

AN INVESTIGATION OF
PRESSURE SOLVENT EXTRACTION
OF
SHALE OIL

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Petroleum Refining Engineering.

Signed

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INTRODUCTION

For over a century, the possibility of using oil shale as a source of hydrocarbons has been of interest to petroleum men throughout the world. Many years ago in countries where crude oil was not available, the possibility of developing this source was considered by scientists.

Since the United States of America had ample supply of crude, the use of oil obtained from "rock" was considered too expensive to be commercially profitable. At the end of world war I, a plan for using oil shale was presented to the oil industry of this country. The engineer presented this plan to develop methods that could be used on a commercial scale to supplement our dwindling supply of crude oil. Unfortunately, the swindler presented this same scheme to drain funds from the public by fair or foul means for his personal benefit. Since this plan did not progress to the point where a

commercial plant could be realized, the development of oil shale was left in the background for many years.

After their experience during World War II, the engineers of our country were convinced that our supply of crude oil must be supplemented in the case of another national emergency. In normal times, of course, we could purchase oil from foreign countries, whereas, in times of national crisis, these imports could easily be cut off. Therefore, the problem of hydrocarbon derivatives from oil shale has once again become of great interest.

United States Bureau of Mines Operations

In view of the international situation and our growing dependence on oil from foreign sources, this country was forced to attempt to develop a practical means of recovering the oil from oil shale. This development was especially desirable since an estimated 250 billion barrels of oil were contained in the oil shale found in this country. Of this amount, approximately 227 billion barrels or 91 per cent lies in the shales of the Green River formation of Colorado, Wyoming, and Utah.^{1/}

^{1/} Murphree, E. V., Natural gas, coal, oil shale as a source of liquid fuels: Oil and Gas Jour., vol. 46, no. 49, p. 69, April 8, 1948.

By an act of Congress, the United States Bureau of Mines was allowed to formulate and carry out plans on the investigation of synthetic fuels. One division of their

plans resulted in the erection of a demonstration plant at Rifle, Colorado, and of laboratories at Laramie, Wyoming, all for the development of oil shale.

The Rifle installation was set up to try to minimize the cost in the operations of mining the shale, to extract the oil from the shale, and to refine the oil into substitutes for petroleum products. In order to make this work possible, facilities had to be constructed at the site before actual operations could commence. Fifty housing units were brought in to provide homes for the staff.

A five and one-half mile road had to be built from the retort site to the top of the mountain where the mining operation was to take place. At the mine site, evacuations were made to an extent which would allow mining operations to take place on the desired scale. The mining operations were set up to determine and demonstrate the best method of mining the shale to minimize the cost.

The shale is mined and then transported by truck to the retort site. This shale is dumped onto a grizzly where the larger pieces are broken. Crushers and grinders reduce the shale to the size which is to be charged into the retort. The shale is transported by conveyor belts to one of three storage bins. The shales from these bins are mixed to give the desired size and oil-content mixture. Conveyor belts then transfer the shale to the top

of one of the two NTU type units which is to be charged with approximately 45 tons of shale. The NTU type of retort was adapted at this plant for comparative studies. Although this unit is definitely not the design for commercial recovery, it was selected because it would give pertinent information required for future work in oil shale. The ignition starts by oil-soaked logs; the lid is placed on the unit, and a controlled quantity of air is circulated from the top of the unit to the bottom. The burning of the carbon deposit on the shale furnishes the heat required in obtaining the oil from the shale. The vapors from the unit are collected from the bottom of the unit and further processed outside the unit.

The heated charge is removed from the bottom of the unit by a hydraulic ram that withdraws the bottom of the unit and allows the charge to fall into a truck below.

Many patents have been procured for the recovery of oil from shale in the past. Some of the patents involve fluid catalysts, externally and internally heated units, and solvent processes.

Object of the Thesis

Work done in the past by the usual solvent extraction methods has not been successful in recovering a large percentage of the hydrocarbons. Only a small amount of this material has been recovered by using various solvents at the normal boiling point.

Since so little has been done on this work, it was decided to use an adaptation of the Soxhlet apparatus for pressure work. By increasing the pressure and thereby increasing the temperature used in solvent extraction, more of the recoverable material should be obtained. Therefore, for this paper, the author undertook the problem of performing the operations necessary to gain information on moderate pressure solvent extraction of shale oil in order to advance the knowledge of the field so that a commercially profitable process might some day be possible.

In proceeding with this work, the problem was divided into the several sections listed below:

1. The first objective was to furnish a background for further continuance of this work. The information necessary for a better understanding of the problem includes the origin of oil shale, the distribution of oil shale, and kerogen.

2. An understanding of the fundamentals involved in the use of solvents in solvent extraction is essential. This discussion on solvents was presented in an effort that an understanding of the principles behind solvents and solvent extraction might lead to a better understanding of the application of solvents to the extraction of oil from shale.

3. The design and construction of the equipment for the moderate pressure solvent extraction of oil from

shale were also studied. A great deal of time was spent on this section as it proved to be a difficult problem to design and then construct a unit that would operate satisfactorily. The development of the pressure extractor unit included the designs of all the units suggested and that of the final unit constructed for the process.

4. A discussion on the source of shale was included. Since each shale differs, the source is very important.

5. The effect of pressure solvent extraction over and above the normal solvent extraction of shale was determined. The effect of the pressure solvent extractions was studied to determine whether the various pressures and temperatures would give any appreciable recovery over the solvent extraction as made at atmospheric pressure and at normal boiling temperatures.

6. The effect of size of shale particles on oil recovery by the use of pressure-temperature solvent extraction methods was determined. The difference in size of particles should have a definite effect on oil recovery. By taking a one-unit-measurement cube of shale and quartering this sample, the surface area is greatly increased. By increasing the area on which the solvent extraction could take place, the recovery should likewise be increased.

OIL SHALE

The Origin of Oil Shale

Black shales occurring in the sedimentary formations from the Belt series of the pre-Cambrian age to the peat-bog clays in present formations are the result of carbonaceous matter derived from plant or animal remains. These deposits may have been chemically changed since their deposition; they may be in their original form and composition, or they may have been partially or wholly bituminized. These shales, containing the volatile carbonaceous material, may lose much of the original gas and oil contained within.^{2/}

^{2/} George, R. D., Origin of oil shale, from McKee, R. H., Shale oil, p. 27, New York, N. Y., The Chemical Catalog Company, Inc., 1925.

True oil shale was thought to be a clay or sand deposit from which petroleum may be obtained by

distillation, but not by treatment with solvents.^{3/} Other

^{3/} McKee, R. H., Shale oil, p. 14, New York, N. Y., The Chemical Catalog Company, Inc., 1925.

material classified as "oil shale" at present might include lignitic and coaly shales, shales partially or completely saturated with oil from outside sources, torbanites, boghead coal, kerosene shale, and cannel coal.^{4/}

^{4/} Idem, pp. 27-36.

In shales partially or completely saturated with oil from outside sources, the deposits fill the openings along fault planes and stratifications or the pores and joint spaces. This liquid oil can be removed by solvents.

Lignitic and coaly shales contain films or laminae of fairly pure, friable coal between layers composed largely of inorganic matter with fine-grained characteristics.

Torbanites, boghead coal, kerosene shale, and cannel coal are deposits which, under proper biochemical, chemical, and dynamochemical conditions, might form the future oil fields.

In comparison with these types is the true "oil shale" in which the organic matter was intimately mingled or in a dispersed phase with inorganic matter at the time of deposition, after which bituminization has taken

place.^{5/} This material rarely contains oil as such, but

^{5/} Idem, p. 25.

is the source of a product by destructive distillation.^{6/}

^{6/} Idem, pp. 27-36.

When oil is found in the shale, it is believed to be the result of dynamic processes that were too short and too feeble to result in an oil field.

Under the microscope, a thin section of rich shale shows an extremely fine-ground mass of more or less altered plant matter in which are bedded such highly resistant plant remains as spores, spore cases, pollen and pollen exines, grains of resin, and wax. It is mainly from these substances that the oil is formed when the shales are subjected to destructive distillation.

The formation of oil shales seems to be similar to the formation of coal in that swamps, lagoons, deltas, estuaries, and lakes provided ideal conditions for deposition. Usually, the water was fresh land water, although in some places marine water conditions existed. Although plant remains are predominant in some shales, animal remains in the form of fish, crustaceans, insects, and larvae are found in others. The deposition of plant and animal remains were covered by very fine inorganic sediments in the form of a seal from the atmospheric and

sub-aerial decay. The relatively high amount of volatile matter in the oil shale remaining in place was the result of the slow progress of devolatilization of these very resistant materials.

Other theories have been suggested as to the origin of oil shale. However, they are essentially the same as the above-mentioned theory.

Distribution of Oil Shales

A commercial process for extracting oil from shales would have world-wide application for vast quantities of oil shale are distributed throughout the world.^{7/}

^{7/} Idem, pp. 37-42.

Europe: In England, the Kimmeridge shales have been worked at intervals since 1848. The Norfolk shales are abundant and have a high oil yield, but the sulfur content is objectionably high.

Scotland has the richest true oil shale deposits in the world, yielding 72-84 gallons of oil per ton. Ireland and Wales each have oil shale deposits but not in great quantities, the strata in Ireland being faulted, and the shale in Wales being cannel coal.

Several other European countries have developed their oil shale deposits to varying degrees. In France, deposits have been worked since 1858. Spain has promise of oil shale of great quality and quantity, and its plants

are producing oil. Oil shales occur in Italy, and some deposits have been developed. In southern Bulgaria there are extensive deposits of oil shale. Considerable development of rich oil shales (70 gallons per ton) has taken place in Estonia, which has great potentialities.

Russia is a country with widely distributed deposits. These shales have been used in gas manufacture and as fuels.

Deposits of oil shale are also found in Sweden, Norway, Austria, Hungary, and Yugoslavia, the shale of the last country being especially rich.

North America: Almost every province in Canada is known to contain shale oil; however, little has been done to develop Canadian deposits. Supply and demand of oil will determine whether or not Canada will turn her national asset into something more than an oil shale reserve.

In eastern United States, the most important body of black shale is the Chattanooga, New Albany, or Ohio shale which occurs in the following states: Alabama, Tennessee, Virginia, Kentucky, Indiana, and Illinois. The average oil content of the shale is 10.5 - 20.0 gallons per ton.

The midwestern states containing known oil shale deposits are Nebraska, Montana, Texas, New Mexico, Colorado, Utah, and Wyoming. The last three states promise to be of major importance in the oil shale

industry and warrant a short discussion. The Green River formation occurs in northwestern Colorado, southwestern Wyoming, and northeastern Utah. Oil shale from this formation contains up to 90 gallons of oil per ton, the average being 20 - 30 gallons of oil per ton. Utah and Wyoming each have larger areas that are underlain by oil shale than does Colorado, but the strata are thinner and kerogen content lower.

Oil shale deposits are found in Nevada and California. Unfortunately, the beds in Nevada are generally faulted and folded. The oil shale of California has a low average yield per ton with high sulfur content; however, because the beds are thick and accessible, California shale deposits must be considered.

The oil shale deposits mentioned above by no means represent all such locations in the United States; it is believed that every state in the Union has oil shale deposits either undiscovered or undeveloped.

Australia and vicinity: The deposits in New South Wales are the best known examples of kerosene shales in the world. They yield 110 - 150 gallons of oil per ton. True oil shales also exist in New South Wales.

Queensland and New Zealand have kerosene and true oil shale beds similar to those found in New South Wales.

South America: South America has an adequate supply of crude oil; therefore the shale oil deposits remain undeveloped. If, however, a need for oil products should

arise that could not be taken care of by crude oil, Brazil, Peru, Argentina, Chile, Uruguay, and possibly other South American countries could furnish shale.

Africa: Oil shale deposits occur in Transvaal, Cape Colony, Natal, Basutoland, Griqualand East, Rhodesia, Mozambique, and Madagascar in moderate quantities.

Asia: Shale deposits occur along the boundary between Burma and Siam, and in Manchuria, Arabia, Syria, and Palestine.

Kerogen

Professor Crum Brown^{B/} first used the word "kerogen"

^{B/} McKee, R. H., and Goodwin, R. T., Kerogen--the oil yielding material of oil shales, from McKee, R. H., Shale oil, p. 74, New York, N. Y., The Chemical Catalog Company, Inc., 1925.

as a means of describing the oil-yielding material of oil shale that is obtainable upon destructive distillation. He described it as a pyrobitumen and not a petroleum or bitumen.

Emphasis should be placed on the fact that kerogen is merely a convenient designation of the organic oil-yielding material of oil shale; that it is not a definite chemical compound, but probably a complex mixture of complex compounds; and that the kerogens of different shales are dissimilar.

Analysis of oil shales from various locations^{9/} has

^{9/} Idem, table I, p. 75 and table II, p. 77.

proved that the chemical and physical properties of the shales vary from location to location. A study of the composition of the hydrocarbons obtained under uniform conditions of recovery from these shales likewise shows that the composition of the hydrocarbons obtained varies greatly in paraffinity, nitrogen content, and sulfur content.

After careful consideration of the theory of cracking, it is apparent that the products from a given shale are dependent upon the conditions of cracking in the system of destructive distillation. Consequently, the problem of refining of shale oil begins with the retorting, or obtaining of the oil. Since each shale is different, each shale must be tested in each process in order to determine whether or not the process is feasible.

In the retorting of oil shale, the production of oil from kerogen takes place in two stages. The primary decomposition occurs in changing the insoluble kerogen into soluble solid, or semi-solid, bitumen. This intermediate product, which is not of the same composition as the original kerogen, is further decomposed into lighter oils of greater stability and higher saturation.

The analysis of oil shale "kerogen" would greatly advance the understanding of the recovery of the

hydrocarbon from the shale by solvents. Some work has been done on the solvent recovery of the product, although a small percentage of the recoverable oil is removed by this method.^{10/ 11/} Since the shales differ, as explained

^{10/} Hall, J. O., Survey of bitumen analyses and extraction methods: Colo. School of Mines Quart, vol. 39, no. 1, pp. 71-115, January 1944.

^{11/} McKee, R. H., and Goodwin, R. T., Kerogen--the oil yielding material of oil shales, from McKee, R. H., Shale oil, table III, p. 83, New York, N. Y., The Chemical Catalog Company, Inc., 1925.

previously, the solubility of the products from the various shales will likewise differ.

SOLVENTS AND SOLVENT EXTRACTION

Fundamentals of Solvents

According to Jordan^{12/} a solvent may be defined as

^{12/} Jordan, Otto, The technology of solvents, pp. 3-13, 92-95, 133-144, New York, N. Y., Chemical Publishing Co., 1937.

a volatile, fluid, organic compound by means of which solid or semisolid organic materials may be converted, without chemical change, into technically useful solutions. A plasticiser may be defined as a non-volatile, or slightly volatile, organic liquid or solid whose function is to form the desirable homogeneous products when mixed with organic vehicles or binders with or without the addition of one or more of the volatile solvents. No chemical action between plasticiser and the other components of the product is assumed to take place, and the

physical properties of the vehicle, such as flexibility, hardness, and so on, are affected by such additions.

By far the most important industrial use of the organic solvents is the preparation of solutions of non-crystalline materials, especially oily substances and the colloidal substances of high molecular weight, known as "lyophile."

Considering the mechanism of solutions and the chemical structure of solvents, two types of solvents may be distinguished. In the first, the atoms and atomic groups from which the molecules are built do not set up electrical stresses across the molecules, and no valence force exists; in the second, individual atoms or atomic groupings give rise to potential differences across the molecule. The latter type is therefore known as a polar compound, and to this class belongs all oxygen-containing solvents, including the very strongly polar water, while the so-called non-polar solvents are represented by the hydrocarbons.

A rule to remember while working with solvents is as follows: non-polar solvents have excellent solvent powers for non-polar solutes, and polar solvents have excellent solvent powers for polar solutes.

In non-polar solvents, the individual atoms are so completely bound together by their primary valences that at no position in the molecule do there exist sources of unsatisfied energy and hence differences of electrical

potential, or dipole moments, as Debye has called them. Therefore, since the individual molecules possess but very small free energies, neighboring molecules in such liquids exert a very slight effect on one another. Since no excessive hindrance takes place between molecules, the vapor pressure and rates of evaporation are higher.

In polar solvents, the atomic groupings are not able to attain a state of complete internal saturation, and certain positions in the molecule possess a quantity of unbalanced or excessive energy. The molecule consists of two portions, an active one possessing a degree of free energy, and an inactive portion between which exists a tension called dipole moments. The forces acting between polar molecules, termed "the forces of cohesion" by van der Waal, are of importance in considering the forces of attraction existing between solvents and solutes.

At normal temperatures there is a constant interchange from high, low, or mean position potential energy; at any one time no one type will predominate. At the surface of the liquid, it is most probable that, in order to have a state of minimum potential energy, the molecules of a polar solvent are so arranged that their active portions are directed toward the interior of the fluid, the inactive portions being adjacent to the air surface. For non-polar solvents, this statement is not true since there is no active portion and each end is of equal energy. When an interface is formed between two solvents, the

molecules of each solvent at the interface arrange themselves so that like types attempt to approach one another -- that is to say, there is a conflict between similar groups on opposite sides of the interface. If one solvent (such as water or methyl alcohol) possesses no hydrocarbon chain, or but a short one, while the other solvent (a petroleum hydrocarbon, for instance) possesses no active group at all, there is no attraction between the two types of molecules, and the liquids do not mix appreciably.

If, however, two surfaces of polar solvents are brought together, the active hydroxyl groups at the surface will attempt to approach each other.

The ratio of active to inactive groups in a molecule may be expressed as:

$$\frac{\text{Hydrocarbon group}}{\text{Oxygen-containing group}} \text{ or } \frac{\text{Molecular weight}}{\text{Active group}}$$

and is of considerable importance in the prediction of solvent power.

As a general rule, non-polar or weakly polar materials, such as fatty oils, are most easily dissolved by the hydrocarbons and their chloro-derivatives. Resins are divided into two classes: the rather strongly polar types, such as the phenol-formaldehyde, glyptal, and acrolein resins, which are soluble in polar liquids, and those that dissolve freely only in non-polar solvents, such as the coumarone resins and the oil-soluble bakelite types containing rosin-modified phenol-formaldehyde or naphthalene-aldehyde products.

Strongly polar solvents, in which the active portion of the molecule predominates, are freely miscible with water but become less so as the hydrocarbon radical increases in chain length. Such fluids are poor solvents for oils and fats.

A mixture of solvents of varying polarity and water miscibility may be able to dissolve a certain material that is insoluble in the individual components of the mixture.

Industrial Use of Solvents

The solvents generally used for industrial purposes can be classified into groups according to their chemical composition as follows:

1. Hydrocarbons. The aliphatic and aromatic hydrocarbons are composed of carbon and hydrogen only and are electrically neutral or non-polar since they contain no hydrophilic groups. They are classified as hydrophobic or lipophile -- good solvents for oils and fats. The members of this group have a pronounced solvent power for non-polar or weakly polar (hydrophobic) materials, especially for oils, fats, bitumens, many resins, rubber, and also for paraffins and waxes at higher temperatures. On the other hand, hydrocarbons are poor solvents for hydrophilic or polar materials.

2. Chlorinated Hydrocarbons. The chlorinated hydrocarbons are also essentially lipophile, although they do possess slight polar properties. They are very

similar to hydrocarbons although their greater polarity permits them to exercise a solvent power for certain cellulose esters.

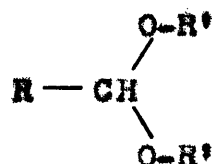
3. Alcohols. Because of the presence of the hydroxyl group, the alcohols are very strongly polar. Their solvent power depends on the proportion of the hydroxyl group to the whole molecule. In the lower alcohols the hydrocarbon radical is relatively small, and the hydroxyl content relatively large. These compounds are water soluble and strongly polar. They possess poor solvent power for non-polar materials such as fats, oils, bitumens, and waxes, but are exceedingly good solvents for strongly polar materials such as many resins, dyestuffs, and some types of nitrocellulose. With a lengthening of the chain, the influence of the hydrophilic hydroxyl group is diminished, and a lower degree of water miscibility and a poorer solubility for polar materials in general result. At the same time, solubility of the non-polar materials, oils for instance, increases. The addition of alcohols to other solvents is of great assistance in adjusting the polar characteristics of the solvents to those of the material to be dissolved.

4. Ketones. The ketones contain the ketonic group -- RCOR' -- in which are weaker polar compounds than the alcohols. The higher ketones are good solvents for oils.

5. Esters. The esters possess the general structure -- RCOOR' . Polar characteristics are possessed by these substances, although to a much lesser degree than in the alcohols, and only the very lowest members are hydrophilic. Most of the esters dissolve oils and resins freely.

6. Ethers. The structures of the ethers show two similar or different hydrocarbon radicals linked by an oxygen atom, $\text{R-O-R}'$. This compound is non-polar from diethyl ether up and has strong solvent power for non-polar materials like fats and oils. The polar characteristics of ethers can be increased by the addition of alcohol, and some mixtures of ether and alcohol are ideal solvents for nitrocellulose.

7. Acetals. The acetals contain two ether groups joined to a common carbon atom:



These groups are somewhat more strongly polar than the simple ethers.

The Use of Solvents for Extraction

The efficiency of a solvent for an extraction process usually depends on the type of apparatus employed. They commonly operate on the principle that oily or fatty substances may be leached out of the raw material by means of a suitable solvent which must be able to penetrate into

the smallest cells of the material in order to dissolve the oil. This process of penetration by the solvent into the cells requires definite time, and in order that the oil or fat may be removed by the solvent as quickly as possible, the latter is circulated so that the fresh solvent continuously passes through the mass, the removal of the oil being thus completed in a minimum time. The apparatus is best constructed on the countercurrent principle, whereby the fresh material to be extracted is washed first by a comparatively concentrated solution of the fatty matter in partially spent solvent, and finally, the last traces of oil are removed by the incoming fresh solvent.

Consideration of the specific gravity of the solvent and solid in the design of the equipment determines whether the solvent should enter from above or below. The temperature and pressure of the operation should also be considered along with the possibility of corrosion by the solvent.

The desired properties of a solvent to be used might include:

1. Great purity and chemical individuality.
2. Resistance to decomposition.
3. High solvent power.
4. Resistance to chemical reaction with the extract or with the residue.
5. Ease of separation.

6. Resistance to reaction with the metals used in the apparatus.
7. Non-inflammability.
8. Economy in industrial use.

The Recovery of Solvents

The process of recovering the solvent used in any unit is of economic importance. Whenever the solvent used is of value, a unit must be set up for the recovery of that solvent for re-use. The recovery of solvents depends on two distinct principles: 1) The distillation of the solvent by the addition of heat and the condensation of the vapors, and 2) the absorption of the solvent vapors by fluids or by absorbent solids.

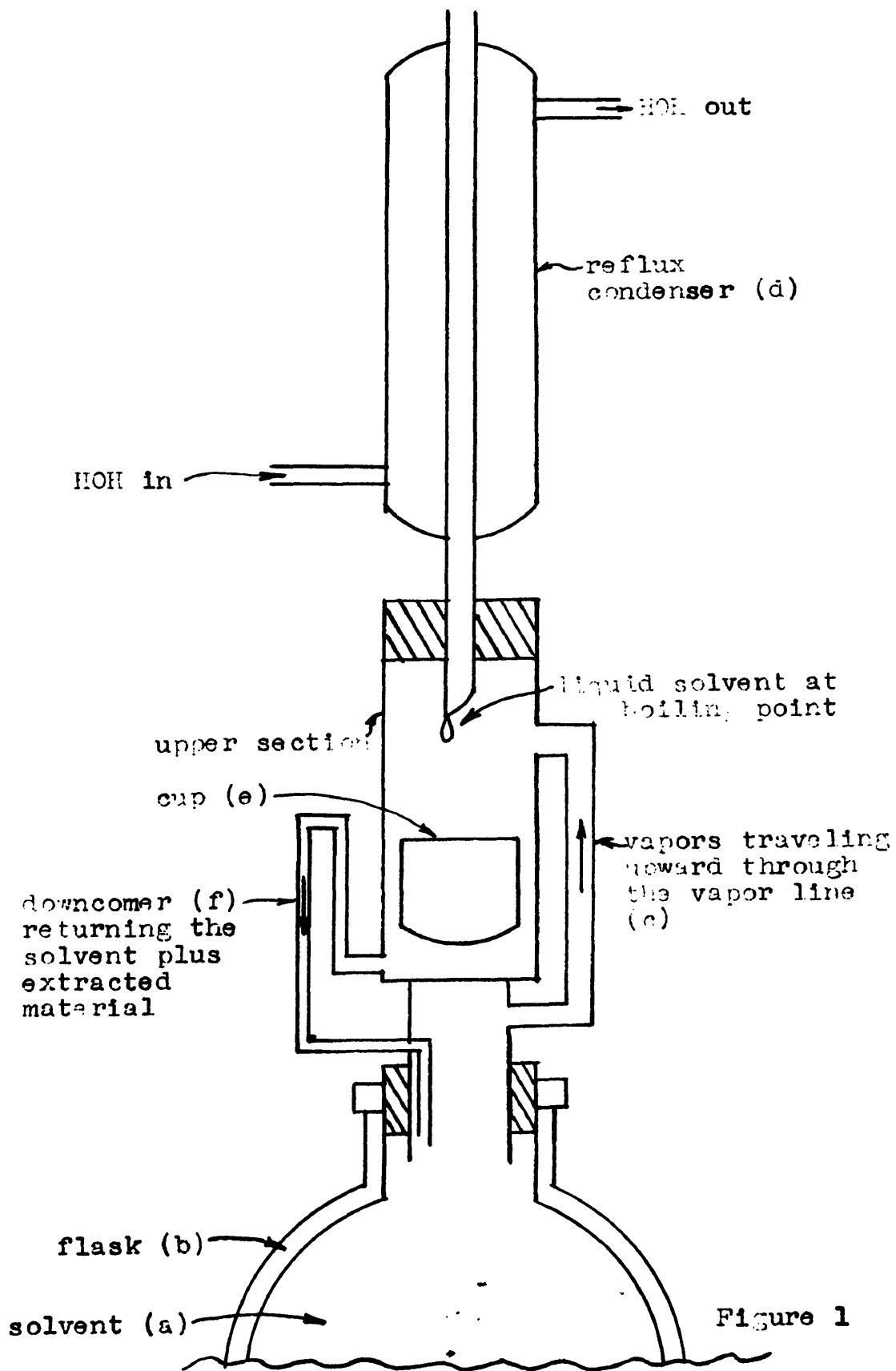
DESIGN OF THE SOLVENT EXTRACTION UNIT

The past work on solvent extraction of oil from shale has not been successful in recovering the hydrocarbons by the use of solvents in the standard equipment used in laboratories. Only a small percentage of the hydrocarbons present in the shale has been recovered by the use of a Soxhlet extracting apparatus using absolute alcohol, acetone, petroleum ether, metacresol, pyridine, benzol, phenol, carbon disulphide, and chloroform.^{13/ 14/}

^{13/} Pier, M., Treatment of shale oil by hydrogenation, from Oil shale and cannel coal, p. 399, London, W.C.2, The Institute of Petroleum, The Adelphi, June 1938.

^{14/} Ball, J. O., Survey of bitumen analyses and extraction methods: Colo. School of Mines Quart., vol. 39, no. 1, p. 14, January 1944.

The Soxhlet extractor (Figure 1, page 26) is constructed of glass and set up so that solvent a in flask b is vaporized by the heat source below the flask. The



vapors then travel upward through vapor line c to the upper section where they are condensed in reflux condenser d. The solvent, now in the liquid state, but essentially at the boiling point of the solvent, is dropped down onto cup e that holds the material to be treated. When the liquid level builds up to the level of downcomer f, it is siphoned back down to the original flask, carrying the extract with it. The cycles continue as the fresh vapors again travel upward.

The condenser is used to remove the heat of vaporization from the vapors and thus leave the liquid at the boiling point of the solvent. This liquid, as mentioned above, removes only a small percentage of the oil that can be obtained from the shale. It was believed that a good solvent, used at a very high temperature, would produce more oil. In order to use a good solvent at an elevated temperature, high pressure would have to be applied. To apply such pressures, a unit would have to be designed from metal which would withstand the strenuous conditions of operation.

The first job to be undertaken was to design the pressure unit. In order to have a unit that would withstand the pressure, standard 1.5-inch pipe was used, the unit being constructed as shown in Figure 2, page 28.

As in the Soxhlet extractor, solvent a was contained in the lower section b. Vaporization took place so that the vapors would pass upward through vapor line c to the

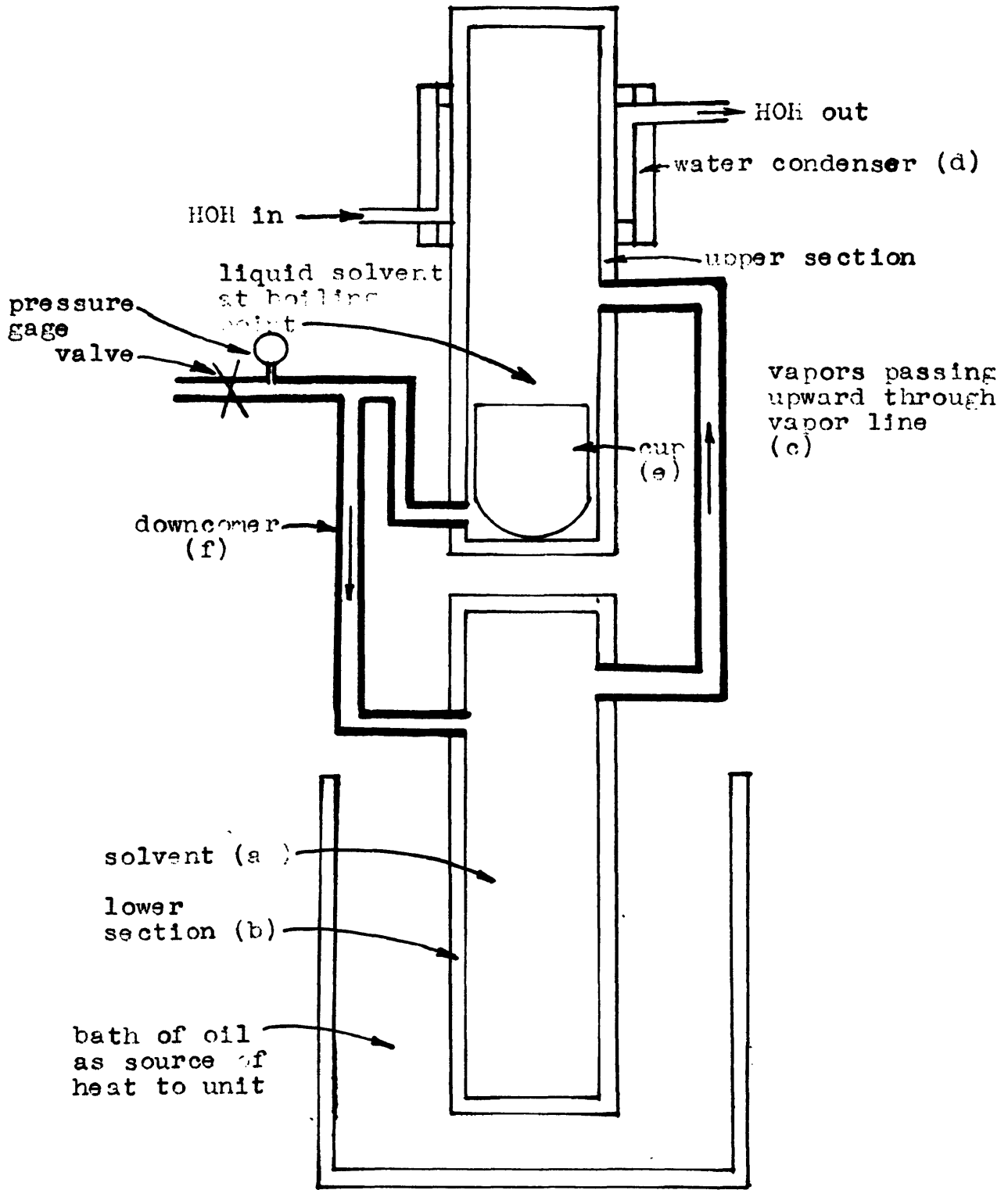


Figure 2

upper section. An outer water jacket was constructed of oversize pipe which would act as the condenser d. The liquid, at its boiling point and at the pressure in the system, was dropped down onto cup e, which held the crushed shale. When the liquid level built up to the level of the downcomer f, it was siphoned back down to the lower section. Fresh vapors again traveled upward for continuous recycling.

The first precautionary step taken was to test the equipment under a hydrostatic head of 300 pounds per square inch gage (psig) to assure safety in operation up to the proposed 200 pounds per square inch gage (psig). After many tests, the equipment was put into a condition considered safe. The pressure gage was then tested on a gage tester to insure accuracy in pressure readings.

The first operation of the unit proved that the water jacket was unnecessary. The heat removed from the upper section was so great that the vapors would condense rapidly and cause the pressure to remain low. Consequently, the design had to be altered to include insulation throughout the unit. Even with this insulation, heat had to be added to the upper section of the equipment to hold the required pressure.

The unit was also changed so that a clear gage glass in the downcomer side would allow timing of the process by cycles instead of by hours. The time set for the test was originally 1 hour. After this clear gage glass was

installed, the number of cycles was counted so that equal quantity of fresh solvent was used in each test. In operation, the solution of solvent plus oil recovered had to be removed from the bottom section. Therefore, an attachment with a valve had to be placed out of the top of the lower container. Accordingly, the revised equipment was constructed as shown in Figure 3, page 31.

A thermometer well was added in the top of the upper container so that the inside temperature could be recorded. When the equipment was operated under pressure, it could be observed that proper circulation was being provided. Since a seal could not be maintained, the gage glass had to be eliminated and the basis of operation changed. The basis for all runs was set at 1 hour.

At this point, the equipment was set up as shown in Figure 4, page 32.

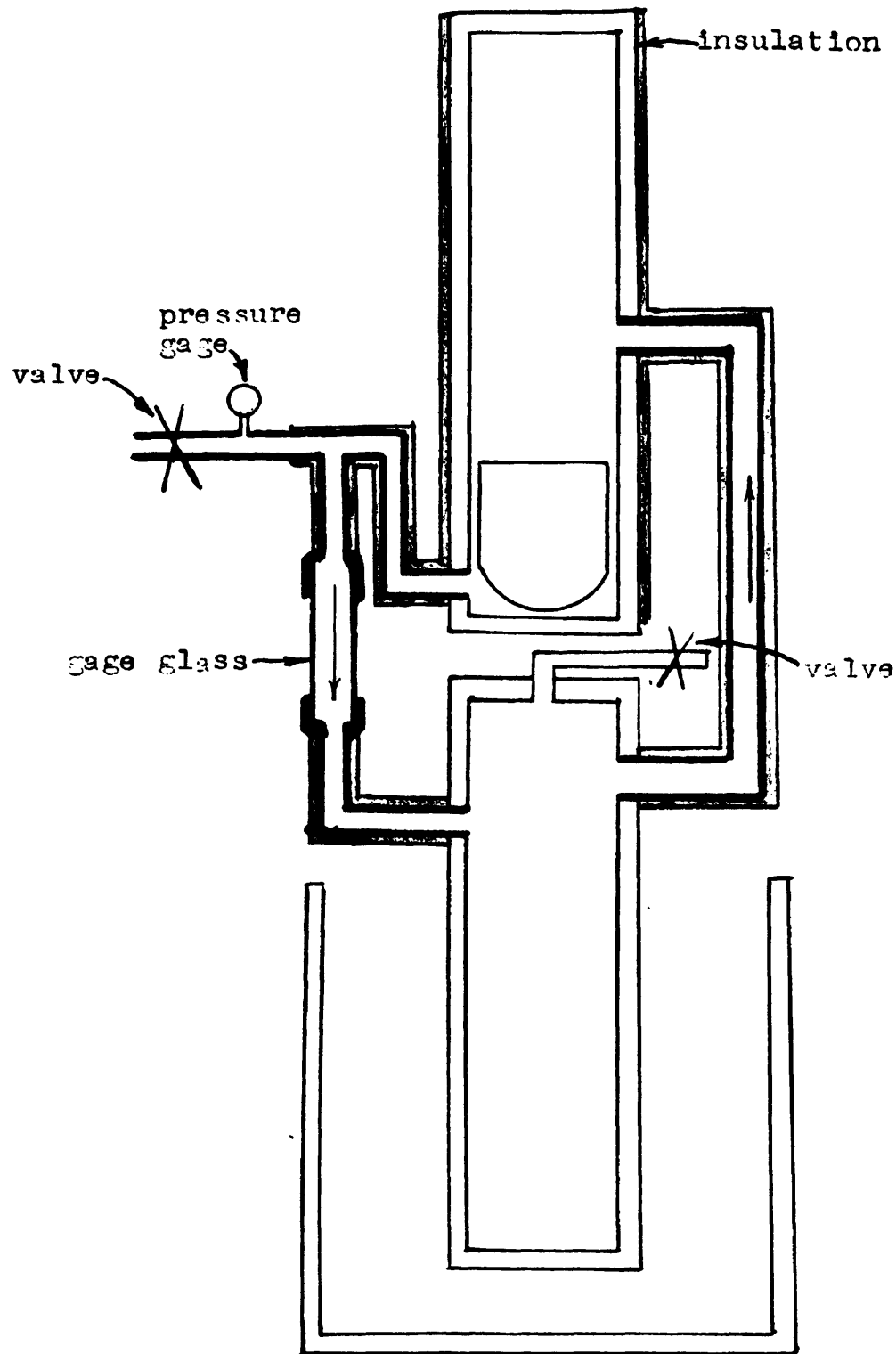


Figure 3

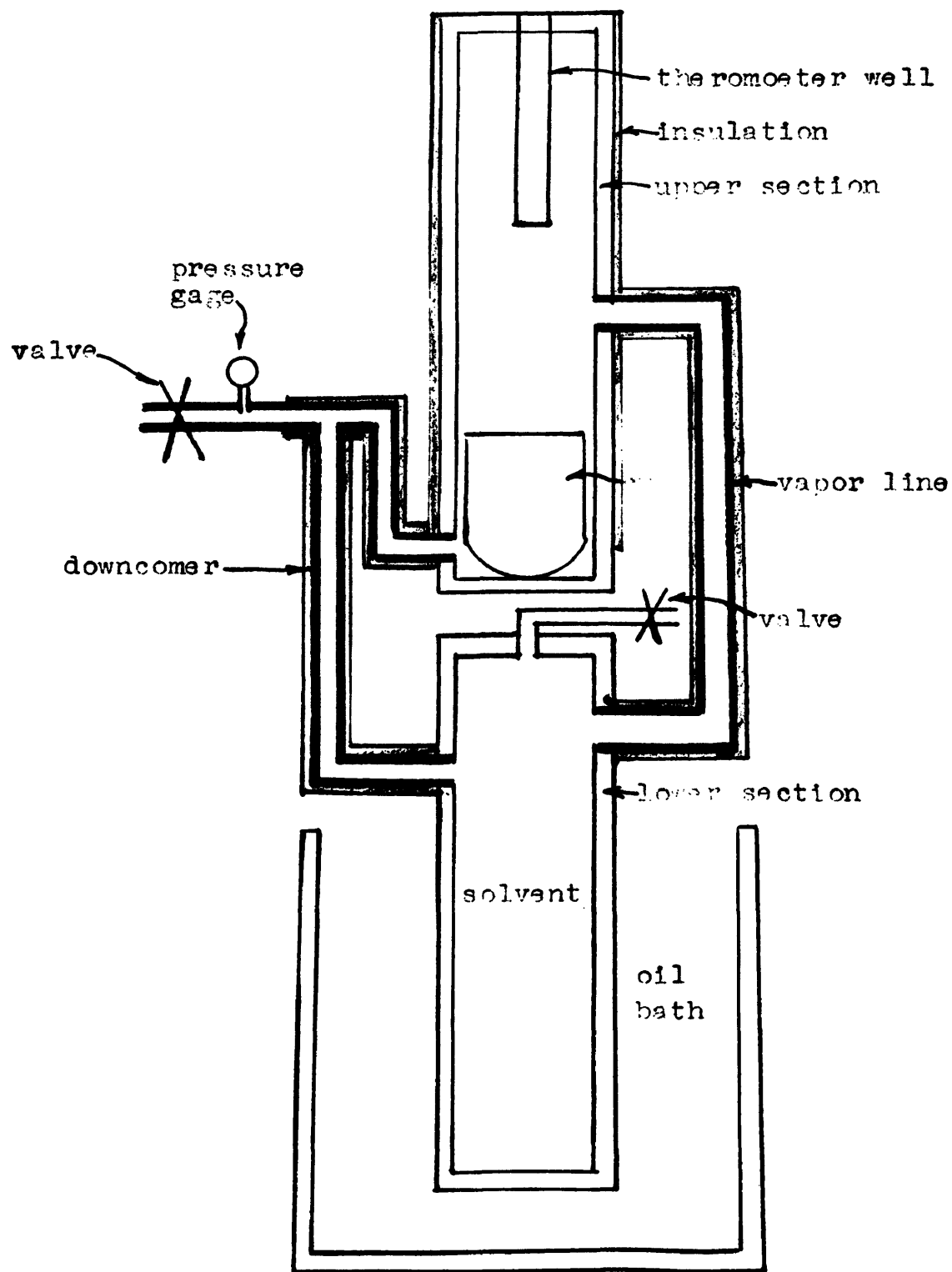


Figure 4

ORIGIN AND PREPARATION OF THE OIL SHALE USED

The shale used in this experimental work was secured through the courtesy of the United States Bureau of Mines laboratory at Golden, Colorado. It was acquired from property owned by the Union Oil Company of California and located in the Grand Valley district of Garfield County, Colorado.^{15/} The point at which the shale was mined was

^{15/} Parry, V. F., Goodman, J. S., Wagner, E. O., Lambers, G. C., and Cook, V. A., Processing Colorado mahogany oil shale in the Parry Retort: pp. 1-8, February 1946.

12.5 miles up Parachute Creek, approximately north of the town of Grand Valley and near the confluence of the middle and east forks of Parachute Creek in the NW $\frac{1}{4}$ of NW $\frac{1}{4}$, Section 30, Township 5, Range 95 west. Geologically, the Grand Valley Colorado shales are in the Green River formation and are sediments deposited in the ancient Lake Uinta of Eocene time.

The weathered shale was removed as completely as possible and discarded. This was done by cutting down to the massive mahogany shale. Then 8 feet of an 11-foot seam was blasted back about 6 feet from the face of the shale by using 40 per cent dynamite in drill holes and in some seams. The Union Oil Company reported that this shale represented an average section of the mahogany shale. The property from which the shale was taken is adjacent to Naval Oil Shale Reserves 1 and 3.

The shale was received at the Golden, Colorado, plant in massive pieces, some weighing as much as 300 pounds. This mahogany shale, splitting fairly easily along the bedded plane, required much power to crush it into pieces that would pass a 1.0-inch screen. After passing this screen, the shale was divided into four sizes for operation: 1) 1-by 1/2-inch, 2) 1/2- by 1/4-inch, 3) 1/4- by 1/8-inch, and 4) 1/8- by 0-inch.

The table presented by the U. S. Bureau of Mines^{16/}

^{16/} Op. cit., table 3, p. 13.

on the Comparison of Results of Fischer Assay Determinations of Various Sizes of Raw Mahogany Shale indicates that the percentage of shale oil obtainable by the Fischer Retort assay at 500 C for the 0- by 1-inch shale was 18.9 per cent or 18.9 grams of oil per 100 grams of shale.

The sample of shale for the tests in this report was the 1/4- by 1/8-inch size. This shale was crushed further at the Colorado School of Mines Experimental Plant so that all of the sample would go through an 8-mesh screen but would be retained on a 10-mesh screen.

A Fischer Retort assay was run on this sample to determine the total oil. The average determination as made by William Laspe, graduate student in Petroleum Refining at the Colorado School of Mines, by the members of the senior class in Petroleum Refining at the Colorado School of Mines, and by the author was 18.7 grams of oil per 100 grams of shale. The deviation of the individual tests was not more than 2 per cent. Although the usual method of expressing this figure is gallons of oil per ton of shale, the small volumes force the use of the term grams of oil per 100 grams of shale. This value, 18.7 grams of oil per 100 grams of shale, was assumed as 100 per cent recovery for the remainder of this report.

EFFECT OF PRESSURE SOLVENT EXTRACTION

Using the equipment as shown, with an oil bath as the source of heat on the lower section, a sample of 34.104 grams of shale was charged into the unit with 400 cc of carbon tetrachloride. The unit was then closed and ready for operation. A pressure of 100 psig was reached and maintained for 1 hour. In order to hold this temperature, a small flame had to be played across the bottom of the upper container. At the end of 1 hour, all sources of heat were removed, and immediate cooling took place.

The solvent containing the oil was removed from the apparatus and placed in a distillation flask of known weight. The carbon tetrachloride was removed from the oil by distillation. A total of 9.71 grams of oil per 100 grams of shale was recovered.

A second sample of 32.805 grams of shale was charged with 425 cc of carbon tetrachloride. Of this sample

4.580 grams of oil were recovered by running at a pressure of 115 psig for 1 hour. This quantity represents 13.95 grams of oil per 100 grams of shale, based on the original weight of shale as received.

Additional runs were made using carbon tetrachloride, acetone, water, butyl alcohol, isopropyl alcohol, methyl ethyl ketone, benzene-acetone mixtures, chloroform, and iso-octane. The author felt that most of the results obtained from the experiments using these solvents, as well as both of the runs mentioned above using carbon tetrachloride, were too high and consequently in error. However, from these determinations, sufficient skill and technique of operation were developed so that, for the remainder of the paper, accurate results could be obtained.

During an inspection trip to the United States Bureau of Mines Laboratory on the University of Wyoming campus at Laramie, Wyoming, definite information was gained on the problem at hand. The results obtained by the work that was being done at this laboratory definitely proved that high pressure and temperature increased the formation of oil hydrocarbons from shale.

Pier^{17/} stated that extraction at atmospheric

^{17/} Pier, M., Treatment of shale oil by hydrogenation, from Oil shale and cannel coal, p. 399, London, W.C. 2, The Institute of Petroleum, The Adelphi, June 1938.

pressure results in only a very small amount of the

organic matter being brought into the solution. He also stated that it is easier to extract more oil from shale by the application of pressure, high temperature, and suitable solvents than at atmospheric conditions by carbonization. As a result of the low extraction temperature, the original high-molecular structure of the organic matter in the shale is only slightly broken down, so that the extract consists of a high-boiling product.

The results of the laboratory work mentioned above, although not precise, also indicated that more oil was extractable from shale by the application of pressure-temperature solvent extraction than is recoverable at the normal boiling point by solvent extraction methods for a given period of operation.

EFFECT OF SIZE OF PARTICLES ON OIL RECOVERY

Since the possibility of increased production by the use of high temperature-pressure had been established, the next problem was to determine the effect of the size of particles on oil recovery under similar operating conditions.

The total sample of 8- to 10-mesh shale was divided into four equal parts. One quarter of the shale was stored. A second quarter of the shale was further crushed to a size that would pass a 14-mesh screen and was then stored. A third quarter was crushed to allow it to pass a 20-mesh screen. The fourth quarter was crushed to pass a 28-mesh screen. The four variable sizes used for the remainder of the work were 10- to 12-mesh, 14-mesh, 20-mesh, and 28-mesh.

Acetone was selected as the solvent for the experimental work because previous results had indicated that the recovery of hydrocarbon product was possible by using acetone.

The pressures selected for this work were 100, 150, and 200 psig (112, 162, and 212 psia). The pressure was controllable to ± 4 psig.

Runs were made on the four sizes of samples at the three different pressures. Sufficient repetition gave satisfactory checks of the experiments completed. The most representative results as determined from this work can be found in Tables 1, 2, and 3, pages 41 and 42, respectively. A summary of the graphs can be found in Table 4, page 42.

The calculations for percentage of recovery were made as grams of oil recovered by solvent extraction per 100 grams of shale used divided by 18.7 grams of oil per 100 grams of shale as determined by the Fischer Retort analysis.

Although the oil recovered from the individual tests was small, it was combined to make a total sample of approximately 300 cc. This material was dark brownish-black in color with an odor similar to that of varnish and also to that given off when the shale was crushed. The material was very sticky to the touch and remained tacky on the fingers for several hours. When the container was turned sideways, the oil proved very resistant to flow.

TABLE I

Solvent -- Acetone

Sample mesh	8-10	14	20	28
Pressure, psig	100	100	100	100
Time, hours	1	1	1	1
Sample, grams	34.508	33.528	33.808	33.418
Temperature, F	254	254	254	254
Oil + container, g	80.065	80.268	105.812	80.405
Container, g	78.695	78.926	104.408	78.877
Oil, grams	1.370	1.342	1.404	1.528
g oil/100 g shale	3.97	4.00	4.15	4.57
Recovery, per cent	21.23	21.40	22.2	24.45

TABLE II

Solvent -- Acetone

Sample mesh	8-10	14	20	28
Pressure, psig	150	150	150	150
Time, hours	1	1	1	1
Sample, grams	31.040	34.181	33.193	33.000
Temperature, F	292	292	292	292
Oil + container, g	105.805	81.712	80.304	80.790
Container, g	104.562	80.305	78.918	79.272
Oil, grams	1.243	1.407	1.386	1.518
g oil/100 g shale	4.00	4.12	4.18	4.6
Recovery, per cent	21.40	22.00	22.35	24.60

TABLE III**Solvent -- Acetone**

Sample mesh	8-10	14	20	28
Pressure, psig	200	200	200	200
Time, hours	1	1	1	1
Sample, grams	33.125	34.030	33.800	33.078
Temperature, F	314	314	314	314
Oil + container, g	105.550	80.218	105.738	105.151
Container, grams	104.185	78.770	104.296	103.600
Oil, grams	1.365	1.448	1.442	1.551
grams oil/100 g shale	4.12	4.24	4.26	4.69
Recovery, per cent	22.00	22.68	22.80	25.1

TABLE IV

Mesh	254° F 100 psig		292° F 150 psig		314° F 200 psig	
	$\frac{\text{g. oil}}{100 \text{ g}} \\ \text{shale}$	Recovery (%)	$\frac{\text{g. oil}}{100 \text{ g}} \\ \text{shale}$	Recovery (%)	$\frac{\text{g. oil}}{100 \text{ g}} \\ \text{shale}$	Recovery (%)
8-10	3.97	21.23	4.0	21.40	4.12	22.00
14	4.00	21.40	4.12	22.00	4.24	22.68
20	4.15	22.20	4.18	22.35	4.26	22.80
28	4.57	24.45	4.6	24.60	4.69	25.1

From the preceding data, the following graphs might be plotted:

	Ordinate	Abscissa	Variables
A	Recovery	Mesh	Pressure <u>a</u>
			Temperature <u>b</u>
			Recovery per cent <u>c</u>
		Pressure	Mesh <u>d</u>
			Temperature <u>e</u>
			Recovery per cent <u>f</u>
		Temperature	Mesh <u>g</u>
			Pressure <u>h</u>
			Recovery per cent <u>i</u>
			Mesh <u>j</u>
B	Pressure	Mesh	Pressure <u>k</u>
			Temperature <u>l</u>
			Temperature <u>m</u>
		Temperature	Recovery per cent <u>n</u>
			Recovery <u>o</u>
			Mesh <u>p</u>
Recovery per cent	Recovery per cent <u>q</u>		
	Recovery <u>r</u>		
	Temperature <u>s</u>		
	Mesh <u>t</u>		
			Recovery <u>u</u>

	Ordinate	Absoissa	Variables
C	Mesh	Temperature	Recovery per cent <u>v</u>
			Recovery <u>w</u>
			Pressure <u>x</u>
			Temperature <u>y</u>
		Recovery per cent	Pressure <u>z</u>
			Recovery <u>aa</u>
D	Temperature	Recovery per cent	Pressure <u>bb</u>
			Recovery <u>cc</u>
			Mesh <u>dd</u>

After a careful study to determine the maximum charts which might be of value, the following charts were prepared:

1. Oil recovery versus Mesh with pressure variable,
2. Oil recovery versus Mesh with temperature variable,
3. Oil recovery versus Pressure with mesh variable,
4. Oil recovery versus Oil recovery per cent,
5. Operating pressure versus Operating temperature, Vapor pressure of acetone versus Temperature of acetone.

These graphs were the only combinations chosen, as other combinations would only be repetition. This is shown in the following table which indicates all the possible combinations represented by one of the above-mentioned graphs.

Graph number I	a, y, z, aa, bb, cc, dd.
Graph number II	b.
Graph number III	d, e, g, h.
Graph number IV	j, k, l.
Graph number V	p, q, r.
Same as Graph I except perpen- dicular	s, t, u.
Points only	m, n, o, v, w, x.
Inaccurate	e, f, i.

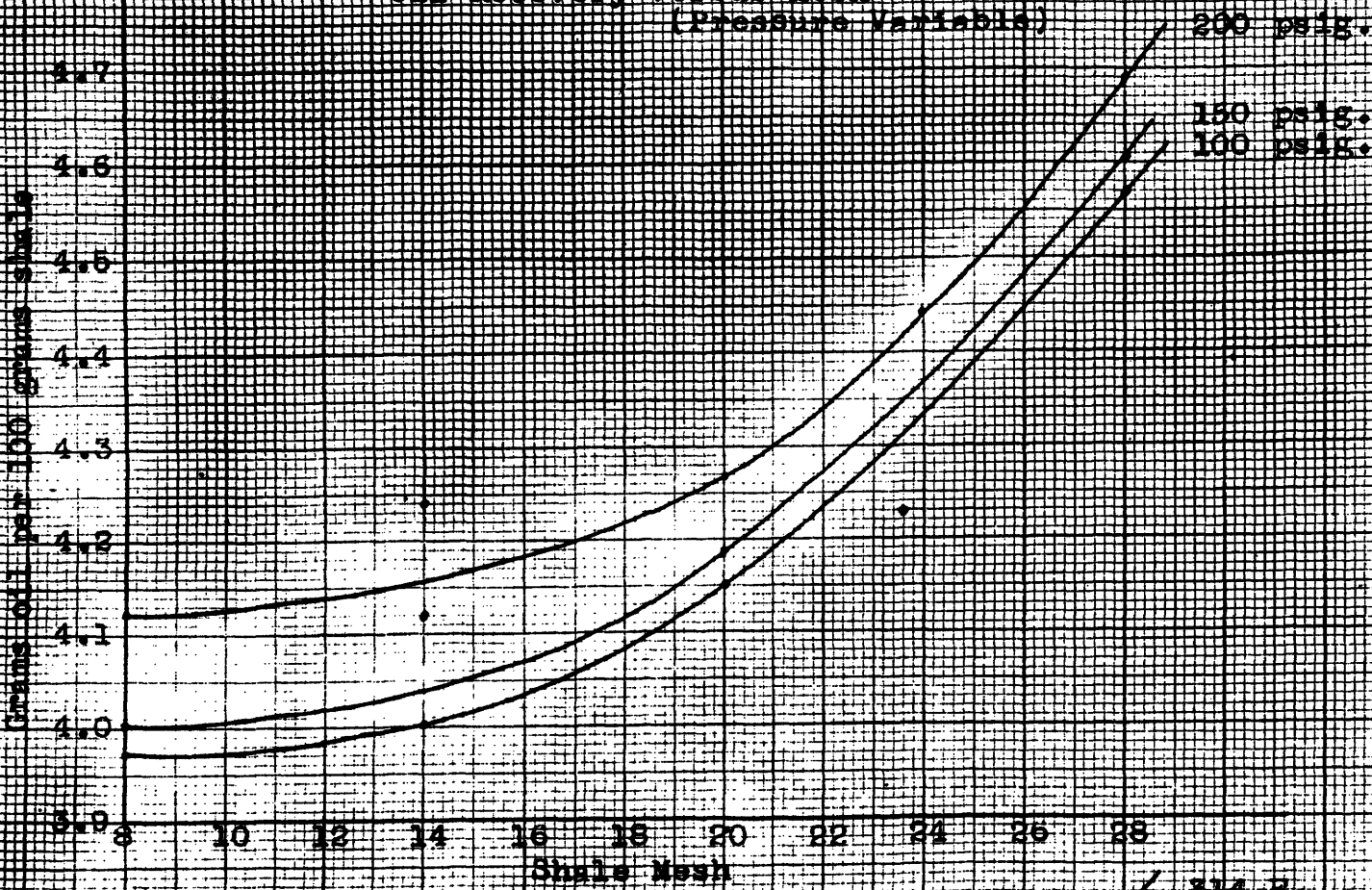
A close inspection of Graph I indicates an increased recovery of oil from the shale by high pressure solvent extraction as the size of the shale is decreased.

Starting with an 8- to 10-mesh shale at 100 psig, the recovery of oil was 3.97 grams of oil per 100 grams of shale. As the size of the shale was reduced from 8- to 10-mesh to 14-mesh, the oil recovery increased to 4.00 grams of oil per 100 grams of shale; to 4.15 grams of oil per 100 grams of shale at 20-mesh; and to 4.57 grams of oil per 100 grams of shale at 28-mesh. Likewise, at 150 psig and 200 psig, the increased oil recovery was very noticeable as the size of the shale was decreased.

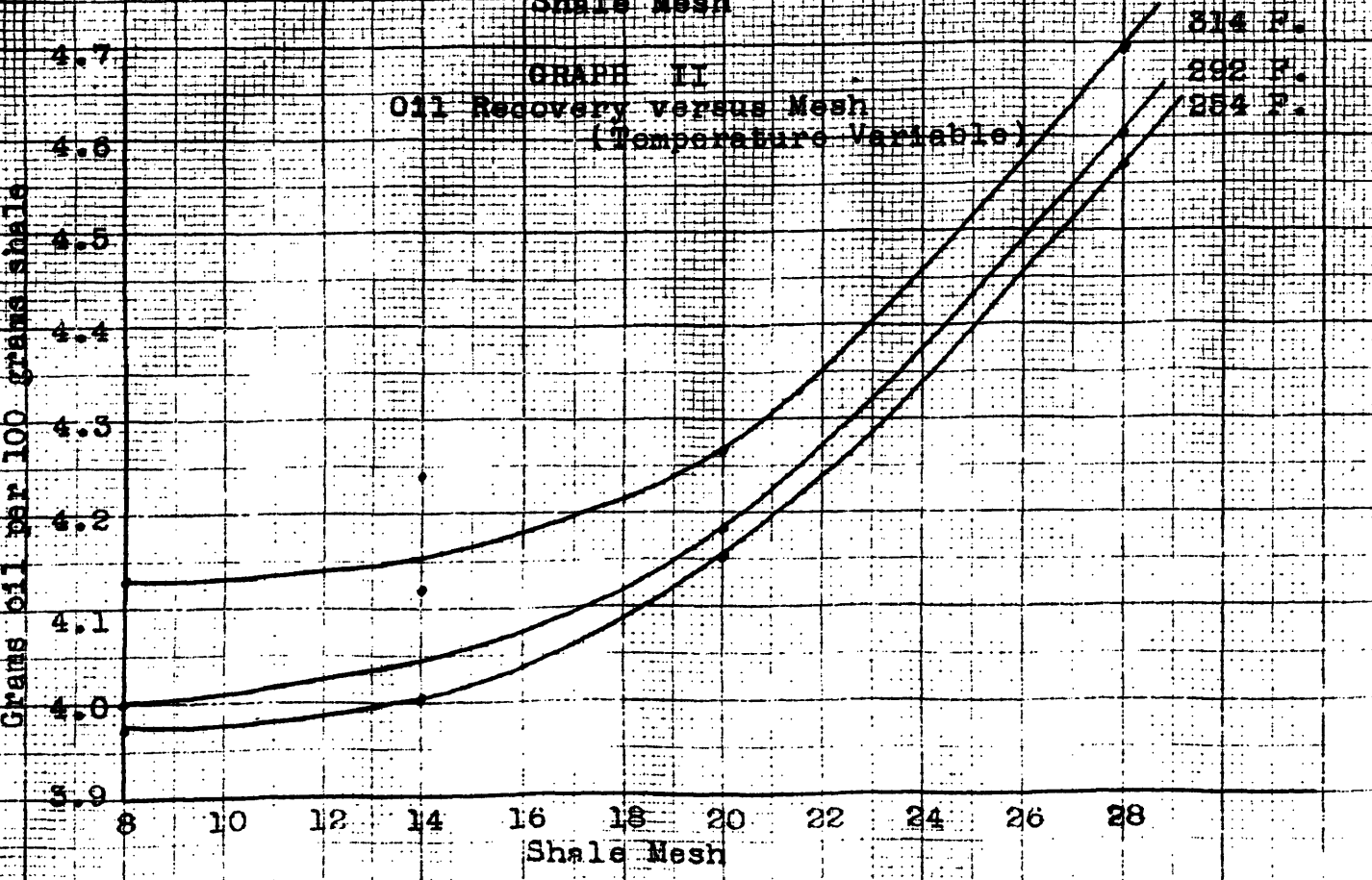
Since the curves for higher pressure fell increasingly higher on the graph, production was increased as the pressure was increased.

Graph II was plotted similarly to the previously mentioned graph. In this graph temperature was

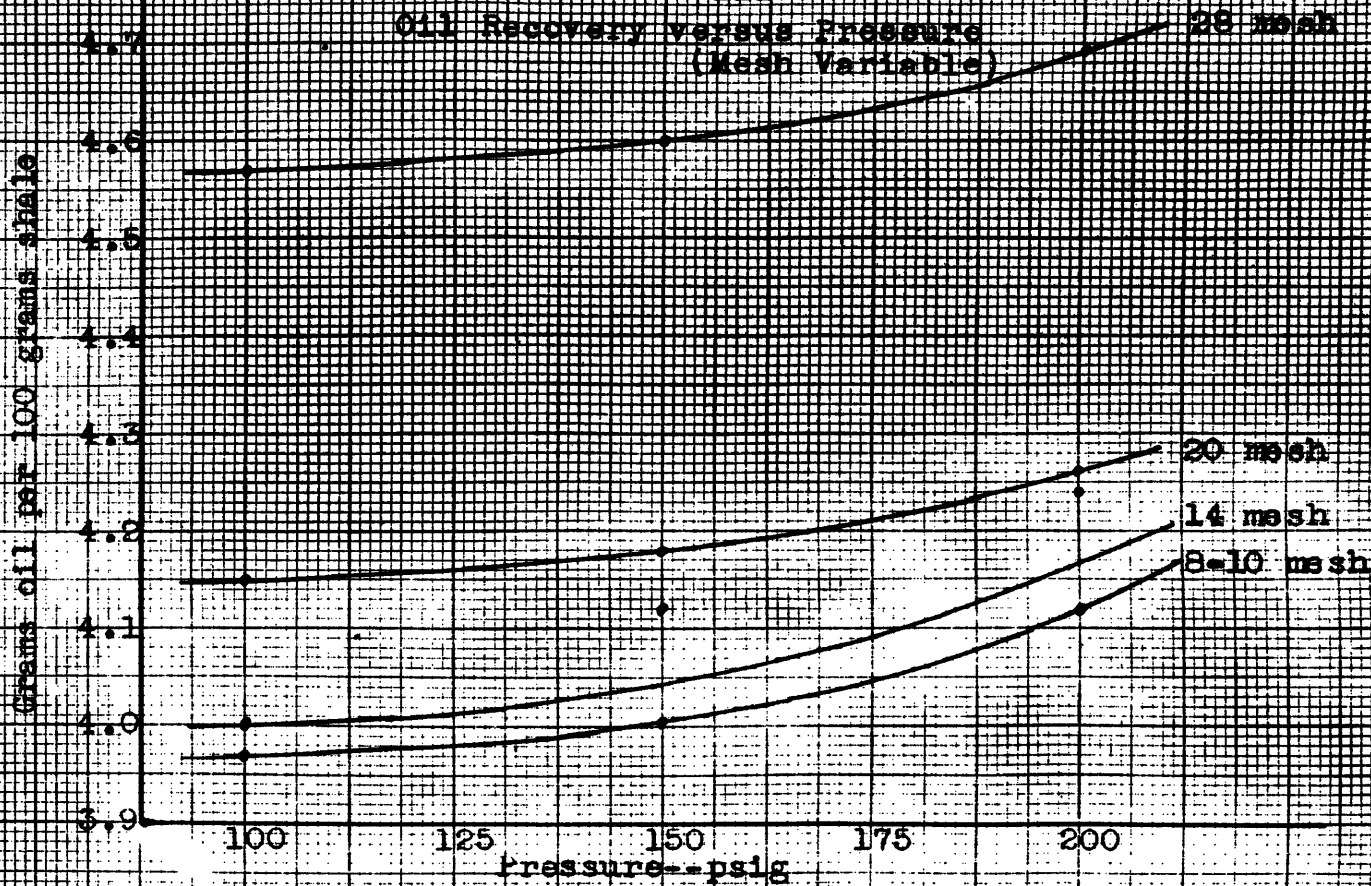
GRAPH I
Oil Recovery versus Mesh
(Pressure Variable)



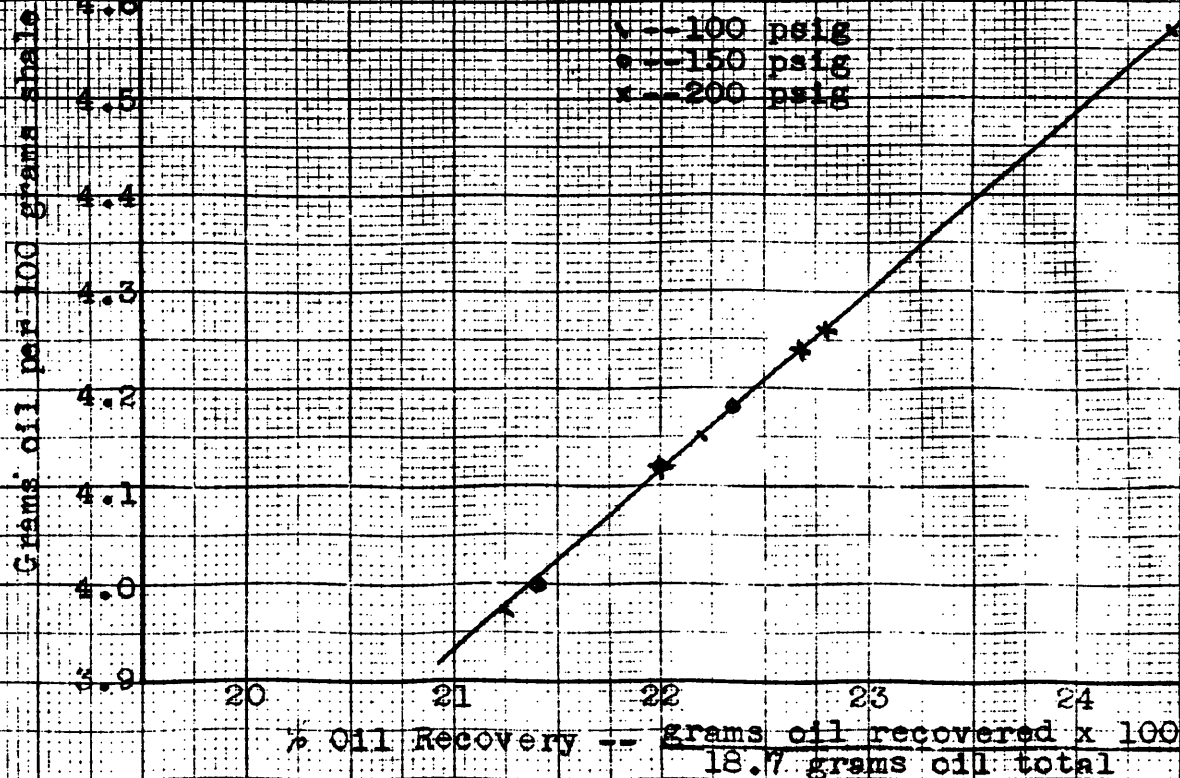
GRAPH II
Oil Recovery versus Mesh
(Temperature Variable)



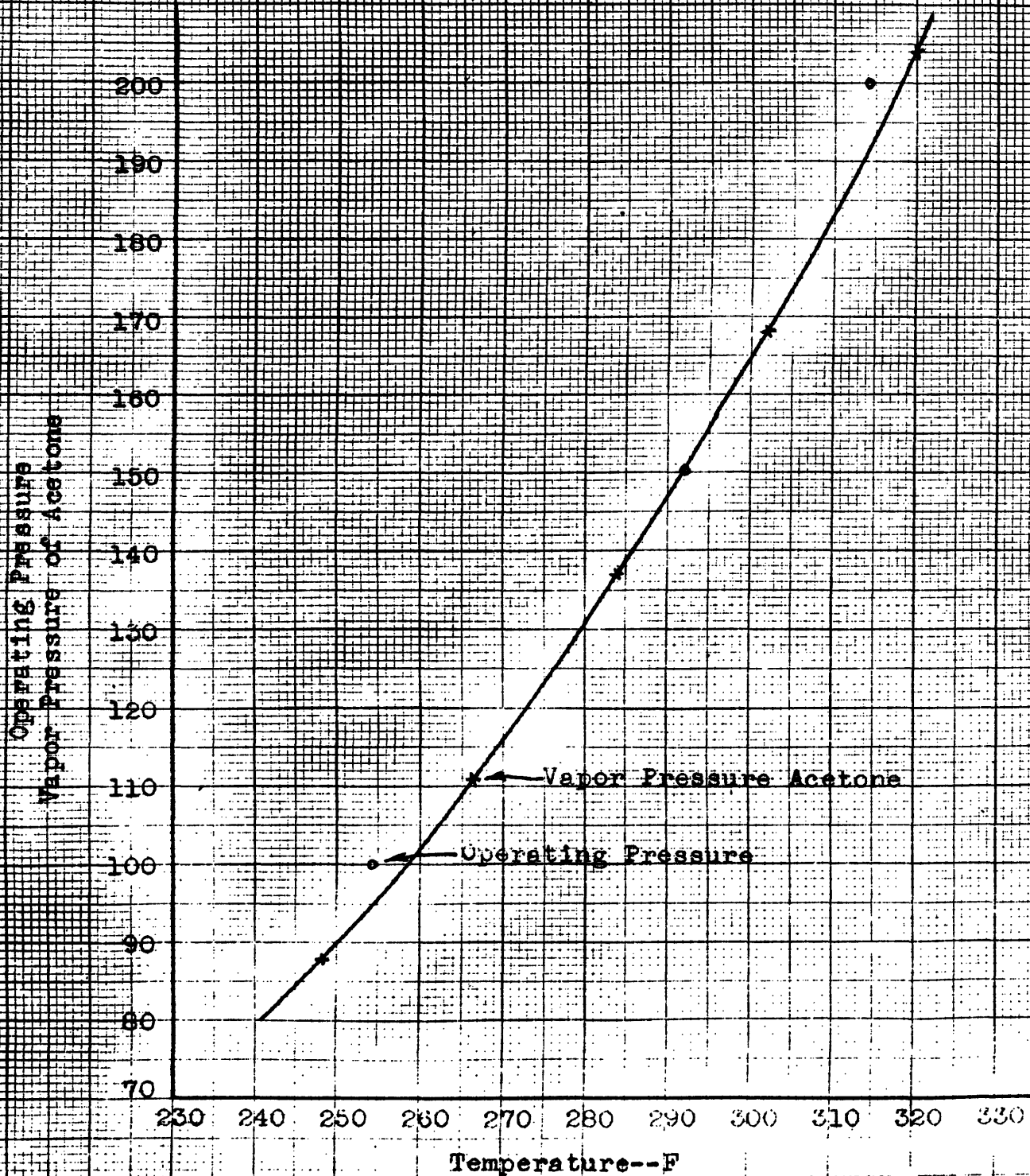
GRAPH III
Oil Recovery versus Pressure
(Mesh Variable)



GRAPH IV
Oil Recovery versus % Oil Recovery
(Mesh Variable)



GRAPH V
Operating Pressure versus Operating Temperature
Vapor Pressure Acetone versus Temperature Acetone



substituted for pressure. As in Graph I, increased production was obtained as the size of shale was decreased and as the temperature was increased.

By assuming that the recovery increased along a line drawn tangent to the curve at 100, 150, and 200 psig at 28-mesh, the size of shale required to obtain 100 per cent recovery would be calculated. The tangent to the 100 psig curve at 28-mesh had a slope of $(4.58-3.9)/(28-16.6)$ or 0.0599. This indicated that 18.7 grams of oil per 100 grams of shale could be recovered at $18.7/0.0599$ or 314-mesh. The tangent to the 150 psig curve at 28-mesh had a slope of $(4.60-3.9)/(28-16.4)$ that indicated an 18.7 gram oil recovery per 100 grams of shale at $(18.7 \times 11.6)/(0.70)$ or 310-mesh. The tangent to the 200 psig curve at 28-mesh had a slope of $(4.69-3.9)/(28-16.5)$ that indicated an 18.7 gram oil recovery per 100 grams of shale at $(18.7 \times 11.5)/(0.79)$ or 272-mesh. Since these figures were extrapolated, they are only approximate. However, they would indicate the reason for using fluid methods for the recovery of the hydrocarbons. As seen, the increase temperature-pressure conditions allowed larger sizes to be used for complete recovery. Furthermore, smaller shale samples allow lower temperature-pressure conditions for complete recovery.

An examination of Graph III likewise showed an increased recovery of hydrocarbon products with an increase of temperature and pressure and also with a decrease of shale size.

In plotting Graph IV, the recovery in grams of oil per 100 grams of shale was plotted against percentage recovery based on 18.7 grams of oil per 100 grams of shale as obtained by retorting the shale in the Fischer Retort. By extending the plotted line, both 100 per cent at 18.7 grams and 0 per cent at 0 grams were crossed.

Graph V was plotted as the vapor pressure of acetone against the temperature as obtained from the Handbook of Chemistry and Physics. Also plotted was the operating pressure against the operating temperature. The variation from the vapor pressure of acetone was probably caused by the partial pressure effect of water and hydrocarbons that were present during the operation.

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SUMMARY AND OBSERVATIONS

Some of the fundamentals of solvents and solvent extraction were presented in an effort to give the reader an understanding of the principles involved.

The design of the equipment for pressure solvent extraction of oil from oil shale was completed so that the work could be continued for this paper.

The pressure-temperature solvent extraction as undertaken proved feasible. The recovery of hydrocarbon products was increased as the pressure-temperature conditions were increased.

In determining the effect of the size of shale particles on the oil recovery by the use of moderate pressure and temperature solvent extraction of shale, four sizes of shale were used at three different conditions of pressure. All runs were made using the same quantity of acetone and for the operating time of 1 hour. The results indicated that increased oil recovery was

obtained as the pressure-temperature conditions were increased and as the size of shale was decreased.

The following observations were made:

1. Oil is recoverable by solvent extraction from "True Oil Shale" by the use of moderate pressure and temperature conditions.
2. Increased temperature in solvent extraction using pressure equipment yields increased recovery from shale.
3. Increased pressure in solvent extraction using pressure equipment yields increased recovery from shale.
4. The smaller the shale used in pressure solvent extraction, the greater the quantity of substance extracted from the shale.
5. A commercial process using solvent extraction is possible. However, further investigation must be undertaken at higher pressure and higher temperature conditions using many solvents to determine the optimum conditions for operations.

SUGGESTIONS FOR FUTURE RESEARCH

The author suggests the following for future research in this work:

1. That the work already undertaken be continued at higher pressure-temperature conditions with both smaller and larger sizes of shale. The information secured will allow the curves to be extended so that pressure, temperature, size of shale, and oil recovery data may be correlated to indicate the possible conditions of operation. With these data, optimum curves can be set up to show the most economical conditions for the recovery of oil from oil shale by pressure solvent extraction.
2. That a large group of solvents be selected, representing the total range of polarity to determine the best solvent or combinations of

solvent for the pressure solvent extraction of oil from shale.

By combining the above-mentioned work the optimum overall conditions of pressure, temperature, and particle size can be selected for the desired solvent to give the best recovery in a commercial process.

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