FIG. 4.

FIG. 5.

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FIG. 6

OIL SHALE HEATED TO 900°F (CUBIC FEET / DAY X 10^3)

DISCHARGE TEMP 800°F

NATURAL GAS FLOW RATE - ATMOSPHERIC PRESSURE (CUBIC FEET / DAY X 10^3)

FIG. 7

NATURAL GAS ENTERS WELL AT 932°F

DISCHARGE TEMPERATURE

60°F

200°F

400°F

600°F

800°F

METHANE RELEASED AND IN DECOMPOSITION GASES

NATURAL GAS FLOW RATE - ATMOSPHERIC PRESSURE (CUBIC FEET / DAY X 10^3)

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The invention relates to the art of heat-treating oil shale for the recovery of thermal decomposition products therefrom, and particularly to such treatment carried out while the oil shale remains in its natural location underground, i.e., in situ, although it is also possible to derive certain advantages of the invention by carrying out the process within a pressurized retort. In either instance, the quality of the decomposition products is superior to that of products obtained by previously known processes.

An efficient and economical process for the recovery of petroleum products from oil shale has long been sought. Because of the high cost of mining the shale for subsequent processing, efforts have been directed in many instances to thermal decomposition of the organic content of the shale in situ. This involves the supplying of decomposing heat to the underground formation and the conditioning of decomposition products from such formation to surface areas.

Most of the in-situ processes proposed heretofore have relied in whole or in part on the burning of a portion of the carbonaceous constituent of the shale, known as kerogen, for supplying much or all of the decomposing heat required. For this purpose, air or an oxygen-containing gas has been introduced into the formation along with heating means capable of raising the temperature of a portion of the shale to the ignition point.

In some special instances it has been proposed that a heated gas, inert to combustion, be introduced into the formation as a heat-transfer agent. In these instances, either the formation concerned is naturally porous, as in the case of porous tar sands of the Athabasca region of Canada, as distinguished from non-porous oil shales, see Pelzer U.S. Patent No. 3,040,809, or the proposal has involved the use of explosives to shatter impervious oil shale formations, see Hocter et al. U.S. Patent No. 1,422,204, the taking advantage of naturally porous strata in such formations, see Huntingdon U.S. Patent No. 2,960,226, or the driving of drifts of gas flow into and through such formation, see Kiel U.S. Patent No. 2,974,937.

The process of the present invention utilizes natural gas-containing methane as a principal constituent, for conveying kerogen-decomposing heat to the formation and products of distillation from the formation. Because this gas contains nothing that contaminates the products produced by the decomposition of kerogen and transmits heat more efficiently than do other gases that could be used, it is an ideal carrier for such products of decomposition. It will not reduce the heating value of the product gases, and it will carry sufficient heat to effect the desired decomposition. Moreover, its own decomposition temperature (between 932° F. and 1292° F., depending upon its composition) is low enough to give automatic protection against any accompanying decomposition of the host rock (decomposition of aluminosilicate metal carbonates occurs at well over 1292° F.). In addition, it is highly significant that natural gas is substantially oxygen-free and, therefore, inert so far as oxidation of the kerogen is concerned.

Another advantage accompanying the use of natural gas as a fluid heating medium is a solvent stripping action. The gas is a solvent for thermally decomposed kerogen and exercises a solvent-stripping action with respect to the oil shale by penetrating whatever pores naturally exist in such shale (although oil shale is generally regarded as impervious it often contains minute pores or hairline cracks) or are artificially developed during treatment (by the dissolving or corroding action of both the introduced carrier gas and the evolved gases), it being realized that the natural gas is introduced under a pressure of from about 150 to 500 p.s.i.g.

A feature of the invention is the changing of the pressure of the solvent carrier gas periodically to effect what may be regarded as a pulsating action of such gas with respect to the shale formation being treated. When the pressure is reduced, gases and vapors within the shale are permitted to escape; when the pressure is increased, the solvent carrier gas is forced into whatever voids are left by decomposition of the kerogen and by escape of the resulting gases and vapors. Thus, there is a periodic cleansing action exerted on the thermally treated oil shale by the very gas which carries the heat to the shale, as well as an intimacy of contact between the gas and shale not heretofore achieved in the art.

The process of the invention is described in detail hereinafter and is illustrated in the accompanying drawings with respect to specific procedures presently regarded as the best mode of carrying out the invention in practice. From these, additional objects and features of the invention will become apparent.

In the drawings:

FIG. 1 schematically represents, in perspective and in vertical section taken on the line 2—2 of FIG. 2, a typical installation of equipment for carrying out the process with respect to a natural underground deposit of oil shale with which it is associated;

FIG. 2, a top plan view of the installation, progressive expansion being indicated by broken lines;

FIG. 3, a fragmentary vertical section taken on the line 3—3 of FIG. 1 and drawn to a considerably larger scale;

FIG. 4, a portion of the installation and of the progressive well-layout pattern of FIG. 2 drawn to a larger scale and amplified to indicate, by dotted lines, well casings, underground flow channels, and initial gas-penetration areas;

FIG. 5, a graph depicting the relationship between flow rate of the natural gas carrier fluid at atmospheric pressure, temperature of discharge gases and vapors, and energy input to the shale zone being treated;

FIG. 6, a graph depicting the relationship between flow rate of the natural gas carrier fluid at atmospheric pressure, temperature of discharge gases and vapors, and quantity of shale which will be heated to a decomposition temperature of 932° F.; and

FIG. 7, a graph depicting the relationship between flow rate of the natural gas carrier fluid at atmospheric pressure, temperature of discharge gases and vapors, and the quantity of methane released by the decomposed kerogen.

Referring to the drawings:

There are a variety of ways in which the natural gas carrier fluid can be injected into the underground deposit of oil shale and the process of distillation carried on. It is preferred, however, and a feature of the invention that one or more extraction wells be drilled to intersect an injection well at the bottom of that portion of the oil shale deposit which is to be treated, the wells being cased and insulated down to the treatment zone, but being uncased within the treatment zone, whereby the hot natural gas will freely circulate from injection well to extraction well or wells and will come into intimate contact with exposed surfaces of the shale within the treatment zone.
An advantageous arrangement of wells, which lends itself to a progressive expansion of the workings in a most economical manner, is illustrated in FIGS. 1, 2, and 3 with respect to a deposit of oil shale 10 covered by barren overburden 11.

There, an injection well 12 is drilled through the overburden and into the deposit of oil shale to a level 18a that establishes the lower limit of a shale treatment zone and that avoids any water zone that may exist. A depth of a thousand feet or more is not unusual in an instance of this type, depending upon the natural formation encountered.

Six extraction wells 13 are drilled symmetrically and concentrically around the injection well in hexagonal formation. They parallel the injection well through much of their depths, but have their lower end portions 13a slanted toward and intersecting its bottom to establish free flow communication therewith.

This hexagonal arrangement makes for economical expansion of the workings in successive similar hexagonal groups indicated by broken lines in FIGS. 2 and 4, such groups having injection wells 12A, 12B, 12C, etc. and new extraction wells 13A, 13B, 13C, etc., but each successive working group making use of two injection wells of a preceding, worked-out group.

Both the injection well 12 and the extraction wells 13 of each hexagonal group of wells are double cased from the surface down to a level which establishes the upper limit 10b of the shale treatment zone, see the casings 14 and 15, respectively, in FIG. 3, and the treatment zone 16 in FIG. 1. Thermal insulation 17 of any suitable type is inserted between the two casings. The extent of the annular space between the casings is determined in each instance by the circumstances, it being realized that the purpose is to prevent undue loss of heat from hot fluid passing through the inner casings. A typical installation will have the wells spaced at twenty foot intervals and will utilize nine inch diameter steel pipe for the outer casing and two and one-half inch diameter steel pipe for the inner casing.

As previously indicated, natural gas is injected into the decomposition zone as a heating medium for the shale and as a carrier fluid for products of distillation. For this purpose, there is provided at the surface suitable gas compressing, heating, and injecting equipment and suitable product recovery equipment. In the illustrated installation, natural gas is supplied through a pipe 18 and a valved bypass 19 to a compressor 20 from any suitable source, such as a storage tank (not shown). After being compressed to a suitable extent, ordinarily about 500 p.s.i.g., it is passed into preferably a gas-fired furnace 21, where it is circulated through a suitable heat exchanger (not shown) and heated to an injection temperature above 662° F. (minimum optimum decomposition temperature of kerogen), but sufficiently below its decomposition temperature to insure stability (about 932° F. in most instances). Then, still under pressure, it is passed through suitable piping 15a into the inner casing 15 of injection well 12.

This pressurized, hot, natural gas travels down into the uncased lower portion 12a of the injection well and into the uncased lower portions 13a of the extraction wells 13, directly contacting the exposed shale faces of the several uncased well portions.

A sufficient quantity of the compressed, hot, natural gas is passed (determined both by the carrying capacity of the inner casing 15, the depth of the working, the pressure, length and diameters of the uncased portions 12a and 13a, and the input pressure) to heat a superficial layer of the shale to the distillation temperature of the contained kerogen, i.e. between 626° F. and 1022° F. In this connection, it should be noted that the heat capacity of natural gas is 0.910 B.t.u. per pound at 932° F., and that it requires 0.314 B.t.u.'s to raise the temperature of one pound of oil shale one degree F. under ordinary conditions. It is significant that this heat capacity is approximately two and a half times as great as that of any other gas that would be practical to use, and that natural gas is substantially oxygen-free and therefore chemically inert with respect to the kerogen.

It has been found experimentally that the optimum temperature for decomposition of kerogen and the rapid evolution of decomposition products is about 824° F. In order to attain that working temperature in the formation, the natural gas will normally be introduced at a temperature of 932° F.

It should be apparent that the exact gas injection temperature, pressure, and rate will depend upon the circumstances in each application of the present process in actual practice and that calculations will have to be made in accordance with sound engineering practice based upon available data concerning the particular deposit and conditions peculiar thereto.

In any event, the thermal decomposing and solvent action of the hot, natural gas carrier fluid, and of such carrier fluid augmented by product gases and vapors, against the exposed faces of the uncased well portions 12a and 13a, will either cause spent portions of the shale to slough off, exposing fresh shale for treatment, or will render such shale permeable and susceptible to extension of the treatment backwards from such well portions, depending upon the nature of the particular host rock.

In this way, the kerogen components of the shale in treatment zone 16 will be decomposed progressively outwardly from the uncased well portions 12a and 13a, somewhat as indicated at 16a in FIG. 4, and the shale in such zone will be effectively worked in situ.

The natural gas carrier fluid, accompanied by decomposition product vapors and gases, passes upwardly through the extraction wells 13 into product recovery lines 22 and into and through condensers 23 interposed in such lines, where the hot and wet gases are cooled, thus separating the natural gas carrier fluid to pass through pipe 24 back to the compressor 20, the heater 21, pipeline 15a, and injection well 12, thereby completing a circuit. The liquefied decomposition products pass through pipes 25 and 26 to storage tanks 27 and 28, respectively.

The natural gas supply line 18 leads directly to the gas burner (not shown) of furnace 21 and supplies furnace fuel. Whenever the quantity of natural gas carrier fluid is sufficiently augmented by methane and other suitable decomposition components of the kerogen content of the shale being treated, the valved by-pass 19 may be opened, permitting passage of the recycled gas to be burned as fuel for the furnace.

In order to achieve maximum contact between the hot natural gas and the kerogen content of the shale, it is a feature of the invention that a pulsating action be imparted to the gas within the bore holes. This can be accomplished by alternately slowing down and speeding up the compressor for time intervals which may vary from a few minutes to an hour or more, or by opening and closing valves (indicated as such) at the upper ends of the extraction wells 13 for such time intervals. The pressure differentials for effecting this pulsating action can vary widely, depending upon the circumstances. A differential of about 50 p.s.i.g. should suffice in most instances.

A preferred procedure in the operation of each successive hexagonal well group when utilizing a constant gas-injection pressure is to commence the operation with the valves of all extraction wells closed and to keep them closed until the gases are collected up to the desired maximum pressure. Then the valve of one of the extraction wells 13 is opened, permitting part of the natural gas carrier fluid and the product vapors carried thereby to flow out of the well system.

When the pressure drops the prescribed extent, the valve is closed and the pressure, and the desired maximum. Thereupon, the valve of the next extraction well 13 is opened, and so on around and around
the circumferential series of extraction wells until the treatment zone associated with the particular hexagonal group of wells is exhausted of its kerogen content.

When the wells of a succeeding hexagonal group are drilled, it is only necessary to plug the slanted lower portions 13a of the two existing extraction wells which are to be used with the new group and to drill new lower portions slanted in the proper direction to intersect the injection well of such new group.

The graph of FIG. 5 is used to determine the quantity of thermal energy in terms of B.T.U.'s per day that is transferred to the shale in the treatment zone when the discharge temperature of the carrier gas leaving such zone and its injection rate in terms of cubic feet per day are known. These can, of course, be easily ascertained by the use of appropriate instruments at the surface. Thus, if the carrier gas were leaving the formation at a measured temperature of 600° F. and the flow rate were maintained at 3.0 x 10^6 cubic ft./day at the injection well, the energy transferred to the shale deposit would be 52.5 x 10^8 B.T.U.

The graph of FIG. 6 is used to determine the quantity of shale that can be heated up to a maximum of 932° F. on the assumption that all the energy transferred to the shale is confined in the particular zone being treated. Again, if the discharge temperature of the carrier gas and its injection rate are measured, the quantity of shale can be read from the graph. Thus, if the carrier gas were leaving the shale formation at a temperature of 600° F. and the flow rate were maintained at 4.0 x 10^6 cubic ft./day at the injection well, 2,300 cubic ft. of shale would be heated from 60°F. to 932°F.

The graph of FIG. 7 indicates how much methane is released from the decomposed kerogen in terms of cubic feet per day when the same temperature and injection rate previously indicated are measured.

Although the composition of natural gas varies somewhat from source to source, a typical composition is as follows:

<table>
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<tr>
<th>Component</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>Methane</td>
<td>91.6</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.9</td>
</tr>
<tr>
<td>Propane</td>
<td>1.1</td>
</tr>
<tr>
<td>Butane</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.1</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td></td>
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</table>

The oxidizing capacity present by reason of the very small quantity of carbon dioxide is inconsequential.

The obtained composition of a decomposition product of the process is unique among shale oils. Thus, the API gravity at 60° F. of shale oil produced by a typical experimental run of the present process, using natural gas at a pressure of 300 psi, was 29.5, whereas the normal API gravity at 60° F. for shale oil is below 20.

In instances where mined shale is treated in a pressurized retort, rather than shale in situ, the procedure is essentially similar so far as use of natural gas as a carrier fluid for both heat and the products of kerogen decomposition is concerned. A mass of oil shale is first introduced into the retort, the retort is sealed, and natural gas is then injected under pressure into intimate contact with the shale, there being a withdrawal of gas and accompanying products of decomposition either continuously or periodically within the limits of a minimum pressure to be maintained, and there being a recycling of the natural gas following extraction of the products. The feature of pulsating the carrier fluid is applicable here also.

Whereas there is here illustrated and specifically described a certain preferred procedure which is presently regarded as the best mode of carrying out the invention, it should be understood that various changes may be made, and other constructions adapted without departing from the inventive subject matter particularly pointed out and claimed herebelow.

I claim:

1. A process of recovering petroleum products from oil shale in situ, comprising introducing into a substantially impermeable and undisturbed natural deposit of oil shale underground a sufficient quantity of natural gas, whose major constituent is methane, at sufficient temperature and sufficient pressure to exert a combined thermal and solvent action thereon for releasing the kerogen from areas of the oil shale with which it comes in contact and for permeabilizing such oil shale to open up normally inaccessible areas thereof to thermal decomposition of kerogen; and withdrawing from said underground deposit said natural gas along with distillation vapors and gases intermingled therewith.

2. The process of claim 1, including pulsating the gas into intimate contact with the shale.

3. The process of claim 1, including separating decomposition vapors from the gases and recycling said gases.

4. The process of claim 2, including bleeding off some of the gases before recycling them.

5. A process of recovering petroleum products from oil shale in situ, comprising drilling at least two wells adjacent each other into a substantially impermeable and undisturbed natural deposit of oil shale underground so that at least their lower portions have oil shale facings; circulating through said wells a sufficient quantity of natural gas, whose major constituent is methane, at sufficient temperature and sufficient pressure to exert a combined thermal and solvent action on the exposed oil shale for releasing the kerogen and for permeabilizing the oil shale to open up normally inaccessible areas thereof to thermal decomposition of kerogen; and separating decomposition vapors from said gas at the surface.

6. The process of claim 3, including insulating the wells against the loss of heat down to the upper level of the oil shale zone to be treated.

7. The process of claim 3, including pulsating the gas into intimate contact with the shale.

8. The process of claim 3, wherein there are six extraction wells concentrically and symmetrically surrounding an injection well in hexagonal formation; and wherein similar groups of wells are drilled successively, following working off of an immediately preceding group, so as to respectively utilize two of the extraction wells of said preceding group.

9. A process of recovering petroleum products from the organic content of normally impermeable, petroleum-producing, mixed organic and inorganic earth materials in situ underground, comprising introducing into such impermeable earth materials substantially undisturbed in situ a sufficient quantity of natural gas, whose major constituent is methane, at sufficient temperature and sufficient pressure to exert a combined thermal and solvent action thereon for releasing the organic component of said earth materials with which it comes in contact and for permeabilizing such earth materials to open up normally inaccessible areas thereof to thermal decomposition of organic constituents thereof.

10. The process of claim 9, including pulsating the gas into intimate contact with the earth materials.

References Cited by the Examiner

UNITED STATES PATENTS

895,612 8/1908 Baker 166—57
1,422,204 7/1922 Hoover 166—40 X
2,148,717 2/1939 Whitney 166—57 X
2,421,528 6/1947 Steffen 166—40 X
2,793,696 5/1957 Morse 166—11
2,813,583 11/1957 Marx et al. 166—40 X
2,875,830 5/1959 Martin 166—7
2,909,337 9/1959 Henning 166—1

(Other references on following page)
<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Date</th>
<th>Inventor</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,911,206</td>
<td>11/1959</td>
<td>Purre</td>
<td>166—11 X</td>
</tr>
<tr>
<td>2,954,218</td>
<td>9/1960</td>
<td>Dew et al.</td>
<td>166—11 X</td>
</tr>
<tr>
<td>2,970,826</td>
<td>2/1961</td>
<td>Woodruff</td>
<td>166—11 X</td>
</tr>
<tr>
<td>3,004,595</td>
<td>10/1961</td>
<td>Crawford et al.</td>
<td>166—11</td>
</tr>
</tbody>
</table>

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