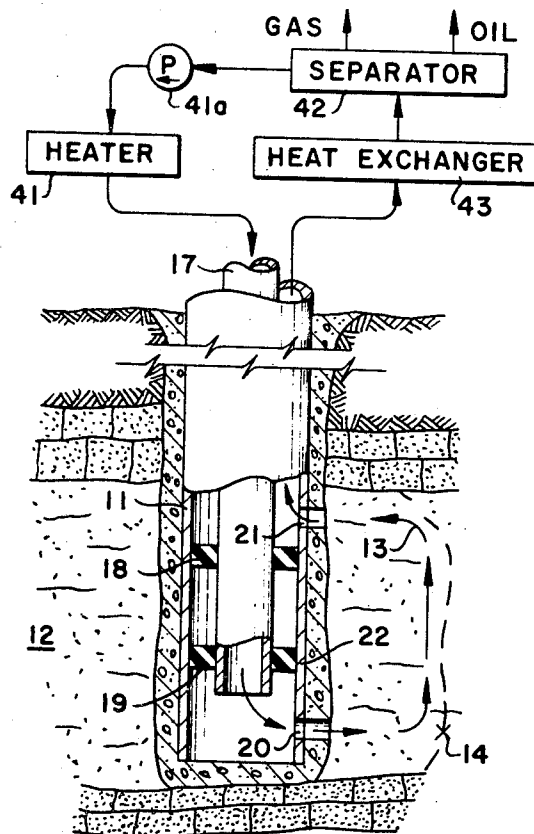


ABSTRACT: A method for producing shale oil from a permeable zone formed within a subterranean oil shale formation by circulating through a well borehole in contact with said permeable zone a fluid containing at least one phenolic compound.



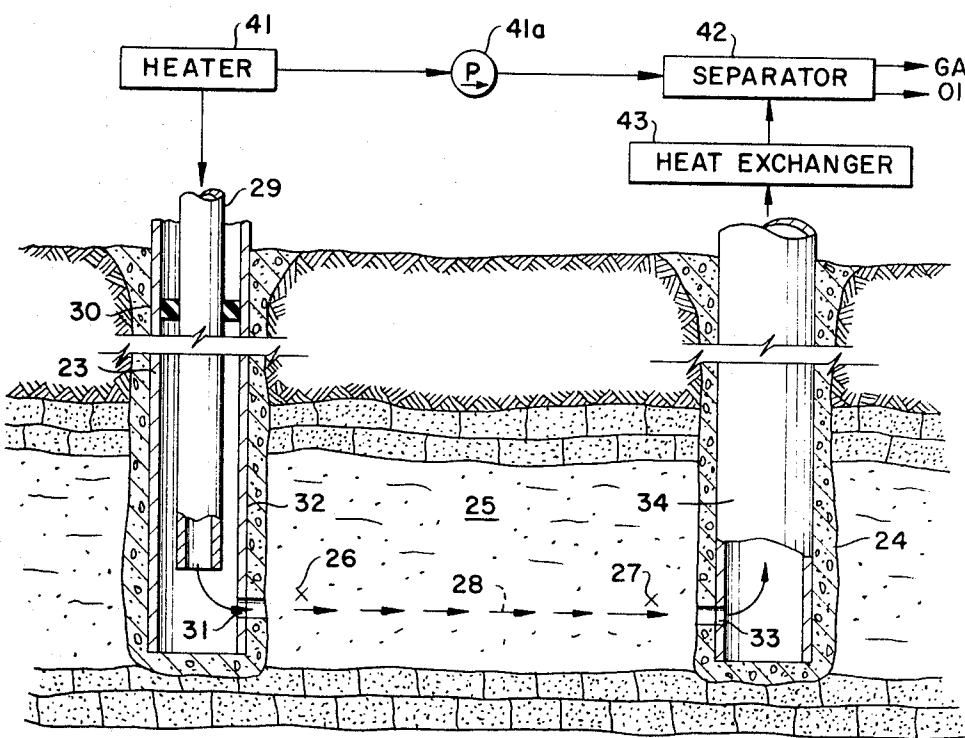


FIG. 2

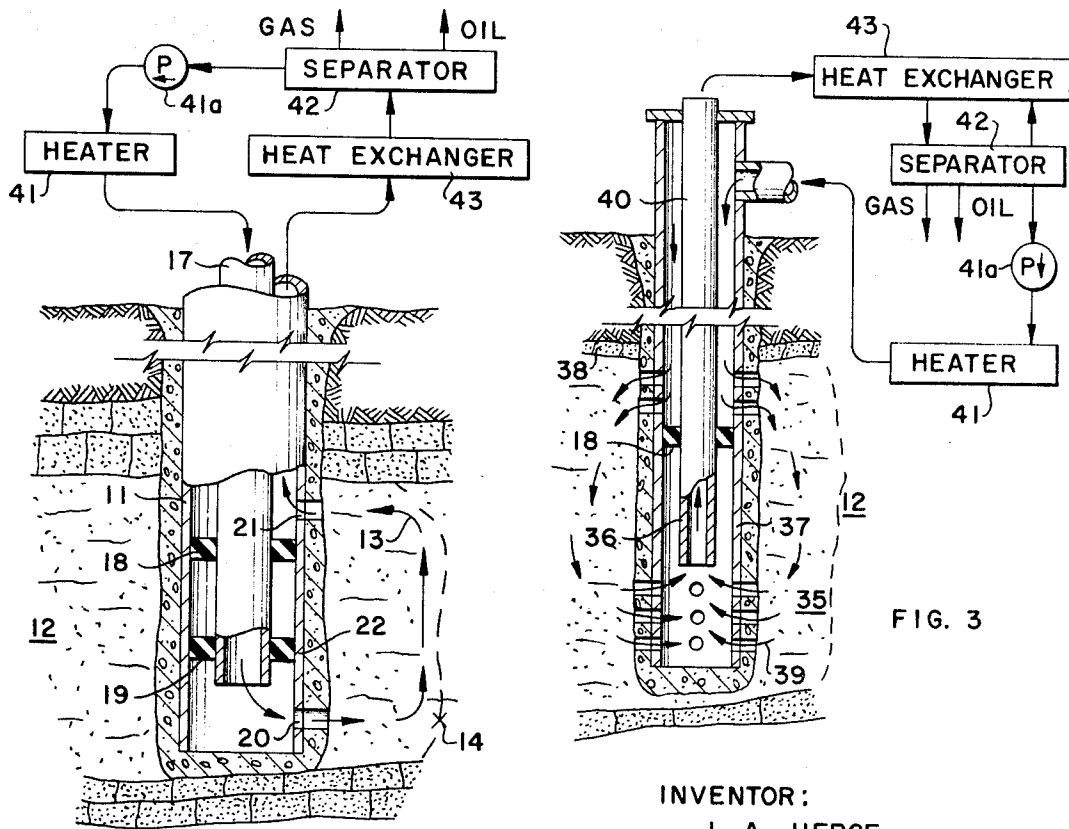


FIG. 3

FIG. 1

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METHOD FOR PRODUCING SHALE OIL FROM AN OIL SHALE FORMATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention relates to a process for solvent extracting shale oil from a subterranean oil shale formation; more particularly, it relates to a process for recovering shale oil from a permeable zone in an oil shale formation by circulating therethrough at least one phenolic compound.

2. Description of the Prior Art

Shale oil as kerogen, which is a bituminous material present in oil shale formations, can be removed from oil shale by pyrolysis at elevated temperatures. A big drawback to the retorting of oil shale to recover shale oil is the need to remove and dispose of a substantial amount of the shale after it has been retorted. In view thereof, in situ retorting has found much favor in recent years as a method of recovering shale oil, particularly from subterranean oil shale formations. One such method is to create a large, permeable zone within the oil shale formation by rubbleizing such a zone by an explosion within the formation, e.g., by utilizing high-energy explosives such as nuclear bombs. One or more access wells are then drilled into the fragmented zone and communication is established between the permeable zone and openings into the wells. Hot fluids are then injected, usually to start an in situ combustion heating process which causes the shale oil (kerogen) to become fluidized. The shale oil is then recovered from a production well by conventional means.

SUMMARY OF THE INVENTION

It is an object of this invention to produce shale oil from a subterranean oil shale formation more efficiently than has been previously accomplished.

It is a further object of this invention to improve the rate of recovery, amount of recovery and/or the nature of the petroleum materials that are recovered from a subterranean oil shale formation by use of at least one phenolic compound having unique oil-extracting properties.

These objects are accomplished by extending at least one well bore hole into a permeable zone formed within a subterranean oil shale formation and circulating an aromatic organic Brønsted acid, such as a phenolic compound therethrough per se or in a fluid carrier. Shale oil and circulating extracting fluid material are then recovered from the permeable zone and the shale oil is separated from the extracting material. The formation should be preheated prior to injection or the circulating fluid should be injected hot in carrying out this process. By "aromatic Brønsted acid" is meant an aromatic substance that loses a proton as defined in "Advanced Organic Chemistry," pp. 491-2, by Fieser and Fieser (1961).

In situations in which it is desirable to mine portions of an oil shale formation and pyrolyze the mined oil shale in a fluid-heated, pressure tight, surface located retort, the pyrolytic recovery of petroleum material is improved by incorporating an effective amount of phenolic compound in the hot fluid with which the oil shale is contacted. In such a process, chunks or fragments of the oil shale are preferably contacted with a hot aqueous and/or hydrocarbon fluid that contains at least about 10 percent by volume of at least one phenolic compound employing a temperature of at least about 650° F. under a pressure sufficient to keep a significant proportion of the fluid in the liquid phase. Where the oil-shale-contacting fluid predominates in hydrocarbon components, e.g., a benzene solution of a phenolic compound, the oil shale is preferably preheated by contacting it with hot aqueous liquid. The contacting of chunks of oil shale with a hot aqueous liquid, (i.e., with hot water utilized in preheating the oil shale and/or a hot aqueous solution containing at least one phenolic compound) tends to exfoliate the pieces of the oil shale. The exfoliation reduces the tendency for clinkers to be formed during the pyrolysis-extraction operation and reduces the ex-

tent to which the oil shale needs to be crushed in order to obtain an efficient recovery of petroleum material.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a vertical sectional view of an oil shale formation to which the recovery process of this invention has been applied, involving a single-well borehole;

FIG. 2 is a vertical sectional view of the oil shale formation of FIG. 1 wherein a pair of well boreholes are disposed in accordance with the teachings of my invention; and

FIG. 3 is a vertical sectional view of an alternate recovery process of the invention applied to the single-well borehole of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Referring to the drawing, FIG. 1 shows a well borehole 11 extending into subterranean oil shale formation 12. Fluid communication may be established between points 13 and 14 in oil shale formation 12 and adjacent to borehole 11 along a vertical fracture by, for example, a conventional hydraulic fracturing procedure. Hot, aromatic Brønsted acid such as a phenolic compound or fluid containing such acid is then circulated through tubing 17 past packers 18 and 19, or the formation should be heated and the fluid injected, until oil shale-derived fluidizable materials are entrained in the circulating fluid. The fluid passes through perforations 20 and 21 in casing 22. Of course, if the wellbore 11 is uncased, such perforations are unnecessary. The fluidizable materials may then be recovered from the outflowing portions of the circulating fluid by any known means. Thus, a single well may be used, although it is generally preferred to use at least a pair of wells. As seen in FIG. 1, if a single well is used, the preferred two points may be a pair of substantially vertically separated points that are apt to be encountered by vertical fractures within the oil shale.

As shown in FIG. 2, a pair of wellbores 23 and 24 extend into subterranean oil shale formation 25. Fluid communication is established between point 26 adjacent to wellbore 23 and point 27 adjacent to wellbore 24. In a preferred embodiment, the depths of such points may be those at which a tuffaceous streak is encountered by a pair of well boreholes between which the streak is continuous. The permeable channel extending through the oil shale may be formed by the process of locating and acidizing a tuffaceous streak as described in an application Ser. No. 619,259 filed Feb. 28, 1967 to Prats, now U.S. Pat. No. 3,481,398. A hot phenolic compound, such as an aromatic Brønsted acid or a fluid containing the acid, is then circulated through tubing 29 past packer 30, until the oil shale-derived fluidizable materials are entrained in the circulating fluid. The circulating fluid passes through perforation 31 in the casing 32 of wellbore 23, through points 26 and 27, and through perforation 33 in the casing 34 or wellbore 24. Again, if the well is uncased, such perforations are unnecessary. Fluidizable materials which are derived from the oil shale can then be recovered from the circulated fluid by any known means.

The circulation of the hot fluid may be a long duration heating operation, and, for some time, the amount of oil production may be insignificant. The temperature of the circulating fluid is preferably monitored either at the point at which the fluid flows out of the permeable path or at the wellhead.

Oil shales are generally impermeable. Once a permeable path has been established between a pair of wells, the permeable path will provide substantially the only zone that can be penetrated by a fluid injected into either of the wells. In view of this, relatively simple equipment can be utilized to circulate the heated fluid through the permeable path between the selected points. The fluid can be pumped through a heating device, through the permeable path, through a temperature-monitoring device, and then recycled back through the heating device. The duration of the heating that is necessary for a given oil shale can be determined by maintaining a sample of

the shale at an equivalent temperature for an equivalent time until a suitable degree of conversion is obtained. This can be done prior to or while circulating the fluid.

In FIG. 3, an alternate recovery process, which can be operated with a single well, is illustrated. Here, the permeable channel formed within oil shale formation 12 is preferably a relatively voluminous permeable fragmented zone 35. The term "permeable fragmented zone" refers to a multiply-fractured zone in which the number of the fractures and the volume of the interconnected openings within the fractures provide a void volume of from about 5 to 40 per cent of the volume of the zone.

Permeable fragmented zones can be formed by known hydraulic and/or explosive techniques for fracturing subsurface earth formations. One suitable fracturing technique was described in 1922, in U.S. Pat. No. 1,422,204. The streak acidizing procedure of application Ser. No. 619,259, filed Feb. 28, 1967 which matured as U.S. Pat. No. 3,481,398 on Dec. 2, 1969, may be used, preferably to form a channel into which a liquid explosive is injected and subsequently detonated to form a generally disc-shaped permeable fragmented zone. High-power explosives, such as those produced by nuclear devices, are particularly suitable means for forming such fragmented zones. In general, the permeable fragmented zone formed by a nuclear device has a vertically extensive and generally cylindrical shape.

In circulating hot fluid through a permeable fragmented zone, the flow paths can be vertical or horizontal and can involve a radially expanding or line-drive type of displacement of the fluid that is circulated through the oil shale. Generally, a substantially vertical downward flow is preferred.

FIG. 3 illustrates a portion of a nuclear chimney type of permeable fragmented zone 35. In treating such a zone, one or more wells 36 are drilled to near the bottom, preferably while the zone is hot, or at least warm, from the explosion energy. In the illustrated arrangement of FIG. 3, the well 36 is drilled and cased to near the bottom and the casing 37 is perforated at 38 and 39 and equipped for injecting fluid through the borehole annulus above packer 18, and through perforations 38 into the upper portion of the fragmented zone. Fluid is produced from near the bottom of the zone through perforations 39 and tubing string 40.

With such an arrangement, the pressure within the permeable fragmented zone is adjusted to one selected for the circulation of heated fluid. The adjustment is affected by controlling the rate of withdrawing fluid from the cavern relative to the rate of injecting fluid into the cavern. As indicated in FIGS. 1 through 3, conventional equipment and techniques, such as heater 41, pump 41a, separator 42 and heat exchanger 43 may be used for pressurizing, heating, injecting, producing, and separating components of the fluid that is circulated through the permeable zone 35. The production of the fluid can be aided by downhole pumping means, now shown, or restricted to the extent necessary to maintain the selected pressure within the zone. The pressure in the zone is preferably maintained at a level suited for economically transferring heat into the zone by circulating a fluid that is economically available at the well site.

A wide variety of aromatic Brønsted acids and fluids containing such acids may be used in this process. The main requirements are that these acids be pumpable at a moderate temperature such as from about 400° to 600° F. Carriers for the aromatic Brønsted Acids can be oil-immiscible fluids such as water; aqueous liquids; steams of various grades, such as a low quality steam, dry steam or supersaturated steam; or oil miscible fluids such as relatively low-cost volatile hydrocarbons that contain or consist essentially of volatile oil shale hydrocarbons that contain or consist essentially of volatile oil shale hydrocarbons may be used. The aqueous fluids, e.g., water, should be softened to inhibit scaling at the temperatures to which they are heated.

In certain situations, it is advantageous to circulate a mixture of relatively low-molecular weight, predominantly aro-

matic hydrocarbons having relatively low critical temperatures and pressures. With such hydrocarbons (which may include significant proportions of shale oil hydrocarbon) the temperatures and pressures within the permeable zone may provide conditions approaching or exceeding the critical conditions for part or all of the circulating hydrocarbons. In the critical or supercritical region, such hydrocarbons have densities and viscosities that are intermediate between their gas and liquid states and are particularly effective in extracting organic components from oil shale.

In a preferred feature of my invention, an aromatic Brønsted acid, a reactive petroleum-extracting material having unique properties, is added to the fluid being circulated through the permeable oil shale formation of FIGS. 1 through 3 in an amount as low as about 10 per cent by volume of the injected fluid. The reactive material may be mixed with either an oil-immiscible or an oil-miscible fluid. The reactive materials also include phenolic or substituted phenolic compounds, e.g., phenol or cresol, which are relatively soluble in either oil or water. In the preferred method of my invention disclosed herein, the reactive material containing circulating fluid may contain the reactive material either as a solute and/or a separate fluid phase that is introduced either continuously or intermittently into the well boreholes of FIGS. 1 through 3.

EXAMPLE

It has been found that the addition of a phenolic or substituted phenolic compound to a fluid (e.g., water or benzene) circulating through a permeable oil shale formation results in the extraction of significant amounts of organic matter from the oil shale within the oil shale formation. Recoveries of 120 percent Fisher Assay have been obtained with such phenolic compounds in much shorter time periods than known prior art processes, as for example the process disclosed in application Ser. No. 656,815, filed July 28, 1967 to Deans et al. which matured as U.S. Pat. No. 3,474,863 on Oct. 28, 1969 in which shale oil is produced by circulating a volatile, normally liquid oil solvent through a permeable fragmented zone within a subterranean oil shale formation under supercritical conditions of temperature and pressure. In the Deans et al. application, it was found that the addition of a normally liquid hydrocarbon solvent, such as benzene, to the circulating fluid gave results far superior to known prior art processes. Solvent extractions utilizing aromatic Brønsted acids, e.g., phenol or cresol, have achieved much greater recovery of oil than benzene solvents. For example, in an eight day period, 120 percent Fisher Assay was extracted by the circulation of pure phenol. Under very long solvent oil shale contact times, recovery by the circulation of phenol still attained 120 percent Fisher Assay. The phenol solvent may be recovered by conventional distillation methods yielding both pure phenol to be recycled back into the oil shale formation and an organic enriched phenolic liquor. Further, a phenolic compound miscible in water may be dissolved in water and then flowed through the permeable oil shale formation. Tests have shown that phenol-water solutions of from about 25 percent phenol / 75 percent water effectively recover the shale oil (kerogen) from oil shale. The phenol water mixture of this method is sufficiently acidic to attack the carbonates which form a portion of the inorganic matrix of the oil shale within the oil shale formation. These acid attacks increase the permeability of the oil shale and lessen the resistance of the oil shale to the circulating fluid.

The Fisher Assay method is a standard analytical method used to determine the richness of an oil shale. The results are commonly given in gallons of shale oil per ton of oil shale. Since this method is essentially a retorting process, much of the organic matter in the oil shale is converted to gas and approximately 20 percent of the kerogen is left in the residue as fixed carbon. Thermal solution processes, such as disclosed herein, on the other hand, may be carried out at much lower temperatures and more organic matter may be recovered without coking it. Therefore, recoveries by a thermal solution

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process, in accordance with the teachings of my invention, resulting in a Fisher Assay greater than 100 percent are not anomalous.

Although good results in accordance with the teachings of the present invention have been obtained with phenolic or substituted phenolic compounds, any suitable aromatic organic Brønsted acid having an active hydrogen proton may be used with varying degrees of effectiveness. Examples of such organic compounds include: phenol, cresol, catechol, resorcinol, aromatic carboxylic acids, substituted aromatic carboxylic acids, etc.

The use of aromatic organic Brønsted acids, such as phenol or cresol, provides a substance which donates active hydrogen ions (protons) for attacking oil shale in situ. The active hydrogen ions attack the acid-soluble inorganic components of the oil shale, causing increased permeability and solution of the inorganic matrix material. The active hydrogen ions may also attack particular functional groups contained in the kerogen molecules in the oil shale by breaking such molecules into smaller fragments more amenable to solution. The remainder of the active hydrogen donor molecule, after donation, is employed both as a solvent for the kerogen fragments and as a transportation medium for bringing the fragments to the earth's surface. Finally, the entire process may take place at elevated temperature (namely above 400 ° F.) and pressure conditions, but these conditions must be such that the solvent employed exists as a liquid.

I claim:

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1. In a method for producing shale oil from a subterranean oil shale formation comprising the steps of:

forming a permeable zone within a subterranean oil shale formation;

extending at least one well borehole into the permeable zone within said subterranean oil shale formation;

circulating a hot fluid containing an aromatic Brønsted acid through said permeable zone;

recovering shale oil and a fluid containing said aromatic Brønsted acid; and

separating the oil from the fluid containing said aromatic Brønsted acid.

2. The method of claim 1, wherein the Brønsted acid is a monomeric phenolic compound.

3. The method of claim 2 wherein the monomeric phenolic compound comprises about 10 percent by volume of the circulating fluid.

4. The method of claim 2 wherein the step of circulating a fluid containing at least one phenolic compound therein includes the step of introducing said phenolic compound continuously into said permeable zone while said fluid is being circulated therethrough.

5. The method of claim 1 wherein the circulating fluid is water containing phenol.

6. The method of claim 1 wherein the circulating fluid is an oil-miscible fluid containing phenol.

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