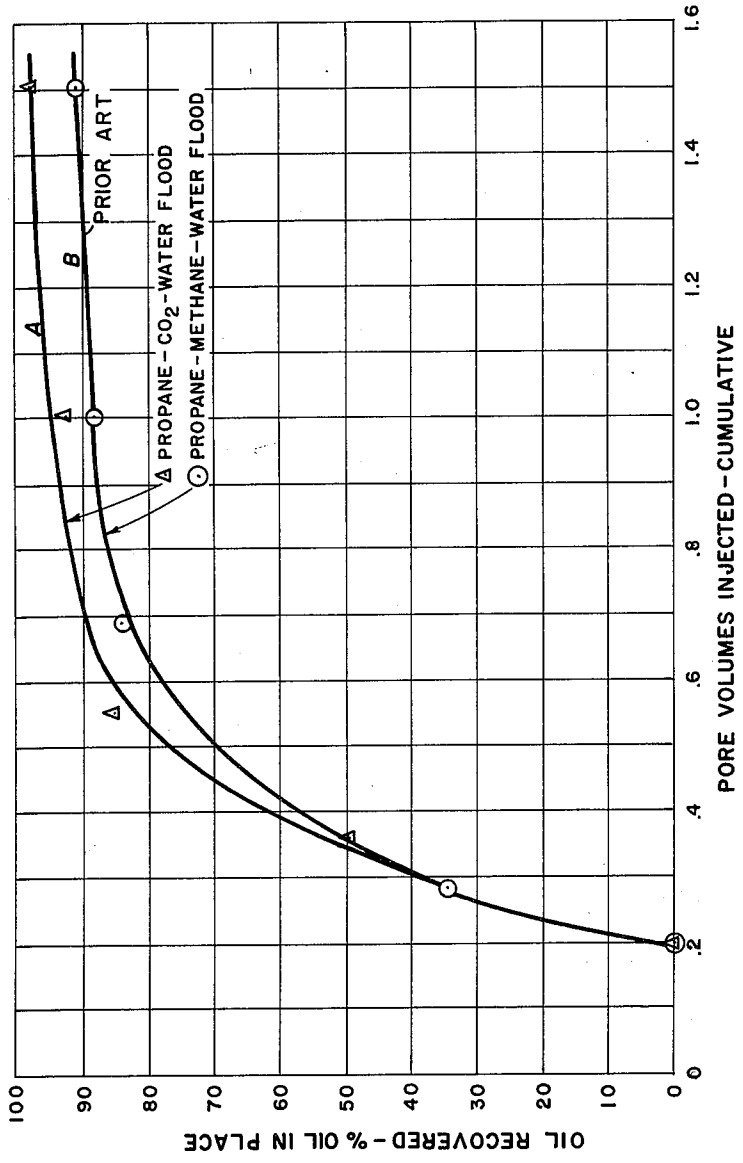
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MISCIBLE DRIVE-WATERFLOODING PROCESS

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MISCIBLE DRIVE-WATERFLOODING PROCESS

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This application is a continuation-in-part of copending application, Serial No. 802,637, filed March 30, 1959, now abandoned.

This invention relates to an improved process for recovering petroleum from underground reservoirs. More specifically, this invention is directed to an improved miscible drive, waterflood process in which the reservoir is contacted first with liquefied light hydrocarbon then with carbon dioxide and lastly with water.

It is known that greater quantities of oil can be recovered from subterranean petroleum reservoirs by displacing the oil with an oil-miscible liquid and then displacing the oil-miscible liquid with a cheap scavenging fluid which may be left in the reservoir. The oil-miscible liquid is preferably one which will dissolve in the oil and substantially reduce the viscosity of the oil with which it mixes. The use of various oil viscosity-reducers has been proposed and it is well known in the art that mixtures of low-molecular-weight hydrocarbons, known commercially as "liquefied petroleum gas" are especially suitable as petroleum solvents. "Liquefied petroleum gas," hereafter referred to as LPG, is a mixture of hydrocarbons consisting principally of propane and butane with minor proportions of ethane and pentane.

It is known further that increased oil recoveries can be obtained when the scavenging fluid used to drive an oil-miscible solvent through a reservoir is a dense fluid having a viscosity greater than that of the fluid which it displaces. The use of a scavenging fluid of lesser density than the petroleum and connate water in the formation, as has been proposed in the past, results in an uneven and inefficient flow distribution. For example when methane is used as the scavenging fluid, the compressed methane, being substantially lighter than the petroleum or connate water, tends to override the formation, with the result that petroleum in only the upper portion of the reservoirs is produced while the petroleum in the lower strata of the formation is substantially bypassed. Moreover, a scavenging fluid, such as methane, which has a viscosity substantially lower than that of the fluid which it displaces tends to finger through the displaced fluids in the more permeable portions of the reservoir resulting in a low sweep efficiency and the bypassing of large areas of the reservoir.

Since water has the same density as the connate water and a density only slightly different from the petroleum in the formation, it is an effective scavenging fluid. In addition, water has a viscosity substantially greater than that of low-molecular-weight hydrocarbons and is relatively inexpensive and abundantly available. Also possessing these attributes is carbonated water. The use of carbonated water not only makes additional CO_2 available for viscosity reduction of the formation oil but also reacts with the formation rocks, producing bicarbonates, which increases formation permeability. The viscosity of the injected water may be conveniently and economically increased by the addition of various natural or synthetic gums.

However, hydrocarbons and water are not readily miscible. Consequently, when water is injected directly behind the hydrocarbon, a hydrocarbon-water interface is produced and a dual rather than a single phase displacement of the petroleum results. When this happens, the scavenging fluid tends to replace only the connate water in the formation and to bypass large quantities of the injected hydrocarbon and petroleum. I have found that much greater efficiency is achieved by injecting between the low-molecular weight hydrocarbon and the scavenging water a fluid which is miscible both with the hydrocarbon and with the water. While this intermediate fluid may be completely miscible with the limited quantity of hydrocarbon which is injected before it, it is desirable that the intermediate fluid be miscible only to a limited extent with water. Otherwise, too large an amount of the intermediate fluid dissolves into the great quantities of water which are injected behind it. This causes a breakdown of the intermediate zone, and water containing the dissolved intermediate fluid comes into contact with the injected hydrocarbon. In order to prevent this, excessive quantities of the intermediate fluid would have to be used. In addition, the intermediate fluid would tend to dissolve in too great an amount in the connate water contained in the formation thereby tending to increase further the amount of intermediate fluid which must be injected.

I have further found that the formation is advantageously scrubbed first with a liquid, then with a gas, and lastly with another liquid. It is therefore desirable (although not necessary) that the intermediate fluid be a gas at reservoir conditions. Carbon dioxide possesses all these qualities and is therefore a superior intermediate fluid. Carbon dioxide is miscible with low-molecular-weight hydrocarbons and, since the reservoir temperatures are almost invariably above the critical temperature of carbon dioxide, the carbon dioxide exists as a dense fluid at typical reservoir temperatures and pressures. The low-molecular-weight hydrocarbon must, of course, be maintained as a liquid and it is therefore necessary that the reservoir pressure be maintained at a high level, preferably in excess of about 700 p.s.i. A further advantage of the use of carbon dioxide as the intermediate fluid results from the fact that carbon dioxide is soluble, but not infinitely soluble, in water at pressures in excess of 700 p.s.i. By using carbonated water for at least part of the drive media, the efficiency of the carbon dioxide slug is increased inasmuch as the carbon dioxide slug will attain greater formation sweep or contact before it is completely lost in mixing with the oil and drive water. Carbon dioxide, when dissolved in water, produces acidic carbonated water which acts as a surfactant to reduce the surface tension between the reservoir rock and a subsequent flood medium, thus enabling the carbonated water to better wet the reservoir rock and thereby minimizing bypassing of the carbon dioxide by the moving waterflood.

Briefly, therefore, the process of this invention comprises injecting into the reservoir a quantity of liquid low-molecular-weight hydrocarbon followed by a quantity of carbon dioxide, and driving these injected fluids through the formation by the injection of floodwater.

It is an object of this invention to provide an improved method of recovering petroleum oil from underground reservoirs.

Another object of this invention is to provide an improved secondary-recovery waterflooding process.

It is another object of this invention to provide an improved miscible-drive, waterflood process in which the reservoir is scrubbed first by a liquid, then by a gas, and lastly by another liquid.

More objects of this invention will become apparent upon reading the following specification in conjunction with the drawing wherein:

The figure discloses a chart which illustrates the unexpected increased recovery obtained by the method of this invention as compared with another well-known process.

The pressure of the injected fluids and the quantity of the various fluids injected must be determined from a study of each individual reservoir. In general, it is de-

sirable to inject the minimum effective quantitites of liquid low-molecular-weight hydrocarbon and carbon dioxide. It is, however, necessary that the quantities injected be sufficient to prevent a complete break-down in either the hydrocarbon or carbon dioxide zone. To maintain the integrity of these zones, carbonated water may be used as the flood medium, thereby replenishing the carbon dioxide previously injected in the slug form or at least preventing loss from the CO_2 slug to the driving flood water.

The quantity of low-molecular-weight hydrocarbon injected generally will be between .01 and 0.1 reservoir pore volume. The quantity of carbon dioxide preferably should be slightly larger than the quantity of injected hydrocarbon, to allow for the loss of some carbon dioxide into the connate water in the formation, and generally will be about .05–.35 reservoir pore volume with the preferred range between about .1–.15 reservoir pore volume. The injection pressures preferably should be in excess of 700 lbs. per square inch. At this pressure carbon dioxide satisfactorily mixes and dissolves in the injected water, and the low-molecular-weight hydrocarbon is maintained as a liquid at ordinary reservoir temperatures.

The process of this invention may be initiated at any time during or following primary depletion of the petroleum-bearing formation. Superior results are dependent on the pressure being at least 700 p.s.i., and therefore, it is preferred to initiate the process while the reservoir pressure is still above this point, preferably well above 700 p.s.i.

The liquid low-molecular-weight hydrocarbon injected into the petroleum reservoir in accordance with this invention may be any low-molecular-weight hydrocarbon or hydrocarbon mixture which can be maintained in the liquid state at reservoir temperature and pressure, and with which the selected intermediate fluid, such as carbon dioxide, is substantially completely miscible. Non-limiting examples of suitable hydrocarbons include propane, butane, gasoline, natural gasoline, "LPG," "compressor condensate," and all hydrocarbon fractions having a boiling point lower than that of kerosine. "LPG" is recognized in the petroleum industry as a term representing certain liquefied petroleum gases, these gases being petroleum fractions lighter than gasoline such as butane, propane, etc. and mixtures thereof which remain in the liquid state when maintained under pressure. As used herein and in the petroleum industry, "compressor condensate" refers to the liquid petroleum fraction obtained as a result of compressing natural gas for pipeline transmission. These condensates are rich in butane and pentane but contain minor amounts of propane and lighter hydrocarbons and of hexane and heavier hydrocarbons.

As an example of the process of this invention, a core of McCook dolomite, 7.5 inches long and 3.5 inches in diameter, is saturated to 48% of a pore volume with Devonian stock tank oil, i.e., weathered Devonian crude oil. In accordance with this invention, the saturated core is flooded at 1200 p.s.i.a. and 120° F. with 0.02 pore volume of propane, and this is followed by flooding with 0.10 pore volume of carbon dioxide (measured as a liquid at 1200 p.s.i.a. and 80° F.). After the carbon dioxide has been injected, the core is flooded with water in a conventional manner. Oil recovery at water breakthrough is 58% of the oil originally in place, and this increases to 60% when the water-to-oil ratio reaches 100/1.

For comparison, a similar core is flooded at the same conditions (1200 p.s.i.a. and 120° F.) with 0.12 pore volume of carbon dioxide, and then is flooded with water. At water break-through, only 54% of the oil originally in place is recovered, and the recovery rises to only 57% when the water-to-oil ratio reaches 100/1. Thus 3–4% more of the oil in place is recovered by applying this invention. Even greater superiority is evident in actual oil-field practice because of the superior sweep efficiency achieved by applying this invention, in comparison to miscible flood projects in which the solvent is displaced by low-viscosity fluids, such as gases, rather than relatively viscous liquids, such as water.

In another example, a similar core is flooded at the same conditions (1200 p.s.i.a. and 120° F.) with 0.02 pore volume of compression condensate rich in material lighter than hexane. The compression condensate is obtained by compressing field gas, produced with crude oil and gathered from low-pressure separators (about 20 p.s.i.g.), to about 500 p.s.i.g., chilling to about 100° F., and separating the condensate from residue gas. The compression-condensate flood is followed by a flood with 0.10 pore volume of carbon dioxide (measured as a liquid at 1200 p.s.i.a. and 80° F.). After the carbon dioxide has been injected, the core is flooded with water in a conventional manner. Oil recovery at water break-through is 57.5% of the oil originally in place, and a total of 60% when the water-to-oil ratio reaches 100/1.

As another specific example of the process of this invention, a petroleum-bearing reservoir, having an input and an output well and an internal pressure of 1000 p.s.i., is produced by injecting through the input well and into the formation 0.05 reservoir pore volume of LPG, then injecting into the formation 0.07 pore volume of carbon dioxide, and finally injecting floodwater into the formation. The LPG and carbon dioxide banks are driven through the formation by the continuing injection of floodwater, and petroleum is produced from the producing well without any substantial reduction in formation pressure.

In view of the results of the foregoing examples, it would be advantageous to note the following experimental data demonstrating the superiority of carbon dioxide as an intermediate fluid over those in the art. For example, Slobod et al. in U.S. Patent 2,968,350 describes a typical miscible-slug secondary recovery process. In accordance with Slobod et al., a slug of miscible fluid, viz., ethane, propane, sulfur dioxide or hydrogen sulfide, is injected into a subterranean oil reservoir followed by the injection of a slug of a normally gaseous hydrocarbon such as natural gas or a similar gas comprising principally methane. Thereafter, a waterflood drives the miscible slug and normally gaseous slug through the reservoir, thus forcing the oil to flow toward a production well through which it is removed to the surface of the earth.

EXPERIMENT 1

An 8′ sandstone core was saturated with a Colorado crude oil, so that the sandstone contained 0.603 pore volume of oil. The core was then flooded with water under pressure of 1150 lb./sq. in. at 180° F. and there was recovered 0.291 pore volume of the oil, leaving 0.312 pore volume of oil remaining in the core. The core was then flooded with 0.25 pore volume of propane, followed by 0.16 pore volume of carbon dioxide, both measured at 1150 lb./sq. in. and 180° F. Water was then injected behind the carbon dioxide at the same pressure and temperature and the oil recovered from the core at various stages in the operation was recorded. The following table accurately sets forth the oil recovered at various stages during the injection.

Table I

Cumulative pore volumes of fluid injected	Oil recovered		
	Pore vol.	Percent of oil in place	Water-oil ratio
0.192	0	0	∞
0.365	0.155	49.8	<0.1
0.55	0.267	85.5	1.0
1.0	0.289	92.6	30
1.5	0.303	97.0	>50

EXPERIMENT 2

An 8' sand core was saturated with the same oil as in Experiment 1 so that the core contained 0.618 pore volume of oil. The core was flooded with water and there was recovered 0.319 pore volume of oil, leaving 0.299 pore volume of oil in the core. There was then injected into the core at 1150 lb./sq. in. and 180° F., 0.25 pore volume of propane, followed by 0.25 pore volume of methane, and then driven with water. The following table accurately represents the recoveries of oil obtained at different stages in the treatment of the core.

Table II

Cumulative pore volumes of fluid injected	Oil recovered		
	Pore vol.	Percent of oil in place	Water-oil ratio
0.196	0	0	∞
0.282	0.103	34.5	<0.1
0.685	0.250	83.7	1.0
1.0	0.263	88.1	35
1.5	0.272	91.1	>50

As can be seen, by the practice of this invention, carbon dioxide, as an intermediate fluid, is superior to those heretofore utilized in the art. In Experiment 1, following the technique of this invention, when a total of 1.0 pore volume of propane, carbon dioxide and water had been injected, the recovery of oil was 0.289 pore volumes, or 92.6% of the oil in place. In contradistinction, using the prior art technique as set forth in Experiment 2, even considering the fact that the amount of methane used was greater than the amount of carbon dioxide used in Experiment 1, when a total of 1.0 pore volume of propane, methane and water had been injected, the oil recovered was only 0.263 pore volume, or 88.1% of the oil in place. Both floods were terminated when the water-to-oil ratio exceeded 50 and at that time both the volume of oil recovered and the percentage of the oil in place recovered by the propane-carbon dioxide waterflood exceeded that recovered by propane, methane and water.

It is to be noted that the prior art method utilizing an intermediate hydrocarbon gas succeeded in recovery of only 91.1% of the original oil in place, whereas by the practice of this invention the significant recovery of 97% is realized. As is well known, the lesser the amount of oil remaining in a reservoir, the more difficult further recovery of oil becomes. However, the data in the foregoing experiments would indicate the superiority of carbon dioxide over that of methane in the aspect of increasing residual oil recovery efficiency.

The figure graphically illustrates a comparison of the oil recoveries obtained by the method of this invention, employing carbon dioxide as an intermediate gas, as compared to the prior art method, utilizing methane as the intermediate gas. This graph, obtained from calculations based on laboratory experiments, shows recovery as the ordinate and volume of fluid injected as the abscissa, therefore eventually indicating the ultimate recoveries. Curve B shows the recovery attained by a propane-methane-waterflood process. Curve A shows the recovery obtained by the use of this invention. From the graph, it is apparent that a larger amount of methane than of carbon dioxide is necessary as the intermediate gas, to achieve

a given recovery of oil, and that less of the oil in place is ultimately recovered when using methane than when using carbon dioxide.

If desired, the viscosity of the initially injected flood water may be increased by the addition of 1–5% of crude dextran. Dextran is a water-soluble carbohydrate which is compatible with the salts generally present in the available waters. Other viscosity-improving additives may, of course, be used, but it is necessary that they be compatible with both dissolved carbon dioxide and the mineral content of the floodwater. The use of a viscosity-increasing additive in the initial portion of the injected water results in the removal of oil from greater areas of the reservoir, and minimizes the tendency of the water drive to finger through the carbon dioxide and liquefied low-molecular-weight hydrocarbon zones at places of unusually high reservoir permeability.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for production of oil from a subterranean reservoir consisting essentially of injecting through an injection well into said reservoir a quantity of low-molecular-weight hydrocarbon, liquid under reservoir conditions, injecting immediately behind said hydrocarbon a quantity of carbon dioxide, driving the hydrocarbon liquid and carbon dioxide through the reservoir by injection of floodwater in the direction of an output well, and maintaining the reservoir at a pressure of at least 700 pounds per square inch.

2. A method according to claim 1 in which a viscosity-increasing additive is added to the initial portion of the floodwater.

3. A method according to claim 1 in which the amount of low-molecular-weight hydrocarbon injected is between 0.01 and 0.1 reservoir pore volume and the amount of carbon dioxide injected is between 0.05 and 0.35 reservoir pore volume of liquid hydrocarbon.

4. A method according to claim 3 in which the low-molecular-weight hydrocarbon comprises propane as the major constituent.

5. A method according to claim 3 in which the low-molecular-weight hydrocarbon comprises butane as the major constituent.

6. A method according to claim 3 in which the low-molecular-weight hydrocarbon comprises L.P.G.

7. A method according to claim 3 in which the low-molecular-weight hydrocarbon comprises compressor condensate.

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