

# OPTICAL ACTIVITY OF SHALE OIL FOR PARAMETER STUDY IN RETORTING

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## INTRODUCTION

Optical activity has been observed in petroleum and in isoprenoid compounds, steranes, and triterpanes extracted from oil shale (1-3). Optical activity is a property that can reflect the molecular integrity of a former biological system and has been used to evaluate the geochemical history of petroleum from different geological ages (1). Optical isomer data have been used as a biological clock in geochronological research (4) and have been used to determine the possible origin of certain carbonaceous chondrite meteorites (5). The key to studying these organic systems is the slow decay of the optically active molecules, as a result of low-level heat (geological time), into optically neutral mixtures. Retorting of oil shale kerogen accelerates this decay process. This paper describes the use of optical activity data as a means of studying this conversion of kerogen into shale oil. Studies at the Laramie Energy Research Center have demonstrated that shale oil produced from bench-scale and field in-situ experiments is optically active. New insights into the retorting process may now be possible by following the changes in optical activity.

## EXPERIMENTAL

### Preparation of Shale Oils

The three sets of shale oils studied were from two laboratory retorting experiments and one field retorting experiment. The laboratory experiments were conducted in the controlled-state retort (CSR), described in detail by Duvall (6). In brief, the retort is an electrically heated, 3-in. by 13-ft stainless steel pipe. The electric heaters are spaced each 6 inches and are monitored by thermocouples inserted in a 1-inch pipe through the center of the 3-inch pipe. Nitrogen, admitted at the top of the retort, is used as a sweep gas.

The first set of oils was prepared by filling the retort with 1/8- to 1/2-inch, 36.5-gal/ton shale from the Anvil Points, Colo., mine and by retorting under the conditions shown in Table I. The shale was heated from the top downward; the produced oil flowed by gravity with assistance from the nitrogen sweep gas and was collected at the bottom of the retort. The collected oil was transferred to a distillation flask and was distilled to remove water and naphtha. The naphtha was separated from the water and was returned to the oil. Properties of the dried oil are shown in Table II. Naphtha and light distillate fractions after tar acid and tar base removal were fractionated, using silica gel chromatography, into saturates, olefins, and aromatics.

TABLE I. - CSR retorting conditions

Heating rate, °F/min	Maximum temp., °F	Zone velocity, in./hr	Sweep gas, ft <sup>3</sup> /hr	Sweep gas, SCF/ft <sup>2</sup>
2	1,000	3	1.5	24
20	1,000	12	14	224

TABLE II. Properties of CSR crude oils

Retort heating rate, °F/min	Oil yield, % of Fischer assay	Specific gravity 60/60°F	Pour point, °F	Viscosity, 100°F SUS	Viscosity, 130°F SUS	Molecular wt.*
2	96.4	.925	45	148	69	282
20	87.6	.921	35	263	131	219

\*Vapor-phase osmometry in benzene

The second set of oils was prepared by filling only the bottom 6-inch zone of the retort with 1/8- to 1/2-inch shale and the next 6-inch zone with ceramic beads. Oils were prepared using heating rates of 0.1, 1, 2, 4, and 10°F per minute and a N<sub>2</sub> flow rate of 14 ft<sup>3</sup> per hour. A maximum spent-shale temperature of 1200°F was reached. The collected oils were dried by centrifugation.

The third set of oils was collected from the in-situ retorting Site 9 near Rock Springs, Wyo.(7). A 40-ft zone of fractured oil shale was retorted in advance of a combustion front that propagated radially from a central air injection well toward surrounding production wells. One production well, No. 7, located 50 feet from the injection well, was sampled four times during a 2-month period. The collected oils were dried by centrifugation.

#### Preparation of Saturate Fraction

The procedure is basically that used by Redfield (8). A 0.5-g sample of dried oil was dissolved in 1 ml of cyclohexane and placed on a 2- by 75-cm column of 150 g of 28- to 200-mesh silica gel (Matheson Grade 10) prewet with n-hexane (Burdick and Jackson Laboratories, Inc.). The column was eluted with 240 ml of n-hexane at a flow rate of 7 to 8 ml per minute. The n-hexane-eluted saturate fraction was concentrated to 20 ml by evaporation under N<sub>2</sub>, and the concentrated solution was used for optical activity measurements.

#### Optical Activity Measurements

Optical activity was measured on the saturate fraction using a 10-cm, strain-free quartz cell in a Jasco J-20 spectropolarimeter in the optical rotary dispersion mode. Data were recorded in the 250- to 600-nm wavelength range. A solvent blank after each run was used to determine the baseline. The observed rotation from 300 to 600 nm wavelengths was converted to degrees of specific rotation,  $[\alpha]^{25}$ , by the following formula:

$$[\alpha]^{25} = \frac{\alpha}{l \cdot c}$$

where  $\alpha$  = observed rotation,  $l$  = sample path length in decimeters, and  $c$  = concentration of sample in g per ml; i.e., the weight of oil charged to the silica gel column divided by the volume of the saturate solution in the cell.

### RESULTS AND DISCUSSION

Shale oils are deeply colored, and thus are not easily amenable to optical activity measurement. Fortunately, the optically active molecules, steranes, di-, tri-, and tetraterpanes (3), are found essentially in the transparent saturate

fraction so that measurements can be made on this fraction. These molecules partly degrade to racemic or optically inactive mixtures during the retorting process.

Optical activity measurements on the first set of oils show that optically active molecules do survive the retorting process, and this occurs to varying degrees. The data plotted in Figure 1 show less activity in the 20°F-per-minute oil at all wavelengths. This activity difference indicates more degradation or cracking in the 20°F-per-minute oil than in the 2°F-per-minute oil.

Other evidence of increased cracking with increased heating rate is shown in Table II where the oil yield, the pour point, and the molecular weight decrease. More definitive cracking evidence is seen in the olefin increase (Table III) from 48 to 54 percent for the naphtha and from 49 to 65 percent for the light distillate.

TABLE III. - Hydrocarbon-type analysis of neutral oils

Retort heating rate, °F/min	Vol. percent					
	Naphtha			Light distillate		
	Saturates	Olefins	Aromatics	Saturates	Olefins	Aromatics
2	38	48	14	30	49	21
20	32	54	14	24	65	11

The second set of oils was chosen for a more detailed study of the effect of heating rate on optical activity. Five heating rates were chosen, and duplicate samples of the resulting oils were separated and measured. The results, Table IV, show good reproducibility since rotational differences between duplicate samples are generally less than 0.1° of rotation. A plot of the data, Figure 2, shows a consistent trend toward decreasing activity with increasing heating rates. The top curve, representing the oil prepared at a 0.1°F per minute heating rate, ranges from above 3.2°[α]<sup>25</sup> to about 0.6°[α]<sup>25</sup>. The 10°F-per-minute heated oil ranges from 1.9 to 0.4°[α]<sup>25</sup>. Shale oils prepared from the controlled state retort show changes in optical activity as an inverse function of heating rate. The oils produced at higher rates show the least activity, implying more thermal energy exposure to the product oil, which causes more oil degradation.

Optical activity measurements were made on four oils collected from the Rock Springs, Site 9, in-situ retorting experiment (Fig. 3). Using data plotted from the 450-nm wavelength, differences are apparent in the oil composition from the four dates over a time span of over two months. These differences seem to reflect changes in operation that altered the rate of combustion. During the period April 5 to 22, propane was burned in the injection well to establish combustion and retorting. The produced oil, because of exposure to hot combustion gases, showed a low optical activity of about 0.3 degrees. Conversion from propane to air-only injection on April 23 probably resulted in a cooler retorting system which produced the higher optically active oil collected on May 5. Propane injection was resumed on May 8, and later air injection in a different well produced hotter combustion conditions, resulting in the lower optically active oils sampled on May 25 and June 8. These conclusions are tentative and do warrant further data evaluation and experimentation. The in-situ oils in general show one-third to one-half the optical activity of the controlled-state produced oils and, therefore, apparently have experienced more degradation or cracking.

TABLE IV Optical activity,  $[\alpha]_{25}^D$ , of five shale oils prepared at different heating rates

Heating rate, °F/min	Degrees specific rotation, $[\alpha]_{25}^D$						
	300	350	400	450	500	550	600
0.1	3.26 ± 0.15	2.28 ± 0.12	1.61 ± 0.08	1.21 ± 0.05	0.96 ± 0.03	0.77 ± 0.03	0.62 ± 0.01
1*	2.59	1.76	1.29	1.02	0.83	0.67	0.68
2	2.56 ± 0.01	1.76 ± 0.01	1.28 ± 0.01	0.96 ± 0.03	0.78 ± 0.01	0.62 ± 0.03	0.55 ± 0.04
4	2.10 ± 0.08	1.38 ± 0.03	1.00 ± 0.02	0.76 ± 0.01	0.58 ± 0.04	0.46 ± 0.03	0.38 ± 0.02
10	1.90 ± 0.08	1.28 ± 0.06	0.90 ± 0.04	0.68 ± 0.01	0.52 ± 0.04	0.41 ± 0.00	0.37 ± 0.04

\*Single determination only

#### SUMMARY

The possibility of using optical activity data to study cracking during oil-shale retorting was confirmed by examining shale oils prepared at different heating rates using the bench-scale controlled-state retort. The results show a relationship between shale oil optical activity and heating rate. The oils prepared from in-situ field experiments have optical activity values that are inversely proportional to the suspected underground retorting temperatures and indicate more severe and variable retorting conditions than the controlled state retort system. Further use of optical activity data may be useful in understanding the retorting process in the laboratory and in controlling the process in the field.

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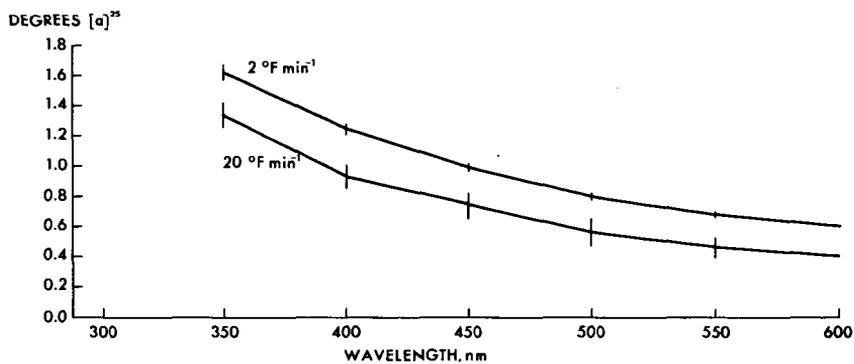


FIGURE 1. - OPTICAL ACTIVITIES, 2 CSR CRUDES.

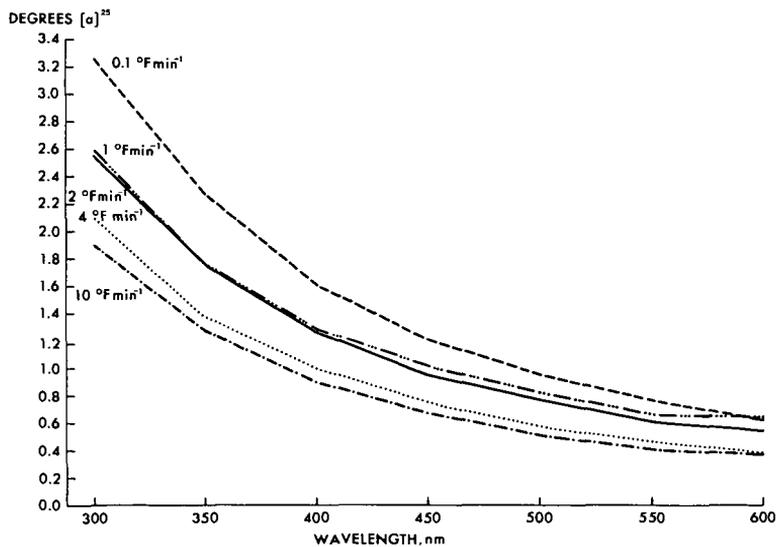


FIGURE 2. - OPTICAL ACTIVITIES, 5 CSR CRUDES.

