ANALYTICAL SCIENCE & TECHNOLOGY
(Journal of the Korean Society of Analytical Sciences)
Vol. 8, No. 4, 1995
Printed in the Republic of Korea

Chemical Compositions and Pyrolysis Characteristics of Oil Shales Distributed in Korea

Moon Yul Yang,[†] **Myoung Kee Yang,**[‡] **Sang Hak Lee**[§*] **and Hisanobu Wakita**[‖]

[†] *Laboratory of Chemical Analysis, Korea Institute of Geology, Mining and Materials, Taedok Sicence Town, Taejon, Korea.*
[‡] *Technical Service Center for Engineering Plastics, Tongyang Nylon Co. Ltd., Anyang, Kyungi-Do, Korea.*
[§] *Department of Chemistry, Kyungpook National University, Taegu, 702-701, Korea.*
[‖] *Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Fukuoka 814-01, Japan.*
(Received August 20, 1995)

Abstract : The chemical compositions and pyrolysis characteristics of oil shales and source rocks distributed in the southwestern and southeastern parts of the Korean peninsular have been investigated. In order to compare the results of Korean samples with those of shales giving high oil yields, two Colorado oil shale samples and one Paris source rock samples were also investigated. Chemical compositions of the samples were analysed by means of gravimetry, CHN analysis, X-ray diffraction method, inductively coupled plasma atomic emission spectrometry and atomic absorption spectrometry. A custom made pyrolyser and a Rock-Eval system were used for the pyrolysis studies. Pyrolyses of the samples were carried out by means of a temperature controlling device to 600 ℃ at a heating rate of 5 ℃/min with a helium flow rate of 1200 mℓ/min. The results of pyrolysis study indicated that Colorado shale samples belong to type I and all the other samples belong to type II.

Keywords : Oil shale, Petroleum source rock, Pyrolysis, Hydrogen index, Oxygen index, Kerogen, Hydrocarbon.

1. Introduction

Oil shale is one of the promising sources for the production of synthetic liquid fuels in the next century. Even though there is actually no geological or chemical definition of an oil shale, any shallow rock yielding oil in commercial amount upon pyrolysis is considered to be an oil shale[1]. Several countries have made continuous surveys on the occurrence of large oil shale deposits, with sufficient reserves to justify important investments and the potential to contribute significantly to the demand in oil[2-7]. The requirements regarding the evolution stage are quite different for a petroleum source rock and an oil shale. A petroleum source rock requires a sufficient burial history and the stage of catagenesis in order to degrade a substantial part of kerogen to generate oil[1]. The nature of petroleum source rock is a powerful guide in petroleum exploration. The requirement for potential source rock is the presence of insoluble matter (kerogen) and it is generally accepted that any source rock containing about 0.5% of organic carbon may produce oil or gas[1]. The quality of source rock is defined in terms of amount and types of kerogen and bitumen, and the evolutionary stages of kerogen which is commonly referred to as maturity. Therefore, the prerequisite of source rock evaluation is the improved analytical technique employed to identify the composition in detail. Frequently used analytical methods have been pyrolysis[8-16], total organic carbon determination[1,17], organic petrography[18,19], optical analysis[20], and various organic geochemical analyses[21,22]. The pyrolysis method is the most widely used screening technique for rapid analyses of oil shales or source rocks[1,8]. The Rock-Eval method developed by Espitalie *et al.* involves the use of temperature programmed pyrolysis under an inert atmosphere and subsequent analysis of the product gases[8]. This method also measures the temperature at which maximum cracking of the organic sturucture occurs.

In the present study, we have investigated the chemical composition and pyrolysis characteristics of the oil shale and source rock samples collected from the southwestern and southeastern parts of the Korean peninsular. The main facet of this report concerns the application of our experimental techniques and results to the offshore exploration for petroleum as well as the evaluation of the samples collected in this study. We studied mineral compositions of the samples by X-ray diffraction spectrometry. The major and minor inorganic constituents were analysed by using inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and gravimetry. In order to further characterize the source rock, the total extractable organic matter (TOM) was determined by extraction method. The Rock-Eval analysis was conducted for the samples to evaluate the rock type. In order to compare the results of Korean samples with those of shales giving high oil yields, two Colorado oil shale samples and one Paris source rock sample were also investigated.

2. Experimental

2.1. Samples and Reagents

Two oil shale samples (Uhang-Ri, Uhang-Po) were collected from the black shale distributed at Uhang-Ri and Uhang-Po, Whangsan-Myun, Haenam-Gun, Cholanam-Do, Korea. Two petroleum source rock samples (Daljun, Daeryun) were collected from the Yongil bay tertiary strata distributed in the southeastern part of Korea. Two Colorado oil shale samples (Colorado-1, Colorado-2) and one Paris source rock sample were kindly supplied by the United States Geological Survey.

Metal standard solutions for ICP-AES and AAS measurements were prepared by diluting 1000 ppm stock solution obtained by Spex Industries, Inc. Water purified by a Milli-Q system was used. All the other reagents used were analytical reagent grade.

2.2. Sample Preparation

For ICP-AES and AAS measurements 3 mℓ of concentrated hydrofluoric acid and 3 mℓ of concentrated nitric acid were slowly added to 1 g of sample. The mixture was then heated in a microwave digestion system (CEM, MDS-81D) until dissolution was achieved. The dissolved solution was diluted with deionized water to give a final volume of 100 mℓ.

2.3. Apparatus and Measurements

The contents of SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO and MgO were determined by a classical scheme of analysis[24]. To determine the contents of Na_2O and

K_2O, a Varian 875 atomic absorption spectrometer was employed. All the other inorganic components were analyzed by using a Jobin-Yvon JY 38 Plus ICP-AES system.

A Philips Model 1730 spectrometer using Cu target and Kα radiation was employed for X-ray diffraction measurements. The instrument operating conditions used are as follows: slits, 1°, 0.1°, 1°; accelerating voltage, 40 KV/20 mA; scanning, 2°/min; chart speed, 2 cm/min; range, 3-55°; X-ray dosage, 400 cps.

A Yanaco Model MT-2 was used for organic elemental analyses with carrier gas of high purity helium at a flow rate of 180 mℓ/min and temperature of 850-900 ℃.

In order to measure TOM, 50-80 g of sample was weighed, and 250 mℓ of a mixture solvent of benzene, acetone and methanol (50:25:25 v/v) was added to the sample. This was followed by the extraction using a soxhlet extractor until color of the solvent siphon completely disappeared. The organic matter in the solvent was dried in a vacuum oven at temperature of 50-80 ℃. The organic matter extracted was weighed repeatedly until a constant weight was reached. The TOM was defined by the weight of organic matter extrated (g)/weight of sample (g).

For the pyrolysis studies a homemade pyrolyser[25] and a IFP Rock-Eval system obtained from Techniq Geoproduction, France were used. Samples were ground (<100 mesh) prior to analysis in a boat made from sintered steel. A portion of 50-100 g sample dried in a oven at a temperature of 105 ℃ was weighed and pyrolysis was performed by programming temperature at 5 ℃/min from ambient temperature up to 600 ℃. Helium was used as the carrier gas and the flow rate was adjusted to 1200 mℓ/min. The gaseous products from pyrolysis were divided into two parts by means of a splitter at the highest temperature used. One part of the products was analysed by a flame ionization detector in oder to detect hydrocarbons. The other part was passed through a CO_2 trap which was collected only below a pyrolysis temperature of 400 ℃. This procedure was conducted to ensure that the CO_2 evolved from mineral decomposition was not included in the analysis. During the recycle phase of the temperature programmer, the CO_2 trap was heated to desorb CO_2. A thermal conductivity detector was used to detect the gas passed through a Porapak column.

3. Results and Discussion

3.1. Chemical Composition

Table I represents the results of determination of inorganic components of the samples. Oil shales (Uhang-Ri, Uhang-Po, Colorado-1 and Colorado-2) were found to have relatively high contents of CaO and MgO comparing with source rocks (Daljun, Daeryun and Paris). The source rocks revealed rich contents in SiO_2, Al_2O_3, Fe_2O_3, Na_2O and K_2O comparing with the oil shales. For the trace elements all of the samples showed high contents of V (250-1000 ppm) and B (70-200 ppm) as expected for sedimentary rocks[23,24].

Mineral compositions of the samples were determined using X-ray diffraction patterns and *Table* II shows the results. Montmorillonite was found to be present only in the Korean samples at detectable levels. On the other hand, dolomite was detected only in the Colorado-1, Colorado-2 and Paris samples. Feldspar was not found in the Uhang-Ri and Uhang-Po samples and mica was not present in the Colorado-1 and Colorado-2 samples. The mineral composition was also analysed for the samples pyrolysed. Only montmorillonite and kaolin were disappeared for the pyrolysed samples, which is attributed to the elimination of OH groups during the pyrolysis process.

The results of organic elemental analyses for the samples are shown in *Table* III. For all of the elements analysed the Colorado-1 and Colorado-2 samples showed much higher contents of organic elements than the other samples. The content of carbon is 1.51, 4.74, 2.14 and 2.34% for Uhang-Ri, Uhang-Po, Daljun and Daeryun, respectively. On the other hand, Colorado-1 and Colorado-2 contains 18.94 and 31.57%, respectively. Similar results were observed for hydrogen contents. The Colorado samples also revealed high TOM values. The TOM values were found to be 0.42, 0.43, 1.93, 1.83, 0.07, 0.18, and 0.16% for Uhang-Ri, Uhang-Po, *Table* I. Analytical Data for Inorganic Compositions of Oil Shales and Source Rocks

Analyte	Sample						
	Uhang-Ri	Uhang-Po	Colorado-1	Colorado-2	Daljun	Daeryun	Paris
SiO_2 (%)	38.94	47.64	19.32	21.62	61.12	70.80	42.22
Al_2O_3 (%)	4.76	6.06	4.44	6.07	15.64	10.74	17.35
Fe_2O_3 (%)	1.01	1.32	0.70	1.33	3.25	2.67	3.82
FeO (%)	0.50	0.71	0.85	1.14	1.49	0.85	1.85
CaO (%)	25.35	17.49	28.11	12.13	2.52	1.20	11.76
MgO (%)	5.58	6.99	3.58	4.40	1.85	1.30	2.31
Na_2O (%)	0.58	0.80	1.46	2.13	1.55	1.04	0.47
K_2O (%)	0.20	0.28	0.81	0.05	2.28	1.59	2.37
TIO_2 (%)	0.19	0.24	0.18	0.20	0.48	0.33	0.63
MnO (%)	0.12	0.09	0.13	0.03	0.04	0.10	0.05
SO_3 (%)	0.47	0.92	1.15	3.58	3.52	4.02	4.27
Ba (ppm)	130	30	20	140	70	60	100
B (ppm)	170	70	85	200	190	180	140
Cr (ppm)	23	10	23	20	30	20	25
Cu (ppm)	120	10	15	25	40	50	150
Pb (ppm)	31	11	25	14	31	30	47
Ni (ppm)	50	10	7	10	50	35	40
Rb (ppm)	101	12	8	46	128	140	57
Sc (ppm)	50	180	220	450	100	60	200
V (ppm)	450	350	1000	250	550	280	650
Zn (ppm)	170	46	28	103	452	122	70
Zr (ppm)	121	140	149	279	252	210	125

Table II. Mineral Compositions of Oil Shales and Source Rocks obtained by X-ray Diffraction Analysis

Sample	Mineral
Uhang-Ri	montmorillonite, quartz, mica, calcite
Uhang-Po	montmorillonite, quartz, mica, calcite
Colorado-1	dolomite, quartz, feldspar, calcite
Colorado-2	dolomite, quartz, feldspar, calcite
Daljun	montmorillonite, quartz, feldspar, mica, calcite
Daeryun	montmorillonite, quartz, feldspar, mica
Paris	dolomite, quartz, feldspar, mica, calcite

Table III. Summary of Results for Elemental Analyses of Oil Shales and Source Rocks[a]

Sample	C	H	N	S	P
Uhang-Ri	1.51	0.39	0.02	0.37	0.02
Uhang-Po	4.74	0.32	-	0.19	0.02
Colorado-1	18.94	1.55	0.32	0.45	0.19
Colorado-2	31.57	3.89	0.34	1.43	0.20
Daljun	2.14	0.34	0.04	1.41	0.03
Daeryun	2.34	0.74	0.10	1.91	0.02
Paris	4.47	0.77	0.23	1.71	0.03

[a]Units are in %.

Colorado-1, Colorado-2, Daljun, Daeryun and Paris, respectively.

3.2 Pyrolysis Characteristics

Table IV represents the values of S_1, S_2, S_3, *Table* IV. Summary of Results for Pyrolyses of Oil Shales and Source Rocks[a]

Sample	S_1[a]	S_2[b]	S_3[c]	T_{max}[d] (℃)	TOC (%)
Uhang-Ri	2.84	0.66	0.36	449	0.94
Uhang-Po	4.40	0.85	0.53	446	1.20
Colorado-1	5.28	65.01	3.76	434	8.60
Colorado-2	6.70	203.0	5.90	443	22.24
Daljun	0.08	1.60	1.05	423	1.48
Daeryun	0.12	4.84	0.31	420	1.84
Paris	0.04	5.54	0.67	429	1.80

[a]S_1: free hydrocarbon present in the sample. [b]S_2: hydrocarbon produced during kerogen cracking. [c]S_3: CO_2 produced from pyrolysis. [d]T_{max}: pyrolysis temperature at the top of S_2 peak.

Table V. Hydrogen Index, Oxygen Index and Production Index for Oil Shales and Source Rocks

Sample	HI[a]	OI[b]	PI[c]
Uhang-Ri	438	442	0.84
Uhang-Po	372	38.3	0.81
Colorado-1	817	43.7	0.08
Colorado-2	943	26.5	0.03
Daljun	114	70.9	0.05
Daeryun	270	16.8	0.02
Paris	313	37.2	0.01

[a]HI : hydrogen index (S_2/TOC). [b]OI : oxygen index (S_3/TOC). [c]PI : production index.

T_{max} and total organic carbon obtained by a Rock-Eval system. S_1 value indicates the free hydrocarbons (HC) present in the sample. S_2 is defined by the HC produced during kerogen cracking. Both S_1 and S_2 are given in mg (HC)/g of sample. Since S_2 value directly gives the quantity of HC produced by thermal conversion of kerogen contained in rock sample, it is a good indicative of rock quality. Quite contrary to the cases of Colorado shales and source rocks, Uhang-Ri and Uhang-Po samples gave higher S_1 values comparing with their S_2 values. This may be ascribed to the small contents of kerogen comparing with the relatively large amount of bitumen included in the samples. T_{max} is definded by the temperature at the top of S_2 peak, which is the temperature in ℃ when maximum generation of HC from kerogen occurs. Therefore, this value gives information about the degree of maturation of organic matter. T_{max} is commonly divided into three categories: T_{max}<430-435 ℃, immature zone; 430-435 ℃ <T_{max}<465 ℃, oil zone; T_{max}>465 ℃, gas zone[1]. According to this classification Uhang-Ri, Uhang-Po, Colorado-1 and Colorado-2 samples fall under the oil zone catagory. On the other hand, Daljun, Daeryun and Paris samples belong to the immature zone.

Using the hydrogen index and the oxgen index the different types of organic matter can be classified[1]: Type Ⅰ, very good source rocks and oil rich shales; Type Ⅱ, good source rocks; Type Ⅲ, mediocre source rock and/or source rocks for gas. The hydorgen index (HI) and oxygen index (OI) are defined as HI=S_2/TOC (mg HC/g TOC) and OI=S_3/TOC (mg CO_2/g TOC), where TOC is total organic carbon. The content of TOC was calculated from the sum of residual and pyrolysed organic carbon. Production index (PI) is the $S_1/(S_1+S_2)$ ratio and this value also gives information on the degree of maturation of the organic matter[1]. *Table* V shows the values of HI, OI and PI for all the samples investigated. The results indicate that Colorado-1 and Colorado-2 shale samples belong to type Ⅰ and all the other samples belong to type Ⅱ.

Acknowledgement

The financial supports from the Ministry of Science and Technology of Korea is greatly acknowledged.

References

1. B. Tissot and D. H. Welte, "Petroleum Formation and Occurence", Springer-Verlag, Berlin, 1978.
2. N. V. Dung, *Fuel*, **68**, 1570 (1989).
3. N. V. Dung, G. C. Wall and G. Kastl, *Fuel*, **66**, 372 (1987).

4. G. C. Wall and P. Udaja, *Fuel*, **67**, 1340 (1988).
5. N. V. Dung, *Fuel*, **68**, 1570 (1989).
6. N. V. Dung, *Fuel*, **69**, 368 (1990).
7. J. Espitalie, M. Madec and B. Tissot, *Am. Assoc. Pet. Geol. Bull.*, **64**, 59 (1980).
8. J. Espitalie, J. L. Laporte, M. Madec, F. Marquis, P. Leplat, J. Poulet and A. Boutefeu, *Rev. Inst. Fr. Petrole*, **32**, 32 (1977).
9. C. Barker, *Am. Assoc. Pet. Geol. Bull.*, **58**, 2349 (1974).
10. J. Espitalie, M. Madec and B. Tissot, "Source Rock Characterization Method Petroleum Exploration", Presented at the 9th Ann. Offshore Tech. Conf., Houston, May, 1977.
11. V. D. Alled, *Chem. Eng. Progr.*, **62**(8), 55 (1966).
12. R. L. Braun and A. J. Rothman, *Feul*, **54**, 129 (1975).
13. K. Kuroda, A. Suzuki, M. Kato and K. Imai, *J. Anal. Appl. Pyrolysis*, **34**, 1 (1995).
14. T. A. Centeno, J. J. Pis, J. A. Pajares and A. B. Fuertes, *J. Anal. Appl. Pyrolysis*, **34**, 13 (1995).
15. S. H. Lee and M.Y. Yang, *J. of Korean Ind. & Eng. Chemistry*, **2**, 185 (1991).
16. M. Y. Yang, S. H. Lee and J. T. Park, J. *Korenan Chem. Soc.*, **35**, 737 (1991).
17. J. M. Hunt, "Petroleum Geochemistry and Geology", W. H. Freeman, San Francisco, 1979.
18. M. Teichmuller and R. Teichmuller, *Bull. Centres Rech. Explor*, 5(2), 491 (1891).
19. W. G. Dow, *J. Geochem. Explor.*, **7**, 79 (1977).
20. O. T. Tuo and E. E. Etuk, *J. Geochem. Explor.*, **37**, 285 (1990).
21. D. H. Welte, M. A. Yukler, M. Radke and D. Leythaeuser, "Origin and Chemistry of Petroleum", A. Gordon and J. J. Zuckermann, Ed., Pergamon Press, Oxford, 1981.
22. A. A. K. Mohammed, *Analyst*, **110**, 1477 (1985).
23. Y. O. Son, D. Y. Song, S. H. Lee, C. H. Eum and J. T. Park, Research Report: No. KR-88-3A-1; KIER, Korea, 1988.
24. P. J. Potts, "A Handbook of Silicate Rock Analysis", Blackie and Son Limited, Glasgow, 1987.
25. M. Y. Yang, Ph. D. Dissertation, Fukuoka University, 1993.