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STUDY OF THE THEORY AND PRACTICE OF THE THERMAL SOLUTION PROCESS, INCLUDING HYDROGENATION

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A STUDY OF THE THEORY AND PRACTICE OF THE THERMAL SOLUTION PROCESS, INCLUDING HYDROGENATION

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Intra-Bureau Report

OSRD 33

Petroleum and Oil-Shale Experiment Station

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July 1949

A STUDY OF THE THEORY AND PRACTICE OF THE THERMAL SOLUTION PROCESS, INCLUDING HYDROGENATION

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INTRODUCTION

The development of methods for producing shale oil from oil shale constitutes one phase of the research and development program being conducted at the Petroleum and Oil-Shale Experiment Station at Laramie, Wyoming, under authority of Public Law 290. The objective of this law is to facilitate the development of liquid fuels from sources other than petroleum.

Customarily, shale oil is produced by heating oil shale to a temperature in the range 800-1000 F. for a sufficient time to convert the organic matter to gas, oil, and coke and to distill the volatile conversion products from the inorganic residue or "spent shale." This retorting process results in recovery usually of not over 80 percent of the organic matter in the shale as volatile products, the balance remaining in the retort as coke or fixed carbon on the spent shale. Even though a quantity of fuel equivalent to or more than this coke may be required to carry out the process, it would be advantageous if all of the organic matter could be recovered economically from the shale as volatile fuels, for the mechanics of utilizing the fuel value of the spent shale are difficult to solve. No retorting process developed to date has succeeded in increasing this recovery by more than a few percent.

A method which appeared from published data and patent claims to convert a higher percentage of the organic matter in oil shale to volatile products consists of heating the shale either alone or in the presence of a solvent and extracting the soluble conversion products rather than distilling them from the shale. This so-called thermal solution process and a modification of it, wherein the conversion and extraction are carried out under a high partial pressure of hydrogen, have been studied at Laramie to determine their applicability to Green River oil shale from Colorado. The results of this work, which was carried out during the period from June 1945 to February 1949, are presented in this report.

SUMMARY

The thermal solution process converts over 90 percent of the organic matter in oil shale to oil and gas. The highest yields of oil obtained without hydrogen pressure were equivalent to 119 weight percent of that obtained from the same shale by Fischer assay while, under pressure, oil yields equivalent to 126 weight percent of Fischer assay were obtained. However, this oil has a higher boiling range than that obtained by retorting methods, particularly when extracted in the absence of hydrogen pressure. Nondistillable oil equivalent to over 100 percent of the organic matter in the shale was obtained without hydrogen pressure in the system. When extracting under hydrogen pressure, the yield of nondistillable oil amounted to 60 to 70 weight percent of the organic matter. This heavy material is formed partly

by polymerization and condensation of the shale-oil solvent used. This reaction together with cracking of the solvent to form gas and a carbonaceous deposit on the shale are unfavorable features of the process when using shale-oil solvents.

The estimated cost of producing shale oil by the thermal solution process without hydrogen pressure is $4.74 per barrel. Under a pressure of 3000 psi with a high partial pressure of hydrogen this cost is raised to $6.00 per barrel. Both of these cost figures allow for no return on the investment.

Advantages of the process are high rates of heat transfer to the shale with consequent short retention time in the reactor, and higher oil yields than are customarily produced by retorting.

Disadvantages of the process are the necessity for fine grinding of the shale, the high boiling-range of the oil produced, the cracking, polymerization, and condensation of the shale-oil solvent, and the difficulty of separating the solvent and product oil from the spent shale. These disadvantages are reflected in the high process costs.

The thermal solution process is considered to be not a practical shale oil production process at the present stage of development.

ACKNOWLEDGMENTS

The work described in this report was done under the general direction of W. I. R. Murphy, Chief, Retorting and Refining Section, and the direct supervision of W. I. Barnet. H. B. Jensen was responsible during the last two years for the actual laboratory work, aided by C. J. Chindgren, W. G. Collins and J. F. Lipstate. H. W. Sohns had a considerable part in the early phases of the study. Others who assisted at various times were E. E. Jukkola, L. E. Mitchell, B. F. McLarry, and J. H. Rainwater. Several others have given valuable assistance and suggestions, including particularly, F. H. Dunlap and J. F. Evitts of the Shops Section.

LITERATURE REVIEW

The organic matter in oil shale usually is associated intimately with the mineral portion and is characterized by its relatively low solubility at low temperatures and by its decomposition to gas, oil, and carbonaceous residue at high temperatures. The extent to which it is soluble is indicated by the work of Gavin and Aydelotte[1], who extracted unheated samples, crushed to 20 to 60 mesh, of several American oil shales with carbon tetrachloride, carbon disulfide, acetone, benzene, and chloroform in soxhlet apparatus. The results of their work are shown in the following table.

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[1] Gavin, M. J., and Aydelotte, J. T., Solubility of Oil Shales in Solvents for Petroleum: Bureau of Mines Rept. of Investigations 2313, 1922, 3 pp.

Solubility of Oil Shale in Various Solvents
for Petroleum[1]

Shale source	Oil yield (gpt)	Solubility (percent of distillation yield)				
		CCl_4	CS_2	$(CH_3)_2CO$	C_6H_6	$CHCl_3$
Kentucky	18.22	0.51	1.44	--	0.82	1.99
Utah (Soldier's Summit)	44.60	4.45	4.57	3.16	5.47	6.32
Colorado (DeBeque)	37.75	15.42	13.97	10.04	16.84	18.22
Wyoming (Green River)	58.65	5.27	5.58	5.35	6.02	7.72
California (Ione)	52.00	33.46	29.68	55.80	--	51.73

These data show that for shale from DeBeque, Colorado, the solubility ranges from 10 to 18 percent, based on the distillation yield of the shale. These percentages probably would represent a solubility of 7 to 12 percent of the total organic content of the shale.

McKinney[2], working with a 30.1 gpt New Brunswick oil shale, found it to be soluble in the following weight percentages in the solvents listed; ethyl alcohol, 1.5; ethyl ether, 2.2; carbon disulfide, 2.8; acetone, 2.6; chloroform, 2.2; carbon tetrachloride, 2.6; benzene, 3.2; pyridine, 2.6; and acetic acid, 6.9. These percentages are based on raw shale and probably should be multiplied by about 3 to put them on an organic matter basis.

Kogerman[3] states that not more than 1 percent of the organic matter in an Estonian kukersite was dissolved in 120 hours by acetone, chloroform, benzene, carbon disulfide, petroleum ether (boiling point 322 F), toluene, xylene, pyridine, ethyl ether, or ethyl alcohol. Apparently due to a chemical change in the organic matter it was found that 2.2 percent was soluble in tetrachloroethane. He later found that 8 percent of the organic matter was soluble in cyclohexanol (boiling point 322 F).

From the above data it is apparent that the organic constituents of oil shale are only slightly soluble at low temperatures in any of the common solvents for petroleum. Work by many investigators has shown that temperatures in the region above about 650 F are necessary to effect conversion of the organic matter to soluble material. A study at this station of the specific rates of this conversion reaction for Green River oil shale from Colorado over the temperature range

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[2] McKinney, J. W., Constitution of Kerogen: Jour. Am. Chem. Soc. 46, 1924, pp. 968-979.

[3] Kogerman, P. N., Hundred Years of the Chemical Investigation of an Oil Shale: Oil Shale and Cannel Coal, The Institute of Petroleum, London, 1938, pp. 119-120.

675 to 825 F indicates that the rate of the reaction is very low at 675 F but approximately doubles for each 18 degree rise in temperature. In the region above 750 F the rate is sufficient to be of practical significance.

J. A. Dulhunty[4] [5] [6] reports some work on the solvent treatment of Australian torbanite. These investigations apparently were made more in an attempt to determine the chemical properties of the organic material in torbanite than to develop a commercial process for its extraction. Preheating of the torbanite to 660-840 F rendered the organic material soluble in benzene. Aromatic solvents were found to be more efficient than aliphatic and it was observed that the organic matter could be extracted also by its own oily conversion product at 660-840 F and 150-300 psi. Considerable work was done by this investigator on the pressure extraction of torbanite with benzene.

Some data are available[7] on the small-scale batch autoclaving of Dunnet, Scotland, oil shale with a heavy, aromatic kerosine. With a 1:1 weight ratio of shale and solvent and an extraction time of 6 hours the optimum temperature was found to be 716-752 F. The maximum pressure developed during these tests at this temperature was 350-470 psi. Batch extraction with the same shale and solvent at 752 F and 320 psi maximum pressure removed 63.3 percent of the organic carbon and 71.9 percent of the hydrogen from the shale. Dry distillation of this shale at 1380-1470 F removed 55.8 percent carbon and 91.9 percent hydrogen. The carbon to hydrogen ratio of the total products was 4.66 for the thermal solution method as compared with 3.22 for the dry retorting method.

Since 1940, Russian investigators have published considerable work on the thermal solution of solid fuels, including oil shales. M. K. D'yakova[8] [9], in 1944, described a pilot plant handling 30 kg of shale per hour. A low-sulfur shale containing 48 percent organic matter was used in a series of tests. A particle size of 0.3 to 5 mm was found to be satisfactory. The solvent was a shale-oil fraction

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4/ Dulhunty, J. A., Solvent Extraction of Torbanite: Proc. Linnean Soc. N. S. W. 67, pt. 3-4, 1942, pp. 238-248.

5/ Idem, The Action of Solvents on Torbanite and the Nature of Extracted Products: Jour. Proc. Royal Soc. N. S. W. 76, 1943, pp. 268-274.

6/ Idem, Preliminary Notes on Solution-Cracking Treatment of Torbanite: Jour. Proc. Royal Soc. N. S. W. 77, 1943, pp. 24-32.

7/ Smith, G. H., and Stewart, D., Extraction of Oil Shale with Solvents at Relatively High Temperatures: Scottish Oils Ltd., Central Laboratory, Report SO. M/168/40, July 16, 1940.

8/ Dyakova, M. K., Production of Liquid [illegible]l from Combustible Shales by the Method of Thermal Solution: Bull. Acad. Sci. U.R.S.S., Classe Sci. Tech., 1944, 258-274.

9/ Idem, Thermal Solution, A New Method for Obtaining Artificial Liquid Fuel: Bull. Acad. Sci. U.R.S.S., Classe Sci. Tech., No. 7-8, 1944, 498-505.

with a boiling range of 428-698 F (48 percent volatile at 572 F) and a specific gravity at 68 F of 0.933. When a mixture of equal weights of shale and solvent was processed at 797-806 F for 20 minutes at a pressure of 470-500 psi, the following yields were obtained, based on original organic content of the shale: gasoline 39.3 percent, diesel fuel 2.9 percent, casinghead gasoline (recovered by absorption from the gas) 0.6 percent, pitch 30.2 percent, gas 8.8 percent, water (pyrogenic) 6.3 percent, and insoluble organic matter 8.4 percent. The removal of 91.7 percent of the organic material of the shale was obtained. The fractions boiling below 428 F were removed from the mixture, the residue was then filtered on a filter press and the spent shale washed by decantation with shale naphtha. The pilot plant consisted of a 100-liter mixing tank, gear pumps, high-pressure paste pumps, a heating coil made from 165 feet of about 0.4-inch ID pipe, a reaction chamber of 8.6-liter capacity and equipped with a mechanical stirrer, a throttle valve, condenser, and product receiver.

The earliest American thermal solution patents were obtained by H. D. Ryan[10] [11] in 1920 and 1928. Ryan proposed to fine-grind oil shale in a 1:1 mixture with heavy shale oil at a temperature of 300 to 400 F. Digestion of the shale was to be completed at 600 to 700 F at atmospheric pressure. The temperature of about 700 F was supposed to be high enough to effect conversion of the kerogen to soluble material but to be not so high as to volatilize too much of the solvent. However, tests made by the Canadian Department of Mines on New Brunswick oil shale, reported by A. A. Swinnerton[12], pointed out the failure of this process when applied to New Brunswick oil shales. These shales require higher temperatures, in the order of 750 F, to effect fairly complete conversion of kerogen in reasonable lengths of time, and are therefore similar to Colorado oil shales. Ryan's process was found to be inoperable at 750 F because of the excessive volatilization and cracking of the solvent that took place. Patents were granted in 1923 to D. T. Day[13] for a process whereby oil shale, crushed to minus 2-inch, was digested in a bath of crude shale oil at temperatures of 550 to 700 F. While the process was supposed to operate at either atmospheric, subatmospheric or superatmospheric pressures, the claim was made that a pressure of at least 70 psi resulted in a gain in efficiency. The cracking of the shale oil during this treatment was acclaimed, credit being given to the mineral

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[10] Ryan, H. D., Bituminous Material from Shale: U. S. 1,327,572, Jan. 6, 1920.

[11] Idem, Digestion of Bituminous Shale: U. S. 1,672,231, June 5, 1928.

[12] Swinnerton, A. A., Treatment of Oil Shale from New Brunswick by the Ryan Oil Digestion Process: Canadian Dept. Mines, Summary Report No. 605, 1922, pp. 210-218.

[13] Day, D. T., Apparatus for Extracting and Distilling Hydrocarbons from Oil Shale: U. S. 1,447,296, U. S. 1,447,297, Mar. 6, 1923.

matter in the shale for increasing the amount of cracking. William H. Hampton[14] [15] [16] received several patents in 1928 and 1929 for a process that is very similar to Ryan's. Hampton also proposed fine grinding of the shale at 300 to 400 F in a slurry with a heavy paraffin-base oil yielding substantially no distillate below 700 F. Digestion was to be carried out at temperatures not in excess of about 700 F; a range of 665 to 675 F was claimed as giving excellent results. The pressure was to be either atmospheric or subatmospheric. The introduction of steam, hydrogen or an inert gas into the retort was suggested. The digested mixture was to be diluted with a light oil, such as kerosine, filtered on a centrifugal filter, and washed with kerosine. The spent shale was to be dried, then retorted at 900 to 1000 F for final recovery of the bitumen. In U. S. Patent 1,707,759, Hampton suggests digestion with a kerosine fraction under a pressure not greater than 100 psi at a temperature of 500 to 700 F. In U. S. Patent 1,778,515, he points out the advantage of heating the shale rapidly, claiming that this procedure will give a materially larger yield of liquid hydrocarbons, and remarking that the extreme fineness finally attained by the mineral matter of the shale may be due to the disrupting effect of this sudden temperature rise. Alfred Fisher[17], in a U. S. Patent granted in 1937, describes a process in which finely-divided oil shale is mixed with a hydrocarbon oil, such as a crude petroleum, distillation residue, tar, pitch, or other heavy oil, preheated by passage through heater coils to 850 to 1050 F and then coked in chambers at a temperature of 900 to 1200 F with final heating to as high as 1600 F. The pressure in the preheating coils was to be 100-800 psi and in the coking chambers preferably subatmospheric.

The bibliography given at the end of this report covers the major portion of the English-language literature on the thermal solution of oil shales. A number of abstracts of foreign-language articles and patents also are included. In this discussion of thermal solution processes the attempt was made to include all references to methods of obtaining oil from oil shales in which the shale was contacted with hydrocarbon solvents either before or during its heat treatment, excluding processes specifically applicable to tar sands rather than to true oil shales. Reference to the bibliography shows a considerable number of United States and British patents on thermal solution processes. The Canadian, Australian and New Zealand patents are largely duplications of British patents. A number of German patents, mostly held by I. G. Farbenindustrie A-G, are listed The abstracted patents and articles have been grouped in accordance with the section entitled "Outline of Bibliography."

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[14] Hampton, William H., Hydrocarbons from Bituminous Shale-Like Material: U. S. 1,668,898, May 8, 1928.

[15] *Idem*, Digesting Shale With Oil and Cracking Evolved Products: U. S. 1,687,763, Oct. 16, 1928.

[16] *Idem*, Digestion and Distillation of Products from Bituminous Shale: U. S. 1,703,192, Feb. 26, 1929.

[17] Fisher, Alfred, Pyrolytic Conversion and Coking of Finely Divided Bituminous Material and Hydrocarbon Oil: U. S. 2,073,367, Mar. 9, 1937.

THERMAL SOLUTION OF OIL SHALE IN A BATCH AUTOCLAVE

The initial laboratory investigation of the thermal solution process conducted at Laramie on Green River oil shale utilized a small batch autoclave constructed of seamless steel tubing 1.5 inches ID and 26 inches long, closed at both ends by threaded plugs and equipped with an axially-located thermocouple tube, a pressure gage, and the necessary high-pressure valves. Auxiliary apparatus consisted of a thermostatically controlled, electrically heated lead bath in which the autoclave and its contents could be immersed for heating and a cold-water quenching bath in which the autoclave and its contents could be immersed upon removal from the lead bath for rapid cooling to stop the conversion reaction. A photograph of this apparatus is shown in figure 1.

Data obtained in these batch thermal solution studies are given in table 1 and compared graphically in figure 2. In this work a 41-gpt shale from DeBeque, Colorado, having an analysis of 23.3 percent organic content, 17.2 percent mineral CO_2, and 59.5 percent ash was used. It was crushed to the following approximate screen analysis and dried at 220 F: 7 percent plus 48 mesh, 18 percent 48-100 mesh, 25 percent 100-200 mesh, and 50 percent minus 200 mesh. Most of the work was done with petroleum kerosine as the solvent, but quinoline and anthracene oil were also used for comparison. The weight ratio of raw shale to solvent was varied between 1.0 and 2.0, little difference being found due to different ratios. To increase the heating rate of the charge a quantity of 0.5-inch stainless steel balls was used in the autoclave. This quantity was proportioned to the shale-solvent charge so that the latter just filled the interstices of the balls. Thus, the heating up period was lowered to 20 to 30 minutes, depending somewhat upon the maximum temperature reached.

Correlation of the data in figure 2 shows a maximum percent conversion of organic matter (to gas and benzene-soluble material) at a different temperature for each "soaking" period, when petroleum kerosine was the solvent. Thus, for a soaking period of one minute the optimum temperature is 840 F with a conversion of 86 percent and for a 60-minute period the temperature is 795 F and the corresponding conversion 87 percent. The tests were not carried to low enough temperatures for the 180-minute runs to ascertain the optimum temperature, but the maximum conversion obtained during this series of tests was 87 percent at 740 F. The optimum temperature for 60 minutes heating with quinoline was about 800 F and for anthracene oil about 770 F, and the respective conversions were 90 and 84 percent. Comparison of the results obtained from the 60-minute runs with petroleum kerosine, quinoline and anthracene oil is of interest. At 740 F, both quinoline and anthracene oil show considerably better conversion than petroleum kerosine, the difference being 13 and 17 percent, respectively. At temperatures up to the optimum of about 800 F, quinoline continues to be at least 3 percent better than kerosine, while the anthracene oil becomes progressively poorer in comparison with the other two solvents. Data obtained for various solvents such as those used in these preliminary experiments is mainly of academic interest, as it seems unlikely that the use of a solvent other than a shale-oil product can be practical for a commercial thermal solution process. However, these data have been of value in showing the small difference in solvent effect of a polar solvent (quinoline) and a non-polar solvent (petroleum kerosine). The importance of the extraction time and its dependence upon the temperature were well demonstrated. As was expected from the investigations of Maier and Zimmerley[18] and of Carlson[19], the length of heating time required to obtain a given percentage conversion decreases as the temperature is increased.

A number of batch tests were made at temperatures in the range of 860 to 950 F, using different fractions of Parry shale oil. These data, given in table 2, show that the relative stability of the three solvents, based on the final cold gas pressure, decreased in the following order: light gas oil, heavy gas oil, and residuum. The relatively large amount of cracking of the residuum is evident from the lower apparent conversion of organic matter that was obtained. Coke produced by cracking of the oil appears as unconverted shale organic matter, because of the analytical method used.

The low vapor pressure of the light gas oil in the range of 900 to 950 F, together with its greater stability, recommends the light gas oil for use as a solvent at these higher temperatures. Although the conversion rate of kerogen is so much faster in this temperature range, difficulty would be experienced in obtaining a short enough heating up period to prevent overtreatment of the shale with consequent loss of oil yield.

STUDY OF THE PROCESS WITH A SEMI-CONTINUOUS UNIT

A semi-continuous thermal solution unit was next constructed to serve as an intermediate step between the batch autoclave and a continuous semi-pilot plant. A diagrammatic sketch of this unit is given in figure 3 and a photograph in figure 4. The purpose of the apparatus was to permit the thermal solution treatment of crushed oil shale at various constant temperatures up to about 850 F under pressures up to 500 psi while maintaining a desired rate of passage of the preheated solvent through the fixed bed of shale. Better yields were expected in this apparatus than by autoclaving since the solvent and extracted shale oil would not be held at the extraction temperature for as long a period of time, thus lessening the amount of cracking and formation of fixed gases and coke.

The extraction column was constructed of a 4-foot length of 1-inch ID seamless steel tubing, with screwed plugs at both ends, a central

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[18] Maier, C. G., and Zimmerley, S. R., The Chemical Dynamics of the Transformation of the Organic Matter to Bitumen in Oil Shale: Bull. Univ. Utah 14, No. 7, 1924, pp. 62-81.

[19] Carlson, A. J., Inorganic Environment in Kerogen Transformations: Univ. Calif. Pub. Eng. 3, 1937, pp. 295-342.

thermocouple tube, and pipe connections for entrance of the preheated solvent at the bottom of the column and exit at the top. The solvent was fed from large burets to a Zenith high-pressure gear pump, thence through preheater tubes in a thermostated lead bath into the bottom of the extraction column. The lower half of the column was filled with steel washers and 1/8-inch stainless-steel balls to provide final preheating of the solvent. Crushed oil shale was charged to the upper half of the column. The apparatus was set in a controlled-temperature electric heater. The solvent was at the extraction temperature when it contacted and passed through the shale charge, removing the kerogen as the latter was converted to gas and soluble bitumen and oil. The solvent and shale oil then passed through a water-cooled heat exchanger, thence through a Grove pressure regulator from which the liquid and gas were discharged at atmospheric pressure to a liquid receiver, the gas being taken off to a gas receiver.

Preliminary runs were made with petroleum kerosine for purposes of comparison with batch autoclaving. Operation was carried out at a pressure of 400 psi since this was sufficient to maintain the solvent in the liquid phase at the operating temperatures. The oil shale used was a sample from Parachute Creek, Colorado, containing 31 percent organic matter and assaying 53 gpt. It was ground and screened to 4 to 8 mesh and dried at 220 F. A charge of 50 grams of oil shale was used for each run. The extraction was continued until the color of the solvent coming out of the column indicated essentially complete removal of extractable organic matter. The data from the series of runs using petroleum kerosine are reported in table 3 and the data from the runs using a shale-oil gas oil in table 4. In figure 5 these data are compared with the results from batch autoclaving with petroleum kerosine. An increase of 6 percent conversion was obtained with petroleum kerosine in the semi-continuous unit over that obtained in the batch autoclave. On plotting the percent conversion against temperature, a curve is obtained which is similar to the plots of the batch autoclaving data; that is, rising to a maximum at some temperature then dropping with a further increase in temperature. In the case of the semi-continuous extraction with petroleum kerosine, the optimum temperature is between 760 and 770 F. A higher maximum conversion of 95 percent was obtained when a similar series of runs was made with a Pumpherston shale-oil gas oil. For the shale-oil gas oil the optimum temperature was slightly lower than for the petroleum kerosine, being about 750 F.

Of special interest in comparing the petroleum kerosine and shale-oil gas oil runs is the relative amount of noncondensable gases formed. In the optimum temperature range of 740 to 760 F about 10 times as much gas was formed with the shale-oil solvent as with the petroleum solvent. The gas amounts to an estimated 28 percent of the organic content of the shale for the shale-oil runs and to less than 3 percent for the petroleum kerosine runs. The gas formation is due, therefore, mainly to the cracking of the solvent rather than to the decomposition of the shale organic matter.

The very complete disintegration of shale upon thermal extraction with a shale-oil solvent led to a further study along this line. Using the small batch autoclave and treating different screen size samples of shale in shale-oil solvent at 775 F for various lengths of time, qualitative notes were taken as to the degree of disintegration that occurred. The data given in table 5 show that shale particles, ranging from 14-mesh to 3/4-inch in size, are all almost completely disintegrated in one hour at 775 F and are all completely broken down after a 2-hour extraction. The rate of disintegration seems about the same for all sizes of shale tested. This physical change appears to accompany the conversion of the kerogen to soluble material. The occurrence of a rubbery state prior to disintegration is similar to that observed by other investigators.

Another series of tests was made, using samples of 11, 27, and 53-gpt shale, each crushed and screened to $\frac{1}{4}$-inch to $\frac{1}{2}$-inch and treated in the same manner as in the previous tests. The data are given in table 6. Although the 27 and 53-gpt shales acted in a similar fashion to the samples previously tested, the 11-gpt shale, while becoming more easily split into laminations, did not break down into fine particles. Larger pieces of shale of about the same grades were treated in a larger autoclave with the same results. Digestion of one-kilogram pieces of 27 and 53-gpt shale with shale oil at 790 F and 500 psi effected disintegration within 2 to 4 hours. Under similar treatment the 11-gpt shale retained its shape but became more easily split into laminations.

For further study of the disintegrating effect of shale-oil upon medium and rich grades of shale a larger semi-continuous thermal solution unit was constructed. The extraction column was 2.5 inches ID and 45 inches inside length, constructed similar to the previous unit, with similar arrangement of auxiliary apparatus. The major change was to carry out all the preheating of the solvent in the bottom half of the column, thus decreasing the retention time of the solvent. A diagrammatic sketch of the new apparatus is shown in figure 6.

Lumps of shale as large as would fit into the column were used in the first series of runs. These were approximately 2 inches by 2 inches by 4 inches in size. Conditions of temperature, pressure and solvent pumping rate were maintained as nearly constant as possible for these runs, being respectively 800 F, 300 psi and 30 cc per minute. Three different shale-oil solvents were used, each being a fraction or combination of fractions from Parry shale oil. The light gas oil was that fractionated between 380 F at 585 mm Hg and 445 F at 2 mm Hg; the heavy gas oil was the cut taken after the light gas oil and up to the cracking point, which was about 650-700 F at 2 mm Hg. A mixture was made of one-third heavy gas oil and two-thirds distillation residuum for use as the third solvent. For all the runs, approximately 60 minutes was required to bring the shale charge up to the operating temperature of 800 F after placing the column in the heater and filling it with the solvent under pressure. When 800 F was reached, solvent pumping was begun and containued for various lengths of time. After this period, the pumping was stopped, the pressure released, and the column removed from the heater. Analyses of the raw and spent shales were used to calculate percentage conversion of kerogen to gas and benzene-soluble oil. These data are given in tables 7 and 8.

Runs 34 to 38, in which the three solvents were pumped through the shale charge for 45 to 50 minutes, show that the heavy gas oil and residuum mixture gave somewhat better results than the other two solvents. With a 63-minute heating period and a 15-minute pumping period, a maximum of 85 percent conversion of the organic matter was obtained. These results are somewhat uncertain, due to the extreme range in quality of different pieces of shale and to the difficulty of obtaining a good representative sample from large pieces. This shale, coming from Bed B of the Anvil Points mine, appeared to vary in grade from 15 to 50 gpt. The apparent assay value was determined on each piece of shale by weighing in water and in air and using a specific gravity versus assay value correlation chart. The main purpose of this portion of the investigation was accomplished, since it was demonstrated that oil shale did not have to be crushed to sizes any smaller than about 2 inches to be extractable by thermal solution. At the same time the poorest grade of shale that would disintegrate during treatment with shale oil was found to be about 20 gpt.

Further semi-continuous extraction work was carried out with 26-gpt shale crushed to minus $\frac{1}{2}$-inch so that more representative shale samples could be obtained for analysis. A number of runs were made with different solvents at 300 psi and 760 or 800 F. Table 9 gives the operating conditions for each run and the percentage conversion of organic matter. The best conversion, 81 percent, was obtained with Parry shale-oil heavy gas oil and with the shale held at 760 F for 60 minutes. The runs made at 800 F all gave somewhat lower apparent percentage conversion of organic matter, probably because of too long a heating period which resulted in excessive coke formation from the oil.

An attempt was made to show whether the assumption was true that the low apparent conversion of organic matter was due largely to the formation of coke from cracking of the solvent oil. In separate runs at 300 psi and approximately 800 F, raw shale, spent shale, and a fine gravel were charged to the semi-continuous unit. The solvents used were petroleum kerosine and three shale oils. The latter were a light gas oil, a heavy gas oil, and a mixture of one-third heavy gas oil and two-thirds residuum. Table 10 gives the resulting data for coke deposition on the solids and also for naphtha formation. The values of coke deposition do not show necessarily the total amount of coke formed since part was probably carried out of the reactor in the oil stream. However, run 56 with light gas oil and spent shale, shows that a considerable amount of coke may be formed. The 5.3 percent coke, based on the weight of the spent shale charge in the reactor, may be calculated to an organic matter basis, assuming that the reactor had been charged with a 26-gpt raw shale. This results in a coke equivalent of approximately 29 percent of the organic matter. Thus, an explanation may be given for the exceedingly low apparent conversion of organic matter that was obtained from most of the runs given in table 9. The naphtha production during the pumping period may be used as a measure of the relative amounts of cracking obtained in the different runs. As compared to the gravel, the spent shale exerted no great catalytic cracking effect on any of the solvents. Also, about the same amount of cracking occurred with the different shale oils. Of particular interest is the approximately three-fold production of naphtha from the shale oils over that from the petroleum kerosine. While the above data are of a more qualitative than quantitative nature, they serve to demonstrate that the maximum conversion of kerogen to gas and benzene-soluble material by thermal solution can be obtained only by careful control of operating conditions so as to keep coke formation at a minimum.

INVESTIGATIONS WITH A CONTINUOUS UNIT

As a step toward more nearly simulating probable commercial-type equipment and mode of operation, a continuous thermal solution unit was next designed and constructed. Figure 7 shows a drawing of the apparatus and figure 8, a wiring diagram. A slurry of shale oil and minus 65-mesh oil shale was mixed thoroughly, then pumped by means of a Hills-McCanna high-pressure pump through the reactor, thence through a water-cooled heat exchanger into a pressure receiver. The gas passed through a brine-cooled condenser and was released by means of a Grove pressure regulator. The data given in table 11 and figure 9 were obtained by treatment of a 27-gpt shale in a 1.15 weight ratio of shale and shale-oil gas oil. A pressure of 300 psi was maintained on the apparatus and runs were made at the temperatures, 750, 780, 810, and 850 F. To obtain a measure of the affect of retention time upon kerogen conversion the batches of slurry were recycled several times at the same operating temperature. A maximum conversion to gas and benzene-soluble oil of 85 percent of the organic matter was obtained by a retention time of 26 minutes at 810 F and also by a retention time of 10 minutes at 850 F. These times do not include the heating-up periods. Figure 9 shows that the maximum conversion is about the same at the various temperatures, but the reaction rate increases rapidly with increasing temperature.

While the 85 percent conversion to oil and gas compares favorably with the average 80 percent by Fischer assay, the net oil yield is probably considerably lower than that obtainable by Fischer assay, due to the formation of gas from cracking of the solvent. The solvent that is lost in the process by being cracked to gas must be replaced by newly produced oil, thus lowering the net oil yield. To determine this value, a measure of the total quantity of gas produced is necessary. Because gas measurements for these runs were of uncertain accuracy, owing to the necessity of prepressurizing the apparatus with carbon dioxide or nitrogen, an estimation of gas production for run 6 was made in the manner shown in table 12.

Based on the composition of the raw shale and spent shale slurries the gas produced was calculated to be equivalent to 23 percent of the of the shale organic matter. This value is comparable to the 19 percent calculated on the basis of the weight of gas collected. For this run the conversion to oil and gas was only 75 percent, apparently due to insufficient processing time, so the net yield of oil is about 55 percent of the shale organic matter. However, the quantity of 400 F end point naphtha produced during the run was 85 percent of the shale organic matter, which is 30 percent more than the net oil yield. Thus, considerably more oil was cracked to gas and naphtha than was produced from the shale.

As the solvent oil becomes somewhat more resistant to cracking upon recycling, the following series of runs was made to obtain a measure of this refractoriness. A sample of shale-oil light gas oil was passed through the continuous thermal solution unit five times at 850 F and 300 psi. The total retention time in the unit, based on the cold specific volume of the oil, was 10 minutes, with 7 to 8 minutes at the maximum temperatures. After each cracking cycle, the product was fractionated into naphtha, light gas oil and polymer (material heavier than the light gas oil). The material balances, given in table 13 for each cycle, show that the light gas oil becomes considerably more refractory with increased cracking treatment. However, even the loss of 8.8 percent of this fraction in the last cycle is an important quantity when calculated to a shale organic matter basis. Insufficient oil in the light gas oil range would be produced from the shale to maintain the necessary supply of solvent. Although this low boiling and low viscosity solvent would be desirable to use, a broader cut is shown to be necessary. In carrying this study further, a mixture of the light and heavy gas oil from N-T-U crude oil was cracked in 7 passes through the thermal solution unit under conditions similar to those used for the light gas oil. Similarly, also, the product from each cycle was fractionated into naphtha, recycle stock, and residuum. The products from the seventh cycle, given as weight percent of the charge to the cycle, are 1.0 percent gas, 5.7 percent naphtha, 90.8 percent recycle stock, and 2.5 percent residuum and coke. For normal thermal solution operations, and calculated to a shale organic matter basis, these products would amount to about 6 percent gas, 34 percent naphtha, and 15 percent residuum and coke. Thus, the loss of solvent still amounts to a large portion of the oil that would be produced from shale by thermal solution.

Four final runs with an oil-shale slurry were made in the continuous unit. For these runs a change was made in the product receivers so that the products from the start and end of the run could be kept separate from the product obtained during the middle part of the run when conditions were stable and uniform. Apparently, due to this change, the percentage conversion of the shale organic matter to gas and benzene-soluble material shown in table 14 was 6 to 11 percent higher than previously obtained. With the exception of the solvent used, the operating conditions were the same for the 4 runs. Raw shale RRS-48-329 containing 14.2 percent organic matter and ground to minus 65 mesh was mixed with the solvent oil in a weight ratio of

1.15. Based on its specific volume at room temperature, the slurry was retained in the reactor for 10 minutes, the operating temperature being 850 F and the pressure 300 psi. For runs 9, 11, and 12, the solvent was the distillable portion of N-T-U shale oil with the naphtha removed. The solvent used in run 10 was the distillable product with the naphtha removed, resulting from the seven-cycle thermal cracking of N-T-U shale oil. No apparent effect in percentage conversion is noted due to the use of the more refractory solvent. The average for the four runs, 93 percent net yield of gas and benzene-soluble material from the shale organic matter, appears to be a good representative value for the thermal solution process.

Analyses were made of the charge and product materials for runs 9 to 12, the respective compositions being given in table 15. Analysis of the product slurry was quite difficult and therefore is subject to some error. The procedure followed was to distill the naphtha and a portion of the heavier oil from the slurry, then to wash the remaining benzene-soluble material out of the spent shale. The benzene was stripped off this extract and a microdistillation was made on the residue to determine the proportion of solvent oil and nondistillable oil. The naphtha was redistilled to the correct end point, and the residue was added to the solvent oil. The benzene-extracted spent shale was analyzed by the usual method. From the data given in table 15, the yield of organic products was calculated and is shown in table 16. The yields are averaged for runs 3, 11, and 12, in which an uncracked solvent oil was used, and are compared with the yields for run 10, in which the more highly cracked and refractory solvent was used. Less than two-thirds as much gas and one-third as much naphtha were produced by run 10 as compared to the average of the other three runs. However, the cracked solvent used for run 10 appeared to be more readily polymerized, as evidenced by the greater amount of nondistillable oil produced. The average total oil yield for runs 9, 11, and 13, was 71 percent of the shale organic matter, and the yield for run 10 was 81 percent. These results, particularly the latter, compare favorably with the average oil yield by Fischer assay, which is about 68 percent. The composition of the gas produced from these four runs is given in table 17. The main constituents are methane, ethane, hydrogen, and carbon dioxide.

The preceding data show the necessity of carrying out the thermal solution process under operating conditions that will reduce cracking and polymerization to a minimum. A reduction in the yield of gas would be desirable, particularly as it is low in unsaturates that might be polymerized to liquid products. The most important problem, however, is reduction or complete prevention of polymerization of the solvent so that a sufficient quantity of a relatively light oil may be recycled. The only apparent method of accomplishing this is by hydrogenation during the thermal solution treatment of the oil shale. The hydrogenation studies that were undertaken as a result of this conclusion are described in the following section of this report.

BATCH THERMAL SOLUTION WITH HYDROGENATION

A preliminary study was planned for the use of hydrogenation concurrent with the thermal solution treatment of oil shale in the expectation that polymerization of the solvent oil could be prevented. Other possible advantages of the use of hydrogen were a better quality product and reduced gas production.

An American Instrument Company 4-3/8 inch series superpressure shaking mechanism, equipped with a stainless steel reaction vessel, was used in this work. It was set up inside the small stall shown in figure 10. The walls of the stall were 1/4-inch steel plate, 10 feet high, bolted together and bolted to the building, floor, and walls. The doorway was shielded by another steel wall. An overhead trolley was located over the hydrogenation unit for easier handling of the reaction vessel and a control panel was constructed of $\frac{1}{4}$-inch steel plate installed outside the barricade. This panel may be partly seen in the photograph of figure 10, a complete view being shown in figure 11. A Tagliabue Celectray temperature controller, Brown Electronik temperature recorder, and various ammeters, variacs, and switches were all mounted at the right end of the panel. On the left end, nearer to the hydrogenation unit, the gas control manifold was mounted. This consisted of the various pressure gauges and valves, shown in the diagrammatic sketch of figure 12, which were used in pressurizing and blowing down the reaction vessel. The gauges had a 5,000-psi range, and were equipped with stainless steel Bourdon tubes and fittings and with safety backs. They were set in the panel above the head level of the operator for safety, in case of bursting and breakage of the glass face. The valves and tubing connections were of stainless steel, rated at 25,000 psi operating pressure. Except on the gauge lines, all valves were arranged in pairs to insure against leakage. Connecting tubing was all stainless steel, 1/4-inch OD by 3/32-inch ID, and having a yield strength of approximately 26,000 psi. The manifold was ridigly fastened to brackets welded to the back of the panel, so all the protruded through the panel were the gauges and the valve handles. For some of the studies a 2-cubic foot stainless steel gas holder (shown mounted under the panel) was evacuated and used as a gas receiver. The manometer mounted on the left end of the panel was used to measure the pressure in this receiver.

Because of its availability and lower cost, helium was used as a flushing gas to remove the air from the system. A further advantage of helium, when operations are such that some of it enters the gas sample, is its ease of determination by the mass spectrometer and calculation out of the gas analysis. Hydrogen was available only in the standard commercial 1,800 psi cylinders. When the cycinder pressure became too low for final pressurizing of the reaction vessel, the remaining hydrogen was used for flushing the apparatus and for partial pressurizing. To provide hydrogen at a pressure greater than 1,800 psi, the unit, shown in figure 11 below the left end of the control panel, was constructed. A spare 4-3/8 inch reaction vessel served as a high-pressure gas holder. A 5-ton hydraulic truck jack was converted to a hand-operated oil pump. Starting with the gas holder full of hydrogen at the maximum cylinder pressure, a light lubricating oil was pumped into it from a reservoir until the desired pressure of as much as 4,500 psi was obtained. The oil reservoir was equipped with a gauge to provide means of determining the quantity of oil pumped into the gas holder.

Later phases of the hydrogenation study utilized an American Instrument Company micro reaction vessel. This vessel was constructed of type 347 stainless steel and had a rated operating pressure of 6,000 psi at 800 F. Its capacity, without liner, was 183 cc. The photograph of figure 13 shows this vessel as it was equipped for use in studies requiring fairly rapid heating and cooling of the vessel and contents. The relatively low heat capacity of the micro reactor made feasible its rapid change of temperature. The heater jacket of the 4-3/8 inch series shaking mechanism was fitted with a carbon steel liner, bored to receive the micro reactor. The reactor was connected to the control panel in the position shown in figure 13 only for pressurizing with hydrogen and for discharging the gaseous products. In starting a run, the heater was brought up to the desired temperature, the cover plate removed, the reactor inserted and bolted in place, and the shaker started. At the end of the run, the shaker was stopped, the heater raised to a vertical position, and the retaining bolts removed. Operating a rope block from the outside of the barricade, the reaction vessel was removed from the heater and lowered into a drum of lubricating oil for quenching. A pump kept the oil circulating in the drum during this process. Runs were made without trouble up to maximum operating conditions of 4,400 psi and 875 F, followed by quenching. As a check on the condition of the reaction vessel, the outside diameter was periodically micrometered at several specific points and occasional hydrostatic tests were made. The micrometer measurements showed no expansion of the vessel's walls during the approximately 40 runs that were made in the above manner.

The initial hydrogenation studies were carried out in the 4-3/8 inch series reaction vessel, equipped with a stainless steel liner having a capacity of 2,080 cc. The first series of tests were 6 runs made at maximum temperatures ranging from 750 to 843 F. Oil shale RRS-48-108, containing 15.2 percent organic matter and ground to minus 65 mesh, was mixed in a weight ratio of 1.15 with N-T-U shale-oil gas oil RRS-48-105. About 750 cc of this slurry was charged to the reactor for each run. After flushing the vessel three times with helium at 500 psi and three times with hydrogen at 500 psi, it was pressurized with hydrogen, while still at room temperature, to 2,000 psi. The heat was then turned on full and the reactor was heated to the maximum temperature as rapidly as possible, being shaken during the entire period. With this unit the heating and cooling rates are quite slow, 65 minutes being required to heat from 650 F to 750 F and to cool back to 650 F again, and 110 minutes for the 650-843-650 F cycle. The temperature of 650 F was selected for this comparison because it appeared to be the point near which hydrogenation commenced.

The heating and cooling curves for these runs are shown in figure 14. The heat was turned off before the maximum temperature was reached, due to the temperature lag in the heater and reactor walls, and the unit was allowed to cool back to room temperature overnight before being discharged. The results, given in table 18, show that increased percentages of organic matter were converted to gas and benzene-soluble material with increasing temperature (and reaction time) up to the maximum of 100 percent, attained with a temperature of 830 F. In comparison, the conversion obtained in the continuous thermal solution unit, without hydrogenation, averaged 93 percent. The gas from these hydrogenation runs was passed through an acetone and dry ice trap, a caustic scrubber which removed the H_2S and some of the CO_2, and a wet test meter, and was finally collected over water in a gas holder. Mass spectrometer analyses of the gas samples, calculated to a hydrogen-free basis, are given in table 19. The gas obtained from hydrogenation of the solvent oil by itself, at a maximum temperature of 775 F, shows no great difference in the proportion of the various hydrocarbons. The consumption of hydrogen by the shale was calculated for each run, assuming the solvent oil and the organic matter of the shale to have absorbed equal weight percentages of hydrogen. The consumption for the two runs which gave 100 percent conversion of the organic matter was estimated to be 750 to 800 std cu ft hydrogen per ton of shale or 1.3 weight percent of the shale organic matter.

To show the effect of a hydrogen atmosphere during thermal solution at high pressures, the following two series of tests were made. In both cases the contents of the reactor were heated to a maximum temperature of 837 to 843 F and held above 650 F for 108 to 113 minutes. The data are given in table 20. When hydrogen was used, the percentage conversion of shale organic matter to gas and benzene-soluble products increased from 75 to 100 percent as the cold initial hydrogen pressure was raised from 500 to 2,005 psi. However, with helium, the maximum conversion obtained was only 63 percent, for the run starting with a cold initial helium pressure of 1,200 psi. The value of the hydrogen in the prevention of coke formation and, to a certain extent, in the reduction of gas formation is thus demonstrated. The gas production, as weight percent of the shale organic matter, was quite uniform for each series of tests, ranging from 35 to 43 percent for the hydrogen runs and from 46 to 49 percent for the helium runs. Compared with the average gas yield of 21 percent that was reported in table 16 for continuous thermal solution operations, even the hydrogenations runs produced an excessive amount of gas. No doubt this is due to the lengthy heating period required by the equipment used for these tests.

To solve the problem of obtaining rapid heating and cooling of the reaction mass, the previously described micro reaction vessel was purchased and used in further batch hydrogenation studies. With this unit, heating from room temperature to 825 F could be attained in 15 to 20 minutes and cooling back to 650 F in 2 to 3 minutes was possible by quenching in the oil bath. The first series of tests made with the micro reactor was a study of the effect of hydrogen pressure and of boiling range of solvent upon the percentage conversion of shale organic matter. The results are given in table 21. Previous work had indicated that a shale-oil solvent in the kerosine and light gas oil distillation range was not as effective in hydrogenation of shale as was a higher-boiling oil. As verification of this factor, tests were made with three fractions of a previously non-catalytically hydrogenated N-T-U shale oil. The boiling ranges were 446 to 530 F at 760 mm Hg for the light fraction, 530 to 608 F at 760 mm Hg for the medium oil, and 608 F and 760 mm Hg to 490 F at 1 mm Hg for the heavy fraction. The light oil gave a consistently lower conversion than the two heavier oils, the difference amounting to as much as 11 percent for the runs at 1,000 psi initial pressure. The probable explanation is that the light oil is a poorer hydrogen carrier than the heavier fractions. For each particular solvent higher conversions were obtained at the lower hydrogen pressures. The optimum results were 95 to 97 percent conversion of shale organic matter with both medium and heavy oil and at 500 and 1,000 psi cold initial hydrogen pressure. No explanation is apparent for the low conversions at 2,000 psi initial pressure compared to the 100 percent conversion obtained at this pressure in the larger reactor. The results of runs 56, 57, and 58 show definitely the need for agitation of the slurry during the hydrogenation process. Mass spectrometer analyses of the gas sample collected from each run were calculated to a hydrogen-free basis and are reported in table 22. Due to the small volume of gas produced, its collection and storage without contacting with water was feasible. This procedure was carried out by evacuating a 2-cubic foot stainless steel gas holder and bleeding in the product gas from the reactor through an acetone and dry ice trap. The volume of gas collected was calculated from its absolute pressure in the holder. The percentages of the various hydrocarbons and of hydrogen sulfide were quite constant for all of the runs during which the reactor was shaken. The lower carbon dioxide content of the gas and higher carbon monoxide content at the higher hydrogen pressures apparently is due to the reduction of the carbon dioxide to the monoxide. Of considerable interest, particularly with respect to other studies now being made on the constitution of gases from shale retorting, is the zero to one percent carbon monoxide in the gas from runs 56 to 58 in which very little hydrogenation took place. These analyses serve to indicate that the carbon monoxide in retort gases is due probably to reduction of the dioxide and is not a direct product of pyrolysis of the shale.

Having ascertained the conditions that would give a high conversion of shale organic matter, a series of ten runs was made in the micro reactor under constant conditions to prepare sufficient hydrogenated slurry for analysis and determination of distillable oil yield. Shale RRS-48-329, containing 14.2 percent organic matter, was mixed in a 1.15 weight ratio with a solvent oil consisting of equal weights of the medium and heavy oils used in the preceding tests. The cold initial hydrogen pressure was 500 psi and the maximum operating pressure averaged 1,200 psi. A period of 15 to 20 minutes was taken to reach the average maximum temperature of 862 F, which was held for an additional 15 to 20 minutes, then followed by a quench in the oil bath. A conversion of 93 percent organic matter was obtained. Of this quantity, approximately 11 percent was gas which separated from the slurry at room temperature and about 20 inches Hg vacuum, 60 percent was nondistillable oil as determined by micro distillation at 2 mm Hg to the cracking temperature, and the remaining 22 percent was distillable oil and dissolved gas. Compared to the continuous thermal solution results, hydrogenation effected a reduction in yield of nondistillable oil amounting to about 40 percent of the shale organic matter.

As the quantity of nondistillable oil produced was still excessive, a number of tests were made in an attempt to find more favorable operating conditions. In all of these runs the cold initial hydrogen pressure was 500 psi. The resulting operating pressures of 1,100 psi and higher were believed to be the maximum that would be economically feasible for this process, so further studies at higher pressures were not made. Reaction temperatures ranged from 753 to 922 F and retention times at these temperatures ranged from 2 to 120 minutes. The data are given in table 23. The best product was obtained from run 95, in which the slurry was heated at 814 F for 60 minutes. This was one of the few runs that showed a net yield of distillable oil. However, the yield of nondistillable oil was still very high, being 66 percent of the shale organic matter. Higher temperatures and shorter heating periods did not give even as good a product as this.

The above tests showed that hydrogenation in a thermal solution medium with a cold initial hydrogen pressure of 500 psi does not yield a satisfactory product. Considerable difficulty would be encountered in attempting recovery of the relatively large quantity of nondistillable oil from the spent shale. Higher hydrogen pressures might produce a more volatile product, but the cost of operating at these high pressures would be excessive. Hydrogenation tests with an added catalyst were not made. On the basis of some catalytic hydrogenation work that had been carried out on shale oils, the quantity and cost of the catalyst that would probably be required would necessitate its recovery from the spent shale. This would be difficult, if not impossible.

SEPARATION OF OIL AND SPENT SHALE

A major problem of the thermal solution process is the economical recovery of the solvent and product oils from the spent shale slurry. Three general methods which may be used have been partially tried out in the laboratory. These are: first, flashing the oil off the hot slurry upon release of the pressure after thermal solution treatment; second, filtering the oil from the spent shale, washing the latter with a light oil, and then stripping the solvent from the spent shale by heating or steaming; and third, filtering the slurry and completing separation by stripping the spent shale with superheated steam.

Separation of the oil and spent shale by flash vaporization of the oil was attempted at two different times. The first experiment was made during run 44 in the semi-continuous unit, the data for which are given in tables 7 and 8. After pumping a heavy solvent oil, consisting of 1/3 shale-oil gas oil and 2/3 residuum, through the shale bed at 800 F for 17 minutes, the pressure was released and the shale held at 800 F for an additional hour. In comparison with run 41, which was made under similar conditions except for the additional heating after release of pressure, a 21 percent decrease in yield of gas and benzene-soluble material was noted for run 44. This was due to coke formation from the oil that failed to vaporize at 800 F. In addition, the spent shale was still impregnated with 12 percent of benzene-soluble material so that a net removal of only 4 percent of the shale organic matter had been effected by the combined thermal solution and flashing treatment.

As the preceding test had been made with a heavy solvent, the procedure was tried again with a shale-oil kerosine solvent, used in connection with the hydrogenation studies. The data in table 24 show the comparative results obtained with and without flash vaporization of the oil, after hydrogenation of an oil shale and shale-oil kerosine slurry in the large batch reactor. Two runs were made in which the pressure was released while the reactor was maintained at the run temperature of 851 F, resulting in 65 and 74 percent removal of organic matter, respectively. Benzene extraction of the spent shale showed that 83 and 82 percent organic matter, respectively, had been converted to gas and benzene-soluble material. Thus, oil equivalent to 8 percent of the shale organic matter was left on the spent shale. Whether additional oil was lost as coke is not certain, as the 4 to 5 percent lower conversion obtained for these two runs, as compared to run 34, may have been due to the shorter heating period. As pointed out in the discussion on hydrogenation, shale-oil kerosine was not a satisfactory hydrogenation solvent, heavier oils being considerable better. However, these heavier solvents would undoubtedly leave even larger quantities of unvolatilized residue on the spent shale. The separation of oil and spent shale by flash vaporization was indicated by these few experiments to be an unsatisfactory procedure.

Laboratory filtration tests showed that filtering rates for spent shale slurry are rather slow at room temperature, but considerably higher above about 200 F. The filterability of the slurry depends largely upon the type of solvent used, the degree of cracking the solvent has undergone, and the degree of conversion of the shale organic matter. A shale in which the organic matter has been converted nearly completely to gas and oil is expected to show better filtering characteristics than one which contains a relatively large amount of unconverted organic matter. After preliminary filtration and washing, some of the spent shales settled with fair rapidity in light solvents, so settling and decantation may prove feasible as part of the oil recovery process.

A series of steam stripping tests were made on a spent shale from which the volatile oil had been flash distilled at temperatures in excess of 750 F. In these experiments superheated steam was passed through a bed of the spent shale maintained at various temperatures. A one-hour treatment at 800 F was found necessary to remove only 82 of the benzene-soluble material originally present in the spent shale. The remainder of the organic matter was converted to coke. In contrast with this result, extraction of the same spent shale with shale-oil kerosine, resulted in removal of 92 to 95 percent of the benzene-soluble material.

Of the three methods of oil recovery listed in the first paragraph of this section, the washing and filtration procedure offers the best possibility. Tests additional to those described above were delayed pending further development of the thermal solution process.

ESTIMATED PROCESS COSTS

The cost of producing shale oil by the thermal solution process, without hydrogenation, has been estimated at $4.74 per barrel[20], without a return on the investment. With high-pressure hydrogenation, the cost of shale oil was roughly estimated at $6.00 per barrel.

The basis of the estimate on the process without hydrogenation was a plant designed to handle 14,000 tons per day of 30-gpt oil shale and producing a net yield of 10,520 bpd of liquid products. These products were assumed to consist of 884 bpd light ends, 4,760 bpd naphtha, 576 bpd heavy distillate, and 4,300 bpd residuum. The material balance for the process is given in table 25 and the calculation of the net yield of liquid products in table 26. Figures 15 to 17 outline the flow of materials and indicate the major items of equipment. With equipment cost figures adjusted to Spring 1947, the capital investment was estimated at $58,620,000, or about $5,600 per barrel of net daily plant capacity. The amount of working capital needed was calculated at $9,066,000. A summary of the estimated operating costs is given in table 27. Allowing $0.85 per ton of raw shale as the cost of mining, crushing to minus 2-inch, and transporting to the plant site, and an amortization rate of 10 percent, the estimated operating cost for production of shale oil was $4.74 per barrel. A 6 percent per annum return on investment adds $1.29 per barrel to the above amount, totaling $6.03 per barrel.

A rough estimate was made at a later date of the probable minimum cost of shale oil by high pressure hydrogenation of pulverized oil shale in the thermal solution process. The assumptions were made that 100 percent conversion of the organic material in the shale with an 85 percent yield of liquid products could be obtained by hydrogenation at an operating pressure of about 3000 psi and 825 F for 15 minutes. The raw material basis was the same as used in the previous cost estimate, that is, an oil shale containing 17.0 percent organic matter and a 1.5 shale to solvent weight ratio.

On the basis of 1947 construction and equipment costs the estimated total plant investment is $112,000,000 for the production of 13,600 bpd of shale oil from 14,000 tons per day of raw shale. This amounts to

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[20] Barnet, W. I., Estimated Cost of Shale Oil by the Thermal Solution Process on a 10,000 BPD Basis, Bureau of Mines Intra-Bureau Report, Laramie, Wyo., May 7, 1948.

$8,200 per daily barrel of plant capacity. The estimated cost of the oil, without allowance for profit, is $6.00 per barrel using an amortization rate of 10 percent. If the 6-2/3 percent rate, set by W. C. Schroeder for the 1948 annual report, is used, the cost of oil is reduced to $5.10 per barrel. In either case a 6 percent return on plant investment adds $1.60 per barrel to the cost.

The equipment required for a hydrogenation plant processing 14,000 tons per day of raw shale was assumed to differ from the thermal solution plant, described in the above cited cost estimate, in the following respects: the reactor system, the addition of a hydrogen preparation plant, and the use of a lower cost distillation unit. The reactor system consists of high-pressure slurry pumps, stalls, converters and heat exchangers, and gas scrubbing and recycling equipment. Costs for these items are calculated in table 28 from data given by J. A. Markovits, et al[21/], in Case II, where the operating pressure was 300 atmospheres. The basis for calculation was taken as the relative number of tons per day of slurry processed in the two proposed plants, except for the cost of the stalls, converters and exchangers. For those latter the basis was the relative converter volume required for the two processes. The cost per unit volume of scrubbed and compressed hydrogen also was taken from the above report, the unit cost of hydrogen per ton of shale being calculated in table 29. The cost of the hydrogen plant was calculated from data by E. E. Donath[22/]. A lower cost distillation unit than that used in the thermal solution cost estimate was considered possible because only a topping process was believed necessary. Hydrogenation was assumed to prevent polymerization of the solvent to heavy nondistillable oil and also to aid in breaking down any heavy oil produced directly from the shale. Removal of the naphtha after each cycle therefore was assumed to produce an oil suitable for use as solvent.

Inspection of the equipment cost summary given in the latter part of table 28 shows that, as also in the thermal solution cost estimate, the oil recovery and distillation system constitutes a considerable proportion of the total plant cost. This further emphasizes the problem of handling, in a thermal solution process, a slurry containing a large proportion of mineral matter. In this connection, a point relating to the technical feasibility of the hydrogenation process should be mentioned. According to present information, a slurry containing more than about 20 percent of mineral matter cannot be satisfactorily discharged from a pressure vessel operating at about 3000 psi. The process on which the above shale hydrogenation costs are based requires the handling of a slurry containing at least 50 percent solids. Increasing the ratio of solvent

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[21/] Markovits, J. A., Skinner, L. C., Donath, E. E., and Hirst, L. L., Preliminary Estimate on Liquefaction of Utah Coal for Fuel, Bureau of Mines, Louisiana, Mo., May 30, 1947.

[22/] Donath, E. E., Estimate of Plant and Production Costs of Hydrogen from Coal and Natural Gas, Bureau of Mines, Louisiana, Mo., August 1, 1947.

oil to raw shale so that the reaction product contained only 20 percent solids probably would not be feasible, owing to the greatly lessened plant capacity that would result.

The summary of estimated operating costs given in table 30 shows that the overhead expense comprises 60 percent of the total cost. Failure to properly value the various equipment items would thus have an appreciable effect on the resulting estimated cost of shale oil. However, the most optimistic oil yield and plant capacity have been used in this estimate, so the cost of oil given above is probably near the minimum figure that might be obtained.

CONCLUSIONS

The thermal solution process for the production of oil from oil shale has several advantages over retorting methods. The chief advantages are: (1) a faster rate of heat transfer to the shale and, consequently, a shorter reaction time, and (2) somewhat greater conversion of the shale organic content to oil and gas. With the shale in a pulverized form and suspended in a slurry, conversion temperatures of 800 to 900 F can be attained in a fraction of the time required to heat crushed shale. A retention time of 10 minutes at 850 F was found sufficient for maximum conversion of organic matter. The heating up period in a commercial type tube heater should be only a few minutes, therefore, the total time the shale must be kept at high temperatures is in the range of only 10 to 15 minutes. This is about the same retention time required for a fluidized solids retort operated at the same temperature, but is much less than the retention time required by an internally gas-heated retort.

Thermal solution treatment of oil shale, without hydrogenation, was found to convert about 93 percent of the shale organic matter to gas and benzene-soluble material. Hydrogenation at 500 psi cold initial hydrogen pressure gave a conversion of 97 percent. These values may be compared with an average Fischer assay conversion to gas and oil of 80 percent of the organic matter. The net oil yield obtained by thermal solution in the continuous unit, without hydrogenation, was 71 percent of the shale organic matter when ordinary shale oil was used as solvent and 81 percent when a more highly cracked and refractory shale-oil solvent was used. The best batch hydrogenation oil yield was 86 percent. The average Fischer assay oil yield is 68 percent of the shale organic matter. Thus, thermal solution without hydrogenation may give a net oil yield of 119 weight percent of Fischer assay and, with hydrogenation, a net yield of as much as 126 weight percent of Fischer assay.

Unfortunately, there are several disadvantages that overbalance the advantages to such an extent as to make the thermal solution process, either with or without hydrogenation, appear commercially impractical. These disadvantages are: (1) the necessity for fine grinding of the shale, (2) the thermal instability of shale oil, and (3) the difficulty of separating the oil and spent shale.

The shale must be ground fine enough to remain in a pumpable suspension in the solvent oil. The extra crushing and grinding adds to the process cost. Oil shale assaying better than 15 to 20 gpt disintegrates upon thermal solution treatment; however, similar disintegration occurs with dry retorting when the shale is in motion, as in the Hayes retort and the fluidized solids retort. Several people have proposed utilizing this phenomenon, so that fine grinding would not be necessary, by heating coarsely crushed shale in an autoclave with solvent oil. Such a scheme does not take advantage of the rapid heating rate obtainable when the shale is in a slurry, and would require large and complicated pressure vessels.

Shale oil usually starts cracking at a temperature of 650 to 700 F. Thus, at the optimum thermal solution temperature of about 850 F, the cracking rate is considerable. The main problem is not the production of gas and naphtha, but the formation of polymerized material that is not distillable. For the runs in the continuous unit, without hydrogenation, the yield of nondistillable oil amounted to 100 percent and more of the shale organic material. Thus, taken altogether, more organic material was converted to gas, naphtha, and nondistillable oil than was supplied by the raw shale. Hydrogenation, with a cold initial hydrogen pressure of 500 psi, failed to reduce the polymerization as much as was desired, as the minimum yield of nondistillable oil was 63 to 67 percent of the shale organic matter.

The most feasible method for the separation of the oil from the spent shale is by dilution of the slurry with light oil, settling with counter-current decantation, and finally filtration and washing of the filter cake with naphtha. The cost of this operation would be high, as it entails much equipment and a large fractionation unit for recovery of the wash oil from the product and solvent oil. An alternative separation method, flash vaporization with or without coking of the residue, would result in excessive loss of organic matter in the spent shale.

The cost of producing shale oil was estimated for a plant processing 14,000 tons per day of a 30-gpt shale, with equipment costs based on Spring 1947 prices and with allowance of 10 percent per annum for amortization. Without hydrogenation the net cost was estimated at $4.74 per barrel, and with hydrogenation at 3000 psi the cost was $6.00 per barrel. Allowance o 6 percent return on capital investment adds $1.29 per barrel in the first case and $1.60 in the second case. The estimated plant investment is $5,600 per barrel of daily capacity, without hydrogenation, and $8,200 with hydrogenation.

Because of the above disadvantages of the process and, especially because of the high estimated operating costs, the thermal solution process is not considered as being commercially feasible.

OUTLINE OF BIBLIOGRAPHY

I. Heating the shale at a temperature high enough to effect conversion of the kerogen to soluble material, then extracting with a solvent.
(Abstracts 1 - 11)

II. Digestion of the mixture of shale and oil at approximately atmospheric pressure with:

A. Liberation of the oil as vapors.
(Abstracts 12 - 28)

B. Distillation of the oil and carbonization of the spent shale.
(Abstracts 29 - 40)

C. Refluxing of a portion of the evolved oil vapors.
(Abstracts 41 - 51)

D. Subsequent separation of the spent shale and oil by mechanical means.
(Abstracts 52 - 61)

III. Preheating the shale and/or oil separately under pressure to temperatures high enough to cause conversion of the kerogen after the shale and oil are mixed.
(Abstracts 62 - 70)

IV. Digestion of the mixed shale and oil under elevated pressure at such a temperature as to cause conversion of the kerogen, with:

A. Subsequent separation of the spent shale and oil by mechanical means.
(Abstracts 71 - 80)

B. Vaporization of the oil and subsequent carbonization of the residue.
(Abstracts 81 - 89)

C. The use of catalysts to aid the extraction, but without hydrogenation.
(Abstracts 90 - 102)

D. Hydrogenation of the mixture.
(Abstracts 103 - 131)

V. Miscellaneous processes.
(Abstracts 132 - 140)

VI. Reports of experimental investigations.
(Abstracts 141 - 158. See also abstracts 71 - 78, D'yakova, et al.)

PATENTEE, ASSIGNEE, AND AUTHOR INDEX TO BIBLIOGRAPHY[1]

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[1] Numbers refer to individual abstracts.

BIBLIOGRAPHY OF THERMAL SOLUTION PROCESSES

I. Heating the shale at a temperature high enough to effect conversion of the kerogen to soluble material, then extracting with a solvent.

1. Freeman, N.H., "Shale oil,"
Brit 248,014 (Sept 4, 1924); C A 21, 647.

Shale or other similar oil-bearing material is heated to render the oil soluble and then extracted with kerosine or other similar suitable solvents.

2. Freeman, N.H., "Process for treating shale,"
Ger 436,889 (Mar 25, 1922).

See Brit 248,014.

3. Freeman, N.H., "Oil from shales, coal, or similar oil-bearing materials,"
Brit 291,475 (Dec 1, 1926); C A 23, 1261.

The material is heated to and maintained at a predetermined critical temperature until substantially all the hydrocarbon content is soluble in a hydrocarbon oil, as described in Brit 248,014, and the oil is removed in a heated entraining agent such as superheated steam, gas or vapor. Heating to about 300 C for about 1 hour is ordinarily suitable. An apparatus and various details are described.

4. Freeman, N.H., "Treating oil-bearing shales,"
New Zealand 60,637 (June 5, 1928).

The process consists in the application of dry heat to the material to be treated, for the purpose of bringing most of its hydrocarbon content into a condition in which it is soluble in a hydrocarbon oil, and then subjecting this product to the action of a heated entraining agent for the purpose of extracting the oil from the mass. The entraining agent may be shale oil, superheated steam, oil vapor, or other gaseous medium. Apparatus consists of a conversion retort and an extracting retort, with means for isolating the extraction retort, except for means for condensing the oil products vaporized from it during operation.

5. Freeman, N.H., "Means for treating oil-bearing shales,"
Australia 13,720 (June 7, 1928).

See Brit 291,475.

6. Freeman, N.H., "Extracting oil from schist,"
Fr 656,542 (June 27, 1928); C A 23, 4338.

See Brit 291,475.

7. Freeman, N.H., "Oil shale processing,"
Can 292,280 (Aug 20, 1929).

3. A process for treating oil-bearing shale which consists of applying dry heat to the substance under treatment to such a degree as to render the oil soluble and to drive off the contained mixture without effecting distillation, and subjecting the product of the heat treatment to an operation to extract a soluble oil.

4. A process for treating an oil-bearing shale which consists of grinding the material to a fine mesh, subjecting the ground material in the form of thin layers to the action of heat to render the oil soluble, and subjecting the product of the heat treatment to an operation to extract the soluble oil.

8. Freeman, N.H., "Process of treating shales or other like oil-bearing minerals,"
Can 297,909 (Mar 4, 1930).

See New Zealand 60,637.

9. I G Farbenindustrie A-G, "Destructive hydrogenation,"
Brit 315,764 (July 17, 1928); C A 24, 1725.

Liquid of readily liquefiable products are obtained from solid distillable carbonaceous materials such as coals, oil shales or other bituminous substances by destructive hydrogenation at "mild conditions" so that the formation of benzine is substantially avoided, followed by extraction with solvents. Various details are given, including the treatment of brown coal at 450 C under 200 atm pressure with a counter-current of H_2.

10. I G Farbenindustrie A-G, "Liquid products from coal,"
Fr 678,328 (July 12, 1929); C A 24, 3632.

Liquid products are extracted from coal of various kinds, schists or other bituminous substances by first submitting the coal, etc., to a hydrogenation under such conditions of temperature and pressure that a formation of benzines is avoided, then extracting with solvents. The fractions of high boiling point are treated to obtain lubricating oils and paraffins.

11. I G Farbenindustrie A-G (assignee of M. Pier), "Treating carbonaceous materials,"
Australia 22,041 (Aug 26, 1929).

See Brit 315,764 and Fr 678,328.

II. Digestion of the mixture of shale and oil at approximately atmospheric pressure with:

A. Liberation of the oil as vapors.

12. Black, A.G., "Distillation of oil shales," Australia 19,644 (Apr 23, 1929).

A process for the generation, distillation and recovery of oil from oil shales and the like, in which the shale is reduced to small lumps and intimately mixed with tar, and is then heated in a retort to a temperature not exceeding the volatilization temperature of the tar, whereby heat is evenly distributed throughout the mass and relatively pure distillates are recovered. The tar absorbs any S present, and the spent shale and tar leave a residue which acts as a filled bitumen.

13. Esling, F., "Distilling shale, coal, etc.," Brit 339,963 (Sept 12, 1929); C A 25, 2845.

Bituminous shales, cannel coals, torbanites, etc., are distilled in admixture with petroleum or its derivatives at ordinary, reduced or slightly increased pressure, to form distillates of low S content and an uncoked pitch-like residue suitable for road-surfacing, roofing, etc. Vegetable oils, such as linseed, cottonseed, rape, olive or tung oil may be added, and the shale is preferably powdered and may be mixed with lime to aid S removal. Steam may be injected during the distillation.

14. Gage, C.H., "Apparatus for distillation of shale or other materials," U S 1,515,103 (Nov 11, 1924); C A 19, 194.

Materials to be subjected to distillation are fed downwardly through successive compartments of a digester and still, each succeeding compartment being at a higher temperature and being provided with a vapor and gas exit pipe for leading products evolved to a condenser or other recovery apparatus. The apparatus is proposed for use in the treatment of shale, cannel coal, or materials yielding turpentine, etc.

15. Gercke, M., "Apparatus for distillation of bituminous materials," U S 1,474,357 (Nov 20, 1923); C A 18, 584.

An endless piston chain conveyer passes through a tubular passage with perforated walls within a distillation chamber. An oil bath surrounds the lower portion of the passage and superheated steam is supplied above the oil bath. The apparatus is especially adapted for the distillation of coal or shale.

16. Gercke, M., "Carbonizing,"
Brit 159,246 (Oct 20, 1919).

See U S 1,474,357.

17. Gercke, M., and Albrecht, J., "Process for distilling bituminous shale,"
Ger 358,605 (Feb 22, 1919); J Soc Chem Ind 42, 137A (1923); Oil Shale, Literature and Patent Survey, The Texas Co (1948).

Oil shale is treated with a stream of heated heavy oil, and the product is distilled using superheated steam.

18. Groeling, A.E.von, "Recent processes for treatment of oil shale,"
Petroleum Z 18, 487-93, 539-45 (1922); C A 16, 4054.

A review of the Scotch and German methods of shale retorting. In the American (Hampton) digestion method the shale, after passing through a series of crushers, is mixed with a stream of heavy preheated oil in a mixing cylinder and passes thence into the digester where the first stage of the distillation takes place. The digester comprises 4 sections and the material is forced through by a screw arrangement. Final distillation is carried out in a separate chamber at approximately 870 F after the oil has been removed from the mass by centrifuging. The apparatus is fired directly. The vapors pass upward to a preheater for the digestion oil while the combustion gases travel counter to the movement of the shale in the apparatus. Colorado shale gave a yield of 87 gpt compared with 50 gpt by the Scottish process. The temperature of the digester is maintained at about 340 F. Oil obtained from the first distillation had a specific gravity of 0.807 and that from the final distillation of 0.798. It is suggested that the use of superheated steam would give better results.

19. Hampton, Wm H., "Shale processing,"
Can 280,272 (May 22, 1928).

7. The process of treating solid bitumeniferous mineral matter to obtain valuable products therefrom, which comprises digesting an intimate fluid commixture of finely divided bitumeniferous material and a finely divided base with a heavy oil, at temperatures within the approximate range of 600-700 F to liberate NH_3 and volatilize certain hydrocarbon fractions.

8. Digesting a finely ground mixture of the material and not more than 5% of its weight of caustic lime with a heavy mineral oil at approximately 680-700 F to liberate NH_3 and volatilize certain hydrocarbon oil fractions.

9. Digesting an intimate mixture of shale, or the like, and a base with an oil at temperatures sufficiently high to liberate NH_3 but not high enough to cause substantial deposition of C, and also recovering hydrocarbons from the mixture.

20. Hampton, Wm. H., "Digesting shale with oil and cracking evolved products," U S 1,687,763 (Oct 16, 1928); C A 23, 275.

Material such as bituminous shale is digested with a heavy mineral oil at temperatures of 260-370 C, steam is mixed with the evolved vapors and the mixture is subjected to cracking at higher temperatures. Products formed are fractionally condensed, and the residual digestion mixture is treated with a lighter oil, solid matter is separated from the diluted mixture and a heavy oil fraction is obtained from the residual oil which together with a heavy fraction from the products of cracking is used for digestion of additional quantities of raw bituminous material. Apparatus is described.

21. Hampton, Wm. H., "Digestion and distillation of products from bituminous shale," U S 1,703,192 (Feb 26, 1929); C A 23, 2030.

After digestion in an ammonia-liberating base, such as lime, and with a mineral oil such as "Congo" cylinder oil, at a temperature not substantially above 370 C, the volatilized products are recovered. An apparatus is described.

22. Heyl, G.E., "Distilling shale," Brit 112,997 (Feb 6, 1917); C A 12, 1250.

The yield of oil obtained by distilling shale is increased by first soaking the shale with about 10% of its volume of a liquid hydrocarbon for a period of 24 hr or longer. Distillation is carried on up to a temperature of about 220 C, and a further 10% of hydrocarbon is then added and the distillation continued up to a temperature of about 400 C.

23. Heyl, G.E., "Distilling shale, etc.," Brit 115,867 (Oct 11, 1917); C A 12, 1926.

Distillation products free from S are obtained from coal or shale by distilling the shale, etc., in a rotary still under a partial vacuum, the shale being mixed with a mineral oil, e.g., tar oil, which causes the shale oil to be distilled at a lower temperature and with metal borings to reduce the amount of S compounds formed. The vapor is freed from S by heating in one or more rotary stills in contact with metal borings. A suitable apparatus is shown.

24. Kirby, W.K., "Shale oil," U S 1,458,983 (June 19, 1923); C A 17, 2780.

A proportioned charge of finely divided oil shale and an entraining oil of high boiling point is caused to flow in a stream of restricted cross-section through a retorting zone heated sufficiently to liberate oil vapors from the shale.

25. Kovarskii, N.S., Nozdreev, V.A., and Tret'yakov, V.I., "Treating shale," Russ 46,877 (May 31, 1936); C A 33, 3579.

To bituminous shale is added 4-20% of mastic, the mixture is heated to 380-400 C, 15-20% tar distilled off, the temperature lowered to 180-200 C, more mastic is added, and the process is repeated.

26. Sociétè Lyonnaise des Eaux et de l'Eclairage, "Destructive distillation," Brit 9,730 (Jul 3, 1915); C A 11, 96.

Oils are extracted from coal, lignite, shale, boghead, bitumen, asphalt, tar, pitch, etc, by distillation at low temperature which may be 300-425 C, solvent oils or vapors being circulated during the heating which may be conducted with or without increased or reduced pressure. The solvent oils and the extracted oils are recovered in condensers, etc, the last traces being expelled from the material by a current of water vapor. The uncondensed gases may be used for heating, and the solid residue may be used for the production of gas or coke, or may be briqueted.

27. Struben, A.M.A., "Distilling carbonaceous materials," Brit 250,699 (Jan 26, 1925); C A 21, 1343.

Solid carbonaceous materials, such as torbanite, oil shale, brown coal, peat, lignite, tar sands, or wood are distilled in admixture with a liquid or fusible solid such as a heavy oil or paraffin, which boils at a temperature above the boiling point of the distillates to be obtained. An apparatus is described.

28. Struben, A.M.A., "Treatment of carbonaceous materials," Australia 26,140 (Nov 30, 1925).

See Brit 250,699.

B. Distillation of the oil and carbonization of the spent shale.

29. Chown, J.A., "Carbonizing," Brit 173,099 (Oct 9, 1920).

Carbonaceous material such as cannel coal or torbanite is soaked in a hydrocarbon oil and heated while in contact with the oil at the same time that some of the pre-soaked material is being distilled and carbonized. An upper chamber in which the soaking and preheating take place communicates with a lower chamber in which the material is carbonized. The two chambers are heated in a setting and have connections whereby the volatile compounds distilled off may be led to condensers. The treated material passes out from the lower chamber through a valve.

30. Consitt, N., Smith, J., and Cowell, R.E., "Cracking and coking coal/oil mixtures," Brit 449,619 (Dec 31, 1934).

In the distillation of coal/oil mixtures to obtain oils of low boiling point and coke, the mixture is first preconditioned by heating under complete refluxing conditions to 325 C, and the mixture thus obtained is heated rapidly under non-refluxing conditions to 600 C, the vapors evolved being removed substantially at their speed of formation. The first stage is carried out in a retort to which oil is fed from a tank and finely divided coal, peat, shale, etc, through a hatch, and which is provided with a reflux condenser and a mixer. From there the charge is fed to another retort where it is distilled to dryness.

31. Day, D.T., "Extracting hydrocarbon compounds," Brit 123,415 (Feb 27, 1918); C A 13, 1529.

Oils and other hydrocarbon products, N bases, e.g., pyridine, and the like, are extracted from shales, coal, etc, by treating the shale, etc, prior to destructive distillation with the vapors, which may be partially condensed, obtained by the distillation process. The condensation of the vapors is completed in passing through the shale, and the hot condensed liquid dissolves part of the oil, etc, from the shale, and this is separated from the solid material prior to the feeding of the material to the distillation retort.

32. Day, D.T., "Extracting hydrocarbon oil from shales and coals," U S 1,280,178 (Oct 1, 1918); C A 12, 2686.

In the continuous treatment of hydrocarbon-bearing shale or coal, the material is subjected to a destructive distillation to recover vapors after previous treatment with vaporous material produced in a similar distillation of a previously treated batch of material and containing an acid solvent such as acetic and other organic acids. The hot extracted material condenses and dissolves hydrocarbons from the freshly supplied material; the combined solvent and extracted substances are recovered in liquid form and the residue is then subjected to the destructive distillation as first mentioned for continuing the process. Apparatus is described.

33. Day, D.T., "Oils; gas," Brit 208,586 (Sept 18, 1922); See U S 1,447,297.

Oils and gas are obtained from shale or oil-bearing sand by immersing the shale in and passing it through a bath of liquid oil, cracking the oil-soaked shale, and condensing the vapor and using the condensate to replenish the bath, preferably by passing the gases and vapors direct into the oil-bath container. The operation may be conducted at reduced, normal or increased pressure, e.g., 70 psi. The temperature of the retort should be about 900-1400 F, that of the inside of the cracking tubes about 550-700 F, and that of the oil-bath chamber about 300 F.

34. Day, D.T., "Apparatus for extracting and distilling hydrocarbons from oil shale,"
U S 1,447,296 (Mar 6, 1923); U S 1,447,297; C A 17, 1713.

The apparatus is adapted for the combined extraction of oil from shale, employing both solvent treatment and distillation. U S 1,447,297 relates to immersion of shale in an oil bath, then separating the solids from the bath, subjecting them to distillation and passing the vapors thus produced into the oil bath to serve for further extraction of shale.

35. Day, R.B., (to UOP), "Treatment of hydrocarbonaceous solids,"
U S 2,406,810 (Sept 3, 1946); C A 40, 7586.

A process is described in which hydrocarbons are distilled from oil shale by direct contact with a preheated hydrocarbon gaseous product subsequently distilled from the shale. A crushed oil shale is passed downwardly as a bed through a distilling retort in countercurrent contact with upwardly passing hot hydrocarbons. To approximately the center of the retort is added a heated heavy hydrocarbon subsequently separated as a fractionator bottoms and to the lower part of the retort bed are added highly heated hydrocarbon gases produced subsequently as fractionator overhead. Vaporous material distilled from the shale is passed to a distillation column in which overhead, one sidestream, and a bottom fraction are taken. The bottoms are heated in a separate heater prior to passage into the upper retort as mentioned. High-boiling and/or residual material remaining on the shale is burned in a separate furnace for supplying heat for the indirect heat exchange of the fractionator overhead prior to its addition to the lower portion of the retort. Hot mineral matter leaving this latter furnace as fully spent shale is used in direct heat exchange with air for preheating air for supporting combustion of the retort bottoms in the gas preheat furnace. Steam is injected into the distilled shale as a separator between the retort and the gas preheat furnace to prevent mixing of the hydrocarbon vapors from the downflowing shale with preheated air in this furnace. Only residual, undistilled carbonaceous matter is intended to be burned in the preheat step. Temperatures of 750-850 F are employed in the upper portion of the retort while the lower portion is heated to 900-1100 F.

36. Fisher, A.,(to UOP), "Conversion and coking of hydrocarbon oils,"
U S 2,050,427 (Aug 11, 1936).

1. A process which comprises coking a mixture of hydrocarbon oil and solid pyrobituminous material in a coking zone, fractionating the resultant vapors to form a relatively heavy and a light fraction. The light fraction is given further cracking treatment and the heavy oils are recycled to the coking process. See Brit 413,927 by A.L. Mond, for similar apparatus for coking coal.

37. Fisher, A., (to UOP), "Conversion and coking of hydrocarbons," U S 2,098,033 (Nov 2, 1937).

1. A process for the pyrolytic conversion and coking of a charging stock mixture of finely divided carbonaceous material in hydrocarbon oil which comprises subjecting the mixture to elevated temperature conditions under non-coking conditions, introducing the heated products into a coking zone wherein the residue is coked in a relatively thin layer on a highly heated surface. The vapors are fractionated and the heavy fraction is recycled to the process.

38. Reed, V.Z., "Extraction of hydrocarbon products from shales and coals," Australia 7704 (June 18, 1918).

See U S 1,280,178, D.T. Day.

39. Reed, V.Z., (assignee of D.T. Day), "Hydrocarbon extraction," Can 188,464 (Jan 28, 1919).

See U S 1,280,178, D.T. Day.

40. Universal Oil Products Co, "Cracking and coking coal and oil mixtures," Brit 409,969 (May 10, 1934); C A 28, 6285.

Mixtures of finely-divided solid carbonaceous materials, e.g., coal, peat, lignite, oil shale and hydrocarbon oils are cracked and coked by bringing them to conversion temperature and introducing the heated products into a coking zone, where they are separated into residues and vapors which are fractionated to produce a light distillate while the residues are coked in thin layers on a highly-heated surface. Alternate arrangement of process is given. Apparatus is described.

C. Refluxing of a portion of the evolved oil vapors.

41. Crozier, R. H., "Distilling coal, shale, etc," Brit 319,224 (May 18, 1928); C A 24, 2581.

In distillation in a vertical retort, the heat contained in the vapors drawn from the various stages of the retort is used to vaporize fractions of lower boiling point and concentrated fractions of higher boiling point. Residual fractions thus concentrated are returned to the retort to be cracked in contact with the residual coke. Various details of apparatus and operation are described.

42. Day, D.T., "Hydrocarbons from shales and coals," U S 1,244,840 (Oct 30, 1917); C A 12, 220.

Shale or coal is subjected to destructive distillation and the vapors thus produced are condensed in and allowed to flow down through and exert a solvent action upon a mass of the coal or shale which is in transit to the distillation chamber. Hydrocarbon oils may thus be obtained at low cost.

43. Engler, C., "Oil shale retorting and extraction," Ger 380,331 (Sept 6, 1923); Oil Shale, Literature and Patent Survey, The Texas Co (1948).

The shale is heated to about 300 C for a short time and the hot shale is then mixed with a solvent in a vessel equipped with a reflux condenser. The solvent used may very well be the benzine already obtained from the shale.

44. Freeman, N.H., "Distilling solid carbonaceous materials," Brit 408,342 (Apr 12, 1934); C A 28, 5968.

In the extraction of liquid hydrocarbons from coal, shale, etc, the material is subjected to progressive stages of heat treatment during its passage through a series of communicating retorts and the condensates from one stage, with or without volatiles, are fed to a preceding or succeeding stage. Apparatus is described.

45. Freeman, N.H., "Liquid hydrocarbons from coal, shale, etc," U S 2,005,863 (Oct 12, 1936); C A 31, 8892.

Apparatus is described, and a process for the extraction of liquid hydrocarbons from coal, shale, and other solid and liquid hydrocarbon material which consists of feeding the raw hydrocarbon material successively into separately heated retorts each of which has a separate reflux condenser, a portion of the condensate from which is distributed to a different retort unit, and in feeding volatile gaseous hydrocarbons into each unit through a heated activating chamber containing an alkali-metal hydroxide, whereby the material in retorts is subjected to prolonged contact with hydrocarbon gas thus resulting in further extraction of volatiles.

46. Freeman, N.H., "Cracking and hydrogenating oils," Brit 468,707 (July 9, 1937); C A 32, 760.

Hydrocarbons of low boiling points are obtained by passing coal, shale or other solid carbonaceous material or heavy oils through a series of heated retorts of increasing temperature, the gases and vapors produced from each retort, or extraneous gases, being activated by passage through a heated alkali or alkaline earth hydroxide and then introduced into a preceding or succeeding retort. Condensate obtained from one retort is similarly introduced into a preceding or succeeding retort as described in Brit 408,342.

47. Macintosh, A.A., "Gas," Australia 24,713 (Jan 21, 1930); C A 26, 4162.

The products of distillation from coal, shale or lignite are subjected to a reflux condensation at a relatively high temperature and then to a condensation at a relatively low temperature. The tarry products from the first condensation and the oils from the second are returned to the retort.

48. Reed, V.Z., "Extraction of hydrocarbon products from shales and coals,"
Australia 6983 (Apr 4, 1918).

See U S 1,244,840, D.T. Day.

49. Reed, V.Z., "Extracting oils, pyridine, etc,"
Brit 119,648 (May 17, 1918); C A 13, 252.

Oils and other hydrocarbon products, N bases, e.g., pyridine and the like are extracted from shales, coal, etc, by treating the shale, etc, prior to destructive distillation with the vapors, which may be partially condensed, obtained by the distillation process, and in the presence of an acid added or obtained by distillation. The condensation of the vapors is completed in passing through the shale, and the hot condensed liquid dissolves part of the oil, etc, from the shale and this is separated from the solid material prior to the feeding of the material to the distillation retort. A suitable apparatus is described.

50. Reed, V.Z., "Hydrocarbon extraction,"
Can 185,181 (June 25, 1918); C A 13, 185; See U S 1,244,840, D.T. Day.

Shale or coal is submitted to destructive distillation in one chamber, the distillate is passed into a second chamber containing similar shale or coal to dissolve material from the shale, and the solvent and extracted matter are recovered.

51. Thompson, C.W., "Process and apparatus for recovery of hydrocarbons from shale,"
U S 1,428,458 (Sept 7, 1922).

1. A process for distillation of hydrocarbons from oil shale comprising heating the shale by external means to free gasoline and light oils, removing gasoline and light oils, then heating the shale at a higher temperature to vaporize the heavy hydrocarbons, and introducing the heavy vapors freed from said light oils and gasoline into a fresh quantity of cold shale prior to the first heat treatment.

D. Subsequent separation of the spent shale and oil by mechanical means.

52. Brown, H.D., "Process for the recovery of oil from shales,"
U S 2,431,677 (Dec 2, 1947); C A 42, 6100.

Digests pulverized shale in shale oil at 200-250 C, using not more than 3% by shale weight of anhydrous $AlCl_3$. Oil vapors boiling below process temperature are taken off. Slurry is filtered on continuous vacuum filter and the spent shale washed by repulping with gasoline and naphtha, the solvent being recovered by drying in a tunnel oven at temperature above 200 C. The $AlCl_3$ is recovered by distillation.

53. Hampton, Wm. H., "Hydrocarbons from bituminous shale-like material," U S 1,668,898 (May 8, 1928); C A 22, 2267.

Bituminous shale or similar material is digested at a temperature above 200 C with a liquid oil, while the materials are agitated, and the solid residue is separated by centrifuging. An apparatis is described.

54. Hampton, Wm. H., "Digestion of bituminous shale," U S 1,778,515 (Oct 14, 1930); C A 24, 6000.

After digestion in an oil such as "Congo cylinder oil" the finely divided material together with the oil and associated substances is centrifuged, without substantial cooling, to separate liquid from solids. Apparatus is described.

55. National Oil Machinery Co,(assignee of Shale Reduction Machinery Corp, assignee of H.D. Ryan), "Recoverying bituminous matter from shale," Can 223,205 (Aug 29, 1922), See U S 1,327,572, H.D. Ryan.

15. The process of obtaining valuable hydrocarbons from bituminous solids such as shale and the like, which comprises digesting a mixture of such a bituminous solid with a hydrocarbon liquid, the digestion being conducted at temperature high enough to effectively liquefy heavy bituminous matter contained in said solid but not high enough to effect substantial distillation of heavy bituminous matter, separating the liquid mixture of hydrocarbons from the solid residue and refining the liquid.

56. Ryan, H.D., "Extracting bitumen, etc," Brit 129,992 (July 16, 1919); C A 13, 3008.

In extracting bitumen, paraffin wax, and other constituents from shale, etc, the latter is digested with heavy oil at a temperature too low to effect destructive distillation, and the hot digest or solution is discharged into a bath of light oil in order to prevent the deposition of bitumen on cooling. The construction and operation of a suitable plant is specified.

57. Ryan, H.D., "Bituminous material from shale," U S 1,327,572 (Jan 6, 1920); C A 14, 625.

Bitumen is recovered from solids such as are found in shale by heating the finely divided raw material with heavy oil in a retort and agitating the mixture. Some light oil extracted is volatilized during the heating and the vapors are led off and condensed. The remaining products of the digestion, while still highly heated, are drawn off into a relatively large bath of light oil in which a rising current is maintained and liquid is withdrawn from the bath near its upper surface. Insoluble non-bituminous constituents are withdrawn from the bottom of the bath and heated to volatilize and recover the light oils with which they are impregnated. The liquid withdrawn from the bath is fractionally distilled and a portion of the heavier oils obtained in this distillation may be used for treatment of additional raw material. An apparatus is described.

58. Ryan, H.D., "Digestion of bituminous shale,"
U S 1,672,231 (June 5, 1928); C A 22, 2661.

Ground bituminous shale or similar material is digested with a hydrocarbon oil such as a heavy shale oil fraction at a temperature (suitably about 315-370 C) sufficiently high to liquefy the shale bitumens. Vaporization is limited to obtain a final product or digestion mixture which is fluid, and residual solids are separated from the mixture.

59. Strevens, J.L., "Oils from shales, etc,"
Brit 323,773 (Oct 6, 1928); C A 24, 3354.

Solid fuels such as torbanites or shales are ground with oil to a fine suspension to which is added an oil-soluble colloid such as soap, asphalt, or an extracted oxidation product of coal, the suspension is subjected to a cracking treatment, light products are distilled off, and the powdered fuel residuum is separated by filtration from the associated oil. Numerous details of procedure are described.

60. Strevens, J.L., "Extraction of oil from solid fuels, shales, etc,"
Australia 22,891 (Oct 7, 1929).

See Brit 323,773.

61. Struben, A.M.A., "Distilling carbonaceous materials,"
U S 1,706,468 (March 26, 1929); C A 23, 2276.

Solid carbonaceous material to be distilled, such as torbanite, oil shales, coal, brown coal, peat, lignite or tar sands, in comminuted form, is suspended in a hydrocarbon material such as a heavy oil or paraffin maintained in bulk in a enlarged zone and having a higher boiling point than that of the desired distillate of the solid carbonaceous material, heat is supplied directly to this zone and distillation is effected at as high a temperature as possible without distilling the bulk of the carrier material; the suspension is agitated, the distillate is removed, and the solid carbonaceous material remaining undistilled together with the hydrocarbon carrier allowed to settle in a separate zone, so that the carrier may be further used in the process. An apparatus is described.

III. Preheating the shale and/or oil separately under pressure to temperatures high enough to cause conversion of the kerogen after the shale and oil are mixed.

62. Carter, R., "Art of recovering blended fuels,"
U S 1,978,984 (Oct 30, 1934).

Solid hydrocarbons are contacted with a liquid hydrocarbon, which is previously heated under pressure to cracking temperature, and held under vacuum for the formation and removal of vapors, which latter are condensed under super-atmospheric pressure.

63. Dubbs, C.P., (to UOP), "Process for distilling coals,"
U S 1,868,732 (July 26, 1932).

1. In the art of recovering values from hydrocarbon sources, raising hydrocarbon liquids to a cracking temperature, in then bringing the heated liquid into the presence of hydrocarbon solids capable of destructive distillation and transferring heat from the hydrocarbon liquid and its vapors to the solids to cause distillation of the volatiles contained therein.

64. Egloff, G., (to UOP), "Distilling bituminous material such as tar, asphalt, shale, etc,"
U S 1,868,733 (July 26, 1932); U S 1,868,734; U S 1,868,735; U S 1,868,736; C A 26, 5405.

A mass of solid bituminous material is charged into an enlarged chamber, and a zone of combustion is maintained in the mass; a separate supply of hydrocarbon liquid material, such as oil, is heated under superatmospheric pressure to about 425 C and then passed into the combustion zone in the mass of bituminous material, and regulated quantities of air are continuously supplied to this combustion zone to effect controlled combustion; a sub-atmospheric pressure is maintained on the bituminous material and values are recovered from the vapors evolved. Apparatus is described. U S 1,868,734 relates to a generally similar process in which steam is also introduced into the material, as does also U S 1,868,735 according to which a temperature is maintained sufficiently high to break down the steam and produce substantial quantities of fixed hydrocarbon gases. U S 1,868,736 broadly claims processes involving charging a chamber with hydrocarbon material capable of undergoing destructive distillation, such as coal, and effecting its distillation by introducing hydrocarbon liquids heated to cracking temperatures. These patents describe apparatus.

65. Egloff, G., (to UOP), "Process of destructively distilling bitumen," U S 1,868,738 (July 26, 1932).

1. A continuous process for producing a low boiling point distillate from hydrocarbon liquids and solids capable of destructive distillation, comprises keeping a mass of the solids at cracking conditions of temperature and superatmospheric pressure in a chamber, separately heating a hydrocarbon liquid to cracking temperature under superatmospheric pressure and passing the liquid into the mass of solids to dissolve the carbonaceous material. The extract is kept at high temperatures and subjected to vacuum to vaporize the constituents, after removal from the chamber.

66. Egloff, G., (to UOP), "Cracking process," U S 1,934,847 (Nov 14, 1933).

1. A process for treating hydrocarbon liquids and solids to produce low boiling point liquids, comprising passing vapors from a chamber in which a hydrocarbon liquid is kept under cracking conditions of temperature and pressure into another chamber filled with the hydrocarbon solid. The vapors distill and dissolve parts of the solid. The heavy liquids from the fractional condensation of the vapors are returned to the oil cracking chamber.

67. Egloff, G., (to UOP), "Cracking bituminous material," Can 341,368 (May 1, 1934); C A 28, 4868.

One or more chambers are charged with a bituminous material such as coal, which may be heated to 800-900 F, and then petroleum or fuel oil heated to 950 F under 500 psi is delivered to the chamber. The hot oil and vapors in chamber act on the coal to dissolve or distill out some of the hydrocarbons, and also to crack some of them, depending on pressure and temperature in chamber. These chambers may be subjected to a vapor press of 200 psi or more with temperature of 850 F in vapor lines leading to a dephlegmator. The temperature of latter may be controlled as desired to condense the vapors. This process applies to destructive distillation of coal, tar, shales, asphaltic material, etc.

68. I G Farbenindustrie A-G, (assignee of J. Jannek and O. Gohre), "Treatment of coaly substances," Australia 13,067 (May 1, 1928).

A process for the production of soluble products from coaly substances consists of heating coal or the like under pressure, and if desired with the addition of gases or vapors which do not react to a substantial extent with the coaly matter under the conditions of working, and treating the product with a solvent at an elevated temperature and pressure, with or without the addition of said gases or vapors. The products obtained by the above treatment may be subjected to a cracking process and/or a destructive hydrogenation. The products may be also separated by the aid of solvents into resins, waxes, and other substances.

69. Johnson, J.Y., (to I G Farbenindustrie A-G), "Extracting oils, etc," Brit 301,946 (Sept 1, 1927).

In the extraction of soluble bodies from coal and like carbonaceous material, the coal is preheated under pressure in a closed vessel and then heated under pressure with the solvent. The pressure in either or both stages may be increased by gases or vapors more or less inert under the conditions, e.g., H_2, steam, CO, and N_2. Pressures specified are 2-20-200 or more atmospheres. Preheating is preferably at 100-600 C for several hours, and under such conditions as do not cause caking. Solvents specified are benzene and its homologs, hydrogenated naphthalenes, alcohols, ketones, petroleum, and mineral and tar oils; cyclo-hexanes and cyclo-hexanone are especially suitable. Carbonaceous materials specified are lignite, peat, coal, oil shale and carbonaceous shale. In an example, brown coal is maintained at 300 C for 10 hr, thus producing a pressure of 100 atm, and is then extracted for 10 hr at 300 C and 100 atm with benzene in a closed vessel. Over 60% of the coal is dissolved. After separation of the undissolved coal and removal of the solvent, the soluble products may be treated with solvents or may be hydrogenated.

70. Morrell, J.C., (to UOP), "Process for treating carbonaceous material," U S 1,940,725 (Dec 26, 1933).

1. A process for producing hydrocarbon distillates from solid bituminous material and heavy hydrocarbon oil which comprises mixing a portion of the heavy oil with the solid material and placing the mixture in an enlarged distillation zone, heating another portion of the heavy oil unadmixed with solid material to vapor phase cracking temperatures of the order of about 1000 F in an independent zone, introducing the resultant vapor phase cracked vapors into said distillation zone to supply heat for the distillation of said mixture, distilling the mixture, and removing and condensing the vapors.

IV. Digestion of the mixed shale and oil under elevated pressure at such a temperature as to cause conversion of the kerogen, with:

A. Subsequent separation of the spent shale and oil by mechanical means.

71. D'yakova, M.K., "Production of liquid fuel from combustible shales by the method of thermal solution," Bull acad sci URSS, Classe sci tech 1944, 258-74; C A 39, 2393.

For the transformation of combustible shales into liquid fuels, thermal solution is the most effective method, Solvents used were anthracene oil, tetralin, primary shale tars, their hydrogenation products and distillates, shale solutions in primary tars and petroleum mazut; mixtures totaling 200-300 g and consisting of 30-70 parts of solvent and 70-30 parts of shale were heated for 40-60 min to 300-430 C, kept at this temperature for a definite time and cooled rapidly. The gases were analyzed, liquid and solid products transferred to a glass flask, and the hygroscopic and pyrogenic water and light distillates (crude gasoline) boiling up to 200 C distilled off and determined. The residue was filtered on a heated Buchner funnel at 90-110 C, the precipitate on filter washed either with benzene or shale naphtha or extracted with benzene. The benzene was distilled off and residue boiling above 130 C was combined with the filtrate. The solid residue extracted with benzene and consisting chiefly of the mineral fraction of the shale and insoluble organic matter was analyzed for ash content (including mineral CO_2). The degree of solution of the organic matter of the shale was determined on the basis of changes in the content of the mineral fraction in the residue after solution according to the equation:

$$x = 100\left[1 - \frac{a(100-b)}{b(100-a)}\right]$$

in which x is percent content of dissolved organic matter, a content of mineral fraction in original shale, and b content of the mineral fraction in the residue after solution. The value of x obtained exceeds the true content of the dissolved organic matter of the shale by y, which is equal to the sum of the yields (in percent of the organic matter of the shale) of gas and pyrogenic water. The pressure created by the vapors of the solvent was usually 30-40 atm. Conditions were found under which 75-95% of the organic matter of the shales dissolved; 35-45% of this was transformed by cracking into gasoline. Thermal solution began at 300 C. At the optimum temperatures (380-430 C) the organic matter of the shale dissolved in 5-15 min. Large-scale laboratory equipment with capacity of 700 kg/day confirmed the laboratory data and indicated that a continuous process is possible. A large-scale method for the separation of the shale solution from the insoluble fraction of the shale was developed and checked experimentally. According to this method, tar shale solution freed from gasoline is filtered on filter presses and the precipitate washed with shale naphtha. It is possible to produce on an industrial scale from a shale containing 48-50% of organic matter; refined gasoline (boiling up to 180 C) 15.5%, naphtha (boiling 180-220 C) 1.9%, phenols (boiling 180-220 C) 0.77%, gas 4.2%, and shale pitch 14.6%. Seven references are included.

72. D'yakova, M.K., "Thermal solution, a new method for obtaining artificial liquid fuel,"
Bull acad sci URSS, Classe sci tech #7-8, 498-505 (1944);
Abs 522, J Inst of Petr 31, 167A (April 1945);
See Abstract; UOP Survey Foreign Petr Lit (June 22-29, 1945).

"Thermal solution" is the solvent extraction of solid fuels at temperatures such that cracking occurs. The yield of liquid products obtained is 3-5 times as great as that from retorting processes.

Various solvents may be used, such as fuel oil, anthracene oil, gas oil, tetralin, etc. The proportion of soluble organic matter decreases with increasing carbonization (age) of the solid fuel. ranging from 80% in the case of peats to 6% for anthracite coals. In the case of shale, on which most work has been done, the utilization of the organic matter present is as high as 85-90%, compared with 35-45% for the conventional distillation process. A typical thermal solution process, applied to shale, is as follows. The shale (organic content 50-60%) is dried to moisture content of 1-3%, and ground to 0.2-0.3 mm. The material is then mixed (1:1) with solvent (shale distillate of boiling range 220-370 C), heated to 415 C, and transferred to a reaction chamber, where it is maintained for 20 min at 425-430 C at pressure of 20-30 atm. The reaction product is freed from gas and products boiling below 225 C, and is then filtered to remove undissolved material. Typical yields (in weight percent) are gasoline (to 225 C) 20%, casinghead gasoline 0.3%, diesel fuel 1.5%, gas 4.5%, tar 15%. Hydrogenation of the latter will yield a further 12% gasoline. (Figures are on original shale containing approximately 50% organic matter.) A pilot plant of 27 kg/hr capacity has been successfully operated.

73. D'yakova, M.K., "Thermal solution, new method for obtaining artificial fuels,"
Petroleum (London) 8, 227, 246 (1945);
Bur Mines Abs Current Lit on Syn Liq Fuels, Abs 1040, (Feb 1946).

This method differs from the method of Pott and Broche, who studied the solvent extraction of coals under pressure and at temperatures below that at which decomposition began, in that the organic portion of the solid fuel undergoes appreciable decomposition. In carrying out the process, the solid ground fuel (0.2-5 mm in size) is mixed with an equal weight of solvent (petroleum fuel oil, tar distillates, hydrogenated heavy oils, anthracene oil, gas oil, tetralin, etc,) and heated to 380-430 C and 30-40 atm for 10-30 min. After completion of the reaction, the mixture is distilled to remove fractions boiling below 220 C and the residual liquid is freed from undissolved substances either by centrifuging or filtering. The products are a light distillate of the gasoline type, a heavy distillate for fuel oil, and a heavy extract suitable for hydrogenation, for fuel or for roads. A wide variety of fuels are applicable but those of sapropelite structure are more easily soluble than those of a humus structure and high (60%)ash; low-calorific value fuels can be used as well as fuels of higher quality. One of the most attractive raw materials is shale, a good quality of which will undergo a conversion of 85-90% of its organic matter into liquid fuel using a shale tar distillate as solvent, thus making the process self-contained. Yields of liquid fuel (percent on organic matter) are stated as follows: wood 42.2, lignite 71.1, peat 48.2, and coals 46.4-69.6%. The properties of the refined gasoline products are tabulated.

74. D'yakova, M.K., and Kardasevich, V.P., "High-temperature extraction and cracking of Gdovsk shale,"
J Applied Chem (USSR) 13, 122-31 (in Fr, 131) (1940); C A 34, 8230.

Organic substances of shale were dissolved in mazut, anthracene oil, primary tar and its hydrogenation product, "schist solution", or in fractions separated from "schist solutions", by heating at 400-430 C for 3-5 min in rotary autoclave. The optimum ratio of shale to solvent was 50:50 or 60:40. During the thermal solution, organic content converted was gasoline 35-40%, kerosine plus heavy material 35-40%, gas 5-10% of total organic. The heavy residue (40%) can be hydrogenated to gasoline, increasing motor fuel to 75%.

75. D'yakova, M. K., and Melent'eva, N.V., "Liquid fuel from wood, the tetralin process,"
J Applied Chem (USSR) 15, 173-81, 237-48 (1942); Chem Age 50, 359-60 (1944);
Bur Mines Abs Current Lit Syn Liq Fuels, Abs 31, (Oct 1944).

The tetralin process for transforming solid into liquid, which is based on the dissolution of coal in tetralin or phenol at high temperature or pressure, has now been applied to wood, peat and similar substances. The total amount of the product soluble in tetralin, and therefore, utilizable as liquid fuel, was found to be much larger than the amount of liquid obtainable by distilling peat, oil shale, etc.

76. D'yakova, M.K., and Stepantseva, T.G., "Thermal solution of combustible shales,"
Compt rendu acad sci URSS 26, 342-5 (1940) (in Eng); C A 34, 5642.

Organic matter can be completely extracted from combustible shales by heating for 3-5 min at 390-420 C finely-divided shale with certain commercial solvents such as fuel oil, anthracene oil and primary tars. The results of the experiments are tabulated. There are obtained up to 40% crude gasoline, 30-40% kerosine and heavy bituminous residue, 3-6% water, and 5-10% gas. From 5-15% of the organic matter is lost in the mineral residue. The solvent is in most cases completely or nearly completely regenerated.

77. D'yakova, M.K., and Stepantseva, T.G., "High-temperature extraction and cracking of combustible shale. II. The River Volga shale of the 'Obshchii Syrt' deposit,"
J Applied Chem (USSR) 13, 1045-52 (in Fr, 1052) (1940); C A 35, 2307.

A previously described method was used for the high-temperature extraction and cracking of the shale. Heating the mixture of shale and solvent (Ishimbaev residuum or anthracene oil) for 5-10 min at 390 C dissolved 75-80% of the organic substance of the shale and 10-15% of the shale was transformed into gas and water. In the thermal transformations (because of partial decomposition) 35-40% of the organic substances were made into gasoline, 30-40% into kerosine and asphaltic-like residue. Gasoline and kerosine have to be carefully rectified, while the asphalt-like residue could be used in road-building. The method was much better than other known methods for this shale.

78. D'yakova, M.K., and Tsitron, L.L., "Thermal solution of Sadki asphaltites as a method of preparation of artificial liquid fuel,"
Bull acad sci URSS Classe sci tech 1944, 740-4;
UOP Survey Foreign Pet Lit, Trans 585, (Mar 8, 1946).

Laboratory batch experiments of thermal solution of Sadki asphaltite in solvents consisting of petroleum solar oil, of the 250-360 C fraction of the products of dry distillation of Sadki asphaltite or the latter solvent after reclaiming, showed that under optimum conditions, i.e., 430-440 C, duration of 15-30 min, pressure of 25-30 atm and weight ratio of 1:1 solvent and asphaltite, 30% crude gasoline with 230 C end point, up to 56% coke, and 8-10% gas can be obtained by this method.

79. Hampton, Wm. H., "Digestion of bituminous shale, etc,"
U S 1,707,759 (April 2, 1929); C A 23, 2567.

Solid material such as bituminous shale is mixed with mineral oil within the kerosine range and digested at a temperature sufficiently high to liquefy bituminous substances present and under sufficient pressure substantially to retard vaporization of the kerosine and heavier fractions. Volatilized products are conducted away and recovered, and solid material is separated from the residue of the digested mixture. An apparatus is described.

80. Johnson, J.Y., (to I G Farbenindustrie, A-G), "Oils from shales, coals, destructive-hydrogenation residues, etc,"
Brit 312,383 (Feb 22, 1928); C A 24, 955.

The material while hot is extracted with organic solvents having great solvent power for the oils present when hot but little solvent power for them when cold, and the oil solution is separated and the oil recovered by cooling or other suitable method. Various details and examples and an arrangement of apparatus are described.

B. Vaporization of the oil and subsequent carbonization of the residue.

81. Egloff, G., (to UOP), "Process for treating bituminous materials and hydrocarbon oils,"
U S 1,954,866 (Apr 17, 1947).

A process in which a finely divided solid bituminous material is mixed with a solvent for bitumen, the latter being not subject to cracking at the conditions of pressure and temperature obtained in the process, heating this mixture in a restricted stream under pressure to such a temperature that, when combined with a heavy hydrocarbon oil in a reaction chamber, and maintaining the temperature, cracking of the heavy oil and the mixture take place. The vapors are separated and condensed.

82. Fisher, A., (to UOP), "Pyrolytic conversion and coking of finely divided bituminous material and hydrocarbon oil," U S 2,073,367 (Mar 9, 1937); C A 31, 3246.

A process for treating materials such as coal, peat, lignite or oil shale comprises adding the solid material to the oil, subjecting the mixture to conversion temperatures under substantially noncoking conditions, introducing the heated products into a coking zone, where the residue is coked in a relatively thin layer on a highly heated surface, subjecting the vapors from the coking zone to fractionation, etc. Recycling a fraction for mixing with solid material, and a heavy fraction direct to coking zone. Finely divided material is mixed with any hydrocarbon oil preheated in coils at 100-800 psi to 850-1050 F, coked in coking chamber at sub-atmospheric pressure and initially 900-1200 F, finally 1600 F.

83. Gotting, H.E., (to J.M. Browne), "Improved process and apparatus for the recovery of oil and spirit from shale, coal, and the like," Australia 16,029/34 (July 4, 1935).

See Brit 448,279, H.E. Gotting and J.M. Browne.

84. Gotting, H.E., "Shale oil and spirit recovery," Can 360,873 (Sept 29, 1936).

See Brit 448,279, H.E. Gotting and J.M. Browne.

85. Gotting, H.E., and Browne, J.M., "Process and apparatus for recovering oil from shales, etc," Brit 448,279 (June 5, 1936); C A 30, 7326.

Hydrocarbon oils boiling below 450 F are obtained from shale, coal, etc, by distilling under a self-generated pressure of at least 25 psi in a retort provided with a reflux column in which the heavier fractions are condensed and returned to the retort where they are cracked. The lighter fractions pass to an air-cooled condenser and receiver where the condensate is collected under pressure, gases passing off through a valve to a scrubber and holder.

86. Mond, A.L., (to UOP), "Cracking coal and oil mixtures," Brit 409,969 (Aug 29, 1933).

Mixtures of finely divided solid carbonaceous material and hydrocarbon oil are cracked and coked by subjecting the mixture to conversion temperatures and introducing the heated products into a coking zone where they are separated into residues and vapors which are fractionated to produce a light distillate while the residues are coked in thin layers on a highly heated surface. Conversion is obtained by pumping the mixture through coils heated to 450-480 C. The coking ovens are preferably maintained under atmospheric or sub-atmospheric pressure. Means are described for fractionating the oils and returning the heavy fraction to the system.

87. Morrell, J.C., (to UOP), "Treatment of hydrocarbon oils and coal," U S 1,972,944 (Sept 11, 1934).

A suspension of a finely divided solid bituminous material in a hydrocarbon oil is passed through a heating coil wherein the mixture is heated to a relatively mild conversion temperature (800-900 F) insufficient to cause substantial coke deposition in the coils, the recommended pressure being in range of 0-500 psi. The mixture is discharged directly into a coking chamber which is maintained at a reduced pressure relative to the coil (0-100 psi) and the vapors fractionated. The heavy oil is returned to the beginning of the process. A middle oil is heated to a higher temperature (900-1050 F) and pressure (100-800 psi) and reintroduced into the coking chamber to aid in carbonization and devolatilization of the contents of the chamber.

88. Strevens, J.L., and Mitford, W.B., "Materials for making coke," Brit 407,360 (July 9, 1932).

Smokeless fuel is made by coking a suspension of coal, torbanite or shale in mineral or coal oils, the suspension being prepared by agitating the solid (ground so as to pass a 200 mesh I M M sieve) with the oil and up to 5% of a non-aqueous wetting or peptizing agent, and digesting in a closed vessel at 300-370 C and pressure up to 50 atm.

89. Woidich, F.S., "Simultaneous treatment of crude petroleums or the like and bituminous coals or the like," U S 1,955,041 (Apr 17, 1934).

A process for the simultaneous distillation of liquid and solid hydrocarbons of the type of mineral oil and coal, consisting of forming an emulsion of the coal-dust and oil, preheating the emulsion with agitation, then gradually heating under pressure hot enough to volatilize the most volatile constituents when the pressure is reduced, separating the most volatile constituents at reduced pressure, then heating at gradually increasing temperatures with separation of the vapors. An apparatus is described.

C. The use of catalysts to aid the extraction, but without hydrogenation.

90. Haase, A., "A process and equipment for the treatment of bituminous shales, especially poor bituminous shales," Fr 860,127 (Jan 7, 1941).

Pulverized bituminous shales are mixed into a paste with heavy oil and the paste is heated in batches in a special retort under pressure to a temperature of 600 C. The charge is heated by electricity, the heating elements traverse the mass and are made of Ni alloy for its catalytic effect. A movable piston in the top of the retort is used to apply and to control pressure in the vessel.

91. I G Farbenindustrie A-G, "Organic compounds from coal, tar, etc," Fr 647,742 (Dec 16, 1927); C A 23, 2557.

Organic compounds of great value are obtained from treatment of coal, tar, wood, bituminous schists, etc, with hydrocarbons of high boiling point or high molecular weight or their derivatives below the coking temperatures of the hydrocarbons and at high pressure, and if necessary with addition of gases, with the exception of H_2, in appreciable amounts, and catalysts. The products may be used for the production of lubricating oils, diesel oils, or motor oils.

92. I G Farbenindustrie A-G, "Oils," Brit 282,691 (Dec 21, 1927).

Liquid or liquefiable products are obtained from solid carbonaceous materials such as coal, brown coal, residues of coal from which bitumen has been extracted, bituminous shales, peat, wood, etc, by heating them under pressure of 10-1000 atm with high boiling hydrocarbons or their derivatives containing no constituent which boils below 300 C, such as anthracene oil, mineral or tar oils, or their distillation products, or products obtained by cracking, destructive hydrogenation, etc, or synthetic high boiling products obtained from H_2 and oxides of C or products from the process. The treatment may be carried out in the presence of gases containing N_2, CO_2, or CO, but substantially no H_2, and of catalytic substances such as sulfides and alkali or alkaline earth metals, or other substances having an alkaline reaction. Substances having a distributive or thermoconductive reaction may be added. Temperatures above 250 C but not exceeding the coking temperature of the oil are used. The process may be carried out by passing the mixture through a heated coil or a vessel provided with stirrers, or the oil may be passed through vessels containing the solid substances. The product is separated by centrifuging or other means. The residual coal is easily ignited, readily absorbs gases and may be transformed into liquid products by treatment with H_2 under pressure. The liquid products are worked up to form lubricating oils, diesel or other fuel oil, etc.

93. I G Farbenindustrie A-G, "Pressure extraction of coal, peat, bituminous shale, etc," Ger 711,380 (Aug 28, 1941); C A 37, 4230.

The extraction is catalyzed by finely divided heavy metals or their oxides or sulfides of elements of groups IV-VIII of the periodic table. These are used together with mineral acids, carboxylic acids, or halogens.

94. I G Farbenindustrie A-G, "Extraction of coal, peat, bituminous shale, etc," Ger 711,711 (Sept 4, 1941); C A 37, 4231.

Oxides of groups IV-VIII of the periodic table or heavy metal sulfides are used as catalysts for extracting these substances. These catalysts are used together with volatile S compounds, however, the sulfides may be used without the volatile compounds.

95. I G Farbenindustrie A-G, "Extraction of coal, etc,"
Ger 711,712 (Sept 4, 1941); C A 37, 4230.

Mo, W or V halides are used to catalize the pressure extraction of coal, peat, bituminous shale and similar substances.

96. I G Farbenindustrie A-G, "Catalyst for extracting coal, peat, bituminous shale, etc,"
Ger 714,909 (Nov 20, 1941); C A 38, 2190.

Organic halogen compounds are used as catalysts for these reactions.

97. I G Farbenindustrie A-G, "Extraction of coal (and shale),"
Ger 719,536 (Mar 12, 1942); C A 37, 1850.

Salts of metals of the Fe group, e.g., Fe_2O_3 or $Ni(NO_3)_2$, are used as catalysts for pressure extraction of coal, peat, bituminous shale, etc, in the presence of alkaline-reacting substances.

98. Johnson, G.W., (to I G Farbenindustrie A-G),"Extracting solid carbonaceous materials with solvents,"
Brit 466,336 (Feb 8, 1936).

The pressure extraction of solid carbonaceous materials is carried out in the presence of catalysts comprising metals of the Fe group or their compounds together with alkaline substances. The metals are preferably used in a finely divided state. Oxides of Ni or Fe or Ni nitrate may be used together with caustic soda or potash solutions or milk of lime. Solvents used comprise benzines, middle oils, tars, cyclic organic compounds, e.g., tetrahydronaphthalene. The extraction is carried out at 200-500 C and 20-200 atm. Finely ground peat is dried and mixed with milk of lime and nickel nitrate and an equal quantity of middle oil obtained by destructive hydrogenation. The mixture is heated for 3 hr. at 380 C under 90 atm pressure, 88% of the peat is extracted. In a similar treatment brown coal is impregnated with solutions of caustic soda and ferric chloride.

99. Johnson, G.W., (to I G Farbenindustrie A-G), "Pressure extraction of solid carbonaceous substances,"
Brit 469,914 (Aug 5, 1937); C A 32, 1076.

The pressure extraction of coal, peat, bituminous shales, etc, in presence of solvents is conducted in presence of catalysts comprising heavy metals (specific gravity of 5 or more) or their compounds plus acids or substances that split off acids under the reaction conditions. The materials may be preheated with the acids and then extracted in the presence of the metals or their compounds. Metals specified are Sn, Pb, Ge, Fe, Ni, Co, Zn, V, Cr, Mo, W, Ti, and Mn, and compounds are oxides, sulfides, salts, halides or organic compounds, e.g., oxalates. Organic or inorganic acids may be used.

Wetting agents, e.g., salts of sulfonic acids, and volatile S compounds, e.g., H_2S, CS_2, and $(NH_4)_2S$, may also be added. As an example, gas coal is impregnated with a solution of Sn oxalate in $(COONH_4)_2$ solution and mixed with an equal amount of tetrahydronaphthalene and the mixture is heated to 400 C for 3 hr under 85 atm pressure in presence of 1% NH_4Cl.

100. Johnson, J.Y., (to I G Farbenindustrie A-G), "Pressure and chemical decomposition of coals, oil-shales and other carbonaceous solids," Brit 311,031 (Mar 1, 1928); C A 24, 714.

Temperatures above 200 C and pressure of preferably over 30 atm are used in the treatment of coal, oil shales, etc, with solvents in the presence of halogens, hydrogen halides, or compounds which set free the halogen or halide. Numerous details and modifications of procedure are given.

101. Krauch, C., Pier, M., and Anthes, E., (to I G Farbenindustrie A-G), "Extracting oils such as lubricating oils from materials such as coal or shale," U S 1,904,477 (Apr 18, 1933); C A 27, 3599.

Solid, non-asphaltic pyrobituminous material such as brown coal is passed through a reaction zone while treated with a hydrocarbon liquid, the major constituents of which boil between 100 and 300 C, and under a pressure of at least 75 atm until at least 50% of the oil contained in the initial material is extracted from it, but only for so long that substantially no low-boiling hydrocarbons are produced (the hydrocarbon liquid being kept in liquid state during process), and the liquid extract is separated from the solid residue. A catalyst may be used, consisting of an alkali or alkaline earth sulfide. Apparatus described.

102. Winkler, K., and Wissel, K., (to I G Farbenindustrie A-G), "Conversion of carbonaceous solids into valuable liquid products," U S 1,904,586 (Apr 18, 1933).

Solid bituminous materials are treated with a liquid hydrocarbon, which contains no material boiling below 300 C, at temperatures higher than 250 C and pressures greater than 10 atm, until at least 55% of the solid is extracted. Catalysts may or may not be used. These catalysts are sulfides of the alkali and alkaline earth metals.

D. Hydrogenation of the mixture.

103. Berl, E., "Obtaining extracts from oil shale," Ger 411,540 (Mar 31, 1925); Oil Shale, Literature and Patent Survey, The Texas Co (1948).

The material is extracted with hydrogenated naphthalene, especially tetrahydronaphthalene, at high temperature and pressure. In an example, oil shale gave an extract yield of 19.9% on treating with tetralin at 250 C, 0.9% at 100 C, and 2% with benzene at 240 C.

104. Egloff, G., (to UOP), "Treatment of hydrocarbons," U S 2,091,354 (Aug 31, 1937).

1. A process for recovering hydrocarbon liquids of motor fuel-like character from hydrocarbon-containing solids and liquids, comprising mixing with a relatively heavy hydrocarbon liquid suitable proportions of a finely comminuted hydrocarbon-containing solid to form a free-flowing fluid mixture, subjecting the mixture to a cracking temperature while flowing in a stream through a heating zone, discharging the heated mixture into an elongated rotary coking zone, introducing H_2 to the mixture in the coking zone, keeping the mixture and the H_2 at conversion temperature for needed time to complete conversion, coking the mixture, fractionating the vapors and recycling the heavy oil.

105. I G Farbenindustrie A-G, "Lubricating oils, etc," Brit 312,050 (May 18, 1928); C A 24, 956.

Lubricating oils and other high-boiling hydrocarbons are obtained by extracting coal, shale or other solid carbonaceous material with an organic solvent and reducing the extracted matter under such conditions that little decomposition into lower boiling products takes place; e.g., a paste of brown coal and a 300-350 C oil obtained by destructuve hydrogenation of coal is forced through a reaction vessel at about 200 atm and 380-400 C until about 60% of the coal is dissolved and the entire mass is passed over a Mo-Zn catalyst at 200 atm and about 400 C in presence of H_2; a condensate containing about 25% lubricating oil is thus obtained. Other examples are also given.

106. I G Farbenindustrie A-G, "Hydrocarbons," Fr 675,073 (May 15, 1929); C A 24, 2874.

Hydrocarbons of high boiling point, particularly lubricating oils, are made by treating coal, lignite, schist, peat, etc, by solvents under pressure and treating the extracted products with H_2 at a higher temperature but not sufficiently high to cause an appreciable dissociation.

107. I G Farbenindustrie A-G, (assignee of M. Pier), "High boiling point hydrocarbons," Australia 19,771/29 (April 29, 1929).

See Brit 312,050 and Fr 675,073.

108. I G Farbenindustrie A-G, "Hard and soft paraffins," Ger 709,022 (June 26, 1941); C A 37, 3929.

Coal, slate or other bituminous substances are extracted with suitable solvents at elevated temperatures below 800 C and under pressure. The extraction continues only until the bitumen is dissolved but not the asphaltic nor phenolic constituents nor the humic acids. The extracts are hydrogenated at below 300 C with fixed catalysts or above 300 C with a finely divided catalyst. The hydrogenation is in the liquid phase and cracking is avoided.

109. International Hydrogenation Patents Co, Ltd, "Bituminous solid carbonaceous material extraction," Australia 105,039 (Jan 5, 1938).

To extract bituminous solid carbonaceous materials under pressure and at elevated temperatures for soluble products, a fraction boiling between 170 and 260 C of the products resulting from the destructive hydrogenation of a previous extract and containing an amount of cresols between 5 and 40% by weight is made into a paste with the carbonaceous materials and subjected to an extraction process at a temperature of between 250 and 470 C at a pressure of 50-300 atm. The resultant extraction agent, extract, and pasting oil are subjected to destructive hydrogenation at from 250-600 C and 200-1000 atm in the presence of a metal of groups V to VIII, of the periodic table, especially finely divided iron or compounds of iron to regenerate the extraction agent and to hydrogenate the pressure extract.

110. International Hydrogenation Patents Co, Ltd, "Destructive hydrogenation," Fr 833,773 (Oct 31, 1938); Fr 833,774; Fr 833,775; C A 33, 3566.

Pastes of carbonaceous materials mixed with middle oil and mud from a previous operation are hydrogenated, the composition of the products which escape as gas and vapor from the reaction space or a neighboring separator being regulated so that the products contain at least the whole of the heavy oil freshly formed in the destructive hydrogenation. The mud from the operation is used at the same time as the middle oil as diluent for the fresh material. In Fr 833,775, lignite, peat or schists are subjected to hydrogenation under pressure under moderate conditions along with oils containing middle oil, or extracted with solvents, the product is freed from solid substances and fraction boiling below about 325 C, fractionated with a selective solvent, e.g., a liquid aliphatic hydrocarbon, to obtain a fraction rich in hydrogen and another poor in hydrogen and asphaltic. The first is hydrogenated under pressure without appreciable cracking in the presence of catalysts at 250-400 C, and the second is hydrogenated to produce gasoline and combustible oil.

111. Johnson, G.W., (to I G Farbenindustrie A-G), "Destructive hydrogenation, extracting oils,"
Brit 505,496 (Nov 8, 1937).

In the destructive hydrogenation or pressure extraction of solid carbonaceous materials with solvents, while flowing the reacting materials through a tower-like reaction vessel, from which the main portion of the products is removed into an adjacent hot separator, a portion of the reacting materials is removed from the lower part of the reaction space before the end of the reaction and the reaction products, after leaving the separator, are freed from solid constituents. The process is applicable to the limited hydrogenation of carbonaceous materials in which a maximum of 5% H_2 is consumed in the reaction.

112. Krauch, C., and Pier, M., (to I G Farbenindustrie A-G), "Conversion of fuel into liquid organic products,"
Australian 1217/26 (Mar 29, 1926); U S Bureau Mines Bull 467, 194 (1948).

A process for the conversion of solid fuels or mineral oils or their products of distillation or extraction or allied products, which consists of employing H_2 under elevated pressure and an added catalyst immune to sulfur poisoning and heat. The use of various catalysts, gas mixtures, and pressures are described and claimed.

113. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels and products derived therefrom or other carbonaceous materials into valuable products,"
U S 1,876,009 (Sept 6, 1932).

Destructive hydrogenation of solid and liquid fuels and distillation and extraction products therefrom with H_2 at pressure above 20 atm and temperature of 300-700 C with solid catalysts of compounds from the Ag and Cu group. Suggest H_2 flow rate in excess of 600 liters per kg of carbonaceous material. Solid materials are preferably treated dispersed in a liquid oil.

114. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,890,434 (Dec 6, 1932).

Destructive hydrogenation of solid and liquid carbonaceous substances with H_2 at pressure above 20 atm and sufficient temperature, in presence of a catalyst immune to S poisoning.

115. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,904,476 (Apr 18, 1933).

Similar to U S 1,876,009, temperature of 300-500 C, sulfur-resisting catalysts, 20 atm, vessels operating above 300 C to be Al alloy lined for prevention of corrosion.

116\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels and products derived therefrom or other materials into valuable liquids,"
U S 1,931,549 (Oct 24, 1933).

Destructive hydrogenation of carbonaceous materials (if solid with or without mixing with liquids) is carried out with H_2 and at temperatures of 300-700 C and pressures in excess of 20 atm. The catalyst that is employed is NH_3, ammonium sulfide, or inorganic nitrides of, e.g., Si or Ti.

117\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,931,550 (Oct 24, 1933).

Same as U S 1,876,009, except that catalyst is a solid inorganic nitride.

118\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,983,234 (Dec 4, 1934).

Same as U S 1,876,009, except that the catalyst is a sulfide of a metal of Group VI. Use of catalyst in finely dispersed state; suggests only 0.02% MoS as being needed.

119\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,994,075 (Mar 12, 1935).

Same as U S 1,876,009, except that the catalyst is a heavy metal sulfide associated with a substance selected from the group consisting of free heavy metals, the oxides of which are difficultly reducible, and difficultly reducible metal oxides.

120\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 1,996,009 (Mar 26, 1935).

Same as U S 1,876,009, except that the catalyst is the oxide of a metal of Group IV.

121\. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 2,005,192 (June 18, 1935).

Same as U S 1,876,009, except that the catalyst contains uranium.

122. Krauch, C., and Pier, M., (to Standard I G Co), "Conversion of solid fuels, etc,"
U S 2,006,996 (July 2, 1935).

Same as U S 1,876,009, except that the catalyst consists of a heavy metal sulfide mixed with a substance from the group consisting of ZnO, $ZnCO_3$, Al_2O_3, MgO, $CaCO_3$, and $MnCO_3$.

123. Pier, M., (to Standard I G Co), "Production of valuable liquid products from solid distillable carbonaceous materials by destructive hydrogenation,"
U S 1,920,887 (Aug 1, 1933).

Destructive hydrogenation of solid distillable carbonaceous materials at 300-600 C and at least 20 atm pressure, with H_2, and with or without S-resistant catalysts, under conditions for minimum production of benzines. The benzines are removed, and the high-boiling oils, with the asphalt in emulsified form, are extracted with an organic solvent that does not precipitate asphalt.

124. Pier, M., (to Standard I G Co), "Production of hydrocarbons of high boiling point range,"
U S 1,988,019 (Jan 15, 1935).

1. A process for producing lubricating oils which comprises subjecting solid pyrobituminous material to an extraction at a temperature below 400 C and at an elevated pressure with an organic liquid having substantially the same solvent action on the initial material as benzene has at a temperature below 400 C for such a time as to effect a substantial extraction of soluble constituents and then subjecting the extract to hydrogenation at temperature below 400 C and elevated pressure for such a time as to saturate the constituents without appreciable formation of low boiling products.

125. Pier, M., and Kroenig, W., (to Standard I G Co), "Destructive hydrogenation,"
U S 1,984,596 (Dec 18, 1934).

Hydrogenation of distillable carbonaceous material at 300-600 C, with H_2 pressure, separation of benzine and middle oil, and hydrogenation of residue again at 300-500 C without coke formation. First stage: 4 to 20 cu m H_2/kg carbonaceous material. Throughput of over 0.5 kg initial carbonaceous material/liter reaction volume per hour. Catalysts, amounting to 0.01-2 weight percent of material in first step and 10-30 weight percent of material in second step, may be destructive hydrogenation type.

126. Potts, H.E., (to International Hydrogenation Patents Co, Ltd), "Paraffin," Brit 450,721 (July 23, 1936); C A 31, 244.

Paraffin is obtained by treating coal, shale or other bituminous material with such organic solvents and under such mild conditions that only waxes, resins or other bituminous materials are dissolved, the asphaltic and phenolic substances and humic acids being practically neither extracted nor decomposed, and hydrogenating, without substantial cracking, the extract at 20-500 atm and either below or above 300 C. The residual coal, etc, may be destructively hydrogenated. The extraction is preferably carried out below 300 C, at 5-200 atm, usually with 1-10 parts by weight of solvent for 0.25-4.0 hr; it may be in stages, e.g., with rising temperatures and/or pressure and successive amounts of solvent. Solvents specified are benzene, toluene, xylene, tetrahydronaphthalene, alcohols, ethers, amyl acetate, acetone, CS_2, $CHCl_3$ and CCl_4.

127. Potts, H.E., (to International Hydrogenation Patents Co, Ltd), "Destructive hydrogenation," Brit 498,300 (Jan 2, 1939); C A 33, 4770.

In destructive hydrogenation of solid, infusible carbonaceous materials, e.g., coal, shale or peat, to produce hydrocarbons of low, middle, and high boiling ranges, all the reaction products remaining after separation of gasoline and gases are divided into parts of substantially the same composition and one of the parts, on which the pressure has been released prior to or subsequent to division, is used as pasting medium for fresh initial material while one or more of the other parts are worked up to fuel oil, lubricating oil or motor fuels. Separation of the reaction products is preferably conducted in hot and cold catchpots, the sludge and major part of the heavy constituent being collected in the hot catchpot while the gasoline and part of the middle and heavy oil is collected in the cold catchpot. The gasoline is distilled off and the middle and heavy oil mixed with the sludge withdrawn from the hot catchpot. Part of the sludge may be recycled to the reaction chamber. The mixture is then divided into parts of the same composition, one of which is used as the pasting medium, while the other(s) is (are) freed from solid constituent by centrifuging and used directly as fuel oil. Preferably, however, the materials are further worked up by limited hydrogenation to obtain an improved fuel oil or diesel oil and gasoline. Hydrogenations are conducted up to 700 atm, known catalysts, limited H_2, so only 2-4% H_2 is used.

128. Potts, H. E., (to International Hydrogenation Patents Co, Ltd), "Destructive hydrogenation of carbonaceous materials; diesel fuels," Brit 500,282 (May 6, 1937).

Diesel fuel is made by subjecting solid or liquid carbonaceous materials to destructive hydrogenation in the liquid phase, separating from the product gasoline, middle oil and heavy oil. The hydrogenation is carried out at 300-550 C and above 20 atm, preferably 200-750 atm, in the presence of catalysts consisting of elements of Group VI or compounds thereof or of Fe, Zn, or Sn. Sulfuric acid halogens or H halides or compounds forming these may be present, e.g., ammonium chloride, CCl_4 or $CHCl_3$. Middle oil is further hydrogenated.

129. Szeszich, L. von, (to Deutsche Gold-und-Silber-Scheideanstalt), "Destructive hydrogenation of carbonaceous materials," U S 1,946,341 (Feb 6, 1934).

Hydrogenation of a mixture of two carbonaceous materials containing high and low quantities of S, respectively, at 350-600 C and pressure above 100 atm with H_2 in presence of a catalyst including a metal from Fe, Ni, and Co group. The continuous presence of H_2S in the process increases the activity of the catalyst.

130. Varga, J., (to Deutsche Gold-und-Silber-Scheideanstalt), "Process for the destructive hydrogenation of carbonaceous substances," U S 1,852,988 (Apr 5, 1932).

The method of destructive hydrogenation of carbonaceous substances which consists of subjecting the substances to temperatures of 250-700 C and pressure of 100-500 atm and treating the substances in the presence of Mo catalyst and H_2S with H_2, so that H_2S is continuously present in optimum amounts of 1-6% by weight of the carbonaceous substance, so that the action of the Mo catalyst is improved over the action of Mo catalysts, including MoS, when used alone, there being continuously present a quantity of H_2 in minimum amount twice the quantity needed for destructive hydrogenation.

131. Varga, J., (to Deutsche Gold-und-Silber-Scheideanstalt), "Process for the destructive hydrogenation of carbonaceous substances," U S 1,894,926 (Jan 17, 1933).

Same as U S 1,852,988, except that W catalysts are used instead of Mo catalysts.

V. Miscellaneous processes.

132. Fisher, A., (to UOP), "Process of treating hydrocarbon oil and bituminous materials," U S 2,010,357 (Aug 6, 1935).

1. A process for treating a substantially solid comminuted pyrobitumen, which consists of mixing said pyrobitumen with an emulsion of water and oil containing $ZnCl_2$ and an emulsifying agent, and then subjecting such mixture to temperature sufficient to decompose the same and produce relatively low boiling hydrocarbons.

133. Hofmann, F., and Wulff, C., (to I G Farbenindustrie A-G), "Oil from shale, etc,"
Brit 283,159 (Jan 5, 1927); C A 22, 3985.

Liquid SO_2 (with or without admixture of benzene or other solvents) is used for extracting oil from shale or similar materials such as residues from the destructive hydrogenation of coal.

134. I G Farbenindustrie A-G, "De-ashing liquid and semisolid hydrogenation and extraction products of coal, oil shale, and peat,"
Ger 722,406 (May 28, 1942); C A 37, 5224.

These products are treated with CO_2 or $(NH_4)_2CO_3$ in the presence of water at an elevated temperature and under pressure. The ash is thereby converted to a coarse aggregate which is subsequently removed by mechanical means.

135. International Hydrogenation Patents Co, Ltd, "Hydrogenating bituminous materials,"
Fr 827,600 (Apr 28, 1938); C A 32, 8749.

Bituminous coals, particularly lignites and coals of recent formation, as well as petroleum schists, peat, wood, etc, are subjected to a preliminary extraction with, e.g., benzene, under moderate conditions. The residue from this extraction is subjected to a more vigorous extraction, e.g., with deca- or tetrahydronaphthalene or hydrogenated anthracene at above 300 C and at 150 kg/sq cm. The product from the second extraction is hydrogenated to obtain gasoline, middle oil, and heavy oil.

136. Nast, H., (to Bergbauunternehmung "Corona," G.m.b.h.), "Extracting bituminous coal and shale,"
Ger 541,829 (Dec 7, 1928); C A 26, 2579.

Small amounts of hydrogenated cyclic hydrocarbons or their derivatives or amines or a solution of NH_4OH or a mixture of these is added to the extracting agent, e.g., C_6H_6. Thus, crude lignite is extracted with C_6H_6 containing 1% cyclohexanol, at 95 C. The yield is 12.4% bitumen against 10.2% by benzene alone.

137. Pier, M., and Jaeckh, W., (to I G Farbenindustrie A-G), "Removing solids from oils,"
Ger 712,230 (Sept 18, 1941); C A 37, 4553.

The oils are first centrifuged, then filtered, to remove solids produced by distillation, extraction or hydrogenation of coal, peat, shale, etc.

138. Pier, M., Kroenig, W., and Jaeckh, W., (to Wm.E. Currie), "Working up liquefaction products of coals, shales or peat,"
U S 2,223,184 (Nov 26, 1940); C A 34, 1971.

A process employed involves extracting "mineral coals," brown coals, shales or peat with a solvent such as tetrahydronaphthalene containing 10% naphthalene at temperatures above 370 C to dissolve both asphaltic and waxy constituents, separating the undissolved portion from the resulting solution, removing at least a portion of the solvent from the solution, then slowly chilling the remainder solution of asphaltic and waxy constituents to a temperature sufficient to cause separation of the asphaltic constituent as a relatively heavier layer from a relatively lighter liquid wax layer and mechanically separating the two layers.

139. Sayer, Wm. F., "Extracting coal or oil shale,"
Can 444,408 (Oct 7, 1947); C A 42, 2420.

Coal, lignite, shale, etc, are digested in NaOH solution, the soluble acids are removed, the residue is dried, and the oily constituents are extracted from the residue by solvents consisting of one or more acids, such as propionic, butyric, isobutyric, 2-ethyl butyric, valeric, or isovaleric and an organic liquid having a molecular weight of 85-400; e.g., phenol 42-65% and ethylbutyric acid 58-35% by volume constitute the solvent.

140. Ulke, T., "Liquid hydrocarbons from peat,"
U S 1,445,423 (Feb 13, 1923); C A 17, 1543.

Peat is hydrogenated with Na formate under a pressure of about 100 atm at a temperature of about 400 C. NaOH in solid form and CO are obtained from the products and are used to regenerate Na formate for treating a new charge of peat. The liquid hydrogenation products formed from the peat are separated. Oil shale, lignite, coal, and sawdust may be similarly treated.

VI. Reports of experimental investigations.

141. Berl, E., and Schmid, W., "Extraction of oil shale and brown coals with tetralin."
Brennstoff Chem 7, 149-53, 181-5 (1926); C A 20, 3231.

Extraction with tetralin at 14 atm and 270 C yielded 19.9% soluble material from an oil shale compared with 2.12% with C_6H_6 at 26 atm and 240 C. Decomposition took place at 22 atm and 280 C with tetralin. The tetralin extract was distilled with superheated steam to 320 C, yielding 33.7% liquids, 19.8% asphalt, and 46.5% gas. Direct distillation of oil shale yielded 93% as much oil as by extraction with tetralin; 2 brown coals yielded 2.17 and 2.07 times as much and one rich in bitumen yielded 1.27 times as much. Composition of substances extracted from brown coal was: 11.2% wax-like plastic material, 40.5% resin, 20.8% pitch, 12.3% phenols and acids, and 15.2% undetermined.

142. Cunningham-Craig, E.H., "The origin and constitution of oil shale, with a practical application," Proc World Eng Cong Tokyo 1929, 32, 1-25 (1931); C A 25, 5546.

Discusses origin of kerogen in oil shale. Proposes passing finely crushed shale through an agitated bath of heavy stable oil (boiling point 662 F) at 572 F, followed by distilling to dryness in a second retort. Oil from the latter is returned to the former as carrier oil. The throughput of such a still is far greater than that of any other of the same size. More oil is recovered than by other methods. The quality of the oil is high, practically no non-condensable gas, little or no cracking, no C deposition and no dust. Examples are given.

143. Dulhunty, J.A., "Solvent extraction of torbanite," Proc Linnean Soc N S Wales 67, Pt 3-4, 238-48 (1942); C A 37, 1033.

A 250-g sample of powdered torbanite was preheated at temperature intervals of 20 C from 300 to 420 C. After each heat treatment it was extracted with 1 liter C_6H_6 at 270 C and 560 psi for 8 hr. The residue after the extraction was reheated for a total period 4 hr longer than at the previous temperature. The yield of products is small up to 340 C. There is a sudden increase in formation of soluble products as the result of heating at 360 C, and the amounts fall off rapidly above 380 C. The quality of products formed by heating above 400 C is negligible. Upon preheating torbanite at 360 C and 840 psi of C_6H_6 vapors for varying periods of time, about 50% of the total extractable material is formed during the first half hour, after which the rate falls off. The last 10% requires about 24 hr.

144. Dulhunty, J.A., "The action of solvents on torbanite and the nature of extracted products," J Proc Roy Soc N S Wales 76, 268-74 (1943); C A 37, 6859.

Aromatic compounds are more efficient solvents for torbanite than aliphatic. Oil can be produced by solvent extraction by preheating torbanite at 350-450 C to make organic matter soluble, followed by extraction with C_6H_6 or by extracting with its own oily extract at 350-450 C and 150-300 psi. The product consists largely of very heavy paraffin compounds. No soluble ulmins or tar acids are present.

145. Dulhunty, J.A., "Preliminary notes on solution-cracking treatment of torbanite," J Proc Roy Soc N S Wales 77, 24-32 (1943); C A 38, 1097.

Solution cracking of torbanite in 7 cycles with temperature increasing from 375-400 C, pressure from 126-230 psi and time from 15-60 min reduced the volatile content of the solid residue to 15%. The yield of 224 gpt of light products is equivalent to 84% conversion of the organic matter. Gas yield is 4 cu ft/gal of light products. Quantity of gasoline boiling below 180 C is 30% of light products boiling below 230 C. Solution cracking in 3 cycles at 375-400 C, 546-406 psi, 60-120 min yields 120 gpt gasoline and 20 cu ft gas/gal gasoline.

146. Franks, A.J., and Goodier, B.D., "Preliminary study of the organic matter of Colorado oil shales,"
Quart Colo School Mines 17, #4, Suppl A, 16 pp (Oct 1922).

By successive heating at 300 to 350 C for periods of 8 hr and extraction, extracted heavy bitumen without producing oil. Concludes transformation of kerogen to bitumen not a depolymerization, does not take place at definite temperature. Rate greater at higher temperatures. Bitumen formed at different temperatures apparently not the same.

147. Gavin, M.J., and Aydelotte, J.T., "Solubility of oil shales in solvents for petroleum,"
U S Bur Mines RI 2313, 3 pp (1922); C A 16, 1500.

The common statement that oil shales contain little or no oil as such, but contain organic matter from which oil is produced by distillation was investigated by extracting samples of unheated shales in a soxhlet apparatus. The samples were ground to minus 20-mesh, and all material minus 60-mesh was rejected. The extracts from CCl_4, CS_2, Me_2CO, Et_2O, C_6H_6, and $CHCl_3$ were similar in appearance, being dark brown or black, and more or less fluid. They were not appreciably affected by cold, concentrated H_2SO_4 or HNO_3, were insoluble in cold EtOH and slightly soluble in hot. The amounts extracted varied from traces to 10.98% of the weight of the shale, and up to 55.8% of the distillation yield. The largest amounts were extracted by Me_2CO and $CHCl_3$. The percent of extraction from solvents is no criterion of the distillation yield.

148. Gillet, A., and Maquet, A., "Experimental studies on the bituminous schist of Belgian Luxemburg,"
Bull soc chim Belg 50, 173-84 (1941); C A 36, 3939.

The bituminous schist contains 73.0% ash, 17.3% C and 2.16% H. At 340 C, 13.5% of the schist is soluble (kerogen) in anthracene oil; of this soluble portion 7.66% (based on weight of schist) is precipitated by acetone and is called kerogen a. Practically all the organic matter can be dissolved in oleic acid during 2 hr at temperatures above 320 C. Below this temperature the extraction is incomplete. The organic matter in the schist can be divided into three portions; 1, substances (hydrocarbons, S and N compounds) soluble in acetone; 2, nonacidic substances which can be esterified readily with oleic acid; and 3, more acidic substances (such as kerogen a) which still combined with oleic acid but with only a small amount of the latter. Oleic acid also attacks the mineral constituents of the schist to an extent depending upon the temperature and duration of the treatment.

149. Klosky, S., Thermal Solution of Kerogen,
U S Bureau of Mines Intra-Bureau Report, Washington, D. C. (1946).

A review of the literature relating to the effect of heat on the solubility of kerogen and its extraction with liquid solvents. Translations are given of several foreign publications. Twenty-one references are included.

150. Luts, K., "Disintegration of kukkersite in organic liquids,"
Brennstoff-Chem 11, 148-50 (1930); C A 25, 196.

This and other oil shales exhibit swelling tendencies, gas evolution, and subsequent disintegration of structure upon immersion in various organic solvents. Gas pressure produced by penetration into capillaries, the size of which has been calculated, is believed responsible. The composition of sieved residue fractions is given. The speed of disintegration is proportional to heat of wetting and also depends on the surface tension. Russian, Estlandish and Scottish shales and bituminous limestone have been investigated with ether, acetone, $CHCl_3$, C_5H_5N, CS_2, EtOAc, MeOH, EtOH, aniline, benzine, petroleum, acetophenone, nitrobenzene, and C_6H_6.

151. Luts, K., The Estonian Combustible Shale Kukersite - Its Chemistry, Technology and Analysis,
Reval Publishing Co, Estonia (1944); Translated by H. W. Sohns,
U S Bureau of Mines, Laramie, Wyo (1947).

A discussion of thermal solution and hydrogenation studies of oil shale is included. Eleven references are given on these subjects.

152. McKinney, J.W., "Constitution of kerogen,"
J Am Chem Soc 46, 968-79 (1924); C A 18, 2244.

Kerogen is the organic matter in pyrobituminous shale. A New Brunswick shale was used, containing 19.44 C, 2.18 H, 1.3 N, 1.18% S, and which yielded 30.1 gpt oil. The percent extracted by various solvents was: EtOH, 1.5; Et_2O, 2.2; C S_2, 2.8; Me_2CO, 2.6; $CHCl_3$, 2.2; CCl_4, 2.6; C_6H_6, 3.2; C_5H_5N, 2.6; and AcOH, 6.9. On the large scale Me_2CO was used and the extracted oil separated into asphaltenes (10%), resins (5%), and hydrocarbons (85%). The oil, filtered through fuller's earth had a density of 0.833, α_D 0.76, and did not react with dilute $KMnO_4$ or bromine water. The yield was 1.36% of the original shale or about 4% of the kerogen. This product was then sepa[illegible]ed by distillation and crystallization until 28 compounds belonging to the paraffin, naphthalene, and hydronaphthalene series were isolated, for which the density, index of refraction and molecular weight were observed and calculated, and analyses given. These compounds, with the exception of two, are probably identical with compounds which have been isolated from varied sources. By the action of C_6H_6 in a sealed tube at 200 C the amount of extract obtainable from pyrobituminous shale is more than tripled. As this amounts to more than 20% of the kerogen it should be investigated in the same way as the Me$_2$CO extract. The kerogen may be completely removed from the shale by HNO_3, though in a highly altered condition, the products obtained being humins.

153. Neppe, S.L., "A technical study of Transvaal torbanite," <u>J Inst Petroleum 28</u>, 104-8 (1942); <u>C A 36</u>, 6332.

Finely-ground Transvaal torbanite was extracted with Shell gasoline under pressure at temperatures up to 335 C. The yield of black, fairly viscous oil increased nearly four-fold when the fineness of of the sample was increased from minus 20 mesh to minus 60 mesh. Not only did the yield of extract increase with increasing time, temperature, pressure, but more decomposition of the torbanite took place, so that at temperatures above 310 C, N_2 formed a large part of the gas production.

154. Petrick, A.J., "The hydrogenation of Ermelo (S Afr) oil shales and shale oil," <u>Brennstoff-Chem</u> 18, 221-4 (1937); <u>C A 31</u>, 8171.

Five samples of shale have been treated in a 5-liter Bergius rotating autoclave previously described (<u>C A 31, 5140</u>). Charges of 250 g mixed with 176 g heavy tar oil, $\overline{20\text{ g }(NH_4)_2MoO_4}$ and 7 g S (to give 5% MoS_2) were treated under following conditions: 95-100 atm initial pressure of H_2, 4 deg/min to 450-460 C, held 1 hr, and then cooled. Gas and liquid products recovered. Oil and water removed from solid residue first by distillation to 350 C, then by soxhlet extraction with benzene. Yields of crude oil were greater than by direct distillation of the shale to 570-80 C in every case, the difference being greater with shales which were lean on distillation. Residues after hydrogenation still contained organic matter. Shale oil fractions boiling above 220 C, obtained by direct distillation, were hydrogenated under similar but varying conditions. Detailed examination of the resulting 150, 230 and 300 C fractions showed that, with increased reaction temperature from 400 to 500 C, absorption of H_2 also increased. At 400 C for 1 hr the product contained 98% of original oil. At 450 C oil content was 89% with 11.7% gas. At 500 C (momentary) oil content was only 49% with 55.6% gas and loss. Very little low-boiling oil was recovered at 400 C but the color improved, S and N were decreased, and density increased. At 450 C, S and N were removed, I number decreased, content of 150 C light oil was 19%, oils boiling to 230 C totaled 41%. At 500 C the oil became aromatic in nature. The influence of increased time at reaction temperature was greater at higher temperatures, increased gas being at cost of oil. Contents of S and paraffines and the I number were also decreased thereby. One-hour treatment at 400 C is enough to improve heavy shale oils for lubricant manufacture. Treatment at 450 C suffices for light oil production. Further study showed that large excess of H_2 was not necessary for highest yields of light oil. Addition of 2% H_2S to provide excess S, also increased oil yield but not light oils. Results were improved and yields increased by use of activated C as carrier for precipitated MoS_2.

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STUDY OF THE THEORY AND PRACTICE OF THE THERMAL SOLUTION PROCESS, INCLUDING HYDROGENATION

155. Pezold, E. von, "The distillation of oil shale from a liquid phase, I and II,"
Chem-Ztg 52, 541-2, 562-4 (1928); C A 22, 4238.

Reviews previous work in which oil shale was heated in the presence of a solvent. In his experiments, Pezold uses shale oil and concludes that this increases the yield materially.

156. Popham, F.J., "Shale - some new reactions,"
Ind Chemist 5, 269-72 (1929); C A 23, 5035.

A discussion of the character of the organic matter in oil shale is followed by a detailed account of experiments carried out on Estonian shale. The ground shale was heated under pressure with various reagents in an autoclave of 3-liter capacity. Conclusions: the organic matter can be decomposed to liquid hydrocarbons by heat and pressure, giving a higher yield of low boiling point hydrocarbons than by ordinary retorting. Similar treatment with superheated steam in absence of catalysts is ineffective. The presence of H_2 is a distinct advantage. The presence of a cracking oil (largely assisted by the inorganic matter in the shale) is a distinct advantage. For this purpose, the heavier portions of the oil produced by the process can be advantageously used. The shale should be heated as rapidly as possible (preferably ground in a liquid medium). The products should be removed rapidly from the reaction, or if this is not possible, the retarding effect of superheated steam may be used to advantage.

157. Smith, G.H., and Stewart, D., "Extraction of oil shale with solvents at relatively high temperatures,"
Scottish Oils Ltd, Central Laboratory, Report SO.M/168/40 (July 16, 1940).

Review of three previous reports, SO/42/38, SO/66/38, and SO/124/38. In the first, tests on Dunnet shale (Westwood pit) showed the benzole had no appreciable solvent action at 250 C, heavy aromatic kerosine gave slight extraction at 350 C; the initial decomposition temperature of raw shale was 350-360 C. The second report compared repeated extraction of Westwood shale with heavy aromatic kerosine at 400 C with dry assay at 750-800 C. Extraction at 400 C, 320 psi maximum, reduced the organic C content of shale by 63.3% as compared with 55.8% by dry heating at 750-800 C; the H content was reduced by 71.9% and 91.9% respectively. Dry heating of the solvent-extracted shale did not further reduce the C content but removed H in the form of water. The third showed similar results on extraction of a rich Australian shale at 400 C; pyridine was unsuccessful as a solvent; the extract obtained with cresol, in which the cresol was removed with boiling caustic soda, was a soft bituminous substance of high specific gravity and high C/H ratio. The present report describes the results obtained from extraction of Westwood shale with a heavy aromatic kerosine in a 250-cc rotating autoclave, heated in a lead bath, and holding 50-g batches of shale. So long as the shale was thoroughly wetted with the solvent, the solvent/shale ratio had no effect on percent extraction. Studies over temperature range of 330-420 C showed: no extraction at 330 C, maximum extraction (one extraction) at 380-400 C of 11.8% of shale, extraction at 420 C fell to 8.3%. Exhaustive extraction (9 times with fresh solvent) at 350 C removed 13.2% of shale; additional extraction at 400 C showed this to be almost complete removal. The gas was shown to be derived from the thermal decomposition of the solvent only.

158. Swinnerton, A. A., "Treatment of oil shale from New Brunswick by the Ryan oil digestion process,"
Can Dept Mines, Summary Report 1922, #605, 210-8; C A 18, 1563.

Several runs made on a laboratory scale resulted in no definite conclusions, owing mainly to excessive handling losses, principally in the centrifuging operation. The process is not recommended for treating New Brunswick shales.

Table 1.--Batch thermal solution of oil shale in small autoclave[1]

Solvent[2]	Run no.	Time held at oper. temp.[3] (min.)	Operating temperature (F)	Conversion of organic matter[4] (%)
Petroleum kerosine[5]	17	1	773	63
	16		799	77
	19		799	66
	23		810	73
	14		834	86
	24		850	86
	21		869	83
Petroleum kerosine[5]	26	60	740	63
	25		760	81
	22		780	86
	18		800	87
	20		800	86
	15		838	76
Petroleum kerosine[5]	29	180	740	87
	28		760	86
	27		780	84
Quinoline[6]	30	60	740	77
	31		790	90
	32		840	84
Anthracene oil[7]	35	60	740	80
	33		790	84
	34		840	71

[1] Oil shale No. 44L-69, from DeBeque, Colorado; assay value - 41 gpt; analysis - 23.3% organic content, 17.2% mineral CO_2, and 59.5% ash; crushed to approximately 7% plus 48 mesh, 18% 48-100 mesh, 25% 100-200 mesh, and 50% minus 200 mesh; and dried at 220 F.

[2] Raw shale to solvent weight ratio in charge: 2.0 for runs 14-18, 1.33 for runs 19-29, and 1.0 for runs 30-35.

[3] Preceded by a heating up period of 15 to 30 minutes.

[4] Organic matter: total organic matter in the raw shale.

[5] Supplied by Standard Oil Company of Indiana.

[6] Supplied by Koppers Company, pure compound, b 458 F.

[7] Supplied by Fisher Scientific Company.

Table 2.--Small-scale batch thermal solution tests at higher temperatures[1]

Run no.	Solvent	Shale to solvent wt. ratio	Max. temp. (F)	Total time (min.)	Time at max. temp. (min.)	Conversion of organic matter (%)	Max. pressure (psi)	Final cold pressure (psi)
B	Residuum[2]	1.00	860	13	5	43	280	200
C	Residuum[2]	1.00	895	7	1	30	400	230
D	Heavy gas oil[3]	1.00	900	7	1	62	375	165
E	Heavy gas oil[3]	1.00	875[5]	3.4	-	66	400	150
F	Light gas oil[4]	1.64	905	10	3	74	190	40
G	Light gas oil[4]	1.64	905	10	1	70	184	45
H	Light gas oil[4]	1.64	950	8	2	65	300	51

[1] Raw shale No. RRS-47-77, from Anvil Points Mine, Rifle, Colorado; ground to pass 65-mesh sieve; Fischer assay - about 26 gpt; analysis - 15.8% organic content, 16.7% mineral CO_2, and 67.5% ash.

[2] Residue after distillation of the heavy gas oil from a sample of Parry shale oil.

[3] Fraction of Parry shale oil taken from 445 F at 2 mm Hg to cracking temperature (approximately 650-700 F at 2 mm Hg).

[4] Fraction of Parry shale oil taken from 380 F at 585 mm Hg to 445 F at 2 mm Hg.

[5] Autoclave bath temperature was 950 F, so the average temperature of the slurry was probably higher than 875 F.

Table 3.--Semi-continuous thermal solution of oil shale petroleum kerosine1/

Run no.	Mean shale temperature (F)2/	Conversion of organic matter (%)3/	Total duration of run (min.)	Period of constant temp. (min.)
13	670	28	192	157
14	720	86	245	185
15	740	92	240	185
16	775	93	249	204
17	815	89	245	210

1/ Oil shale No. RRS-45-30, from Parachute Creek, Colorado; assay value of 53 gpt; analysis - 31.0% organic content, 12.4% mineral CO_2, and 56.6% ash; ground and screened to 4 to 8 mesh and dried at 220 F. Petroleum kerosine was supplied by Standard Oil Company of Indiana.

2/ Mean temperature of the charge of shale during the constant temperature period of the run.

3/ Operating pressure of 400 psi, solvent pumping rate of 11-20 cc/min.

Table 4.--Semi-continuous thermal solution of oil shale shale-oil gas oil[1]

Run no.	Mean shale temperature (F)[2]	Conversion of organic matter (%)[3]	Total duration of run (min.)	Period of constant temp. (min.)
21	720	93	273	240
18	740	87	240	180
24	750	95	220	190
23	760	95	210	180
22	780	92	210	160

[1] Oil shale No. RRS-45-30, from Parachute Creek, Colorado, assay value of 53 gpt; analysis - 31.0% organic content, 12.4% mineral CO_2, and 56.6% ash; ground and screened to 4 to 8 mesh, and dried at 220 F; solvent was gas oil cut of Pumpherston shale oil, fractionated between 305 and 380 F at 3 mm Hg.

[2] Mean temperature of the charge of shale during the constant temperature part of the run.

[3] Operating pressure of 400 psi, solvent pumping rate of 13 cc/min.

Table 5.--Effect of particle size of oil shale and heating time on conversion of organic matter and on degree of disintegration of the shale[1]

Particle size	Reaction time[2] (hr.)	Conversion of organic matter (%)	Degree of disintegration of the shale
8-14 mesh	0.5	88	[5]
	1.0	89	[5]
	2.0	84	[6]
4-8 mesh	0.25	26	[3]
	0.5	71	[5]
	1.0	87	[5]
	2.0	82	[6]
1/4"-1/2"	0.5	83	[4]
	1.0	90	[5]
	2.0	86	[6]
1/2"-3/4"	0.5	88	[4]
	1.0	92	[5]
	2.0	87	[6]

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[1] Shale samples prepared from a Parachute Creek, Colorado, oil shale, assaying 53 gpt; extracted in a small batch autoclave at 775 F, with a Pumpherston shale-oil gas oil fraction distilling between 305 and 380 F at 3 mm Hg; raw shale to solvent weight ratio of 0.8.

[2] Period of heating at 775 F after initial heating up period of approximately 10 minutes.

[3] Very little visual disintegration, particles rubbery and easily pulverized.

[4] Some sludge formed, considerable particles left intact, these were very rubbery and very easily broken down.

[5] Very few of the particles left intact, very much sludge formed.

[6] No particles left intact.

Table 6.--Effect of oil shale-richness and heating time on conversion of organic matter and on degree of disintegration of the shale[1]

Assay value of shale (gpt)	Reaction time[2] (hr.)	Conversion of organic matter (%)	Degree of disintegration
11	0.5	85	Very little visual change, particles retained sharp corners and were broken down only with difficulty.
	1.0	99	Same as above, except particles were more easily broken down into laminations.
	2.0	62	No sludge,particles retained sharp corners and were quite easily broken down into laminations.
27	0.5	81	Some sludge, numerous particles which were left intact were broken down with difficulty into laminations.
	1.0	75	Much sludge, also considerable particles were left intact which were spongy and easily broken down.
	2.0	64	Very few particles left intact.
53	0.5	83	Some sludge, numerous particles which were left intact were very easily broken down.
	1.0	90	Much sludge, very few particles left intact.
	2.0	86	No particles left intact.

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[1] Oil shales from Green River formation, near Rifle, Colorado; crushed and screened to 1/4"-1/2", extracted in a small batch autoclave at 775 F, with a Pumpherston shale-oil gas oil fraction distilling between 305 and 380 F at 3 mm Hg; raw shale to solvent weight ratio of 0.8.

[2] Period of heating at 775 F after initial heating up period of approximately 10 minutes.

Table 7.--Semi-continuous thermal solution of oil shale[1]

	Light gas oil solvent [2]		Heavy gas oil solvent[3]	1/3 heavy gas cil and 2/3 residuum as solvent[4]					Steam stripping [5]		
Run number	34	35	37	38	39	41	42	44	45	46	47
Temperature (F)	800	800	800	800	800	800	800	800	800	800	800
Pressure (psi)	300	300	300	300	300	300	300	300	300 to 0	0	0
Size of shale used	.... Lumps approximately 2" x 2" x 4" in size										-1/2"
Heating time (min.)											
To temperature	60	60	60	60	70	63	80	70	50	60	60
While pumping at temp.	45	48	50	45	0	15	75	17	130	90	60
After pumping[6]	-	-	-	-	-	-	-	60	-	-	-
Total time	105	108	110	105	70	78	155	147	180	150	120
Approx. pumping rate (cc./min.)	30	30	30	30	30	30	30	30	23	21	16
Organic matter converted (%)	47	67	76	81	75	85	49	64	75	72	82

[1] Oil shale of the Green River formation from the Anvil Points Mine near Rifle, Colorado; see table 8 for analyses.

[2] Parry shale-oil fraction between 380 F at 585 mm Hg and 445 F at 2 mm Hg.

[3] Parry shale-oil fraction between 445 F at 2 mm Hg and cracking temperature (approx. 650-700 F at 2 mm Hg).

[4] Mixture of Parry shale-oil heavy gas oil and distillation residuum.

[5] Steam, preheated in preheating section of column to 800 F.

[6] Period column was left in heater at 800 F after stopping the pumping and blowing down the pressure.

Table 8.--Material balance and analyses of raw and spent shales for the semi-continuous thermal solution runs

	Run number										
	34	35	37	38	39	41	42	44	45	46	47
Material balance (Wt. %, raw shale basis)											
Input: Raw shale	100	100	100	100	100	100	100	100	100	100	100
Solvent	177	90	148	115	74	125	199	126	192	192	96
Total input	277	190	248	215	174	225	299	226	292	292	196
Output: Spent shale (unwashed)	93	94	85	75	98	83	97	75	87	81	84
Solvent & oil recovered	170	79	146	122	69	122	187	143	199	200	108
Gas & loss	14	17	17	18	7	20	15	8	6	11	4
Total output	277	190	248	215	174	225	299	226	292	292	196
Average gas density (g/cu ft at 585 mm Hg, 75 F)	---	30.5	30.2	30.0	---	---	26.2	28.2	29.8	26.2	24.0
Analyses (Wt. %)											
Raw shale:											
Organic content	21.0	13.5	21.0	21.9	13.9	23.7	17.1	17.4	13.6	21.0	18.1
Mineral CO_2	15.0	18.8	15.4	18.8	21.1	13.6	17.2	20.1	19.7	9.3	16.4
Ash	64.0	67.7	63.6	59.3	65.0	62.7	65.7	62.5	66.7	69.7	65.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Benzene-washed spent shale:											
Residual organic content	12.4	5.0	6.0	5.0	4.1	4.6	9.5	7.0	3.9	7.1	3.8
Mineral CO_2	16.2	19.3	17.4	22.9	19.0	15.9	19.0	22.7	20.8	10.7	18.7
Ash	71.4	75.7	76.6	72.1	76.9	79.5	71.5	70.3	75.3	82.2	77.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Unwashed spent shale:											
Residual organic content	11.8	4.8	5.5	4.1	3.7	3.9	8.4	6.2	3.9	7.1	3.8
Benzene-soluble oil	5.0	4.1	8.6	17.7	10.3	20.0	11.8	10.6	0.3	0.0	0.0
Mineral CO_2	15.4	18.5	15.9	18.9	17.0	12.7	16.7	20.3	20.8	10.7	18.7
Ash	67.8	72.6	70.0	59.3	69.0	63.4	63.1	62.9	75.0	82.2	77.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 9.--Semi-continuous thermal solution of minus ½-inch shale[1]

Run no.	Heating time (min.)	Pumping time (min.)	Conversion of organic matter (%)
	With petroleum kerosine[2] at 800 F		
62	70	45	71
	With light gas oil[3] at 800 F		
53	60	45	67
	With heavy gas oil[4] at 760 F		
67	75	0	75
70	75	30	79
69	75	60	81
68	75	120	73
	With heavy gas oil[4] at 800 F		
65	55	45	69
	With 1/3 heavy gas oil plus 2/3 residuum[5] at 800 F		
51	65	0	41
49	50	15	38
52	65	15	38
48	65	30	42
50	60	40	54

[1] Raw shale No. RRS-46-168, from Anvil Points Mine, Rifle, Colorado; Fischer assay - 26.5 gpt; analysis - 18.1% organic content, 16.7% mineral CO_2, and 65.5% ash. Operating pressure for all runs was 300 psi.

[2] Petroleum kerosine supplied by Standard Oil Company of Indiana.

[3] Parry shale-oil fraction between 380 F at 585 mm Hg and 445 F at 2 mm Hg.

[4] Parry shale-oil fraction between 445 F at 2 mm Hg and cracking temperature (approximately 650-700 F at 2 mm Hg).

[5] Mixture of Parry shale-oil heavy gas oil and distillation residuum.

Table 10.--Products from treatment of various thermal solution solvents in semi-continuous unit[1]

	Petroleum Kerosine[2]		Shale-oil light gas oil[3]		Shale-oil heavy gas oil[4]			1/3 heavy gas oil and 2/3 residuum[5]	
Run number	62	66	56	58	65	64	63	55	59
Solid material charged	Raw shale[6]	Gravel[7]	Raw shale[8]	Gravel[7]	Raw shale[6]	Raw shale[8]	Gravel[7]	Raw shale[8]	Gravel[7]
Heating period (min.)									
Time between 700 & 800 F	---	27	16	36	31	27	31	38	36
Time after reaching 800 F	---	33	10	0	0	11	8	0	0
Total heating time above 700 F	---	60	26	36	31	38	39	38	36
Pumping period (min.)[9]	45	45	45	45	45	40	45	45	45
Total solvent used (as wt. % of solid material charged)	129	95	203	104	137	190	113	192	88
Coke deposited on solids									
(as wt. % of solids)	---	0	5.3	0	---	2.7	0.5	1.3	0.2
(as wt. % of solvent)	---	0	2.6	0	---	1.4	0.4	0.7	0.2
400 F, EP naphtha produced (as wt. % of solvent)									
While heating	5	---	7	7	4	10	5	8	6
While pumping	4	3	10	10	12	14	10	10	11

[1] Operating pressure - 300 psi; mean temperature during pumping period - 796 to 805 F.

[2] Petroleum kerosine supplied by Standard Oil Company of Indiana.

[3] Parry shale-oil fraction between 380 F at 585 mm Hg and 445 F at 2 mm Hg.

[4] Parry shale-oil fraction between 445 F at 2 mm Hg and cracking temperature (approximately 650-700 F at 2 mm Hg).

[5] Mixture of Parry shale-oil heavy gas oil and distillation residuum.

[6] Raw shale No. RRS-46-168, from Anvil Points Mine, Rifle, Colorado; Fischer assay - 26.5 gpt; analysis - 18.1% organic content, 16.7% mineral CO_2, and 65.5% ash; crushed to minus $\frac{1}{2}$-inch.

[7] Fine gravel, analysis - 0.1% volatile material, 1.1% mineral CO_2, and 98.8% ash.

[8] Spent shale from steam extraction runs containing no benzene-soluble oil or oil by Fischer assay.

[9] All of the pumping periods were at temperatures above 800 F, except run 65 in which 6 minutes of the period was at temperatures below 800 F.

Table 11.--Continuous thermal solution runs with recycling of the slurry[1]

Cycle no.	Cumulative residence time (min.)	Cumulative time at temperature (min.)	Conversion of organic matter (%)
		Run No. 5; temperature 750 F	
1	19	14	44
2	34	25	52
3	51	39	64
		Run No. 2; temperature 780 F	
1	19	14	57
2	32	23	72
3	58	45	82
4	80	63	80
5	107	85	79
		Run No. 4; temperature 810 F	
1	6	4	55
2	14	10	76
3	33	26	85
4	50	40	81
		Run No. 3; temperature 850 F	
1	6	4	76
2	15	10	85
3	30	23	76
4	45	36	68
		Run No. 6; temperature 850 F	
1	10	4	75

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[1] Raw shale No. RRS-47-52, from Anvil Points Mine, Rifle, Colorado; Fischer assay - 27 gpt; analysis - 15.8% organic content, 16.7% mineral CO_2, and 67.5% ash; crushed to minus 65 mesh. Solvent was Parry shale-oil heavy gas oil distilling from 445 F at 2 mm Hg to cracking temperature (approximately 650-700 F at 2 mm Hg). Shale to solvent weight ratio of 1.15. Operating pressure of 300 psi.

Table 12.--Calculation of gas production from continuous run 6[1]

By spent shale slurry analysis

(Basis: Ash = 1.000)

	Raw shale slurry	Spent shale slurry
Total ignition loss	1.763	1.692
Mineral CO_2	-0.247	-0.229
Organic matter plus oil	1.516	1.463
Solid organic matter	-0.234	-0.059
Oil in slurry	1.282	1.404

Organic matter extracted = 0.234 - 0.059 =	0.175
Oil produced = 1.404 - 1.282 =	-0.122
Gas produced from organic matter	0.053
Organic matter extracted (wt. %)	74.8
Oil produced (wt. %)	-52.1
Oil produced from organic matter (wt. %)	22.7

* * * * * * * * *

From quantity of gas collected

Weight of organic matter in raw slurry used in run = (7,345 g raw slurry) (37.1% ash in slurry)(23.4% OM on ash basis) = 638 g OM)

Weight of mineral CO_2 in gas = (7,345 g raw slurry) (37.1% ash) (1.8% CO_2 lost from mineral matter on ash basis) = 49 g CO_2.

Weight of gas from organic matter and oil = (Total weight of gas collected) - (pressurizing N_2) - (mineral CO_2 in gas) = 188 - 18 - 49 = 121 g gas.

Percent weight of gas from organic matter and oil (organic matter basis), = $\frac{(121)(100)}{(638)}$ = 18.9%

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[1] Slurry containing [illegible] wt. ratio of oil shale to shale-oil heavy gas oil was heated at 850 F for 4 min.

Table 13.--Thermal cracking products from shale-oil light gas oil[1]
(Basis: Charge stock to each cycle)

Cycle no.	Gas[2] (wt. %)	Naphtha[3] (wt. %)	Light gas oil (wt. %)	Polymer[4] (wt. %)	Loss or gain of product (wt. %)
1	2.8	12.8	70.3	14.3	+ 0.2
2	1.8	10.1	80.5	7.3	- 0.3
3	2.4	7.2	87.7	3.0	+ 0.3
4	1.8	5.6	85.9	6.3	- 0.4
5	1.3	4.4	91.2	3.4	+ 0.3

[1] Parry shale oil, cut between 400 and 675 F (760 mm Hg), recycled through continuous thermal solution unit at 850 F, and 300 psi, total retention time in unit of 10 minutes per pass, approximate time at 850 F of 7 to 8 minutes per pass.

[2] Includes light ends from distillation.

[3] 400 F end point (760 mm Hg).

[4] Residue after distillation of light gas oil.

Table 14.--Percentage conversion of shale[1] organic matter for runs 9 to 12 in continuous thermal solution unit[2]

	Run 9[3]	Run 10[4]	Run 11[3]	Run 12[3]
Conversion to gas and benzene-soluble oil	96[5]	93	91	91

[1] Oil shale No. RRS-48-329, analysis: 14.2% organic matter, 0.5% water (by Fischer assay), 20.4% CO_2, and 64.9% ash. Minus 65 mesh.

[2] Operating temperature - 850 F, operating pressure - 300 psi, retention time (based on specific volume of slurry at 70 F) - 10 minutes, shale to solvent weight ratio - 1.15 approx.

[3] Solvent was the distillable portion of N-T-U shale oil with the 400 F EP naphtha removed.

[4] Solvent was the distillable portion of cracked N-T-U shale oil, with the 400 F EP naphtha removed, after seven cycles of thermal cracking at 850 F and 300 psi with 10-minute retention time based on specific volume at 70 F.

[5] This value may be slightly high, as conversion calculated on the basis of C and H determination of the raw and spent shale gave only 94%.

Table 15.--Composition of charge and product materials for runs 9 to 12 in continuous thermal solution unit[1]

	Run 9	Run 10	Run 11	Run 12
Shale[2]:				
Solvent weight ratio in charge slurry	1.15	1.12	1.15	1.14
Composition of charge slurry (wt. %)				
Organic matter in shale	7.58	7.49	7.57	7.54
Solvent oil	46.54	47.17	46.59	46.82
Water (by Fischer assay)	0.27	0.26	0.27	0.27
Mineral CO_2	10.92	10.80	10.92	10.87
Ash	34.69	34.28	34.65	34.50
Total	100.00	100.00	100.00	100.00
Composition of total products (wt. %)				
Gas	1.33	0.92	2.00	1.59
Naphtha (400 F EP)	3.29	1.82	7.26	7.21
Solvent oil	41.25	43.04	37.85	36.78
Nondistillable oil produced	8.17	8.47	6.48	8.22
Coke on spent shale	0.31	0.49	0.41	0.71
Water (by distillation)	0.29	0.16	0.25	0.25
Mineral CO_2 in spent shale	11.03	10.79	10.80	10.74
Ash in spent shale	34.33	34.31	34.65	34.50
Total	100.00	100.00	100.00	100.00

---

[1] See table 14 for operating conditions and raw shale analysis.

Table 16.--Yield of organic products from runs 9 to 12 in continuous thermal solution unit[1]

	Run 9	Run 11	Run 12	Avg. of runs 9, 11, & 12	Run 10
Composition of total organic products (wt. %)					
Gas	2.4	3.7	2.9	3.0	1.7
Naphtha (400 F EP)	6.1	13.4	13.2	10.9	3.3
Solvent oil	75.9	69.7	67.5	71.0	78.6
Nondistillable oil	15.0	11.9	15.1	14.0	15.5
Coke	0.6	1.3	1.3	1.1	0.9
Total	100.0	100.0	100.0	100.0	100.0
Net yields of organic products (wt. % organic matter)[2]					
Gas	17	26	21	21	12
Naphtha (400 F EP)	42	96	95	78	24
Solvent oil (lost during process)	-68	-116	-134	-107	-55
Nondistillable oil	105	85	109	100	112
Coke	4	9	9	8	7
Total	100	100	100	100	100

---

[1] See table 14 for operating conditions and raw shale analysis.

[2] Calculated from composition of total organic products, of which 14.0% was from shale organic matter and 86% from the original solvent.

Table 17.--Composition of gas from runs 9 to 12 in continuous thermal solution unit[1]

Gas component	Gas analysis (vol. %)[2]				
	Run 9	Run 11	Run 12	Avg. of runs 9, 11, & 12	Run 10
CH_4	48	48	48	48	43
C_2H_6	11	11	13	11	10
C_3H_8	5	4	5	5	4
C_4H_{10+}	2	2	2	2	2
C_nH_{2n}	5	5	5	5	4
H_2S[3]	--	1	1	1	--
N_2	--	2	3	2	6
CO	7	5	5	6	5
CO_2[3]	8	10	9	9	11
H_2	14	12	9	11	15
Total	100	100	100	100	100

---

[1] See table 14 for operating conditions.

[2] Calculated helium-free.

[3] Values may be low due to samples being collected over water.

Table 18.—Batch hydrogenation[1] of oil shale and shale-oil gas oil slurry[2] with various maximum temperatures

Run no.	Maximum temperature (F)	Maximum pressure[3] (psi)	Time above 650 F (min.)	Conversion of organic matter (%)	Hydrogen consumption by the shale[5] (Std cu ft H_2 per ton shale)	Hydrogen consumption by the shale[5] (wt. % organic matter)	Hydrocarbon gas production[6] (Std cu ft H_2 per ton shale)
19	750	3925	65	63	440	0.73	260
20	766	3935	72	71	590	1.00	370
17	780	4620	78	83	510	0.85	590
18	803	3990	89	93	680	1.13	780
22	830	3975	100	100	750	1.27	1030
23	843	3965	110	100	800	1.34	1400

[1] In 4-3/8 inch series hydrogenation unit.

[2] Slurry: 1.15 wt. ratio of raw shale to solvent.
Raw shale: No. RRS-48-108; 15.2% organic content, 0.5% water by Fischer assay, 20.2% mineral CO_2, and 64.1% ash; ground to minus 65 mesh.
Solvent: No. RRS-48-105; N-T-U gas oil.

[3] Cold initial hydrogen pressure - 2000 psi, no hydrogen added during the run.

[4] Converted to gas and benzene-soluble material.

[5] Calculated on assumption of proportional hydrogen consumption by organic matter in shale and by solvent.

[6] Gas production from both shale and solvent.

Table 19.--Analyses[1] of gases from slurry and solvent oil batch hydrogenation[2]

	Oil shale and shale-oil gas oil slurry						Solvent only
	Run 19	Run 20	Run 17	Run 18	Run 22	Run 23	Run 21
Maximum temperature (F)	750	766	780	803	830	843	775
Analysis (vol. %, H_2 - free):							
CH_4	43	37	38	52	50	50	56
C_2H_6	20	16	26	20	17	18	23
C_3H_8	10	8	11	9	9	10	12
C_4H_{10}	7	3	4	4	4	5	5
C_5H_{12}	0	0	1	2	0	0	0
Olefins	7	3	1	3	1	1	1
CO_2	0	3	5	5	4	4	1
CO	0	10	4	5	15	12	1
N_2	13	20	10	0	0	0	1
Total	100	100	100	100	100	100	100
H_2 in total sample (%)	97.0	94.1	93.0	90.3	85.7	80.8	84.8

[1] Due to high dilution of gas sample with hydrogen the possible error of these percentage values is about ± 2.

[2] Gas passed through acetone and dry ice trap, caustic scrubber for H_2S removal, and wet test meter, and collected over water. See table 18 for other operating details.

Table 20.--Batch thermal solution[1] of oil shale[2] with various pressures of hydrogen and helium

Run no.	Initial cold pressure[3] (psi)	Maximum hot pressure (psi)	Maximum temp. (F)	Time above 650 F (min.)	Conversion of organic matter[4] (%)	Gas production[4] (wt. % organic matter
			With hydrogen pressure			
23	2005	3695	843	110	100	38
26	1490	3045	842	110	96	38
27	1000	2185	840	110	93	35
25	1000	2100	840	108	93	38
28	510	1595	839	112	75	43
			With helium pressure			
31	1400	4180	840	113	51	49
29	1200	3600	837	110	63	47
30	1000	3170	838	112	57	48
32	650	2530	841	113	50	46

---

[1] In 4-3/8 inch series batch hydrogenation unit.

[2] Shale No. RRS-48-108, minus 65 mesh; 15.2% organic matter, 0.5% water (by Fischer assay), 20.2% CO_2, and 64.1% ash.
Oil No. RRS-48-105, N-T-U shale-oil gas oil.
Slurry 1.15 weight ratio of shale to oil.

[3] Cold pressure measured in temperature range of 70 to 90 F.

[4] To gas and benzene-soluble products.

[5] Includes only gas passing through an acetone and dry ice trap.

Table 21.--Batch hydrogenation of oil shale[1] in micro reactor[2] at various pressures and with various solvent oils

Run no.	Reactor pressure (psi)[3] Cold Initial	Maximum Operating	Cold Final	Solvent[4]	Maximum operating temp. (F)	Conversion of organic matter[5] (%)	Hydrogen consumption (std cu ft)	Gas made (wt. % organic matter)[6]
50	500	1390	395	Light	845	91	0.04	11
51	500	1210	375	Medium	845	97	0.05	10
52	500	1150	370	Heavy	845	97	0.05	14
53	1000	2230	835	Light	845	84	0.04	10
54	1015	2080	810	Medium	850	95	0.07	15
55	990	2060	775	Heavy	855	95	0.07	15
59	2015	4400	1780	Light	875	79	0.11	7
60	2000	4100	1720	Medium	860	81	0.08	11
61	1990	4000	1635	Heavy	865	84	0.20	8
56[7]	1000	2600	1000	Light	860	85	0.00	6
57[7]	1000	2630	1005	Medium	865	88	0.00	10
58[7]	1000	2500	980	Heavy	868	83	0.00	4

[1] Raw shale RRS-48-329; analysis - 14.2% organic matter (by ignition loss method), 0.5% water (by Fischer assay), 20.4% mineral CO_2, and 64.9% ash. Shale to solvent weight ratio of 1.15, with slurry charge of about 100 g for each run. Shale ground to pass 65-mesh sieve.

[2] Runs made in 183-cc reactor with shaking except for runs 56, 57, and 58; average heating time - 15 to 20 minutes to heat to 825 F, 15 to 20 minutes above 825 F, and 2 to 3 minutes to cool from 825 to 650 F by quenching.

[3] Cold initial pressure measured at 75 to 79 F, cold final pressure measured at 72 to 77 F, except run 56 which was at 69 F.

[4] Solvents were fractions of a non-catalytically hydrogenated N-T-U shale oil; light fraction RRS-48-417-17, boiling range 446-530 F at 760 mm Hg; medium fraction RRS-48-417-18, boiling range 530-608F at 760 mm Hg; heavy fraction RRS-48-417-19, boiling range 608 F at 760 mm Hg to 490 F at 1 mm Hg.

[5] Conversion to gas and benzene-soluble products.

[6] Includes CO_2 from shale mineral matter.

[7] Runs made without shaking.

Table 22.--Composition of product gas from batch hydrogenation of oil shale in micro reactor[1]

Run no.	Volume percent of hydrogen-free gas[2]									
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_nH_{2n}	H_2S	N_2	CO	CO_2[3]	Total
50	39	12	7	2	1	7	1	7	24	100
51	46	12	5	2	2	4	3	5	21	100
52	43	14	7	3	1	5	2	3	22	100
Avg.	44	13	6	2	1	5	2	5	22	100
53	34	10	5	7	1	7	1	16	19	100
54	44	13	6	2	1	4	1	11	18	100
55	47	13	6	2	1	5	1	7	18	100
Avg.	42	12	6	4	1	5	1	11	18	100
59	35	8	5	tr.	3	5	0	30	14	100
60	45	11	5	2	tr.	4	tr.	21	12	100
61	46	12	6	2	0	5	0	16	13	100
Avg.	43	10	5	1	1	5	0	22	13	100
56	42	15	6	1	1	3	3	0	29	100
57	43	16	7	4	3	4	0	1	22	100
58	38	14	11	4	4	4	0	0	25	100
Avg.	41	15	8	3	3	4	1	0	25	100

[1] See table 21 for operating conditions.

[2] Gas was collected in evacuated stainless steel holder.

[3] Includes CO_2 produced from mineral matter of shale.

Table 23.--Batch hydrogenation of oil shale[1] in micro reactor[2] at various temperatures and heating periods

Run no.	Average slurry temp. (F)	Time at avg. temp.[3] (min.)	Maximum pressure[4] (psi)	Conversion of organic matter (%)	Organic products (% organic matter) Gas[5]	Distillable oil[6]	Non-distillable oil[7]	Coke	Total
84	753	120	1175	73	9	-19	83	27[8]	100
85	814	30	1175	86	10	-33	109	14[8]	100
86	814	60	1150	97	--	--	(75)[9]	3	--
95	814	60	1090	97	11	19	67	3	100
93	862	6	1200	92	7	1	84	8[8]	100
87	865	11	1180	97	21	2	74	3	100
88	867	30	1360	91	28	-8	71	9	100
94	920	3	1450	94	22	9	63	6	100
89	917	5	1550	92	21	-5	76	8	100
90	922	15	2160	77	56	-54	75	23	100

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[1] Raw shale RRS-48-329; analysis - 14.2% organic matter, 0.5% water (by Fischer assay), 20.4% mineral CO_2, and 64.9% ash; minus 65 mesh. Solvent oil RRS-48-551, non-catalytically hydrogenated shale-oil gas oil, distillation range - 350 F at 40 mm Hg to 500 F at 1 mm Hg, contained 1.7% nondistillable oil. Shale to solvent weight ratio of 1.15, with slurry charge of about 100 g for each run.

[2] 183-cc micro reaction vessel, heated in shaker unit.

[3] 11 to 18 minutes additional time was required to heat from 650 F to run temperature and 3 minutes to cool back to 650 F.

[4] Initial cold hydrogen pressure was 500 psi at 70 to 78 F.

[5] Includes gas measured when pressure was released on reactor and gas liberated from the slurry on standing at room temperature for 8 hours.

[6] Determined by difference.

[7] Residue from micro distillation of 2 mm Hg to the cracking temperature.

[8] Includes unconverted shale organic matter.

[9] An approximation.

Table 24.--Batch hydrogenation[1] of oil shale[2] with flash separation of the oil

Run no.	Maximum temperature (F)	Maximum pressure (psi)[3]	Time at pressure above 650 F[4] (min.)	Conversion of organic matter[5] (%)	Removal of by flashing[6] (%)
35	851	4225	40	83	65
37	851	4140	42	82	74
34	850	4325	98	87	--[7]
38	831	4280	93	90	--[7]

[1] In 4-3/8 inch series reaction vessel.

[2] Raw shale No. RRS-48-108; minus 65 mesh; 15.2% organic matter, 0.5% water (by Fischer assay), 20.2% CO_2, and 64.1% ash.
Oil: No. RRS-48-275, N-T-U shale-oil kerosine.
Slurry: 1.15 weight ratio of shale to oil.

[3] Cold pressure of 2000 psi measured in the temperature range of 70 to 90 F.

[4] Time measured to blow-down for runs 35 and 37. Run 37 heated to 920 F during blow-down.

[5] To gas and benzene-soluble material.

[6] Removal of organic matter as gas and oil distilled from shale during flashing.

[7] Reactor cooled to room temperature before discharging.

Table 25.--Material balance for 10,000-bpd thermal solution plant, without hydrogenation.

Input

Raw shale (Fischer assay--30 gpt, 17.0% organic matter)		14,000 tpd
Organic matter	2,380 tpd	
Mineral matter	11,620	
Total	14,000 tpd	

Circulating

Solvent oil (66.7 wt % of raw shale)	9,300 tpd

Output

	From OM (tpd)	From solvent (tpd)	Total	
			(tpd)	(% OM)
Dry gas	238	93	331	13.9
Light ends	28	65	93	3.9
Naphtha	163	493	656	27.6
Solvent	1,116	(8,277) (-9,300)	93	3.9
Residuum	571	279	850	35.7
Coke	264	93	357	15.0
Total	2,380	0	2,380	100.0

Mineral matter in spent shale	11,620 tpd
Total output	14,000 tpd

Table 26.--Net yield of liquid products from 10,000-bpd plant.

	Sp g	Bbl/ton	TPD	Bbl/day
Light ends	0.60	9.5	93	884
Naphtha	0.75	7.6	626[1]	4,760
Solvent[2]	0.92	6.2	93	576
Residuum	1.00	5.7	755[3]	4,300
Totals			1,567	10,520

[1] Output of 656 tpd, less 30 tpd lost in washing spent shale.

[2] Consisting of all distillate heavier than naphtha.

[3] Output of 850 tpd, less 95 tpd used in plant as fuel.

Table 27.--Summary of operating costs for 10,000-bpd plant, without hydrogenation.

	$/year	$/ton raw shale[1]
Plant expense		
Power		0.17
Water (2,400,000 gal/day at $0.25 per M gal)		0.04
Operating labor		0.16
Maintenance, materials and labor (4% of equipment cost)	1,288,000	0.31
Works expense (clerical, accounting and laboratory costs, extra pay, engineering, superintendent's expense, plant protection and safety, storehouse and shipping expense; 100% of operating labor)		0.16
Process materials		0.05
Total plant expense		$0.89
Raw material expense		
Mining, crushing to minus 2-inch, and transporting raw shale to plant site		$0.85
Overhead expense		
Amortization of capital investment (10% of investment)	5,862,000	1.40
Insurance and taxes (2% of investment)	1,172,000	0.28
Executive and administrative costs (1% of investment)	586,000	0.14
Total overhead expense		$1.82
Total operating cost		$3.56

Operating cost for 10,520 bpd of liquid products

$$= \frac{(3.56)(14,000)}{(10,520)} = \$4.74 \text{ per bbl.}$$

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[1] Costs per ton, when calculated from annual charges, are based on 14,000 tpd and 300 operating days per year.

Table 28.--Estimation of equipment costs and power requirements for thermal solution plant, with hydrogenation

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Hydrogen plant

Hydrogen requirement estimated on basis of experimental work; 800 std cu ft per ton raw shale or 11,200 M std cu ft per day.

Unit hydrogen plant cost (data from Estimate of Plant and Production Costs of Hydrogen from Coal and Natural Gas, by E. E. Donath, Aug. 1, 1947) = $\frac{(22,000,000)}{130,000)}$ = \$169 per M std cu ft of H_2 per day.

Hydrogen plant cost = (11,200) (169) = \$1,900,000.

Slurry preparation

Equipment cost (data from Estimated Cost of Shale Oil by the Thermal Solution Process on a 10,000 - BPD Basis, by W. I. Barnet, May 7, 1948) including installation, foundations, piping, etc. = \$2,300,000.

Power requirement = 13,600 hp.

High-pressure slurry pumps

Unit cost (from Preliminary Estimates on Liquefaction of Utah Coal for Fuel, by J. A. Markovits, et al, May 30, 1947) = $\frac{(5,000,000)}{(535)\ (24)}$ = \$390 per tpd slurry capacity.

Equipment cost for 23,300 tpd slurry = (23,300)(390) = \$9,100,000.

Power requirement = $\frac{(4,000)\ (23,300)}{(535)\ (24)}$ = 7,300 hp.

Stalls, converters, and exchangers

Unit cost (from J. A. Markovits, et al) = $\frac{(12,000,000)}{(4)(1060)}$ = \$2,830 per cu ft converter capacity. (Assume 15-min. retnetion time, based on specific volume of slurry at 70 F).

Convertor volume required for 95,000 bpd slurry = $\frac{(95,000)\ (42)\ (15)}{(7.48)\ (1440)}$ = 5,560 cu ft.

Equipment cost = (5,560) (2,830) = \$15,700,000.

Gas scrubbing

Unit cost (from J. A. Markovits, et al) = $\frac{(4,000,000)}{(535)\ (24)}$ = \$310 per tpd slurry

Equipment cost = (23,300) (230) = \$5,400,000.

Table 28.--Estimation of equipment costs and power requirements for thermal solution plant, with hydrogenation--Continued

Power requirement = $\frac{(1,600)\ (23,300)}{(535)\ (24)}$ = 2,900 hp.

Gas recycle

Unit cost (from J. A. Markovits, et al) = $\frac{(3,000,000)}{(535)\ (24)}$ = \$230 per tpd slurry.

Equipment cost = (23,300) (230) = \$5,400,000.

Power requirement = $\frac{(6,000)\ (23,300)}{(0.746)(535)(24)}$ = 14,600 hp.

Oil recovery and distillation

Equipment cost for oil recovery system, not including distillation unit (from thermal solution cost estimate) but including installation, foundations, piping, etc. = \$12,400,000.

Distillation equipment for topping naphtha from approximately 115,000 bpd of oil at unit cost of \$50 per bpd = \$5,800,000.

Total cost of oil recovery and distillation equipment = \$18,200,000.

Power requirement = 2,100 hp.

Miscellaneous

Instruments, laboratory and office equipment, and furniture, tools, etc. = \$2,000,000.

Summary of equipment cost and power requirement

	$	HP
Hydrogen plant	1,900,000	1/
Slurry preparation	2,300,000	13,600
High-pressure slurry pumps	9,100,000	7,300
Stalls, converters and exchangers	15,700,000	-
Gas scrubbing	7,200,000	2,900
Gas recycle	5,400,000	14,600
Oil recovery and distillation	18,200,000	2,100
Miscellaneous	2,000,000	-
Total	61,800,000	40,500

Estimated total plant cost (at 182% of equipment cost) = (61,800,000) (1.82) = \$112,000,000.

Power cost (at \$0.008 per kwhr) = $\frac{(40,500)(0.746)(24)(0.008)}{(14,000)}$ = \$0.41 per ton of raw shale.

1/ Included in hydrogen unit cost.

Table 29.--Hydrogen cost.

Hydrogen unit cost (from J. A. Markovits, et al) scrubbed and compressed = \$0.25 per M std cu ft.

Hydrogen cost (including hydrogen plant maintenance and overhead expense) = (0.25) (0.800) = \$0.20 per ton of raw shale.

Overhead expense and maintenance cost of hydrogen plant

$$= \frac{(1,900,000)\ (0.17)}{(14,000)\ (300)} = \$0.08 \text{ per ton of raw shale.}$$

Hydrogen cost (not including hydrogen plant maintenance and overhead expense)

= 0.20 - 0.08 = \$0.12 per ton of raw shale.

Table 30.--Summary of operating costs for 13,600-bpd plant, with hydrogenation

Plant expense	$/year	$/ton[1] raw shale
Power (not including hydrogen plant)		$0.41
Water (not including hydrogen plant)		0.04
Operating labor (not including hydrogen plant		0.16
Maintenance, materials and labor (4% of equipment cost)	$2,470,000	0.59
Works expense (not including hydrogen plant)		0.16
Hydrogen (scrubbed and compressed, not including maintenance and overhead expense)		0.12
Process materials other than hydrogen		0.05
Total plant expense[2]		$1.53
Raw material expense		
Mining, crushing to minus 2-inch, and transporting raw shale to plant site		$0.85
Overhead expense		
Amortization of capital investment (10% of investment)	$11,200,000	2.67
Insurance and taxes (2% of investment)	2,240,000	0.53
Executive and administrative costs (1% of investment)	1,120,000	0.27
Total overhead expense		$3.47
Total operating cost		$5.85

(Assuming 85% conversion of the organic content of the shale to oil with average specific gravity of 0.85, production of oil = 13,600 bpd.)

$$\text{Cost of oil} = \frac{(5.85)\ (14,000)}{(13,600)} = \$6.00 \text{ per bbl.}$$

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[1] Costs per ton, when calculated from annual charges, are based on 14,000 tpd and 300 operating days per year.

[2] No charge is included for fuel as it is assumed that the gas and coke will provide sufficient fuel for the plant. The hydrogen cost includes a charge for raw material.

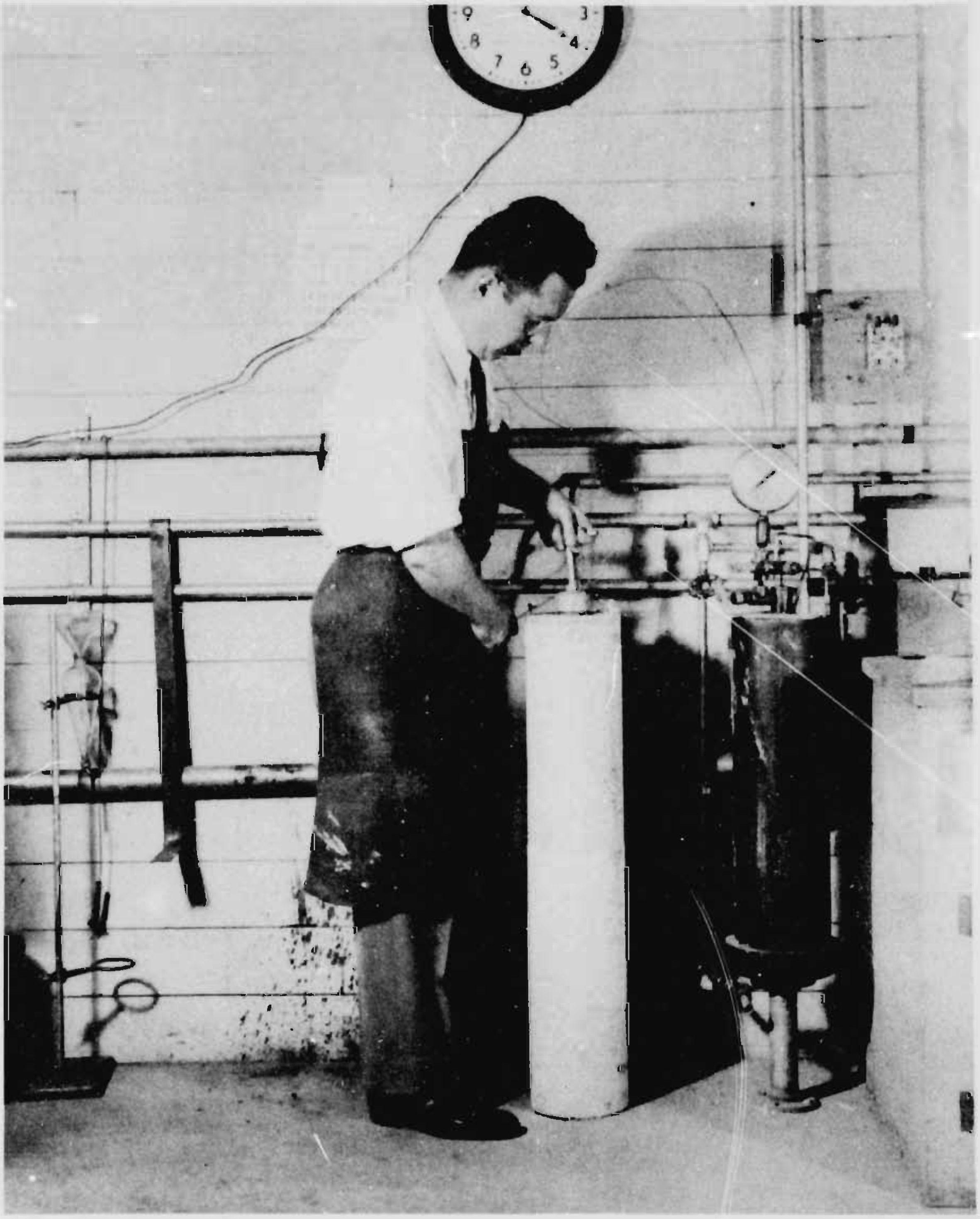


Figure 1. - Batch thermal solution apparatus.

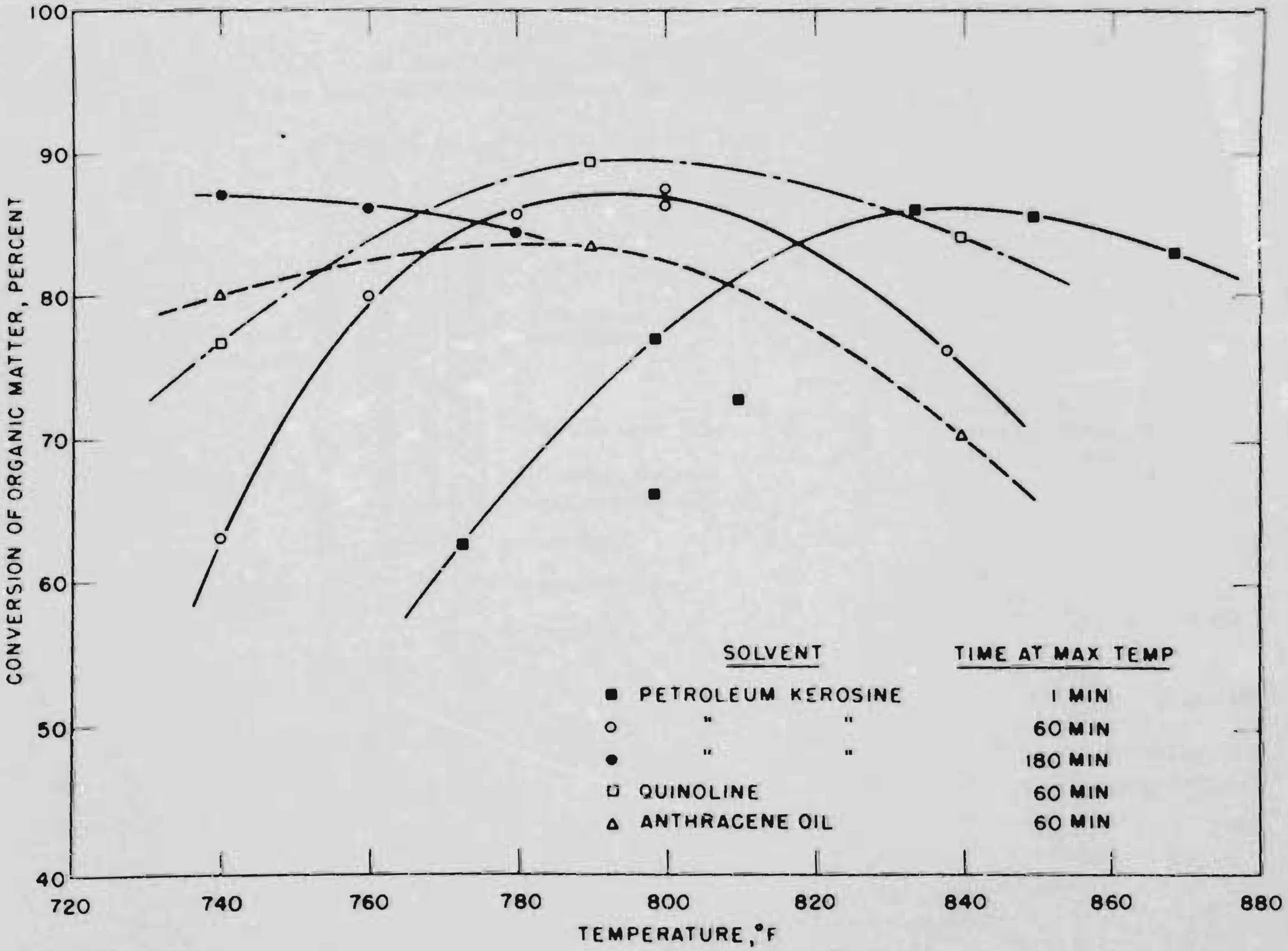


Figure 2. —THERMAL SOLUTION OF OIL SHALE IN A BATCH AUTOCLAVE

Figure 3
DIAGRAMMATIC SKETCH OF
SEMI-CONTINUOUS THERMAL SOLUTION UNIT NO. I

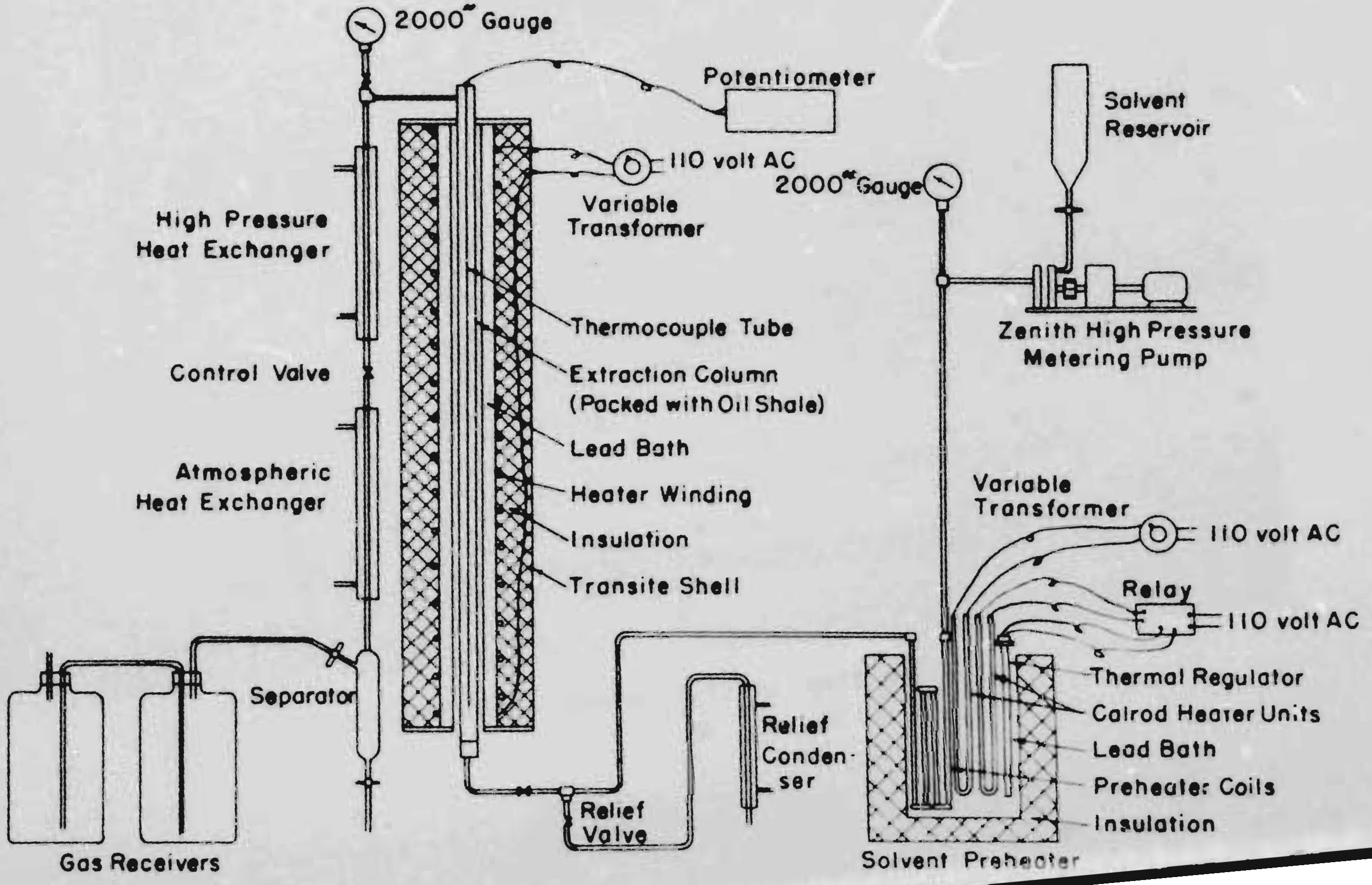
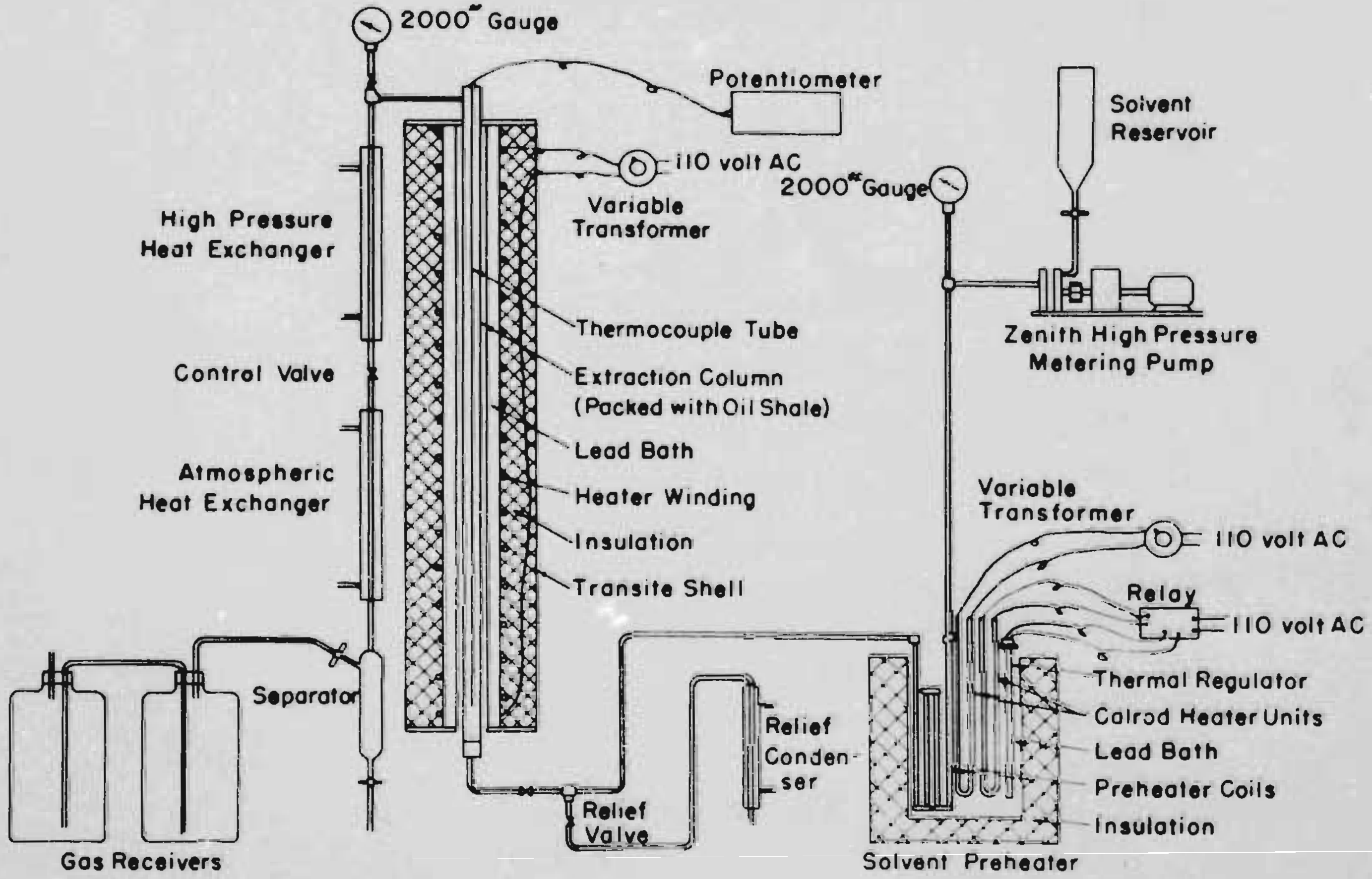


Figure 3
DIAGRAMMATIC SKETCH OF
SEMI-CONTINUOUS THERMAL SOLUTION UNIT NO. I



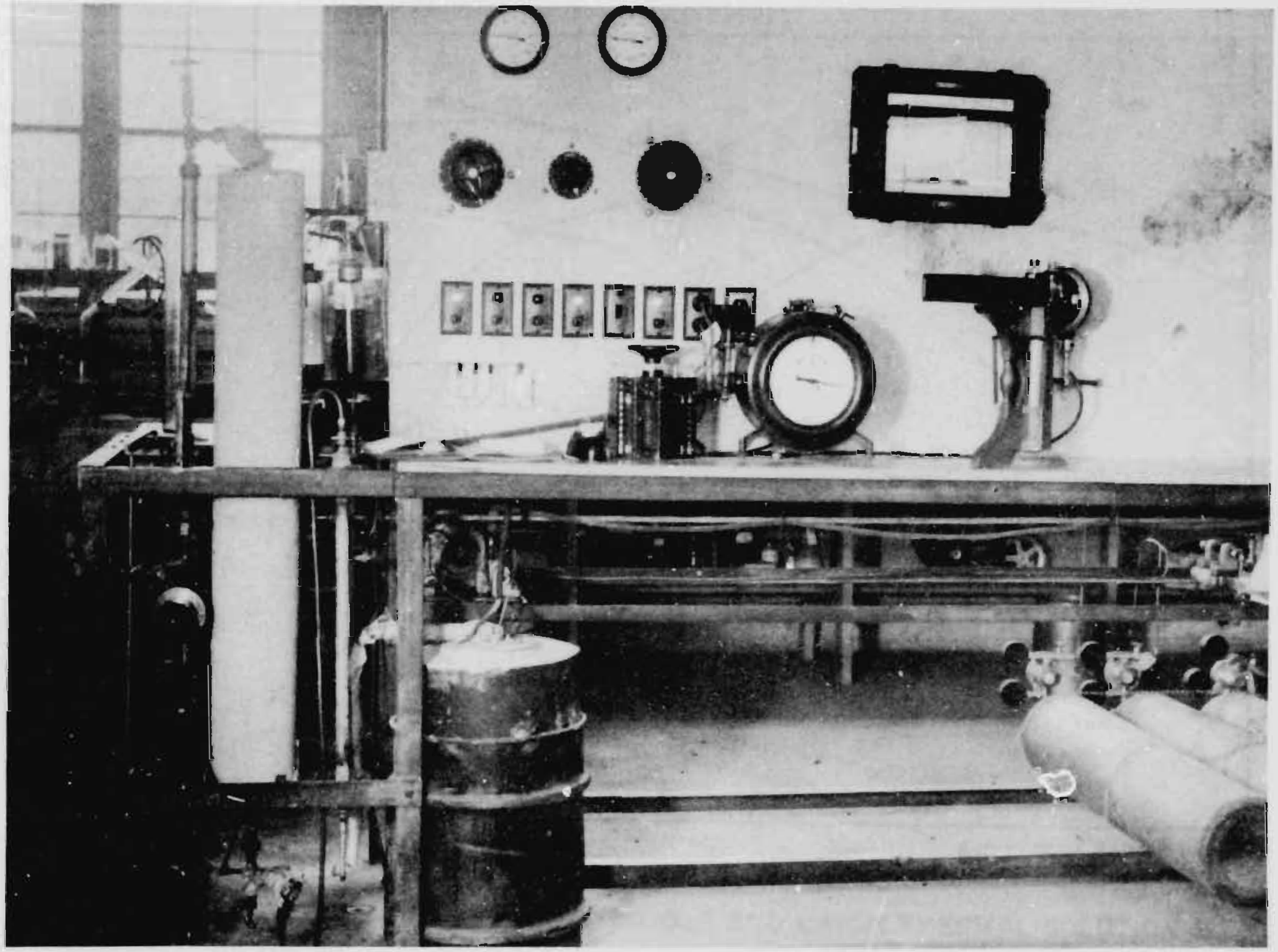


Figure 4. - Semi-continuous thermal solution unit No. 1.

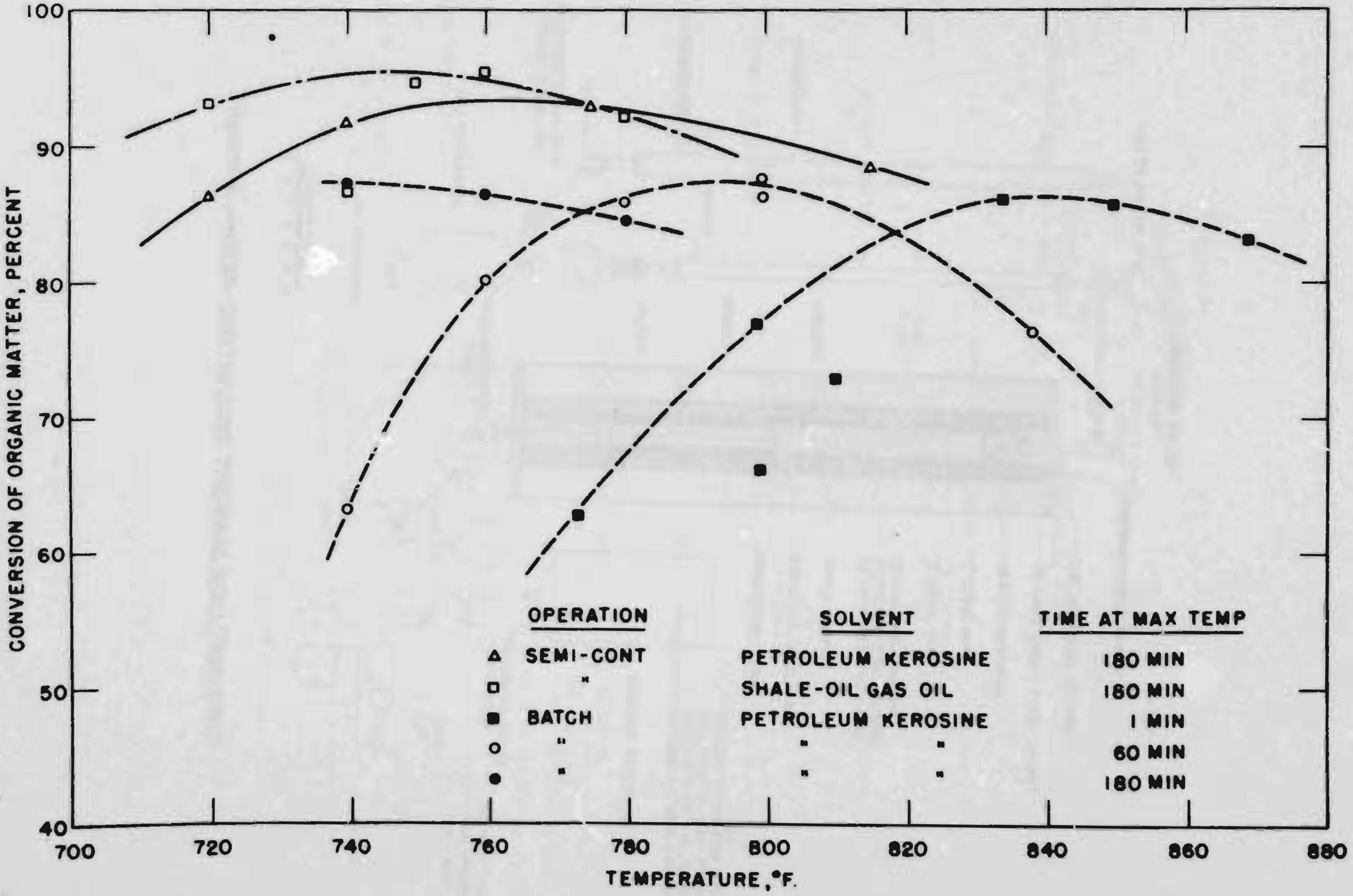


Figure 5.-- COMPARISON OF SEMI-CONTINUOUS AND BATCH THERMAL SOLUTION OF OIL SHALE.

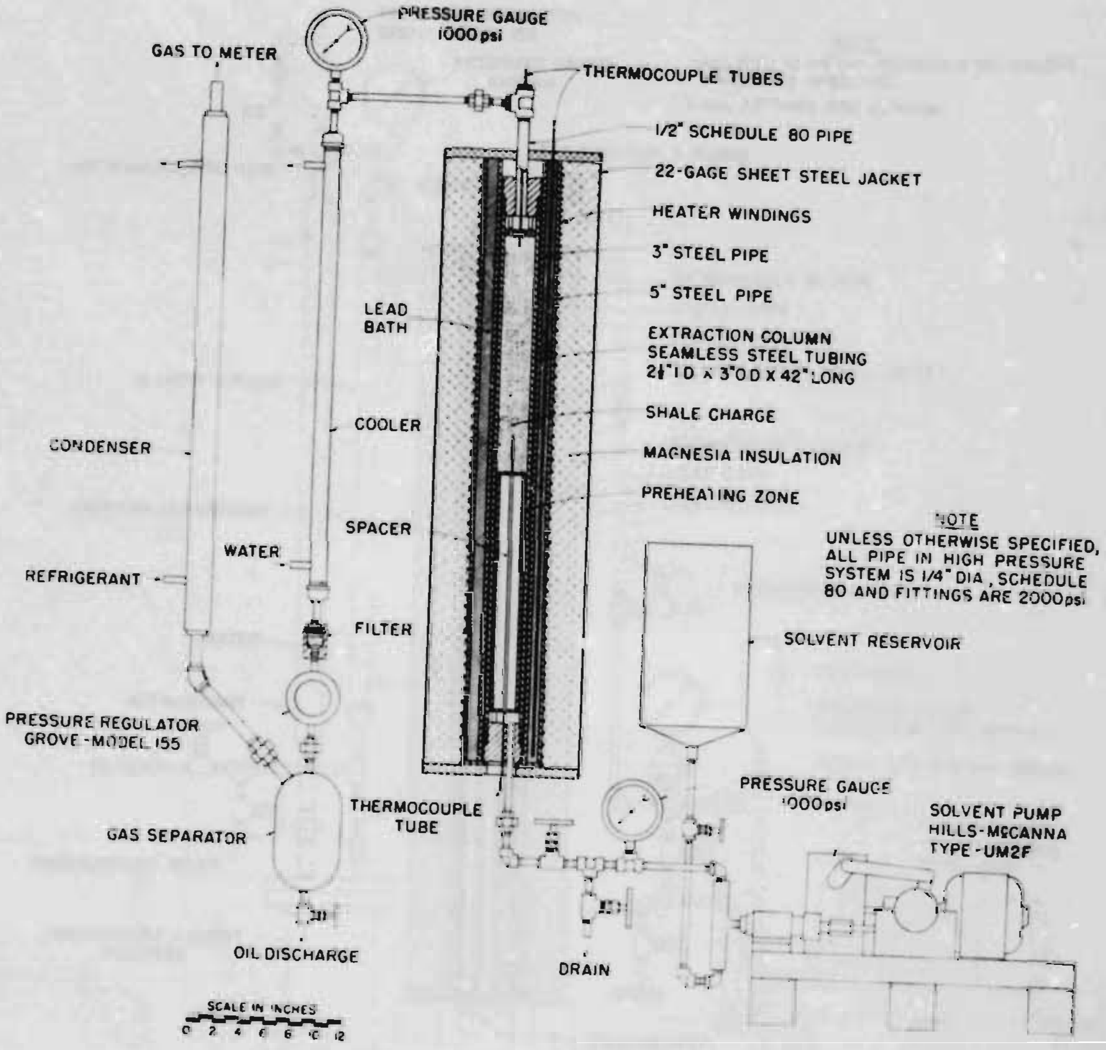


Figure 6.--SEMI-CONTINUOUS THERMAL SOLUTION UNIT

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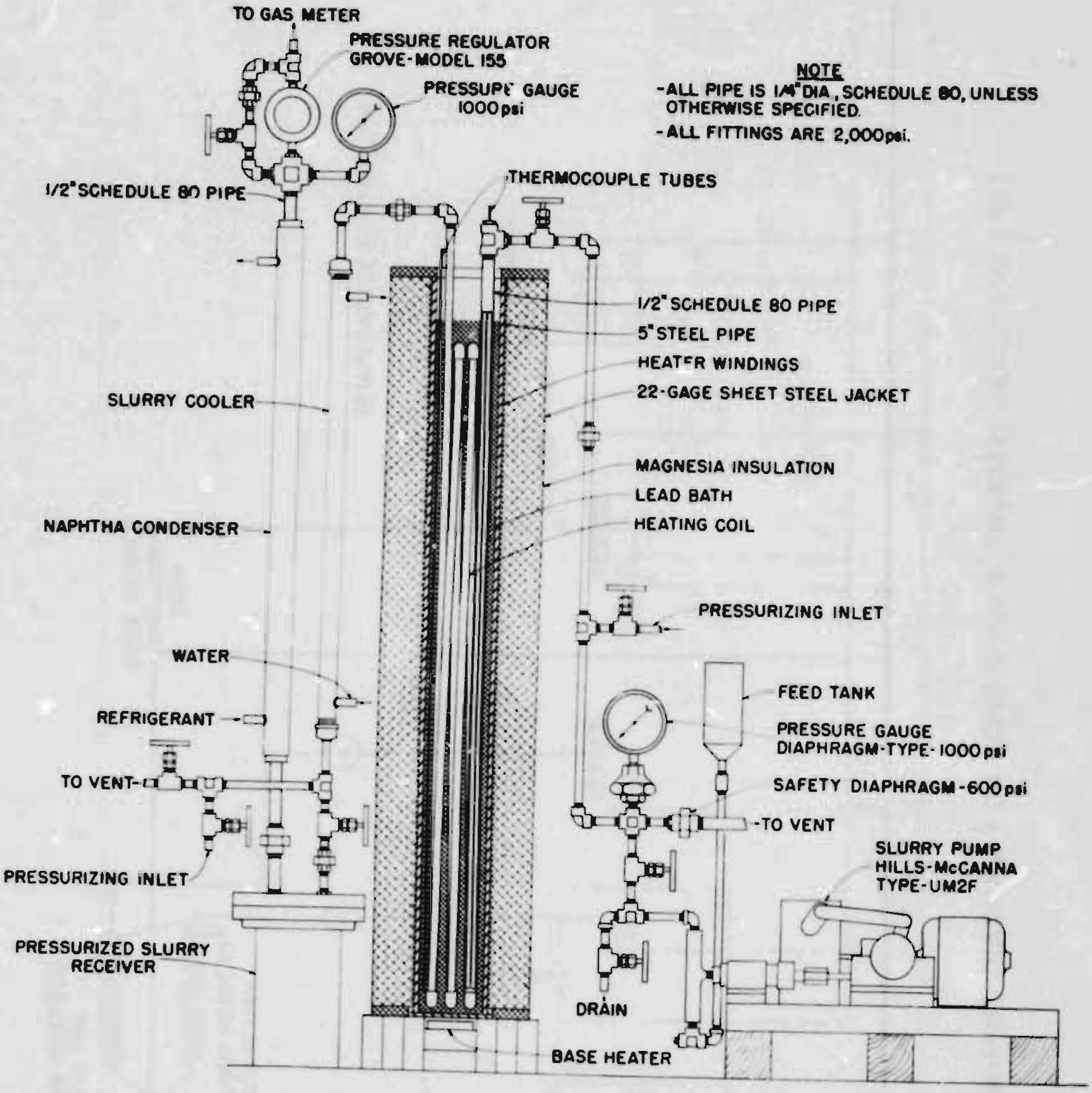

NOTE
- ALL PIPE IS 1/4" DIA, SCHEDULE 80, UNLESS OTHERWISE SPECIFIED.
- ALL FITTINGS ARE 2,000 psi.

Figure 7.—CONTINUOUS THERMAL SOLUTION UNIT

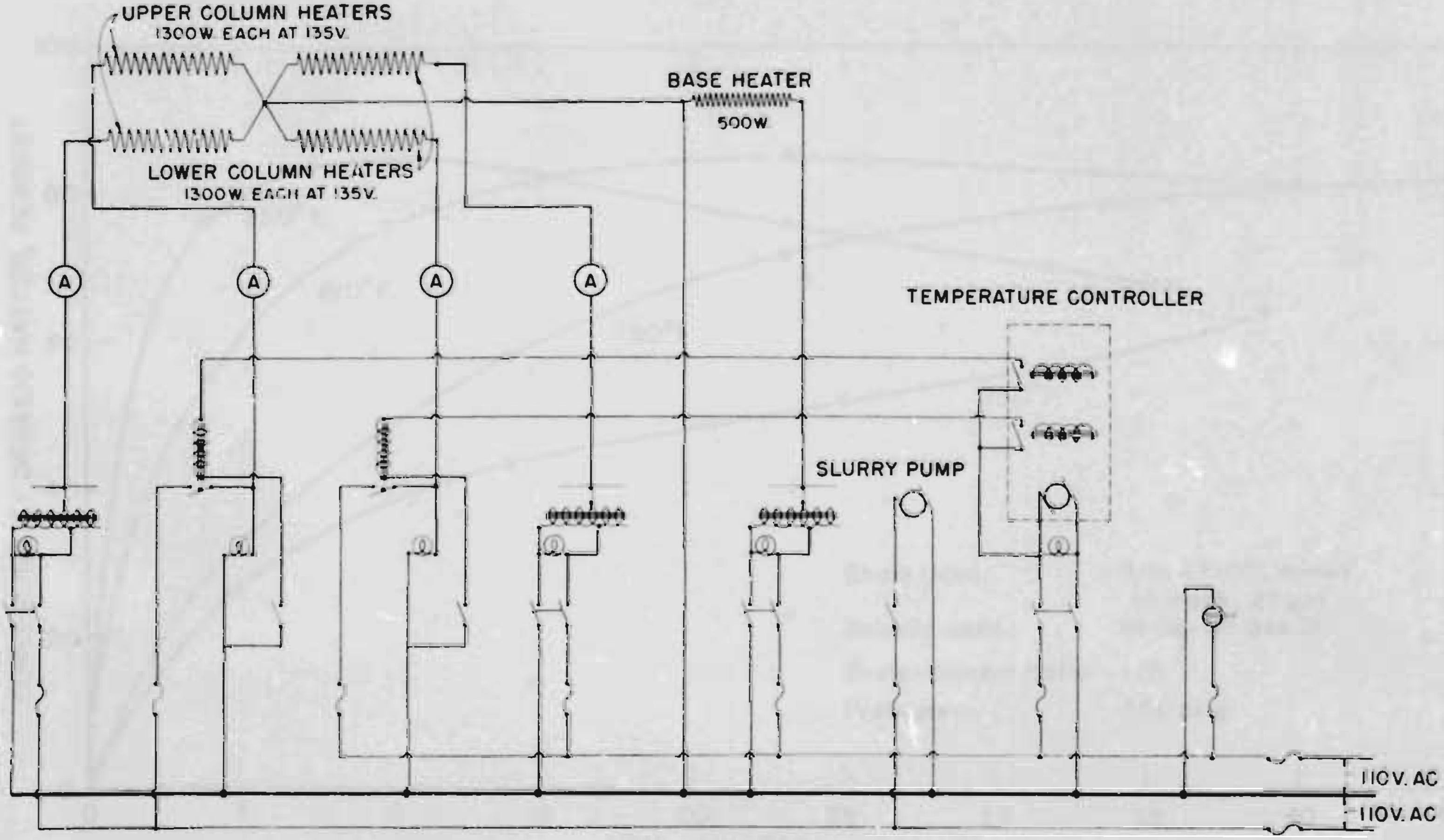

Figure 8-WIRING DIAGRAM FOR CONTINUOUS THERMAL SOLUTION UNIT

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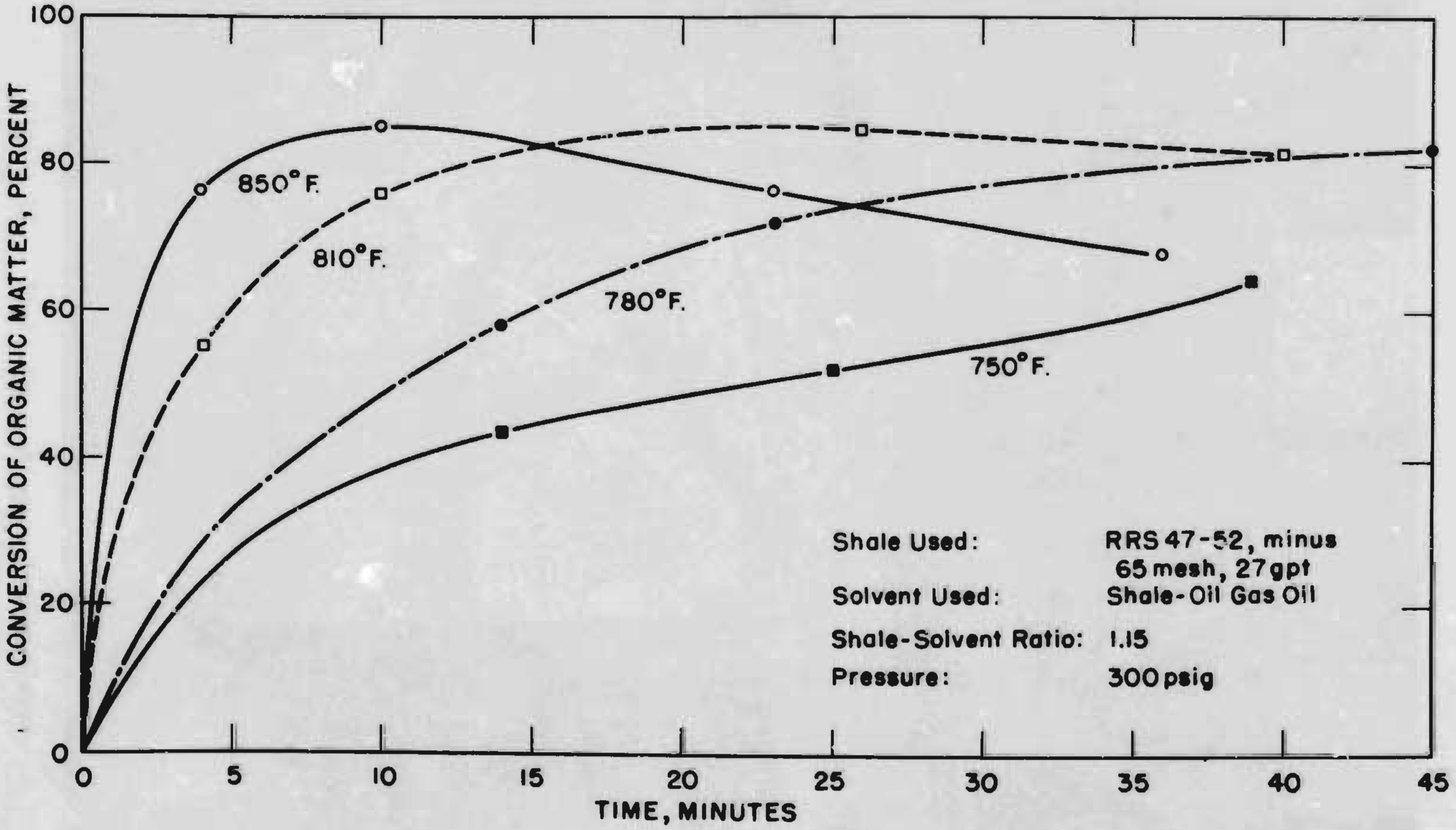

Shale Used: RRS 47-52, minus 65 mesh, 27 gpt
Solvent Used: Shale-Oil Gas Oil
Shale-Solvent Ratio: 1.15
Pressure: 300 psig

Figure 9.--THERMAL SOLUTION OF OIL SHALE IN CONTINUOUS UNIT.

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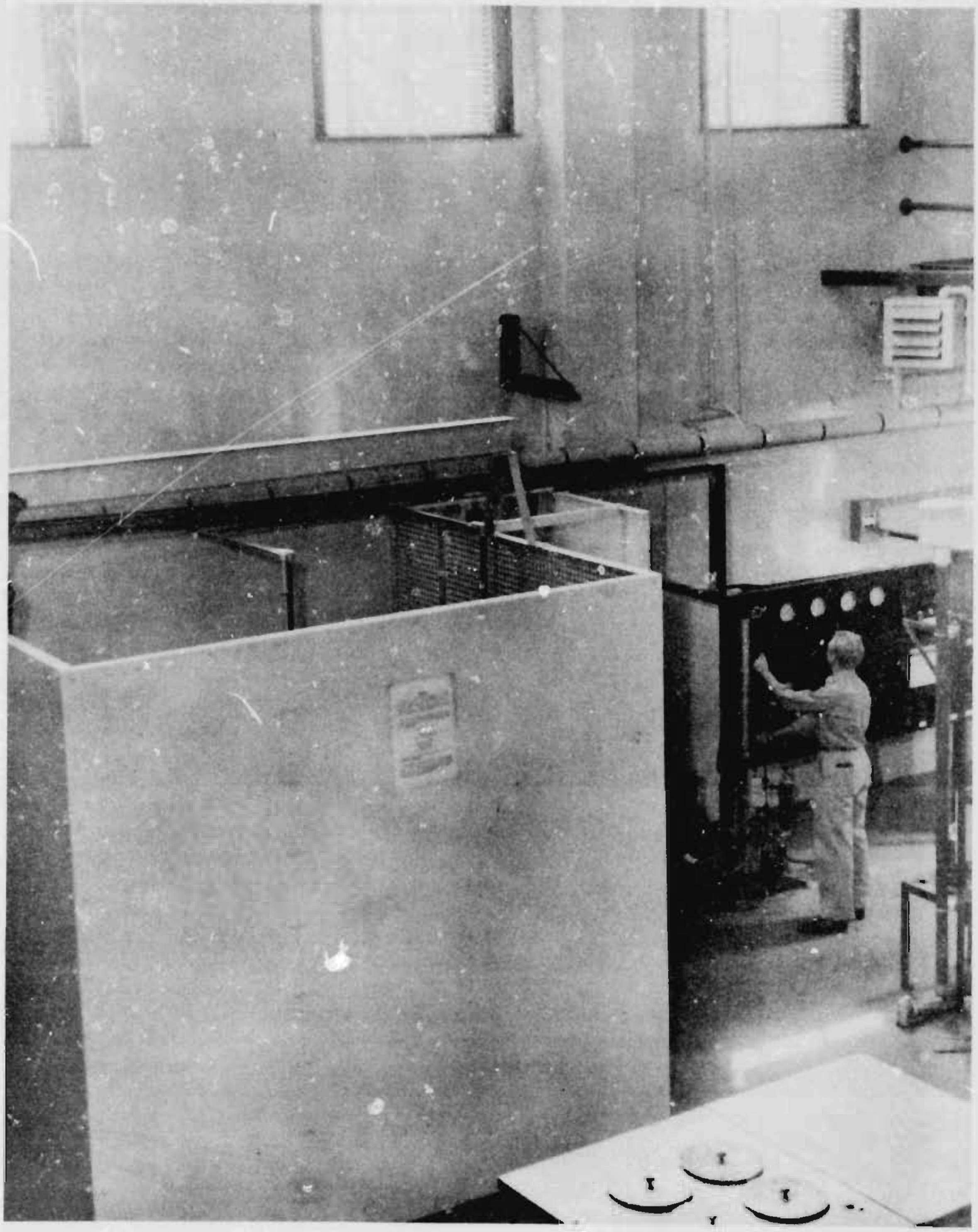

Figure 10. - Stall for hydrogenation equipment.

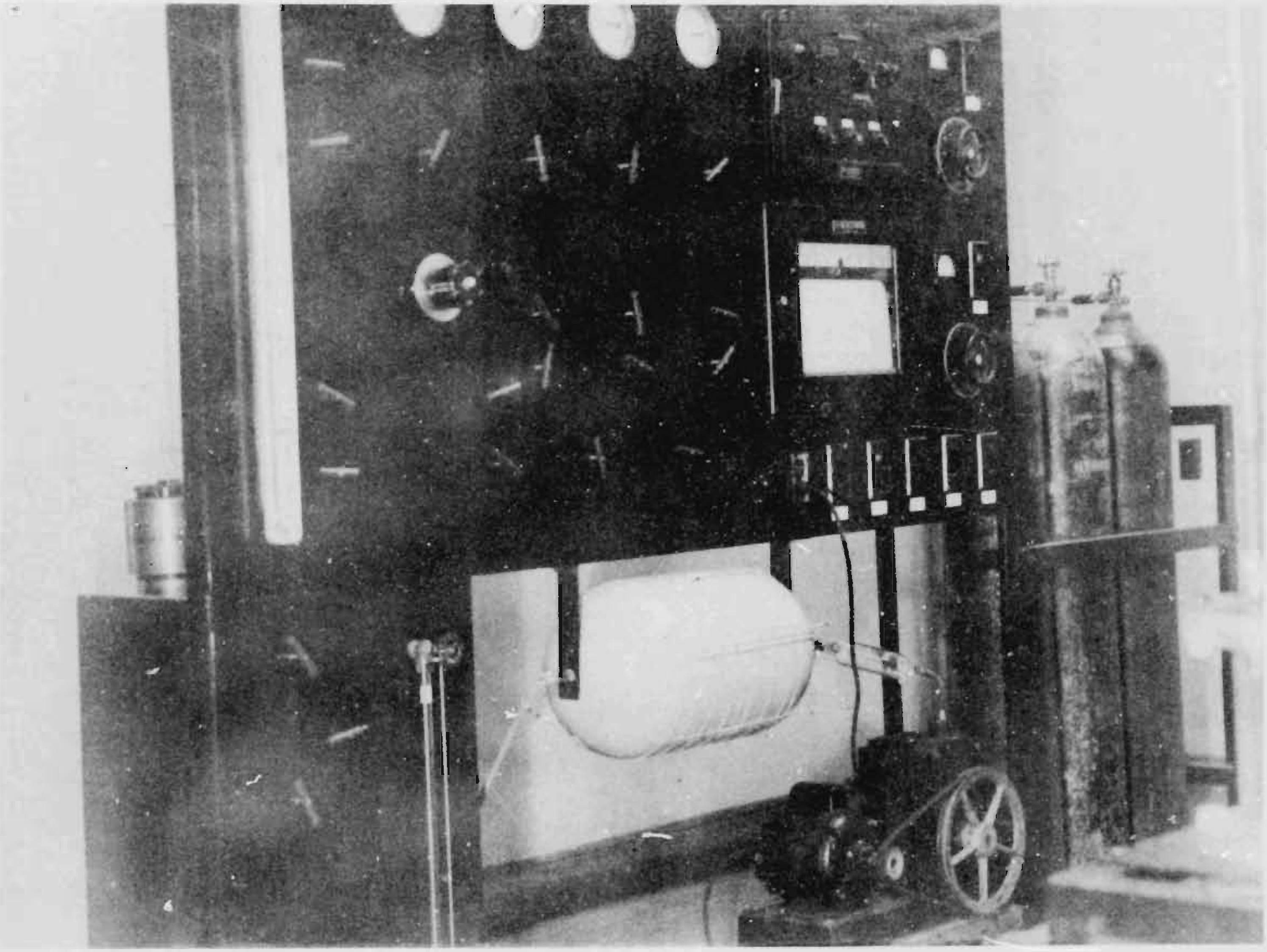

Figure 11. - Control panel for hydrogenation unit.

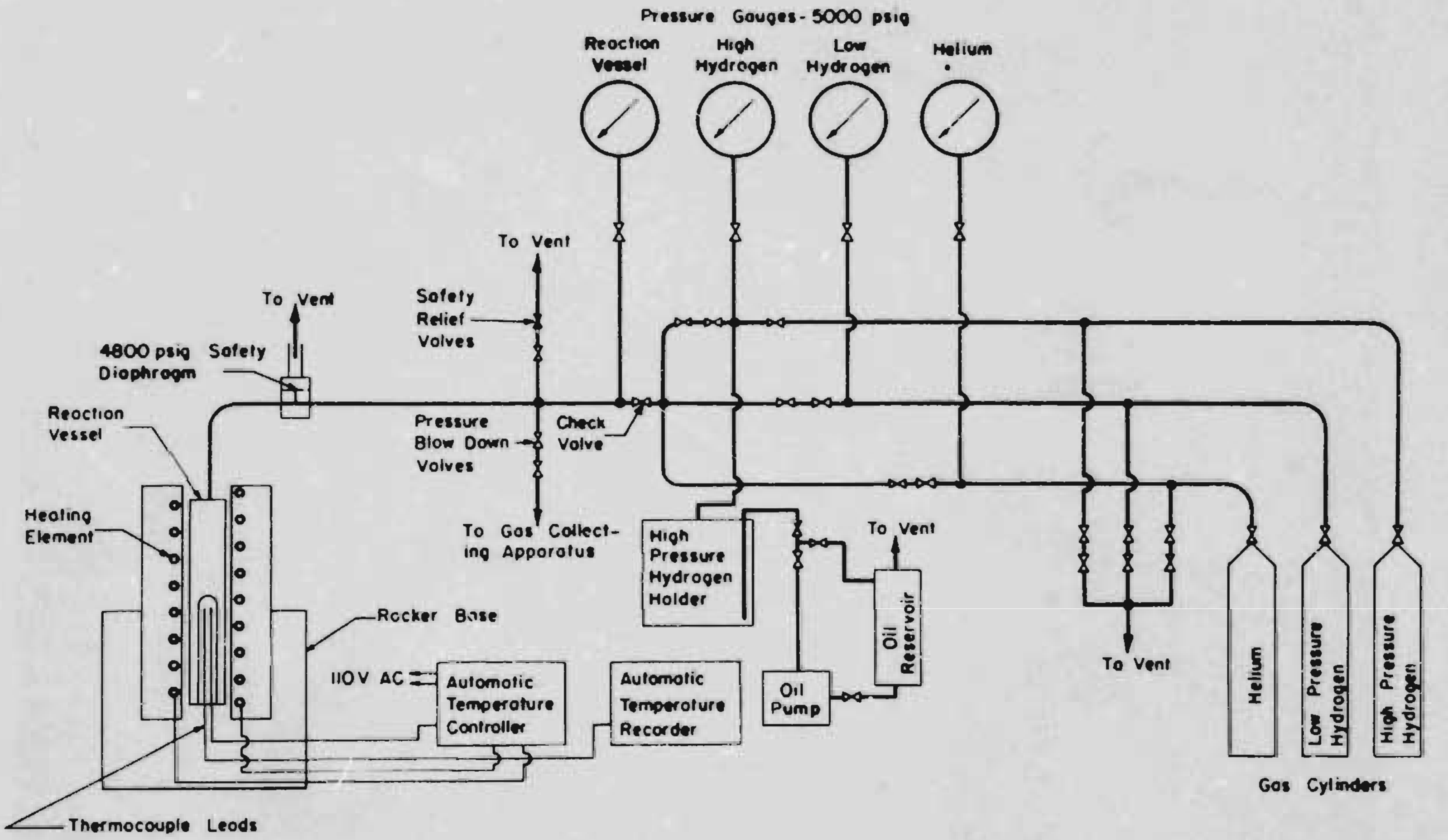

Figure 12.-- BATCH HYDROGENATION UNIT.

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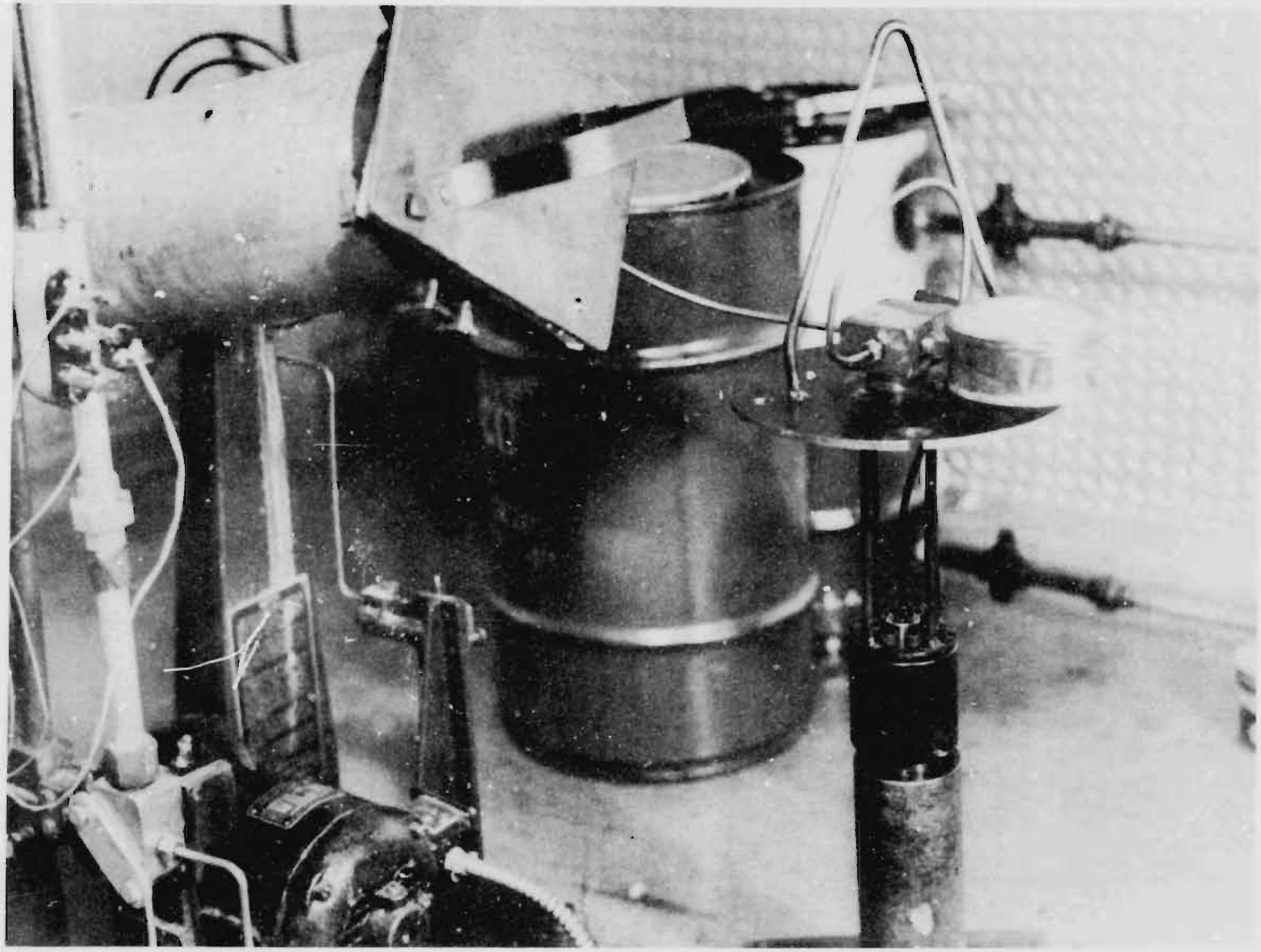


Figure 13. - Micro reaction vessel and shaker used in hydrogenation studies.

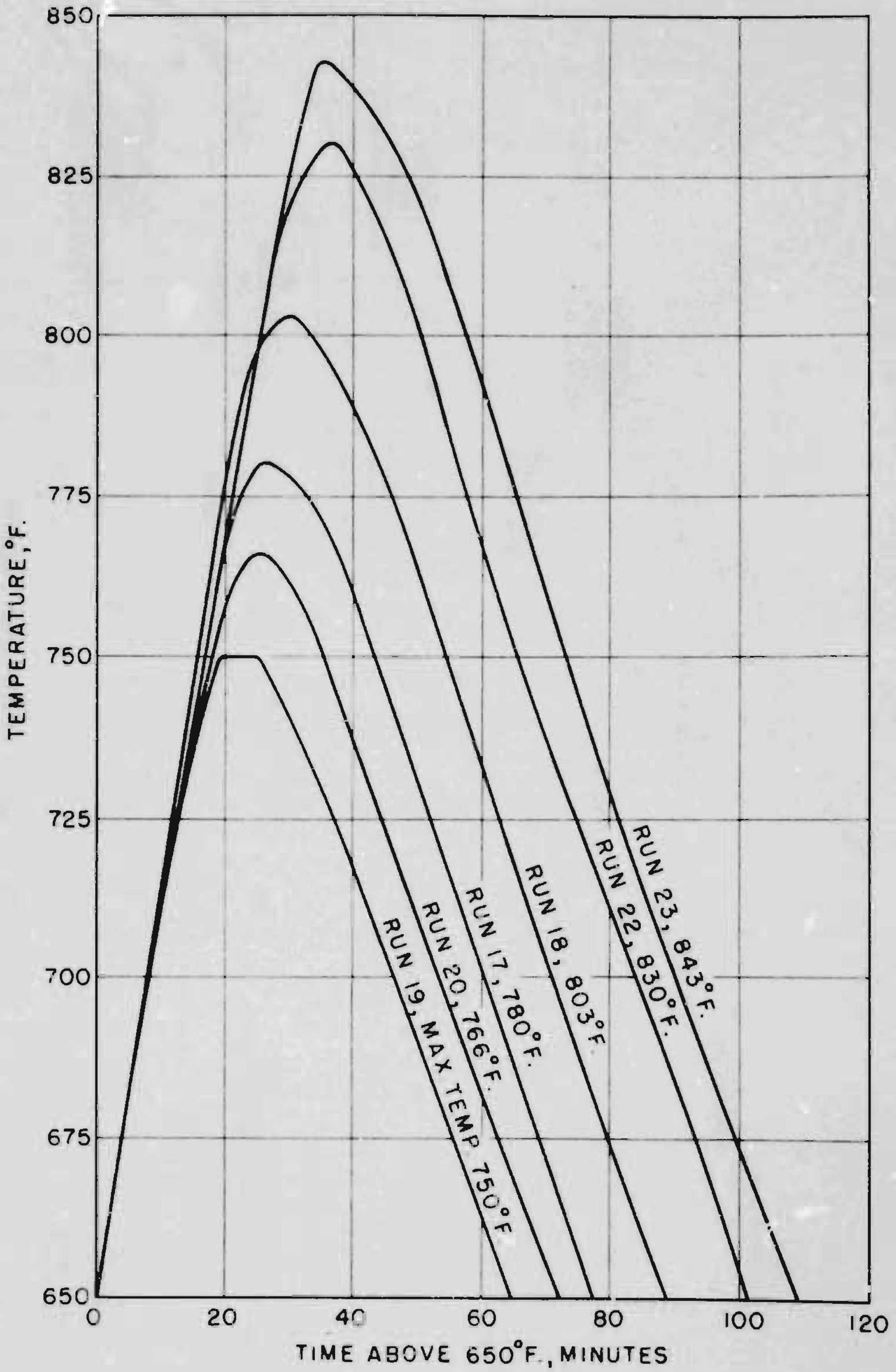


Figure 14.-- HEATING CURVES FOR SLURRY HYDROGENATION (BATCH UNIT)

Figure 15

FLOW DIAGRAM FOR THERMAL SOLUTION PROCESS RAW SLURRY PREPARATION SYSTEM

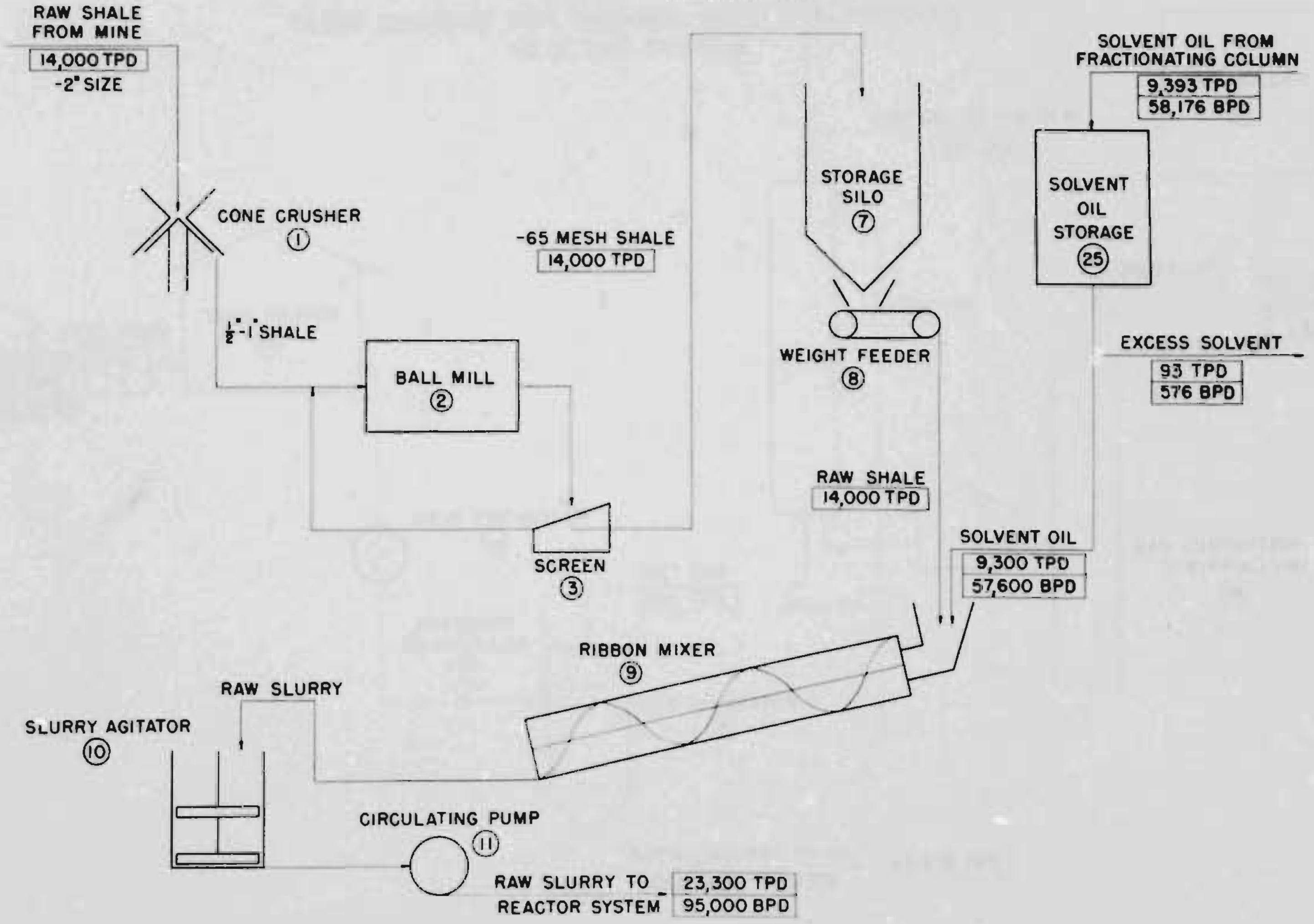
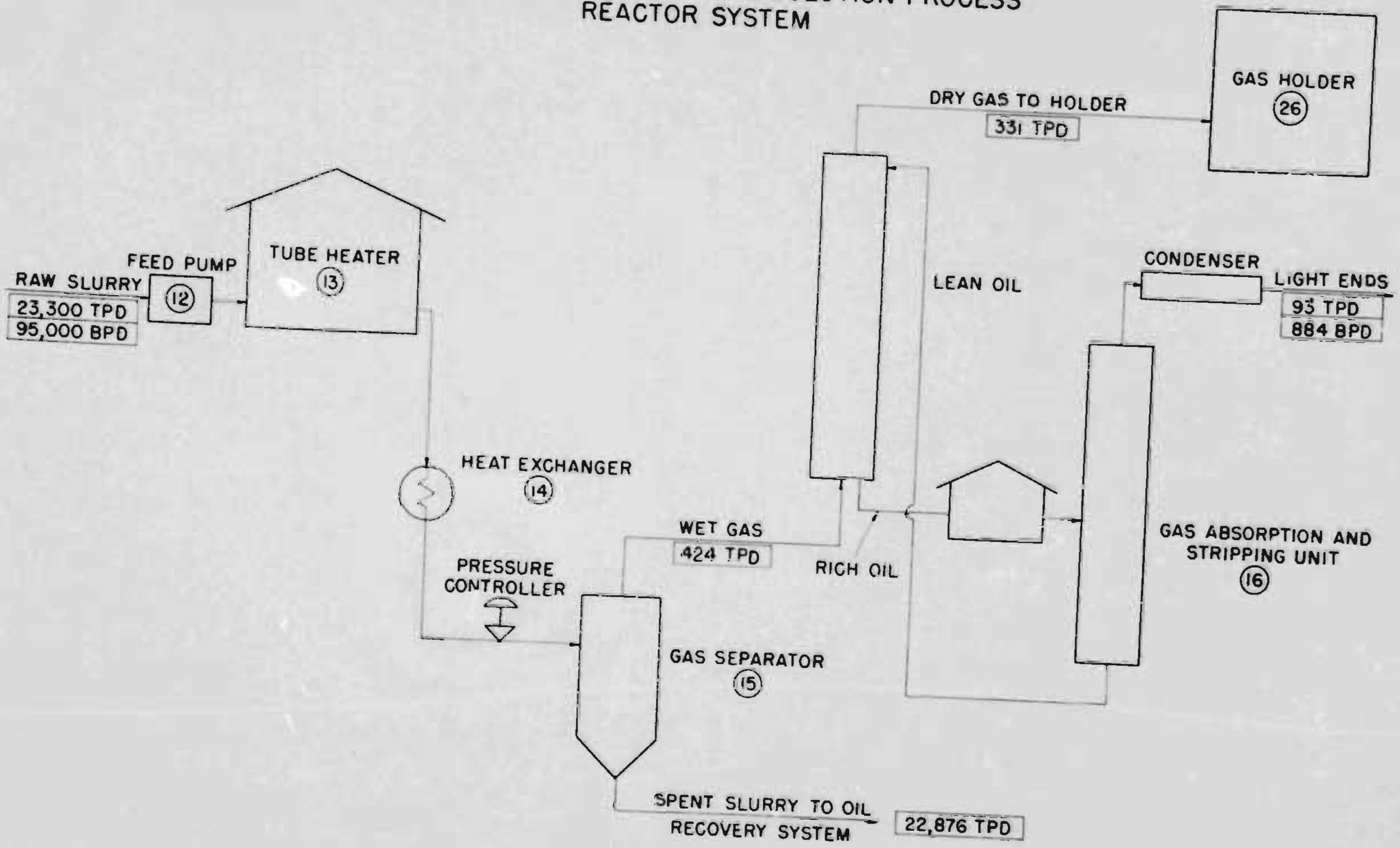


Figure 16

FLOW DIAGRAM FOR THERMAL SOLUTION PROCESS
REACTOR SYSTEM



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