RETORTING UNGRADED OIL SHALE AS RELATED TO IN SITU PROCESSING, II

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INTRODUCTION

For many years the Bureau of Mines has engaged in research to provide technology for the development of methods for producing oil from oil shale. The world's known reserves of oil shale in deposits 10 feet or more in thickness and with an assay of 10 or more gallons of oil per ton are estimated to represent 3.1 trillion barrels of oil (1).[1/] The bulk of the world's known oil shale reserves are in the United States in the Green River Formation which underlies parts of Colorado, Utah, and Wyoming. The known oil shale deposits in this formation are estimated to represent 600 billion barrels of oil in deposits assaying 25 or more gallons of oil per ton. If the shales assaying from 10 to 25 gallons per ton are included, the total known shale oil potential of this formation is about 2 trillion barrels. To put the importance of this shale oil potential in its proper light, note that the proved crude oil reserves in the United States at the end of 1969 were 29.6 billion barrels (not including the recent discoveries on Alaska's North Slope which have not been evaluated), and that 3.2 billion barrels of crude oil were produced in the United States in 1969 (2).

Many different ways to produce the oil from oil shale have been proposed and tried. One method which may have economic and environmental advantages over the others, should it prove technically feasible, is retorting the shale in the formation where it occurs. This process is commonly called in situ retorting. Basically, this method consists of fracturing the nearly impermeable oil shale in place, heating the fractured oil shale by some method to retort it, and recovering the oil produced via wells or other suitable recovery systems.

Under current plans, the fracturing required for in situ retorting will probably be accomplished by the use of either conventional or nuclear explosives. Either method could produce a large mass of broken shale with pieces varying in size from dust to several feet in diameter and varying in assay value from nil to as much as 50 or more gallons of oil per ton.

The present study was conducted to determine the retorting characteristics of oil shale ungraded in size and varying in richness, simulating to some degree the physical conditions of in situ retorting. In general, the oil shale charge has been mine-run material with pieces as large as 20 inches in two dimensions. The third dimension was as large as 36 inches. Grade of the charge, as determined by Fischer assay, ranged from 20.4 to 48.0 gallons of oil per ton. Air rates that have been investigated ranged from 0.58 to 3.74 standard cubic feet per minute per square foot of retort cross section. Yields of oil as high as 80 percent of Fischer assay have been obtained.

Multiple linear regression analysis was used to generate equations predicting the oil yield for given sets of retorting conditions. Using only controlled operating variables, an equation was developed that accounts for 83 percent of the variability in oil yield. Including ambient conditions in the regression improves the percentage to 93.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Construction of a small, 10-ton batch-type retort was completed at the Bureau of Mines

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

Center in Laramie, Wyo., in late 1965 (4). A schematic diagram of the retort and its auxiliary equipment is presented in figure 1.

The retort consists of a cylindrical steel shell 6 feet in outside diameter by 12 feet tall surrounding a tapered refractory lining 6 inches thick at the bottom and 8 inches thick at the top. A hinged grate is made of 1-inch steel plate perforated with 3/8-inch holes. A natural gas burner in the top of the retort is used to ignite the shale. The gas inlet to the retort is designed to permit injection of either air, recycle gas, steam, or any combination of the three. The oil recovery system includes three separation tanks, or demisters, to remove the oil from the gaseous products.

The retorting system is instrumented to obtain process temperatures and flow rates. Sets of four thermocouples are evenly spaced from the center to the outside edge of the bed at 18-inch vertical intervals to obtain bed temperatures during retorting. Gas samples taken downstream from the recycle gas blower are analyzed by a multiple stream process chromatograph.

For all experiments, a 3- to 4-inch layer of crushed and sized granite was placed on top of the grate to prevent oil shale fines from falling through the grate to protect the grate from excessive temperatures during the retorting of the bottom portion of the oil shale bed. When the crushed rock layer was in place, the oil shale charge was loaded into the retort, taking care to limit size degradation or segregation. After the oil shale was loaded, the retort was closed and the retorting operation was started.

In most experiments performed during this study, the oil shale bed was ignited at the top using the natural gas burner. Combustion was maintained by injecting air and recycle gas, if used, into the top of the retort. The combustion zone traveled down through the bed, retorting the oil shale ahead of it. Retorting was assumed to be completed when the bottom set of thermocouples in the bed indicated an average temperature of about 900°F. For two experiments, steam was used as the heat transfer medium.

Oil shale charges for most of the experiments performed in the 10-ton retort were prepared from mine-run shale obtained from the Bureau of Mines Anvil Points mine near Rifle, Colo. Four experiments (experiments 27 through 30) were made with oil shale from an area near Rock Springs, Wyo.

To prepare a sample for analysis for each charge, the smaller pieces of the mine-run shale were sampled by cone and quarter methods. Larger pieces, over 12 inches and limited to 20 inches, were broken perpendicular to the bedding planes, and approximately one-fourth of each piece was added to the sample. This total sample was crushed to about 1 inch. Samples for analysis were prepared from the 1-inch material, and the unused remainder was returned to the retort charge.

For all of the experiments performed on Colorado oil shale in this and a previous study, the potential oil content of the shale as determined by Fischer assay ranged from 20.4 to 48.0 gallons per ton. Table 1 shows the oil content of the charges used in the current study, including four charges of Wyoming oil shale ranging from 23.5 to 27.3 gallons of oil per ton.

Determination of particle size distribution for these retort charges, ranging in particle size from sand-grain size to pieces as large as 20 inches, was difficult. Screening equipment of sufficient capacity was not available; thus, it was necessary to determine the size distribution of each charge by separating the particles into size categories by actual measurement. Average particle sizes for the charges used in this study are shown in table 1. These average sizes range from 4.2 inches to 12.4 inches. When the previous work (4) is included, the range is extended from 4.2 inches to 14.1 inches.

TABLE 1. - Summary of operations of the 10-ton retort

Experiment number1/	22	23	19	282/	18	24	26	292/	32
Oil yield, vol pct of Fischer assay	9.4	38.6	42.0	45.3	47.0	47.0	50.8	51.2	53.0
Run time, days	10.77	2.87	4.19	4.75	2.91	5.79	6.62	7.3	8.0
Fischer assay of charge, gal/ton	23.4	20.4	21.7	23.7	36.8	23.4	24.7	26.3	23.7
Air rate, scf/min/ft^2 of bed	Steam	-	1.16	1.29	1.86	0.70	1.03	0.75	0.89
Recycle gas-to-air ratio	do.	-	0	1.28	0	1.46	1.00	0.90	0.88
Total air, scf/ton	do.	-	17,897	19,257	20,328	14,100	13,962	16,561	21,755
Total recycle gas, scf/ton	do.	-	0	24,583	0	20,595	26,017	14,916	19,082
Maximum bed temp., °F	1,125	1,380	1,260	1,240	1,600	1,340	1,140	1,320	-
Average particle size, inches	4.2	7.5	4.6	11.5	9.9	9.9	8.6	9.9	10.2
Selected oil properties:									
Specific gravity, 60°/60°F	0.919	0.921	0.908	0.909	0.914	0.909	0.914	0.915	0.910
Pour point, °F	65	75	10	35	65	65	65	45	40
Viscosity, SUS at 100°F	184	157	72	84	91	82	87	85	71
Nitrogen, wt pct	1.56	1.74	1.54	1.25	1.85	1.56	1.65	1.20	1.21
Sulfur, wt pct	0.70	0.72	1.16	0.48	1.10	0.76	0.64	0.63	1.21
Naphtha, vol pct of crude	5.2	1.3	6.9	6.1	8.5	5.8	5.1	5.0	6.3
Light distillate, vol pct of crude	8.6	17.2	24.1	24.0	20.9	29.8	27.4	26.3	27.6
Heavy distillate, vol pct of crude	45.1	51.6	42.8	47.2	43.4	43.5	35.6	49.0	44.5
Residuum, vol pct of crude	42.1	30.6	25.0	23.7	28.2	21.1	33.3	20.4	21.1
Stack gas composition, vol pct:									
Nitrogen	3/	73.3	76.6	77.5	69.4	78.4	74.9	75.4	76.8
Oxygen	3/	9.4	11.0	8.5	4.9	6.9	4.8	5.7	8.4
Carbon dioxide	3/	15.6	10.8	12.5	20.9	13.5	18.6	16.5	13.4
Carbon monoxide	3/	0.4	0.5	0.8	1.9	0.8	1.0	0.9	0.6
Methane	3/	0.6	0.8	0.5	1.5	0.3	0.5	0.7	0.5
Higher hydrocarbons	3/	0.7	0.3	0.2	1.4	0.1	0.2	0.8	0.3

1/ Experiment number:
18 - Made with air and steam injected for 12.5 percent of run.
19 - Air, no recycle gas.
22 - Made with superheated steam only.
23 - Made with superheated steam and air. No air rate available.
24 - Made with heated air and recycle gas.
26 - Heated air and recycle gas used during 58 percent of run. Recycle gas to air ratio, 1.00.
28, 29, 32 - Made with air and recycle gas.

2/ Wyoming oil shale.
3/ Not determined.

TABLE 1. - Summary of operations of the 10-ton retort (con.)

Experiment number[1]	21	31	30[2]	16	20	17	25	27[2]
Oil yield, vol pct of Fischer assay	56.0	57.5	61.9	66.8	70.0	72.0	73.7	76.3
Run time, days	2.62	7.96	7.59	2.16	4.0	13.33	4.2	4.75
Fischer assay of charge, gal/ton	24.8	28.3	23.5	32.3	26.2	36.7	23.9	27.3
Air rate, scf/min/ft^2 of bed	1.67	0.74	0.74	3.74	1.46	1.47	1.00	1.00
Recycle gas to air ratio	0.29	0.99	1.02	0	0.32	0.53	1.04	1.00
Total air, scf/ton	14,597	20,748	16,971	29,898	18,584	76,126	10,251	14,580
Total recycle gas, scf/ton	777	20,475	17,373	0	5,050	40,351	15,377	14,665
Maximum bed temp., °F	1,550	1,400	1,250	1,475	1,380	1,200	1,300	1,330
Average particle size, inches	6.2	7.9	11.5	12.4	8.7	12.1	9.4	7.7
Selected oil properties:								
Specific gravity, 60°/60°F	0.914	0.914	0.919	0.932	0.918	0.900	0.912	0.916
Pour point, °F	75	50	40	70	65	60	70	55
Viscosity, SUS at 100°F	100	83	101	184	105	77	88	98
Nitrogen, wt pct	1.86	1.09	1.22	2.21	1.81	1.67	1.66	1.38
Sulfur, wt pct	0.99	0.54	0.67	1.05	0.89	0.76	0.80	0.42
Naphtha, vol pct of crude	7.0	4.8	7.3	4.5	6.1	5.3	2.8	8.6
Light distillate, vol pct of crude	21.2	28.3	21.1	16.9	22.3	22.4	25.9	21.7
Heavy distillate, vol pct of crude	39.1	49.3	48.3	40.4	42.3	47.2	31.7	38.3
Residuum, vol pct of crude	32.9	19.9	24.9	38.9	30.9	26.6	41.1	33.1
Stack gas composition, vol pct:								
Nitrogen	69.9	75.9	75.8	70.8	72.0	79.3	73.1	73.6
Oxygen	5.8	8.5	5.9	6.8	4.9	3.0	4.7	4.2
Carbon dioxide	21.3	14.2	16.2	18.2	18.4	13.1	20.4	20.6
Carbon monoxide	1.8	0.7	0.9	3.1	1.9	1.8	1.0	0.8
Methane	1.0	0.5	0.2	0.6	1.5	2.4	0.5	0.6
Higher hydrocarbons	0.2	0.2	1.0	0.5	1.3	0.4	0.3	0.2

1/ Experiment number:
16 - Made with air, no recycle gas.
17 - Made with gas burner operating 94 percent of run.
20 - Recycle gas used 84 percent of run. Recycle gas to air ratio during this time, 0.32.
21 - Recycle gas used 18 percent of run. Recycle gas to air ratio during this time, 0.29.
25 - Started with heated recycle gas at a rate of 1.6 scf/min/ft^2 for 22 hr. Recycle rate then reduced and heated air injected at recycle gas to air ratio of 1.04.
27, 30, 31 - Made with air and recycle gas.

2/ Wyoming oil shale.

RESULTS AND DISCUSSION

A summary of the experiments performed in the 10-ton retort since the last report to the American Chemical Society (4) is presented in table 1. The experiments are arranged in increasing order of oil yield. The oil recovery for this series of experiments ranged from 9.4 percent of Fischer assay for experiment 22 in which steam was used for retorting, to 76.3 percent for experiment 27 on Wyoming shale in which air and recycle gas were used for retorting.

Various methods involving the use of supplementary energy were used in attempts to improve the oil yield during this series of experiments. Additional heat was supplied by the following: In experiment 17 the natural gas burner was operated; in experiments 24 through 26 air and recycle gas were externally heated; in experiment 18 steam was used instead of recycle gas. Experiments 22 and 23 used superheated steam and a mixture of superheated steam and heated air, respectively, to retort charges of unignited oil shale.

Experiment 17, which had additional heat supplied by the natural gas burner, yielded 72 percent oil, while experiment 20 with similar operating conditions yielded 70 percent oil without additional heat. Of the three experiments using heated air and recycle gas (24, 25, and 26), two had yields of about 50 percent, and one had a yield of 74 percent. The high-yield experiment (25) had operating conditions almost identical to those of experiment 27 which yielded 76 percent oil without heated air or recycle gas. Superheated steam proved to be of little value as oil yields from experiments 18, 22, and 23 were low. Based on these results, the addition of supplementary energy appears to be of doubtful benefit. This study indicates that the highest oil yields were obtained with a recycle gas-to-air ratio of about 1:1 while injecting 1 cubic foot of air per minute per square foot of retort cross section. Some of the major factors which may contribute to low oil yields are:

(1) Incomplete retorting caused by channeling or excessive retorting rates.
(2) Burning of the oil as it is formed during retorting.
(3) Loss of oil as a stable mist which was not separated from the stack gas.

Losses from these causes may be minimized by adequate control of air and recycle gas rates and an improved recovery system.

Properties of the crude shale oils produced during this investigation are shown in table 1. These oils are similar to oils produced by other internally heated retorts, in that they are dark and viscous and have a characteristic odor. They also contain material concentrations of sulfur and nitrogen compounds. However, as shown in table 2, the oils produced during the current series of experiments have higher API gravities, lower pour points, and a higher percentage of naphtha and light distillates than oils produced from other internally heated retorts previously studied by the Bureau.

The four experiments (27 through 30) made with Wyoming oil shale produced oil with properties similar to those of the Colorado shale. The nitrogen and sulfur concentrations were slightly lower in the oil produced from Wyoming shale.

REGRESSION ANALYSIS OF RETORTING VARIABLES

In a study of the effects of retorting variables, a convenient measurement of the results of these effects is oil yield. Oil yield, in this study, is expressed as volume percent of Fischer assay; that is, the percent of the total potentially available oil actually recovered during the retorting process.

From a theoretical standpoint the yield should be a function of shale assay, shale particle size, shale mineral matter composition, retorting gas flow rate and oxygen

TABLE 2. - Selected properties of shale oils

Retort	Gravity API	Sulfur, wt pct	Nitrogen, wt pct	Pour point, °F	Volume percent			
					Naphtha	Light distillate	Heavy distillate	Residuum
N-T-U1/	19.8	0.74	1.78	90	2.7	15.7	34.4	45.8
Gas combustion1/	18.6	0.69	2.13	85	4.4	14.6	31.3	49.7
10-ton, Colorado shale2/	23.2	0.89	1.49	60	6.1	24.9	43.8	26.2
10-ton, Wyoming shale3/	23.2	0.55	1.26	45	6.5	23.3	45.7	25.5

1/ Reference (3).
2/ Average from experiments 20, 21, 31, 32.
3/ Average from experiments 27, 28, 29, 30.

content, and the rate of heat loss from the retort. The retorting-gas flow rate (space velocity) and its oxygen content are functions of the air and recycle gas rates. Of these variables, only air rate, recycle rate, and to a certain extent, shale size can be controlled when retorting oil shale from a given oil shale deposit. Heat losses from the retort can be reduced, but not controlled except by an elaborate and expensive heat shield.

Using the data available from all of the experiments made in the 10-ton retort, from this study, and the preceding work (4), a series of statistical regression analyses were performed in an effort to generate an equation that would predict yield as a function of the retorting variables.

A first order equation for predicting oil yield using all of the data, with the exception of the data from experiments 22 and 23 in which steam was used, proved unsatisfactory. The regression analysis was then upgraded by eliminating data from the experiments on Wyoming oil shales (27 through 30) and data from all experiments in which operating conditions were changed during the course of the experiment (1, 5, 6, 12, 13, 17, 18, 24-26, 31, 32). The results from regression analyses on the remaining 14 experiments (2-4, 7-11, 14-16, 19-21) with Colorado oil shales are presented in table 3.

The first two equations in table 3 are first order linear equations generated by computerized multiple linear regression and are of the form

$$Y = B_0 + B_1X_1 + B_2X_2 + \cdots.$$

Equation 1 predicts oil yield using Fischer assay, shale size, and retorting-gas space velocity and retorting-gas oxygen content as variables. This equation accounts for only 33 percent of the variation in the data, and the F-test indicates a 50-percent chance that no correlation exists. Because this equation provided such poor correlation, the average wind velocity and ambient temperature prevailing during each run were added to the data in an attempt to include an approximate heat loss function in the correlation. Equation 2, generated using these additional variables, showed essentially no improvement in correlation over equation 1. If anything, the accuracy of the predicted yield was decreased. These regression analyses show that the variability in the data is such that the yield cannot be predicted using a first order equation.

To determine whether second order effects might be important, equations of the form:

$$Y = B_0 + B_1X_1 + B_2X_1X_2 + B_3X_2 + B_4X_1^2 + B_5X_2^2 + \cdots$$

were investigated. Equations 3, 4, and 5 of table 3 are of this form and were generated using a computerized stepwise regression analysis program. This program generates a sequence of multiple linear regression equations by adding or removing one variable to or from the equation at each step. The variable added or removed at each step is the one which causes the greatest reduction in the error sum of squares term for the equation.

Using this stepwise regression program, equations 3 and 4 were generated from a selection of 35 terms including seven variables, their cross products, and their squares. The original variables for equation 3 were shale assay and size, retorting gas space velocity and oxygen content, ambient temperature, wind velocity, and average bed temperature.[2/] For equation 4 the space velocity and oxygen content were replaced by

2/ Average bed temperature was calculated by adding all temperatures at 5-hour intervals and dividing by the total number of temperatures used.

TABLE 3. - Summary of regression analyses

Equations[1]	Number of independent variables in equation	Standard error of estimated yield	Index of determination, R^2	F-statistic	Significance level of F test
1	4	11.4	0.33	1.1	0.50
2	6	12.8	0.34	0.59	>0.50
3	7	6.1	0.87	5.8	0.025
4	7	4.4	0.93	12.0	0.005
5	7	7.0	0.83	4.1	0.10

1/ Equations generated:

1. Y = 106.45 - 1.68 (OXY) - .804(ASY) + 1.82(SIZ) - 2.57(SPV)
2. Y = 110.20 - 1.82(OXY) - .775(ASY) + 1.54(SIZ) - 3.03(SPV) + .405(WND) - .0591(TEM)
3. Y = 39.26 - .105(TEM)(OXY) + 1.66(TEM) + 1.57(SPV)(OXY) + .0737(BTM) - .412(ASY)(SPV) - 1.03(WND)(SPV) - .00053(TEM)(BTM)
4. Y = 93.48 - .239(TEM)(WND) + .681(AIR)(TEM) + .795(REC)(TEM) - 2.82(REC)(SIZ) + .245(WND)(WND) + .00004(BTM)(BTM) - 3.94(AIR)(AIR)
5. Y = 18.74 + 107(REC) + 1.77(ASY)(AIR) - 1.99(ASY)(REC) - 11.0(AIR)(AIR) - 8.42(REC)(REC) - 13.8(AIR)(REC) - 0.0122(ASY)(ASY)

where:
Y = oil yield, volume percent of Fischer assay,
ASY = oil content of shale by Fischer assay, gal/ton,
AIR = air rate, scfm/ft^2 of bed,
BTM = average temperature of bed during run, °F,
OXY = oxygen content of retorting gas, pct,
REC = recycle gas rate, scfm/ft^2 of bed,
SPV = retorting gas space velocity, scfm/ft^2 of bed,
SIZ = average shale particle size, inches,
TEM = average ambient temperature during run, °F,
WND = average wind velocity during run, mph.

the air and recycle rates. Equations 3 and 4 account for 87 and 93 percent of the total variation in the data, respectively, and there is only a 2.5- and 0.5-percent chance, respectively, that no correlation exists.

Equations 3 and 4 include several uncontrolled variables--wind velocity, ambient temperature, and average bed temperature--and are useful for evaluating the results of experiments performed under different ambient conditions. Direct comparisons of the effects of the controlled operating variables on oil yield can be made because the effects of changes in ambient conditions on yield can be accounted for by these equations. Equation 5 was generated using only controlled variables--Fischer assay, size, air rates, and recycle rates--to predict the oil yield under a proposed set of retorting conditions. This equation accounts for 83 percent of the total variation in the data and has a 10-percent chance that no correlation exists.

In all five equations the terms are presented in decreasing order of the average effect on the yield by the variables involved. From this the importance of heat loss to the surroundings during retorting can be observed, in that the first two terms of both equations 3 and 4 include the ambient temperature. The size of the retorted shale seems to have little effect on the yield as it was not included in equations 3 and 5 and was included only as a cross-product in equation 4.

The size terms used in the regression analyses of the 14 experiments with Colorado oil shale were average particle sizes ranging from 4.6 to 13.4 inches. Over this rather limited range, the variability in oil yield as a result of changes in size is small. Previous studies by the Bureau of Mines (3) show that, although oil yields are not affected appreciably by changes in size of the largest particles in the shale feed, there is a fairly well defined trend for the oil yield to decrease with increased size. In the present study using mine-run shale with a maximum particle size of 20 inches, a somewhat lower oil yield would be expected than was obtained with the gas-combustion retort (3) operating on relatively narrow particle size range charges.

SUMMARY

This paper further substantiates data presented earlier (4) indicating that retorting oil shale ungraded as to size or oil content is technically feasible. During this series of experiments on mine-run shale having pieces up to 20 inches in two dimensions, yields of up to 76 percent of Fischer assay were attained.

The shale oils produced during this series of retorting operations are similar in appearance to oils produced by other internally heated retorts; however, the oils produced in the 10-ton retort had a higher API gravity, a lower pour point, and higher percentage of distillables than oils produced in other retorts. These differences all make the oil produced in the 10-ton retort more desirable for transporting and further processing. The Wyoming oil shale produced an oil containing less sulfur and nitrogen, but this advantage requires further investigation before concluding that it is typical.

Heating the air and recycle gas before injection into the retort proved to be of doubtful value as a method to increase oil yields. Use of superheated steam as a retorting medium also proved unsatisfactory.

Several equations for predicting oil yield from operating variables were developed by regression analysis. Using only controlled operating variables, an equation was developed that accounts for 83 percent of the variability in oil yield; by including ambient conditions in the equation this percentage was increased to 93.

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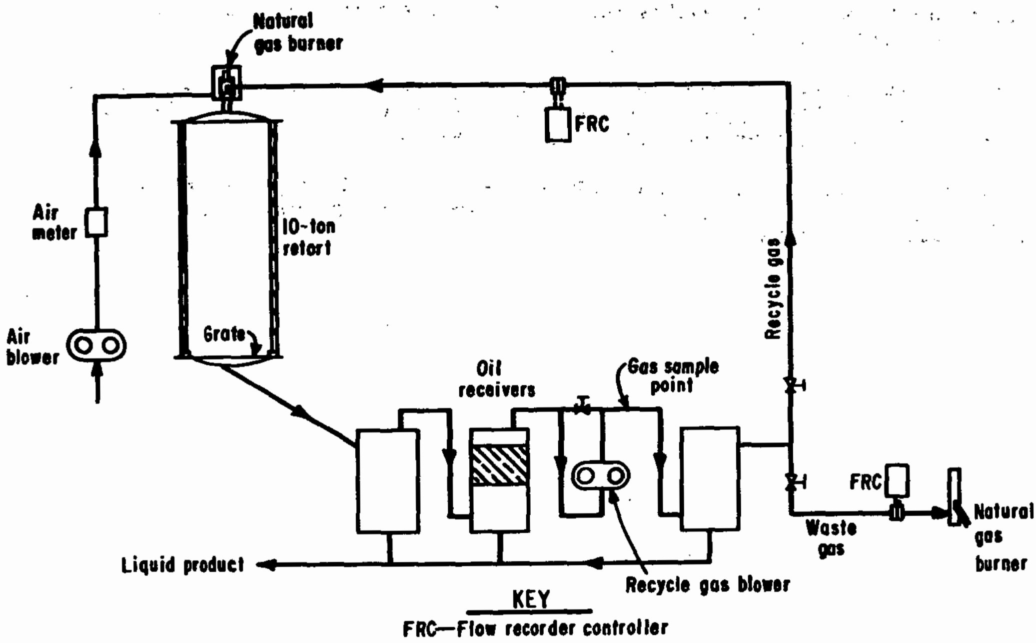

FIGURE 1. - Schematic diagram of experimental 10-ton retort.