

RETORTING INDEXES FOR OIL-SHALE PYROLYSES FROM  
ETHYLENE-ETHANE RATIOS OF PRODUCT GASES

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## INTRODUCTION

The production of shale oil from oil shale is currently practical only by thermally decomposing (retorting) the organic materials in the shale and collecting the liquid products. Investigations to develop processes for retorting oil shale have resulted in many proposed designs for the equipment. However, to maintain control of any of the processes, measurements of appropriate input and output parameters are required to indicate conditions during the decomposition and the subsequent collection of products. The direct measurement of retort temperatures is not always possible. Flow rates through the retorts give only an indirect measure of residence times for material in the heated zones. Both residence times and temperature are important control parameters--related to economy of operation and quality of product.

The pyrolysis of oil-shale kerogen is a very complex reaction or group of reactions that results in the production of a myriad of hydrocarbons and hydrocarbon derivatives. These products range from compounds containing one carbon atom per molecule (methane) to compounds containing greater than 30 carbon atoms per molecule. It is not currently feasible to set forth the mathematical relationships of the pyrolysis reactions with great certainty. This inability to set down the exact mathematical relationships of the overall pyrolysis reaction should not preclude the gleaning of certain useful empirical data that can be used to assist in the interpretation or control of the retorting processes.

Shale-oil production by thermal decomposition of the organic material in the shale has been described as a pseudo first-order process.<sup>1,6</sup> In a practical process the shale is heated to the maximum temperature over a finite period of time. The products of retorting remain in a heated zone for varying periods of time. The nature of the products depends on both the temperature range over which thermal decomposition takes place and on the residence time of the products in a hot zone. Temperature measurements in a retort are not readily related to the product even if coupled with flow rates through the retort. This paper develops a parameter that combines the elements of temperature and residence time into a single number that can be used to indicate instantaneous retorting conditions or can be used to compare various thermal processing techniques for oil shale.

The parameter developed for comparison or control of the retorting process has the dimension of temperature. It could be defined as an "effective temperature" or a "Retorting Index." In the laboratory this index was developed by relating the ethylene/ethane ratio in the product gases from retorting of shale to a measured temperature in the retorting zone. Residence times of the products in the hot zone were nearly constant. In a commercial-size retort, residence times could vary over wide ranges. Residence time variation causes a change in the observed ratio. The calculated parameter also changes and so reflects the changing retorting conditions. Application of the parameter to Fischer assay retorts, gas combustion retorts, and to entrained solids retorts is illustrated with examples. The easily calculatable Retorting Index is applicable to in situ retorting as well as those retorts used as examples.

## EXPERIMENTAL PROCEDURE

Equipment

The equipment consists of an electrically heated quartz tube 2.1-cm i.d. by 83.8-cm long with 24/40 standard taper joints at the ends. A section of the tube, 15-cm minimum length, 43-cm from the inlet was heated to the desired retorting temperature. Heating was accomplished by a three-unit tube furnace, and the temperature was maintained by potentiometer controllers. Oil-shale samples were contained in a 1.25-cm by 7.62-cm boat made from stainless-steel screen. The sample boat was moved in and out of the retorting zone by means of a 1-mm stainless-steel rod which extended from the boat out through the quartz tube inlet.

A tube receiver, a U-tube trap, and an evacuated gas receiver made up the product collection system. The receiver and U-tube were cooled with liquid nitrogen when nitrogen was used for the sweep gas and with dry ice when oxygen was used in the sweep gas for oxidative retorting runs. Sweep gases into the retort tube were metered through a metering valve. Pressure in the retorting section, as monitored by an open-end manometer, was maintained at atmospheric pressure by venting gases from the U-tube through a stopcock into the gas collection system.

Oil-Shale Samples

Oil-shale samples from Colorado, Wyoming, and Utah were used in this study. The sizes of the oil shale used were (A) 20 to 30 mesh, (B) 10 to 14 mesh, (C) 1/8 in to 30 mesh, and (D) 1/4 in to 1/2 in. Most of the retorting work was performed on size C shale. Three different Colorado oil-shale samples were obtained from the Bureau of Mines mine at Rifle, Colorado and assayed 53.8, 52.5, and 22 gpt. The 53.8-gpt oil shale had been ground to sizes A and C, the 52.5-gpt shale ground to size D, and the 22-gpt shale ground to sizes B and C. Wyoming oil-shale samples were a 12.4-gpt sample from a Washakie Basin, Sweetwater County corehole and 13.4-, 19.9-, 30.5-, and 34.4-gpt shales from the Bureau of Mines Rock Springs site 6, well No. 6-2 core. The Utah shales were from the Gulf Evacuation No. 1 core drilled by Gulf Minerals, and the shale samples assayed 14.5, 20.3, 29.0, and 42.7 gpt. All of the Wyoming and Utah oil shales had been ground to size C. A summary description of the oil-shale samples used is presented in Table I.

TABLE I. - Description of oil-shale samples used in the procedure

Sample No.	Geographical source	Assay, gpt <sup>1/</sup>	Sample mesh size
1	Colorado	53.8	20 to 30 mesh
2	do.	53.8	1/8 in to 30 mesh
3	do.	52.5	1/4 in to 1/2 in
4	do.	22.0	10 to 14 mesh
5	do.	22.0	1/8 in to 30 mesh
6	Wyoming	34.4	do.
7	do.	30.5	do.
8	do.	19.9	do.
9	do.	13.4	do.
10	do.	12.4	do.
11	do.	42.7	do.
12	do.	29.0	do.
13	do.	20.3	do.
14	do.	14.5	do.

<sup>1/</sup> Potential oil yields were determined by the modified Fischer assay method (reference 10).

### Pyrolysis Procedure

Temperature profiles of the reaction tube were determined by measuring the temperature inside the tube at 2.54-cm intervals with a thermocouple and potentiometer with sweep gas flowing. Determination of temperature profiles was performed only when work at a new temperature was begun. The temperature at which the furnace was set remained constant and the temperature variation at any point within the quartz tube would fluctuate  $\pm 2^\circ\text{C}$  ( $3.6^\circ\text{F}$ ) maximum.

In making a retorting run, about 7 grams of oil shale were weighed into the sample boat, and the boat was placed at the inlet of the cold reaction tube. The entire retorting system was flushed by evacuation and filling several times with the intended sweep gas. Both the receiver and U-tube trap were cooled and the sweep gas flow adjusted to the desired rate and the vent opened to the atmosphere.

The furnace was then turned on and allowed to come to temperature. After retorting temperature was reached, the sample boat was moved into the retorting zone and kept there for 20 to 25 minutes to insure complete retorting. The boat was then moved back to the inlet, and the furnace turned off. To insure complete collection of the gaseous products, gas collection was started 10 minutes before the furnace reached temperature and continued for 10 minutes after the furnace was turned off. The coolant baths were removed from the receiver and U-tube trap, the traps were warmed to room temperature, and any liberated gases were swept into the gas collection system. When the retorting run was finished, the pressure in the gas collection system was measured and the shale oil and spent shale were weighed.

For the cracking runs the sample boat was not placed as far down the reaction tube. For these runs the boat position was generally 15.24-cm upstream from the "normal" position, and the retorting temperature was about  $100^\circ$  to  $150^\circ\text{F}$  lower.

The majority of the retorting runs were made with a nitrogen sweep through the retort tube. Gas flow was maintained at 2.5 standard  $\text{cm}^3/\text{min}$  (superficial space velocity of  $0.023\text{ ft}^3/\text{min}/\text{ft}^2$ ). Several runs were made with the nitrogen flow increased to 20 standard  $\text{cm}^3/\text{min}$  (superficial space velocity of  $0.19\text{ ft}^3/\text{min}/\text{ft}^2$ ). In addition to these basic retorting runs, others were made using air and nitrogen as sweep gas with the oxygen content varying from 3 to 21 percent and a total gas flow of 2.5 to 20 standard  $\text{cm}^3/\text{min}$ , steam and nitrogen as the sweep gas with the nitrogen flow at 2.5 standard  $\text{cm}^3/\text{min}$  and a steam rate of 1 g/min.

### Gas Analyses

Gas analyses were performed by gas liquid chromatography (GLC) using a 1/8-in o.d. by 10-ft stainless-steel column packed with 150 to 200 mesh Poropak Q. GLC operating conditions were a helium flow of 18  $\text{cm}^3/\text{min}$  and oven temperature programed from  $50^\circ$  to  $180^\circ\text{C}$  at  $4^\circ\text{C}/\text{min}$ . Detection was by thermal conductivity. For quantitative analyses the GLC peak areas were corrected for molar response by the method of Messner.<sup>8</sup>

## RESULTS AND DISCUSSION

Table II is a tabulation of the recoveries and ethylene-ethane ratios for retorting runs performed at  $1,064.4^\circ$  and  $1,297.5^\circ\text{F}$ . These data show the type of recovery experienced during the work. It is felt that most of the loss was due to nonrecovery of liquid, which condensed in inaccessible parts of the system. As can be seen, the ethylene-ethane ratio changes when the retorting temperature changes.

TABLE II. - Recovery and ethylene-ethane ratio for selected temperatures of laboratory retorting using nitrogen sweep gas

Source <sup>1/</sup>	Oil shale Assay, gpt		Total flow cm <sup>3</sup> /min	Retort temp., ° F	Charge, gram	Recovery, wt. pct			Wt pct ratio, ethylene/ethane	
	Size <sup>2/</sup>					Spent shale	Oil + water	Gas		Loss
C	53.8	C	2.5	1,064.4	7,6052	71.69	22.27	5.05	0.73	0.7012
C	53.8	C	20.0		7,3051	71.82	20.86	6.30	1.02	0.7124
C	53.8	A	2.5		5,9429	72.14	20.84	5.22	1.80	0.7638
C	53.8	C	2.5		7,5043	71.82	22.29	5.15	0.74	0.7207
C	52.5	D	2.5		7,4783	73.73	19.73	5.29	1.25	0.7867
C	53.8	A	2.5		6,1041	72.02	21.36	5.27	1.35	0.7565
C	52.5	D	2.5		8,2537	73.98	19.46	5.02	1.54	0.7979
C	53.8	C	20.0		7,4921	71.99	20.91	6.42	0.67	0.7213
W	12.4		2.5		7,5210	88.25	8.49	2.46	0.80	0.6968
C	3/	B+C	2.5		8,4510	80.83	14.70	3.44	1.03	0.7950
C	53.8	C	2.5	1,297.5	7,7834	66.29	13.57	15.88	4.26	1.6135
C	53.8	C	2.5		7,8141	66.13	14.97	15.85	3.05	1.7003
C	53.8	C	2.5		7,8151	66.95	13.53	16.92	2.60	1.6762
C	53.8	C	2.5		7,8141	66.38	13.59	17.32	2.71	1.6975

1/ C = Colorado, W = Wyoming.

2/ Particle size, A = 20-30 mesh, B = 10-14 mesh, C = 1/8-in to 30 mesh, D = 1/2- to 1/4-in.

3/ A mixture of 53.8- and 22-gpt oil shales to give an approximate 36-gpt oil shale.

The change in ethylene-ethane ratio is not linear with change in temperature. A linear relationship can be obtained by using logarithm of the ethylene-ethane ratio and reciprocal of the temperature. Other combinations of saturates and unsaturates, while showing similar changes with temperature, cannot be transformed to linear relationship as readily.

When a linear least-squares regression of the log (ethylene/ethane) with reciprocal temperature is performed, the resulting regression equation has a coefficient of determination ( $100 r^2$ ) of 95. This means that all but 5 percent of the variation of log (ethylene/ethane) can be explained as reciprocal temperature dependence. Data from retorting runs on oil shales from different locations, of different particle size, and of different assay richness were included in the regression.

The regression equation so derived is

$$\frac{1,000}{T} = 0.8868 - 0.4007 \log (\text{ethylene/ethane}). \quad 1)$$

where T = temperature, °F. When Equation 1 is recast for the prediction of the Retorting Index, it is

$$RI = T = 1,000/[0.8868 - 0.4007 \log (\text{ethylene/ethane})]. \quad 2)$$

When ethylene and ethane are determined with a 2 percent accuracy, it is possible to calculate the Retorting Index to  $\pm 25^\circ \text{ F}$  (95 percent confidence).

Oxygen was added to the sweep gas to determine its effects, if any, on the ethylene/ethane ratio. Total amounts of oxygen had to be kept low so the exothermic oxidation reactions would not upset the thermal balance in the retorting zone by increasing the shale temperature above the furnace temperature. In Table III are listed the results from the retorting runs made with added oxygen. These runs were made at 1,187° F using the 53.8-gpt, size C, Colorado oil shale. When the Retorting Index is calculated for the oxidation retorting runs, it is not significantly different from the furnace temperature. This shows that the presence of oxygen in the sweep gas has no effect on the Retorting Index. A similar conclusion can be drawn from the one retorting run where steam was included in the sweep gas.

Table III also lists data obtained from the cracking runs. These data produce a Retorting Index which generally is higher than the retorting temperature. The retorting temperatures for these runs were 100° to 150° F lower than the furnace temperature. This apparent anomaly can be readily explained. Both ethylene and ethane production in retorting and cracking are controlled by the laws of kinetics. The ethylene-ethane ratio is increased in a thermal cracker by increasing the temperature. The ratio can also be increased by holding the temperature constant and increasing the residence time. The same temperature-residence time control of the ethylene-ethane ratio is found in oil-shale retorting. Therefore, increasing the temperature with a small decrease in residence time or holding the temperature constant with an increase in residence time will increase the ethylene-ethane ratio, and the products of retorting will be essentially the same in either case. In most retorts the retorting products are in the high-temperature zone for only a small fraction of a second before they are swept to a cooler temperature. When the retort products were cracked in the bench retort, they spent a longer time in the high-temperature zone so more cracking could take place. Consequently, the products are the same as if they were produced at a higher temperature. Because we cannot determine the residence time for the retorting process, the composition of the retort products is compared to temperature and a higher Retorting Index is correct.



For further information on the validity of the Retorting Index, the calculations will be applied to data from four different retorting methods. Table IV lists the reported retorting temperature, ethylene-ethane ratio, and Retorting Index for (A) Fischer assay, (B) gas combustion, and (C) entrained solids retorting.

TABLE IV. - Reported retorting temperatures and Retorting Indexes

Retort	Wt pct ratio, ethylene/ethane	Reported retorting temp, °F	Retorting Index, °F	
Fischer assay	0.3107	932	918	
	.2585	932	892	
	.3472	932	934	
	$\frac{1}{2}$ .2933	932	909	
	.4338	932	969	
Entrained solids, steam <sup>2/</sup>	1.8884	1,000	1,287	
	2.3494	1,100	1,353	
	3.8667	1,200	1,532	
	5.5556	1,300	1,695	
	6.6316	1,400	1,787	
	9.6216	1,500	2,020	
Entrained solids, steam + air <sup>2/</sup>	12.9153	1,650	2,252	
	5.3243	1,085	1,674	
	8.4408	1,205	1,932	
	5.2889	1,230	1,670	
	12.9937	1,295	2,258	
13.5381	1,315	2,294		
Gas combustion <sup>3/</sup>				
	6-ton/day, Run 311-C	1.8000	$\frac{4}{5}$ 1,400	1,273
	150-ton/day, Run 25-1	1.4000	$\frac{5}{5}$ 1,310	1,206
150-ton/day, Run 25-3	.5333	$\frac{5}{5}$ 1,625	1,004	

<sup>1/</sup> Reference 5.

<sup>2/</sup> Reference 9.

<sup>3/</sup> Reference 7.

<sup>4/</sup> Maximum bed temperature.

<sup>5/</sup> Maximum distributor temperature.

#### Fischer Assay

Ethylene-ethane ratios are listed for five Fischer assay runs. Four were reported in intra-Bureau reports, and the fifth was reported by Goodfellow.<sup>5</sup> The Retorting Index for these data cluster around the 932° F point, which is the maximum temperature used in the assay. In Fischer assay the oil shale is heated at a relatively slow rate to the maximum temperature of 932° F. Variation in heating rate could easily affect the Retorting Index.

#### Gas Combustion

Results from three gas-combustion retort runs<sup>7</sup> are reported. These data are for one run of the 6-ton-per-day retort and two runs of the 150-ton-per-day retort, and the reported temperatures

are for maximum bed temperature and maximum distributor temperature, respectively. Maximum distributor temperature is the highest combustion temperature in the retort and does not give an indication of the temperature of retorting any more than the maximum bed temperature does. Here the use of the calculated Retorting Index gives a meaningful value for a temperature of retorting. Reported yield data follow more closely with the Retorting Index than the maximum distributor or maximum bed temperature.

#### Entrained Solids

Retorting Indexes calculated from the data from the Bureau of Mines entrained-solids retort<sup>9</sup> deviates greatly from reported retorting temperatures. In fact, it is possible to calculate two new regression equations that have essentially the same slope as Equation 1, but different intercepts. One equation would be for the steam only entrainment, and the other for steam plus air entrainment. The fact that the entrained-solids retort data give regression equations with essentially the same slope as was obtained from the laboratory data indicates that the same kinetic mechanism producing ethylene and ethane is applicable. The steam-entrainment data show a higher ethylene-ethane ratio and therefore a higher Retorting Index because of the effect of residence time in the retort. The retort products in this retort have to pass through about 35 feet of heated retort, which would give the products a residence time of several seconds. This is considerably longer than the contact time found in most other types of retorting. At 1,000° F, for example, the residence time in the entrained-solids retort is about 2.5 to 3 seconds as compared to less than 0.5 seconds estimated for the bench retort. Severe cracking of the retorted products takes place in the entrained-solids retort producing final products that appear to have been made at a higher temperature, hence a higher Retorting Index. This argument is also borne out by the increased aromaticity of the oil produced in the entrained-solids retort. The steam plus air retorting data show even higher Retorting Index than the steam-entrained data because of the added heat from the exothermic, oxidation reactions.

#### 10-Ton Aboveground Retort

Two retorting runs of the 10-ton aboveground retort<sup>2-4</sup> provided the necessary data (unpublished) to allow the calculation of Retorting Indexes. Temperatures of the shale bed were measured every 5 hours with thermocouples placed at about 18-in intervals in bed depth. Gas analyses were performed at the same time. Retorting run 28 had an average maximum bed temperature of 1,020.9° F and an average Retorting Index of 1,070.9° F. This run suffered from extreme channeling resulting in a retorting rate of 2.28 ft/day. In this retorting run the calculated Retorting Index follows quite closely the maximum bed temperature. Retorting run 29 had no channeling, and its retorting rate was 1.59 ft/day so that the shale bed could soak and obtain a higher temperature. For this run the Retorting Index is lower than the maximum bed temperature. The average Retorting Index was 964.7° F, and the average maximum bed temperature was 1,180.3° F.

#### SUMMARY

A method of calculating a Retorting Index for oil-shale retorting has been presented. The method utilizes the relative amounts of ethylene and ethane in the retort gas and allows the determination of the Retorting Index or effective retorting temperature to  $\pm 25^\circ$  F. Calculation of the Retorting Index is possible for aboveground and in situ retorting. Factors such as particle size, rate of heating, and oil-shale assay have no apparent effect on the Retorting Index. Because of the kinetics involved, such things as retort product residence time and cracking are reflected in the Retorting Index. Thus, the Retorting Index will be more nearly associated with retort-product composition than such things as maximum temperature of the oil-shale bed.

## ACKNOWLEDGMENTS

The work upon which this report is based was done under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the University of Wyoming.

Reference to specific trade names or manufacturers does not imply endorsement by the Bureau of Mines.

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