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J. N. DEW ETAL

3,208,514

RECOVERY OF HYDROCARBONS BY IN-SITU HYDROGENATION

Filed Oct. 31, 1962

2 Sheets-Sheet 1

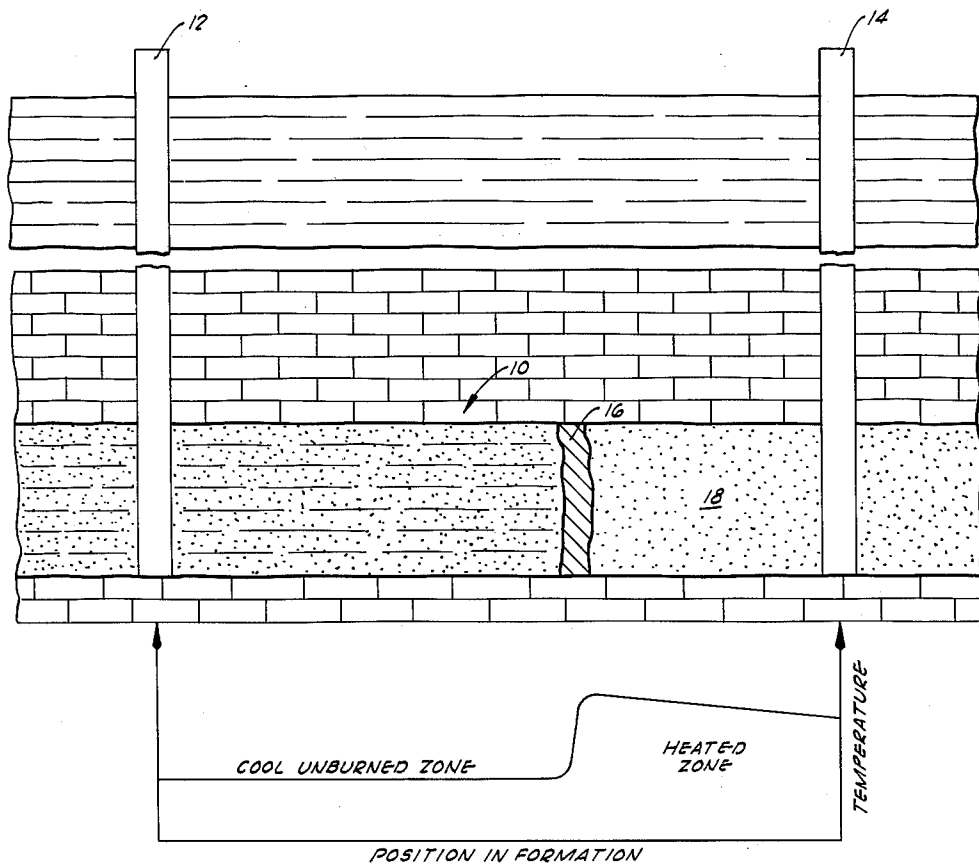


FIG. 1

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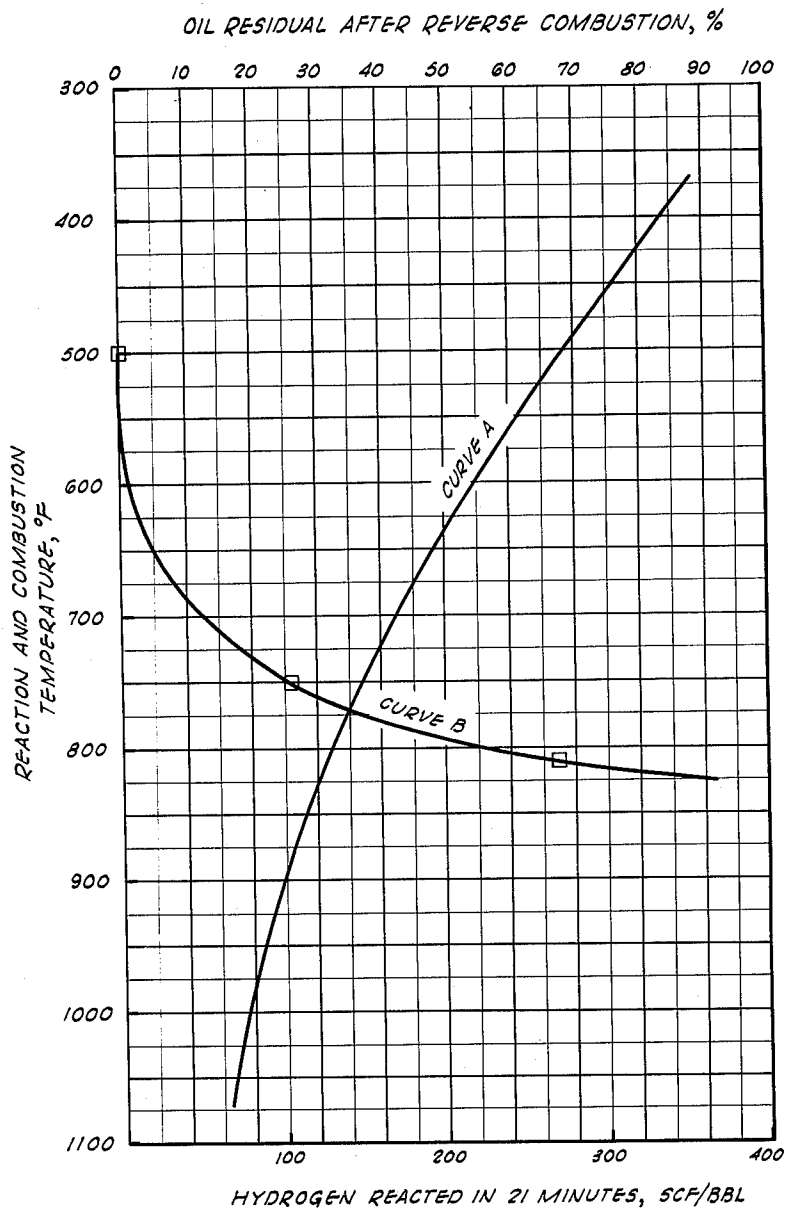


FIG. 2

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3,208,514 RECOVERY OF HYDROCARBONS BY IN-SITU HYDROGENATION

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17 Claims. (Cl. 166—2)

This invention relates to secondary recovery methods for producing subterranean deposits of crude oil. More particularly, the present invention relates to a method for hydrogenating underground deposits of crude oil, thereby upgrading the oil and lowering its viscosity so that it may be more easily moved through a formation to a producing well.

As is well known in the art after recovery from a subterranean formation, crude petroleum requires removal of certain materials, such as sulfur, oxygen and nitrogen in order to prevent interference by these materials with subsequent refining operations. The removal of these materials has been accomplished previously by hydro-refining procedures in which the recovered crude oil is subjected to contact with hydrogen in suitable reaction vessels under requisite conditions of temperature and pressure prior to further refining operations. During such contact, reduction reactions occur in which the loosely bound oxygen, nitrogen and sulfur in the crude oil are converted to more easily removed water, ammonia and hydrogen sulfide, respectively. Further, by using excess hydrogen, high pressures, and appropriate temperature ranges, desirable destructive hydrogenation of the crude oil may be made to occur whereby stable, lower molecular weight materials are formed which are more suitable stocks for use in the production of gasoline. Destructive hydrogenation also results in the reduction of the viscosity of the crude oil.

It has heretofore been recognized that if there were available some practical method for hydrogenating petroleum deposits in place—that is, in their natural subterranean locations—a very considerable economic advantage would be achieved over the present hydro-refining procedures conducted at the surface in that the necessity for reaction vessels and other equipment might be obviated. Moreover, the consequent lowering of the viscosity of the crude oil by in-situ hydrogenation would make possible the recovery of large quantities of low gravity, viscous crude oils which have previously not been possible to recover by conventional recovery methods.

A relatively recently proposed process for the in-situ hydrogenation of viscous crude oils suggests that the hydrogenation reaction may be carried out by placing electrical heating units in casings extending radially into the formation from a bore hole, passing a hydrogen-containing gas through the casings and over the heating units, and finally, contacting the viscous crude oil with the heated hydrogen to hydrogenate the oil. The hydrogenated oil is reduced in viscosity and flows back into the bore hole through the radially extending casings. The described method of hydrogenation poses a number of problems and has enjoyed very little commercial success. Only small parts of an oil-bearing formation can actually be heated to the temperature necessary to achieve substantial hydrogenation. Moreover, the electrical heaters and the equipment necessary to position the radially extending casings are expensive and render use of the process economically unfeasible in many instances.

The present invention provides an improved, more practical method for recovering crude oil from subterranean formations by the process of in-situ hydrogenation,

and achieves relatively improved results by reason of the establishment in the formation of an environment and conditions which are conducive to efficient hydrogenation of the hydrocarbon materials therein. The method of this invention initially provides for the conversion of the crude oil in the major part of the formation to a heated, hydrogenatable carbonaceous material. The hydrogenatable carbonaceous material is, by this initial step, heated to a temperature which is optimum for the progression of the hydrogenation reaction.

A hydrogen-containing gas is next injected into the formation in a sufficient amount and at a sufficient pressure to assure the efficient progression of the hydrogenation reaction and an adequate supply of hydrogen is utilized to assure the substantially complete hydrogenation of the carbonaceous residue.

As a final step of the method, the hydrogenated material of lowered viscosity is produced from the formation by passing a fire or water flood therethrough in accordance with these conventional and well known secondary recovery techniques.

To yet more specifically summarize the method of the present invention, the crude oil in the formation is initially converted to soft coke and oil-like, hydrogenatable material by passing a combustion front through the formation. A preferred technique for propagating the combustion front through the formation is that which is termed reverse in-situ combustion, the details of which are discussed hereinafter. Forward drive in-situ combustion, as contrasted with reverse in-situ combustion, may also be utilized to convert the oil to hydrogenatable material and to heat the material sufficiently for the subsequent progression of the hydrogenation reaction. However, for reasons subsequently explained herein, the maintenance of the temperature of the combustion front within optimum limits for the production of hydrogenatable carbonaceous material is more difficult in the case of forward drive in-situ combustion than in the reverse in-situ combustion technique. When utilizing reverse in-situ combustion, the temperature at the combustion front is maintained in the range of from about 400° F. to about 1000° F., and preferably from about 400° F. to about 850° F., so that the residual hydrocarbon material left in the formation after passage of the combustion front therethrough is maximized in quantity and is heated to a temperature within the optimum range for the progression of the subsequent reaction by which the material is hydrogenated.

After the passage of the combustion front through the formation, a hydrogen-containing gas is injected into the formation and is maintained therein at a pressure of at least 500 p.s.i.g. and a temperature of from about 400° F. to about 950° F. for a period of time sufficient to hydrogenate the residual carbonaceous material remaining in the formation. This period of time varies considerably, according to the temperature and pressure employed and the nature of the formation. As indicated above, the completion of the hydrogenation reaction within the formation is followed by the recovery of the hydrogenated material of lowered viscosity by any suitable technique, such as fire flooding or water flooding.

From the foregoing description of the present invention, it will have become apparent that an important object of the invention is to provide an improved method of hydrogenating viscous petroleum deposits in place so that such deposits may be more easily and more completely recovered from the formation in which they occur.

Another object of the present invention is to provide a process for the in-situ hydrogenation of viscous petroleum deposits, which process may be more economically practiced than those which have heretofore been proposed.

A further object of the present invention is to provide a method for effecting the recovery of crude oil from a subterranean formation in an upgraded, partially refined condition.

Other objects and advantages of the invention will be apparent upon reading the following detailed description of the invention in conjunction with the accompanying drawings.

In the drawings, FIGURE 1 schematically illustrates the manner in which one embodiment of the invention is practiced. FIGURE 2 is a graph showing the relation between the combustion front temperature and the amount of residual material left in the formation, and also showing the rate of progression of the hydrogenation reaction as the temperature of the residual material to be hydrogenated is varied.

In hydrogenating crude oil, the oil must be subjected to a minimum temperature of 400° F. in order for the hydrogenation reaction to proceed efficiently. Although the reaction is exothermic, it does not develop sufficient heat to sustain the reaction throughout the formation and to hydrogenate the oil to the maximum extent. Thus, even assuming that all of the oil in the formation were available for hydrogenation and that the maximum possible amount of hydrogen (about 460 standard cubic feet per barrel) were reacted therewith, the formation temperature would only be raised about 100° F. by the exothermic heat of reaction. From these considerations, it will be apparent that supplementary heat must be provided to raise the temperature of the formation to above 400° F.

One of the widely used techniques of secondary recovery of deposits of less viscous petroleum is that of in-situ combustion. Because of the employment in this procedure of a high temperature combustion front which is propagated through the formation, we have determined that this technique offers a suitable and relatively economical supplementary source of heat for raising the temperature in the formation to a level sufficiently high to support a subsequent hydrogenation reaction.

Two general types of in-situ combustion are presently practiced. In the so-called forward drive in-situ combustion, the fire or combustion front is initiated in the formation adjacent the injection well and propagated through the formation from an injection well toward a producing well or wells. A driving, combustion-supporting gas is introduced into the formation from the injection well and moves to, and across, the combustion front toward the producing wells. The combustion-supporting gas (oxygen-containing gas) promotes the combustion of a portion of the hydrocarbon at the combustion front and drives the hydrocarbon gases and less viscous hydrocarbons ahead of the front toward the producing wells where they are ultimately recovered.

The second type of in-situ combustion secondary recovery is referred to as reverse or inverse in-situ combustion. In this procedure, the combustion front is initiated in the formation adjacent the producing well or wells and moves through the formation toward an injection well spaced from the producing wells. The combustion-supporting gas, on the other hand, is injected into the formation through the injection well and thus moves through the formation in the opposite direction to the direction in which the combustion front is propagated. The hydrocarbons which are highly heated by the passage of the combustion front, but which are not combusted, are driven by the combustion-supporting gas through the formation from the combustion front to the producing wells.

In both forward drive and reverse in-situ combustion, varying amounts of coke, tarry material and heavy viscous petroleum remain in the formation after the passage of the combustion front. Some or substantially all of this material is hydrogenatable, depending upon the temperature of the combustion front being passed through the formation, whether a forward drive or reverse in-situ combustion technique is used, and the conditions of tem-

perature and pressure imposed during the subjection of the residual material to contact with hydrogen or a hydrogen-containing gas during the hydrogenation.

When a forward drive is utilized to propagate a combustion front through the formation, we have found that when the temperature at the combustion front exceeds 700° F., very little residual carbonaceous material is left in the formation after passage of the front therethrough. Moreover, in the forward drive in-situ combustion, when the front temperature exceeds 700° F., the carbonaceous material which does remain in the formation is largely constituted by hard coke which is very difficult to hydrogenate. At temperatures not exceeding 600° F., however, a substantial deposit of residual hydrogenatable carbonaceous material is left in the formation after passage of the front. It is frequently difficult to conduct the forward drive in-situ hydrogenation with the temperature of the combustion front maintained as low, or lower, than 700° F. so as to leave any appreciable quantity of hydrogenatable carbonaceous material in the formation. However, in some instances, the flux rate at which the combustion-supporting gas is injected may be reduced substantially without failing to sustain the drive, thereby lowering the temperature at the combustion front, and yielding a larger residual amount of more easily hydrogenated soft coke and tarry materials. In such circumstances, subsequent recovery of the residual material by in-situ hydrogenation, as hereinafter described, becomes economically feasible and may be coupled with the preheating afforded by the forward drive in-situ combustion to upgrade and recover the tarry and oily materials remaining in the pores of the formation. This allows recovery of the residual material normally coked or combusted, thereby increasing recoveries.

As hereinbefore indicated, however, the reverse in-situ combustion procedure is preferred as a preheating or supplementary heating technique preceding the in-situ hydrogenation under almost all formation conditions, including that described above wherein the forward drive combustion is effective for preheating. This is due to the fact that the temperature at the combustion front is more easily controlled in reverse in-situ combustion, lower flux rates of combustion-supporting gas are required and a substantially larger portion of the crude oil originally present is retained in the interstices of the formation as hydrogenatable residual material when operating at temperatures between 600° and 1000° F. Moreover, a much larger portion of the zone which has been swept out by the moving combustion front may be retained at a temperature within the optimum range for the progression of the hydrogenation reaction. This is possible by reason of the continuous passage of heated gases and hydrocarbons en route to the production wells through this swept out zone which has already been heated by passage therethrough of the combustion front as it is propagated toward the injection well.

The manner in which residual hydrogenatable carbonaceous material is deposited and retained in a heated condition in the formation by the propagation of a combustion front therethrough by the preferred reverse drive technique will be more clearly understood when reference is made to FIGURE 1 of the drawings.

In FIGURE 1, reference character 10 refers to a subterranean formation in which is located a deposit of crude oil which it is proposed to upgrade and recover by the in-situ hydrogenation process of the present invention. The subterranean formation 10 is traversed by a pair of spaced wells 12 and 14 which may be employed as the injection well and the producing well, respectively. It will be understood, of course, that a plurality of injection wells and producing wells may also be utilized in a manner similar to that disclosed in United States Patent 2,958,519 to J. R. Hurley. In contradistinction to the forward drive procedure of originating a combustion front at or adjacent the injection well 12 and propagating the

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front toward the production well 14, in the reverse in-situ combustion technique, the hydrocarbons in the formation are ignited adjacent the production well 14 and the combustion front designated by reference numeral 16 moves away from the production well 14 and toward the injection well 12.

Combustion may be initiated by any suitable means, such as an air-gas burner or electrical heater. While the formation hydrocarbons are being ignited, a combustion-supporting gas, such as air or oxygen, is passed into the formation through the production well 14 for a short period of time so as to establish and enlarge the combustion front and propagate this front a short distance outwardly in the formation away from the base of the production well 14.

Injection of combustion-supporting gas through the production well 14 is then terminated and the injection well 12 is then utilized to supply air or other combustion-supporting gas to the formation. As air is passed into the formation from the injection well 12, the air moves through the formation and crosses the combustion front 16 where oxygen reacts with the hydrocarbons. The gaseous combustion products pass on through a high temperature zone 18 which has been swept out by the front 16 until they reach the production well 14. The air moving through the formation from the injection well 12 toward the production well 14 supports combustion at the combustion front 16 and serves to drive hot oil vapors, gaseous cracked products and low viscosity liquid hydrocarbons from the combustion front 16 through the heated zone 18 to the production well 14.

As the combustion front 16 moves through the formation, it enlarges the heated area 18 and leaves in the interstices of the formation within this area a deposit of soft coke, tarry materials and viscous liquid hydrocarbons. The zone 18 remains very hot as a result of the continued flow of heated hydrocarbon gases and liquids therethrough from the combustion front 16 to the production well 14.

The relative temperatures in the unburned portion of the formation 10 ahead of the moving combustion front 16 and the heated portion 18 of the formation are illustrated by the temperature profile graphically portrayed in the lower part of FIGURE 1. It will there be noted that the heated portion 18 of the formation 10 and the residual carbonaceous material which remains therein after the passage of the combustion front 16 therethrough are retained at a temperature which is only slightly lower than the temperature existing at the combustion front 16. Thus, if the temperature in the combustion front 16 can be brought within the range which is suitable for the subsequent in-situ hydrogenation of the residual material remaining in the formation, the heated portion 18 of the formation 10 which remains after passage of the front therethrough may also be retained in substantially the same range.

We have determined that by controlling the flux rate of air introduced to the formation 10 via the injection well 12, the temperature of the combustion front 16 may be kept within a range which is most suitable for the deposition of a maximum amount of residual hydrogenatable material and for the progression of the hydrogenation reaction. Since, as indicated above, the hydrogenation reaction cannot be carried out successfully at temperatures lower than 400° F., such temperature constitutes the lowest temperature at which the combustion front 16 should be maintained.

With respect to the upper limit of temperature which should optimally obtain at the combustion front 16, laboratory tests have shown that, though some hydrogenatable residual material remains in the formation when a reverse combustion front having a temperature as high as 1000° F. is passed therethrough, temperatures not exceeding 850° F. are preferred because operation at temperatures exceeding this value results in excessive cracking of hydrocarbon materials in the formation and

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consumes excessive fuel, with the result that more of the hydrocarbon material is displaced from the formation and consumed by the combustion-supporting gas passed therethrough. The relation between the amount of residual material left in the formation and the combustion front temperature is portrayed by curve A in the graph illustrated in FIGURE 2.

Besides the disadvantage posed by the undesirably small quantities of residual material left in the formation when combustion front temperatures exceeding about 850° F. are utilized, the small amount of material which is left in the formation is primarily deposited as a hard coke which is difficult to hydrogenate. At temperatures of about 850° F. or less, on the other hand, only an optimum degree of thermal reaction will occur at the time of passage of the combustion front through the formation and during the subsequent hydrogenation. Also, as the temperature in the combustion front 16 and in the heated zone 18 is decreased from 850° F. toward the minimum operative temperature of 400° F., increasing quantities of tarry and oil-like materials are left in the pore spaces of the zone 18.

The subsequent hydrogenation reaction is, in actuality, destructive hydrogenation in which the larger molecules of the hydrocarbon material are cracked and the products of the cracking are subsequently hydrogenated to reduce their viscosity and permit them to be more easily recovered from the formation. Temperatures exceeding about 500° F. are required for any substantial degree of cracking to occur and at temperatures exceeding about 850° F., the cracking reaction becomes undesirably predominant relative to the destructive hydrogenation reaction in the sense that more solid coke is produced as a result of such cracking and less hydrogenated liquid material is produced as a result of destructive hydrogenation. Carrying out the destructive hydrogenation at superatmospheric pressures of at least 500 p.s.i.g. in the manner hereinafter prescribed greatly aids in suppressing coke formation as a result of cracking and in promoting the formation of low viscosity, hydrogenated liquid materials. In general, the higher the pressure, the more the hydrogenation reaction is favored.

As will be noted from the graph shown in FIGURE 2, the hydrogenation reaction (as indicated by the consumption of hydrogen) proceeds most rapidly at temperatures exceeding 600° F., and preferably falling within the range of from about 800° F. to 850° F. Thus, when considered only from the standpoint of achieving an optimum balance between the destructive hydrogenation and cracking reactions, a temperature of between about 800° F. and 850° F. would appear to be indicated for most effectively carrying out the hydrogenation of the residual material in the formation. However, as has been indicated, the deposition of larger quantities of hydrogenatable residual material is favored by the use of lower combustion front temperatures, so that rather than operating in the temperature range which would provide the maximum rate of progression of the hydrogenation reaction and still avoid excessive cracking and coke formation, it is preferably to propagate a lower temperature combustion front through the formation to leave more hydrogenatable residual material. Consequently, the hydrogenation reaction temperature is also lowered from the otherwise optimum range of 800° F. to 850° F. so that, in effect, a compromise temperature range of from about 600° F. to 700° F. is preferably utilized for the hydrogenation reaction. Since the hydrogenation reaction per se generates approximately 100° F. as the exothermic heat of reaction, this means that the combustion front temperature should be between about 500° F. and 600° F. for optimum operation. At this temperature, curve A on the graph of FIGURE 2 indicates that between about 55 percent and 70 percent of the total oil in the formation remains as residual hydrogenatable material.

Although the hydrogenation reaction rate is considerably slower in the preferred temperature range of from 600° F. to 700° F. than at higher temperatures, it may be increased by hydrogenating at higher pressures. Moreover, in in-situ hydrogenation of subterranean oil deposits, the reaction rate is not especially critical, since the hydrogen gas may be injected into the formation, the injection and production wells then shut in, and the reaction allowed to proceed to completion over several weeks or months.

In order to maintain the combustion front 16 at a temperature such that the temperature of the heated zone 18 of the formation 10 will fall within the broad operative range for the hydrogenation reaction of from about 400° F. to about 950° F., the air flux through the injection well 12 should be adjusted to from about 2 standard cubic feet per hour per square foot of the combustion front area to about 50 standard cubic feet per hour per square foot in the combustion front area. The combustion-supporting gas is continuously injected into the formation through the injection well 12 at a rate within this range until the combustion front 16 has reached the injection well.

In one embodiment of the invention, after the combustion front 16 has reached the injection well 12, the injection of air or other combustion-supporting gas into the formation is stopped. The injection well is then purged and the injection of hydrogen or a hydrogen-containing gas into the formation via the injection well 12 is commenced. As an aid to maintaining the temperature in the burned-out formation within the range of from 400° F. to 850° F., which is desirable, or to within the range of from 600° F. to 700° F., which is most preferred, the hydrogenating gas may, if desired, be preheated to some temperature above about 400° F. prior to its injection into the formation. The hydrogenating gas which is employed may be manufactured free hydrogen, or it may be a hydrogen-containing gas, such as the gaseous effluent from a catalytic reformer containing associated normally gaseous hydrocarbons, such as methane, ethane, propane, butane and the like.

The injection of the hydrogen or hydrogen-containing gas into the formation 10 is continued until free hydrogen is observed at the production well 14. At this time, the production well is closed in and the injection of hydrogen is continued until the pressure in the formation exceeds 500 pounds p.s.i.g., and preferably is between about 1000 pounds p.s.i.g. and 4000 pounds p.s.i.g. We have found that, in general, the higher the hydrogen pressure in the formation, the more efficient the hydrogenation reaction which occurs therein and the faster its rate of progression.

As discussed in detail hereinbefore, the rate of progression of the hydrogenation reaction has also been determined to be dependent, to a substantial extent, upon the temperature obtaining within the formation during the hydrogenation reaction. For example, based on laboratory tests, it was found that hydrogenation of the residual carbonaceous material was completed in about five days when the formation temperature was about 700° F. and a pressure of 1000 pounds was maintained in the formation. When the temperature was lowered to 600° F. and the hydrogenation reaction was conducted at the same pressure of 1000 p.s.i.g., thirty-five days were required to complete the hydrogenation reaction. When the pressure in the formation is increased to 4000 p.s.i.g., the time required to complete the hydrogenation reaction is reduced by about one-third.

When the pressure within the formation has reached the desired magnitude, the injection well is then closed in and the entire formation remains pressurized and in a heated state for a sufficient length of time for the hydrogenation reaction to reach equilibrium. As indicated, this period of time may vary over a wide range and will depend upon the formation temperature, the formation pressure, the amount of residual carbonaceous

material remaining in the formation, and the porosity and permeability of the formation.

Following the completion of the hydrogenation reaction, the hydrogenated material in the formation is upgraded from the original material and is of substantially reduced viscosity. This lower viscosity material may be recovered from the formation by conventional water flooding, or a forward drive in-situ combustion recovery operation of the type hereinbefore described may be conducted to drive the hydrogenated oil to the producing wells.

Several alternatives to the procedure hereinbefore described may be practiced in carrying out the process of the invention without departure from the basic principles which are utilized. For example, after the formation has been traversed by the combustion front and the residual carbonaceous material which remains therein is ready to be hydrogenated, the hydrogenating gas may be injected through the producing well, instead of the injection well, if this procedure is preferred. Also, economic advantages may frequently be gained by terminating the reverse in-situ combustion prior to the propagation of the combustion front to the injection well. In other words, the combustion front is moved only a part of the distance between the production well and the injection well before the supply of combustion-supporting gas is terminated. Hydrogen or a hydrogen-containing gas is then injected into the formation at the production well and that portion of the formation which has been burned out is the situs for the hydrogenation reaction. Following the hydrogenation reaction a forward drive in-situ combustion may be initiated at either of the wells and the hydrogenated material, as well as the material remaining in the portion of the formation which has not been traversed by the combustion front, recovered.

A further alternative procedure which is sometimes desirable is that of partially closing in the production well shortly prior to the termination of the reverse in-situ combustion so that the pressure in the formation commences to build up as a result of the continued injection of the combustion-supporting gas through the injection well. The pressure built up by virtue of the partially throttled production well continues until a minimum pressure of about 500 pounds p.s.i.g. is achieved in the formation. At this point, the reverse in-situ combustion is terminated and a hydrogen-containing gas is then injected into the formation in the manner previously described to further increase the pressure therein to in excess of 1000 p.s.i.g. By this procedure, a saving in time is realized over the time required to build up the pressure in the formation to the required extent solely through the injection of the hydrogenating gas. Moreover, the use of the combustion-supporting gas to partially pressure the formation prior to the injection of the hydrogenating gas results in an economic saving since combustion-supporting gases, such as air or oxygen, are, of course, much less expensive than hydrogen or hydrogen-containing gases.

While there have been shown, described and pointed out the fundamental novel features of this invention, as applied to the preferred embodiment entailing the use of a reverse in-situ combustion in combination with in-situ hydrogenation for the recovery of viscous crude oils from a subterranean formation, it will be understood that various omissions, substitutions and changes in the form and details of the process illustrated and described may be made by those skilled in the art of petroleum production without departing from the spirit of the invention. It is therefore our intention to be limited only as required by the scope of the appended claims and reasonable equivalents thereof.

What is claimed is:

1. A secondary recovery method for recovering residual liquid hydrocarbons from a permeable underground

formation traversed by injection and production wells which comprises:

- (a) continuously subjecting the hydrocarbons in the formation between said wells to controlled in-situ combustion in which a combustion front having a temperature of between about 400° F. and about 850° F. is propagated through said formation to convert a portion of the hydrocarbons therein to hydrogenatable, residual carbonaceous material;
- (b) contacting the residual carbonaceous material with a hydrogenating gas at a pressure exceeding about 500 p.s.i.g. and a temperature of from about 400° F. to about 950° F. for a period sufficient to substantially lower the viscosity of said residual carbonaceous material by injecting hydrogenating gas through a first one of said wells;
- (c) recovering said hydrogenated residual material from the formation through a second one of said wells.

2. A secondary recovery method as claimed in claim 1 wherein said residual carbonaceous material is contacted with a hydrogenating gas at a temperature of between about 600° F. and 700° F.

3. A secondary recovery method as claimed in claim 1 wherein said combustion front is propagated through said formation by passing a combustion-supporting gas through said formation from the second of said wells to said first well at a rate of between 2 and 50 standard cubic feet per hour per square foot of combustion front area.

4. A secondary recovery method as claimed in claim 3 wherein contact of said residual hydrocarbons with a hydrogenating gas is effected by

- (a) partially shutting in said first well after the in-situ combustion is substantially completed to restrict the flow of said combustion-supporting gas from said first well;
- (b) continuing to pass combustion-supporting gas into said formation at a rate exceeding the rate at which said combustion-supporting gas flows from said first well until said formation is back pressured to about 500 p.s.i.g.; then
- (c) closing in said first well and terminating the introduction of said combustion-supporting gas into the formation;
- (d) introducing said hydrogenating gas into the formation to increase the pressure therein to in excess of 1000 p.s.i.g.; and
- (e) closing in said second well to maintain the pressure in said formation in excess of 1000 p.s.i.g. while maintaining the temperature therein between 400° F. and 950° F.

5. The method claimed in claim 4 and further characterized to include the steps of:

- (a) blocking the escape of hydrogenating gas from the formation to increase the pressure therein to in excess of 1000 p.s.i.g.;
- (b) retaining the hydrogenating gas in the formation until the maximum hydrogenation of residual material has occurred.

6. The method claimed in claim 4 wherein the combustion-supporting fluid is introduced to said formation at a rate predetermined to maintain the temperature at the combustion front at between about 500° F. and 600° F.

7. A method for hydrogenating subterranean hydrocarbons in place in a formation traversed by injection and production wells which comprises:

- (a) continuously subjecting the hydrocarbons in said formation between said wells to controlled reverse in-situ combustion in which a driving, combustion-supporting gas is passed through the formation toward a producing well, said combustion front is

propagated in a direction opposite to the direction of movement of said combustion-supporting gas, and the rate of introduction into the formation of said combustion-supporting gas is controlled to maintain the temperature at the combustion front between about 400° F. and about 850° F.;

- (b) injecting a hydrogenating gas into said formation through one of said wells to hydrogenate the residual carbonaceous material remaining in the formation following said controlled reverse in-situ combustion; and then

- (c) recovering said hydrogenated residual material from the formation through one of said wells.

8. The method claimed in claim 7 wherein said hydrogenating gas is hydrogen and the hydrogen is injected into the formation until a pressure exceeding 1000 p.s.i.g. is reached in the formation.

9. The method claimed in claim 7 wherein said combustion-supporting gas is introduced to the formation at a rate of between 2 and 50 standard cubic feet per hour per square foot of formation area in the combustion front.

10. A process for recovering residual carbonaceous materials remaining in a formation traversed by injection and production wells after passing a continuous reverse in-situ combustion front controlled to have a temperature in the range of about 400° F. to about 850° F. through the formation between said wells, which process comprises:

- (a) injecting a hydrogenating gas into the formation through one of said wells at a pressure exceeding 1000 p.s.i.g. while maintaining the temperature in the formation between 400° F. and 850° F. so as to hydrogenate said residual carbonaceous materials; and

- (b) recovering hydrogenated residual material from the formation through one of said wells.

11. The process as claimed in claim 10 wherein said hydrogenating gas is hydrogen and the temperature of the carbonaceous materials in the formation during the injection of the hydrogen gas is maintained between 500° F. and 700° F.

12. A process as claimed in claim 10 and further characterized to include the step of preheating the hydrogenating gas to at least 400° F. prior to the injection thereof into the formation.

13. A process as claimed in claim 10 wherein the hydrogenated residual material is removed by water flooding the formation.

14. A process as claimed in claim 10 wherein the hydrogenated residual material is recovered by passing a combustion front through the formation.

15. The method of recovering viscous crude oil from a subterranean formation which comprises:

- (a) penetrating the formation with a pair of wells spaced from each other and adapted for use as an injection well and a producing well;

- (b) initiating combustion of the oil in said formation adjacent the producing well;

- (c) continuously injecting a combustion-supporting gas into said formation from said injection well to maintain the combustion of oil in said formation and propagate the combustion front at a temperature of between about 400° F. and about 850° F. in a direction away from said producing well and toward said injection well; then, following the movement of the combustion front from adjacent the producing well to adjacent the injection well;

- (d) injecting a hydrogenating gas into the formation via one of said wells while at least partially shutting in the other of said wells to build up the gas pressure in said formation to greater than 500 p.s.i.g.

- (e) maintaining the hydrogenating gas in the formation at a pressure exceeding 500 p.s.i.g. until maxi-

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mum hydrogenation of the residual carbonaceous material in the formation is achieved; then

(f) recovering the hydrogenated carbonaceous material from the formation through one of said wells.

16. The method claimed in claim 15 wherein said hydrogenating gas is hydrogen.

17. The method claimed in claim 15 wherein the hydrogenating gas pressure in said formation is built up to in excess of 1000 p.s.i.g. and said pressure is maintained until maximum hydrogenation of the residual carbonaceous material in the formation is achieved.

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