Oil Shale Distillation Techniques on Oklahoma Shales

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Oils were derived from rocks as early as the 14th century in England (3). British records in 1694 describe the distillation of "Oyl from Stones," presumably shales (2). Sellique (1) developed an oil shale distillation process and later, in 1839, the first commercial exploitation of oil from shale occurred in France.

Considerable research has continued on oil shales in many countries. Activities in oil shale development began in the United States about 1916 and continued until strong competition developed in petroleum-derived products about 1927. The work since then has been concerned largely with the development of suitable retorting techniques in order to meet this competition. Public interest in oil shales was revived about 1944 when the 78th Congress through Public Law 290 provided adequate funds for research devoted especially to oil shales in Colorado and Wyoming, mostly under the direction of the United States Bureau of Mines. These investigations devoted to oil shales are sound and include extensive experimental studies on processes for recovering the organic matter from the shales as shale-oil or kerogen.

Numerous methods for retorting oil shales have been designed and patented. They have all been based essentially on the principle of controlled heat varying from about 350°C. to 500°C. in suitable apparatus. Each type of retort has had to face the problem of heat economy. The volatile bitumen must be removed from the shale with the minimum cracking at high temperatures. The purpose of this paper is to describe the results of experimental apparatus and techniques designed to obtain more accurate and efficient oil-shale assay procedures on shales.

Any laboratory-scale investigation is always confronted with one of several methods of sampling the shale formation. There are no means of anticipating how nearly the quality of the shale in the selective-mine operations will parallel the quality of the samples used in the laboratory assay analyses. However, analyses of samples of shale collected from the Green River formation in Colorado have proved remarkably close to the results in commercial runs.

Four retorting processes (4) developed and recognized at present are as follows:

1. Designed for heat transfer through a wall to the shale.
2. Designed for heat transfer from the combustion gases generated in the retort by burning the residual carbon on the retorted shale.
3. Designed to receive incoming previously heated gases or liquids through the shale in the retort.
4. Designed for the introduction of hot solids into the retorting shale.

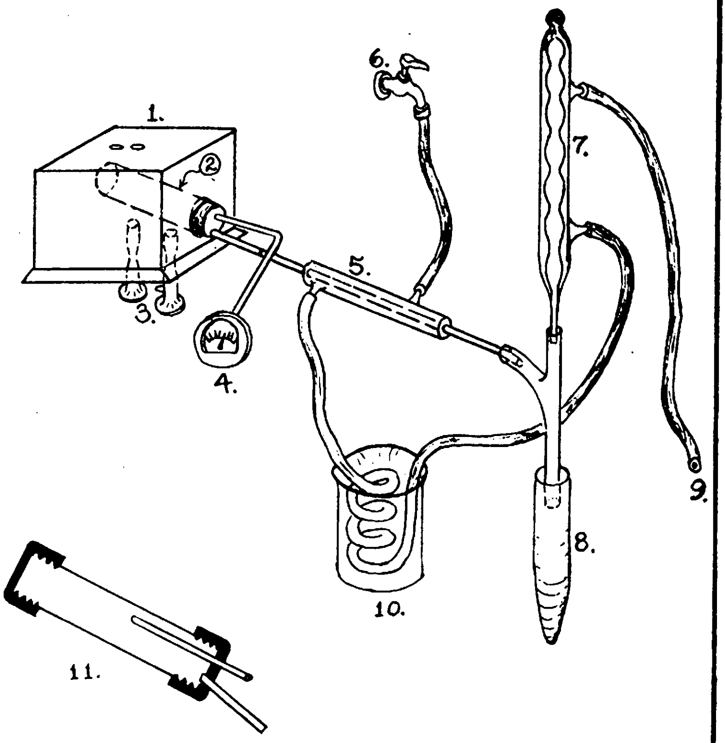
Experimental procedures at the beginning of this investigation followed the line of the first type using the well known mercury retort and the modified Fischer retort. Further experimenting led to two modified retorts of this type designed for shale distillation with emphasis placed on temperature control and heat economy. The steps taken were guided to a great extent by information presented in formal papers and accompanying discussions at the Second Oil-Shale and Cannel Coal Conference (4) held in Glasgow, Scotland, July 3-7, 1950.

The actual assaying of oil shales in experimental retorts at the University of Oklahoma was started in 1951 with the mercury retort (Karrick) method as a basis for comparison of oil shales in Oklahoma and Colorado. The modified Fischer retort was set up in 1952-53 and was operated with the assistance of three graduate students, H. S. Cook, Troy F. Hicks and F. W. Lipshultz. Research on apparatus and techniques of operation is continuing in the 1953-54 academic year with the assistance of two other graduate students, Don Coldiron and J. L. Morgan.

The United States Bureau of Mines uses the modified Fischer retort (5) and up to 1949 had made over 5000 oil shale assays on the shales of the Green River formation. Considerable information is available based upon oil-shale analyses in many parts of the world, but real comparisons are difficult to make because some samples were taken from outcrops of the shale and others from cores, and the composition and physical properties of the shale vary. The variation of data obtained from a given shale also depends upon the difference in the analytical procedure used. Further, the methods of oil shale pyrolysis are dependent upon the nature of the shale oil derived from them. A workable procedure suitable for one shale may have to be revised for satisfactory analysis of another shale or entirely new methods may have to be developed.

The apparatus and methods used in this investigation are as follows:

1. The modified Fischer retort proved to be satisfactory. It is housed in an asbestos enclosure and heat is supplied through an opening at the base of two fisher burners. A thermo-couple is inserted in an opening provided on one side of the retort. The fumes are



1. STEEL ENCLOSURE ASBESTOS LINED
2. RETORT IN HOUSING
3. FISHER BURNERS
4. PYROMETER
5. COPPER CONDENSER
6. WATER FAUCET
7. GLASS CONDENSER
8. GLASS GRADUATE
9. SINK
10. BEAKER ICE WATER
11. RETORT CROSS SECTION

FIGURE 1. Oil Shale Assay Retort.

conducted to a vertical glass seven-bulb condensing tube. One hundred grams of the oil shale broken to about one-fourth-inch particles are used for the retort load. The volume of shale-oil in ml. is converted to gallons per ton by the formula: Gallons of oil per ton equal ml. of oil times 239.66 divided by grams of shale used in the retort.

2. Another retort was designed which consists of a three-inch vertical steel pipe immersed in a bath consisting of sodium and potassium nitrate in equal proportions. The bath is contained in an outer vertical steel pipe eight inches in diameter, which is enclosed in a thick asbestos jacket. Two fisher burners supply heat from below and the fumes are condensed in a glass spiral type condenser. This design has the advantage of more uniform heat control within the retort. The danger point of the nitrate is apparently not reached at 500°C., since the possible explosion of the material requires a temperature of about 900°C.
3. The third retort was designed especially for heat economy and ease and accuracy of heat control. It was first put to use in the experimental work conducted in 1953-54, and is illustrated in Figure 1.

Samples of shale from the Woodford chert of southern Oklahoma were tested in all three types of apparatus. The best results were obtained by using the third type. The following analysis gives results of the test in this apparatus.

Sample No. 1c.
100 grams retorted.
3.9 ml. of kerogen—approximately 9.34 gallons per ton.
3.8 ml. of water.
Gases unknown.
Ash left or spent shale—89 grams
Color long-wave black light—light green.

Best results are obtained when the procedure outlined below is followed: low flame is maintained for about 30 minutes, after which the heat is increased gradually to approximately 250°C. during the second 30 minutes. The first show of oil appears at approximately 175°C. The heat must be kept uniformly distributed in the retort as the temperature is inceased in order to prevent the condensation of vapors in slightly cooler areas inside the retort. If the vapor does not pass from the retort soon after it is formed, over-cracking or burning of the shale-oil results. After about two ml. have accumulated, the temperature can be increased gradually to about 350°C. during the third 30 minutes, provided that the condenser capacity is not exceeded by the accumulation of excess fumes.

Oil shale has a low thermal conductivity and the particles should not be larger than one-fourth inch. If the particles are too large, it is thought that the excessive heat in the outer zone may "scorch" the fumes being driven from the cooler interior portion. Distillation allowed to progress at a relatively slow and gradual rate will recover the greatest amount of high quality oil from the average shale.

A rather sudden decline in shale oil accumulation is noticeable near the end of the above procedure of distillation. The temperature should then be increased to about 500°C over a period of ten minutes to complete the distillation. The heat should remain at about 500°C. for another period of ten minutes or more in order to burn away excess carbon and reduce the time and effort to clean and prepare the apparatus for the next run.

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