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HYDROCARBON RECOVERY PROCESS

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This invention relates to the recovery of hydrocarbon materials from a subterranean formation and relates more particularly to the recovery of such materials by the method involving combustion in place of a portion of the hydrocarbons in the subterranean formation. In a more restricted sense, the invention relates to obtaining information concerning the flame front in a subterranean formation during recovery of hydrocarbons by the combustion method.

It has been proposed to recover hydrocarbon materials from a hydrocarbon-containing subterranean formation by a method which involves combustion of a portion of the hydrocarbons within the formation. In this method, combustion supporting gas is injected into the formation through an input well and combustion of hydrocarbon within the formation is initiated by suitable means. The formation is provided with a single output well, or is provided with a plurality of output wells. Output wells may be positioned equidistantly from each other or otherwise on a circle or plurality of circles having the input well as the center. As the flow of combustion supporting gas to the formation is continued, a flame front migrates from the input well to the output well or output wells. Combustion gases, oil, and distillation and viscosity breaking products of the hydrocarbon migrate in advance of the flame front to the output well or output wells from which they are removed to be treated for recovery of the desired valuable hydrocarbon material or other constituents. The heat of the fluids migrating in advance of the flame front strips the hydrocarbon-containing formation of water and the greater portion of the hydrocarbon leaving behind a carbonaceous deposit. This carbonaceous deposit is essentially the fuel consumed in the process and the flame front migrating from the input well to the output well or wells is the zone of combustion progressively moving through the carbonaceous deposit.

In carrying out the combustion process, it is often necessary or desirable to obtain information concerning the flame front in the subterranean formation. It is often necessary or desirable also to determine whether combustion is continuing or whether combustion has completely ceased within the formation. Further, it is often necessary or desirable to determine whether combustion has ceased at particular places along the previously established flame front and, if so, to determine where the discontinuities in the flame front are located with respect to a position between any particular output well and the input well.

It is an object of this invention to provide a method for obtaining information concerning the flame front in a subterranean formation wherein combustion has been effected for the purpose of recovering hydrocarbon materials. It is another object of this invention to determine whether combustion is continuing within a subterranean formation wherein combustion has been effected. It is another object of this invention to determine with respect to a position between a particular output well and an input well the location of a discontinuity in a flame front within a subterranean formation wherein combustion has been effected. It is another object of this invention to control the migration of the flame front in a subterranean formation wherein combustion has been effected. These and other objects of the invention will become apparent from the following detailed description.

In accordance with the invention, tritium in addition to the combustion supporting gas is passed to an input well leading to a subterranean formation in which combustion has been effected for recovery of hydrocarbon materials therefrom and thereafter analysis is made of gas issuing from an output well leading from said formation for the quantity of tritium therein contained.

Tritium, as is known, is an isotope of hydrogen and has a mass of 3.0221. The chemical properties of tritium resemble those of ordinary hydrogen including the property of combining with oxygen and combining with other elements to form various compounds. However, tritium is radioactive. The half life of tritium is 12.1 years and its gamma radiation energy is 0.0189 m. e. v. (million electron volt).

In the subterranean formation, oxidation of tritium to form water containing tritium as one of the hydrogen atoms in the molecule will occur at the flame front. The medium supplying the oxygen can be the combustion supporting gas passed through the input well to the subterranean formation. The water formed by oxidation of the tritium will not accompany the gas after leaving the flame front but will rather condense, unless formed sufficiently close to an output well, in cooler portions of the subterranean formation ahead of the formation in the direction of an output well. The condensed water will remain in the subterranean formation at the point of condensation until the flame front advances to this point. At this time the water will vaporize. This vaporized water may condense in the subterranean formation and will remain in the subterranean formation at the point of condensation until vaporized again. This procedure can be repeated until the water reaches the output well or is condensed at a point in the subterranean formation never reached by the flame front. However, by condensation in the subterranean formation of the water containing tritium as one of the hydrogen atoms in the molecule, the tritium contained in this water is prevented from arriving at the output well with the non-radioactive gas with which it was admixed upon passing into the input well. Thus, a delay in the time of arrival of the tritium at the output well or the arrival of the tritium at an output well in diminished or undiminished quantity but at the same time as the gas with which it was admixed upon passing into the input well supplies information concerning the flame front.

The tritium passed to the subterranean formation through the input well must be, in view of the foregoing, in a chemical form capable of oxidation under the conditions prevailing within the subterranean formation. The tritium may be in the molecular hydrogen form. The tritium may also be in the form of an oxidizable chemical compound containing the tritium as an atom in the molecule. Oxidizable compounds which may contain tritium in the molecule and which may be employed include methane, ethane, ethylene, acetylene, and other aliphatic hydrocarbons.

In the practice of the invention, the tritium is admixed with gas passed through the input well to the subterranean formation in which combustion has been effected. This gas is generally a combustion supporting, i. e., oxidizing gas passed to the formation to maintain combustion. However, the gas may be another gas passed to the formation through the input well temporarily for a particular

purpose and need not be a combustion supporting gas. If the gas is non-oxidizing, the amount thereof should be such that, upon mixing with gas in the subterranean formation, a mixture capable of oxidizing the tritium contained therein is formed. The tritium may be admixed continuously or intermittently or as a single isolated step with the gas passed through the input well.

The amount of tritium to be admixed per unit amount of gas passed through the input well to the subterranean formation may be as desired. However, the amount should be such that, if the same amount were contained in the effluent gas from an output well leading from the subterranean formation, quantitative determination thereof would be possible. Tritium is quantitatively determinable by measurement of intensity of radioactivity. However, to be quantitatively determinable by measurement of intensity of radioactivity, the tritium should be in a concentration between about two parts of tritium to 10^{12} parts of non-radioactive material and one part of tritium to 10^9 parts of non-radioactive material, depending upon the sensitivity of the means employed for measurement of the intensity of radioactivity. Accordingly, where analysis of gas from an output well leading from the formation for the quantity of tritium is to be made by measurement of intensity of radioactivity, the amount of tritium added to the gas passed to the input well leading to the formation should be between two parts of tritium to 10^{12} parts of non-radioactive gas and one part of tritium to 10^9 parts of non-radioactive gas. If desired, concentrations higher than one part to 10^9 parts of non-radioactive gas may be employed. In connection with the use of high concentrations of tritium, the question of personnel hazard must be considered. Concentrations lower than two parts of tritium to 10^{12} parts of non-radioactive gas may also be employed, although with present day equipment for analysis of gas from an output well for the quantity of tritium contained therein, the sensitivity is such that the use of such small amounts could affect accuracy.

Regardless of the amount of tritium admixed with the gas passed to the subterranean formation through the input well, the amount of tritium in proportion to the amount of gas must be known in order that any change in amount can be determined. Proportionation of the tritium and the gas entering the input well may be effected by any suitable means. The amount of tritium to be employed can be quite small as compared to the total amount of gas passed through the input well. It may therefore be convenient for proportionation to admix the tritium in a known amount in a tank, for example, with a known amount of gas such as the gas to be passed to the input well. A larger amount of gas containing a known amount of tritium is thus obtained and this larger amount of gas may then be more easily proportioned with the gas passed through the input well. A pressure above the pressure of the gas entering the input well is then imposed on the mixture in the tank and the mixture is bled into the gas entering the input well.

Knowledge of the amount of tritium to the amount of gas entering the input well may be obtained by various means. For example, knowledge of the amount of tritium to the amount of non-radioactive gas may be obtained by direct measurement of the amount of tritium and the amount of gas admixed together. Knowledge of the amount of tritium to the amount of non-radioactive gas may also be obtained by measuring the intensity of radioactivity of the mixture entering the input well. Knowing the intensity of radioactivity per unit amount of tritium, the amount of tritium to the amount of non-radioactive gas can be calculated.

Analysis of the effluent gas from an output well leading from the formation is made for its contained quantity of tritium. This analysis may be made by any suitable means. Most conveniently, the analysis is made by measuring the intensity of radioactivity from the effluent gas. For example, the effluent gas may be passed through an air ionization chamber and the magnitude of the ionization current measured. The magnitude of the ionization current will be proportional to the intensity of the radioactivity of the effluent gas. Where analysis of the effluent gas for the amount of tritium is made in this manner, it will usually be found desirable to dry the effluent gas of any water contained therein prior to being passed through the ionization chamber in order to avoid any effect of water on the accuracy of analysis.

Where tritium has been added to the gas passed to the input well in a molecular hydrogen form, measurement of the amount of tritium in the effluent gas from an output well may be made by passing the gas through an air ionization chamber as described. However, analysis for the tritium may be made by other suitable means. For example, a unit amount of the effluent gas from the output well may be treated to convert any tritium and, of necessity, any other molecular hydrogen contained therein to a compound, such as methane, ethane, ethylene, acetylene, etc. The compound may then be separated from the other constituents of the effluent gas and the intensity of the radioactivity measured. The intensity of the measured radioactivity may then be related to the volume of effluent gas from which the compound was obtained. Where tritium has been added to the gas passed to the input well in the form of an oxidizable compound other than the molecular hydrogen form, the effluent gas from the output well may also be treated to separate and concentrate the tritium-containing compound. However, if desired, the entire amount of effluent gas irrespective of the form of the tritium may be passed to an air ionization chamber for measurement of the intensity of the radioactivity.

While measurement of the intensity of radioactivity has been described in connection with the use of an ionization chamber, it will be understood that other apparatus may be employed for measuring the intensity of radioactivity. For example, a Geiger-Muller counter or a liquid scintillation counter may be used by introducing the tritium into the counter gas or liquid. Generally, however, it will be preferred to employ an ionization chamber in view of its greater sensitivity and ease of introducing the tritium into the sensitive volume of the counter.

Knowing the quantity of tritium in the effluent gas, comparison can be made with the quantity of tritium in the gas passed to the input well. Any changes or lack of changes in the quantity of tritium in the gas between the time it passes through the input well and the time it leaves the output well are significant with respect to combustion and the flame front within the subterranean formation. In determining whether a change or lack of change occurs in the quantity of tritium in the gas between the time it passes through the input well to the time it leaves the output well, consideration must be given to the fact that passage of oxidizing gas through the flame front may result in change in the volume of gas by formation of combustion products from the combustible material in the subterranean formation. For example, in passage of oxidizing gas through the flame front with oxidation of a paraffin hydrocarbon, two volumes of oxygen will produce one volume of carbon dioxide and two volumes of water. Since the water will condense in the cooler portions of the subterranean formation, a reduction of one volume of oxygen in the oxidizing gas will thereby have occurred as a result of formation of combustion products. Correction for changes in the volume of oxidizing gas as a result of the formation of combustion products is readily made by those skilled in the art employing, if necessary or desired, analysis of the effluent gas from the output well for combustion products of the combustible material in the subterranean formation.

It is also necessary, in determining whether a change or lack of change in the gas occurs between the time it passes through the input well and the time it leaves the output well to know when a particular unit volume of gas,

whose tritium content was known at the time it passed through the input well, arrives at an output well. This is readily determined by admixing a tracer material with the gas passing through the input well. This tracer material may be any of the known tracer materials that will accompany the gas from the input well to the output well even if combustion products thereof are formed by passage through the flame front. This tracer material may be admixed with the gas passed through the input well prior or subsequent to admixture of the gas with the tritium. Analysis of the effluent gas from the output well is made for the tracer material and the time required for passage of the gas through the subterranean formation from the input well to the particular output well is thereby determined. The tracer material may also be admixed with the gas passed through the input well at the same time as the tritium is admixed, and analysis of the gas from the output well for the tracer material may be made when analysis is made for the quantity of tritium.

Where tritium does not arrive at an output well at the same time as the gas with which it was admixed upon passage through the input well, passage of the entire amount of gas through a flame front has occurred. Accordingly, the presence of a flame front without a discontinuity is indicated within the subterranean formation across the entire path of flow of the gas between the input well and the output well. Where tritium arrives at an output well at the same time as the gas with which it was admixed upon passage through the input well and in undiminished quantity, passage of none of the gas through a flame front has occurred. Accordingly, in this case, the absence of a flame front is indicated within the subterranean formation across the entire path of flow of the gas between the input well and the output well. In the event that tritium arrives at an output well at the same time as the gas with which it was admixed upon passage through the input well but in diminished quantity, passage of a portion of the gas through a flame front has occurred. Thus, a discontinuity in a flame front is indicated within the subterranean formation across the path of the flow of gas at a point between the input well and the output well.

Admixture of the tritium gas with the gas passed to the input well may be effected in a manner to provide a square wave curve in a plot of concentration of tritium in the gas with time. The shape of the curve in a plot of the concentration of tritium in the gas from an output well with time is indicative of the distribution of the gas flow in the subterranean formation and the presence or absence of channeling. Where a plurality of output wells lead from the subterranean formation, the shape of the curve in a plot of the concentration of tritium in the gas from the wells with time, where the plot of the concentration of tritium with time at the input well was a square wave curve, indicates the shape and the relative position of the flame front with respect to each of the output wells. In similar manner, other information concerning the flame front may be determined.

Having determined the presence or absence of a flame front, or a discontinuity in the flame front, in the path of flow of gas between the input well and an output well, measures can be taken to control the migration of the flame front. Efficient operation might require, for example, that migration of the flame front be directed toward or away from a particular output well. Also, it might be desired in some instances to extinguish the flame front in the path of flow of gas from the input well to a particular output well. On the other hand, it might be desired to eliminate any discontinuities which may be present in the flame front in the path of flow of gas between the input well and a particular output well.

Changes in the migration of the flame front may be effected by changing the rate of flow of combustion supporting medium in the subterranean formation. For example, migration of the flame front toward or way from a particular output well can be effected by increasing or decreasing, respectively, the rate of flow of combustion supporting medium in the subterranean formation. Extinguishment of a flame front in the path of flow of gas through the formation between the input well and an output well can be effected by completely stopping the flow of combustion supporting medium until the flame front extinguishes or decreasing the rate of flow of combustion supporting medium to the point that combustion is no longer supported. Elimination of discontinuities in a flame front may be effected by increasing the rate of flow of combustion supporting medium.

Change in the rate of flow of combustion supporting medium may be effected by changing the concentration of combustion supporting medium in the combustion supporting gas passed through the subterranean formation from the input well to the output well. Increase in the concentration of combustion supporting medium in the combustion supporting gas can be effected by adding combustion supporting medium to the gas and decrease in the concentration of combustion supporting medium in the combustion supporting gas can be effected by adding an inert diluent to the gas. Thus, where air is the combustion supporting gas, increase in the concentration of combustion supporting medium is effected by adding oxygen to the air and decrease in the concentration of combustion supporting medium is effected by adding flue gas, nitrogen, or other inert gas.

Change in the rate of flow of combustion supporting medium may also be effected by changing the rate of flow of combustion supporting gas through the subterranean formation from the input well to the output well. The rate of flow of combustion supporting gas through the subterranean formation between the input well and an output well is proportional to the difference in the square of the pressure at which the combustion supporting gas is passed to the input well and the square of the pressure imposed upon the gas at the output well. This latter pressure is known as the back pressure. Thus, the rate of flow of combustion supporting gas through the subterranean formation can be changed by changing the pressure of the gas at either the input well or the output well. Change in the rate of flow can also be effected by changing the pressure at both the input well and the output well provided that a change in the difference between the squares of the two pressures results. Increase in flow of gas can be effected by increasing the difference in the squares of the pressures at the two wells and decrease in the rate of flow of gas can be effected by decreasing the difference in the squares of the pressures at the two wells.

This application is a continuation-in-part of my copending application Serial No. 492,731, filed March 7, 1955.

Having thus described my invention, it will be understood that such description has been given by way of illustration and not by way of limitation, reference for the latter purpose being had to the appended claims.

I claim:

1. In the process for the recovery of hydrocarbon material from a subterranean formation containing hydrocarbons and having an input well leading thereto and at least one output well leading therefrom wherein combustion of hydrocarbon material within said subterranean formation is initiated, combustion supporting gas containing a combustion supporting medium is passed into said subterranean formation through said input well in the direction of an output well and as a result thereof a flame front preceded by combustion gas and hydrocarbon products recoverable from an output well migrate through said subterranean formation from said input well in the direction of said output well and gas issues from said subterranean formation through said output well, the steps comprising determining the time required for gas to pass through said subterranean formation from said

input well to said output well, passing into said subterranean formation through said input well in addition to said combustion supporting gas tritium in known amount with respect to said combustion supporting gas whereby said tritium in admixture in known amount with said gas advances through said subterranean formation from said input well in the direction of said output well, analyzing at a time subsequent to passing said tritium into said subterranean formation and equal to said time required for gas to pass through said subterranean formation from said input well to said output well gas issuing from said output well for the amount with respect to said gas of tritium contained therein whereby the presence of tritium in undiminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the absence of a flame front within said subterranean formation across the entire path of flow of gas between said input well and said output well, the presence of tritium in partially diminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the presence of a flame front in said subterranean formation across a portion of the path of flow of gas between said input well and said output well, and the absence of tritium in said gas indicates the presence of a flame front in said subterranean formation across the entire path of flow of gas between said input well and said output well, and thereafter changing the rate of flow of said combustion supporting medium into said input well through said subterranean formation in the direction of said output well such that said rate of flow may be increased to eliminate discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front has any such discontinuity across the path of flow of gas between said input well and said output well and said rate of flow may be decreased to create discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front is present across the entire path of flow of gas between said input well and said output well.

2. The process of claim 1 wherein analysis of said gas issuing from said output well is made for the amount with respect to said gas of tritium contained therein by measurement of the intensity of radioactivity of said gas.

3. The process of claim 1 wherein said tritium passed into said subterranean formation through said input well is in the form of molecular hydrogen.

4. The process of claim 1 wherein said tritium passed into said subterranean formation through said input well is in the form of an oxidizable compound containing said tritium as an atom in the molecule.

5. The process of claim 1 wherein said tritium passed into said subterranean formation through said input well is upon passage through said input well in admixture with combustion supporting gas passed to said subterranean formation through said input well.

6. The process of claim 3 wherein analysis of said gas issuing from said output well for the amount with respect to said gas of tritium contained therein is made by a procedure involving conversion of said tritium in the molecular hydrogen form to a compound containing said tritium.

7. In the process for the recovery of hydrocarbon material from a subterranean formation containing hydrocarbons and having an input well leading thereto and at least one output well leading therefrom wherein combustion of hydrocarbon material within said subterranean formation is initiated, combustion supporting gas containing a combustion supporting medium is passed into said subterranean formation through said input well in the direction of an output well and as a result thereof a flame front preceded by combustion gas and hydrocarbon products recoverable from an output well migrate through said subterranean formation from said input well in the direction of said output well and gas issues from said subterranean formation through said output well, the steps comprising passing into said subterranean formation through said input well in addition to said combustion supporting gas a tracer material, analyzing gas issuing from said output well for said tracer material whereby the time required for gas to pass through said subterranean formation from said input well to said output well is determined, passing into said subterranean formation through said input well in addition to said combustion supporting gas tritium in known amount with respect to said combustion supporting gas whereby said tritium in admixture in known amount with said gas advances through said subterranean formation from said input well in the direction of said output well, analyzing at a time subsequent to passing said tritium into said subterranean formation and equal to said time required for gas to pass through said subterranean formation from said input well to said output well gas issuing from said output well for the amount with respect to said gas of tritium contained therein whereby the presence of tritium in undiminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the absence of a flame front within said subterranean formation across the entire path of flow of gas between said input well and said output well, the presence of tritium in partially diminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the presence of a flame front in said subterranean formation across a portion of the path of flow of gas between said input well and said output well, and the absence of tritium in said gas indicates the presence of a flame front in said subterranean formation across the entire path of flow of gas between said input well and said output well, and thereafter changing the rate of flow of said combustion supporting medium into said input well through said subterranean formation in the direction of said output well such that said rate of flow may be increased to eliminate discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front has any such discontinuity across the path of flow of gas between said input well and said output well and said rate of flow may be decreased to create discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front is present across the entire path of flow of gas between said input well and said output well.

8. In the process for the recovery of hydrocarbon material from a subterranean formation containing hydrocarbons and having an input well leading thereto and at least one output well leading therefrom wherein combustion of hydrocarbon material within said subterranean formation is initiated, combustion supporting gas containing a combustion supporting medium is passed into said subterranean formation through said input well in the direction of an output well and as a result thereof a flame front preceded by combustion gas and hydrocarbon products recoverable from an output well migrate through said subterranean formation from said input well in the direction of said output well and gas issues from said subterranean formation through said output well, the steps comprising passing into said subterranean formation through said input well in addition to said combustion supporting gas tritium in known amount with respect to said combustion supporting gas and simultaneously therewith a tracer material whereby said tritium in admixture in known amount with said gas and said tracer material advances through said subterranean formation from said input well in the direction of said output well, analyzing gas issuing from said output well and containing said tracer material for the amount with respect to

said gas of tritium contained therein whereby the presence of tritium in undiminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the absence of a flame front within said subterranean formation across the entire path of flow of gas between said input well and said output well, the presence of tritium in partially diminished amount with respect to said gas compared with the amount of tritium with respect to said combustion supporting gas passed into said input well indicates the presence of a flame front in said subterranean formation across a portion of the path of flow of gas between said input well and said output well, and the absence of tritium in said gas indicates the presence of a flame front in said subterranean formation across the entire path of flow of gas between said input well and said output well, and thereafter changing the rate of flow of said combustion supporting medium into said input well through said subterranean formation in the direction of said output well such that said rate of flow may be increased to eliminate discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front has any such discontinuity across the path of flow of gas between said input well and said output well and said rate of flow may be decreased to create discontinuity in the flame front in said subterranean formation between said input well and said output well in the event the flame front is present across the entire path of flow of gas between said input well and said output well.

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