COMPARISON BETWEEN CHINESE AND COLORADO OIL SHALES

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ABSTRACT

Three oil shale samples from the People's Republic of China were analyzed and compared with a typical Colorado oil shale sample. Two of the samples were taken from the Fushun area in Manchuria, and the third one was from the Maoming area in Southern China.

Although the total organic carbon contents are higher, the Chinese shales yielded less oil and significantly more chars than a typical Colorado shale. Also, unlike Colorado shale, the Chinese shales have very low levels of carbonate carbon and all carbonates appeared to decompose during retorting. These unique characteristics will allow a relatively lean Chinese shale to be processed in a heat-balanced char burning retort, such as Chevron's Staged Turbulent Bed (STB) process, with minimum external energy.

The Chinese shale oils had higher API gravity and lower nitrogen. Their refining values are therefore probably higher.

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1. INTRODUCTION

The People's Republic of China (PRC) has a 50-year history of nearly continuous shale oil production.[1] Because of differences in geological age and genesis, Chinese shales are different from those found in the United States.[2]

Recent interactions between PRC and Chevron Research Company in oil shale dated back about a decade ago. Professor Zhu Yajie, Director of the Beijing Graduate School of the East China Petroleum Institute, visited Chevron in 1981 and discussed oil shale programs with Chevron researchers. It was later decided that Chevron and PRC would exchange some oil shale samples for evaluation purposes.

As a result of these interactions, three Chinese oil shales were received at Chevron Research in the spring of 1983. Two of the samples were taken from the Fushun area in Manchuria, and the third one was from the Maoming area in Southern China. These samples were analyzed and compared with a typical Colorado oil shale sample. The results are summarized in this paper.

2. THERMOGRAVIMETRIC ANALYSES

The three Chinese samples were subject to thermogravimetric (TGA) analyses. A small sample was heated at 10°C/Min. in nitrogen atmosphere to 550°C, and in air between 550°C and 900°C. Both weight and differential weight loss were plotted as a function of sample temperature.

FIGURE 1
THERMOGRAVIMETRIC ANALYSIS OF COLORADO SHALE

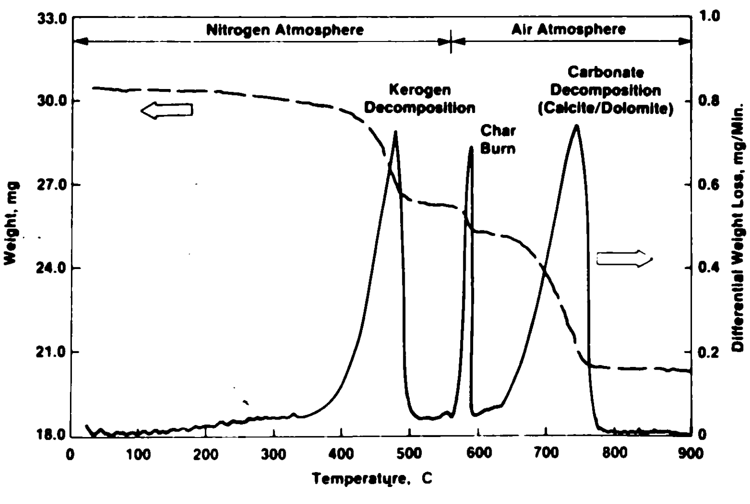

FIGURE 2
THERMOGRAVIMETRIC ANALYSIS OF FUSHUN-I SHALE

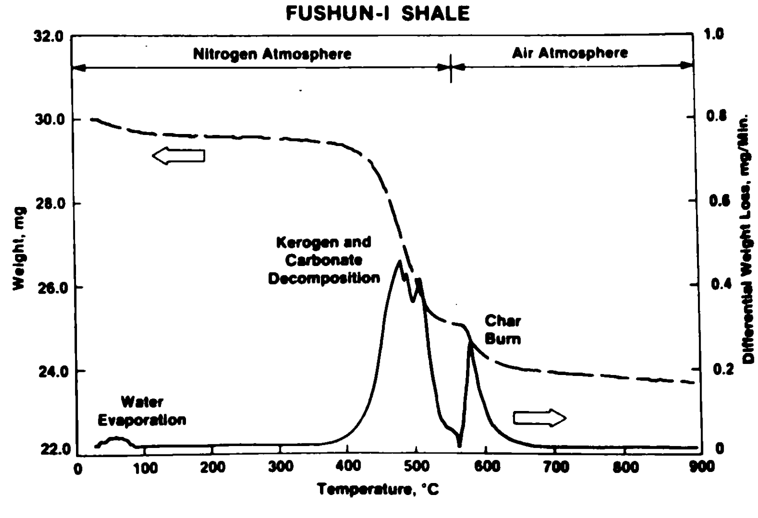

Figure 1 shows the result with a typical Colorado shale. Between 450°C and 500°C, kerogen decomposition took place. The resulting char was burned off as soon as air was introduced at 550°C. At about 730°C carbonates, mostly calcite and dolomite, decomposed.

Although the TGA patterns for the three Chinese shales were similar to each other, they were different from that of the Colorado shale. Figure 2 displays the result with a Fushun shale. The volatiles observed at about 50°C were probably surface water. The peaks at 470°C and 570°C were similar to those observed with the Colorado shale. This similarity implies that retort and combustion temperatures in a process developed for a Colorado shale may be applied directly to the Chinese shales.

One major difference in Figure 2 is the lack of a carbonate decomposition peak at 730°C, an indication that the Chinese shales have little or no carbonates which would decompose at this temperature. A shoulder observed near 500°C suggested that a small amount of carbonates might have decomposed at retort temperature. Since carbonate decomposition is highly endothermic, this is an important advantage of the Chinese shales in a heat-balanced operation.

3. ELEMENTAL ANALYSES

The total and carbonate carbon were measured by coulometric analyses. Carbon, hydrogen, and nitrogen were analyzed with Carlo Erba. Sulfur was determined with LECO SC-32. Table I summarizes the elemental analyses of the Chinese shales and the typical Colorado shale.

Table I. Elemental Analyses of Shales

Sample	Fushun-I	Fushun-II	Maoming	Colorado
Grade, Gallons/Ton	16.2	18.2	16.3	25.4
Composition, Wt % Fresh Shale				
Total Carbon	10.20	14.12	15.00	16.37
Carbonate Carbon	0.81	0.63	0.46	4.65
Organic Carbon (By Difference)	9.39	13.48	14.54	11.72
Hydrogen	1.81	2.12	2.37	1.62
Nitrogen	0.80	0.84	0.49	0.58
Sulfur	0.49	0.69	1.29	0.71

Compared to Colorado shale, the Chinese shales have very low levels of carbonate carbon. As discussed earlier, TGA analyses of these samples indicated essentially no carbonate decomposition at temperatures higher than 550°C. What little carbonates which were present in the Chinese shales decomposed readily during retorting. Iron carbonates such as ferroan have been found in some Colorado shales. These carbonates decompose at retorting temperatures, and, therefore, might be present in the Chinese shales.

Except for Fushun-I, Table I indicates that the Chinese shales contained higher amounts of organic carbon than the Colorado shale. The Fushun samples had slightly higher nitrogen content while the Maoming sample had more sulfur than the Colorado shale.

4. FISCHER ASSAY

Table II summarizes the Fischer Assay (ASTM D 3904-80) results. In addition to standard procedure, the Fischer Assay gas was collected and analyzed by gas chromatography so that the entrained C_5+ liquid could be determined.

Although the Chinese shales contained higher amount of organic carbon than the Colorado shale as noted earlier, their grades by Fischer Assay were only 16-18 gallons of liquid products per ton of shale, compared to about 25 gal./ton for the Colorado sample. The gas yields were similar. On the other hand, the char yields for the Chinese shales were very high.

Table II. Fischer Assay Yields

Sample	Fushun-I	Fushun-II	Maoming	Colorado
Grade, Gallons/Ton	16.2	18.2	16.3	25.4
Yields, Wt % Fresh Shale				
Rundown Oil	6.0	6.9	6.1	9.7
Char Carbon	3.3	5.5	6.7	2.4
C_4- Gas	0.6	0.8	0.8	0.8
C_5+ Gas (Entrained Liquid)	0.1	0.2	0.2	0.2
H_2O	4.6	6.0	9.1	1.4
CO_2	1.7	2.0	1.7	0.6
CO	0.1	0.1	0.1	0.1
H_2S	0	0	0	0.2
Spent Shale (Including Char)	85.1	81.4	80.6	86.0
Losses	1.8	2.6	1.4	1.0

Table II also indicates that the Chinese shales had very high Fischer Assay water yields. About 30-40% of this water was probably surface moisture judging from the low temperature peaks observed in TGA analyses. The remaining water was either generated from kerogen retorting or from dehydration of a mineral at retorting temperature.

The CO_2 yields with the Chinese samples were also high. Stoichiometry calculations showed that these yields account for essentially all of the carbonates in the Maoming sample, and 57-87% of the carbonates in the Fushun samples. The balance may be from retorting of the kerogen.

Another interesting observation is that no H_2S was detected in any of the Fischer Assay gases of the Chinese shales despite 0.5-1.3% total sulfur measured in elemental analyses. This implies that, relative to Colorado shales, the forms of sulfur, i.e., organic versus inorganic, are very different in the Chinese shales.

Table III summarizes the Fischer Assay organic products on a relative basis. The liquid products represent 50-59% of the total kerogen in the Fushun samples, and only 43% of the Maoming sample. The gas yields are relatively constant. On the other hand, the char yields of the Chinese shales account for 36-52% of the total organics, more than twice what was observed for the Colorado shale. In fact, the char carbon factors, defined as pounds of char carbon per pound of rundown oil, were two to four times as large with the Chinese shales as that found for the Colorado shale. On a similar basis, the gas factors are also higher for the Chinese shales. These differences can significantly change the operation of a heat-balanced char burning retort, such as Chevron's Staged Turbulent Bed (STB) process.

Table III. Fischer Assay Products Distribution

Sample	Fushun-I	Fushun-II	Maoming	Colorado
Grade, Gallons/Ton	16.2	18.2	16.3	25.4
Distribution,				
Wt % of Kerogen				
C_5+ Oil	58.5	50.3	43.1	74.0
C_4- Gas	5.8	5.3	5.2	5.8
Char*	35.7	44.4	51.6	20.2
Factors, Lb/Lb Rundown Oil				
Char Carbon Factor	0.56	0.81	1.09	0.25
Gas Factor	0.10	0.11	0.12	0.08

*Char stoichiometry of $CH_{0.44}N_{0.051}S_{0.008}$ found for the Colorado shale was assumed for all samples.

Table IV summarizes selected analyses of the Fischer Assay spent shales. The low carbonate carbon concentrations with the Chinese shales are consistent with TGA results. The sulfur contents in the Chinese shale chars account for 75-90% of the total sulfur in shales, compared to about 50% observed for the Colorado shale.

Table IV. Fischer Assay Spent Shale Analyses

Sample	Fushun-I	Fushun-II	Maoming	Colorado
Grade, Gallons/Ton	16.2	18.2	16.3	25.4
Composition,				
Wt % Fresh Shale				
Spent Shale	85.1	81.4	80.6	86.0
Composition,				
Wt % Spent Shale				
Total Carbon	4.16	6.88	8.23	7.97
Carbonate Carbon	0.25	0.21	0.03	5.32
Organic Carbon				
(By Difference)	3.91	6.66	8.20	2.65
Hydrogen	0.81	0.79	0.90	0.27
Nitrogen	0.56	0.65	0.41	0.55
Sulfur	0.48	0.63	1.49	0.40

Table V summarizes selected analyses of the rundown oils. The Chinese shale oils had higher °API gravities and lower nitrogen contents than the Colorado shale oil. Due to limited oil samples the sulfur contents were not analyzed. These observations suggest that the Chinese shale oils may have higher refining values than the Colorado shale oil.

Table V. Fischer Assay Oil Analyses

Sample	Fushun-I	Fushun-II	Maoming	Colorado
Grade, Gallons/Ton	16.2	18.2	16.3	25.4
Gravity, °API	27.0	25.2	25.8	22.0
Composition, Wt % Oil				
Carbon	84.90	84.10	84.06	84.40
Hydrogen	11.82	11.26	11.25	11.3
Nitrogen	1.50	1.60	1.16	2.30

5. PROCESS CONSIDERATION

In oil shale retorting the thermal efficiency is defined as the percent of the hydrocarbon resource which is recovered as saleable products. A high thermal efficiency is usually achieved by operating a process in a heat-balanced mode with minimum external energy. An example is Chevron's Staged Turbulent Bed (STB) Process.[3] In this process retorted shale is burned in a separate combustor and recycled to the retort to supply the process-heat requirement.

For a given type of shale, there is a limit on the minimum grade which would generate enough residual carbon in the spent shale in order to satisfy all the heat requirement. This minimum grade depends on the thermal efficiency of a specific process, and on the carbonate decomposition, and Fischer Assay char factor of the shale. Since the Chinese shales have essentially no carbonates and very high char factor, the minimum grade required are expected to be much lower than that for a Colorado shale. The additional heat required to vaporize the additional retort water in the Chinese shales is small compared to the additional heat generated from the incremental amount of char that would be burned.

6. SUMMARY

Three shale samples received from the People's Republic of China were found to be very different from a typical Colorado oil shale. These samples were taken from the Fushun area in Manchuria and the Maoming area in Southern China.

Although the total organic carbon contents are higher, the Chinese shales yielded less oil and significantly more chars than a typical Colorado shale. Also, unlike Colorado shale, the Chinese shales have very low levels of carbonate carbon and all carbonates appeared to decompose during retorting. These unique characteristics will allow a relatively lean Chinese shale to be processed in a heat-balanced char burning retort, such as Chevron's Staged Turbulent Bed (STB) process, with minimum external energy.

The Chinese shale oils had higher API gravity and lower nitrogen than Colorado shale oil. Their refining values are therefore probably higher.

7. REFERENCES

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