested and verified the readiness of oxidation of Huangxian (Shandong province) oil shale and Maoming (Guangdong province) oil shale without being treated and concentrated<sup>[2]</sup> and then selected mild oxidation conditions to produce carboxylic acids economically. Preliminary results showed that using 8 kg/cm<sup>3</sup> air at 155°C in sodium hydroxide solution could get higher conversion ratio. Under the above conditions, the cost of processing and the investment of equipment are both low, and so it has certain actual significance and is worth further investigating.

In this paper, the feasible oxidation conditions and the mechanism and kinetics of oxidation were studied.

## EXPERIMENT

Three oil shales, one lignite and one coal were studied. The analytical data of the samples are given in Table 1.

Table 1. Analytical data of samples.

Samples	C <sub>Y</sub> <sup>f</sup>	H <sup>f</sup>	A <sup>g</sup>	V <sup>g</sup>	W <sup>f</sup>
Huangxian black oil shale	55.01	5.75	15.90	40.20	13.30
Maoming oil shale	13.43	2.35	72.40	24.70	2.40
Fushun oil shale	11.06	1.73	72.10	23.70	2.82
Huangxian lightite	51.11	3.69	10.00	43.00	10.40
Huainan Bitumous coal	58.63	3.81	6.52	34.00	11.40

f -- analytical sample basis

g -- dry basis

C<sub>Y</sub>-- organic carbon

The experimental oxidation process was in batch operation, using air stirring and temperature controller. The laboratory flow chart of oil shale oxidation is shown in Fig. 1.

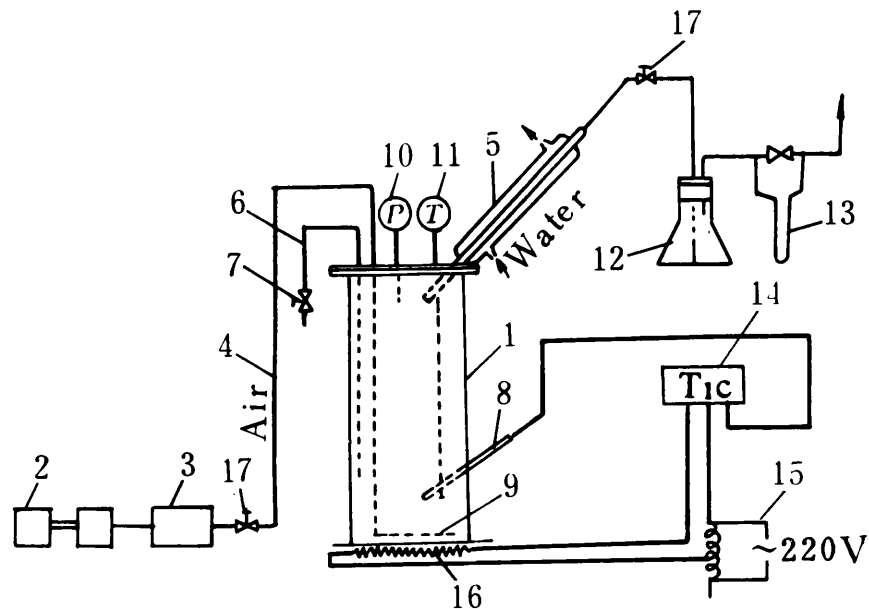


Fig. 1. Flow chart of lab. oxidn of oil shale

1--reactor; 2--air compressor; 3--air reservoir; 4--air-entry tube; 5--condenser; 6--sampling tube; 7--sampling valve; 8--temp measure unit; 9--air distributor; 10--manometer; 11--thermometer; 12--buffer; 13--flow meter; 14--temp. controller; 15--transformer; 16--electric stove; 17--valve.

## RESULTS AND DISCUSSION

### 1. Feasible oxidation processing conditions.

From the point of view of economy of processing, the main factors are sample size and oxidation temperature. Table 2 represents the effect of sample size on oxidation. In Table 2, with the decrease of sample size (from <5mm to <0.12mm), the conversion rate increases. While the sample

Table 2. The effect of sample size on oxidation

Reaction condition	Sample size (mm)	Sample weight(g)	NaOH weight(g)	Total volume(ml)	Effective conc.ratio(%)	Remark
155°C 8 kg/cm <sup>2</sup> 3.5 hours	0.074	20.0	30.0	500	51.09	PH=13
	0.12	20.0	30.0	500	51.01	
	0.589	10.3	16.0	250	33.88	
	1.50	13.6	22.0	340	30.72	
	5.0	10.1	16.0	250	22.68	

size is reduced to <0.12mm, the conversion rate does not go up further, indicating that the reaction is in the range of chemical reaction control. As a result, the sample size was chosen  $\leq 0.12$ mm.

Because of the high chemical activity of these oil shales, it is quite possible to choose a proper temperature suitable for oxidation and an air compressor for providing an adequate (8-10 kg/cm<sup>2</sup>) pressure so as to acquire rather sufficient conversion rate. The effects of temperature are listed in Table 3. The highest effective conversion rate (E. C. R.) can reach 50% (based on organic carbon) for Huangxian oil shale. The results of oxidation of other samples, such as Fushun oil shale, Maoming oil shale, Huangxian lighthouse and Huainan (Anhui province) bituminous coal are shown in Table 4. It is shown that Huangxian lignite and Maoming oil shale can be easily oxidized but Fushun oil shale and Huainan bituminous coal are not. It will be explained in next section.

Table 3. The oxidation effect of Huangxian black oil shale.

Oxidn. condns.	Oil shale wt (g)	NaOH wt (g)	Reactn time (hr)	Residue wt (g)	WIA wt (g)	WSA wt (g)	Total C R (%)	WIA FR (%)	WSA FR (%)	Effective C R (%)
155°C 8 kg/cm <sup>2</sup>	20	20	0.25	7.64			30.54			17.64
	20	20	1.0	5.40	3.04	0.79	50.91	27.63	7.81	35.44
	20	27	2.0	4.26	3.90	0.97	61.27	35.45	8.92	44.37
	18	36	3.0	3.35	3.36	1.60	66.65	33.6	16.6	49.60
	20	30	3.5	3.19	3.22	2.40	71.45	29.27	21.82	51.29
	10	20	5.0	1.60	0.96	0.92	71.0	17.45	16.94	34.04
135°C 8 kg/cm <sup>2</sup>	20	20	1.0	7.50	1.85	0.49	31.82	16.64	4.50	16.55
	20	20	2.0	6.24	2.83	0.65	43.27	25.73	5.91	31.64
	20	20	3.0	5.34	2.96	1.08	51.45	26.91	9.82	36.73
	20	20	4.0	4.37	3.41	1.03	60.27	30.10	9.36	40.18
	20	20	5.0	3.37	3.05	1.95	69.36	27.72	17.13	45.45
115°C 8 kg/cm <sup>2</sup>	20	20	3.0	6.29	2.72	0.90	42.82	24.73	8.18	32.91
	20	20	5.25	4.10	3.60	1.07	62.73	32.73	9.73	42.46
	20	20	7.0	3.10	3.08	1.87	71.82	28.00	16.09	44.09

Table 4. The oxidation of different sample.

samples	oxidation time(hr)	Total C.R(%)	Remarks
Huangxian black oil shale	3.5	70.0	oxidn. condn. 155° 8 kg/cm <sup>2</sup>
Maoming oil shale	3.5	65.1	sample size 0.12 mm
Fushun oil shale	5.0	34.2	
Huangxian lignite	4.0	67.5	
Huainan coal	7.0	46.6	

## 2. Mechanism and kinetics of oxidation of Huangxian black oil shale

The results of oxidation of Huangxian black oil shale in Table 3 can be illustrated by Fig. 2. It can be seen that

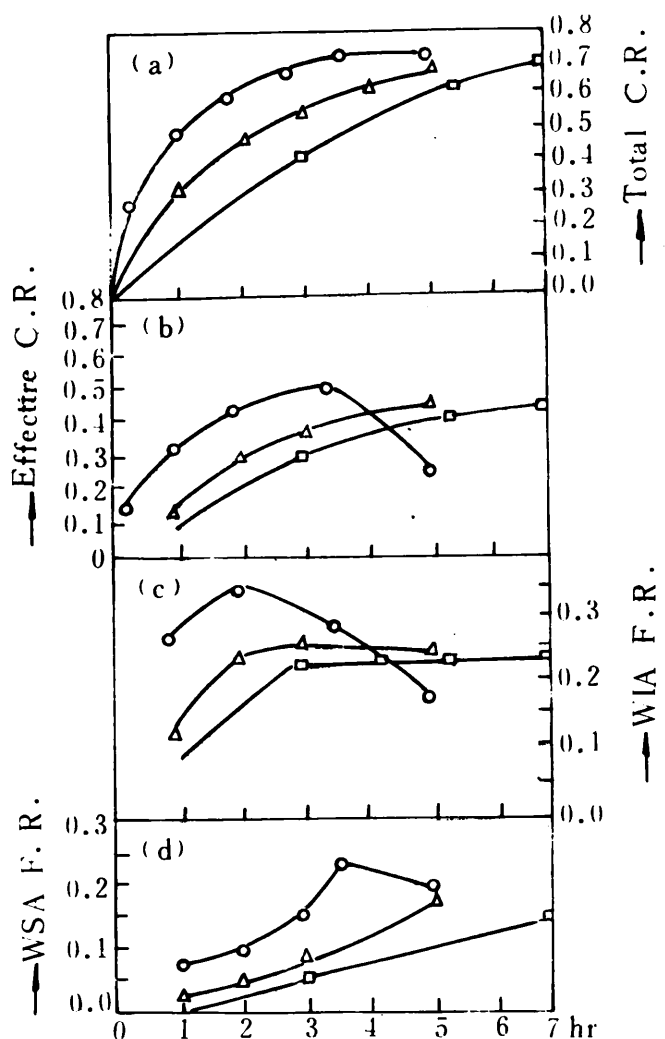


Fig. 2. The oxidn effect of Huangxian black oil shale. (According to Table 3)

○ --155°C; △ --135°C; □ --115°C.

(a) At 155°C, the original organic carbons in the beginning period reacted at a great rate, considered as the neutralization of humic acid-like material in kerogens with alkali and the organic salts formed to be dispersed or dissolved into the solution. (This period remained about one hour.)

In the middle period (1-3 hr), the conversion rate became slow, the humic acid-like material being quite little and the reaction being mainly the oxidation of side chain and other easily-oxidizable groups of kerogens.

In the last period (3-3.5 hr), the conversion rate decreased remarkably. It can be considered as the oxidation of least reactive crosslink-

ing structures of kerogens.

(b) At 135°C and 115°C, the total conversion rate (TCR) was lower than at 155°C. In the beginning period, the TCR was 20% lower at 135°C and 30% lower at 115°C than that of 155°C. It can be considered that in this period, the humic acid-like substances were not mainly extracted by alkali but directly oxidized by air. Only in the latter period (135°C after 4 hrs; 115°C after 5 hrs) predominated the oxidation of the cross-linking structure.

This mechanism could be verified by direct extraction with alkali without oxidation (at 155°C), the extraction yield reaching 20% (based on organic carbons). It can be inferred that the beginning period reaction at 155°C was mainly alkali-extraction. Besides, IR can be used to give the relative proportion of aliphatic part to aromatic part and the relative content of carbonyl, the former revealed by  $D_{2920}/D_{1630}$  and the latter by  $D_{1700}/(D_{2920}+D_{1630})$ . The IR of organic matter of Huangxian black oil shale and its oxidation residue for different reaction time at 155°C is shown in Fig. 3, and the results are listed in Table 5.

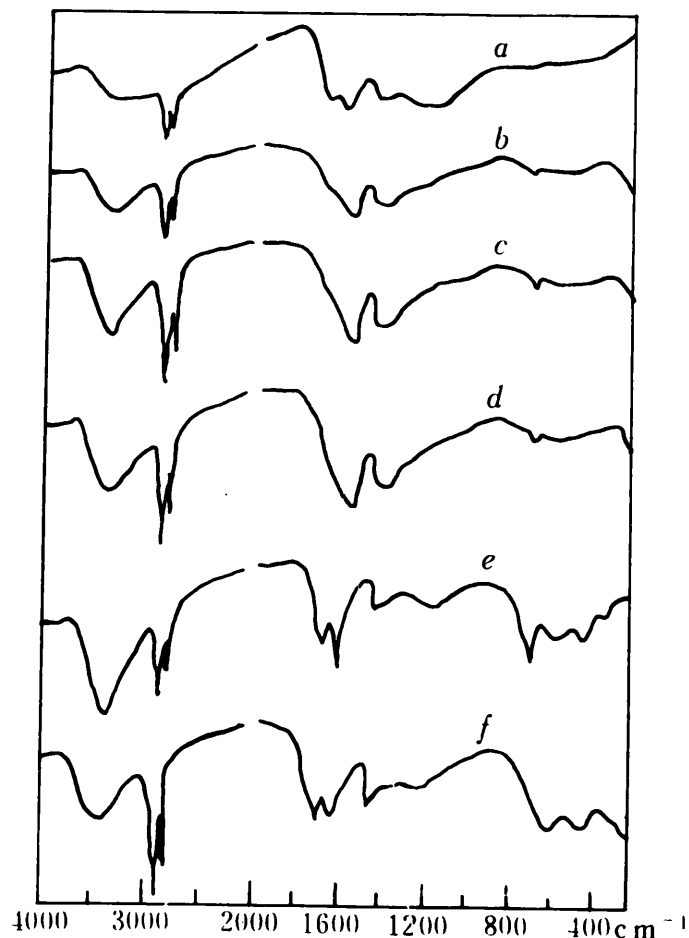


Fig. 3. The IR of organic matter of Huangxian black oil shale and its oxidation residue of different time at 155°C.

a -- oil shale; b -- residue of 1 hr; c -- 2 hrs;  
d -- 3 hrs; e -- 3.5 hrs; f -- 5 hrs.

Table 5. The relative proportion of aliphatic part to aromatic part and the relative content of carbonyl of each residue in different time.

oxidation time (hr)	$D_{2920}/D_{1630}$	$D_{1700}/(D_{2920}+D_{1630})$
a	0.0	0.22
b	1.0	0.27
c	2.0	0.28
d	3.0	0.29
e	3.5	0.38
f	5.0	0.40

From Table 5, it can be seen that

(1) In the beginning period (0-1 hr), the relative proportion of aliphatics to aromatics increases, the relative content of carbonyl decreases remarkably. This indicates that the humic acid-like substances which are mainly composed of aromatics are substantially extracted by alkali solution.

(2) In the middle period (1-3 hr), the proportion of  $D_{2920}/D_{1630}$  is almost constant, this shows that there are few alkali-extractable substance left in the residue, while the oxidation of the side chain and active group becomes the major reaction.

(3) In the later period (3-3.5 hr), the relative content of aromatics decreases but that of carbonyl increases. It is obvious that the reaction is mainly the oxidation of the aromatics of cross-linking structures of kerogen, and some carboxylic acids formed remains in the residues, not dissolved in the alkali solution.

(4) In the last period (after 3.5 hr), the organic carbon in the residues changes scarcely, and relative carbonyl content decreases. This shows that there occurs decomposition of the carboxylic groups.

Based on the conversion of organic carbon, the overall kinetics equation can be expressed as follows;

$$-\frac{dC_s}{dt} = kC_s^n$$

$C_s$  --- the weight of organic carbon of residue (g)

The reaction orders and rate constants at different temperature are calculated by differential method, and the results are listed in Table 6. It can be seen that the time range of similar reaction order corresponds to the time range of similar reaction mechanism. The reaction order at these three temperatures becomes greater at last period, and approaches Similarly.

Table 6. The reaction orders and velocity constants at different temp.

Temp.	Period	Time (hr)	C.R (%)	n	$k(g^{1-n} \cdot hr^{-1})$
155°C	I	1.0	40.0	3.2	$6.51 \times 10^{-3}$
	II	2.5	62.0	2.5	$7.32 \times 10^{-3}$
	III	3.5	68.8	3.5	$8.86 \times 10^{-3}$
135°C	I	4.0	60.0	1.9	0.05
	II	5.0	67.5	3.6	$4.60 \times 10^{-3}$
115°C	I	5.0	59.0	1.2	0.138
	II	7.0	76.2	4.0	$2.67 \times 10^{-3}$

As to the oxidation characteristics of different samples, it is learned that the kerogen of Maoming oil shale is composed of aliphatics with branched chain and that of Fushun is mostly normal aliphatics. Therefore, the former is more readily oxidized and the latter less readily oxidized.

### 3. Analyses of oxidation products.

Primarily, the oxidation products were separated into water-soluble acids (WSA) and water-insoluble acids (WIA) by acidification.

Because of insolubility and high molecular weight, it is difficult to analyze WIAs. The IR and NMR spectrometry have been used for these acids.

Fig. 4 is the IR of the WIA of different samples of 155°C. It shows that  $1630 \text{ cm}^{-1}$  peaks which represent the aromatics of WIAs of Huangxian black oil shale and lignite and Huainan bitumous coal are quite strong, but the  $2920 \text{ cm}^{-1}$  peaks which represent the aliphatics are weak. But the Maoming and Fushun oil shales have a contrary result. It can be considered that there are quite a large amount of aromatics in WIAs of Huangxian black oil shale and lignite and Huainan bitumous coal, while in Maoming and Fushun oil shales, the aliphatics predominate.



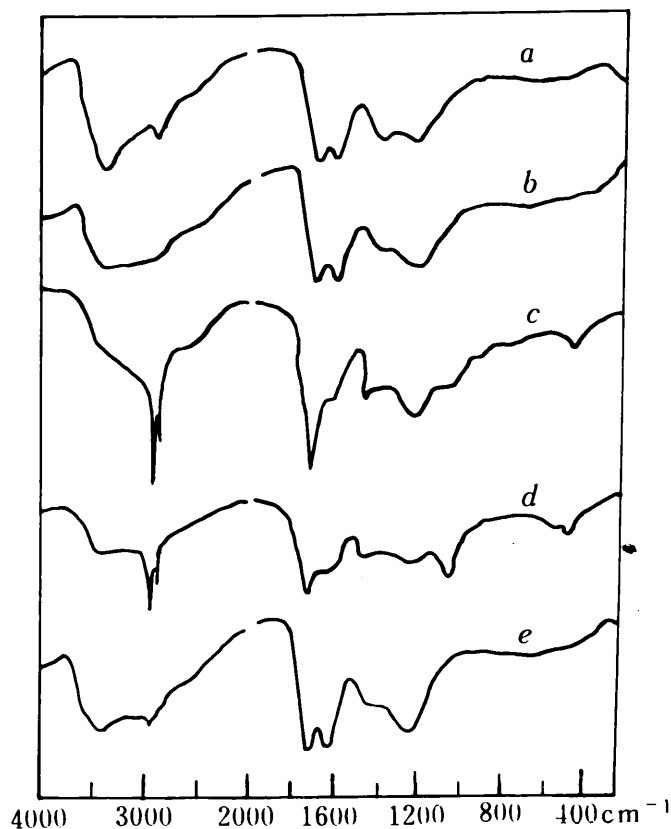


Fig. 4. The IR of WIA of different samples of 155°C  
 a--Huangxian black oil shale; b--Huangxian lignite;  
 c--Maoming oil shale; d--Fushun oil shale;  
 e--Huainan bituminous coal.

#### CONCLUSION

Due to the high chemical activity, Huangxian and Maoming oil shales can be oxidized directly by air. This may be considered as a feasible process for producing carboxylic acids.

#### REFERENCES

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- (2) Yang Qiushui, Fan Weiyu and Cao Zhongyuan: "Study on Oxidation of Oil Shale for Producing Organic acids" (in Chinese) Collected Papers on Oil Shale Research, pp 168-171, (1984).