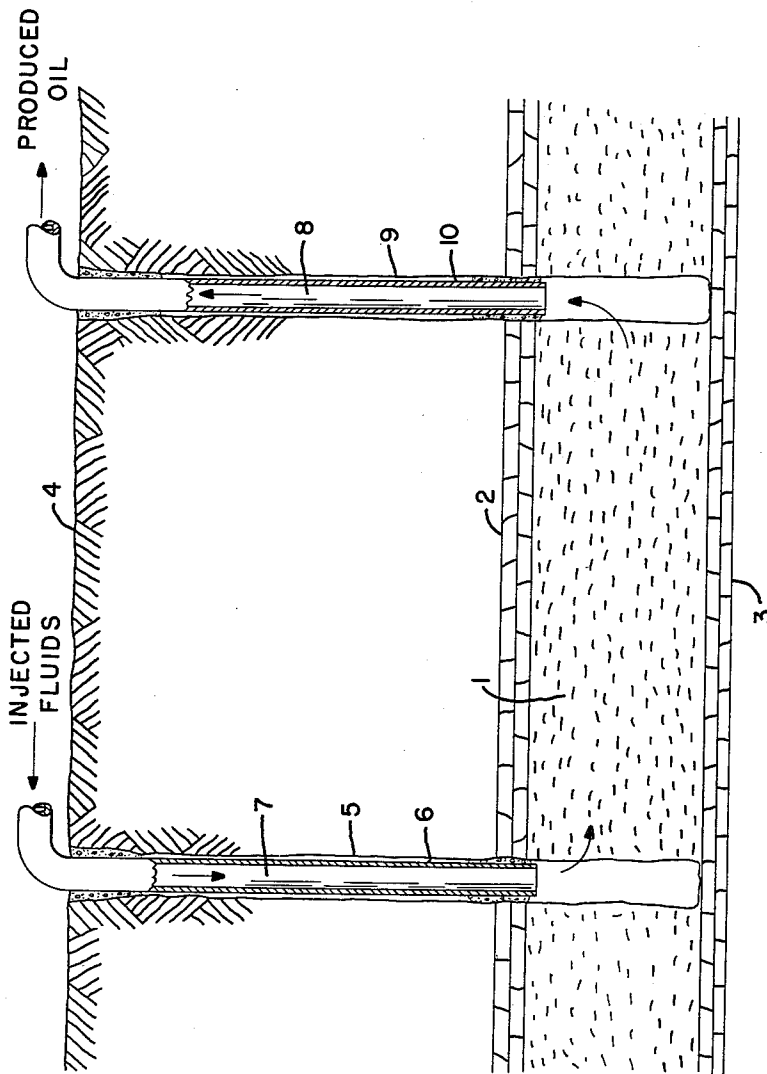


Aug. 28, 1962

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RECOVERY OF PETROLEUM CRUDE OIL BY IN SITU
COMBUSTION AND IN SITU HYDROGENATION
Filed Feb. 24, 1958

3,051,235



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**RECOVERY OF PETROLEUM CRUDE OIL, BY
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DROGENATION**

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Filed Feb. 24, 1958, Ser. No. 717,256
1 Claim. (Cl. 166—11)

This present invention generally relates to a method of recovering petroleum oil from a subterranean oil reservoir. The invention more particularly concerns a secondary recovery type procedure for producing oil, and it is especially adapted for use in reservoirs that contain relatively viscous oil. In accordance with this invention, petroleum crude oils are hydrogenated in-situ within a reservoir by injecting hydrogen and a catalyst into the reservoir.

Petroleum crude oil is generally recovered from an oil-bearing earth formation initially as a result of gas pressure, rock pressure, or natural water drive forcing the oil from the formation through a producing well to the surface. As oil production continues, the initial reservoir energy gradually decreases and finally becomes insufficient to force the oil to the production well. It is well known by the petroleum industry that a relatively small proportion of the oil in a subterranean oil reservoir is produced from the reservoir during this primary stage of production. It is also generally recognized that almost all reservoirs retain from about 30% to 90% of their original oil when they have ceased primary production; and it is not unusual for a reservoir containing highly viscous crude to retain at least 90% of the oil originally in place following primary production.

It has, accordingly, been a continuing problem and object in the petroleum industry to recover the large amounts of oil that remain within a reservoir following primary production. Numerous methods have been suggested or employed to date for this purpose. In general, the methods used have involved injecting a scavenging fluid into a reservoir through one or more injection wells and thereby displacing the oil from the reservoir through one or more spaced production wells. Fluids which have been employed or suggested thus far as a scavenging media in oil recovery operations include gases such as natural gas, carbon dioxide, methane, flue gas, and various hydrocarbons; and liquids such as water, petroleum fractions, aqueous sugar solutions, and the like. Unfortunately, none of these procedures are markedly effective in recovering a heavy viscous oil from a reservoir. The primary reason that these methods have not proved themselves of value in the production of viscous crudes is the high capillary resistance within the interstices of reservoir rocks to the flow of viscous oil.

Methods that have appeared to be very attractive for the production of viscous oil are ones involving the use of scavenging fluids such as steam and hot combustion gases which heat up a reservoir, thereby reducing the viscosity of the oil within the reservoir and rendering it much more mobile. The hot combustion gases may be generated by combustion processes conducted either outside or directly within a reservoir.

While methods of heating a reservoir for scavenging oil from the reservoir have been recognized to possess very desirable advantages, they have also been recognized to have serious disadvantages. For example, in the case of combustion processes, it is difficult to regulate and maintain a combustion front throughout a reservoir. Frequently, the combustion process is interrupted and the flame front disappears—all too often necessitating abandonment of the operation.

In the case of steam-injection processes, it has been

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found that such processes are very slow; and they take very long periods of time for the steam to effectively penetrate and raise the temperature of a reservoir. Furthermore, when the pressure of the steam is increased in an effort to speed up the recovery process, the accompanying rise in the temperature of the steam causes large amounts of heat to be lost to the surrounding formations in which oil is not present. Even at low operating pressures, heat losses in a steam injection process are undesirably high—thereby tending to make this type of operation inefficient and uneconomical.

Accordingly, it is an object of the present invention to provide an oil recovery method wherein highly viscous petroleum is readily recovered from subterranean reservoirs. More specifically, the object of this invention is a process for the in-situ hydrogenation of petroleum within a reservoir whereby the petroleum is made readily mobile and high recovery of the oil in place is obtained. It is especially an object of the invention to provide a method for petroleum recovery which is rapid and efficient. These and related objects of this invention will become more apparent from the ensuing description.

In the process of this invention, petroleum is hydrogenated within a reservoir so that an enhancement of its recovery is realized. The first step of the process lies in the injection of a mixture of a gaseous catalyst and hydrogen through an injection well into the reservoir. These materials as they are injected into the reservoir tend to flow through the reservoir in multiple flow paths. That is, the injected fluid tends to seek paths that are "fingers" through the reservoir extending from an injection well toward a production well. Preferably, the operation in any given reservoir is carried out concurrently throughout the reservoir so that the multiple paths extend substantially throughout the reservoir. Thus, injection wells are preferably spaced in a pattern that covers the entire lateral extent of the reservoir in a manner consistent with conventional well patterns. In this way, multiple wells are provided from which the petroleum can be produced.

The injection of the gaseous catalyst and hydrogen may be performed either sequentially or simultaneously. For example, a mass of catalyst may be injected, followed by a mass of hydrogen—or an admixture of catalyst and hydrogen may be injected. The mass of hydrogen may be about 1% to 4% by weight of the oil in place; and the mass of catalyst may be about 1% to 6% by weight of the oil in place.

In the operation of this process, hydrogen can be injected first and followed by the catalyst. However, the preferred method for the operation of this invention is the injection of a hydrogenating mixture of hydrogen and a gaseous catalyst such as methyl iodide, hydrogen iodide, or nickel carbonyl. This hydrogenating mixture can be injected continuously until ultimate oil recovery is obtained. However, it is preferred that the volume of hydrogen and catalyst be injected only at the beginning of the process and that it be limited to from about 1% to 10% by weight of the oil in place. A supplemental driving or scavenging agent such as water or gas is then injected until ultimate oil recovery is obtained. The mass of the hydrogenating mixture serves to increase oil recovery beyond that obtainable by a conventional water or gas drive operation.

In the process of this invention, reservoir oil is hydrogenated in-situ at a temperature above 400° F. and generally within the range of 400° F. and 1200° F. by direct contact between the oil and hydrogen in the presence of a catalyst. Suitable injection pressures are those above 50 pounds per square inch but not so great as to lift the overburden above the reservoir and thereby fracture the formations. The pressure required to lift the overburden

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is usually equal to about one pound per square inch per foot of depth and is usually referred to as the fracturing pressure. Structural limitations of shallow petroleum formations—such as shallow oil sands, tar sands, and oil shale deposits—usually require the maintenance of relatively low pressures, since the higher pressures tend to create fractures in the formation extending into the overburden. These fractures in turn permit undesirable leakage of fluids from the oil-bearing formations into adjacent structures.

The process of this invention may be controlled in various ways. In general, the rate of reaction of the process may be readily adjusted and controlled by simply regulating the pressure within a reservoir. High pressures tend to accelerate the rate of reaction; and, conversely, low pressures tend to retard the reaction.

Controlling the pressure of a reservoir in the practice of this invention may be accomplished in effect by regulating the relative rates of fluid injection and production. Thus, it will be apparent that the pressure on any given reservoir may be readily controlled by simply controlling the back pressure on the production wells. The maximum pressure attainable, of course, is determined by the depth of the reservoir in question as well as the pressure of the fluids injected into the reservoir.

Other conditions being fixed, the rate at which catalyst and hydrogen are injected within a reservoir also has a bearing upon the rate at which the reactions of this invention take place. In this connection, it is desirable that the hydrogen and catalyst—and any scavenging agents—be passed through a reservoir at a rate sufficient to stimulate intimate mixing and contacting. In conventional oil recovery processes (e.g., conventional gas and water drives), apparent rates of advance of the driving fluids of about one-tenth to one foot per day are usually employed. In the practice of this invention, however, it is preferred that the hydrogen and catalyst be injected in a quantity and at a rate sufficient to provide an apparent rate of advance through a reservoir of about one to two feet per day. Rates of advance of this magnitude assure fingering of the hydrogen and catalyst into the reservoir oil and thus promote their mixing and reaction with the oil. Once the hydrogen and catalyst have been injected, it is generally preferred that any scavenging agents subsequently injected advance through a reservoir at a rate less than one foot per day in order to maintain an essentially bank-type displacement of fluids from the reservoir. It will be recognized, of course, that the hydrogen-containing gases and the catalysts used in this invention may be circulated repeatedly through a reservoir as may be necessary or desirable.

In carrying out the present process, a well bore penetrating an oil-bearing formation should be cased with pipe in a conventional manner whereby a mixture of gaseous catalyst and hydrogen may be injected into the formation. Well bores laterally spaced from the injection borehole are also drilled as necessary, and oil produced by the process is withdrawn from these wells. The mixture of catalyst and hydrogen is forced under pressure through the injection well into direct contact with the oil in the formation. The hydrogen permeates the oil thoroughly and produces—in the presence of the catalyst and by reaction with the reservoir—an upgraded oil. The upgraded oil has a lower specific gravity and viscosity than the original oil and is an excellent hydrogen-transfer agent. In other words, it tends to absorb hydrogen from injected gases and later release it to the reservoir oil. Thus, hydrogenation of the reservoir oil occurs by direct reaction with injected hydrogen and also by a transfer mechanism involving oil previously hydrogenated.

In addition to this upgrading phenomenon, several other actions occur in the process of the invention which further promote oil recovery. For example, as beforementioned, any driving fluid employed in the production of oil tends to select zones or "fingers" in traveling from

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an injection well to a production well. This is especially true when the driving or scavenging fluid has a viscosity markedly lower than that of the driven fluid. In the present invention, this characteristic is deliberately exploited so as to enhance the production of oil, since it promotes contact between the hydrogenating agents and viscous oil.

As the hydrogen and catalyst in a process of this invention finger through a reservoir—and as hydrogenation takes place, transforming viscous petroleum to products of lower viscosity—heat released by the hydrogenation is transmitted through the reservoir, thereby further reducing the viscosity of the oil substantially. As the viscosity of the oil decreases, its mobility within the reservoir rapidly increases. The mobility of oil within a reservoir is by definition proportional to formation permeability and inversely proportional to the viscosity of the oil. Due to its increased mobility, the oil flows readily within the reservoir rock and drains into the production wells. The increased mobility also further promotes mixing of heated oil within the reservoir with unheated oil and with the injected gases.

The injected hydrogen and catalyst gases and the oil as it is hydrogenated tend to move up-structure in a reservoir, while the heavier reservoir fluids tend to flow downward. In other words, the low-density materials—hydrogen, gaseous catalyst, and hydrogenated oil—tend to diffuse upward through the denser reservoir oil. An efficient contacting and mixing system is thus provided which further enhances oil hydrogenation.

The reaction of this invention may be initiated within a reservoir by raising the temperature at the borehole face of the reservoir to reaction temperature. Any suitable means of supplying heat may be used. Preferred methods are those involving liberation of heat near the face of the oil-productive formation. A borehole heater—activated by electrical energy or combustion products—may be placed in the well bore to preheat the reactants. Once initiated, the reaction sustains itself due to the heat supplied by the hydrogenation process.

Insofar as injection or flooding patterns are concerned, it should be noted that any conventional flooding program used in the recovery of oil such as linear, 4-spot, 5-spot, and related flooding patterns may be employed. Obviously, in these patterns it will be understood that the wells conventionally designated as injection and production wells will be similarly employed in carrying out the present process. The process of this invention is illustrated diagrammatically by the accompanying drawing.

The accompanying drawing illustrates diagrammatically and in vertical section an oil reservoir and its relationship to the earth's surface, and an oil production method as practiced according to this invention.

With reference to the drawing, the numeral 1 designates a subterranean oil-bearing formation, above which is a relatively impervious stratum 2, and below which is another relatively impervious stratum 3. These impervious layers are usually of a shale or other relatively impermeable composition. A well bore is drilled from the surface of the earth 4 through the oil-bearing formation—this borehole being shown by the legend 5. A steel casing 6 is placed in the borehole and may terminate at the top of the oil sand. The annulus between the casing and borehole is sealed with cement or other sealing material in a conventional manner. The casing placed in this manner leaves a borehole within the oil sand which is completely uncased for the injection of fluids into the oil-bearing formation.

As in conventional oil field practice, the casing may also be extended through the oil sand and, after being sealed in place, perforated by conventional means whereby an injected fluid will pass through the perforations into the formation. By using this technique of placing the casing and then perforating the casing at desired points, control of the injection points for fluids into the forma-

tion may be effected. For example, perforations may be made in a selected part of the casing and the catalyst-hydrogen mixture thereby injected into a selected zone of the oil-bearing formation. This and other obvious procedures may be practiced without departing from the scope of this invention.

As beforementioned, the injected fluids are pumped through injection well 7 into the productive formation, and oil production is realized through production well 8. This well, like injection well 7, is drilled from the surface of the earth through the productive sand formation as shown by the borehole 9. Here again a casing 10 is placed within the borehole and may be set at the top of the productive formation 1 or may extend through this formation and be perforated by conventional means. The annular space between borehole 9 and casing 10 may be cemented or sealed in a manner analogous to conventional oil field practice.

As may be noted, the surface equipment which would normally be employed in injecting or producing fluids via wells penetrating an oil reservoir is not shown. The inclusion of such equipment is not considered essential for the purpose of describing this invention.

Another illustrative embodiment of this invention lies in a combination-type operation wherein the hydrogenation step of the invention is preceded by an in-situ combustion step. After the in-situ combustion reaction has proceeded a substantial preselected distance within a reservoir from an injection well, an inert gas such as nitrogen is injected into the reservoir to flush oxygen from the vicinity of the injection well. Thereafter, quantities of hydrogen and gaseous hydrogenation catalyst are injected into the reservoir in the manner described hereinbefore so as to effect hydrogenation of the oil in place. A scavenging fluid may be injected after the hydrogen and catalyst, also as described hereinbefore.

The in-situ combustion step described above achieves several desirable objectives. First, it heats up a substantial portion of the reservoir and brings it up to a temperature favorable to the hydrogenation step which follows. Second, it reduces the viscosity of the oil in place, thereby rendering the oil much more mobile and readily contacted by the hydrogenating gases and catalyst.

The in-situ combustion step may make use of any conventional technique of this type. For example, it is contemplated that a combustible mixture of fuel gas and oxygen may be passed down an injection well bore. The combustible mixture may then be ignited and its heat of combustion used to start the combustion of part of the oil within the surrounding formation. Injection of the

combustible mixture may then be suspended and oxygen alone supplied to move the combustion front away from the injection borehole. When the combustion front has proceeded an adequate predetermined distance into the formation, the injection of an inert gas followed by the injection of hydrogen and a gaseous hydrogenation catalyst may be practiced as described hereinabove. Generally speaking, the combustion front need not penetrate within a formation much more than 20 to 40 feet to achieve the objects of the in-situ combustion step. It will also be noted that the in-situ combustion step may be used to help build up the pressure of the reservoir to whatever level is desired. The combustion process will tend to generate large volumes of gas which may be held within the reservoir by simply keeping the production wells shut down.

The invention claimed is:

A method of producing petroleum crude oil from a subterranean oil bearing formation which comprises injecting an oxygen-containing gas into the formation through an input well under conditions to effect combustion within a zone of the formation adjacent said input well, continuing said injection of oxygen-containing gas until the temperature within said zone is between 400° F. and 1200° F., thereafter discontinuing the injection of said oxygen-containing gas to terminate said combustion, injecting an inert gas within said formation through said input well to flush said oxygen-containing gas from said zone adjacent said input well, then injecting hydrogen and a gaseous hydrogenation catalyst within the formation through said input well whereby to hydrogenate oil within the formation in the presence of said catalyst, maintaining the pressure of the formation in excess of 50 p.s.i.g., and recovering oil from the formation through an output well laterally spaced from said input well.

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