BRANTLEY FE COX RJ 02/00/1952
RETORTING OIL SHALE AT HIGH TEMPERATURES. 4. INCLINED SURFACE RETORT

Reference #

Data Inventory Sheet

1. Commodity OS

2. Author LETC

3. Title (or description)

Intra-Bureau Report OSRD - 51 "Retorting Oil Shale at High Temperatures. 4. Inclined-Surface Retort", by F. E. Brantley and R. J. Cox, Feb. 1952.

4. Date

5. Reference

29 pp

6. Source

in house

7. Location of Data

Lib. closet

8. Form of Data

9. Type of Work

10. Description of Work

11. Types of Data

12. Quantity of Data

13. Quality of Data

14. Priority

Ref. OK

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RETORTING OIL SHALE AT HIGH TEMPERATURES

4. Inclined-Surface Retort

by

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Laramie, Wyoming

Intra-Bureau Report OSRD-51
February 1952

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INTRODUCTION

Use of the inclined-surface retort as a means of producing aromatics is the last in a series of four methods investigated for high-temperature retorting of oil shale. The first three methods have been described in Intra-Bureau Reports OSRD-48, 49, and 50, issued by the Laramie Station. The purpose of these investigations, as well as a cost estimate of a commercial-size plant based on the inclined-surface retort, has been presented in Intra-Bureau Report OSRD-46, "Production of Benzene, Ethyl Alcohol, and other Products from Oil Shale," by Walter I. R. Murphy and W. I. Barnet, dated August 12, 1951.

The inclined-surface retort appears to have several advantages. Based on a similar retort for carbonization of coal, the materials of construction would be largely ceramics. Thus the large amounts of steel necessary in some of the other types of retorts would not be necessary. Mass shale rates are high for this type of retort, and use of a gravity feed simplifies handling of the shale. Estimates of heat requirements have indicated that sufficient heat for the process can be obtained from the carbon residue on the spent shale and the gas remaining after removal of ethylene. The retorting system does not require introduction of fluids; therefore, the problem of product dilution by steam or other substances is not encountered.

Attempts were made in this series of experiments to retort in the same temperature range used in the vertical-tube retort experiments (1200°-1700° F.), and to obtain conditions favorable to maximum benzene production.

Several variations in operating procedure were used. For some runs inert sweep gases were used to reduce vapor residence time in the retort, while in other runs, an extension of the retort in the form of a reactor, heated electrically, was used to increase residence time of the vapors at the retorting temperatures. This reactor was also used to study the possibility of retorting at a low temperature and then subjecting the vapors to higher temperatures before condensation had taken place.

APPARATUS AND METHOD

The experimental retort used in this investigation is shown by the diagrammatic sketch in figure 1. A photograph of the apparatus is given in figure 2. The retort was constructed from a 3.5-foot length of 10-inch

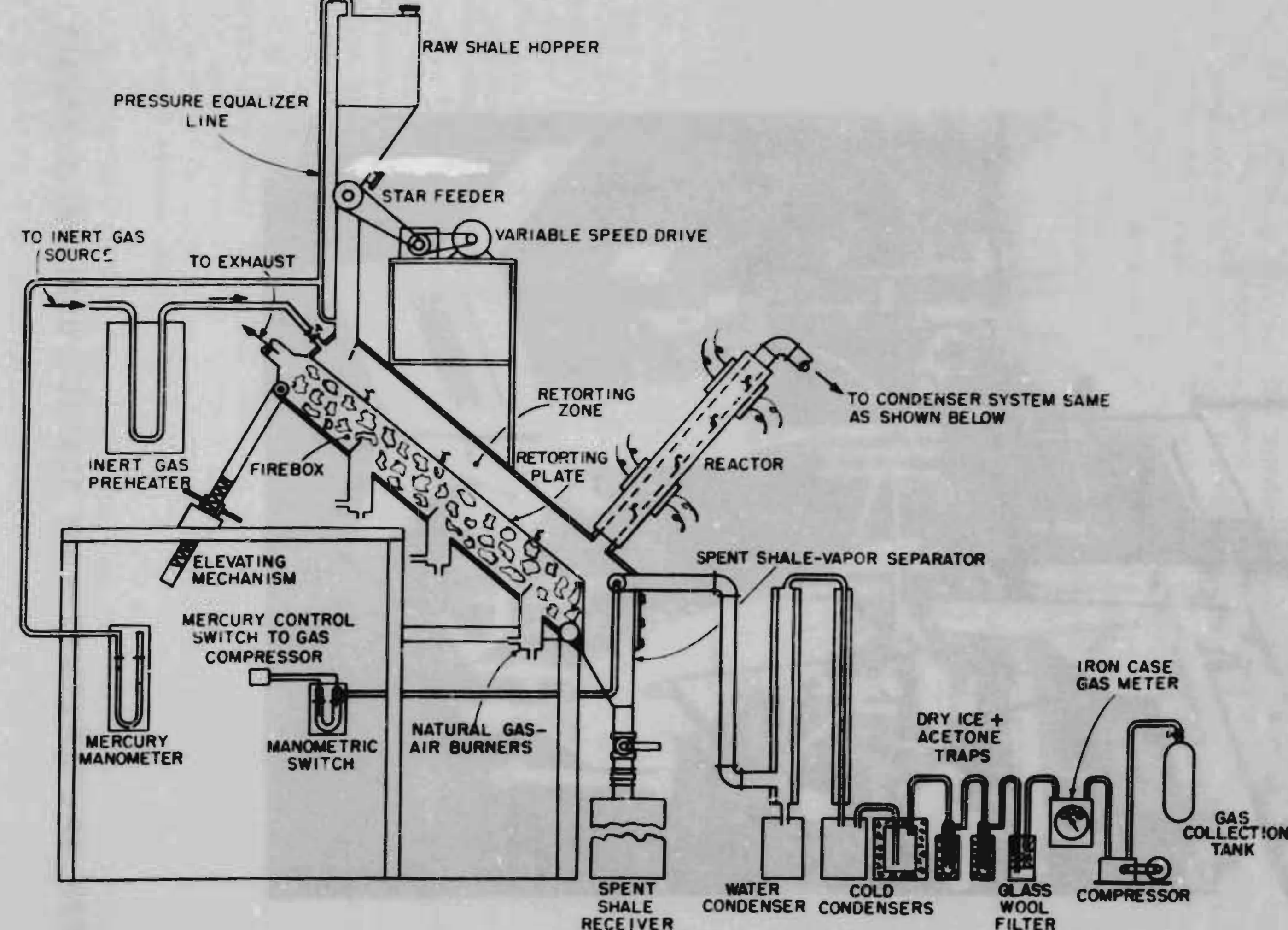

FIGURE I. INCLINED-SURFACE HIGH-TEMPERATURE RETORT.

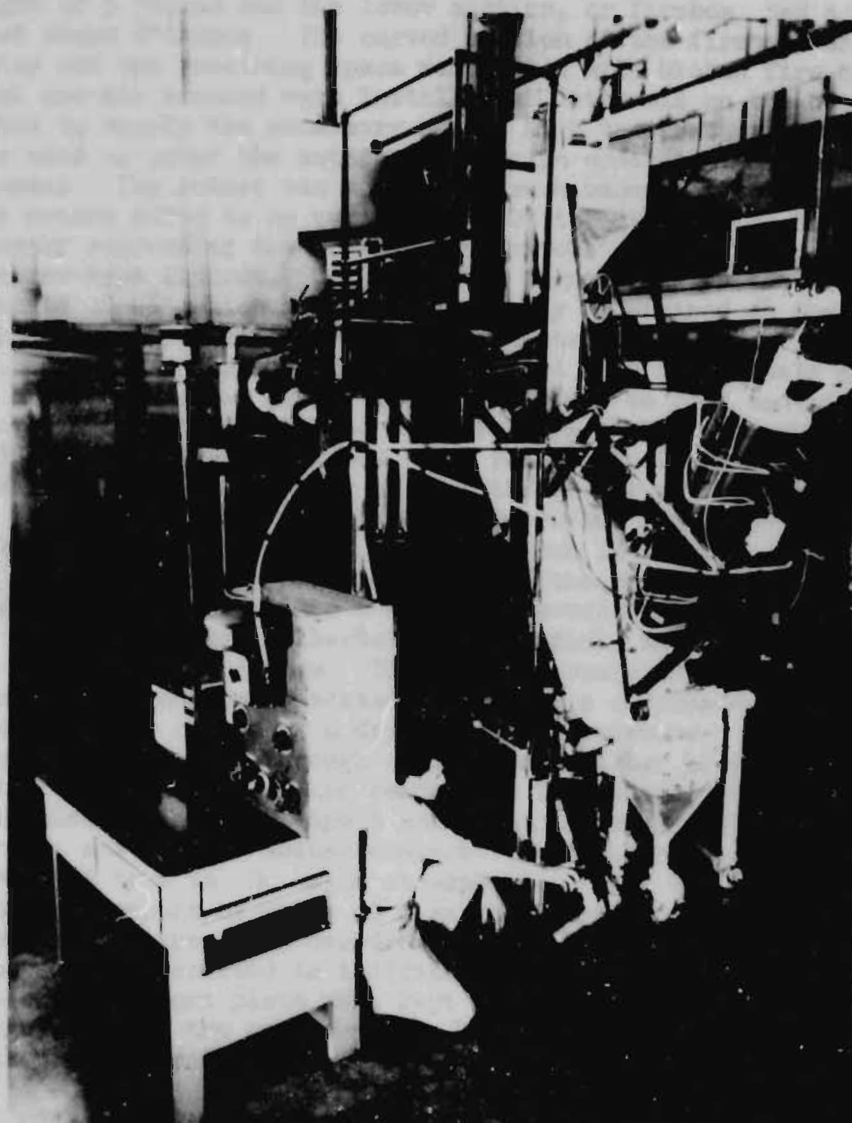

FIGURE 2. INCLINED-SURFACE HIGH-TEMPERATURE RETORT

steel pipe, which was divided into two longitudinal sections by means of a 1/2-inch steel plate. The upper section, or retorting chamber, had a maximum height of 3 inches and the lower section, or firebox, had a maximum height of about 9 inches. The curved section of the firebox was lined with fire clay and the remaining space was packed with broken fire brick. Three natural gas-air burners were installed at intervals on the bottom of the firebox to supply the necessary heat. High-temperature insulating material was used to cover the entire assembly in order to prevent excessive heat losses. The retort was mounted in such manner as to allow the angle of the retort plate to be varied from 30° to 55° with the horizontal. This was done by suspending the lower end on pivots and the other on an adjustable screw-type support, which could be turned to give the desired angle. An angle of 45°, which had been previously determined as the minimum that would give a satisfactory flow of raw shale, was used for most of the runs. Crushed shale was fed to the retort from a raw shale hopper by means of a variable-speed star feeder and allowed to flow continuously by gravity over the entire length of the retorting plate. The shale used was obtained from the Bureau of Mines Anvil Points mine near Rifle, Colo., and averaged 30 gal./ton by Fischer assay methods. It was crushed and screened to the following sizes: 28/100 mesh, 20/100 mesh, and 14/100 mesh. Fischer assays of the shales used are shown in table 1. Feed rates ranged from 109 to 1361 grams per minute. From the retorting zone the vapors and spent shale passed into a spent shale-vapor separator. The spent shale was retained and collected at this point, while the vapors passed into the condensing system. This system consisted of a water-cooled condenser, a condenser operated at 15° F., a condenser cooled by dry ice, and two traps cooled by a dry ice-acetone mixture. The noncondensible gases were filtered through a glass-wool filter to remove any remaining oil fog, then metered and compressed into storage cylinders from which samples were taken. Spent shale samples were collected and analyzed for CO_2 and organic matter content. The retort was operated at a pressure of 1 to 2 in. Hg below atmospheric. This was accomplished by withdrawing the vapors by means of a gas compressor controlled by a manometric switch. Temperature measurements were made by means of chromel-alumel thermocouples connected to indicating and recording pyrometers. Temperatures of the retort plate were kept as nearly constant as possible by manual regulation of the gas burners. The average of the plate temperatures was taken as the run temperature.

Initial runs were made to determine the amount of benzene that could be obtained by means of high-temperature retorting using an inclined-surface type of retort. For these runs, retorting temperatures were maintained in the range which produced maximum aromatic yields in the vertical tube retort (1400°-1600° F.).

A modification to allow use of a sweep gas was installed for several runs in order to determine the effect of reducing vapor residence time in the hot zone of the retort. Two 1/4-inch stainless steel lines were connected to sources of helium and natural gas. Each component was metered

Table 1.--Fischer assays and analyses of raw shales

Run No.	Mesh	Oil		Water		Organic matter, percent	Mineral CO_2, percent	Ash, percent
		Gal./ton	Wt. percent	Gal./ton	Wt. percent			
2	28/100	29.6	11.4	2.4	1.0	16.4	17.1	65.5
3	14/100	29.0	11.1	2.4	1.0	16.3	16.6	66.1
4,5,6,7	20/100	27.4	10.5	3.1	1.3	15.3	17.0	66.4
8,9,10,12,13,14,16,17,18	20/100	29.6	11.4	2.4	1.0	16.4	17.0	65.6
23,24,26,27,28,29,30,31,32 33,34,35	14/100	28.3	10.9	3.6	1.5	15.3	20.0	63.2

and the two mixed in a single line. The mixed gas was passed through a preheater where it attained a temperature of 1000°-1200° F. and was then introduced into the upper end of the vapor chamber of the retort.

Another modification was made for a few runs by addition of a reactor to the offtake end of the vapor chamber, which allowed additional high temperature treatment of the vapors after they had been formed in the retort. This reactor, consisting of a length of 2-inch stainless steel pipe, was heated over a 2.5-foot section by means of an electric reactor furnace controlled by rheostats. Vapors passed without condensation from the retort to the reactor while the spent shale collected in the spent-shale receiver. Provision was also made to withdraw part of the vapors through the regular vapor offtake and at the same time take the remainder off through the reactor. Temperatures of the reactor, which were varied from 1200° to 1700° F., were measured by means of thermocouples attached to the reactor wall at intervals and connected to an indicating pyrometer. After passing through the reactor the products were collected in a condensing and collecting system similar to the one previously described.

DISCUSSION OF RESULTS

Operating data for retorting under varying conditions are given in table 2. Removal of organic matter ranged from 51 to 89 percent. This variation, as with the vertical-tube retort, was due largely to changes in temperature, and in a lesser degree to changes in feed rates and shale size. Removal of CO_2 varied from 0 to 55 percent; however, it was not consistent with the organic removal. One run at 1500° F. showed 89 percent organic matter removal and 2 percent CO_2 removal, whereas another run at the same temperature showed 88 percent organic removal and 22 percent CO_2 removal. Operating conditions were approximately the same in both cases. Another run made at 1450° with an exceptionally high feed rate of 1361 g./min. and an organic removal of 85 percent, showed a CO_2 removal of 0 percent. This run indicated that high throughput with high percentage of organic matter removal is possible with the inclined-surface type of retort. No conclusions can be drawn from the discrepancies in CO_2 removal, although it is possible that the feed rate in some instances may have been irregular due to raw shale holdup in the feeder, or the plate temperature may have been uneven. Either of these factors could have caused the variations. Air leakage into the system also may have occurred and caused autothermic reactions to take place. Temperature control was not satisfactory at 1700° F. and above; consequently, 1700° was the highest retorting temperature attempted.

Seven runs were made using a mixture of natural gas and helium to reduce residence time of vapors in the retort. This apparently had a beneficial effect on liquid yields in all cases. While higher liquid yields were obtained from some runs not using inert gas, yields for those runs in which the gas was used were all above average. Total low-boiling aromatic yields varied, and in the temperature range of highest benzene and toluene formation (1500°-1600°), the best results were about evenly

Table 2.--Operating data for retorting oil shale with inclined-surface retort

Run No.	Average temperature °F. Retort plate	Reactor	Feed rate g./min.	Feed size mesh	Raw shale analysis: Organic matter percent	CO_2 percent	Removal of organic matter percent (1/)	(2/)	Removal of mineral CO_2 percent
28	1200	----	332	14/100	15.3	20.0	61.1	----	2.0
29	1200	----	343	14/100	15.3	20.0	56.5	64.6	0.0
26	1200	1200	384	14/100	15.3	20.0	56.5	65.0	0.0
31	1200	1200	518	14/100	15.3	20.0	67.3	75.1	1.0
27	1200	1500	441	14/100	15.3	20.0	63.0	77.4	0.0
30	1200	1700	476	14/100	15.3	20.0	----	81.3	3.7
32	1200	1700	465	14/100	15.3	20.0	63.4	72.8	2.0
33	1200	1700	565	14/100	15.3	20.0	----	75.1	2.9
18	1250	1500	338	20/100	16.4	17.0	77.3	81.1	0.0
12	1350	----	508	20/100	16.4	17.0	84.4	84.4	6.7
3	1400	----	252	14/100	16.3	16.6	50.6	59.9	10.0
16	1400	----	490	20/100	16.4	17.0	64.4	64.8	12.0
13	1450	----	1361	20/100	16.4	17.0	84.4	85.6	0.0
2	1475	----	123	28/100	16.4	17.1	81.3	82.1	35.2
34	1500	----	655	14/100	15.3	20.0	87.9	88.3	3.0
8	1500	----	282	20/100	16.4	17.0	88.4	89.2	21.7
14	1500	----	254	20/100	16.4	17.0	89.2	89.2	1.6
7	1550	----	118	20/100	15.3	17.0	86.5	88.2	55.4
9	1550	----	195	20/100	16.4	17.0	86.4	85.6	19.4
5	1550	----	202	20/100	15.3	17.0	83.0	81.2	37.1
10	1600	----	109	20/100	16.4	17.0	86.0	----	36.8
6	1600	----	169	20/100	15.3	17.0	83.0	82.5	33.6
35	1700	----	685	14/100	15.3	20.0	87.9	88.3	12.0

1/ Before benzene extraction.
2/ After benzene extraction.

divided between the runs using inert sweep gas and those in which it was not used. Calculated yields of products for runs carried out under varying operating conditions are given in table 3. The optimum retorting temperature for aromatic production seems to be 1500°-1600° F. Ethylene yields were also highest in this temperature range. Run 7, with a retorting temperature of 1550°, produced the maximum yield of 2.97 gallons of benzene per ton of shale. An unusually large part of this benzene was recovered in the gas. Small amounts of acetone and methyl alcohol were also present in this gas sample but since these compounds have not been observed in samples from any other run, it is possible that they, as well as part of the benzene, may have resulted from a contaminated sample bottle. A trace of acetone was present among the water-soluble compounds reported for one run, although methyl alcohol was not. Benzene was usually present in small percentages in the gas samples, although it was above average in run 7. The highest ethylene yield was also obtained with a retorting temperature of 1550° F. Feed rates for runs having maximum yields of aromatics were 100 to 200 g./min., although one of the highest total oil yields was obtained in run 13, with a feed rate of 1361 g./min. Benzene yield for this run in which sweep gas was used was 0.9 gal./ton.

The angle of the retorting plate for all runs reported, except two, was set at 45° with the horizontal, which gave an estimated retention time of the shale in passage over the plate of 1.5 seconds. Runs 6 and 7 were made with the plate at 35° and 30° respectively. Shale holdup on the retort plate was considerable in both of these runs. Run 7 gave the highest benzene yield of the series; 1.0 weight percent on a raw shale basis or 21.0 weight percent on a dry crude basis. Because a considerable amount of spent shale was retained on the plate in run 7, a catalytic action by the spent shale at high temperatures may be indicated.

Gas formation for the inclined-surface retort runs increased with increase in retorting temperature and, based on equivalent organic content, was comparable in most cases to the vertical-tube retort yields. However, passing the vapors formed at a lower retort temperature through the auxiliary reactor at elevated temperatures did not result in as high a gas yield as did an equivalent retorting temperature. The vapor space of the retort was not maintained at the same temperature as the retorting plate because heat was supplied only to the retorting plate, and once this was covered by the shale during the run, the quantity of heat radiated to the vapor space was reduced. The top of the vapor chamber was approximately 100° to 200° F. cooler than the retorting plate. The maximum ethylene yield with the inclined-surface retort was 44 lbs./ton. This compares with a calculated maximum of 43.4 lbs./ton obtained from a shale of equivalent organic content by use of the vertical tube retort.

Material balances for the various runs are given in table 4. These balances were calculated on an over-all, no-loss basis, and on an organic basis, the latter comparing favorably with similar balances on runs made with the vertical-tube retort.

Table 3.--Yields of products under varying operating conditions

Run	Temperature, °F.		Feed rate	Sweep gas, cu.ft./min.		Weight percent of raw shale, organic basis				Weight percent of dry crude		Gallons per ton of raw shale		Pounds per ton of raw shale	Total gas
No.	Retort	Reactor	g./min.	Helium	Methane	Dry crude	Benzene[1]	Toluene[1]	Ethylene	Benzene	Toluene	Benzene[1]	Toluene[1]	Ethylene	cu.ft./ton
28	1200	----	332			6.1	----	----	0.58	----	----			11.6	1190
29	1200	----	343			6.0	0.23	0.11	0.56	3.55	1.82	.64	.30	11.2	1350
26	1200	1200	384			4.8	----	----	0.53	----	----			10.7	1240
31	1200	1200	518			5.7	0.35	0.43	0.82	5.79	7.48	.97	1.19	16.4	1820
27	1200	1500	441			4.3	0.35	0.26	1.06	7.59	6.12	.96	.73	21.3	1740
30	1200	1700	476			4.9	0.56	0.18	1.31	9.93	3.67	1.54	0.50	26.2	1840
32	1200	1700	465			5.1	----	----	0.86	----	----			17.2	1920
33	1200	1700	565			5.9	----	----	1.55	----	----			33.0	2040
18	1250	----	356			2.1	0.09	0.06	0.47	4.3	3.0	0.24	0.17	9.4	2430
18	1250	1500				1.8	0.34	0.13	0.96	19.1	7.4	0.93	0.36	19.2	2880
12	1350	----	508	0.5	0.1	5.8	0.24	0.18	----	4.2	3.1	0.67	0.50		----
19	1360	----	350			4.1	0.25	0.14	----	5.7	3.4	0.69	0.39		----
19	1360	1500				1.2	0.17	0.06	----	14.1	5.2	0.47	0.17		----
20	1375	----	285			2.5	0.15	0.10	----	6.1	4.1	0.41	0.28		----
20	1375	1500				1.7	0.38	0.14	----	15.1	5.5	1.04	0.39		----
3	1400	----	252			2.1	0.37	0.09	1.14	14.9	4.3	1.01	0.25	22.8	2050
16	1400	----	490	----	0.6	5.0	0.34	----	----	6.7	----	0.93			----
13	1450	----	1361	0.04	0.2	5.8	0.34	0.22	----	5.8	3.8	0.92	0.61		----
2	1450-1500	----	123			2.8	0.29	----	----	10.6	----	0.81	----		----
34	1500	----	655			7.5	0.38	0.32	1.23	4.65	4.24	1.07	0.87	24.6	2520
4	1500	----	205			4.2	0.68	0.27	2.20	13.9	5.0	1.87	0.74	44.0	4000
8	1500	----	282	0.2	1.1	5.0	0.36	0.18		7.0	3.6	0.96	0.50		----
14	1500	----	254	0.2	0.7	4.5	0.45	0.22		9.9	4.8	1.22	0.60		----
9	1550	----	195	0.4	1.2	5.5	0.53			9.6		1.45	----		----
5	1550	----	202			3.5	0.44	0.10	1.98	7.9	3.0	1.24	0.29	39.6	4063
7	1550	----	118			3.0	1.06	0.09	1.66	21.0	3.1	2.97	0.26	33.2	4500
10	1600	----	109	0.6	0.8	4.6	0.79	0.23		16.5	4.7	2.10	0.59		----
6	1600	----	169			0.8	0.19	----	0.83	5.8	1.4	0.48	----	16.6	4550
35	1700	----	685			4.3	0.58	0.18	1.74	11.12	4.20	1.60	0.50	34.8	4375

1/ Including material recovered from gas with exception of runs 10, 12, 13, 14, 19, and 20.

Table 4.--Material balances of runs with inclined-surface retort

Run No.	28	29	31	26	27	30	32	18	12	3	16
Temperature, °F., plate	1200	1200	1200	1200	1200	1200	1200	1250	1350	1400	1400
Temperature, °F., reactor	----	----	1200	1200	1500	1700	1700	1500	----	----	----
Feed rate, g./min.	332	343	518	384	441	476	465	338	508	252	490
Shale size, mesh	14/100	14/100	14/100	14/100	14/100	14/100	14/100	20/100	20/100	14/100	20/100
Over-all material balance, no loss basis, percent											
Oil	6.8	8.1	5.8	4.9	5.3	4.9	4.7	3.9	5.8	2.0	6.2
Gas	4.0	4.0	5.3	3.7	5.1	6.1	5.0	8.4	14.7*	6.9	10.2*
Water	0.7	0.9	0.9	0.7	1.1	1.2	1.0	0.2	0.6	0.8	0.8
Spent shale	87.1	86.7	87.4	89.7	87.5	86.8	87.7	87.5	78.9	90.3	81.6
Coke	1.4	0.3	0.6	1.0	1.0	1.0	1.6	----	----	----	1.2
Organic balance raw shale basis, percent											
Oil	6.1	6.0	5.7	4.8	4.3	5.4	4.5	3.9	5.8	2.1	5.0
Gas	2.3	3.0	4.2	3.6	4.3	4.9	3.8	9.0	8.1	5.5	6.6
Benzene soluble on spent shale	1.2	1.0	1.3	1.3	1.8	1.5	1.4	0.6	0.0	1.7	0.1
Coke on spent shale	5.7	5.3	4.1	5.6	4.9	3.5	5.6	2.9	2.5	7.0	4.7
Organic balance, organic basis, percent											
Oil	40	39	37	31	28	35	30	24	35	13	30
Gas	15	20	27	24	28	32	24	55	49	34	40
Benzene soluble on spent shale	8	7	9	8	12	10	9	4	0	10	1
Coke on spent shale	37	34	27	37	32	23	37	17	16	43	29

*Plus loss.

Table 4.--Material balances of runs with inclined-surface retort--continued

Run No.	13	2	34	4	8	14	9	7	5	10	35
Temperature, °F., plate	1450	1475	1500	1500	1500	1500	1550	1550	1550	1600	1700
Temperature, °F., reactor	----	----	----	----	----	----	----	----	----	----	----
Feed rate, g./min.	1361	123	655	205	282	254	195	118	202	109	685
Shale size, mesh	20/100	28/100	14/100	20/100	20/100	20/100	20/100	20/100	20/100	20/100	14/100
Over-all material balance, no loss basis, percent											
Oil	6.6	2.5	7.8	4.2	4.5	5.5	4.3	2.6	3.6	4.8	4.7
Gas	9.3	20.2*	7.4	13.1	12.3*	13.1*	9.9*	16.6*	15.8	16.4*	13.3
Water	0.9	0.8	1.0	0.8	1.6	0.6	1.2	1.3	1.1	1.0	1.2
Spent shale	83.2	76.5	83.3	81.9	81.6	80.8	84.6	79.5	79.5	77.8	78.8
Coke	----	----	0.5	----	----	----	----	----	----	----	2.0
Organic balance, raw shale basis, percent											
Oil	5.8	2.8	7.6	----	5.0	4.4	5.5	3.0	3.5	4.6	4.3
Gas	8.2	10.2	5.7	----	9.3	10.5	8.3	10.2	9.2	9.6	9.1
Benzene soluble on spent shale	0.3	0.1	0.1	----	0.1	0.0	0.0	0.3	0.0	0.0	0.1
Coke on spent shale	2.1	3.3	1.9	----	2.0	1.5	2.6	1.8	2.6	2.2	1.8
Organic balance, organic basis, percent											
Oil	35	17	50	----	31	27	34	20	23	28	28
Gas	50	62	37	----	57	64	50	66	60	59	59
Benzene soluble on spent shale	2	1	1	----	1	0	0	2	0	0	1
Coke on spent shale	13	20	12	----	11	9	16	12	17	13	12

*Plus loss.

Table 5.—Calculated yields with and without use of reactor

Run No.	Temperature, °F. Plate	Reactor	Total dry crude (wt. percent)	Wt. percent of dry crude Benzene	Toluene	Gals. per ton Benzene	Toluene	Ethylene lb./ton
1/18	1250	----	4.6	4.3	3.0	0.55	0.38	20.8
2/18	1250	1500	3.3	19.1	7.4	1.75	0.67	35.4
1/19	1360	----	6.7	5.7	3.4	1.06	0.63	----
2/19	1360	1500	4.8	14.1	5.2	1.88	0.69	----
1/20	1375	----	6.1	6.1	4.1	1.04	0.69	----
2/20	1375	1500	4.4	15.1	5.5	1.85	0.66	----

1/ Yields recalculated for no vapors passing through reactor.
2/ Yields recalculated for all vapors passing through reactor.

Analysis of water-soluble compounds present in the inclined-surface retort oil from run 34 (1500°) was made by the Research and Analysis Section. No quantitative estimates were attempted due to the small amounts involved. Hydrogen cyanide and carbon dioxide were present in greatest quantity, with minor amounts of acetone, H_2S, and hydrocarbons. Traces of acetic and propionic acid were observed. No other compounds were reported.

For three runs, 18, 19, and 20, the retort was arranged so that two vapor streams were withdrawn simultaneously. One stream passed through the regular condensing system while the other passed through the reactor at 1500° and then through a condensing system. Liquid products from the reactor stream showed a considerably higher percentage of benzene and toluene than the products from the stream passed directly to the condensing system. Table 5 gives yields of these runs which were calculated to compare results of passing all vapors through the reactor with those of condensing the vapors directly without passage of any of the products through the reactor. Higher benzene and toluene yields resulted in all cases with use of the reactor. A higher ethylene yield was also obtained when the reactor was used, as indicated by run 18 in which the gas was analyzed. In addition to the above, six runs were made using the reactor and in each case where analyses were obtained the benzene and toluene yield was increased, at corresponding retorting temperatures, over runs without the reactor. For purposes of comparison, three runs were made by retorting shale at 1200° and passing the vapors formed through the reactor at 1200°, 1500°, and 1700° F., respectively. The reactor served essentially as an extension to the retort, by means of which additional heat at varying temperatures could be supplied to the vapors. Vapor retention times in the reactor for the various runs were estimated to range from one to two seconds depending on reactor temperature. Three additional runs, without use of the reactor, were made at 1200°, 1500°, and 1700° F., other operating conditions being kept as nearly constant as possible. Vapor retention times for these runs were calculated to be approximately five, two, and one second, respectively. Modified Hempel analyses of the oils from the six runs, 31, 27, 30, 29, 34, and 35, are given in tables 6, 7, 8, 9, 10, and 11, respectively. Sulfur and nitrogen analyses were made on individual distillation fractions from runs 30 and 35. These analyses are included in tables 8 and 11. Benzene and toluene contents of the fractions from each of the runs were obtained by mass spectrometer analysis. Distribution of these two compounds in the various fractions is shown in table 12. In analyzing results of runs 29, 34, and 35, several changes were noted in properties of the crude oil as the retorting temperature was increased. The specific gravity and nitrogen content increased while viscosity and sulfur content decreased with increase in operating temperature. Pour points in all cases were below 5° F. The volume of naphtha and specific gravities of all fractions of the oil increased as retorting temperature was raised. Carbon residues of the residuum and of the crude increased in a like manner, whereas the ash decreased.

Table 6.--Summary of properties of oil from inclined-surface retort. Run No. 31 (1200°-1200° F.)

Properties of dry* crude shale oil

Specific gravity	0.998
Sulfur, percent	0.93
Nitrogen, percent	2.88
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	64.2
*Water removed, wt. %	13.0
API gravity	10.3
Benzene, wt. %	5.79
Toluene, wt. %	7.48

Distillation summary

	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	38.4	0.829
Light distillate (fractions 8-10)	12.5	0.983
Heavy distillate (fractions 11-14)	21.9	1.070
Residuum	24.4	1.269
Loss	2.8	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure (first drop at 82° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.
1	50	122	4.5	4.5	0.692
2	75	167	4.2	8.7	.736
3	100	212	5.8	14.5	.803
4	125	257	7.7	22.2	.837
5	150	302	6.4	28.6	.851
6	175	347	4.7	33.3	.871
7	200	392	5.1	38.4	.906

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity S.U. Seconds 100° F.
8	150	302	2.1	40.5	0.958	
9	175	347	6.1	46.6	.977	
10	200	392	4.3	50.9	1.003	
11	225	437	3.7	54.6	1.026	73.3
12	250	482	4.3	58.9	1.054	[illegible]
13	275	527	5.3	64.2	1.073	595
14	300	572	8.6	72.8	1.094	2715
Residuum			24.4	97.2	1.269	

Carbon residue of residuum, 60.5 percent; carbon residue of crude, 18.8 percent.
Ash on residuum, 7.31 percent; ash on crude, 2.27 percent.

Table 7.--Summary of properties of oil from inclined-surface retort. Run No. 27 (1200°-1500° F.)

Properties of dry* crude shale oil

Specific gravity	1.070
Sulfur, percent	.875
Nitrogen, percent	3.03
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	109.2
*Water removed, wt. %	18.0
API gravity	0.7
Benzene, wt. %	7.59
Toluene, wt. %	6.12

Distillation summary

	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	32.5	0.872
Light distillate (fractions 8-10)	15.2	1.004
Heavy distillate (fractions 11-14)	23.2	1.086
Residuum	27.7	1.353
Loss	1.4	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure (first drop at 142° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.
1	50	122	---	---	---
2	75	167	1.1	1.1	0.773
3	100	212	9.0	10.1	.849
4	125	257	6.9	17.0	.863
5	150	302	5.9	22.9	.871
6	175	347	4.6	27.5	.892
7	200	392	5.0	32.5	.931

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity S.U. seconds 100° F.	Saybolt viscosity S.U. seconds 210° F.	Viscosity index
8	150	302	4.3	36.8	0.983			
9	175	347	6.2	43.0	1.003			
10	200	392	4.7	47.7	1.024			
11	225	437	2.9	50.6	1.044	73.4	33.8	Minus 176
12	250	482	4.7	55.3	1.068	166.4	37.2	Minus 382
13	275	527	5.7	61.0	1.091	525		
14	300	572	9.9	70.9	1.103	1713		
Residuum			27.7	98.6	1.353			

Carbon residue of residuum, 67.6 percent; carbon residue of crude, 23.7 percent.
Ash on residuum, 8.60 percent; ash on crude, 3.01 percent.

Gas evolved during the drying procedure = 8481 ml. (S.T.P.) gas from 842 g. wet crude (671 g. dry crude; 627 ml. dry crude).

Table 8.--Summary of properties of oil from inclined-surface retort.
Run No. 30 (1200°-1700° F.)

Properties of dry* crude shale oil	
Specific gravity	1.141
Sulfur, percent	0.840
Nitrogen, percent	3.03
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	257
*Water removed, wt. %	18.6
API gravity	Below 0.1
Benzene, wt. %	9.93
Toluene, wt. %	3.69

Distillation summary

	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	26.1	0.894
Light distillate (fractions 8-10)	15.9	1.035
Heavy distillate (fractions 11-14)	25.7	1.117
Residuum	32.2	1.357
Loss	0.1	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure
(first drop at 172° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Sulfur percent	Nitrogen percent
1	50	122	---	---	---	---	---
2	75	167	---	---	---	---	---
3	100	212	12.1	12.1	0.875	0.60	0.31
4	125	257	4.5	16.6	.881	.87	0.99
5	150	302	3.9	20.5	.894	.97	1.53
6	175	347	2.6	23.1	.921	.84	3.08
7	200	392	3.0	26.1	.964	.82	3.32

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity, S.U. seconds 100° F.	Sulfur percent	Nitrogen percent
8	150	302	5.0	31.1	1.025		1.05	2.37
9	175	347	6.5	37.6	1.033		0.90	2.92
10	200	392	4.4	42.0	1.051		.95	3.71
11	225	437	4.1	46.1	1.075	62.3	.96	3.97
12	250	482	5.3	51.4	1.106	151.0	.96	3.66
13	275	527	6.0	57.4	1.124	473.	.90	3.52
14	300	572	10.3	67.7	1.136	1712.	.75	3.48
Residuum			32.2	99.9	1.357		.43	3.31

Carbon residue of residuum, 78.1 percent; carbon residue of crude, 29.9 percent.
Ash on residuum, 7.93 percent; ash on crude, 3.04 percent.

Table 9.—Summary of properties of oil from inclined-surface retort.
Run No. 29 (1200° F.)

Properties of dry* crude shale oil	
Specific gravity	0.968
Sulfur, percent	.890
Nitrogen, percent	2.57
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	86.7
*Water removed, wt. %	9.6
API gravity	14.7
Benzene, wt. %	3.55
Toluene, wt. %	1.82

Distillation summary	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	26.9	0.823
Light distillate (fractions 8-10)	15.4	0.931
Heavy distillate (fractions 11-14)	26.9	0.995
Residuum	28.9	1.153
Loss	1.9	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure
(first drop at 135° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.
1	50	122	—	—	—
2	75	167	1.4	1.4	0.732
3	100	212	4.4	5.8	.782
4	125	257	5.9	11.7	.811
5	150	302	5.1	16.8	.826
6	175	347	4.6	21.4	.842
7	200	392	5.5	26.9	.872

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity S.U. seconds 100° F.	Saybolt viscosity S.U. seconds 210° F.	Viscosity index
8	150	302	3.6	30.5	0.908			
9	175	347	6.5	37.0	.928			
10	200	392	5.3	42.3	.950			
11	225	437	4.3	46.6	.965	63.8		
12	250	482	5.7	52.3	.982	120.9	37.2	Minus 140
13	275	527	7.3	59.6	1.000	291		
14	300	572	9.6	69.2	1.013	933		
Residuum			28.9	98.1	1.153			

Carbon residue of residuum, 34.6 percent; carbon residue of crude, 11.9 percent.
Ash on residuum, 5.48 percent; ash on crude, 1.89 percent.

Gas evolved during the drying procedure - 18,400 ml. (S.T.P.) gas from 1242 g. wet crude, (1031 g. dry crude; 1065 ml. dry crude).

Table 10.--Summary of properties of oil from inclined-surface retort.
Run No. 34 (1500° F.)

Properties of dry* crude shale oil

Specific gravity	0.995
Sulfur, percent	0.71
Nitrogen, percent	2.88
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	60.5
*Water removed, wt. %	11.6
API gravity	10.7
Benzene, wt. %	4.65
Toluene, wt. %	4.24

Distillation summary

	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	33.6	0.827
Light distillate (fractions 8-10)	14.2	0.962
Heavy distillate (fractions 11-14)	23.8	1.030
Residuum	26.7	1.215
Loss	1.7	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure (first drop at 86° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.
1	50	122	1.6	1.6	0.692
2	75	167	3.4	5.0	.742
3	100	212	8.7	13.7	.814
4	125	257	5.9	19.6	.835
5	150	302	5.1	24.7	.843
6	175	347	3.6	28.3	.861
7	200	392	5.3	33.6	.899

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity S.U. seconds 100° F.
8	150	302	3.6	37.2	0.945	
9	175	347	6.1	43.3	.960	
10	200	392	4.5	47.8	.977	
11	225	437	4.5	52.3	.994	62.2
12	250	482	5.0	57.3	1.019	129.7
13	275	527	5.8	63.1	1.037	339
14	300	572	8.5	71.6	1.050	1267
Residuum			26.7	98.3	1.215	

Carbon residue of residuum, 45.2 percent; carbon residue of crude, 14.7 percent.
Ash on residuum, 4.66 percent; ash on crude, 1.52 percent.

Table 11.--Summary of properties of oil from inclined-surface retort. Run No. 35 (1700° F.)

Properties of dry* crude shale oil	
Specific gravity	1.049
Sulfur, percent	0.690
Nitrogen, percent	2.92
Pour point, °F.	Below 5
Viscosity, S.U. seconds at 100° F.	61.9
*Water removed, wt. %	19.5
API gravity	3.4
Benzene, wt. %	11.12
Toluene, wt. %	4.20

Distillation summary

	Percent	Sp. gr. at 60° F.
Naphtha (fractions 1-7)	32.2	0.879
Light distillate (fractions 8-10)	17.8	1.012
Heavy distillate (fractions 11-14)	25.2	1.092
Residuum	22.2	1.299
Loss	2.6	

ANALYTICAL DATA

Distillation at 760 mm. Hg pressure (first drop at 158° F.)

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60°F.	Sulfur percent	Nitrogen percent
1	50	122	—	—	—	—	—
2	75	167	—	—	—	—	—
3	100	212	15.4	15.4	0.862	0.52	0.32
4	125	257	4.9	20.3	.868	.79	0.90
5	150	302	3.3	23.6	.873	.856	1.73
6	175	347	3.4	27.0	.892	.786	2.46
7	200	392	5.2	32.2	.938	.67	2.92

Distillation at 40 mm. Hg pressure

Fraction No.	Cut at °C.	Cut at °F.	Percent	Sum percent	Gravity, specific 60/60° F.	Saybolt viscosity, S.U. seconds 100° F.	Sulfur percent	Nitrogen percent
8	150	302	7.3	39.5	1.001		0.55	2.27
9	175	347	6.1	45.6	1.013		.79	2.83
10	200	392	4.4	50.0	1.029		.79	3.76
11	225	437	4.7	54.7	1.052	65.9	.84	3.96
12	250	482	6.3	61.0	1.082	144.4	.84	3.59
13	275	527	6.3	67.3	1.103	459	.72	3.54
14	300	572	7.9	75.2	1.115	2150	.82	3.44
Residuum			22.2	97.4	1.299		.43	3.56

Carbon residue of residuum, 67.8 percent; carbon residue of crude, 18.6 percent.
Ash on residuum, 2.45 percent; ash on crude, 0.67 percent.

Table 12.--Distribution of benzene and toluene in distillation fractions

Run No.	Temperature, °F. Plate	Temperature, °F. Reactor	Specific gravity of crude	Benzene, weight percent of dry crude: 1	2	3	4	5	6	7	Total	Toluene, weight percent of dry crude: 1	2	3	4	5	6	7	Total
29	1200	----	0.968	----	0.30	1.44	1.40	0.08	0.08	0.25	3.55	----	0.02	0.15	0.60	0.55	0.33	0.17	1.82
34	1500	----	0.995	0.16	0.88	3.13	0.06	0.22	0.09	0.11	4.65	----	0.37	1.55	0.91	1.04	0.21	0.16	4.24
35	1700	----	1.049	----	----	9.32	1.24	0.33	0.22	0.01	11.12	----	----	1.40	1.41	0.95	0.39	0.05	4.20
31	1200	1200	0.998	0.51	0.93	1.86	1.83	0.48	0.10	0.08	5.79	0.005	0.04	0.89	3.11	2.99	0.28	0.17	7.48
27	1200	1500	1.070	----	0.36	4.71	1.74	0.52	0.19	0.07	7.59	----	0.002	0.96	1.89	2.16	1.03	0.08	6.12
30	1200	1700	1.141	----	----	7.28	1.67	0.58	0.20	0.20	9.93	----	----	0.96	1.44	0.90	0.26	0.13	3.69

Analyses of oils from runs 31, 27, and 30, wherein the shale was retorted at 1200°, and the vapors passed through the reactor at 1200°, 1500°, and 1700°, respectively, when compared with results obtained by retorting at 1200° F. without the reactor show that the naphtha content, specific gravity, viscosity, and carbon residue of the oils increased with reactor temperature while sulfur content was reduced and nitrogen content remained about the same. Sulfur and nitrogen analyses of individual fractions of oils from runs 30 and 35 followed the same general pattern, the lower boiling fractions having the lowest nitrogen content, and fraction 11 (boiling range 392°-437° F.), the maximum nitrogen content. Curves for both sulfur and nitrogen contents of fractions of these two oils are irregular as shown in figure 3. This probably indicates the presence of specific nitrogen and sulfur compounds. The sulfur contents of the various fractions of the oils from the two runs showed a decided difference in fraction 8; the fraction from the run retorted directly at 1700° having approximately one-half the sulfur content of the correspond-ing fraction from the run using the reactor.

Benzene and toluene percentages on a dry crude basis, of the six oils on which Hempel analyses were made, are presented in figure 4. Retorting at 1200° produced low yields of benzene and toluene with a benzene-toluene ratio of about two to one. As the temperature was increased to 1500° the total percentage of benzene and toluene increased about one-third and the ratio of benzene to toluene decreased to one. Further increase in temperature to 1700° almost doubled the total percentage of the two aromatics. This increase was due almost entirely to increased benzene yield. Retorting at 1200° and then subjecting the vapors to the same and higher reactor temperatures showed that the sum percentage of benzene and toluene tended to remain constant. As the reactor temperature was raised, benzene yield increased with a corresponding decrease in toluene. This indicates a dealkylation of toluene. It would seem from the analyses that retorting at 1200° results in a constant percentage of low-boiling aromatics, which can be converted, within limits, to either benzene or toluene by temperature control. On the other hand, direct retorting at increased temperature levels showed increased percentages of both benzene and toluene, with a toluene peak at about 1500°-1600°. The benzene yield showed a marked increase at 1700° F. Additional increase might be expected at somewhat higher temperatures, but because of apparatus limitations, 1700° was the maximum temperature at which satisfactory control was possible.

More gas and also more ethylene was produced when the shale was retorted at 1500° and 1700° than when it was retorted at 1200° F. with subsequent soaking of vapors in the reactor at 1500° or 1700° F. Ethylene, on a percentage composition basis, was highest for the reactor runs with the reactor at 1500° and 1700°. Mass spectrometer analyses of the retort gases for the various runs are given in table 13. No attempt was made to analyze the gases from the runs in which sweep gas was used.

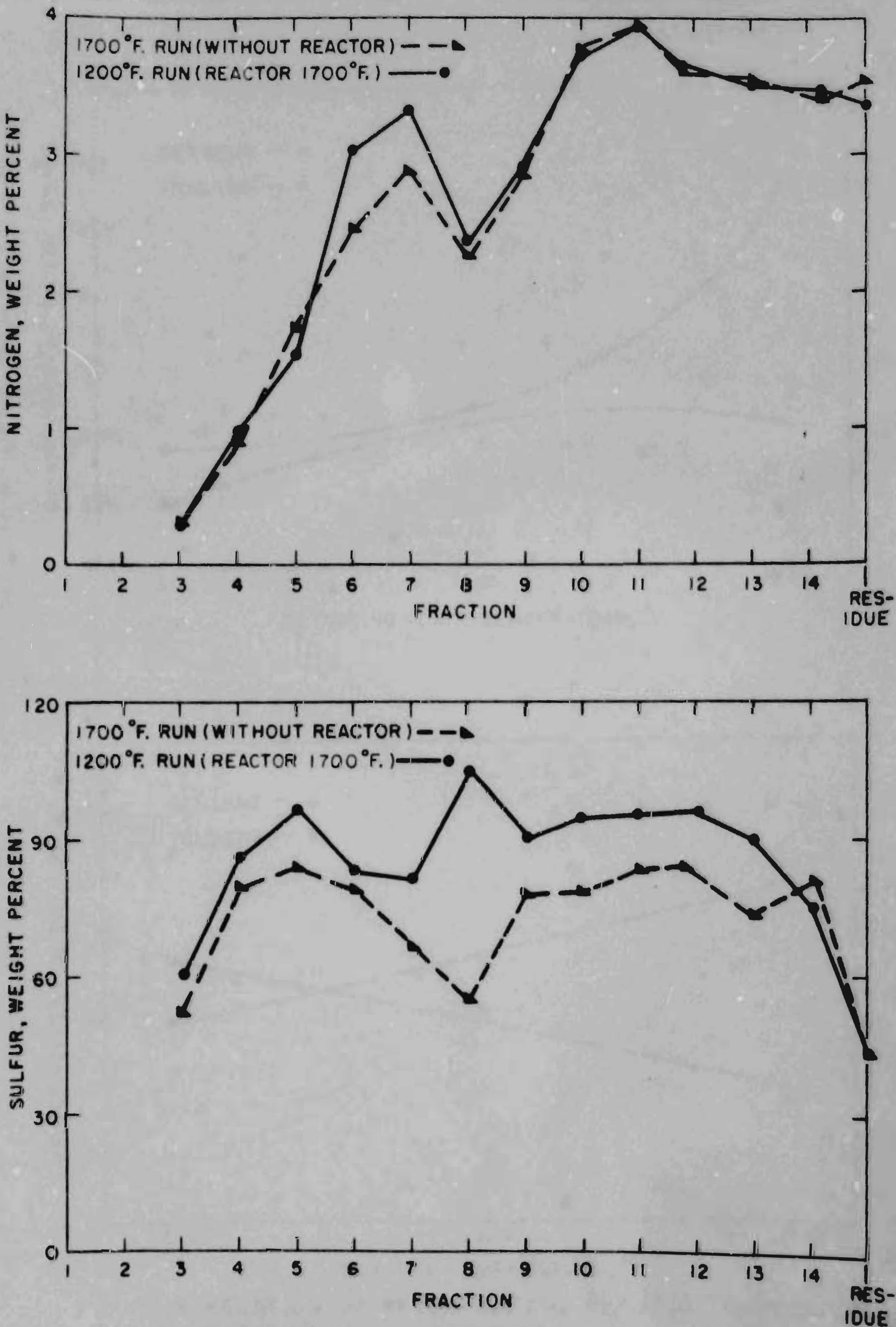

FIGURE 3. SULFUR-NITROGEN CONTENT OF DISTILLATION FRACTIONS AND RESIDUE.

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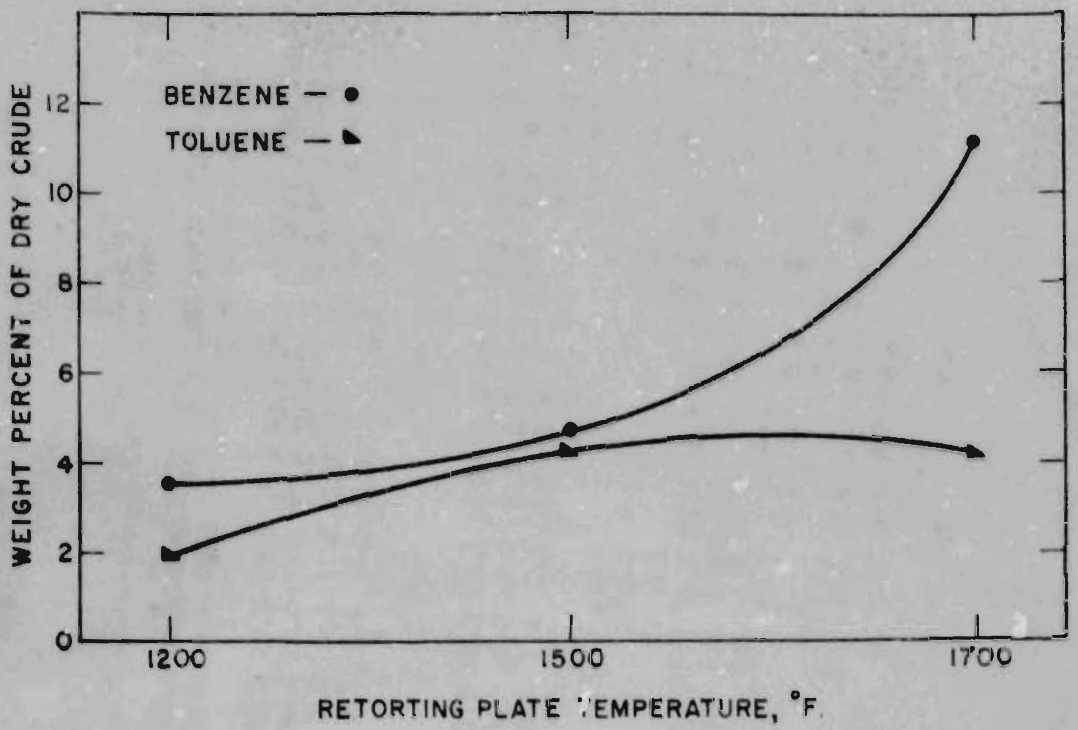
RRS-534



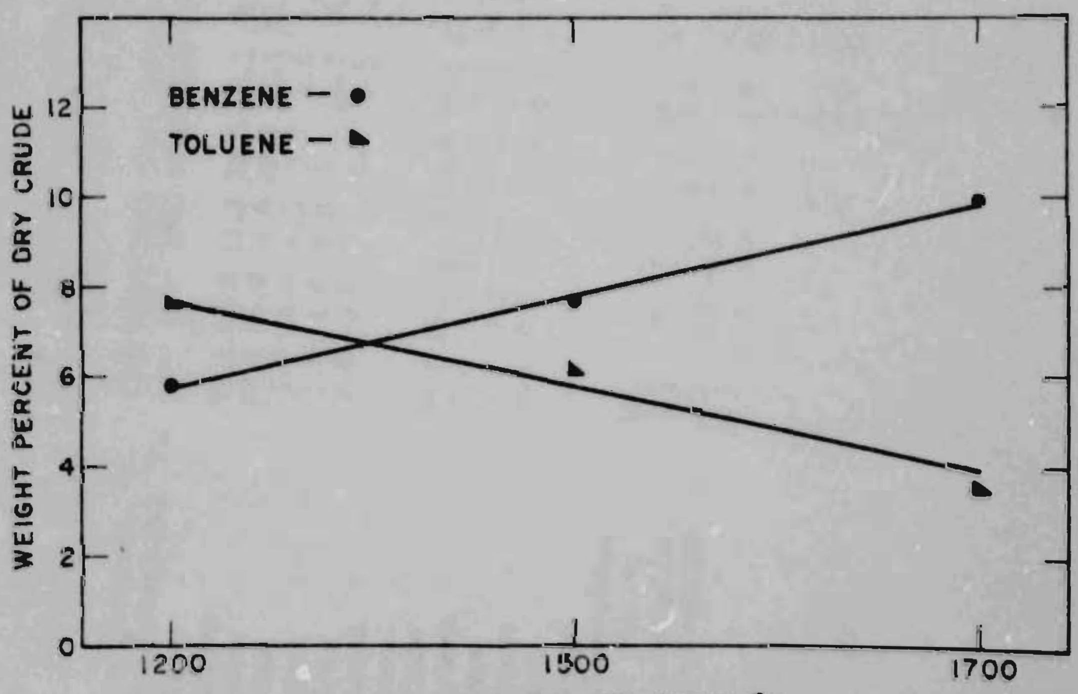


FIGURE 4. RELATION OF RETORTING AND REACTOR TEMPERATURES TO BENZENE-TOLUENE FORMATION IN INCLINED-SURFACE RETORT

Table 13.--Mass spectrometer analyses of high-temperature retort gases (Percent on air, N_2, A, and He free basis)

Run No.	28	29	26	31	27	30	32	33	18	18	3	34	4	1/ 7	5	6	35
Retort temperature, °F.	1200	1200	1200	1200	1200	1200	1200	1200	1250	1250	1400	1500	1500	1550	1550	1600	1700
Reactor temperature, °F.	----	----	1200	1200	1500	1700	1700	1700	----	1500	----	----	----	----	----	----	----
Constituent																	
Hydrogen	17.1	16.8	13.3	16.6	16.1	8.1	21.0	21.1	19.5	19.2	18.5	22.7	20.3	30.6	23.3	21.9	25.5
Methane	27.8	28.0	28.6	29.3	33.1	39.3	34.8	34.8	24.4	33.1	27.8	30.0	25.6	14.4	22.2	10.0	24.8
Ethane	5.7	6.0	6.5	5.9	4.6	3.2	3.0	2.8	5.1	3.2	1.9	3.5	1.9	0.6	1.0	0.6	1.6
Propane	1.4	1.6	2.0	1.1	1.2	0.3	0.3	0.4	0.8	0.1	0.1	1.7	0.1	0.2			0.1
Butanes	2.8	0.9		0.1	0.5	3.0	0.1					0.1					0.2
Pentanes						0.8											
Hexanes						0.2											
Ethylene	15.7	15.4	17.2	16.8	20.0	22.5	19.2	19.9	14.1	18.1	14.9	16.8	16.7	5.0	12.9	5.7	10.9
Propylene	7.6	8.5	9.7	8.5	7.2	4.2	4.0	4.0	6.2	3.6	2.3	4.5	2.3	0.6	1.2	0.9	2.1
Butenes	1.9	2.1	2.7	1.8	1.9	1.2	0.8	0.7	1.1	0.5	0.4	1.3	0.4		0.2	0.2	0.6
Pentenes	0.5	0.5	0.9	0.3	0.5							0.3				0.1	0.1
Hexenes																	
Acetylene							0.4			0.2				0.4		0.1	0.5
Methylacetylene							0.3			0.3				0.1		0.1	0.1
Carbon dioxide	16.2	18.4	14.6	13.4	10.7	14.2	11.1	10.7	21.9	16.2	21.8	18.8	22.3	12.2	21.2	12.6	17.7
Carbon monoxide	1.8		0.9	4.9	1.4		4.4	5.2	6.1	2.5	11.2		9.2	34.9	17.4	47.2	14.9
Hydrogen sulfide	0.5	0.5	0.5	0.3		0.3	0.3	0.2	0.2	0.2	0.1	0.1					
Benzene	0.1	0.2	1.3	0.1	0.1	0.5	0.1	0.1			0.3	0.1	0.2	0.8	0.3	0.3	0.2
Toluene													0.1	0.1		0.1	
Butadienes	0.9	1.1	1.4	0.8	1.6	1.7			0.6	0.7	0.6		0.7	0.1	0.3	0.2	0.5
Pentadienes				0.1	0.5	0.5	0.1	0.1		0.1	0.1	0.1	0.1				0.1
Hexadienes																	
Cyclopentadiene			0.4		0.6		0.1						0.1				0.1

1/ 3.0 percent methyl alcohol and 5.0 percent acetone calculated out.

Spent shale analyses for the runs are given in table 14. Generally, organic and CO_2 removal increased with retorting temperatures, although feed rates affected results to some extent.

SUMMARY

These results must be considered as a preliminary evaluation of the performance of an inclined-surface type of retort. Optimum conditions have been established only over a broad range for most of the variables; adequate temperature control and difficulties in maintaining constant feed rates being limiting factors in carrying out the experiments.

Organic matter removal ranged from 51 percent to 89 percent, the maximum removal being obtained with temperatures at or above 1500° and with feed rates below 300 g./min.

Removal of carbon dioxide ranged from 0 percent to 55 percent, the highest percentage being removed at the higher retorting temperatures and with low feed rates.

Oil yields, on an organic basis, ranged from 13 to 50 percent, the highest yield being obtained with a retorting temperature of 1500° F.

Gas yields generally increased with increase in retorting temperatures, but the maximum ethylene yield was obtained at 1500°.

The use of inert sweep gas apparently improved liquid yields in all cases, since the yields for those runs in which the gas was used were all above average. Use of a reactor to treat vapors further immediately after retorting resulted in products having higher benzene, toluene, and ethylene content than those of untreated vapors.

The highest benzene yield was obtained by direct plate retorting at 1550° F., while the maximum toluene yield was obtained by passing vapors formed by retorting at 1200° through the reactor at the same temperature. Benzene and toluene yields for the inclined-surface retort were found to compare favorably with those obtained by the vertical-tube retort when calculated on an equal organic basis

ACKNOWLEDGMENT

This work was carried out under the direct supervision of H. W. Sohns and general supervision of W. I. R. Murphy, Chief, Retorting and Refining Section. Assisting in the experimental work were: C. M. Johnson, D. M. Beahm, W. B. Nelson, and W. G. Collins.

Table 14.--Spent shale analyses for high-temperature runs

Run No.	Retorting Temperature, °F. Plate	Retorting Temperature, °F. Reactor	Feed rate g./min.	Ignition loss percent (ash basis)	CO_2 percent (ash basis)	Organic matter percent (ash basis)	Ash percent
28	1200	----	332	39.5	29.5	10.0	71.7
29	1200	----	343	42.8	31.6	11.2	70.0
23	1200	----	323	35.0	30.8	4.2	74.1
24	1200	----	1321	48.9	32.5	16.4	67.2
26	1200	1200	384	42.9	31.8	11.1	70.0
31	1200	1200	518	36.3	29.9	6.4	72.2
27	1200	1500	441	41.2	31.7	9.5	70.7
30	1200	1700	476	33.8	29.0	4.8	74.7
32	1200	1700	465	38.6	29.2	9.4	72.1
33	1200	1700	565	35.7	29.0	6.7	73.8
18	1250	1500	338	35.9	30.6	5.3	74.1
12	1350	----	508	27.7	23.9	3.8	78.3
3	1400	----	252	34.8	22.6	12.2	74.2
16	1400	----	490	31.6	22.7	8.9	76.0
13	1450	----	1361	30.2	26.3	3.9	76.8
2	1475	----	123	21.6	16.9	4.7	82.2
34	1500	----	655	32.8	29.7	3.1	73.5
8	1500	----	282	23.1	20.2	2.9	81.2
14	1500	----	254	28.1	25.4	2.7	78.1
9	1550	----	195	24.2	20.8	3.4	80.6
7	1550	----	118	14.5	11.4	3.1	87.4
5	1550	----	202	20.0	16.1	3.9	83.3
10	1600	----	109	19.8	16.3	3.5	83.5
6	1600	----	169	20.9	16.9	4.0	82.7
35	1700	----	685	29.6	26.5	3.1	75.0

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