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METHOD OF RECOVERING OIL FROM UNDERGROUND RESERVOIR

Filed Jan. 21, 1963  2 Sheets-Sheet 1

**Fig. 1**

![Graph showing C4, C7, and C10 hydrocarbon pressures](image)

**Fig. 2**

![Graph showing miscible displacement pressure](image)

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BY [Signature]
**Fig. 3**

**Fig. 4**

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METHOD OF RECOVERING OIL FROM UNDERGROUND RESERVOIR

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10 Claims. (Cl. 166—9)

The present application is a continuation-in-part of application Serial No. 755,480, filed August 18, 1958, now abandoned.

The present invention relates to a method of recovering oil from subsurface earth formations. In a more particular aspect, the present invention relates to a method of recovering oil from subsurface earth formations by the injection of gases comprising gas, with minor amounts of other gases at pressures within a critical range.

In the recovery of oil from subsurface earth formations by the application of external energy, as opposed to natural reservoir energy, it has heretofore been proposed to inject natural gas and other gases which are sparingly soluble in reservoir oil under conventional reservoir pressure or nitrogen, air or other gases which are inert so far as their action or reaction with reservoir oil is concerned and are substantially insoluble therein. At the conventional pressures employed in such operations, generally below about 1500 p.s.i.g., any fluid in its gaseous state merely acts as a pusher; and, due to vast differences between the mobility of the gas as compared with the mobility of the more viscous oil, substantial amounts of the oil are bypassed and cannot be recovered. In addition, nitrogen, air, or other gases containing inert components, are much less efficient than natural gas since inert gases are substantially less soluble in reservoir oil than is natural gas.

It is, therefore, an object of the present invention to provide an improved method of recovering oil from a non-depleted oil reservoir by the injection of gases comprising nitrogen with minor amounts of other gases at a pressure within a critical range.

Another object of the present invention is to provide an improved method of recovering oil from a non-depleted oil reservoir by the injection of gases comprising nitrogen with minor amounts of other gases at a pressure below that pressure which will fracture the subsurface formation and above a pressure which will maintain the injected gas and reservoir oil miscible at all points of contact.

Another and further object of the present invention is to provide an improved method of producing oil from a non-depleted oil reservoir by the injection of gases containing nitrogen at a pressure below that pressure which will fracture the subsurface formation and above a pressure which will maintain the injected gas and reservoir oil miscible at all points of contact.

A further object of the present invention is to provide an improved method for producing oil from a non-depleted oil reservoir by the injection of nitrogen, air, flue gas or other gases containing at least about 80 percent by volume of nitrogen at a pressure below that pressure which will fracture the subsurface formation and above a pressure which will maintain the injected gas and reservoir oil miscible at all points of contact.

A still further object of the present invention is to provide an improved method for recovering oil from a non-depleted oil reservoir by the injection of a gas containing at least about 80 percent by volume of nitrogen, in which less than the first 0.10 pore volume of such gas initially contains at least about 90 percent by volume of \( C_1 \) to \( C_4 \) hydrocarbons gradually decreasing to 0 percent, at a pressure above that pressure which will maintain the injected gas and the oil miscible at all points of contact.

Other and further objects of the present invention will be apparent from the following detailed description when read in conjunction with the drawings, wherein;

FIGURE 1 is a plot of critical pressures for methane-\( C_4 \) hydrocarbon systems versus cricondenbar pressures for nitrogen-\( C_4 \) hydrocarbon systems.

FIGURE 2 is a plot of percent by volume of nitrogen in a nitrogen-natural gas mixture versus miscible displacement pressure.

FIGURE 3 shows plots of percent oil displaced from the first 123 feet and the last 22 feet of a 145 foot core by flue gas at various pressures, and

FIGURE 4 is a plot of the nitrogen content of the free gas produced after breakthrough of displacement gas versus the volume of free gas produced during the displacement of oil from a 145 foot core by flue gas at 3850 p.s.i.

Although, classically, the term "cricondenbar" has been used to denote the maximum pressure at which a given binary system of a given composition can exist in two phases (Chemical Engineering Thermo-Dynamics, Dodge-McGraw-Hill, first edition, page 545), for purposes of the present invention, the term, cricondenbar, shall mean the maximum pressure at reservoir temperature at which two phases can exist for any mixture consisting of the reservoir oil and the injection gases proposed to be injected into the reservoir. An example of the cricondenbar pressure as used in this sense is disclosed in Petroleum Transactions, AIME, volume 195, page 181, 1952.

The terms "nondepleted reservoir" or "producing reservoir" as used herein are meant to include an oil reservoir which, at the beginning of treatment by the method of this invention, contains reservoir oil which is undersaturated with gas or an oil reservoir which, at the beginning of treatment by the method of this invention, contains reservoir oil saturated with gas and a small volume of free gas but which, upon application of the preselected pressure in accordance with the present invention, will become undersaturated by solution in the oil of the free gas phase.

It has been taught in United States Patents Nos. 2,724,437 and 2,724,438 that substantially improved oil recovery can be obtained by injecting into a nondepleted reservoir natural gas or other normally gaseous hydrocarbons at pressures which will maintain miscibility between the injected gas and the reservoir oil. In some instances, such miscibility can be attained by injecting the natural gas at pressures above the cricondenbar pressure provided the formation can withstand such high pressure without formation fracturing occurring. However, as specifically taught in accordance with United States Patent No. 2,724,438, miscibility at all points of contact between the injected gas and the reservoir oil can be attained at pressures well below the cricondenbar pressure, and substantially the same ultimate production can be obtained at these lower pressures as can be obtained at pressures above the cricondenbar pressure.

In view of the prior art disclosures that nitrogen and gases containing substantial amounts of nitrogen can be employed in low pressure gas injection processes coupled with the teachings of United States Patent No. 2,724,438, one would assume that nitrogen could be substituted directly for normally gaseous hydrocarbons in the miscible displacement process of the subject patent. However, based on all available data concerning nitrogen hydrocarbon systems, it becomes rather obvious that such substitution is not practical. Based on available data concerning cricondenbar pressures for nitrogen and various \( C_4 \) hydrocarbons and available data concerning the cri-
condenbar pressures of methane-CA hydrocarbon systems, the relationship of the cricondenbars for nitrogen-hydrocarbon systems and methane-hydrocarbon systems can be illustrated by the plot of FIGURE 1. It can be observed from FIGURE 1 that the cricondenbar pressures for nitrogen-hydrocarbon systems are severalfold greater than those for methane-hydrocarbon systems and that, as the molecular weight of the hydrocarbon increases, the spread between the two cricondenbar pressures for the same hydrocarbon becomes even greater. Based on the plot of FIGURE 1, one may predict the cricondenbar pressure for a given reservoir oil based on the known or measured cricondenbar pressure for the same oil and methane. For example, for an undersaturated reservoir fluid having the following composition:

<table>
<thead>
<tr>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
</tr>
<tr>
<td>C2</td>
</tr>
<tr>
<td>C3</td>
</tr>
<tr>
<td>C4</td>
</tr>
<tr>
<td>C5</td>
</tr>
</tbody>
</table>

It is known that the cricondenbar pressure of mixtures of this reservoir oil with methane is 8800 p.s.i. Referring to FIGURE 1, the estimated cricondenbar pressure of mixtures of nitrogen with this same oil would be 36,000 p.s.i. Obviously, the latter pressure is well above practical limits. It is also recognized that this pressure would cause fracturing of the oil producing formation and is also much greater than the pressure which available laboratory equipment employed in the study of gas injection processes can withstand. Therefore, one would obviously not be able to obtain miscibility by injecting nitrogen into a reservoir at or above the cricondenbar pressure.

However, as taught in United States Patent No. 2,724,438, miscibility at all points of contact between an injected natural gas and a reservoir oil can be attained at pressures well below the cricondenbar pressure and ultimate oil recovery equivalent to that obtainable by operations at or above the cricondenbar pressure can be obtained at this lower pressure. Employing natural gas, containing 85 percent methane and 15 percent ethane, as a driving fluid, it has been found that miscibility can be attained at a pressure of 3,500 p.s.i. when this gas is employed to displace a reservoir oil of the composition previously set forth. The cricondenbar pressure is approximately 60 percent lower than the cricondenbar pressure for the same system. Using these teachings of the subject patent, one could, therefore, predict that miscibility could be attained between the reservoir fluid referred to and nitrogen at a pressure somewhat above 14,000 p.s.i. This predicted miscible pressure for the nitrogen-oil system is, however, little help since, again, the pressure is above all practical limits.

Contrary to these teachings of the prior art and the conclusions which one skilled in the art would reach based on these teachings, it has been found in accordance with the present invention that nitrogen or gases containing substantial amounts of nitrogen can be employed to miscibly displace reservoir oil from nondepleted reservoirs at pressures only slightly greater than those necessary to attain miscible displacement with normally gaseous hydrocarbons. This is particularly true when one has previously exemplified, it has been found in accordance with the present invention that miscibility can be attained and a miscible displacement process carried out by injecting pure nitrogen at a pressure of 3870 p.s.i. For this particular system, the difference between the miscible pressure for natural gas and that for pure nitrogen is only 370 p.s.i., and this miscible pressure for nitrogen is 10,130 p.s.i. lower than the miscible pressure which one would expect.

Work in connection with the process of United States Patent No. 2,724,438 and related miscible displacement processes had also taught that miscibility between the reservoir oil and the injected gas could be created within a few feet of travel of the injected gas and the miscibility pressure could in all cases be determined in a laboratory core 25 feet in length. In the patented process it was further taught that miscibility could be obtained by injecting a mixture of C2 to C4 hydrocarbons from the reservoir oil to the leading edge of injected gas thereby building up a short transition zone in which the fluids at any given point were miscible with one another. In addition, it was well settled that the gas in contact with the oil must be a hydrocarbon gas and that at least 0.1 percent volume of such gas must be injected before any other fluid in order to carry out the process and displace oil at practical reservoir pressures.

It has also been found, in accordance with the present invention, that miscibility between oil and nitrogen or gases containing substantial amounts of nitrogen is not created until the gas has traveled at least about 100 feet and the miscibility pressure in this case cannot be determined in a core less than about 100 feet in length. The comparatively long path length required to create miscibility between nitrogen and oil is attributable to the additional discovery that nitrogen must be transferred from the injected gas to the oil and C2 to C4 hydrocarbons, must be transferred from the oil to the injected gas to build up a transition zone with miscibility throughout.

Therefore, in accordance with the present invention, substantially improved results can be obtained over conventional low pressure injection processes by injecting gases containing at least about 80 percent by volume of nitrogen into the reservoir at a pressure in excess of that necessary to maintain miscibility, as determined by a conventional laboratory procedure hereinafter described, but below that pressure which will cause fracturing of the reservoir formation.

FIGURE 2 illustrates the unexpectedly low pressures at which miscibility can be attained when nitrogen or mixtures of nitrogen with C1 are used to displace the previously mentioned reservoir oil as compared with pure C1. In this series of runs, C1, nitrogen and mixtures of C1 and nitrogen were used to displace the oil from an artificial sand column 123 feet in length at a temperature of 140° F. The ultimate stock tank recovery at abandonment gas-oil ratio (30,000 scf/STB) was calculated as percent of the oil initially in place in the core. The percent ultimate recovery for mixtures containing at least 5 percent nitrogen was found to range between 83.6 and 87.3 percent of the oil initially in place. The difference between this recovery and the 95 percent recovery obtained when methane or natural gasmiscibly displaces oil will be apparent from the following discussion of FIGURE 3.

FIGURE 3 plots the results of a number of tests conducted in the same manner as the tests of FIGURE 2 except that flue gas (87.5 percent nitrogen and 12.5 percent CO2) was employed as the displacing gas in all cases and a detachable 22 foot section was added to the 123 foot core to give an overall length of 147 feet. In addition, in each test miscibility or lack of miscibility was determined at the end of the 123 foot core and the 22 foot extension and ultimate recoveries from the 123 foot core and the 22 foot extension were measured. These results are recorded in FIGURE 3. It is to be observed that at 3600 p.s.i. miscibility had not been attained by the time the gas had reached the 123 foot core or the 22 foot extension. At 3750 p.s.i. none of the oil had been miscibly displaced in the 123 foot core and only part of the oil was miscibly displaced in the terminal end of the 22 foot extension. At 3850 p.s.i. and 4000 p.s.i. part of the oil was miscibly displaced from the terminal part of the 123 foot core and all of the oil was miscibly displaced from the 22 foot extension. Thus, it is obvious that gases containing substantial amounts of nitrogen must travel at least about 100 feet in order to create miscibility and if a sufficiently long travel path is available miscibility can be attained.
at pressures only slightly above the miscible pressure of methane and the reservoir oil (3500 p.s.i.). This effect also explains the lower than anticipated recoveries for nitrogen as compared with methane since about 10 percent of the oil was bypassed due to immiscible hydrocarbon displacement through part of the runs. However, the small amount of oil thus bypassed in the first 100 feet of travel of the gas is much less significant when an actual reservoir is treated and the overall recovery will still be substantially 95 percent of the oil in place in the area of the reservoir contacted.

The effect of using the runs of FIGURE 3, the free gas (gas in excess of solution gas) was analyzed after gas breakthrough at the end of the 145 foot core. FIGURE 4 is a plot of the nitrogen content of the free gas produced in the 3850 p.s.i. run. It is to be observed that the gas in immediate contact with the oil contained 9.0 percent nitrogen, the remainder being C3 through C6 hydrocarbons transferred from the oil. Therefore, the nitrogen content of the free gas increased rapidly and the C2 through C6 hydrocarbons decreased. It was further determined that in all cases the nitrogen content of the first gas was less than 10 percent and specifically between 3 and 7 percent. The ratio of C1 to C6 hydrocarbons in the free gas was also found to be between about 3 to 1 and 2 to 1. Thus, in order for nitrogen to miscibly displace oil at practical reservoir pressures the oil must be substantially free of nitrogen and there must be a transfer of nitrogen from the gas to the oil and C1 from the oil to the nitrogen.

Although it was previously indicated that nitrogen must travel at least 100 feet in order to build up a transition zone with miscibility throughout, it was found as a result of the previously described gas analysis that the transition zone (nitrogen mixed with C3 through C6 hydrocarbons) itself was only 25 feet long. Accordingly, in a variation of the present invention the length of the path necessary to create miscibility can be reduced and the pressure necessary for miscibility can be reduced slightly by preinjecting the mixed transition zone. Specifically, less than the first 0.10 pore volume, and preferably 0.05 pore volume, of the injected nitrogen gas would have added thereto C1 through C6 hydrocarbons in a gradually decreasing volume from at least 90 percent to 0 percent. The added hydrocarbon gas should preferably have a ratio of C1 to C6 through C6 hydrocarbons of between about 3 to 1 and 2 to 1.

As stated previously, the upper limit of pressures to be employed in accordance with the present invention is that pressure which would be sufficient to fracture the oil-producing formation in which the process is to be practiced. Generally, the formation breakdown pressure for formations deeper than 4000 feet consists predominantly of the pressure necessary to lift the overburden. This formation breakdown pressure can be calculated with reasonable accuracy and is equal to between 0.57 and 0.83 p.s.i. per foot of depth for formations deeper than 4000 feet. At depths less than 4000 feet, the formation breakdown pressure is made up predominantly of the pressure necessary to overcome the rock-bonding strength which also can be calculated by well-known means but, in general, is 4000 p.s.i. or less.

The minimum pressure in accordance with the present invention must be attained between the reservoir oil and the injection gas exists as determined by laboratory long core displacement runs. Such long core displacement runs are described and illustrated in detail in the United States Patent No. 2,724,438 and briefly consist of displacing reservoir oil from a core filled with such oil by means of the injection gas at a series of different pressures as observed through the visual cell the lowest pressure at which all effluent is a single phase. At or above this miscible pressure, the effluent of the core is a single phase at all times and as observed through the visual cell the effluent changes gradually from a single phase liquid oil before gas breakthrough to a single phase gas when a substantial change in the gas-oil ratio occurs (about 10,000 s.c.f./STB to 15,000 s.c.f./STB). As a practical matter, the run is usually continued until abandonment gas-oil ratio (generally selected at 30,000 s.c.f./STB of oil) is reached.

In short, two simultaneously flowing phases of gas and liquid will not appear at any time during a miscible displacement; that is, at no time will gas bubbles appear in a liquid phase, and at no time will liquid droplets appear in a gaseous phase.

In conducting long core displacement runs in accordance with this invention, an artificial core is constructed by filling a 100 foot or longer length of 2-inch tubing with a 140 to 200 mesh sand. The length of the sand core is important since a core shorter than 100 feet has been found to be too short to permit adequate mixing and contact at the point of contact between the oil and the gas. Oil which has been stabilized at atmospheric pressure, which is generally referred to as "dead oil," is then pumped into the core at a pressure of about 500 p.s.i. to displace any air or gas which might be present therein. The core is then heated by a fluid-filled jacket or an electrical coil to bring the temperature of the core to the desired reservoir temperature. Reservoir oil having the same composition and characteristics as that of the reservoir to be treated is then pumped into the core until all of the dead oil has been displaced and the core is filled with reservoir oil at reservoir temperature and existing reservoir pressure. The injection gas, in this case nitrogen or mixtures of nitrogen with minor amounts of other gases, is pumped into the core at a preselected pressure while simultaneously producing fluids from the effluent end of the core. A back pressure is maintained on the effluent end of the core which is sufficient to maintain a pressure differential of approximately 50 p.s.i. so that oil will flow from the core due to the slightly higher pressure of the injection gas. Immediately adjacent the effluent end of the core, the effluent passes through a visual cell in which the operator may observe the nature of the effluent at all times. By repeating this procedure at several different gas injection pressures, a pressure will be found at which the oil and the injection gas are miscible and at which a single phase will be observed at all times throughout the course of the run. Below this pressure, two phases will be observed to be flowing simultaneously at some point during the run. Various such modifications of this procedure which are well-known to those skilled in the art may be practiced without departing from the present invention. For example, a tube of smaller diameter may be employed so long as it is sufficient in length to permit adequate mixing and contact (at least 100 feet) or naptha rather than dead oil may be employed to purge the core of air or gas.

While any pressure below formation breakdown pressure but above the miscible pressure, as determined above, can be employed in the practice of the present invention, it is obvious that the miscible pressure or a pressure slightly above the miscible pressure will be most convenient and economical.

As has been pointed out, the present invention is applicable to a producing or nondepleted reservoir, as defined, since it is only in this type of reservoir that miscibility can be attained between the reservoir oil and the injection gas and that the unexpectedly high recoveries of oil that are possible. In depleted reservoirs which are not undersaturated or cannot be made undersaturated at the operating pressure, the injection gas will bypass a substantial amount of the oil and no advantage will be obtained over that of conventional low pressure displacement processes carried out at a pressure of 500 p.s.i. or lower.

In the actual application of the method of this invention to a reservoir, the basic steps are the same as those previously described in connection with the conduct of a long core displacement run. Briefly, having predeter-
mined the operating pressure, as outlined above, the gas is continuously injected into one or more injection wells at a pressure sufficient to maintain such predetermined pressure at the zone of contact between reservoir oil and the injection gas, such gas injection and pressure maintenance is continued to force the gas through the reservoir and displace oil from the reservoir ahead of the gas, and, simultaneously with such injection fluids are recovered through one or more production wells. Obviously, the surface pressure at the producing wells should be slightly lower than that at the injection wells in order to obtain production and maintain flow through the reservoir. Fluids recovered through the production wells will initially consist of a liquid oil phase with minor amounts of natural gas in solution until breakthrough of the injection gas. Following injection gas breakthrough, the gas-oil ratio will begin to rise due to the presence of increasing amounts of injection gas in the fluid but the produced fluid will still be a single phase fluid gradually changing from liquid to oil to injection gas. Finally, at abandonment gas-oil ratio, conventionally 30,000 s.c.f./STB, the fluid will be substantially an injection gas phase with oil dispersed therein, at which time the process is discontinued. Various patterns of injection and production wells may be selected, depending upon field geometry and other factors well-known to those skilled in the art.

Gases, containing substantial amounts of nitrogen, to be used in accordance with the present invention, include nitrogen, air, flue gas, and other gases containing at least about 80 percent by volume of nitrogen. Flue gas is the preferred gas in accordance with the present invention. It should be apparent that a substantial economic advantage exists in the use of flue gas as opposed to natural gas since combustion of one volume of natural gas will produce nine volumes of flue gas. Accordingly, the present invention is particularly adapted to use in areas where natural gas is in short supply since simply converting the available natural gas to flue gas, a ninefold increase in volume is obtained. A typical flue gas will contain approximately 85 to 90 percent by volume of nitrogen and 15 to 10 percent by volume of carbon dioxide.

Having described the present invention and illustrated the same by specific examples, it is to be understood that such examples are illustrative only and are not to be construed as limiting the present invention, and that equivalent materials and techniques or modifications thereof will be apparent to one skilled in the art and such equivalents and modifications are intended to be covered by the appended claims.

We claim:
1. A method of recovering oil substantially free of nitrogen from a nondepleted oil reservoir having in communication therewith at least one injection well and at least one production well at least 100 feet apart; comprising, injecting into said reservoir through said injection well in direct contact with the liquid oil in said reservoir and displacing said oil, through at least 100 feet of travel path in said reservoir, by direct contact with a gas containing at least 80% by volume of nitrogen at a predetermined pressure below that pressure which will fracture the formation of said reservoir but above the lowest pressure at which said gas is miscible with said oil; and, simultaneously with said injection and displacement, withdrawing through said production well fluids displaced from said reservoir by said injection gas.

2. A method in accordance with claim 1 wherein the gas containing nitrogen is substantially pure nitrogen.

3. A method in accordance with claim 1 wherein the gas containing nitrogen is air.

4. A method in accordance with claim 1 wherein the gas containing nitrogen is flue gas.

5. The method of recovering oil substantially free of nitrogen from a nondepleted oil reservoir having in communication therewith at least one injection well and at least one production well; comprising, injecting into said reservoir through said injection well and displacing through said reservoir a gas containing at least about 80 percent by volume of nitrogen, the first injected portion of said gas, equal in volume to less than about 0.10 pore volume, also having added thereto C1 to C5 hydrocarbons graded in concentration from at least 90 percent by volume of C1 to C5 hydrocarbons based on the total volume of gas at the front end of said portion to 0 percent by volume of C1 to C5 hydrocarbons at the back end of said portion, at a predetermined pressure below that pressure which will fracture the formation of said reservoir but above the lowest pressure at which said gas is miscible with said oil; and, simultaneously with said injection and displacement, withdrawing through said production well fluid displaced from said reservoir by said injection gas.

6. A method in accordance with claim 5 wherein the first injected portion of said gas is equal in volume to about 0.05 pore volume.

7. A method in accordance with claim 5 wherein the first injected portion of said gas has added thereto both C1 and C2 to C4 hydrocarbons in a ratio of C1 to C2 to C4 between about 3 to 1 and 2 to 1 parts by volume.

8. A method in accordance with claim 5 wherein the gas containing nitrogen is substantially pure nitrogen.

9. A method in accordance with claim 5 wherein the gas containing nitrogen is air.

10. A method in accordance with claim 5 wherein the gas containing nitrogen is flue gas.

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2,609,051 9/52 Brownsonbe 166—7
2,623,596 12/52 Whorton 166—7

CHARLES E. O'CONNELL, Primary Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,209,824

Howard A. Koch, Jr., et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 51, for "is to" read -- is to be --;
column 7, line 20, for "liquid to oil" read -- liquid oil --.

Signed and sealed this 24th day of May 1966.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents