Analysis of the Organic Matter in Oil Shales Distributed in Korea

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The organic matter in source rocks and oil shales distributed in the southeastern and southwestern parts of the Korean peninsular has been analyzed. A mixture of benzene, acetone and methanol was used to extract bitumen by Soxhlet extraction method. The extractable organic matter was separated into aliphatic hydrocarbons, aromatic hydrocarbons, and asphaltene by preparative thin layer chromatography. By urea adduction method, aliphatic hydrocarbons were separated into linear aliphatic hydrocarbons and cyclic or branched aliphatic hydrocarbons. The aliphatic hydrocarbons were analyzed by GC/FID and GC/MS. The gas chromatograms for linear aliphatic hydrocarbons showed the distribution of C_{12} – C_{35} compounds. Generally, the odd number hydrocarbons were detected more than the even number hydrocarbons. From the total ion chromatograms and mass spectra of cyclic and branched aliphatic hydrocarbons, several compounds including 1-methylpropyl-cyclohexane were identified.

Keywords Soxhlet extraction, bitumen, preparative thin layer chromatography, aliphatic hydrocarbons, oil shale

Oil shales 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 oil shale, any shallow rock yielding oil in commercial amount upon pyrolysis is considered to be an oil shale.¹ The quality of oil shale is generally evaluated by the amount and types of kerogen and bitumen, and the evolutionary stages of kerogen which is commonly referred to as maturity.² Bitumen is termed for the naturally occurring hydrocarbon substances such as oil, asphalt and ozocerite (mineral wax), and the organic solvent extracts from various sedimentary rocks, soils, coal and oil shale.¹ Hydrocarbons are the main constituents of naturally occurring bitumen. It is widely accepted from geological and chemical evidence that hydrocarbons result from alteration of organic matter within sedimentary rocks under the influence of temperature and pressure.¹ The occurrence of hydrocarbons and related substances is known from a wide range of living organisms, many of which have been found in sediments and in crude oils. Numerous types of hydrocarbons or substances with a similar carbon skeleton have been traced from the living organisms into sediments.³⁻⁵ Source potential for hydrocarbons is dependent on the type and quantity of the organic matter, whereas the

generation potential for hydrocarbon is controlled by the extent of thermal evolution of organic matter.⁴ Therefore, the prerequisite of source rock evaluation is the improved analytical techniques employed to determine the composition in detail. Frequently used analytical methods have been pyrolysis,⁶⁻¹¹ total organic carbon determination,^{11,12} organic petrography,^{1,4,13} optical analysis,¹⁴ and various organic geochemical analyses.^{15,16}

In the present study, we have investigated the chemical composition and organic geochemical 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 methods for the extraction of organic matter, separation of extracts into different groups and identification of individual compounds. Bitumen was extracted by a soxhlet extraction method and the extracts were separated into saturated hydrocarbons, aromatics and asphaltene by preparative thin layer chromatography (prep-TLC). The n-alkanes were separated by urea adduction method and the distribution of n-alkanes for each sample was investigated by gas chromatography. The branched and cyclic hydrocarbons were characterized by gas chromatography mass spectrometry and some individual compounds were identified.

Experimental

Samples

Three petroleum source rock samples were collected from the Yongil bay tertiary strata distributed in the southeastern part of Korea (Kyungpook Province): sample A (Uhyun-Dong, Pohang-Si); sample B (Yongheung-Dong, Pohang); sample C (Hakjon-Dong, Yonil-Eub). Samples D and E were collected from the southwestern part of Korea (Chunnam Province): sample D (Uhangpo); sample E (Sinseongri). The E sample was taken from the 33.1 m section of the Sinseongri-1 well.

Materials and reagents

The sources of the reagents were as follows: magnesium sulfate (GR), calcium chloride (GR), benzene (GR) and hexane (GR) from Junsei (Tokyo, Japan); silica gel and TLC plate from Merck (Darmstadt, Germany); concentrated hydrochloric acid and berberine sulfate (neutral sulfate) from Sigma (St. Louis, MO, USA); chloroform (HPLC grade) and cupric sulfate from J. T. Baker (Phillipsburg, NJ, USA); methanol (LC grade) from Fluka (Buchs, Switzerland); cyclohexane (EP) from Yakuri (Osaka, Japan). All other chemicals were of analytical reagent grade. Thimble filters (23×90 mm) used for Soxhlet extraction were purchased from Whatman (Maidstone, England).

Instrumentation

A Yanaco Model MT-2 (Kyoto, Japan) 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 °C. The apparatus used for prep-TLC was a Model Linomat III (CAMAG, Muttenz, Switzerland). A Hewlett-Packard (HP) 5890 series II gas chromatograph was used with a flame ionization detector, a HP 7673A autosampler and a HP 5895A Chemstation for GC analysis. GC/MS analyses were carried out on a Varian Model 3700 GC (Varian, Australia) equipped with a Varian MAT 212 mass spectrometer. The instrumental components and operating conditions used in this work are summarized in Table 1. These operating conditions were selected after the optimization of each parameter.

Analytical method

The schematic outline of the analytical procedures used in this study is given in Fig. 1. The raw samples were crushed using a jaw crusher (DFCC, 2P2P5) and were then pulverized with a pulverizer (BICO, MFD, UD 32) to pass a 140 mesh screen. The resulting powder was dried at 80 °C over anhydrous MgSO₄ in an oven for 24 h, re-dried over anhydrous CaCl₂ at room temperature under reduced pressure (0.2 torr) in a vacuum oven, and stored in a

Table 1 Instrument components and operating conditions for GC and GC/MS

GC	HP 5890 II
	HP 7673A autosampler
	HP 5895A Chemstation
Column	capillary ^a
Oven Temp ^b	30–150 °C, 15 °C/min
	150–290 °C, 3 °C/min
	10-min hold
Injection	
Type	split (30:1)
Temp	270 °C
Detector	
Type	FID
Temp	300 °C
Flow rate	
Column	2 mL/min (N ₂)
Make-up gas	23 mL/min (N ₂)
H ₂	42 mL/min
Air	350 mL/min
GC-MS	
GC	Varian 3700
Column	capillary ^c
Injection	
Type	Open
Temp	25 °C
MS	Varian MAT 212
Ionization	electron impact
Electron energy	70 eV
Emission current	1 mA
Source temp	200 °C

a. Fused silica capillary column (SE-30, 0.25 mm id×30 m, 0.25 µm film thickness). b. These conditions are also used in GC-MS. c. Fused silica capillary column (HP-1, 0.53 mm id×5 m).

desiccator.

The extraction of organic matter from sample (50g) was performed in a Soxhlet apparatus with a 250 mL mixture of benzene, acetone and methanol (50:25:25, v/v) for 72 h. The solvent was removed by rotary evaporation at room temperature and the resulting extractable organic matter (EOM) was weighed.

For prep-TLC, a Merk TLC plate coated with 2 mm silica gel without fluorescence indicator was used. The plate was prewashed in two directions using a mixture of chloroform/methanol (1:1, v/v) and ethylacetate respectively. Prior to use the plate was activated for 30 min at 110 °C. The extract was spotted on to the plate by using a CAMAG apparatus. Elution was carried out using cyclohexane for 2 h. Visualization was performed using 0.5% methanol solution of berberine sulfate and examination of the bands with UV lamp. The

Fig. 1 Schematic outline of the experimental procedures to analyze extractable organic matter in sedimentary rocks.

resulting bands were then removed. The aliphatic and aromatic bands were extracted with chloroform. The asphaltene band was extracted with chloroform and methanol in sequence. Elemental sulfur was removed from the fractions of aliphatic compounds by precipitating in the form of CuSO_4 .¹⁷

Results and Discussion

Extractable organic matter

The analytical results of total organic carbon (TOC) and extractable organic matter (EOM) are summarized in Table 2. The contents of TOC ranged from 1.18–1.25% for all of the samples except sample B. The EOM content of sample B was also lower than those of the rest of the samples. In general, samples collected from the southeastern part of Korea (D and E) gave higher contents of EOM and bitumen ratio than samples collected from the southwestern part of Korea. The differences in bitumen ratio between the samples of the two different area may suggest different degree of maturity and/or different source input.

The results of prep-TLC are summarized in Table

Table 2 Total organic carbon (TOC) and extractable organic matter (EOM)

Sample	TOC	EOM	Bitumen ratio ^a
A	1.18	0.20	17
B	0.35	0.08	20
C	1.23	0.58	47
D	1.20	0.59	49
E	1.25	0.45	36

a. Ratio of EOM/TOC.

Table 3 Summary of fractions separated by preparative thin layer chromatography from the extractable organic matter

Sample	SAT ^a (%)	ARO ^b (%)	ASP ^c (%)	Ratio (SAT/ASP)
A	68.9	8.5	22.5	3.1
B	45.5	15.7	38.8	1.5
C	52.0	17.3	30.5	1.7
D	80.7	8.0	11.3	7.1
E	73.9	11.4	14.8	5.0

a. Saturated. b. Aromatics. c. Asphaltene.

Table 4 Summary of gas chromatographic analyses of n-alkane compounds in the saturated hydrocarbon fraction

Sample	Distribution	Maxima	Ratio ^a
A	C ₁₁ –C ₂₇	C ₁₇	0.74
B	C ₁₂ –C ₂₇	C ₁₅ , C ₁₇ , C ₁₉	0.68
C	C ₁₁ –C ₂₈	C ₁₅ , C ₁₇	1.9
D	C ₁₄ –C ₃₃	C ₂₁ , C ₂₃	0.32
E	C ₁₃ –C ₃₄	C ₂₁ , C ₂₂ , C ₂₃	0.28

a. Ratio of branched and cyclic hydrocarbons/n-alkanes.

3. The contents of saturated hydrocarbon (SAT) and the ratio of SAT to asphaltene for D and E samples were generally higher than A, B and C samples. It is interesting to note that sample C gave relatively higher contents of aromatic compounds.

Analysis of saturated hydrocarbons

The separation of straight-chain alkanes from the saturated hydrocarbon fraction was performed by using the urea adduction method.¹⁸ The GC chromatograms recorded by using fused silica capillary column were well-shaped and similar in shape for all of the samples, with the distribution of n-alkane in the range of approximately C₁₁–C₃₄ and maxima at C₁₅–C₂₃. The Bimodal n-alkane distribution reported for the sample collected from the

Table 5 Branched and cyclic hydrocarbons in the saturated hydrocarbon fraction identified by GC/MS for sample C

RT, min	Compound (Characteristic ions)
6.79	(1-Methylpropyl)-cyclohexane (55,83,179)
7.00	2,9-Dimethyldecane (43,57,99,170)
7.85	6-Ethyl-2-methyldecane (43,57,71,113)
8.49	2,3,7-Trimethyldecane (43,57,97,127)
8.85	2,6,10-Trimethyldodecane (57,71,141,196)
8.94	2-Cyclohexyloctane (41,111,141)
9.06	5,8-Diethyldodecane (41,111,141)
9.69	3-Methyl-8-propyldodecane (57,71,119,246)
10.51	3-Methylhexadecane (57,85,126)
10.64	4-Methylheptadecane (43,154,179)
11.08	1-Nonadecene (41,97,207)
11.58	2-Methylhexadecane (43,71,183,193)
12.79	1-Octadecane (57,85,183,207)
12.90	2-Methylnonadecane (43,71,179)
13.22	3-Methyleicosane (43,83,119)
14.16	(1-Propylheptadecyl)-cyclohexane (55,83,238)
16.40	(1-Hexyltetradecyl)-cyclohexane (41,83,165,196)
17.42	9-Cyclohexyleicosane (57,71,239,253)
17.96	17-Pentatriacontene (43,71,273)

base of the cliff at Port Mulgrove, North Yorkshire was not observed for all of the samples studied in the present work.¹⁹ In addition, for all of the samples, the odd-carbon-number predominance was observed in n-alkanes of medium molecular weight (C_{15} – C_{25}). The summary of n-alkane distribution and its maxima for each sample is represented in Table 4. For the A, B and C samples, the maxima abundances observed at C_{15} – C_{19} indicate that the origin for the organic matters in these samples is a lower plant such as cyanobacteria and algae. The D and E samples gave similar gas chromatographic results in terms of the n-alkane distribution and the most abundant compounds. Maxima in abundance at C_{21} – C_{23} for these samples suggest that the organic matters in this sample originate from lower land plants such as mosses. The ratios of branched and cyclic hydrocarbons to n-alkanes are also given in Table 4. Of importance to note is that the Sample C is unique in this ratio within the samples studied in the present work. The exceptionally high concentration of branched-alkane compound in this sample may be explained as due to the process of biodegradation. The n-alkanes are known to be depleted in the oils when certain bacteria contacts oils.^{1,4}

The analyses of branched and cyclic hydrocarbons were performed by using GC/MS. Identification of compounds was accomplished by comparison of obtained spectra with archived and literature spectra, and, in most cases, was verified by comparison with

known compounds. Selected ion monitoring was also carried out by monitoring different m/z values to characterize each compound. The GC/MS results for sample C is summarized in Table 5. To be noted here is that the compounds identified in the present study are not complete. The detailed structural identification of iso-alkanes, aromatics, asphaltenes and kerogen is being studied in this laboratory.

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