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SUBTERRANEAN RECOVERY PROCESS
BY COMBUSTION

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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 irregularly or they 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 fluid 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 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 within the subterranean formation 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

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and other objects of the invention will become apparent from the following detailed description.

In accordance with the invention, there is passed to an input well leading to the subterranean formation in which combustion has been effected for recovery of hydrocarbon materials therefrom, in addition to the combustion supporting gas, a material capable of irreversible reaction upon passage through the flame front and being either quantitatively identifiable in the gaseous products of combustion or producing upon passage through the flame front a reaction product quantitatively identifiable in the gaseous products of combustion and thereafter analysis is made of gas issuing from an output well for the quantity contained therein of the material or a reaction product of the material.

Hereinafter, the material capable of irreversible reaction upon passage through the flame front and being either quantitatively identifiable in the gaseous products of combustion, or producing upon passage through the flame front a reaction product quantitatively identifiable in the gaseous products of combustion, will be termed the "reactive" material. By capable of irreversible reaction is meant capable of irreversible reaction under the conditions prevailing within the subterranean formation.

In the subterranean formation, the reactive material will, upon passage through the flame front, enter into an irreversible reaction. The form of the material will, therefore, change upon passage through the flame front. By analysis of the gas issuing from an output well for the quantity of the reactive material which was admixed with the gas passed to the input well or the quantity of a reaction product of the material, the amount of the reactive material changed in form is determined. The amount of material changed in form will be dependent upon the amount passing through a flame front and, therefore, upon the amount of gas passing through the flame front. From the amount, information concerning the flame front is obtained.

In the practice of the invention, the reactive material is admixed in known amount with the gas passed through the input well to the subterranean formation. This amount 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. The gas issuing from the output well leading from the formation is analyzed for the quantity of the reactive material or a reaction product of the reactive material. By determination of the quantity of either, the amount of reactive material changed in form is determined. In determining whether a change or lack of change occurs in the quantity of the reactive material in the gas between the time it passes through the input well and the time it leaves the output well, consideration must be given, of course, to the fact that passage of oxidizing gas through the flame front may result in change of the volume of gas by formation from the combustible material in the subterranean formation of combustion products. 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 gas will thereby have occurred as a result of formation of combustion products. Correction for changes in the volume of 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.

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It is also necessary, in determining whether a change or lack of change in the quantity of reactive material occurs in the gas between the time it passes through the input well and the time it leaves the output well, to know when a particular unit or volume of gas, containing reactive material at the time it passed through the input well, arrives at an output well. This is readily ascertained by admixing a tracer material with the gas passing through the input well. This tracer material, which may be any of the known tracer materials, may be admixed with the gas passed through the input well prior or subsequent to admixture of the gas with the reactive material. Analysis of the effluent gas from the output well can be made for the tracer material and the time required for passage of the gas through the subterranean formation from the input well to the 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 reactive material 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 the reactive material or a reaction product of the reactive material. Knowing the quantity of the reactive material or reaction product of the reactive material in the effluent gas from the output well, comparison can be made with the quantity of the reactive material in the gas passed to the input well. From the comparison, the amount of reactive material and thus the amount of gas passing through the flame front can be determined.

The reactive material may be a material capable of oxidation upon passage through the flame front. The reactive material may also be a material capable of combination with a material other than oxygen upon passage through the flame front. The material, further, may be a material capable of other change as a result of passage through the flame front. Additionally, the material may be a radioactive material and may be a material capable upon passage through the flame front of oxidation or combination with a material other than oxygen or other change.

Gas issuing from the output well leading from the subterranean formation will contain, if passage through a flame front has occurred, a lesser quantity of the reactive material in the same form than it contained upon passage through the input well to the subterranean formation. Assuming that none of the reactive material arrives in the same form at an output well with 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 gas between the input well and the output well. Where the reactive material arrives in the same form at an output well with 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 the reactive material arrives in the same form at an output well with 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 between the input well and the output well. The magnitude of the discontinuity is indicated by the extent to which the quantity of reactive material has been diminished.

A suitable reactive material capable of oxidation upon passage through the flame front is hydrogen. Where hydrogen or other reactive material capable of oxidation is employed, the reactive material must be in admixture with oxygen in order to be oxidized. Admixture with oxygen will be effected where the reactive material and combus-

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tion supporting gas, i.e., oxidizing gas, passed to the subterranean formation to support combustion enter the input well together. However, it is not essential that the reactive material and the combustion supporting gas enter the input well together but the reactive material may be in admixture with, upon entering the input well, another gas, which need not be an oxidizing gas, passed to the formation for a particular purpose. If the gas is non-oxidizing, the amount thereof should be such that, upon mixing with the gas present in the subterranean formation, a mixture capable of oxidizing the reactive material is formed. The reactive material capable of oxidation may be in admixture with, upon entering the input well, an oxidizing medium employed particularly for the oxidation of the reactive material.

Hydrogen may be employed in the form of molecular hydrogen or in the form of an oxidizable compound containing hydrogen as an atom in the molecule. Oxidation of hydrogen will result in the formation of water. This water, however, 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 flame front 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 water may condense in the subterranean formation again and 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. Thus, where hydrogen is employed, a flame front may be present between the input well and an output well and neither the hydrogen nor the product of the oxidation of the hydrogen, namely, the water, will arrive at the output well at the same time as the gas. However, where the hydrogen 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 and the presence of a flame front across the entire path of flow of gas between the input well and the output well is indicated. Arrival of the hydrogen at the output well at the same time as the gas with which it was admixed upon passage through the input well, either in diminished or undiminished quantity, has the same significance with respect to the flame front in the subterranean formation as described hereinabove in connection with the arrival in the same form of the reactive material with the gas with which it was admixed upon passage through the input well.

Where hydrogen is employed as the reactive material capable of oxidation, it is preferred to employ the hydrogen in the form of one of its heavy isotopes. The use of heavy hydrogen is particularly preferred where hydrogen may be formed as a product of combustion, and differentiation in the gas from the output well between hydrogen produced by combustion and the hydrogen admixed with the gas passed through the input well is difficult or impossible. Where heavy hydrogen is employed in admixture with protium, it is intended that the ratio of the heavy hydrogen to protium will be higher than in hydrogen not treated to increase this ratio. Heavy hydrogen may be employed in the form of molecular hydrogen, the molecular hydrogen containing any combination of the various isotopes, or in the form of an oxidizable compound containing heavy hydrogen as an atom in the molecule. Oxidizable compounds containing heavy hydrogen as an atom in the molecule and suitable for use in the invention include methane, ethane, ethylene, and acetylene.

Where deuterium is employed as the reactive material capable of oxidation, analysis of the gas from the output well leading from the subterranean formation for the quantity of deuterium may be made by any suitable

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method. For example, analysis may be made employing a mass spectrometer. Employing a mass spectrometer, the quantity of deuterium may be determined whether in the form of molecular hydrogen or a compound containing the deuterium as an atom in the molecule.

Various other reactive materials capable of oxidation upon passage through the flame front may be employed in the practice of the invention. Such materials include hydrocarbons such as methane, ethane, ethylene, and acetylene. Other materials of this type that may be employed include carbon monoxide, carbon disulfide, and hydrogen sulfide. In the case of reactive materials containing carbon as an atom in the molecule, the carbon may be carbon having an atomic weight of 12 or may be carbon having an atomic weight of 14. This latter isotope of carbon is radioactive.

A suitable reactive material capable of combination upon passage through the flame front is heavy oxygen. Either of the heavy isotopes of oxygen may be employed. The heavy oxygen is preferably employed in the form of molecular oxygen. Combination of the oxygen upon passage through the flame front may be with carbonaceous material naturally present in the subterranean formation. Combustion may also be with a compound or material admixed with the gas passed to the subterranean formation through the input well at the time the heavy oxygen is admixed with this gas. Such a material may be a hydrocarbon. Analysis of the gas from an output well leading from the subterranean formation may be made for the quantity therein of heavy oxygen by any suitable method. For example, analysis may be made employing a mass spectrometer.

The reactive material may be passed continuously or alternately or for an isolated period of time to the subterranean formation through the input well. In this connection, admixture of the reactive material with the gas passed to the input well may be effected in a manner to provide a square wave curve in a plot of the concentration of the reactive material in the gas with time. The shape of the curve in a plot of the concentration of the reactive material 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 leads from the subterranean formation, the shape of the curve in a plot of the concentration of the reactive material in the gas from the wells with time where the plot of the concentration of the reactive material 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 away 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

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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 co-pending application Serial No. 492,737, 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 through 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 in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio

whereby said gaseous, oxidizable material in admixture in known amount with said combustion supporting 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 gaseous, oxidizable material 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 said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in a flame front in said subterranean formation across the 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 through 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. 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 through 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 in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase said ratio, whereby said gaseous, oxidizable material in admixture in known amount with said combustion supporting 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 gaseous, oxidizable material 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 said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in the presence of a flame front in said subterranean formation across the 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 through said subterranean formation between said input well and said output well whereby change in the continuity of said flame front in said subterranean formation between said input well and said output well is effected.

3. The process of claim 2 wherein said heavy isotope of hydrogen is deuterium.

4. The process of claim 2 wherein said gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen is heavy molecular hydrogen.

5. The process of claim 2 wherein said gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen is a gaseous, oxidizable compound having said heavy isotope of hydrogen as an atom in the molecule.

6. The process of claim 2 wherein said gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen is molecular deuterium.

7. The process of claim 2 wherein said gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen is a gaseous, oxidizable compound having deuterium as an atom in the molecule.

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 through 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 through 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 a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio whereby said gaseous, oxidizable material in admixture in known amount with said combustion supporting 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 gaseous, oxidizable material 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 said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and thereafter changing the rate of flow of combustion supporting medium through said subterranean formation between said input well and said output well whereby change in the continuity of said flame front in said subterranean formation between said input well and said output well is effected.

9. 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 through 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 through said subterranean formation through said input well in addition to said combustion supporting gas in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio and simultaneously therewith a tracer material whereby said gaseous, oxidizable material in known amount with respect to said combustion supporting gas and said tracer material advance 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 said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said out-

put well, and thereafter changing the rate of flow of combustion supporting medium through said subterranean formation between said input well and said output well whereby change in the continuity of the flame front in said subterranean formation between said input well and said output well is effected.

10. 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 through 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 said combustion supporting gas to pass through said subterranean formation from said input well to an output well, passing into said subterranean formation through said input well in addition to said combustion supporting gas in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio whereby said gaseous, oxidizable material in admixture in known amount with said combustion supporting 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 gaseous, oxidizable material 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 said heavy isotope of hydrogen whereby information concerning the presence of said flame front in the path of gas flow between said input well and said output well is obtained, and thereafter changing the rate of flow of combustion supporting medium through said subterranean formation between said input well and said output well whereby change of migration of said flame front in said subterranean formation is effected.

11. 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 through 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 in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio, analyzing at a time subsequent to passing said gaseous, oxidizable material into said subterranean formation and equal to said time required for gas to pass through said subterranean

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formation from said input well to said output well gas issuing from said output well for the amount with respect to said gas of said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in a flame front in said subterranean formation across the 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 through said input well through said subterranean formation in the direction of said output well such that said rate of flow is 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 is 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.

12. 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 through 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 forma-

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tion through said input well in addition to said combustion supporting gas in known amount with respect to said combustion supporting gas a gaseous, oxidizable material having as a constituent element thereof a heavy isotope of hydrogen in which gaseous, oxidizable material the ratio of said heavy isotope of hydrogen to protium is greater than in hydrogen not treated to increase this ratio whereby said gaseous, oxidizable material in admixture in known amount with said combustion supporting gas advances through said subterranean formation from said input well in the direction of said output well, and analyzing at a time subsequent to passing said gaseous, oxidizable material 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 said heavy isotope of hydrogen whereby the presence of said heavy isotope of hydrogen in undiminished amount with respect to said gas compared with the amount of said heavy isotope of hydrogen 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 said heavy isotope of hydrogen in partially diminished amount with respect to said gas compared with the amount of heavy isotope of hydrogen with respect to said combustion supporting gas passed into said input well indicates the lack of continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well, and the absence of said heavy isotope of hydrogen from said gas indicates continuity in a flame front in said subterranean formation across the path of flow of gas between said input well and said output well.

References Cited in the file of this patent

UNITED STATES PATENTS

40	2,429,577	French	Oct. 21, 1947
	2,584,606	Merriam	Feb. 5, 1952
	2,642,943	Smith	June 23, 1953
	2,734,579	Elkins	Feb. 14, 1956
	2,800,183	Jenkins	July 23, 1957
45	2,843,207	Clewell	July 15, 1958

OTHER REFERENCES

Glasstone: Sourcebook on Atomic Energy, pub. by D. Van Nostrand, New York, N.Y., 1950, pp. 443, 444 and 456 to 570.

Laubengayer, A.: 1949 General Chemistry, Rinehart and Co., Inc., page 486 relied on.