

SYMPOSIUM ON CHARACTERIZATION AND CHEMISTRY OF OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF FUEL CHEMISTRY AND
PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
ST. LOUIS MEETING, APRIL 8 - 13, 1984

STRUCTURAL CHARACTERIZATION OF SUPERCRITICAL GAS EXTRACTS AND
RESIDUES OF FUSHUN AND MAOMING OIL SHALE

By

K. Z. Qin, R. A. Wang, S. S. Jia, Y. X. Lao and S. H. Guo
East China Petroleum Institute, Dongying, Shandong, PRE 22996-7

INTRODUCTION

An ideal degradation process used to elucidate oil shale kerogen structure involves cautious split of kerogen to such an appropriate extent that the high yield fragments will be soluble in common solvents for application of various instrumental analyses, yet still preserve most of kerogen structure in the fragments. Several investigators have employed different methods, such as mild thermosolvolyis by tetralin in autoclaves (1) and stepwise oxidation by alkaline potassium permanganate (2) to achieve these ends, yet the semicontinuous supercritical gas extraction (SCGE) appears to be a more effective means. During the process, kerogen matrix swells and loses its structure due to the dense phase solvent gas penetrating into the crosslinked network. As the framework of kerogen is broken down at the weakened linkages, the thermally depolymerized bitumen fragment just being extractable by supercritical gas escapes from the reaction zone immediately together with the gas stream and is condensed under reduced temperature and pressure, so the minimization of the secondary degradation occurs. Different Chinese oil shales have been extracted by supercritical toluene in a semicontinuous apparatus successfully (3), for instance, Maoming oil shale yields 79% of bitumen extracted on the basis of organic matter content at 385°C and 15 MPa with low yields of gas and water. Much valuable information can be provided by analyses of bitumen and its constituents. Furthermore, determination of the voidage and porous structure of extracted shale will reveal the distribution pattern of organic matter in the raw shale, since the major part of organic matter has been removed from its mineral matrix, which is primary inert to the extraction. The semi-quantitative data measured by porosimeter give a distinct description of that important physical property of oil shale. The present work is such an experiment with Fushun and Maoming oil shale, two of the most famous oil shale deposits in China.

EXPERIMENTAL

Extraction

The extraction was carried out in a home-made semi-continuous apparatus consisting of a stainless steel preheater and a extractor. For each run, 100 g of 20-60 mesh oil shale sample was charged. A constant flow rate stream of toluene was pumped upward through the extractor and a definite temperature and pressure were maintained automatically all over the extraction. Supercritical toluene carrying the dissolved bitumen was condensed in a water cooler, it was removed from the condensate at 80°C under vacuum and the extract obtained was preserved under nitrogen atmosphere. The extracted shale was discharged after cooling the system to room temperature by nitrogen.

Charaterization of Extract

During the fractionating of the extract, asphaltenes were precipitated by heptane extraction. The solubles were fractioned by adsorption chromatography on alumina. The aliphatics, aromatics and resins were eluted successively with petroleum ether (b. p. 60-90°C), benzene and benzene-ethanol mixture (1:1 by volume).

Gas-liquid chromatographic analyses (GLC) of the aliphatics were carried out using a HP-5734-A chromatograph on a 12 m x 0.2 mm i. d. capillary column with ov-101 silicone fluid as stationary phase and He as carrier gas. The column was heated from 100°C to 280°C with a heating rate of 8°C/min. Combined gas chromatography-mass spectrometry analyses (GC-MS) were carried out using a Finnigan model 4201-c GC-MS and data reduction system. Separated components were identified by comparison of standard mass spectra.

Proton and C-13 nmr were performed for bitumen and its constituents on a Bruker WH-90 nmr spectrometer with CDCl₃ as solvent.

Molecular weights were determined using a Knauer vapor pressure osmometer with

benzene as solvent.

Proximate and ultimate analysis procedure follows that of National Standards of China for coals to solid samples and for petroleum products to bitumen samples.

Infrared spectra were measured by a Hitachi 260-50 grating spectrophotometer. Samples were prepared as smears on NaCl cells.

Characterization of Extracted Shale

Preliminary microscope examination shows that the pore size of extracted shale distributes in the range of macropores. A CARLO ERBA-1520 automatic mercury porosimeter was adapted to the determination. It was operated under 0-150 MPa of mercury for the pore radii range 50 to 75,000 Å. The samples were dried at 105°C for 2 hours before hand. Pore radius r is calculated by the Washburn equation in which surface tension of mercury is assumed to be 480 dyne/cm and contact angle, 140°.

True density of samples was determined by water pycnometer and particle density by mercury displacement. Total open pore volume was calculated by the difference between reciprocals of particle and true densities.

For the examination of mineral constituents, above mentioned infrared spectrophotometer was used. The samples were prepared as KBr pellets.

The porous structure of extracted shale was examined by a Hitachi HU-11A transmission electron microscope (TEM) using microtomy for section preparation. Morphology of the minerals was also examined by scanning electronic microscopy (SEM) techniques. (TEM was carried out by Beijing Petro-chemical Research Institute and SEM by Shengli Geological Research Institute.)

RESULTS AND DISCUSSION

Table I summarizes the ultimate analyses of organic matter, bitumen (SCGE) and its group constituents. Kerogen of Maoming and Fushun oil shale will be classified as type 1 according to H/C and O/C diagram suggested by Tissot et al. (4), as well as to their infrared spectra. Detailed analyses of these two shales and description of SCGE experiment conditions are stated elsewhere (3, 5).

TABLE I

ULTIMATE ANALYSIS OF ORGANIC MATTER, SCG EXTRACTS AND GROUP CONSTITUENTS

Sample	Origin	Ultimate Analysis (Wt %)						Weight Yield % (basis)	
		C	H	N	S	O	H/C		
Organic Matter	F	79.1	9.9	2.1	1.9	7.0	1.51	21.1	(d. a. f. shale)
SCG	M	79.4	9.7	1.6	1.1	8.2	1.46	19.2	(d. a. f. shale)
Extract	F	84.5	10.3	1.5	0.2	3.5	1.46	70.9	(org. matter)
Aliphatic fraction	M	84.1	10.1	1.5	0.6	3.7	1.44	79.1	(org. matter)
	F	-	-	-	-	-	-	8	(extract)
	M	-	-	-	-	-	-	7	(extract)
Aromatic Fraction	F	85.7	11.1	-	-	-	1.55	8	(extract)
	M	84.4	10.8	-	-	-	1.54	8	(extract)
Resins	F	79.6	9.4	1.7	0.4	8.9	1.42	52	(extract)
	M	79.9	9.6	1.5	0.3	8.7	1.44	43	(extract)
Asphaltenes	F	80.5	8.7	2.3	0.9	7.6	1.30	32	(extract)
	M	81.6	9.3	1.8	0.5	6.8	1.37	42	(extract)

F: Fushun oil Shale; M: Maoming oil shale.

GLC and GC-MS Analyses

Figure 1 is a total ionization plot of a gas chromatogram of the petroleum ether eluate of Maoming extract. It reveals primarily a homologous series of alkanes from C₁₂ to C₃₃, and also an olefin series, as the weaker peaks are adjacent to respective alkanes. The structure of some individual olefins has been identified as α -mono-olefins by computer comparison of mass spectra. Figure 1 shows that there is a distinct major peak of C₂₇ and the n-alkane homologues exhibited a predominance of odd carbon numbers over even ones, but no such regular pattern for the olefin series. The relative amount of olefins to alkanes decreases as the temperature of extraction goes down. It implies that olefins are the fragments split from the side chains of kerogen structure and unlike the alkanes are indigenous components. In the aliphatics, a lot of isoprenoids, steranes and pentacyclic triterpanes such as pristane, phytane, cholestane, ergostane, stigmastane, hopane and

their isomers and homologues have been verified by mass spectra. These biological markers are valuable to the geochemists for the studies of kerogen genesis and maturity.

GLC analysis of Fushun aliphatics gives analogous results to that of Maoming.

It is evident that branched and cyclic aliphatic structures are present. However, the overwhelming majority are the unbranched aliphatic hydrocarbons. As shown in Table I, the weight fraction of aliphatics reaches 7-8.5%. There is a considerable amount of alkanes in the total extract. Will all the alkanes be originally entrapped in the cage structure of kerogen matrix? It is an interesting problem of the kerogen structure, but it is not clear yet.

Structure Similarities Between Extract and Kerogen

A noticeable feature in Table I is the hydrogen carbon atomic ratio of the extracts which are very close to that of their kerogen matrix. Generally, a cracking process should give the light products a higher H/C than the crude stock, but a depolymerizing process gives the degradation products a same H/C as its precursor.

The infrared spectra of SCG extract bear striking resemblance to those of original kerogen. The strongest absorption bands are around 2920, 2855 and 1455 cm^{-1} contributed by CH_2 and CH_3 groups of aliphatics; another specific band at 720 cm^{-1} shows predominant $(\text{CH}_2)_n$ structures (n larger than 4), exists both in extract and kerogen.

The carbon aromaticities determined by proton nmr are 0.33 and 0.34 for Fushun and Maoming SCG extracts. Recently, we have got the information that the carbon aromaticities directly measured by C-13 nmr with cross polarization/magic angle spinning techniques carried out in Colorado State University for these two raw oil shales are 0.35 and 0.32, respectively (6). This fact may well be taken as one of the reliable indications of a polymer character of kerogen.

Asphaltene of bitumens extracted from oil shale at ordinary conditions is known as having similar structures of kerogen, SCG asphaltene, the major constituent of extract, will naturally give more similarities. For instance, carbon aromaticity of Maoming SCE asphaltene determined by C-13 nmr is 0.33; their X-ray diffraction curves are also having remarkable resemblance. A special report of this item is under preparation.

These structural similarities between SCG extract and kerogen lead to the conclusion that thermo-depolymerization is the main reaction experienced during SCGE and a great portion, if not all, of the kerogen matrix has characters of a multipolymer.

"Building Block" of Kerogen

Although the SCG extract is not just the "monomer" of the multipolymer structure of kerogen, it may be considered as a specimen composed of different "monomers" of kerogen. An average "building block" of kerogen can be described, therefore, with the group constituents used to describe a bitumen. The molecular ratio of these constituents in SCE extracts are tabulated as follows:

Group Constituent	Average M. W. (VPO)		Weight Fraction		Molecular Fraction		Molecular Ratio	
	1	2	1	2	1	2	1	2
	Aliphatics	330	326	0.07	0.08	0.17	0.19	1.0
Aromatics	390	390	0.08	0.08	0.16	0.15	0.9	0.8
Resins	690	710	0.43	0.52	0.49	0.53	2.9	2.8
Asphaltenes	1870	1667	0.42	0.32	0.18	0.14	1.0	0.8

Note: 1 - Maoming oil extract; 2 - Fushun oil shale extract.

Accordingly, average "building blocks" of kerogen keep their constitutional molecular numbers in the ratio of 1:1.3:1 approximately, so the unit weight of an average "building block" of these two kerogens may be estimated as 4400-4600. It has a good agreement with the results of our other work (7), in which the average unit weight was calculated from the correlation of refraction index, density, aromaticity and ultimate analyses of kerogens.

Density of Maoming and Fushun oil shale kerogen has been assessed to be nearly 1.10 (8); then the average molecular volume of a "building block" be spheric in form, the diameter of sphere would be 24Å. It appears somewhat smaller than the dimension of Green River oil shale kerogen, $39 \times 27 \times 25 \text{ \AA}^3$, suggested by Yen (9), but still in the same magnitude order. Using ultimate analysis data of kerogen as those of "building block", their chemical formulas can be written as $\text{C}_{302}\text{H}_{440}\text{O}_{23}\text{N}_6\text{S}_2$ for Maoming and $\text{C}_{296}\text{H}_{446}\text{O}_{20}\text{N}_7\text{S}_2$ for Fushun. It is logical that the carbon constitutional fractions of SCG extract may be taken as those of kerogen (10) and are listed in Table II.

TABLE II

PROTON MUR SPECTROSCOPY AND STRUCTURAL PARAMETERS OF SCG EXTRACT
(per average molecule)

<u>Item</u>	<u>Fushun Extract</u>	<u>Maoming Extract</u>
Total C atoms	53.4	55.3
Total H atoms	77.9	79.6
Molecular Weight (VPO)	758	789
Hydrogen Distribution:		
aromatic	6.2	6.3
naphthenic	8.4	11.6
olefinic	0.3	0.5
alpha to ar. ring	10.7	13.0
beta to ar. ring	44.3	40.0
gama to ar. ring	8.1	8.1
Structural parameters:		
aromatic C fraction	0.33	0.34
naphthenic C fraction	0.16	0.23
paraffinic C fraction	0.51	0.43
no. of total rings	6.6	7.1
no. of aromatic rings	4.0	3.9
no. of naphthenic rings	2.2	3.2
no. of fused carbon	-0.5	-1.0

In the light of characterization of SCG extract, an aspect of the carbon skeleton structure of these two kerogens may be described. Nearly one half of the total carbon atoms are shown to be paraffinic, one third aromatic and the rest naphthenic. It appears more paraffinic in nature for Fushun kerogen but nearly the same aromatic for these two. It implies that they are close in maturity but perhaps differ in origin precursors to some extent. Unbranched long chains are the overwhelming majority in the paraffinic structure. For the cyclic ring cluster, aromatics are rather cata-condensed with long side chains and adjacent with naphthenics to form hydroaromatic structure. Several clusters linked randomly by different bridges constitute a unit "building block" of the multipolymer --oil shale kerogen.

Minerals in Extracted Shale

X-Ray diffraction and infrared spectra have identified that the bulk mineralogy of those two shales primarily consists of quartz, kaolinite and illite and with few percent of carbonates and pyrite (5). Small changes in sieve analysis of shales before and after extraction indicates that, despite the removal of most of the organic matter, no severe fragmentation of the shale results. This is consistent with SEM morphology observations, minerals are cemented together in various patterns with indigenous clay components to form a continuous phase although the individual inorganic crystals such as quartz and calcite are either partly or entirely encased by organic matter.

Some clay minerals such as montmorillonite will lose crystal layer water at 150-200°C. Samples of these two shales dried at 105°C have been further dehydrated in vacuo at 200°C for two hours, their weight loss is no more than 0.1%. It means that, for these two shales, loss of crystal layer water of clay may be ignored.

Siderite is the carbonate most sensitive to heat, beginning its decarbonization at 370°C. These two shales do contain a little carbonate but they are primarily calcite. The good balance of inorganic carbon dioxide of the shale before and after extraction shows that nearly all the carbonates remain unchanged in the residue.

Quartz and kaolinites are rather stable at extraction temperature. Thermogravimetric analysis of minerals of Maoming oil shale has shown that weight loss detected is negligible below 400°C (11).

The case of pyrite is somewhat different. It is reported (12) that pyrite crystals in the oil shale usually coated with a layer of organic matter are distributed evenly in the kerogen matrix. Microscopic examination has proved that Maoming and Fushun oil shale are not the exception. The finely dispersed bright points in the microphotograph of Maoming kerogen present a distinctive picture of pyrite distribution. As large amount of organic matter is extracted by the solvent, pyrite crystal in kerogen will be entrained with the extracts. The pyrite sulfur content of Maoming shale decreases from 0.96% to 0.57%, which affirms the loss of pyrite in extraction. Fushun oil shale has a lower pyrite content, its loss should be less.

Infrared spectra examinations of the shales before and after extraction show that the characteristic absorption bands of minerals, such as 3620-3670 cm^{-1} for kaolinite, 1070-1160 cm^{-1}

and 910-920 cm^{-1} for Si-O bond, 790-800 cm^{-1} for quartz, either the shape or the intensity, are unaltered; only the bands of pyrite (390, 410 cm^{-1}) are weakened.

Tisot et al. (13) observed that gypsum and iron oxide were formed in heat treatment of Green River oil shale at 750°F exposed to air. It is not the case here, since no oxidation will take place in SCGE process.

It comes to the conclusion that, under the operation conditions of SCGE, no remarkable change has happened to the minerals of these two shales. Accordingly, the pore volume increment and porous structure change of the shale due to the extraction are primarily caused by the removal of the organic matter, though the loss of some pyrite and other individual crystal particles must be borne in mind.

Pore Size Distribution and Pore Volume Increment

Figure 2 shows the relation between the pore radius and accumulative pore volume of two shales before and after SCGE. The solid lines (50-75,000 Å) are plotted according to the data of mercury porosimeter and prolonged in dotted lines (<50 Å) to the total pore volume points. The curve sections at radius larger than 500 Å of these two raw shales coincide with each other but diverge sharply in the smaller radius range. It shows that Maoming oil shale is abundant in micropores and has a much higher porosity (up to 20.9%) than that of Fushun (8.3%). It is not surprising that to such a high porosity of oil shale the average moisture content up to 17% is reported.

Data listed in Table III show that the pore volume increment measured is somewhat larger than the calculated volume of the extract, a little ineluctable loss of mineral slits may lead to the difference. However, it still confirms that the pore volume increment is mainly due to the removal of organic matter.

TABLE III

SOME PROPERTIES OF OIL SHALE AND SCG EXTRACTED SHALE

Item	Fushun		Maoming	
	Oil Shale	Ext. Shale	Oil Shale	Ext. Shale
Organic carbon, wt % ^a	16.3	4.9	17.5	4.4
Ash content, wt %	71.9	84.2	72.0	87.3
Mineral CO ₂ , wt %	3.0	3.5	1.4	1.7
Pyrite S, wt %	-	-	0.96	0.57
True density	2.0428	2.2852	2.0353	2.5731
Particle density	1.3594	1.7457	1.1337	1.4281
Total pore volume (ml/g)	0.083	0.298	0.209	0.494
Extracted shale yield, wt %		85.8		82.2
Pore volume increment (ml/g) ^b		0.173		0.197
Volume of extract (ml/g) ^b		14.0		17.5

a. All weight fractions are on dry basis.

b. On oil shale basis.

In Figure 3, the pore radius is plotted against the pore volume increment fraction, which is the quotient of pore volume increment of different radius and total volume increment. The curve represents distribution structure of organic matter in raw oil shale. Nearly 90% of the organic matter of Maoming oil shale is distributed in the size of radius 300-10,000 Å, one half of which being smaller than 1200 Å; for Fushun oil shale, the corresponding figures are 80-6,000 Å and 500 Å. It reveals that the organic matters of these shales are distributed very finely and evenly in the mineral matrix, especially for Fushun oil shale. The results are consistent with TEM porous structure examinations of the extracted shales. This is another significant difference in physical properties of these two oil shales.

From the view point of oil shale processing technology, the properties of porous structure and organic matter distribution structure are of great importance as related to the reaction mechanism and kinetics of the processes, such as drying, extraction, pyrolysis, gasification and combustion. During these fluid-solid multiphase processes, the fluid reactants should diffuse into the solid phase through the micropores, while the fluid reactants should do the opposite. In our experiments, either in the solvent extraction or in the low temperature oxidation, the reaction speed of Maoming oil shale is much faster than that of Fushun. The structural difference between the pore structure and organic matter distribution must be playing an important part, in addition to the factor of difference in chemical properties of kerogen.

Moreover, the moisture content of oil shale is usually directly related to its porosity. As

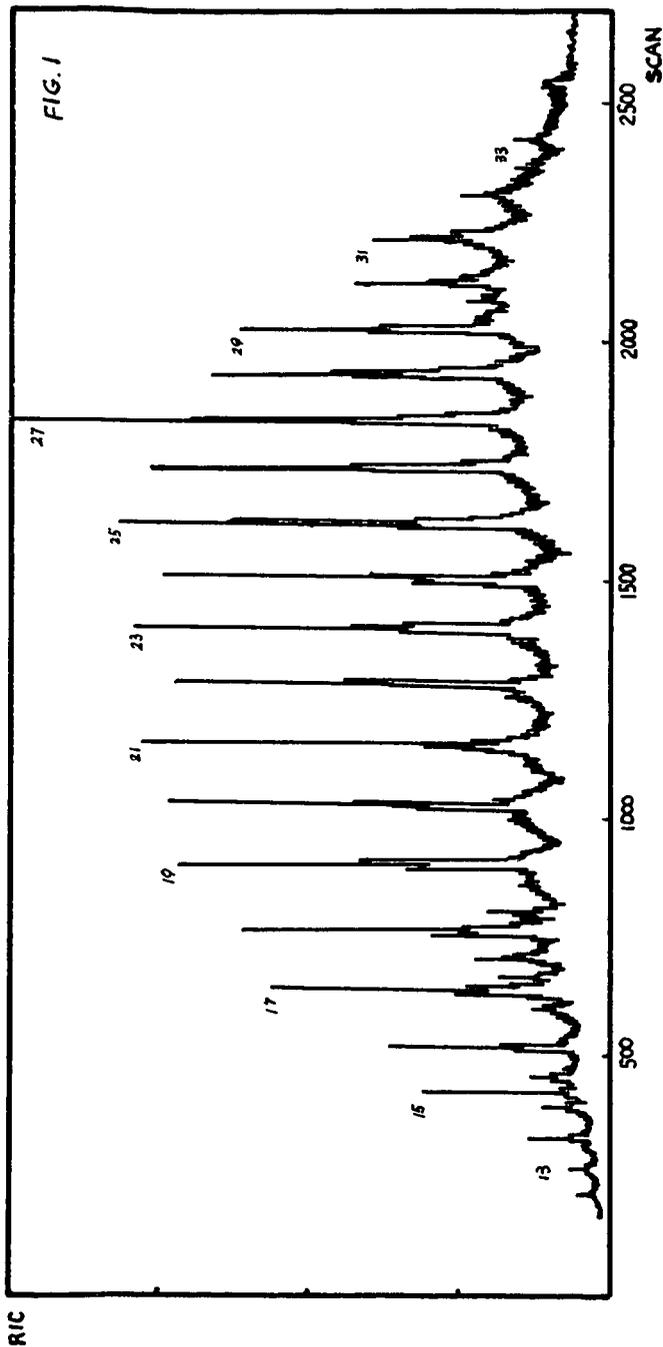


FIGURE 1 TOTAL IONIZATION PLOT OF GAS CHROMATOGRAM OF PETROLEUM ETHER
 ELUATE (MAOMENG OIL SHALE SCG EXTRACT)
 (Arabic numbers indicate number of carbons of n-alkanes)

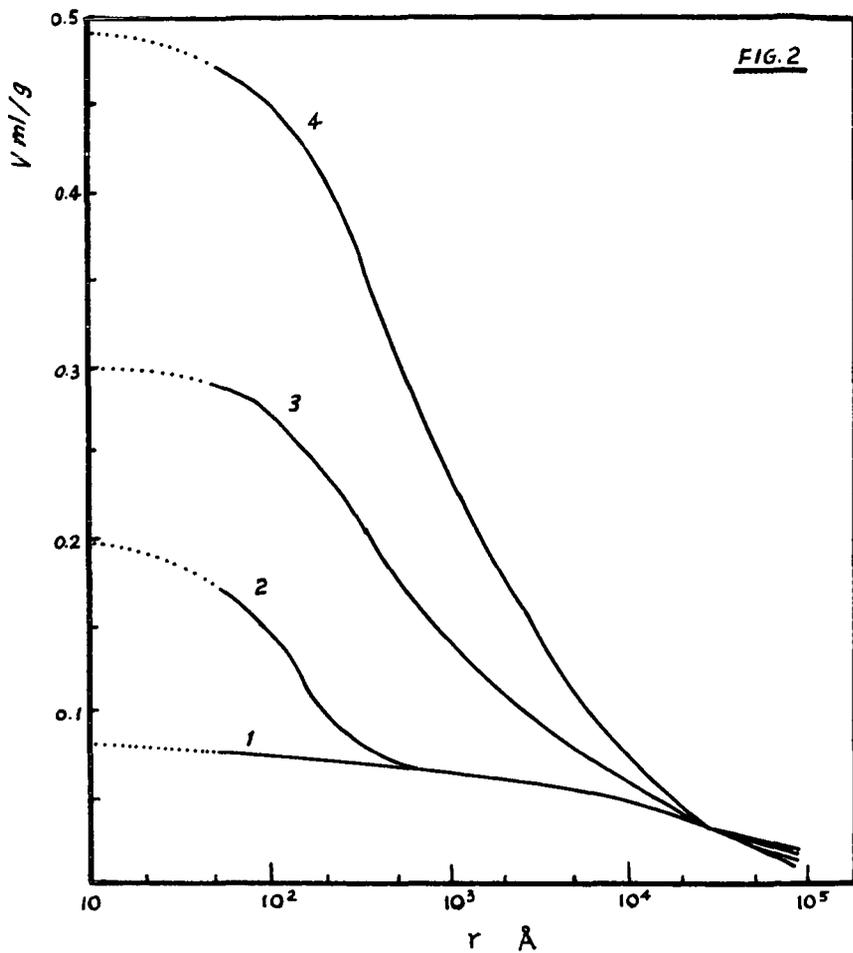


FIGURE 2 RELATION OF PORE RADIUS (r) AND ACCUMULATIVE PORE VOLUME (V)

- 1: Fushun oil shale
- 2: Maoming oil shale
- 3: Fushun extracted shale
- 4: Maoming extracted shale

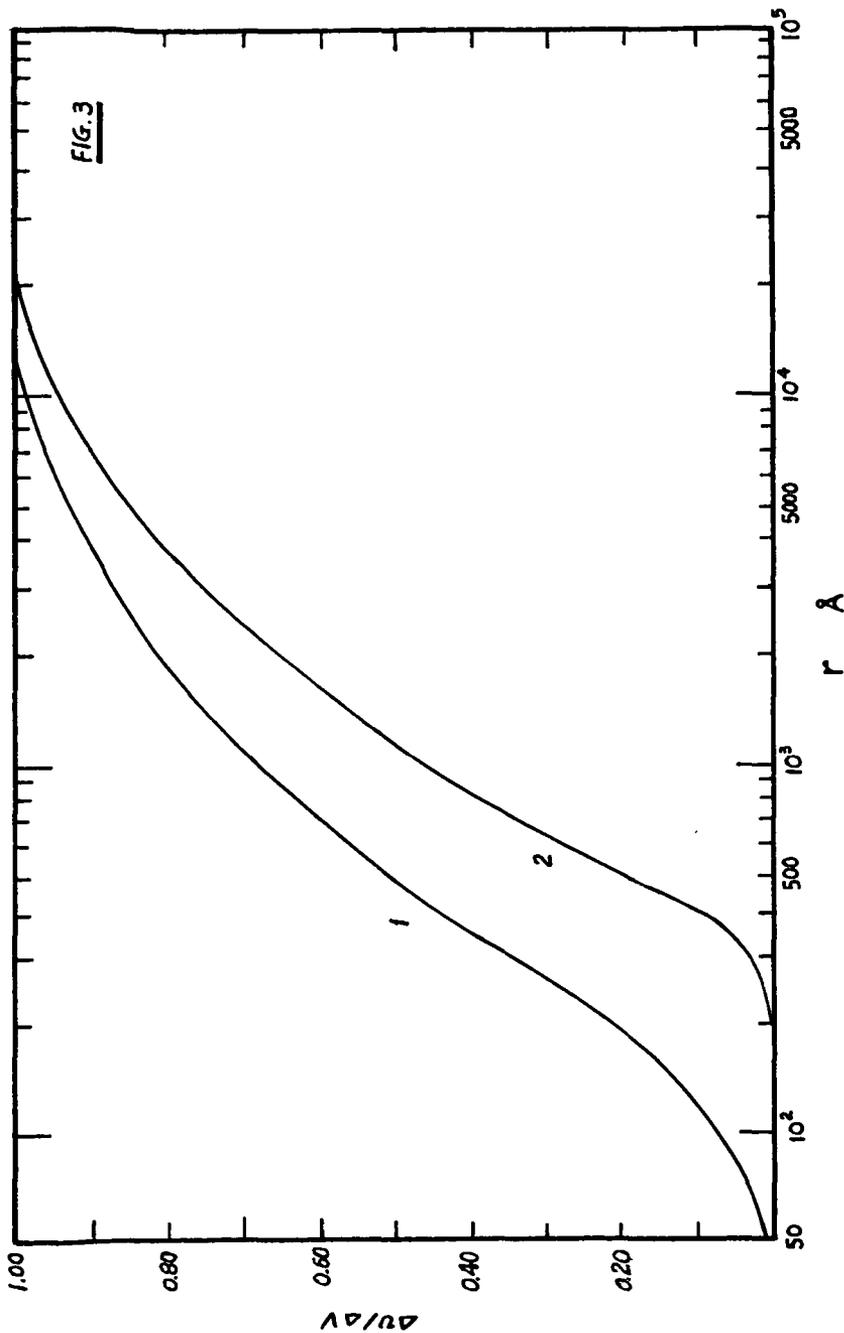


FIGURE 3 RELATION OF PORE RADIUS AND PORE VOLUME INCREMENT FRACTION

mentioned above, Maoming oil shale not only has a high porosity, but also has a very fine pore structure, so that the drying of the shale becomes a tedious process in practice.

Another example is the beneficiation of oil shale. Density of kerogen is nearly 1.0-1.1, density of minerals usually larger than 2.4. It seems to be a simple process to beneficiate the organic matter from shale by density difference, but practically, it is not the case. Many tests of this kind on Fushun and Maoming oil shale failed. It can be found from our present work that the organic matter is mingled so intimately with the minerals that, for Maoming oil shale, successful separation and beneficiation cannot be realized until it is powdered to the size smaller than 1 μm , and for Fushun shale, however, much more powdering is required to achieve the same result. It seems impractical for the conventional mechanical grinding and washing to meet such a requirement.

LITERATURE CITED

- (1) Robinson, W. E. and Cummins, J. J., *J. Chem. Eng. Data*, 5, 74 (1960).
- (2) Young, D. K. and Yen, T. F., *Geochim. et Cosmochim. Acta*, 41, 1411 (1977).
- (3) Wang, R. A., Jia, S. S. and Qin, K. Z., *J. East China Petro. Inst.* 6 (4), 87 (1982).
- (4) Tissot, B., Durand, B., Espitalie, J. and Combas, A., *Amer. Assoc. Petro. Geol. Bull.*, 58, 499 (1974).
- (5) Qin, K. Z., *J. East China Petro. Inst.*, 6 (2), 71 (1982).
- (6) Nutall, H. E., Private communication (1983).
- (7) Qin, K. Z., unpublished data.
- (8) Qin, K. Z., *Symp. of Oil Shale Research Works of East China Petro. Inst.*, in press (1983).
- (9) Yen, T. F., "Oil Shale", Chap. 7, 143, Elsevier, Amsterdam (1976).
- (10) Qin, K. Z., Wang, R. A. and Jia, S. S., *Energy Source* 7 (3), in press (1983).
- (11) Yang, R. T., Chen, D. R. and Qin, K. Z., *Symp. of Oil Shale Research Works of East China Petro. Inst.*, in press (1983).
- (12) Kombaz, A., *Kerogen*, Chap. 3, I. F. P. Paris (1980).
- (13) Tissot, P. R. and Murphy, W. I., *J. Chem. Eng. Data*, 5, 558 (1960).