

[54] **RECOVERY OF VISCOUS PETROLEUM FROM ASPHALTIC PETROLEUM CONTAINING FORMATIONS SUCH AS TAR SAND DEPOSITS**

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[58] Field of Search **166/256-262, 166/272, 270, 288, 300, 305 R**

[56] References Cited

UNITED STATES PATENTS

2,788,071	4/1957	Pelzer	166/261
2,876,840	3/1959	Berry	166/305 R
2,914,309	11/1959	Salomonsson	166/288
3,062,282	11/1962	Schleicher	166/256
3,093,191	6/1963	Glass	166/261
3,167,121	1/1965	Sharp	166/261
3,179,171	4/1965	Beale	166/305 R
3,275,076	9/1966	Sharp	166/261
3,285,336	11/1966	Gardner	166/260

3,294,729	12/1966	Hort et al.	166/305 R
3,314,477	4/1967	Boevers et al.	166/260
3,500,925	3/1970	Beiswanger et al.	166/305 R
3,542,129	11/1970	Bauer	166/261
3,587,739	6/1971	Parker	166/261
3,603,396	9/1971	Braun	166/261

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[57] ABSTRACT

Viscous, asphaltic petroleum may be effectively recovered from subterranean viscous, asphaltic petroleum containing formations such as tar sand deposits by first injecting into the tar sand formation a quantity of N-methyl-2-pyrrolidone or furfural or a mixture thereof which precipitates asphaltic material from the bituminous petroleum portion of the formation petroleum. Next, solvent injection is terminated and air is injected into the formation, and the formation is ignited by heating or other means to initiate in situ combustion within the petroleum formation utilizing the precipitated asphaltic materials for fuel for the in situ combustion reaction. Reaction temperature higher than normal in situ combustion temperatures are produced, facilitating thermal cracking and in situ hydrogenation to up grade the produced crude within the tar sand reservoir.

12 Claims, No Drawings

RECOVERY OF VISCOUS PETROLEUM FROM ASPHALTIC PETROLEUM CONTAINING FORMATIONS SUCH AS TAR SAND DEPOSITS

CROSS REFERENCE TO RELATED APPLICATION

This application is a Continuation-in-Part of copending application, Ser. No. 344,302, filed Mar. 23, 1973 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention concerns a method for recovering hydrocarbon materials from tar sand deposits utilizing a combined in situ solvent deasphalting process with in situ combustion.

2. Description of the Prior Art

There are known to exist in many locations throughout the world gigantic deposits of petroleum in a unique form variously referred to as tar sands, oil sands, or bituminous sands. The largest and most famous such deposit is the Athabasca Tar Sand Deposit located in the northeastern part of the Province of Alberta, Canada, which contains over 700 billion barrels of petroleum. Other large tar sand deposits are found in the western part of the United States and Venezuela, and smaller deposits are located in Europe and Asia.

Tar sand deposits differ from conventional petroleum reservoirs in a number of respects. The hydrocarbon portion is highly bituminous in character, and is much more viscous than conventional petroleum. The deposits contain sand, predominantly fine quartz sand, which is covered with a film of water. Surrounding the water wetted sand grains and essentially filling the void volume is the bituminous hydrocarbon. The balance of the void volume may be filled with connate water, and sometimes small quantities of gas are encountered, which is usually air or methane. The sand grains represent about 65 percent by volume of the total volume of the deposit, which is equivalent to about 83 percent by weight. The sum of the bitumen and water concentration will generally equal about 17 percent, with the bitumen portion thereof varying from about 3 percent to about 15 percent by weight. The most unique difference between the tar sand deposit and conventional petroleum reservoirs is the fact that in the best developed tar sands intervals the bitumen is in fact the continuous phase of the reservoir, and the sand grains are suspended in the bitumen.

The bitumen properties vary throughout the world, although they are fairly constant in broad geographic areas. For example, the bitumen characteristics of the United States tar sand deposits are fairly consistently the same. The density of the bitumen is generally slightly greater than the density of water at 60°F. About 50 percent of the bitumen is distillable without cracking. The sulfur content of the bitumen varies from 4.5 to 5 percent. Thus it can be appreciated that considerable on site processing must be undertaken in order to transport and utilize the hydrocarbons contained from tar sand deposits.

There are two basic approaches for recovering the hydrocarbon or bituminous material from tar sand deposits. The tar sands may be mined and transported to a processing plant where the bitumen is extracted and the sand is discharged, or the separation of bitumen from sand may be accomplished within the reservoir by

an in situ process. In situ recovery processes are closely related to so-called supplemental recovery or secondary recovery of crude oils from conventional oil reservoirs, although there are differences imposed by the unique characteristics of tar sand deposits. The in situ processes for recovering bitumen from tar sand deposits may generally be classified as

1. Thermal methods, including fire flooding or in situ combustion and steam injection, and

2. Emulsion steam processes in which an emulsifier is injected into the formation via a previously created fluid communication path, and steam is injected to partially liquefy the bitumen and to form an oil-in-water emulsion in order to create a fluid having suitable flow properties for recovery from the subterranean deposit.

In application of the in situ combustion or fire flooding process, heat for petroleum viscosity reduction is generated within the formation by injecting air into the formation and igniting the portion of the formations adjacent the injection well bore so as to produce a combustion reaction within the tar sand deposit itself. Some of the hydrocarbons are consumed in the in situ combustion reaction, but a substantial proportion of the hydrocarbons are recovered.

If it is desired to apply in situ combustion techniques to formations containing very viscous hydrocarbon, specifically tar sand deposits, it is often impossible to raise the reaction temperature high enough to achieve the desired mobility of the fluid by thermal means alone. It is recognized in the prior art that some in situ thermal cracking of the hydrocarbon materials may be accomplished if the temperatures can be raised to a sufficiently high level. In conventional oil reservoirs it is possible to operate under conditions so as to achieve a limited degree of thermal cracking by increasing the air injection pressure so as to increase the temperature of the combustion reaction. This is usually not possible in tar sand deposits, a great many of these deposits are generally relatively shallow, e.g., in order of 100 to 500 feet deep as compared to the more conventional hydrocarbon deposits. If the air injection pressure is raised in shallow deposits, fracturing of the formation and/or overburden results, which is detrimental to oil recovery by in situ combustion. Furthermore, a higher degree of thermal cracking must be accomplished in tar sand deposits in order to achieve a fluid mobility sufficient to permit its recovery.

Thus it can be seen that there is a substantial unfulfilled need for a method for performing in situ combustion in tar sand deposits in such a way that a relatively high combustion temperature is obtained, so that appreciable viscosity reduction by thermal cracking of the bituminous hydrocarbon materials occurs.

Most tar sand deposits contain hydrocarbon materials which are a mixture of high molecular weight bituminous materials and more conventional lower molecular weight petroleum components. Since the bituminous materials require surface treating to render them sufficiently mobile for pipeline transportation to remotely located refineries, the more mobile conventional petroleum materials have a higher dollar value. Accordingly, if any of the hydrocarbon material present in tar sands must be consumed by the in situ combustion reaction, it would be highly desirable to utilize the less valuable, less mobile bituminous fraction of the petroleum selectively as the fuel for the in situ combustion reaction. Accordingly, there is also a substantial

need for a method for conducting in situ combustion oil recovery under conditions which preferably consume the high molecular weight bituminous materials as fuel for the in situ combustion reaction.

SUMMARY OF THE INVENTION

We have discovered, and this constitutes our invention, that viscous petroleum may be recovered from viscous, asphaltic petroleum containing formations such as tar sand deposits by first injecting into the tar sand deposit a deasphalting solvent such as N-methyl-2-pyrrolidone, furfural or a mixture thereof which solubilizes the non-asphaltic materials present in the tar sand, and causes precipitation of the asphaltic materials on and/or around the sand grains in the tar sand deposit. After the quantity of asphalt precipitating solvent is injected, air injection is initiated in the tar sand deposit and the formation is ignited by conventional means to cause the initiation and propagation of an in situ combustion reaction front thru the reservoir. The precipitated asphaltic materials are utilized selectively as the fuel for the in situ combustion reaction, driving the more volatile materials ahead of the combustion front. The temperature of the combustion is higher than conventional in situ combustion reactions, sufficiently high to induce an appreciable degree of thermal cracking of heavy hydrocarbons. Air injection may be continued thereafter until the reservoir has been completely depleted, or it may be followed after a period of time by the injection of water into the burned out portion of the reservoir.

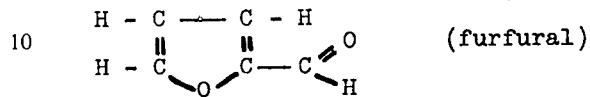
DESCRIPTION OF THE PREFERRED EMBODIMENTS

Generally our invention pertains to a novel method for recovering hydrocarbons from a subterranean reservoir which contains hydrocarbons having abnormally high content of asphaltic materials. This method is especially applicable to tar sand or bitumen sand reservoirs, but may be applied to any oil reservoir containing petroleum having a high content of asphaltic materials. It is an especially attractive feature of our invention that the asphaltic materials present in the formation hydrocarbon fluid are selectively utilized as the fuel for the in situ combustion reaction which accomplishes the enhanced oil recovery. Since the asphaltic materials are the least desirable and least valuable of the hydrocarbon fluids, the economics of the oil recovery process are especially enhanced by the selective utilization of asphaltic materials as the fuel for in situ combustion. Furthermore, the precipitation of the asphaltic materials by the injected deasphalting solvent in the first step of our process insures that a high fuel density will be available for the ensuing in situ combustion phase. The presence of a high fuel density will provide a high reaction temperature in the reservoir, which will result in a considerable amount of thermal cracking and in situ hydrogenation so that the viscosity of the produced fluid is reduced in situ in the reservoir. The thermal cracking and in situ hydrogenation operations aid in the improved oil recovery, and also increases the value of the crude produced on the surface.

In a preferred embodiment of our invention a solvent which also causes asphaltic material precipitation is injected into the reservoir. The solvent is N-methyl-2-pyrrolidone or furfural or a mixture of N-methyl-2-pyrrolidone and furfural.

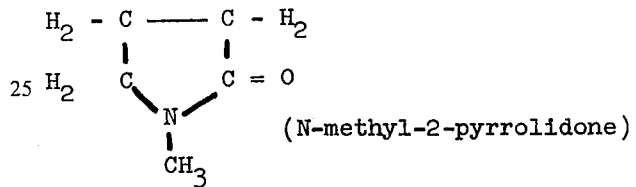
It is desired that the pore space of that portion of the formation adjacent to the well bore be essentially saturated with the deasphalting solvent in order to achieve a high ratio of solvent to petroleum, needed to achieve effective selective asphalt precipitation.

Furfural is a derivative of furan and has the following structure:



Furfural is readily available commercially and may be synthesized from the pentosans of straw, corn cobs, oat hulls, etc., to pentoses which are dehydrated by heating with dilute sulfuric acid. Furfural is used extensively in refinery processes for deasphalting crude oil.

N-methyl-2-pyrrolidone, also available commercially, has the following structure.



The use of deasphalting solvent in the first phase of our procedure represents a dramatic contrast to what would normally be good field procedure for miscible flooding operations in such reservoirs. Ordinarily, if one desired to operate a miscible flood recovery operation, the solvent would be carefully chosen so as not to cause precipitation of asphaltic materials. We have discovered, however, that the precipitation can be an advantage when used as a first phase of a multiple step operation wherein the solvent is followed by injection of air, and ignition of the formation to achieve in situ combustion. Furthermore, it is not necessary to inject the same quantity of solvent as would be required in the instance of a conventional miscible placement procedure. Ordinarily, from about 0.01 to about 0.5 pore volumes of solvent will be adequate to affect the required degree of asphaltic material precipitation necessary to achieve the benefits of our invention.

After deasphalting solvent injection has been completed, air is injected into the formation and sufficient heat is applied to the injection well bore to initiate a combustion reaction within the formation. The in situ combustion phase of our operation will be accomplished in essentially the same manner as any conventional in situ combustion or fire flooding secondary recovery operation. Ordinarily the preferred embodiment will involve the compression of air on the surface and injection of the compressed air into the formation, although any oxygen containing gas or pure oxygen may be used. The pressure will ordinarily be limited by the overburden thickness, since injection of high pressure air into a relatively shallow formation will cause fracturing of the formation, with channeling of the air through the formation without efficient displacement of oil. Since many of the tar sand deposits in which our invention will be especially applicable are relatively shallow, for example around 100-500 feet, the air pressure must be held below about 100-500 pounds per

square inch in order to avoid the undesirable fracturing of the formation. As a general rule, the air injection pressure in pounds per square inch should not exceed numerically the overburden thickness expressed in feet. The air injection rate will be limited by the injectivity of the formation itself, and air should be injected at about the maximum rate it can be injected without exceeding the overburden related pressure limitation described above. Ordinarily the injectivity will increase as the combustion front moves away from the well bore, and so the air rate will increase with time as the in situ combustion phase of our recovery method proceeds.

In order to achieve the maximum benefit possible from the application of our process to a tar sand deposit, it is essential that the reaction temperature be raised to as high a level as possible. Thermal cracking of bitumen such as occurs in tar sand deposits will not begin until the reaction temperatures in the formation exceeds about 500°F. Thermal cracking will produce some viscosity reduction of the bitumen, but the magnitude of the reduction will not be as great as possible if the temperature can be raised sufficiently to achieve in situ hydrogenation. If the temperature can be raised at about 1,300°F., steam reforming will occur, and hydrogen will be generated in situ which will provide spontaneous hydrogenation of the bitumen in place in the reservoir. Hydrogenation can effect a greater viscosity reduction than is possible with thermal cracking, and the production rate and recovery efficiency will be improved dramatically.

In order to achieve the high reaction temperatures necessary to accomplish steam flooding to generate hydrogen and in situ hydrogenation of crude to bring about the desired viscosity reduction, either the air injection rate and pressure must be increased considerably over the pressure and flow rates discussed above, or else the fuel utilized in the combustion reaction must be modified in some manner. Since the relatively shallow tar sand deposits cannot be subjected to high injection air pressures, the only possible way of achieving high reaction temperatures is by modification of the fuel utilized in the reaction process. This is the reason for the preliminary step of our process, wherein N-methyl-2-pyrrolidone or furfural or a mixture thereof is injected for the purpose of accomplishing asphalt precipitation. The asphalt deposits on the sand particles and as portions of the formation ahead of the combustion front are heated by combustion gases from the in situ combustion reaction front, the asphaltic petroleum will yield and lay down on the solid surfaces much more fuel in the form of a coke-like material for burning than would be provided by the whole crude. Thus, it is possible by following the procedures of our invention to operate a high temperature in situ combustion operation in a tar sand deposit which is too shallow to permit high pressure air injection to achieve the high temperatures necessary to accomplish thermal cracking and in situ hydrogenation.

Once air injection into the formation is initiated, some heating step must be taken to ignite the deposited asphaltic materials so as to initiate the in situ combustion reaction. There are many means available in the art for accomplishing this, for example, the spontaneous chemical method described in U.S. Pat. No. 3,180,412 may be used effectively. Also, there are gas-fired or electric heating devices which may be inserted

into the air injection well bore to raise the temperature of the formation adjacent to the well bore to a temperature of at least 300°F., which will be sufficient to initiate the desired combustion reaction. Once the deposited asphaltic material is ignited, the combustion front is self sustaining, and no additional extraneous heat need be supplied to the formation. Once it is determined by temperature measurements that ignition has been accomplished, the ignition devices are removed from the well bore and air injection is continued. The previously injected deasphalting solvent slug will continue to move ahead of the combustion front because of its low volatility compared to the viscous petroleum, so it will continue to deposit sufficient asphaltic materials to provide the fuel for the continued in situ combustion front movement.

In situ combustion processes are generally continued until the temperature at the production well begins to rise, indicating that the in situ combustion front is approaching the production well.

A slightly different embodiment of our invention involves terminating air injection after it determined that the in situ combustion front has proceeded some distance away from the injection well, and is, for example, halfway between the injection well and the production well, and thereafter injecting water into the formation. There is sufficient air still contained in the formation in advance of the finally injected water to insure that combustion will continue for a period of time, and the desired thermal cracking and steam reforming, in situ hydrogenation will continue in conjunction with the combustion front to achieve the desired viscosity reduction of the bituminous hydrocarbon fluids ahead of the injected water. The water injection will scavenge heat from the burned out areas of the formation, and the final phase of oil recovery will be achieved at a reduced cost since the cost of water injection is substantially less than the cost of air compression and injection. In this latter instance the water injection may be continued until water breaks through at the producing well, in which point is necessary to shut in the well since the water/oil ratio will generally rise rather quickly in a short period of time once water breakthrough has occurred.

Alternately, water injection may be initiated with air injection continued. Simultaneous air and water injection continues, with the upper limit of quantity of water injected being the amount just short of quenching the in situ combustion front. Ideally, water injection will be initiated as soon as the combustion front is from 20 to 100 feet away from the injection well. Simultaneous air and water injection will continue for some time, with the air injection being eventually terminated when the oil production rate has declined to a stable low value or when the production well temperature increases. Water injection is continued until the water cut rises to about 95 percent.

Another attractive embodiment of our process especially as applied to large fields, involves conversion of producing wells to injection wells after the water cut has reached about 95 percent. Air and water injection may be continued into the converted well with the combustion front being propagated without having been extinguished into a new pattern.

The process of our invention is better understood by reference to the following field example, which is offered only for purpose of illustration and is not in-

tended to be limitative or restrictive of our invention.

FIELD EXAMPLE

A tar sand deposit is discovered at a depth of 350 feet, and it is determined that the thickness of the tar sand deposit is 60 feet. Production wells are drilled on a square grid pattern approximately 400 feet apart, and injection wells are drilled in center of each square grid pattern. It is determined that the hydrocarbon content of the tar sand deposit is relatively high, but the viscosity of the hydrocarbon material is too high to recover any part thereof by conventional production means. That is to say, the hydrocarbon material is essentially immobile at reservoir conditions, and some treatment to reduce the viscosity of the hydrocarbons must be undertaken in order to recover any part thereof.

It is determined that the permeability of the tar sand deposit averages about 30 percent, and so the total pore volume in each square grid pattern will be $0.30 \times 400 \times 400 \times 60 = 2,880,000$ cubic feet. Since the sweep efficiency of a pattern such as described above is 70 percent and the vertical conformance is 50 percent, the total swept area will be $0.7 \times 2,880,000 \times 0.50$ or 1,008,000 cubic feet.

It is determined that furfural is available for low cost in the area, which is satisfactory as the asphalt precipitation solvent. A 0.2 pore volume slug or 20,160 cubic feet (155,800 gallons) of this material is injected into the injection well. Care is taken to avoid exceeding approximately 350 pounds per square inch injection pressure, since it is desired to accomplish injection of the deasphalting solvent into the tar sand deposit without causing a fracture to occur, which would interfere with efficiency sweep of the formation. Injection of the solvent is completed in approximately 200 days.

After completion of solvent injection, air compressors are placed in operation and air is injected into the injection well at the maximum rate possible without exceeding 350 pounds per square inch. After air injection for approximately 24 hours, the well bore is subjected to heating by a 100 KW downhole electric heater to initiate the combustion reaction. Since the injection well bore is perforated essentially the entire thickness of the tar sand interval, a relatively long heating element is positioned adjacent to these perforations so that air entering the perforations is heated to a temperature approximately 500°F., which is sufficient to heat the formation so as to initiate the combustion reaction. It is only necessary to heat the formation utilizing this electric heater for approximately 36 hours in order to initiate a stable combustion reaction within the formation, which can thereafter be propagated without additional extraneous heat being supplied to the formation. The electric heater is then removed from the injection well bore, and air injection is continued without interruption.

After air injection has been continued for approximately 600 days, calculations indicate that slightly more than half of the volume to be swept by the injected fluid should have been contacted by the injected air. Air injection is then terminated, and water injection is initiated to sweep the burned out area of the tar sand deposit, scavenging heat therefrom and pushing the previously injected air the rest of the way through the formation. The production well bore temperature begins to increase after approximately 800 days, and the water/oil ratio also increases indicating the ap-

proach of the injected water. The produced water is utilized for a period as injection water, but after the water/oil ratio exceeds about 30, the water injection of the operation is terminated.

The foregoing field example demonstrates the method for employing our invention, but it will be obvious to persons skilled in the art of oil recovery that many variations are possible without departing from the true spirit and scope of our invention. Similarly, while mechanisms have been proposed to explain the benefits resulting from application of the process of our invention, it is not represented hereby that these are the only or even the principal mechanisms responsible for the operability of the process of our invention. It is our intention that the scope of our invention be limited or restricted only by the limitations or restrictions in the claims appended hereto.

We claim:

1. A method for recovering hydrocarbons from a subterranean, porous formation containing viscous petroleum having a high asphaltic content including tar sand deposits, penetrated by at least one injection well and at least one production well comprising:

- a. injecting into the formation via the injection well, a deasphalting solvent selected from the group consisting of N-methyl-2-pyrrolidone, furfural, and mixtures thereof, precipitating asphaltic petroleum on solid surfaces of the formation, the precipitated asphaltic petroleum being utilized as a fuel;
- b. injecting air into the formation via the injection well following the solvent injection;
- c. igniting a portion of the formation adjacent the injection well; and
- d. continuing air injection while recovering petroleum from the production well.

2. A method as recited in claim 1 wherein the deasphalting solvent is N-methyl-2-pyrrolidone.

3. A method as recited in claim 1 wherein the deasphalting solvent is furfural.

4. A method as recited in claim 1 wherein the solvent is a mixture of furfural and N-methyl-2-pyrrolidone.

5. A method as recited in claim 1 wherein from about 0.01 to about 1.0 pore volumes of the deasphalting solvent is injected into the formation.

6. A method as recited in claim 1 wherein ignition of the formation to initiate the in situ combustion reaction is accomplished by locating an electric heater in the injection well.

7. A method as recited in claim 1 wherein the ignition of the formation to initiate the in situ combustion reaction is accomplished by locating a gas heating device in the injection well.

8. A method as recited in claim 1 wherein ignition of the formation to initiate the in situ combustion reaction is accomplished by injecting spontaneous igniting chemicals into the formation.

9. A method as recited in claim 1 comprising the additional step of injecting water into the well bore simultaneously with air injection after the in situ combustion front has moved at least 20 feet away from the injection well.

10. A method as recited in claim 1 comprising the additional step of injecting water into the injection well after termination of air injection.

11. A method as recited in claim 1 comprising the additional step of converting the producing well into an injection well after the water-oil ratio of the fluid being produced has risen to a predetermined value.

12. A method as recited in claim 1 comprising the additional step of converting the producing well into an injection well after the temperature of the produced fluid has risen to a predetermined value.

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