

COMPOSITIONAL VARIATION OF RETORTED SHALE OILS WITH STRATIGRAPHY:
WYOMING CORE, NORTHERN GREEN RIVER BASIN

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INTRODUCTION

Current plans for the commercial development of oil shale resources are designed to obtain the maximum amount of oil from the least amount of shale. Within the United States, the industry would use the thick, rich seams which are reasonably close to the surface in the Green River Formation in the Rocky Mountain region. This formation is made up of four principal basins, the Piceance Creek Basin in Colorado, the Uinta Basin in Utah, and the Green River and Washakie Basins in Wyoming. The construction of mining operations, both surface and subsurface, to support aboveground retorting processes will be designed in such a manner that the thickest seams of rich shale will be used. Modified in situ retorts will be designed to develop the tallest rubble chimneys technically feasible. True in situ retorting sites will be located in those shale seams which are inaccessible to the other technologies and will produce the maximum amount of high quality product oil.

Of all the possible variables which can affect the quality of shale oil, the retorting method is by far the most significant (1, 2).¹ It is also known that shale type can affect oil quality. A detailed study of Colorado shale oils and Paraiba Valley (Brazil) shale oils showed significant differences between the two in such characteristics as residuum content, nitrogen content, distribution of nitrogen by boiling range in the oil and hydrocarbon types (3). Consideration of the quality of the shale from a given location has generally been confined to the variations in yield (gallons of oil per ton of shale) and its mining and retorting properties.

To date, the stratigraphic variation of oil shale as it relates to oil quality has received little attention. Robinson and Cook (4, 5, 6) have published a three part study on the variations of the organic source material within three basins in the Green River Formation. Differences in the organic source material between basins were noted and variations with depth within basins were also observed. To date, three systematic, depth-related studies on shale oils have been completed. Two are concerned primarily with the decreasing specific gravity of some (but not all) oils with increasing depth (5, 7) the other study deals with the nitrogen compound types in Green River oil shale and its kerogen degradation products (8).

Smith (7) compared the oil from a 30 foot section of the Mahogany Zone and a composite oil from two discontinuous lower zone sections (total length 310 ft). The analysis was done on Fischer Assay oils composited from drill cuttings. The two composite oils were produced from shales 1,030 feet apart. Variations were noted in specific gravity, elemental composition for nitrogen and sulfur, viscosity and boiling range distribution. In the other study (8), it was found that the nitrogen types in low temperature thermal degradation products of shale (>200°C) were mostly very weak bases and neutral nitrogen types.

¹ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The current study was undertaken to provide information on potential variations in oil quality and composition with increasing depth of burial of the source rock. Such variations would be encountered by any production facility which obtains its raw materials from the vertical development of an oil shale deposit by mining or in situ retorting.

Knowledge of these potential variations is useful for two reasons. First, it will help assure that the technology chosen for any particular site will be sufficient to handle these product variables and allow optimum resource recovery as production proceeds down through the shale bed. Secondly, sound planning is essential to guarantee that oil shale development occurs in a manner which precludes any significant environmental degradation. The evaluation of the potential impact of oil shale products and effluents on the biosphere is just beginning to produce preliminary results (9). As an aid in answering environmental questions by the time full scale development begins, this study will provide the initial data on oil characteristics as produced through a vertical shale bed. This will allow potential problems to be recognized as soon as they are delineated by the environmental impact research effort and will permit the most rapid development of the control technology which must supplement the production technology for orderly development of the resource.

EXPERIMENTAL

A core was obtained in the Northern Green River Basin in T 21 N, R 107 W, Sweetwater Co., WY. The lithographic description was obtained on the core at approximately one foot intervals and the Fischer Assay was carried out on the sections containing kerogen by the Oil Shale Characteristics Division, Modified Fischer Assay Laboratory of the Laramie Energy Research Center. The Fischer Assay oils were collected in 11 composite oils comprising the oil produced from shale seams of similar appearance. The 11 composite oils were obtained from the three principal members of the Green River Oil Shale Formation appearing in this basin. The first two composite oils, L1 and L2, are from the Laney member, the next eight composite oils, WP1 to WP8 are from the Wilken's Peak member, the last oil is T1 and is from the Tipton member which is the lowest strata.

The 11 oils produced by the modified Fischer Assay analysis of the oil bearing strata of the core were characterized by major and trace element analysis, pour point, viscosity, and specific gravity. Boiling range distribution of the total oils and hydrocarbon type analysis as a function of percent composition and boiling range distribution was determined as described elsewhere (10). The nonaqueous titration of the bases was done in acetic anhydride-benzene (1 to 1) with perchloric acid (11, 12) and the acids were titrated with tetrabutylammonium hydroxide in 1 to 1 benzene-acetonitrile (13). These data provide information relevant to site selection, production, and refining technology, environmental planning, and control technology.

RESULTS AND DISCUSSION

A description of the various sections of core and the resulting oils is given in Table 1. The pour point data demonstrates a pattern found in the analyses of these oils, namely the oils L1 and L2 lie at one extreme and WP1 lies at the other extreme while WP2 through WP8 lie in between in irregular order, T1 is usually found at either extreme. This pattern is also found in the elemental analysis for nitrogen and sulfur (Table 2), saturate hydrocarbon analysis (Table 3), polar, material analysis (Table 3), and acid-base analysis (Table 4 and Table 5). The list of physical properties on the oils is completed by Table 6 which gives the percent composition of the oils by 200°F boiling range increments.

TABLE 1. - Description of Wyoming core and Fischer Assay oils

Section	Depth ¹	Length ²	Gal/ton	Viscosity ³	Sp. gr.	Pour pt.
L1	771.5	38.1	5.3	228	0.964	90
L2	870.5	59.6	10.3	112	0.917	85
WP1	1064.7	44.3	13.5	84	0.918	50
WP2	1109.0	48.6	15.1	106	0.921	60
WP3	1157.6	41.2	11.0	86	0.923	60
WP4	1250.0 ⁴	26.2	8.0	172	0.923	75
WP5	1276.4	45.6	15.9	118	0.928	70
WP6	1322.0	193.0	6.1	102	0.927	65
WP7	1515.0	101.0	8.9	94	0.933	65
WP8	1616.0	94.0	7.3	124	0.919	70
T1	1710.0	7.0	4.5	82	0.907	85

¹ Top of section, depth in feet.

² Excluding barren sections, length in feet.

³ S.U.S at 100°F.

⁴ 51.2 ft of core missing between WP3 and WP4.

TABLE 2. - Analysis of major elements in Fischer Assay oils from Wyoming core

Section	C	H	H/C	N	S	O ¹
L1	84.06	10.77	1.54	1.66	1.62	1.89
L2	82.85	11.26	1.63	1.59	1.86	2.44
WP1	84.42	11.23	1.60	2.26	0.76	1.33
WP2	83.84	11.39	1.63	2.11	1.14	1.52
WP3	83.79	11.13	1.59	2.03	1.40	1.65
WP4	84.26	11.14	1.59	2.12	0.97	1.51
WP5	84.06	11.11	1.59	2.32	0.99	1.52
WP6	84.02	11.00	1.59	2.03	0.68	2.27
WP7	84.45	11.07	1.59	2.21	0.53	1.74
WP8	84.66	11.06	1.58	1.86	0.57	1.85

¹ By difference.

Variations in Oil Properties

As shown in Table 1, the lengths of the various sections range from 7.0 to 193.0 feet, with the lengths being determined by intervals of lithologic homogeneity. The first two sections, total length 97.7 feet, are located in the Laney member of the Green River Formation. The Laney member is an oil shale marlstone section which begins at the base of the Bridger Formation and continues to the top of the sodium-salt mineral oil shale section known as the Wilken's Peak member. The Wilken's Peak member is composed of Lacustrine sediments containing oil shale marlstone and trona (sodium carbonate and sodium bicarbonate), shortite, and other exotic carbonate mineral combinations. Eight sections with a total length of 500.1 feet were obtained from this section. An interval of 51.2 feet was missing from the core near the top of the Wilken's Peak member and is not included in these results. The Tipton member is very thin in this region and yielded only one 7.0 ft section of core. This sample should not be considered representative of the oil shales which make up the Tipton. The results of the analysis on the oil from this section is not discussed and included for comparison only.

TABLE 3. - Analysis of Fischer Assay oils for percentage saturate hydrocarbon, polar, and nonpolar material

Section	Polar	Nonpolar ¹	Saturates ²
L2	43	57	11.1
WP1	55	45	8.90
WP2	53	47	9.67
WP3	50	50	10.2
WP4	54	46	9.80
WP5	54	46	9.73
WP6	54	46	9.85
WP7	52	48	9.76
WP8	51	49	9.98
T1	40	60	13.3

¹ Removed from Florisil column with cyclohexane.

² By absorption.

TABLE 4. - Acid type analysis of Fischer Assay oils from Wyoming core¹

Section	Acid type, Meq/g oil		
	Weak acids	Very weak acids	Total acids
L1	0.045	0.302	0.347
L2	0.034	0.228	0.262
WP1	0.021	0.206	0.227
WP2	0.021	0.196	0.217
WP3	0.020	0.207	0.227
WP4	0.025	0.228	0.253
WP5	0.015	0.222	0.237
WP6	0.014	0.232	0.246
WP7	0.014	0.226	0.240
WP8	0.028	0.258	0.286

¹ Determined by nonaqueous titration with tetrabutyl ammonium hydroxide in benzene-acetonitrile.

The oil shales from this region of Wyoming are generally classed as very lean to lean indicating that their oil yield on retorting is low. This is supported by the assay data in Table 1 where the values range from 5.3 gallons per ton in L1 to 15.9 gallons per ton in WP5. The viscosity at 100°F, specific gravity and pour point of L1 are all unusually high when compared to the other oils but aside from this one example no relationship appears to exist among these properties and their depth of burial or yield in gallons per ton.

The elemental analysis of the oils are given in Table 2 and several comments can be made comparing these data and the material presented in Tables 3 through 6. (a) The oils with a H/C ratio of 1.60 or more, L2, WP1, and WP2 show a significant increase in the amount of material with a boiling point of less than 400°F (Table 6). (b) The amount of total nitrogen in the oil is directly proportional to the total bases and total basic nitrogen in the oils (Table 5). (c) The oils from the Laney member contain less than 2% nitrogen and the weak/very weak base ratio is about one whereas the Wilken's Peak oils contain greater than 2% nitrogen and the

TABLE 5. - Base type analysis of Fischer Assay oils from Wyoming core¹

Section	Base types, Meq/g oil			Basic nitrogen type, wt%			Nonbasic ⁴ N, wt%
	Weak ²	Very weak ³	Total	Weak ²	Very weak ³	Total	
L1	0.486	0.373	0.859	0.681	0.522	1.203	0.46
L2	0.435	0.501	0.936	0.610	0.710	1.320	0.27
WP1	0.832	0.399	1.231	1.169	0.559	1.728	0.52
WP2	0.752	0.436	1.188	1.054	0.610	1.664	0.45
WP3	0.732	0.420	1.152	1.025	0.588	1.613	0.42
WP4	0.698	0.416	1.114	0.977	0.583	1.560	0.56
WP5	0.764	0.470	1.234	1.069	0.658	1.727	0.59
WP6	0.736	0.388	1.124	1.030	0.543	1.573	0.50
WP7	0.771	0.438	1.209	1.108	0.613	1.721	0.49
WP8	0.650	0.416	1.066	0.910	0.582	1.492	0.37

¹ Determined by nonaqueous titration with perchloric acid in acetic anhydride-benzene (1:1).

² pK_a = +8 to +2, pyridines, quinolines, anilines, alkylated pyrroles.

³ pK_a = +2 to -2, pyrroles, indoles, amides.

⁴ Determined by difference using total N analysis from table 2, nitriles, carbazoles.

TABLE 6. - Composition by boiling range for the oils obtained by Fischer Assay of Wyoming core¹

Section	Boiling range fractions, percent of total				Residue
	ibp to 400	400 to 600	600 to 800	800 to 1,000	
L1	1	20.8	31.4	31.1	16.5
L2	12.0	23.9	27.5	24.0	13.1
WP1	15.5	24.3	26.1	21.9	12.2
WP2	13.0	23.6	26.1	21.4	15.9
WP3	7.8	22.4	28.0	26.7	15.1
WP4	3.6	23.4	29.5	28.1	15.4
WP5	7.0	22.7	28.4	27.6	14.3
WP6	6.7	24.0	28.9	28.3	12.1
WP7	7.6	24.1	29.0	28.9	10.4
WP8	6.2	23.5	30.9	30.8	8.6
T1	8.9	24.9	28.9	22.1	15.3

¹ Determined by simulated distillation.

weak/very weak base ratio is about two (Table 5). (d) The amount and types of acids present in the oils do not follow the sequence of percent oxygen in the oils (Table 4). (e) With the exception of WP1, the amount of nonpolar material in the oils generally decreases with the nitrogen content of the oil but sulfur has little or no effect (Table 3).

The variation in the oils when analyzed by simulated distillation for boiling range distribution is given in Table 6. The L1 section is deficient in material boiling below 400°F. Sections L2, WP1, and WP2 show 12.0 to 15.0 percent of material boiling below 400°F with 21.4 to 24.0 percent in the 800 to 1,000°F range. The remaining oils are generally heavier, showing less than 8% below 400°F and more than 28% in this 800-1,000°F range. Section WP8 shows less than 9% material boiling above 1,000°F while the other oils vary between 16.5% and 10.4%.

Processing Considerations

The bulk properties which relate to handling the oils specific gravity, pour point, and viscosity are given in Table 1 and show very little variation from one section to another. These values are well within the range expected for shale oils so that handling these products in a production facility will present no new problems.

When the initial shale-oil product is refined, either on or off the site, provisions will have to be made to handle a high-nitrogen feed with modest sulfur levels. These facts are already well known and it seems from the data in Table 2 that the variations in nitrogen and sulfur levels are not sufficient to cause any problems in the refining step not already predicted. In Table 2 the hydrogen-to-carbon ratios are very nearly the same for all oils so it is apparent that hydrogen demand for a hydrotreating plant will depend primarily on the final levels of nitrogen and sulfur in the hydrotreated product. The role of nitrogen and sulfur in the refining of shale oils has been discussed by Poulson (14). Some of the sulfur levels in these oils are slightly higher than those mentioned in that paper but it is generally acknowledged that the sulfur will present no problems because it will be removed before denitrification is complete.

The data in Tables 4 and 5 were obtained by means of nonaqueous titrimetry on the total crude oils. This method was chosen for its applicability to whole oils and to shale oil distillates (15, 16). The data is detailed and therefore gives a good picture of the oil with respect to nitrogen content. The total oils follow the trends established for the various distillation cuts, that is, total bases exceed the total acids, very weak acids predominate over weak acids, and weak bases predominate over very weak bases. Since denitrification is the most troublesome factor in refining, the relative amounts of weak and very weak bases in the oils are worth noting because it is known that weak bases (pyridines and quinolines) are more easily reduced than very weak bases (pyrroles and indoles) at low temperature and pressure, while the situation is reversed at high temperatures and pressures (17). The ratio of weakly basic nitrogen to very weakly basic nitrogen varies from 2.09 to 0.86 in the oils, this changing quality of the feedstock may require a hydrotreater design which is flexible to assure efficient operation of that phase of production. If a fixed hydrotreater design is chosen because of operating and/or economic considerations, judicious consideration will have to be given as to which shale seams will be exploited.

Another result of this study is presented in Table 6. If a given set of retorting parameters are chosen as the most ideal for a particular facility, the boiling range distribution of the product can be markedly affected by the choice of shale seams which are processed. The amount of material in the IBP to 600°F range (naphtha to light distillate) can be increased from about 30 percent of total oil to about 38 percent by selecting the shales in the seams represented by L2, WP1, and WP2. Residuum (1,000°F+) can be lowered from about 16 percent to less than 9. This type of product mix flexibility can occur without changing retorting conditions and could be capitalized on, making an industry much more responsive to changing fuel demands. This varying product mix with stable retort conditions may also have significant economic implications.

Environmental Considerations

As stated earlier, the potential impact of shale products on the biosphere is just beginning to be delineated and evaluated. With this qualification, a few general comments can be made at this time concerning the environmental implications of the varying product quality of these oils.

The physical properties of these oils do not differ markedly from any other known shale oil, so no unusual problems should arise from the retorting or processing of oils from this region as compared to any other. As for unique chemical properties which may be significant, none are apparent. The oils have been analyzed for all stable elements and they are very similar to oils with which we are familiar (18). The analyses were obtained by spark source mass spectrometry. Table 7 gives

TABLE 7. - Elemental analysis of three oils produced by Fischer Assay on Wyoming core¹

Element	Section		
	L2	WP3	WP7
Molybdenum	-	0.46	-
Arsenic	5.8	2.7	5.4
Zinc	-	0.40	-
Nickel	0.43	3.1	3.3
Cobalt	-	0.56	0.62
Iron	17	26	29
Calcium	1.1	8.8	3.5
Potassium	0.61	6.5	2.8
Chlorine	-	-	0.28
Sulfur	0.54	5.0	1.2
Phosphorus	-	0.77	1.7
Silicon	8.5	40	15
Aluminum	4.4	11	1.1
Magnesium	0.79	7.9	4.6
Sodium	1.4	4.9	2.8

¹ All values in ppm; elements for which values are not listed are less than 0.25 ppm.

the results of analysis on these oils. The character of the organic materials is under active investigation as to compound types and specific examples of each type. This work will allow the evaluation of the biological effects of these oils to be made as soon as the suspect agents in shale oil are identified. The suspect nature of the various components of petroleum is well known (19) and the analysis for these materials in shale oils is proceeding.

In an investigation of the mutagenic effects of a shale oil and a petroleum crude, the basic material in the shale oil (8% of the total oil) was significantly more active on a weight basis than the corresponding basic material in the petroleum (>1.0% of the total oil) (20). Since this is the first report of this type it is very important that additional data be gathered on other samples before the results are generalized to all petroleum or shale oils. As the biological significance of the various basic materials in shale oils is reported further, a more comprehensive statement of the possible environmental impact of the variations of oil with depth of burial will be possible. The results of the study on compound types and specific compounds found in these shale oil fraction will be forthcoming in the near future.

SUMMARY

A series of oils produced by Fischer Assay of a core representing 11 major strata of Northern Green River Basin--Green River Formation oil shale have been

analyzed for physical and chemical properties. Three major points concerning the retorting and processing of various strata of shale can be made. First, the physical properties of all oils are similar and as such, the oils will require much the same handling. Second, the types of basic nitrogen vary significantly in their concentration which may require a flexible hydrotreating facility to operate at maximum efficiency. Under the static retorting conditions of the Fischer Assay, product mix varies significantly with the shale strata being used as source material.

Shale from these different strata can be handled and processed in the same way, requiring no unique environmental control technology. Total elemental analysis reveals no significant variations between strata and no potentially harmful elements in unusual concentration.

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A LABORATORY APPARATUS FOR CONTROLLED TIME/TEMPERATURE RETORTING OF OIL SHALE

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INTRODUCTION

The Lawrence Livermore Laboratory (LLL) is currently developing technology for modified in-situ retorting of oil shale.(1) Under this concept, a column of oil shale would be broken up using mining techniques, and then the rubblized oil shale would be retorted either through combustion or hot-inert-gas methods.

As part of the research effort we have designed and built an oil shale assay apparatus that can be used to simulate and evaluate the effects of various heating schedules that might be encountered in-situ.(2)

Our apparatus is a modification of the standard Fischer assay vessel and apparatus.(3,4) Changes were made primarily to simulate phenomena common in in-situ retorting (e.g., the descent of gas and possibly liquid products through reacting shale under variable thermal conditions). The collection system allows for complete gas and liquid product recovery (and hence, for good mass balance). The apparatus can be operated in either autogenous (self-generated) gas or gas-sweep conditions.(2)

In the following discussion, we describe the apparatus and compare our experimental results with those from a typical Fischer assay apparatus.(3) We refer to our assay method as the Koskinas, Stout, Santor (KSS) assay.

APPARATUS

The KSS apparatus is shown in Fig. 1. It has three major parts: a retort chamber, a furnace and controller unit, and a gas manifold and oil collection system. The design and construction of each component is described in detail below.

RETORT CHAMBER

Our retort differs from the usual Fischer assay retort in three respects. First, the product is collected from a delivery tube at the bottom of the retort chamber. Second, our retort is a stainless steel chamber, sealed by welding and hence capable of operating leak-free at high temperatures (1000°C) for long periods of time (> 1 month). Third, the simple physical design of the chamber is compatible with a cylindrical furnace readily available commercially.

The retort chamber (Fig. 2) is made in two parts: the body (with downspout) and the lid. The main body is a cylindrical stainless steel pipe 3.8 cm (1.25 in.) in diameter with a stainless steel frit of 165- μ m mesh, 0.45 cm (3/16 in.) thick, heliarc welded in the bottom. The frit provides a porous path for gases and liquids flowing from the retort, while retaining solid particles in the chamber. The downspout is 0.64-cm-diameter (1/4-in.) type 304 stainless steel pipe, 25.4 cm (10 in.) in length. It has a 0.64-cm (1/4-in.) Cajon Ultratorr O-ring fitting on the exit end. The lid is a flat disk with a thermocouple well at the center. The thermocouple well dimensions are such that when the retort is assembled, the tip is roughly in the middle of the retort chamber. A stainless-steel-sheathed, chromel-alumel (type K) thermocouple is inserted into the well.

The lid is heliarc-welded onto the body after the sample has been put into the retort. To maintain the sample in its natural state and to eliminate any degradation during welding, there is a small void space between the sample and the cap.