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3,024,840

IN SITU COMBUSTION

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This invention relates to the production of hydrocarbons from hydrocarbon-containing formations. More particularly, this invention relates to a method of carrying out an in situ combustion operation for the production and recovery of hydrocarbons from a subsurface formation, such as a petroleum-producing formation, tar sands, oil shales and the like. In accordance with one specific embodiment this invention is directed to an in situ combustion operation whereby the in situ combustion operation is maintained within an underground formation which otherwise would not support an in situ combustion operation or wherein it would otherwise be difficult to maintain an in situ combustion operation.

Various techniques have been proposed for the recovery of hydrocarbons and the like from subsurface formations such as petroleum, oil shale, tar sands, etc. for the recovery of values therefrom. For example, for the recovery of petroleum from petroleum-producing formations secondary recovery operations which involve water flooding or thermal recovery methods such as in situ combustion, employing at least one injection well and at least one producing or production well, have been proposed. As indicated hereinabove, the practice of this invention is particularly directed to thermal recovery methods such as methods involving in situ combustion for the production of petroleum and the like from underground formations.

Explanatory of an in situ combustion operation and indicative as to how an in situ combustion operation may be carried out, a high temperature zone is established in an underground hydrocarbon or petroleum-containing formation in the vicinity of a well bore penetrating the same. Suitable means for establishing or creating a high temperature zone within the well bore penetrating the hydrocarbon-containing formation may comprise an electric heating device or a gas fired bottom hole igniter or heater. A suitable device for initiating in situ combustion and for establishing a high temperature zone in a formation surrounding a well bore is described in U.S. 2,722,278. Upon introducing a combustion-supporting gas, such as air, into the heated well bore adjacent the petroleum-containing formation a resulting high temperature combustion zone is generated therein by the reaction between the oxygen and the combustible petroleum hydrocarbons or residues within the formation, such as combustible residues resulting from the distillation and/or thermal cracking or decomposition of the petroleum hydrocarbons originally in place. This high temperature combustion zone (temperature in the range 700–2000° F., more or less) will commence to move into the formation outwardly from the well bore upon continued introduction of air into the well bore. Leaving this high temperature zone is a relatively high temperature gas stream which, as it moves outwardly into the formation, loses heat to the formation. By this method the high temperature combustion zone is moved for a considerable distance outwardly from the well bore into the formation without further direct application of heat to the well bore at the location therein adjacent the formation undergoing in situ combustion. Continued direct application of heat to the formation at the well bore, however, may sometimes be desirable.

The distances which the high temperature zone moves outwardly, and as a result the volume of the formation swept by or comprised within the high temperature of the

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in situ combustion zone, is determined by the relative magnitude of the rate of heat generation (combustion of combustible residues) and the rate of heat loss to the surrounding formation.

It has been postulated that the following mechanisms are important in the movement of the high temperature combustion zone outwardly from the well bore into the subsurface formation during an in situ combustion operation therein. Although the exact mechanism of an in situ combustion operation is not completely known, the following sequence of events are postulated and are presented herein for the purpose of enabling one skilled in the art to better understand this invention.

As the high temperature combustion zone approaches any given volume of the hydrocarbon or petroleum-containing formation the temperature of this volume of formation rises. This results, first, in a reduction in the viscosity of the formation fluids therein (oil, water) due to temperature increase. These fluids may then be moved more readily under the influence of the hot combustion gas stream continuously emanating from the high temperature combustion zone. As the temperature continues to rise distillations of the formation fluids begin. The products of these distillations condense in cooler regions of the formation removed from the high temperature combustion zone in the direction of flow of the hot combustion gases therein. The distillations continue as the temperature rises within the given portion of the formation until the heavier components remaining from the hydrocarbons or petroleum originally in place within the formation begin to crack and to yield hydrocarbon gases, oxygenated hydrocarbons, oxides of carbon, other combustion products as well as coke and similar solid carbonaceous residues. As the temperature continues to rise and the oxygen content of the incoming combustion-supporting gas increases due to depletion of the combustible residues in the preceding regions of the formation, a temperature will be reached at which the coke or other solid combustible residues will begin to react with the oxygen with the resulting release of heat to the formation and the combustion gas stream emanating therefrom. This heat is carried away by the on-moving combustion gas stream and also to some extent by thermal conduction to adjoining regions of the formation. When the coke or combustible residues have been burned away there remains a volume of substantially liquid-free formation.

Another method of carrying out an in situ combustion operation, involving operations as disclosed hereinabove, i.e., initiation of a high temperature zone within a well bore and then causing an in situ combustion zone to move outwardly therefrom into the formation toward a production well, is known. In this method, after the high temperature combustion zone has moved a sufficient distance outwardly from the well bore, such as a distance in the range 3–50 feet, air or other combustion-supporting gas is injected into another well removed from the well wherein the in situ combustion process was initiated and forced in the direction of the well wherein in situ combustion was initiated. When these operations are carried out, the in situ combustion zone or flame front moves countercurrently with respect to the flow of the combustion-supporting gas (air) introduced into the formation undergoing treatment, i.e., the in situ combustion zone moves toward the other well into which the combustion-supporting gas is injected while a combustion-supporting gas as well as the resulting hot combustion gases and displaced hydrocarbons, partially oxygenated hydrocarbons, etc. move in the direction from this other well toward the well wherein the in situ combustion was initiated. The mechanisms and technique of carrying out an in situ com-

bustion operation in accordance with this method are fully described in U.S. 2,793,696.

The foregoing discussions indicate that the rate of heat energy released within the formation during an in situ combustion operation is some function of the quantity of fuel or combustible residues present therein, which, in turn, is dependent upon the type and quantity of the petroleum originally in place and/or combustible material or fuel caused to be deposited within the formation in the zone of in situ combustion. The rate of heat released within the formation is also dependent upon the rate at which the oxygen is supplied through the combustion zone and consumed therein, or, in other words, the rate at which the exothermic combustion process within the formation undergoing treatment is effected. The rate at which heat can be transferred ahead of the high temperature reaction or combustion zone is dependent upon the temperature and the rate at which the gaseous products of combustion leave the high temperature combustion or reaction zone and also should be to some extent dependent upon thermal conduction through the formation itself. Accordingly, some control of an in situ combustion process can be exercised by controlling the combustion process occurring during the in situ combustion operation, such as by controlling the amount of solid carbonaceous material or combustible residues present within the high temperature combustion zone.

It has been observed that in some underground petroleum containing formations it is difficult, and in some instances impossible, to sustain an in situ combustion operation therein. It is a characteristic of these particular petroleum-containing formations that the petroleum or hydrocarbons generated or contained therein, fluid hydrocarbons and the like, are relatively low molecular weight material containing relatively little carbonaceous, tarry or asphaltic material therein, e.g., are relatively high gravity crudes and do not tend to deposit a solid carbonaceous residue or coke upon distillation and/or thermal decomposition or cracking when subjected to the high temperatures of in situ combustion. When an underground formation containing these materials, such as a crude having an API gravity greater than 20°, or light hydrocarbons is subjected to an in situ combustion operation the on-moving hot combustion gases effectively distill or strip substantially all of the combustible hydrocarbons and material from the formation in front of the in situ combustion zone with the result that continued onward movement of the in situ combustion zone within the formation becomes substantially impossible since there remains insufficient combustible material or solid carbonaceous residue within the formation to sustain the in situ combustion operation therein.

Accordingly it is an object of this invention to provide an improved method for the treatment of hydrocarbon-containing or petroleum-containing or producing formations and the like such as tar sands, etc., to enhance or otherwise improve the recovery of petroleum or fluid hydrocarbons therefrom by an operation involving in situ combustion.

It is another object of this invention to provide an improved method for carrying out an in situ combustion operation.

Still another object of this invention is to provide a method for effecting control of an in situ combustion operation.

Yet another object of this invention is to provide a method for initiating and/or maintaining an underground in situ combustion operation.

Yet another object of this invention is to provide a method for initiating and/or maintaining an in situ combustion operation within an underground formation containing a relatively high gravity crude oil, such as a crude oil having characteristics such that substantially all of the combustible material therein distills upon the appli-

cation of heat, leaving behind relatively little or substantially no solid carbonaceous residue or coke.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure. In at least one embodiment of the practice of this invention at least one of the foregoing objects will be achieved.

In accordance with the practice of this invention in an in situ combustion operation wherein a subsurface formation containing combustible material, such as hydrocarbons and the like, is subjected to an elevated temperature, in situ combustion is initiated and/or maintained therein by introducing into said formation prior to subjecting the same to said elevated temperature a water soluble or water dispersible organic compound which undergoes thermal decomposition to yield a solid carbonaceous residue. The water soluble or water dispersible organic compound is suitably introduced into the formation undergoing treatment in accordance with this invention in the form of an aqueous solution or aqueous admixture thereof. Accordingly, when a subsurface formation has been treated in accordance with the practice of this invention and during heating of the treated formation, the water distills away from the aqueous solution or admixture leaving behind a solid residue of the thermally decomposable organic compound. Thereupon, upon continued application of heat and resulting increase in temperature the organic compound thermally decomposes to yield a solid carbonaceous residue. Subsequently, or during the heating operation which results in the thermal decomposition of the organic compound, an oxygen-containing stream, such as air, employed to initiate and/or maintain in situ combustion, reacts with the thus-deposited solid carbonaceous material or residue to burn the same with the resultant release of heat of combustion to the formation.

Thermally decomposable organic compounds which are suitably employed in the practice of this invention include among the carbohydrates the monosaccharides such as the trioses, the tetroses such as erythrose, the pentoses such as arabinose, xylose and ribose, the hexoses such as glucose, mannose, galactose, fructose, sorbose etc., the disaccharides, i.e., compounds which yield two molecules of monosaccharides upon hydrolysis, such as sucrose, maltose, lactose, the trisaccharides such as raffinose, the polysaccharides, i.e., compounds which upon hydrolysis yield more than three molecules of monosaccharides, such as starch, cellulose, dextrin, glycogen, inulin, gums, pectins, pentosans, etc. Other organic compounds other than carbohydrates or compounds which contain only carbon, hydrogen and oxygen atoms, are suitably employed in the practice of this invention and include the phosphorus-containing organic compounds such as the alkyl phosphates, the aryl phosphates, the alkaryl phosphates, the alkaryl phosphites, the aryl phosphites, the aralkyl phosphites, the aralkyl phosphates, the water soluble glycols, e.g., polyethylene glycol, polypropylene glycol, the polyoxypolyalkylene glycols, the glycol ethers, etc.

As indicated hereinbefore, the practice of this invention is particularly applicable to water soluble thermally decomposable organic compounds and water dispersible thermally decomposable organic compounds. The terms water soluble and water dispersible as used herein are meant to include the water soluble organic compounds or derivatives thereof as well as those organic compounds which, although not truly water soluble, disperse or readily admix in water to form a colloidal dispersion or suspension therein or a thin gel or paste-like admixture which is capable of being injected or forced into an underground formation. Also, the thermally decomposable organic compound suitable for use in the practice of this invention should undergo thermal decomposition with the resulting formation of a solid carbonaceous residue at a suitably elevated temperature, such as a temperature

of about 300° F. or in the range 275–700° F., more or less. More specifically, a thermally decomposable organic compound when employed in the practice of this invention should undergo thermal decomposition when under the influence of those relatively elevated temperatures encountered or experienced during an in situ combustion operation.

Specific materials which are suitably employed in the practice of this invention include aqueous solutions of sugar, sucrose, and such available commercial materials as black strap molasses, etc. Other materials include watery pastes or admixtures of starch and other carbohydrates and the like.

The subject invention may be practiced in a single well or in a multi-well in situ combustion operation. In a single well in situ combustion operation, as set forth in copending, coassigned patent application Serial No. 576,486, filed April 5, 1956 in the name of Gerhard Herzog, issued on September 29, 1959, as Pat. No. 2,906,340, the disclosures of which are herein incorporated and made a part of this disclosure, there is described a single well in situ combustion operation as a remedial treatment to increase the productivity and/or permeability of an underground petroleum producing or petroleum-containing formation. The practice of this invention is particularly applicable to a well remedial treatment since by following the practice of this invention an adequate in situ combustion operation can be assured in the immediate vicinity of the well bore penetrating the formation undergoing treatment.

The practice of this invention is also particularly applicable to an in situ combustion operation employing a plurality of wells, that is, at least one injection well and at least one production well. This invention is also applicable to a multi-well, combination water flooding-in situ combustion operation for the recovery of petroleum. In accordance with this embodiment, a water solution of the thermally decomposable organic compound comprises at least a portion of the water flood. When the water flood operation is terminated, in situ combustion of the flooded formation is initiated and carried out, the organic compound being decomposed to yield a combustible residue which, upon combustion, supplies at least a portion of the heat required to sustain the in situ combustion operation.

Exemplary of the practice of this invention a concentrated aqueous solution of a water soluble carbohydrate, such as sugar, e.g., black strap molasses, is introduced into a subsurface petroleum-containing formation in a volume sufficient to displace the formation water or brine therein for a substantial radial distance surrounding the well bore, e.g., an amount of solution sufficient to displace the formation water or brine for a distance of 3–25 radial feet from the well bore. Thereafter a bottom hole igniter is introduced into the well bore and positioned adjacent the thus-treated petroleum-containing formation. That section of the formation immediately surrounding the well bore is heated to a temperature of at least about 500° F., preferably in the range 800–1300° F. At the same time while the formation surrounding the well bore is being heated a gaseous stream containing elemental oxygen, such as air, is introduced into the thus-treated formation via the well bore. After a period of time the water in the aqueous solution introduced into the formation surrounding the well bore is evaporated, leaving behind as a solid residue the thermally decomposable organic compounds, e.g., sugar, in the aqueous solution, molasses, introduced into the formation. Upon continued temperature increase the resulting deposited sugars and other thermally decomposable materials, decompose with the evolution of water and the formation of a solid carbonaceous residue of coke or carbon. The solid carbonaceous residue upon continued contact with the relatively high temperature oxygen-containing gaseous stream burns with the result-

ing release of heat to better maintain and carry on the in situ combustion operation.

In accordance with another feature of the practice of this invention there is also disposed or introduced in the subsurface formation undergoing treatment in accordance with this invention, preferably in admixture with the thermally decomposable organic compound introduced therein, a water soluble oxidation catalyst such as an alkali metal hydroxide, e.g., potassium hydroxide, or an alkali metal carbonate such as potassium carbonate or the corresponding lithium, barium and calcium compounds. These particular oxidation catalysts exhibit a catalytic effect or otherwise function as oxidation catalysts thereby permitting the in situ combustion of the solid carbonaceous residues deposited due to the thermal decomposition of the organic compounds therein to proceed more readily. In accordance with yet another embodiment of the practice of this invention there is also introduced into the formation undergoing treatment, preferably in admixture with the thermally decomposable organic compound, a compound which undergoes thermal decomposition due to the high temperatures experienced in an in situ combustion operation with the resultant release of an oxidizing agent such as oxygen, an oxide of nitrogen and the like, which reacts with solid carbonaceous residues deposited during the thermal decomposition of the thermally decomposable organic compound within the formation to supplement or to supply at least a portion of the oxygen requirements in the in situ combustion operation. Exemplary water soluble materials which undergo thermal decomposition to yield an oxidizing agent such as oxygen include the alkali metal nitrates, chlorates, perchlorates, etc. such as sodium nitrate. The use of a water soluble material which thermally decomposes during the in situ combustion operation to yield an oxidizing agent to promote the in situ combustion operation is more completely described and claimed in copending, coassigned patent application Serial No. 624,998, filed November 29, 1956, in the names of Joseph C. Allen and Robert E. Kunetka and issued on February 3, 1959 as Pat. No. 2,871,941. The disclosures of this patent application are herein incorporated and made part of this disclosure. Further, the use of an oxidation catalyst to aid or to improve an in situ combustion operation is adequately described in copending, coassigned patent application Serial No. 624,999, filed November 29, 1956, in the names of Allen D. Garrison and Robert E. Kunetka and issued on February 3, 1959 as Pat. No. 2,871,942. The disclosures of this latter patent application are also incorporated and made part of this disclosure.

As will be apparent to those skilled in the art many changes and substitutions are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of initiating or maintaining in situ combustion in a subsurface formation containing in place hydrocarbons which comprises introducing into said formation an aqueous solution of a water soluble organic compound which undergoes thermal decomposition to yield a solid carbonaceous residue, subjecting that portion of the formation into which said compound is introduced to a temperature sufficiently high to effect thermal decomposition of said compound to yield a solid carbonaceous residue, and providing to the last mentioned formation portion a combustion supporting gas for initiating in situ combustion of said carbonaceous residue.

2. A method in accordance with claim 1 wherein said compound is a carbohydrate.

3. A method in accordance with claim 1 wherein said compound is a sugar.

4. A method in accordance with claim 1 wherein said aqueous solution comprises black strap molasses.

5. A method of initiating or maintaining in situ combustion within a subsurface formation containing petroleum hydrocarbons therein which comprises introducing into said formation an aqueous admixture of an organic compound which thermally decomposes to yield a solid carbonaceous residue, subjecting that portion of the formation containing the thus-introduced aqueous admixture of said compound to a temperature sufficient to effect thermal decomposition of said compound therein to yield a solid carbonaceous residue, and providing a stream of an oxygen-containing gas to said last mentioned portion of the formation for initiating in situ combustion of said carbonaceous residue.

6. A method of displacing fluid petroleum hydrocarbons from a subsurface formation containing the same which comprises introducing into said formation an aqueous admixture of an organic compound which thermally decomposes to yield a solid carbonaceous residue, continuing the injection of said aqueous admixture to displace at least a portion of said fluid petroleum hydrocarbons from said formation toward a producing well therein from which the resulting displaced hydrocarbons are produced, subjecting the thus-treated formation, now containing said aqueous admixture therein, to a temperature sufficient to effect thermal decomposition of said organic compound therein to yield a solid carbonaceous residue, providing a combustion-supporting gas to said thus-treated formation and initiating in situ combustion of the carbonaceous residue to displace additional fluid petroleum hydrocarbons from said formation toward said producing well.

7. A method in accordance with claim 6 wherein said aqueous admixture comprises a carbohydrate.

8. A method in accordance with claim 7 wherein said carbohydrate is a sugar.

9. A method in accordance with claim 6 wherein said aqueous admixture comprises black strap molasses.

10. A method of initiating or maintaining in situ com-

bustion in a subsurface formation containing in place hydrocarbons which comprises introducing into said formation an aqueous mixture of an organic compound which undergoes thermal decomposition to yield a solid carbonaceous residue, subjecting that portion of the formation to which said compound is introduced to a temperature sufficiently high to effect thermal decomposition of said compound to yield a solid carbonaceous residue injecting a stream of oxygen-containing gas to the last mentioned formation portion, and initiating in situ combustion of the carbonaceous residue by subjecting said residue to elevated temperatures of at least about 500° F. in the presence of a continuously injected oxygen-containing gas.

11. A method in accordance with claim 10 wherein said aqueous mixture also contains a water soluble compound which undergoes thermal decomposition to yield an oxidizing agent and wherein the oxidizing agent generated by the thermal decomposition of said compound serves to oxidize or to supply at least a portion of the oxygen requirements during the in situ combustion operation to oxidize said solid carbonaceous residue within said formation.

12. A method in accordance with claim 10 wherein said organic compound is a water soluble sugar.

13. A method in accordance with claim 10 wherein said organic compound is a water dispersible carbohydrate.

14. A method in accordance with claim 10 wherein said organic compound contains only carbon, hydrogen and oxygen atoms.

References Cited in the file of this patent

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2,862,557	Van Utenhove et al.	Dec. 2, 1958
2,863,510	Tadema et al.	Dec. 9, 1958
2,906,340	Herzog	Sept. 29, 1959