

COMPARISON OF FISCHER ASSAY SHALE OILS PRODUCED FROM DIFFERENT OIL SHALES

by

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ABSTRACT

Twelve oil shales from various deposits throughout the world were compared by studying the chemical composition of their Fischer assay-produced oils. Two Chinese oil shales, four United States oil shales, two Australian oil shales, two Israeli oil shales, one Turkish oil shale, and one Moroccan oil shale were Fischer assayed to produce shale oils that were then characterized by separation techniques. The oil shales ranged in geologic age from Devonian to Tertiary and represented widely different depositional environments and precursor source materials. Fischer assay oils were fractionated into different compound types before characterization. The isolated fractions were characterized by gas chromatography. In addition, elemental analyses of all shale oils and solid-state carbon-13 nuclear magnetic resonance spectra of the raw shales were obtained for comparison with other results.

The Chinese, Green River, Australian and Turkish oil shales, which were of Tertiary age and lacustrine environment, produced more aliphatic shale oils containing larger amounts of both low and high carbon number alkanes. On the contrary, the other six older oil shales, which were of marine sediments, produced more aromatic shale oils containing lower carbon number alkanes.

INTRODUCTION

There are many oil shale deposits throughout the world that were formed from different geological environments during different geological times. It is of interest to compare the composition of these oil shales so that the oil potential of each major oil shale deposit can be predicted. Robinson and Dinneen (1) compared the kerogen and the benzene-extracted bitumen in the oil shales from 12 countries with various physical and chemical methods. The kerogen types in several worldwide oil shales were classified by Tissot et al. (2) using a Van Krevelen diagram. Nuttall et al. (3) studied the pyrolysis kinetics of 16 key world oil shales using thermogravimetric analysis. Miknis et al. (4) used solid-state nuclear magnetic resonance (NMR) to measure the genetic potential of a variety of oil shales. In our work, the Fischer assay was used to convert 12 oil shales from six countries into shale oils that were then

characterized. The compositional differences in these shale oils and in the corresponding oil shales are discussed.

EXPERIMENTAL SECTION

Sample Preparation and Analyses

Shale oils were produced for characterization using the Fischer assay procedure. The procedure consists of heating a 100 g sample of oil shale to 500°C at a rate of 12°C/min, and maintaining this temperature for 40 minutes. The produced shale oils are collected and the assay results reported in weight percentage of the raw shale.

Elemental analyses were obtained on the oil shales and produced oils. Solid-state ^{13}C NMR determinations of the aliphatic and aromatic carbon fractions in the oil shales were made at the NSF Regional NMR Center at Colorado State University in Fort Collins, Colorado. Analytical and geological data for the oil shales are summarized in Table 1.

Separation Procedures and Fraction Analyses

The light end (<C9) was removed from each Fischer assay shale oil by first distilling the shale oil at the condition required to strip solvents from all the fractions obtained from various separations. The separation method used is similar to those reported previously (5). The asphaltene was removed by using normal pentane. The deasphalted oil was separated on an alumina column into hydrocarbons and polars. Hydrocarbons were further separated into alkanes-plus-alkenes and aromatics on a silica gel column. Twenty percent silver nitrate-silica gel was used to separate alkanes and alkenes. The overall material recovery for all the above column separations was over 93%. The amounts for all isolated fractions reported in this work were normalized to 100%.

The alkanes and alkenes were independently analyzed on a Hewlett-Packard 5830A gas chromatograph (GC) with a flame ionization detector using helium as a carrier gas. The GC column was a 60m x 0.259 mm i.d. DB-1 fused silica capillary column.

RESULTS AND DISCUSSION

The Tertiary lacustrine oil shales are characterized by high aliphatic carbon fractions (>0.65), and high percentages (>56%) of organic carbon converted to oil during Fischer assay (Table 1). The marine shales have lower percentages of organic carbon conversions to oil and generally lower aliphatic carbon fractions, i.e., are more aromatic. However, there are noticeable exceptions in both the NMR and conversion data for both types of shales. For example, one marine oil shale from Alaska (sample 10), which is comprised mainly of the algae microfossil Tasmanites, has the highest aliphatic carbon

Table 1. Analytical and Geological Data of Oil Shales

| Sample | Country | Oil, Wt % | Shale Org. C, Wt % | Fraction of Aliphatic Carbon | % of Carbon Converted to Oil | Remarks |
|--------|------------------|--------------|--------------------------|------------------------------------|------------------------------------|---|
| 1 | China | 12.6 | 18.1 | 0.65 | 59.3 | Fushun, Tertiary, Lacustrine |
| 2 | China | 8.2 | 12.4 | 0.68 | 56.1 | Maoming, Tertiary, Lacustrine |
| 3 | United States | 10.2 | 13.8 | 0.74 | 61.5 | Colorado Green River Formation, Tertiary, Lacustrine |
| 4 | Australia | 11.3 | 15.3 | 0.74 | 62.5 | Rundle Deposit, Kerosene Creek Member, Tertiary, Lacustrine |
| 5 | Australia | 10.0 | 13.2 | 0.77 | 64.4 | Rundle Deposit, Ramsey Crossing Member, Tertiary, Lacustrine |
| 6 | Turkey | 3.2 | 9.1 | 0.69 | 29.4 | Goynuk Deposit, Tertiary, Lacustrine |
| 7 | Morocco | 4.0 | 7.6 | 0.60 | 41.5 | Timahdit Deposit, Cretaceous, Marine |
| 8 | Israel | 8.6 | 14.6 | 0.65 | 46.3 | Rotem Deposit, Cretaceous, Marine |
| 9 | Israel | 2.9 | 11.9 | 0.61 | 18.8 | N. Tsin Deposit, Cretaceous, Marine |
| 10 | United States | 54.2 | 59.4 | 0.80 | 77.9 | Alaska, Jurassic, Marine |
| 11 | United States | 8.3 | 18.1 | - | 37.1 | Alaska, Jurassic, Marine |
| 12 | United States | 5.6 | 13.7 | 0.55 | 34.6 | Kentucky New Albany Formation, Devonian, Marine |

fraction and carbon conversion during Fischer assay. Also, the Turkish oil shale (sample 2) and one of the oil shales from Israel (sample 9) have low carbon conversions to oil during Fischer assay, despite their high aliphatic carbon fractions. In the authors' opinion, the low conversion yields of these shales is more anomalous than it is typical of shales from these deposits.

The composition of the Fischer assay oils from the 12 oil shales are listed in Table 2. The organic carbon contents of the oils varies from 77.2 wt % to 85.4 wt %. The atomic H/C ratio ranges between 1.31 and 1.73. The shale oils derived from the six Tertiary lacustrine oil shales, including two Chinese oil shales, have higher atomic H/C ratios than those obtained from the marine oil shales, except sample 10. The specific gravities of the six lacustrine shale oils all ranges from 0.87 to 0.91, and the amounts of N+S+O% are all less than 3.7%, except in the Turkish shale oil. Other older oil shales, except sample 10, produced shale oils with specific gravities larger than 0.9 and N+S+O% larger than 5%. The N+S+O% in the shale oils derived from Moroccan and two Israeli oil shales are even larger than 10%. Nevertheless, the shale oil produced from the relatively old Jurassic marine Alaskan oil shale (sample 10) has a high H/C ratio (1.69), low specific gravity and low N+S+O% (2.6). This exception to the above general trend is probably caused by the different biological precursors for the shale. The above results suggest that the properties of Fischer assay oil derived from each oil shale not only relate to depositional environment of the oil shale but also correlate to the kerogen type (6).

The amounts of various compound types isolated from 12 shale oils are also given in Table 2. These results show that the amount of each fraction may vary with geological time, depositional environment and kerogen type of the oil shale. The amounts of alkanes, aromatics and polars differ significantly and have their own pattern. The Fischer assay oils of six Tertiary lacustrine oil shales contain alkanes from 13.41 to 25.14%, but those of marine oil shales except sample 10, only contain alkanes from 2.41 to 12.29%. The variation in the amount of aromatic hydrocarbons is just the opposite. The lacustrine shale oils, except Turkish shale oil, only contain 4.87-8.46% aromatic hydrocarbons, but the marine shale oils contain 11.55%-21.74% aromatic hydrocarbons.

To summarize the above results, the amounts of alkanes and aromatics in the shale oils seem to depend upon the depositional environment of the corresponding oil shales. Furthermore, Tissot et al. (2) pointed out that the kerogen type directly affects the hydrocarbon composition of the pyrolysis products of oil shale. It is known that Green River, Chinese Fushun and Maoming oil shales, the two Australian shales, and the Turkish oil shale all represent type I kerogen. Their precursors are basically similar and they were deposited under lacustrine environments. Because of these similarities, their pyrolysis products obtained under the same

Table 2. Composition of Fischer Assay Oils

| Composition | Oil Shale Sample | | | | | | | | | | | | |
|--------------------------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | |
| Elemental Analysis, wt % | | | | | | | | | | | | | |
| C | 85.2 | 84.8 | 83.2 | 84.6 | 85.0 | 83.7 | 78.9 | 78.6 | 77.2 | 85.4 | 81.0 | 84.6 | |
| H | 12.3 | 11.5 | 12.2 | 11.9 | 12.2 | 11.1 | 9.6 | 10.0 | 8.4 | 12.0 | 10.3 | 10.0 | |
| N | 1.3 | 1.2 | 1.7 | 1.2 | 1.0 | 0.8 | 1.4 | 1.2 | 1.9 | 0.4 | 0.3 | 1.5 | |
| S | 0.6 | 0.4 | 0.7 | 0.8 | 0.6 | 1.5 | 7.2 | 7.6 | 6.0 | 0.9 | 3.6 | 1.6 | |
| O | 0.6 | 2.1 | 2.2 | 1.5 | 1.2 | 2.9 | 2.9 | 2.6 | 6.5 | 1.3 | 4.8 | 2.3 | |
| H/C | 1.73 | 1.63 | 1.76 | 1.69 | 1.72 | 1.59 | 1.46 | 1.53 | 1.31 | 1.69 | 1.53 | 1.42 | |
| Specific gravity | 0.880 | 0.907 | 0.890 | 0.888 | 0.873 | 0.882 | 0.966 | 0.964 | - | 0.873 | 0.914 | 0.940 | |
| Fractions, wt % | | | | | | | | | | | | | |
| Light end | 1.09 | 1.63 | 4.99 | 1.76 | 1.26 | 4.25 | 2.49 | 2.09 | 4.40 | 3.79 | 2.01 | 2.69 | |
| Asphaltene | 3.31 | 5.71 | 2.42 | 3.55 | 2.00 | 1.47 | 3.62 | 3.23 | 12.82 | 1.85 | 0.97 | 8.86 | |
| Alkanes | 25.14 | 16.92 | 18.03 | 15.65 | 19.09 | 13.41 | 6.44 | 5.76 | 2.41 | 16.41 | 12.29 | 7.68 | |
| Alkenes | 26.22 | 22.98 | 22.31 | 24.24 | 24.86 | 22.48 | 9.90 | 11.18 | 5.94 | 30.36 | 18.68 | 10.32 | |
| Aromatics | 4.87 | 6.16 | 5.36 | 8.46 | 7.06 | 16.38 | 15.49 | 21.74 | 11.55 | 11.78 | 21.04 | 15.91 | |
| Polars | 39.37 | 46.60 | 46.89 | 46.34 | 45.73 | 42.01 | 62.06 | 56.00 | 62.88 | 35.81 | 45.01 | 54.54 | |

conditions should be similar, as found in this work. These results also agree well with the kerogen pyrolysis products diagram obtained by Tissot (2). After pyrolysis, six type I kerogens, except Turkish oil shale, produced shale oils with ratios of (alkanes+alkenes)/aromatics between 4.77 and 10.55. However, the other six shale oils contained (alkanes+alkenes)/aromatics in ratios between 0.72 and 3.97, reflecting the predominance of aromatics in the pyrolysis products.

Alkanes isolated from the 12 shale oils were analyzed by GC. Figure 1 shows the distribution of normal alkanes. The alkane distribution below C20 and the carbon preference indexes of C15 to C19 are very similar for all 12 shale oils, even though they are from different parts of the world, different geological ages, different precursors and different depositional environments. This similarity suggests that the severe artificial pyrolysis (Fischer assay) becomes a determining factor for the products. However, there are differences in the whole pattern of the distribution curves in Figure 1. The n-alkane distributions for six Tertiary lacustrine oil shales generally have a bimodal pattern. One peak varies from C12 to C15 and the other peak maximizes at C27. This kind of distribution indicates that these oil shales have low maturity and their precursors contained higher plants (7). For the six older oil shales formed from a marine environment, the normal alkane distributions of their pyrolysis products have only one peak and the main normal alkanes are less than C18.

The Fischer assay oils all contain a significant amount of alkenes that are not present in natural crude oils. The normal alkene distributions for these shale oils are found to be very similar to those for the normal alkanes. This suggests that the normal alkene distribution in Fischer assay oil also can be used as an indicator for the oil shale depositional environment.

SUMMARY AND CONCLUSIONS

Twelve world oils shales were studied by characterizing their Fischer assay oils. The shale oils were separated into various compound types. The amounts and the characteristics were compared. Solid-state NMR spectra were also obtained for all the oil shales to determine the amounts of aliphatic and aromatic carbon fractions. In general, two Chinese shales, U.S. Green River shale, and two Australian shales of Tertiary age from lacustrine sediments yield more aliphatic oils with low N+S+O% and lower specific gravity. The oils contain n-alkanes with a bimodal distribution. Two Israeli shales, a Moroccan shale, the U.S. Alaskan (sample 11) and New Albany shales, which were of older age and from marine sediments, yield more aromatic oils, with higher N+S+O% and higher specific gravity. They contain n-alkanes with a single-peak distribution. It appears that the compositions of the shale oils tend to relate to geological age and depositional environment. However, oils from the Turkish shale

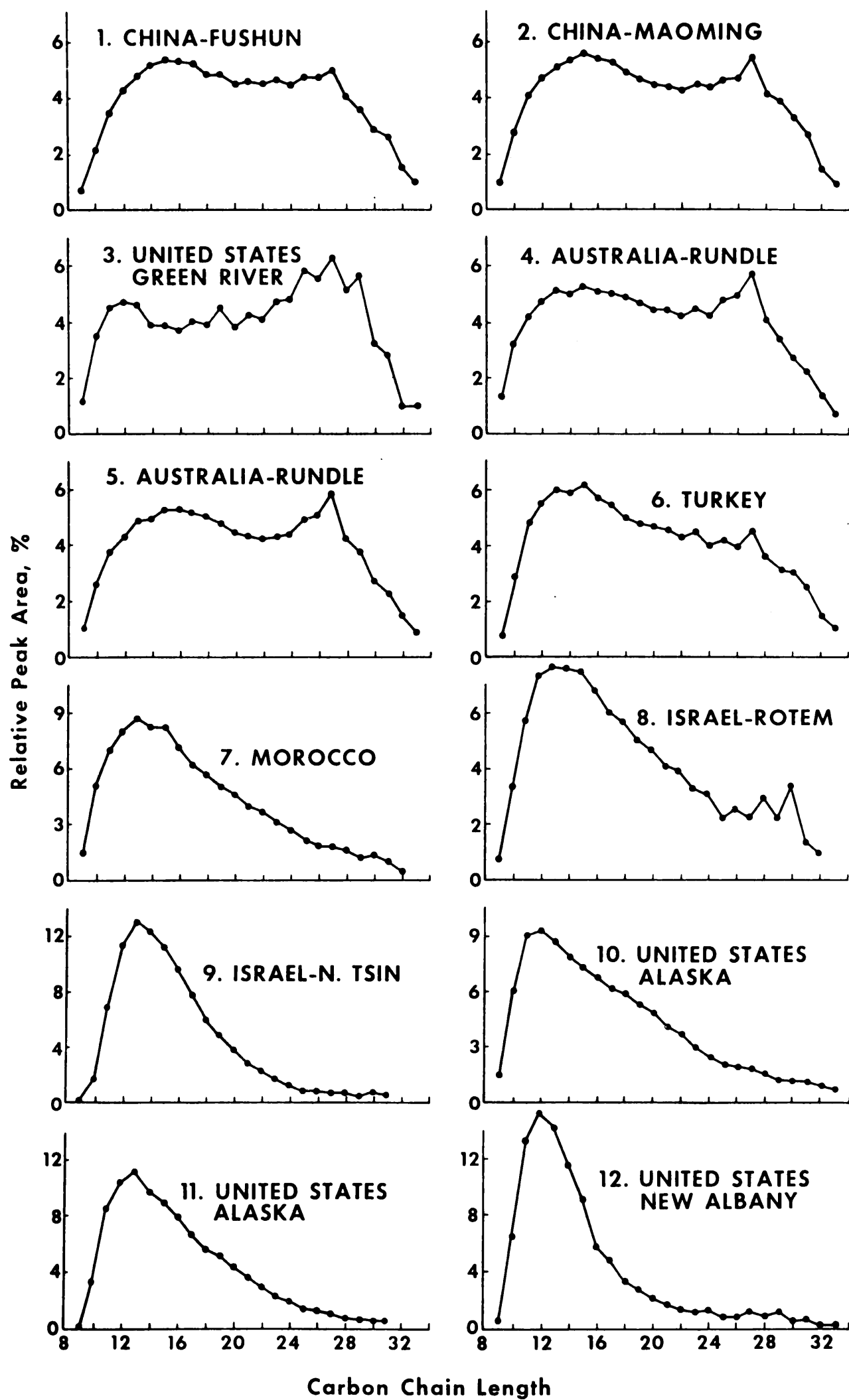


Figure 1. Distribution of n-Alkanes of Fischer Assay Oils

and one Alaskan (sample 10) shale were somewhat different. Their characteristics were mixed and overlapped the above two types. This discrepancy may be caused by the different source material and thermal history of the two oil shales.

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