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M. G. HUNTINGTON
PRESSURE PULSING PERPENDICULAR PERMEABILITY PROCESS FOR
WINNING STABILIZED PRIMARY VOLATILES FROM
OIL SHALE IN SITU

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2 Sheets-Sheet 1

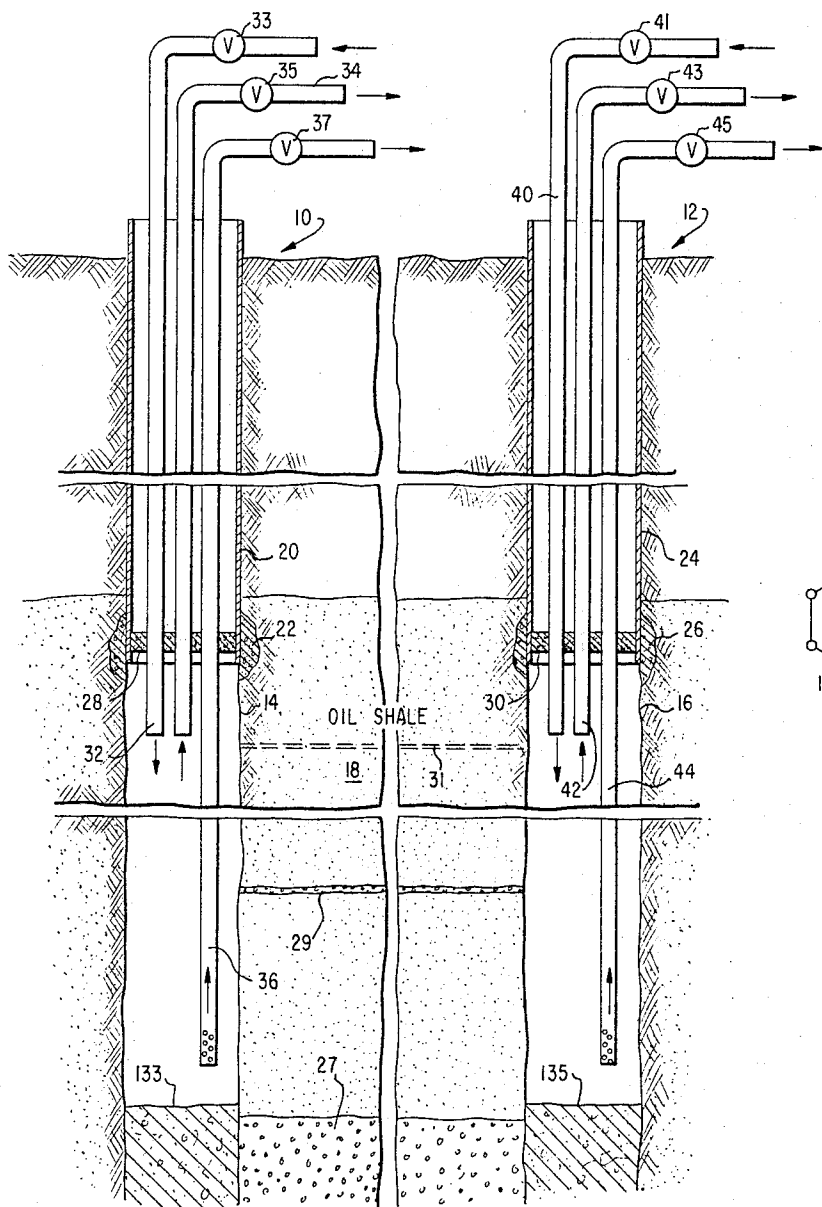


FIG. 1

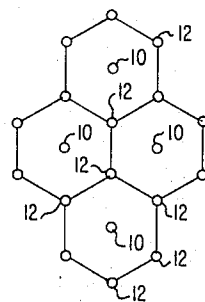


FIG. 3

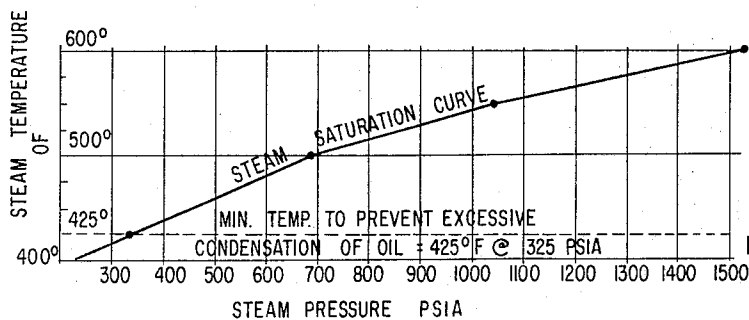


FIG. 4

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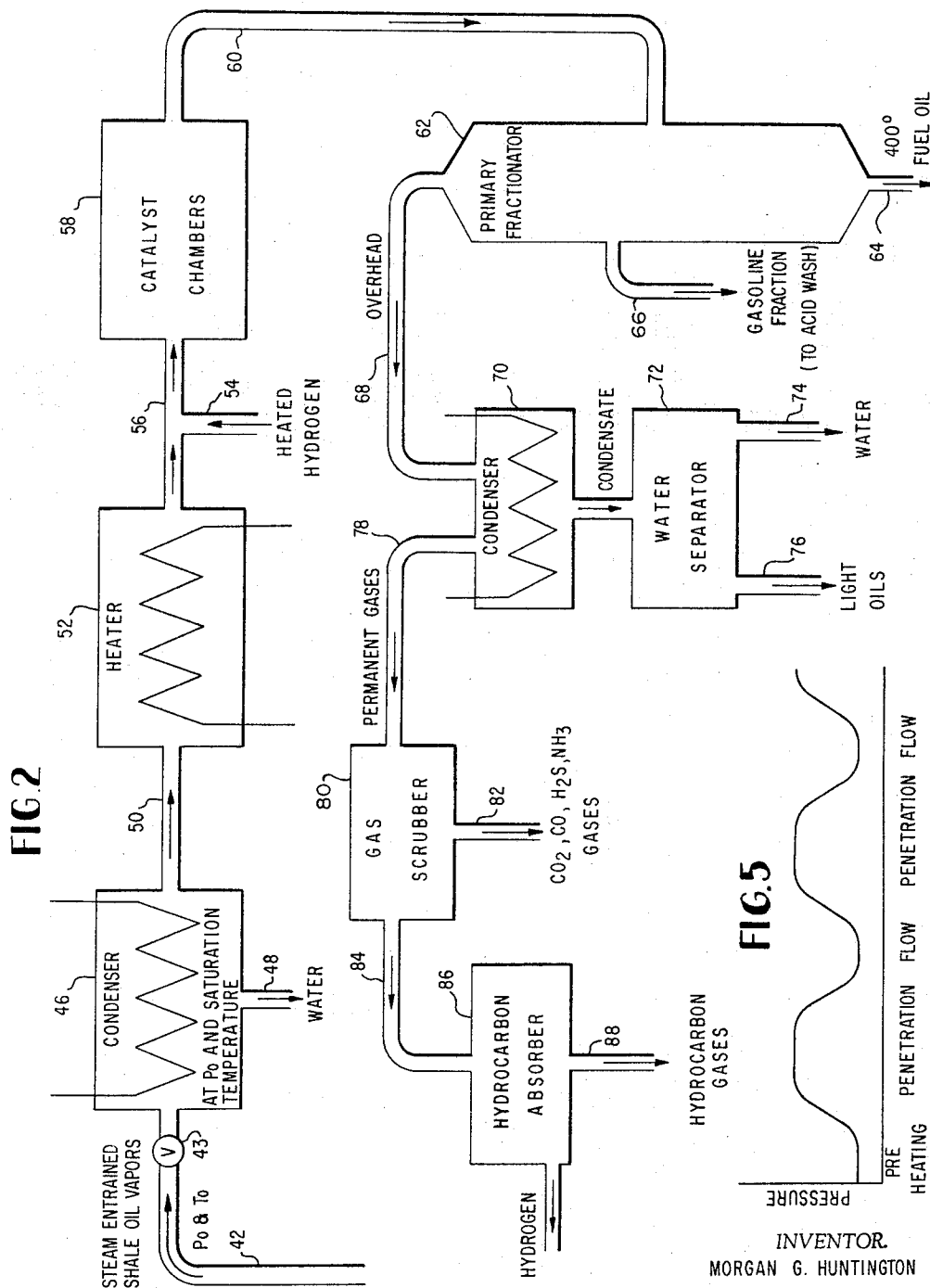
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PRESSURE PULSING PERPENDICULAR PERMEABILITY PROCESS FOR WINNING STABILIZED PRIMARY VOLATILES FROM OIL SHALE IN SITU

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9 Claims. (Cl. 166—7)

This invention relates to improvements in the in situ exploitation of oil shale and other hydrocarbonaceous impregnations and particularly relates to the pyrolysis, destructive steam distillation and to the initial vapor phase catalytic hydrogenation of the volatile matter. This invention further relates to the production of a primary condensate oil which is substantially free of reactive hydrocarbon unsaturates and of oxygenated organic compounds and which is, therefore, essentially stable in respect to molecular size.

Although a very great deal of engineering knowledge has been accumulated in the exploitation of various types of liquid petroleum reservoirs, very little of such conventional oil field experience is immediately and directly applicable to the in situ winning of oil from such impervious and benzene insoluble impregnations as the Rocky Mountain oil shales.

No in situ shale oil recovery process has so far been successfully demonstrated. A number of retorting systems which involve mining, crushing and heating the shale in the absence of air have established the fact that about two-thirds of the initial calorific value of the shale is slowly converted to condensable oil vapors upon heating to a temperature of about 700° F. and more rapidly converted between 800° and 900° F. One-third of the remainder is in the form of permanent hydrocarbon gases and the balance of the original heating value is retained as a coke polymer in the calcined host. About 300 B.t.u. of heat is absorbed per pound of shale during the processes of pyrolysis and of destructive distillation above 800° F. but below the temperature of carbonate destruction which begins above 1150° F.

All grades and types of shale oil which have so far been extracted from Rocky Mountain oil shales by potentially large scale processes, other than those methods disclosed by the present inventor, are less valuable than commercial grades of petroleum because of the lower gasoline yield and because of excessive processing and investment costs. The inferior quality of all previously produced shale oil is due particularly to the average high molecular weight of compounds formed in such oils by intermolecular reaction subsequent to pyrolysis and distillation and which have been allowed to condense from the vapor phase without prior catalytic hydro-stabilization.

While it is well known that kerogen, the impregnating hydrocarbonaceous solid material which occurs in the Rocky Mountain magnesium marls commonly called "oil shales" can be largely converted to benzene-soluble liquids by heating, a second and a very serious problem of physical recovery remains to be solved. In order to extract fluids from impregnated rock hosts through bore holes drilled therein, two conditions must be met as is the case in all oil field practice: (1) The impregnated material must be permeable to the fluid, and (2) some kind of driving and/or displacing force, such as gas, water or gravity, must already exist in the reservoir or it must be artificially supplied.

Rocky Mountain oil shale is an impervious and impermeable laminar sequence of magnesium marlstone containing very finely divided grains of hydrocarbonaceous solids which are petrographically similar to certain con-

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stituents of cannel and boghead coals. Oil shale resembles dark colored marble and has a hardness of about five on Mohs' scale, which is about as hard as window glass. Its shear strength perpendicular to the bedding planes is 3000 to 4600 pounds per square inch, while parallel to the bedding planes, its shear strength is only 900 to 1800 pounds per square inch. Its tensile strength is 340 to 800 pounds per square inch.

The hydrocarbonaceous matter called kerogen is a mixture of amorphous, structureless solids ranging in color from yellow to brown or black. Occasional identifiable pollen grains, spores and microfossils are embedded in the organic matter. Only about 15 percent of it is soluble in common solvent such as benzene at moderate temperatures and pressures. Despite extreme variation in richness of the various beds, the composition of kerogen is fairly constant as is represented by the following data:

Carbon	80 to 81%
Hydrogen	10 to 11%
Nitrogen	2 to 2½%
Sulfur	1 to 1½%
Oxygen	4 to 7½%

It should be noted that part of the kerogen bears a remarkable and close resemblance to the petrographic constituents of certain high volatile coals. (Compare Bureau of Mines Technical Paper 642.) This is not unexpected since geologically, the origins of oil shale and coal are similar in that they are both fresh water deposits and the organic content of each is the result of vegetable matter decaying and coalifying in place.

Following the destructive distillation of oil shale at 800° F.-900° F., the porosity of the calcine ranges from 15 to 40 percent. Because the primary mineral matter (chiefly volcanic dust) has an average grain size between 0.5 and 50 microns, the pore size is very small, being for the most part between ten and one-tenth microns. Obviously, this host rock can be considered permeable only to gases and vapors at low pressures and to liquids only at very high differential pressures.

Oil recovered from oil shale by destructive distillation retains most of the oxygen, sulfur and nitrogen occurring in the original kerogen and these elements, for the most part, are found in chemically functional groups, attached to what otherwise would be pure hydrocarbon molecules. Because of the disproportionating reactions of thermal cracking which accompany pyrolysis, about half of the hydrocarbon molecules in typical shale oil vapors are characterized by at least one double bond due to the insufficiency of hydrogen. These characteristics produce a highly reactive mixture of tar acids, tar bases, organic compounds of sulfur and unstable hydrocarbons which combine to form the typical molecular complex which is commonly called "shale oil."

As disclosed in my Patent 3,106,521, granted October 8, 1963, and in my co-pending application Serial No. 307,162, filed September 6, 1963, shale oil produced by any other means than the inventions therein described is highly reactive and unstable. When allowed to condense from the initial vapor phase, the condensate immediately begins to change its molecular structure by polymerization of olefins and by intermolecular reaction between olefins, tar bases, tar acids and organic sulfur compounds. As a result, re-distillation yields some 50 to 60 percent of residuum having a molecular weight in the order of 200 to 5000 and even higher and which is solid at room temperature. The distillation of shale oil by all processes except that of the present invention, my co-pending application Serial No. 307,162 and of my Patent 3,106,521, noted above, produces about 40 percent of light fraction

and about 60 percent of very heavy residuum. The lighter fraction, which boils below 600° F., invariably consists of 40 to 50% of unsaturated and very reactive hydrocarbons. These olefins, if not saturated by hydrogen immediately, combine with themselves and other hydrocarbon molecules to form high molecular weight complexes which are not readily converted into marketable products.

It is a principal object of this invention to inject heated hydrogen into the extracted primary shale oil vapors and to maintain most of the organic vapors at a sufficiently high temperature to prevent condensation before and while being led over suitable solid catalysts to promote the saturation of olefins into hydrocarbons and to remove all organically combined oxygen as water vapor and thereby destroy the tar acid content of the vapors before condensation occurs; and it is particularly an object of this invention to prevent subsequent liquid phase polymerization and intermolecular reactions so far as is possible by completing substantial catalytic hydrogenation before allowing the steam-entrained vapors to condense from the initial vapor phase.

The physical functions of this process invention may incorporate some or all of the controlled rock-parting principles disclosed in my U.S. Patent No. 2,969,226 when the object is to exploit a sequence of selected strata and to maximize the horizontal area exploited from each borehole.

In order to extract valuable hydrocarbons from oil shale by the in situ means of this invention, it is first necessary to establish fluid flow of a thermal carrier medium such as hot water and/or steam, through a pressure parted and sand fractured plane of weakness between an injection borehole and one or more production wells, as is known in oil field art. Secondly, it is necessary to pre-heat the host shale adjacent to the parted seam and the boreholes and conduits to a temperature above that at which most all vapors condense but below that temperature at which appreciable and rapid pyrolysis occurs. Thirdly, the host rock must be further heated to a temperature at which the organic impregnation converts to oil vapors, gas and residual carbon. Fourth, the host rock must become permeable to steam and to oil vapors and to gases immediately above and below the horizontal plane made pervious by sand fracturing. Fifth, a driving or extracting force must be provided which will expel the recoverable substances from the host rock, and at the same time, perform as a displacing medium to effectively prevent the re-impregnation of the once-impo-
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Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings, which disclose, by way of example, the principle of the invention and the best mode which has been contemplated of applying that principle.

In the drawings:

FIG. 1 is a schematic view in vertical section through the ground and a strata of oil shale showing injection and production boreholes therein.

FIG. 2 is a flow sheet diagram of the processing of steam entrained oil shale volatiles of this invention.

FIG. 3 is a diagrammatic representation of the pattern of drilling the production and injection boreholes.

FIG. 4 is a graph of steam pressure against temperature showing the steam saturation curve and illustrating the temperature and pressure limits within which the process operates.

FIG. 5 is a graph of pressure against time illustrating the pre-heating of the host rock and the pulsating pressure applied to the host by the process of this invention.

Referring now to the drawings for a description in detail of the process of this invention, there is shown in FIG. 1 an injection well 10 and a production well 12. These wells are produced by drilling an injection borehole 14 and a production borehole 16 from the surface of the ground through a known strata of oil shale 18.

The wells 10 and 12 will have casings 20 and 24 respectively which are placed and cemented at 22 and 26 respectively to be gas tight to just about the top of the oil shale formation 18 under exploitation.

The oil shale formation 18 will have a number of planes of weakness which may be opened up between the injection well 10 and production well 12 by sand fracturing methods as are known in the art. In the illustration in FIG. 1 there is graphically illustrated a bedding plane 29 which has been sand fractured by processes known in the art to provide a series of horizontal pervious planes tributary between the boreholes. The pressure parting is accomplished by inserting granular material and the planes are held open by the granular material within the parted planes as is known in the oil field production practice art.

The borehole 20 has three fluid conduits 32, 34 and 36 therein controlled by valves 33, 35 and 37 respectively. Similarly, production well 12 has fluid conduits 40, 42 and 44 controlled by valves 41, 43 and 45. Fluid is injected through conduit 32 under the control of valve 33, vapors may be withdrawn if desired from conduit 34 under control of valve 35 and liquids such as water condensate may be withdrawn through deep pipe 36 by a pump or the like under the control of valve 37. In the production well 12, the vapors including steam entrained oil shale volatiles may pass out conduit 42 under the control of valve 43, additional fluid may be injected if desired through conduit 40 under the control of valve 41 and condensate may be removed through deep pipe 44 under the control of valve 45.

After parting the plane of weakness 29, the next step in the process is pre-heating the formation including the sides of the parted plane 29 by pumping hot water at substantially steam saturation temperature in through one of the pipes in injection well 10 and removed through pipe 44 in production well 12. Water at a high temperature is used for pre-heating due to the superior heat transfer characteristics of water over that provided by a gas or vapor such as steam. The water is preferably at a temperature within the range of 400 to 550° F. That is, the temperature of the water is above the temperature at which excessive condensation of the oil entrained vapors in steam might occur. That is, the formation must be pre-heated to a temperature such that the steam and oil entrained vapors would not condense. As shown in the steam saturation curve of FIG. 4, this would be about 425° at 325 p.s.i.g. The upper limit of pre-heating by the water is the temperature at which pyrolysis of the oil shale 18 begins, i.e., in the order of 550 to 600° F. It is however desirable to preheat as high as possible with pressurized water as it provides more efficient heat transfer as noted above.

After the pre-heating step, the hot water is removed through pipe 44 and the recovery of the volatiles from the shale formation begins by introducing superheated steam through pipe 32 under the control of valve 33 to raise the temperature of the oil shale in the formation 18 to about 825°, or at least to a temperature sufficient to accomplish pyrolysis or distillation of the kerogen entrained within the shale.

The pyrolyzed shale will leave certain voids and the shortest paths for steam penetration into the voids are those which extend transversely to the plane of parting 29, and since the plane of parting is substantially horizontal, the interstices in the shortest path will be perpen-

dicular thereto; hence, the portion of the title, "Perpendicular Permeability."

The next step in the process is for promoting permeability and for obtaining an output from the formation above and below the parted plane or seam 29 by a pulsing effect applied to the superheated steam. This is graphically illustrated in FIG. 5 wherein the pressure after pre-heating is pulsed with respect to time so that with high pressure the steam penetrates into the voids and edges of the oil shale formation in the bedding plane and then the pressure is lowered to allow flow out of the formation and on out of the production well. The highest pressure in the pressure pulsing is about equal to rock pressure (which may be roughly figured as approximately 1 p.s.i. per foot of overburden). The lowest pressure of the pressure pulsing is, in the illustrated example, between 325 and 350 p.s.i. which is the minimum system pressure which will allow separation of vapor phase oils from liquid water in the partial condenser 46 without excessive condensation of oil vapors. See the saturation curve of FIG. 4. In essence, the high pressure pulsing is for first penetrating to open up the tributaries to the plane of parting and put the oil shale in the vapor phase by pyrolysis while the second and lower pressure cycle is to force the steam entrained volatiles to the major pervious plane and make the host rock more permeable for the next penetration by high pressure steam.

The pulsating pressure allows the oil shale entrained vapors and steam to be bled toward the production well 12 by the driving and extracting force and especially the extracting force of the pressure pulsing steam.

The next step in the process is to separate a certain portion of the steam entraining the oil vapors from the vapors by condensing the entraining steam at a temperature and pressure sufficient so that the oil vapors remain in the vapor phase. This step is accomplished in order to reduce the partial pressure of steam before a later step of catalysts and it is necessary that the oil vapors remain in the vapor phase. This step may be accomplished partially in the upper portion of production well 24 by cooling the output pipe 42 or may be accomplished as illustrated in a separate condenser shown in FIG. 2.

As shown in FIG. 2, the steam entrained vapors at output pressure and temperature are taken off line 42 under the control of valve 43 and passed to a condenser 46. This condenser accomplishes partial steam condensation at the output pressure and at steam saturation temperature and the condensed steam is drawn off as water through line 48. As a result of such condensation of steam the oil vapors exhibit a much higher partial pressure while still entrained in some steam at saturation temperature, are passed through line 50 to heater 52 wherein a source of heat is utilized to raise the vapors in temperature to that beneficial for a subsequent step of catalysis. This temperature will be within the range of 600° F. to 1300° F.

The heated vapors then are removed from the heater through lines 56 and are joined by heated hydrogen 54 and the heated hydrogen and oil shale vapors in the vapor phase are passed to catalysis chambers illustrated schematically at 58. The purpose of catalysis of the oil shale vapors while still in the vapor phase is set forth more in detail in my co-pending application Serial No. 307,162, referenced above and in essence it is so that the olefins may be saturated.

Without prompt vapor phase hydrogenation, conventional shale oil may contain approximately 40% olefins which combine with each other and with oxygenated compounds to form unmanageable polymers. However, if the shale oil distillate is kept in the vapor phase and hydrogen is added thereto and vapors are passed through and over a solid catalyst (such as suitably supported cobalt molybdate or the best solid non-poisoning catalyst known in the art for the use of saturating olefins in producing stable hydrocarbons) then the beneficial result mentioned

above will occur. This same type of contact catalysis removes organic oxygen as water vapor almost as readily thereby eliminating tar acids.

The stabilized distillate is then drawn through line 60 and passed to a primary fractionator 62 of the type known in the art. From the bottom of the fractionator 64 may be withdrawn the plus 400° F. fuel oils while the gasoline fraction may be taken off line 66 of the fractionator and passed to an acid wash to remove pyridine and its homologs and any other basic compounds. The 200° F. overhead from the fractionator passes out through line 68 to a condenser 70. The condensate from condenser 70 passes to a water separator 72 where water is separated from light oils, the water being taken off line 74 and the light oils off line 76. The permanent gases from condenser 70 are taken through line 78 to a gas scrubber 80 for absorbing most of the carbon dioxide, carbon monoxide, H₂S and NH₃. These dissolved and combined gases are removed with liquids through line 82 and the remaining permanent gases passed through line 84 to a hydrocarbon absorber system 86 to remove the hydrocarbon gases through line 88 leaving only substantially hydrogen to be taken off line 90 and this hydrogen may then be re-heated by waste heat in the system and recycled to line 54 to be used in the system.

After one plane 29 has been operated on, the pipes may be moved upwardly a predetermined distance and cement, such as shown in holes 10 and 12 as cement plugs 133 and 135 respectively, may be filled in to cover the exploited seam 29. Then another bedding plane illustrated diagrammatically in 31 may be opened up by sand fracturing and the process repeated on the next adjacent desirable bedding plane. In a similar manner, plane 27 has already been worked and has been sealed off as shown by the cement 133 and 135. The system will not leak substantial amounts of the pre-heating hot water or the driving and entraining steam due to the nature of the oil shale which is quite hard and impermeable in its natural state. Where sealing of pervious zones becomes necessary, conventional methods are applicable.

The arrangement of production and injection wells 12 and 10 shown in FIG. 3 is one possible arrangement drilling on a hexagonal pattern wherein each of the injection wells drives the distilled steam entrained vapors toward any one of the six production wells by selective valving arrangements.

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to the preferred embodiment, it will be understood that various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art without departing from the spirit of the invention. It is the intention, therefore, to be limited only as indicated by the scope of the following claims.

What is claimed is:

1. An in situ process for winning oil shale from an oil shale formation, the formation including a production bore hole and an injection bore hole drilled therein, as well as a path of lateral fluid communication through the otherwise impervious oil shale between the production and injection bore holes, the process comprising;

- (a) preheating the oil shale adjacent the path of lateral fluid communication with hot water to a temperature just below that at which pyrolysis of the oil shale begins,
- (b) introducing superheated steam under pressure into the path of lateral fluid communication through the injection bore hole,
- (c) cyclically varying the superheated steam pressure between the limits of rock pressure and a lower pressure sufficient to prevent undue steam condensation,
- (d) removing steam and oil shale entrained vapor from the production well, and

(e) treating the removed steam and oil entrained vapor after first reducing the partial pressure of steam by contact catalysis in the presence of hydrogen.

2. An in situ process for winning oil shale from an oil shale formation having a production well and an injection well extending therein, the process comprising;

(a) establishing a path of lateral fluid communication between the injection well and the production well through the oil shale formation,

(b) introducing steam under pressure and at a temperature and in sufficient quantity to cause pyrolysis of the shale into the path of lateral fluid communication from the injection well,

(c) cyclically varying the pressure of the steam in the path of lateral fluid communication,

(d) removing steam and oil entrained vapors from the production well,

(e) reducing the partial pressure of steam in the removed vapors without condensing the oil shale vapors, and

(f) treating the oil shale vapors in the presence of hydrogen by contact catalysis to stabilize the product by saturating olefins.

3. A process as defined in claim 2 further comprising heating the oil shale vapors to a temperature beneficial to catalysis before the contact catalysis step and also preheating hydrogen prior to contact catalysis.

4. A process as defined in claim 2 further comprising pre-heating the path of lateral fluid communication through the shale by hot water prior to introducing steam.

5. A process as defined in claim 4 wherein the pre-heating is accomplished at a temperature just below where pyrolysis of the oil shale begins, in the order of 550° F.

6. A process as defined in claim 5 wherein the approximate limits of the cyclically varying pressure are rock pressure and a lower pressure sufficient to prevent undue steam condensation.

7. An in situ process for winning stabilized primary volatiles from oil shale by pressure pulsing techniques comprising; providing at least one injection well and one production well, pressure parting a bedding plane in the in situ oil shale formation between the injection and production wells, pre-heating the formation on the sides of the parted plane to a temperature between a lower temperature at which there would be excessive condensation of steam and oil entrained vapors and an upper limit at which pyrolysis of the oil shale formation begins, further heating the oil shale adjacent the parted plane after said pre-heating with superheated steam injected into the oil shale via the injection well to a temperature sufficient to cause pyrolysis of the host oil shale, cyclically varying the pressure of the superheated steam to open up tributaries perpendicular to the plane of parting and volatilize the oil shale and to displace the steam and make the host formation permeable, bleeding the steam and oil shale entrained vapors out through the production well, condensing at least some of the entraining steam at a

temperature and pressure such that the entrained oil vapors remain in the vapor phase in order to reduce the partial pressure of steam, re-heating the vapors after the condensing step to a temperature beneficial for catalysis, and accomplishing contact catalysis on the oil shale vapors in the presence of heated hydrogen.

8. An in situ process for winning stabilized primary volatiles from oil shale by pressure pulsing techniques comprising drilling at least one injection and one production well, pressure parting and holding open a bedding plane in the oil shale formation between injection and production wells, pre-heating the formation on the sides of the parted planes by means of hot water to a temperature between the lowest temperature in which there would be excessive condensation of oil, and an upper temperature at which pyrolysis of the oil shale begins, in the order of 550° F., removing the pre-heating hot water, further heating the oil shale adjacent the parted plane after said pre-heating by injecting superheated steam into the oil shale via the injection well at a temperature sufficient to cause pyrolysis of the host oil shale, in the order of 850° F. upwards, cyclically varying the pressure of the superheated steam between an upper pressure equal substantially to rock pressure and a lower pressure sufficient to prevent undue steam condensation, thereby open up tributaries perpendicular to the plane of parting, pyrolyze the oil shale, and then displace the steam and make the host rock permeable, driving the steam entrained vapors out through the production well, condensing enough of the steam from the steam entrained vapors at the output pressure and saturation temperature to significantly lower the partial pressure of steam in the vapor mixture, reheating the vapors to a temperature beneficial to catalysis, and accomplishing contact catalysis on the reheated vapors in the presence of hydrogen.

9. An in situ oil shale process as defined in claim 8 wherein there are a plurality of production wells for each injection well.

References Cited by the Examiner

UNITED STATES PATENTS

1,422,204	7/1922	Hoover et al.	166—11
2,421,528	6/1947	Steffen	166—40 X
2,692,226	10/1954	Smith	208—11
2,813,583	11/1957	Marx et al.	166—11
2,969,226	1/1961	Huntington	166—11 X
3,042,114	7/1962	Willman	166—40 X
3,106,521	10/1963	Huntington	208—11
3,117,072	1/1964	Eastman et al.	208—11
3,155,160	11/1964	Craig et al.	166—40

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