April 5, 1966 H. GREKEL ETAL 3,244,231

METHOD FOR CATALYTICALLY HEATING OIL BEARING FORMATIONS

Filed April 9, 1963 4 Sheets-Sheet 1

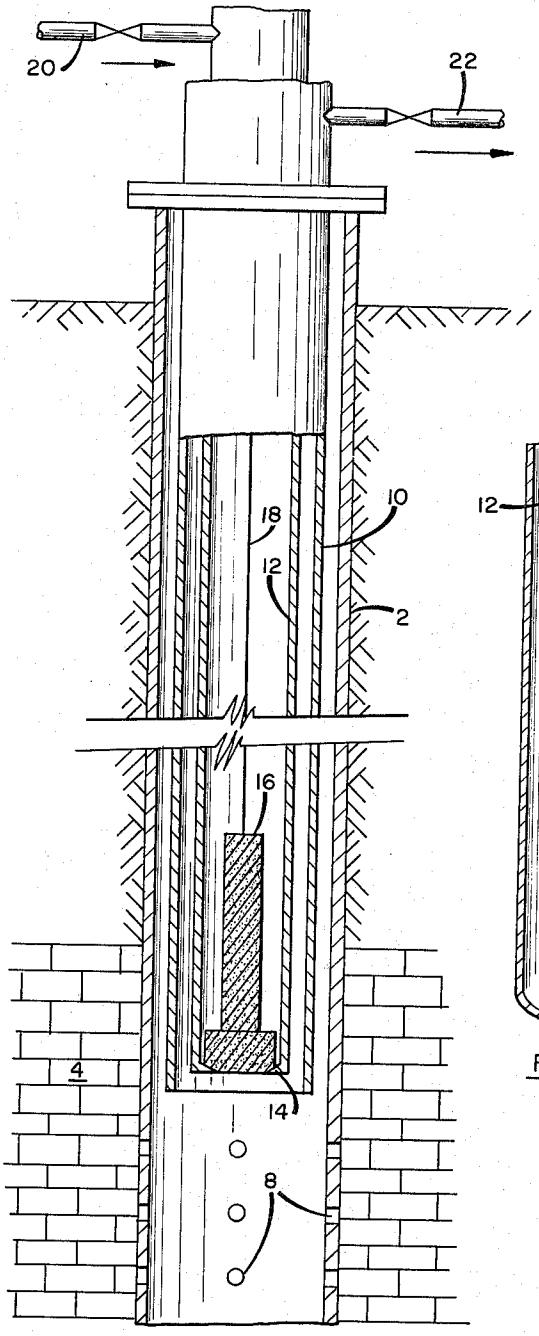

FIG. -1

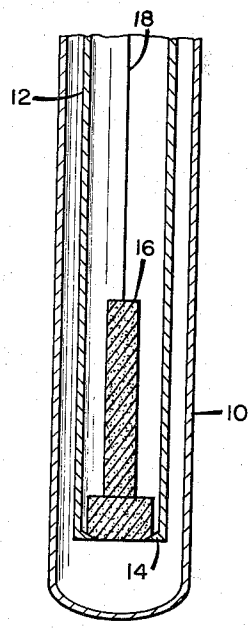

FIG. -2

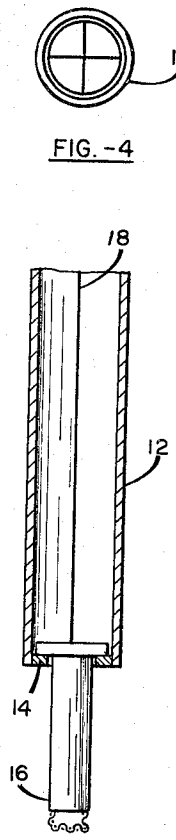

FIG. -3

FIG. -4

HOWARD GREKEL
KAROL L. HUJSAK
INVENTORS.

BY Arthur McElroy

ATTORNEY.

METHOD FOR CATALYTICALLY HEATING OIL BEARING FORMATIONS

Filed April 9, 1963 4 Sheets-Sheet 2

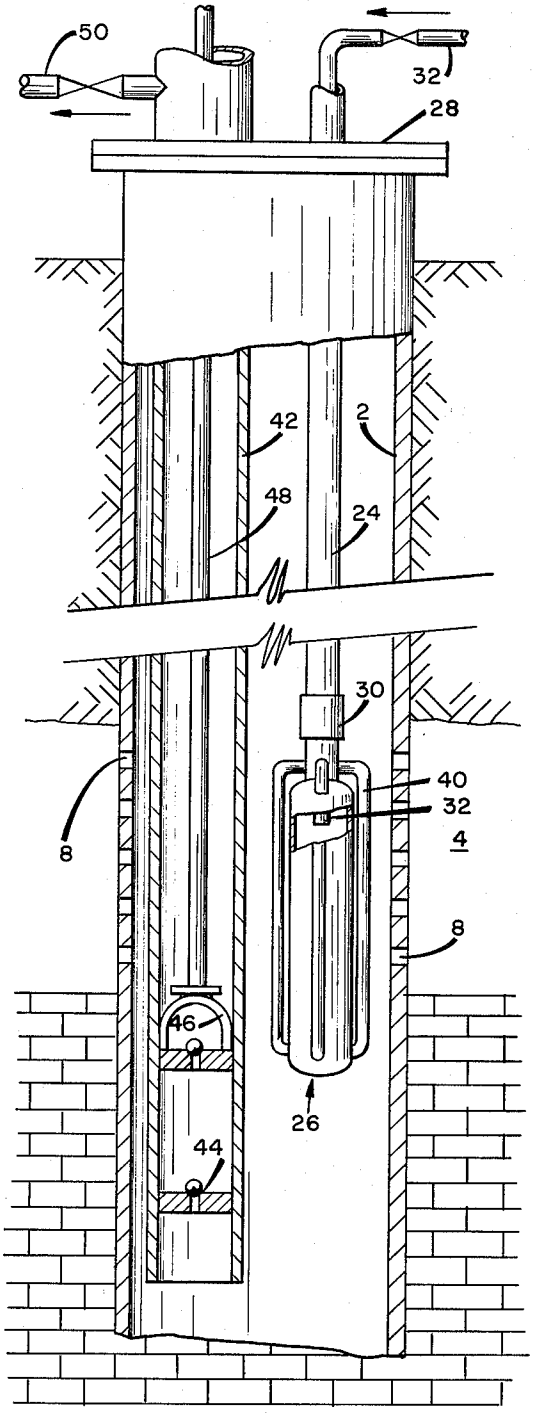

FIG. - 5

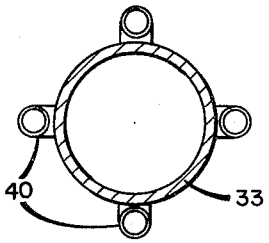

FIG. - 7

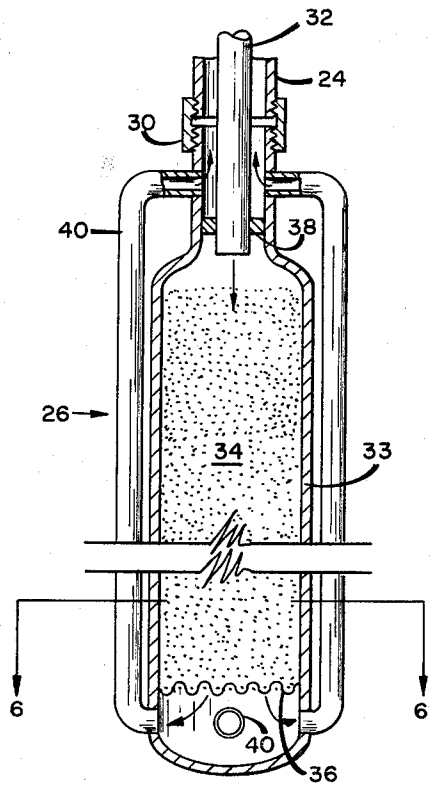

FIG. - 6

HOWARD GREKEL
KAROL L. HUJSAK
INVENTORS.

BY Arthur McAlroy

ATTORNEY.

METHOD FOR CATALYTICALLY HEATING OIL BEARING FORMATIONS

Filed April 9, 1963 4 Sheets-Sheet 3

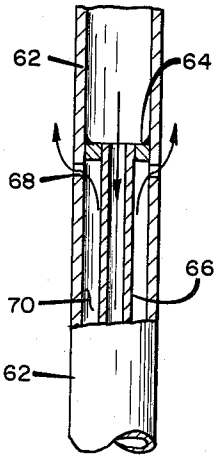

FIG. - 9

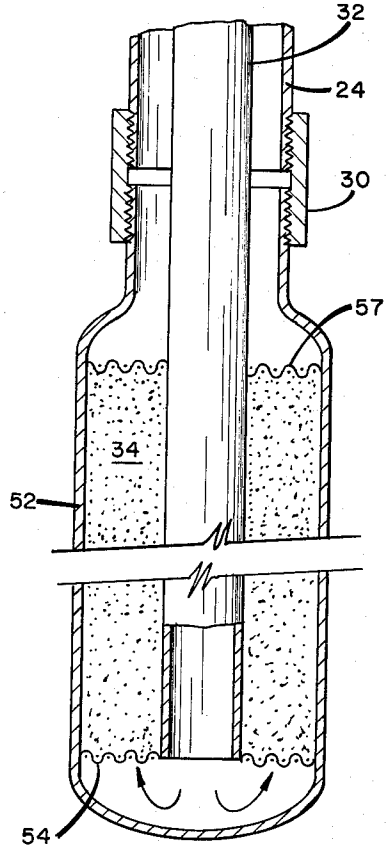

FIG. - 8

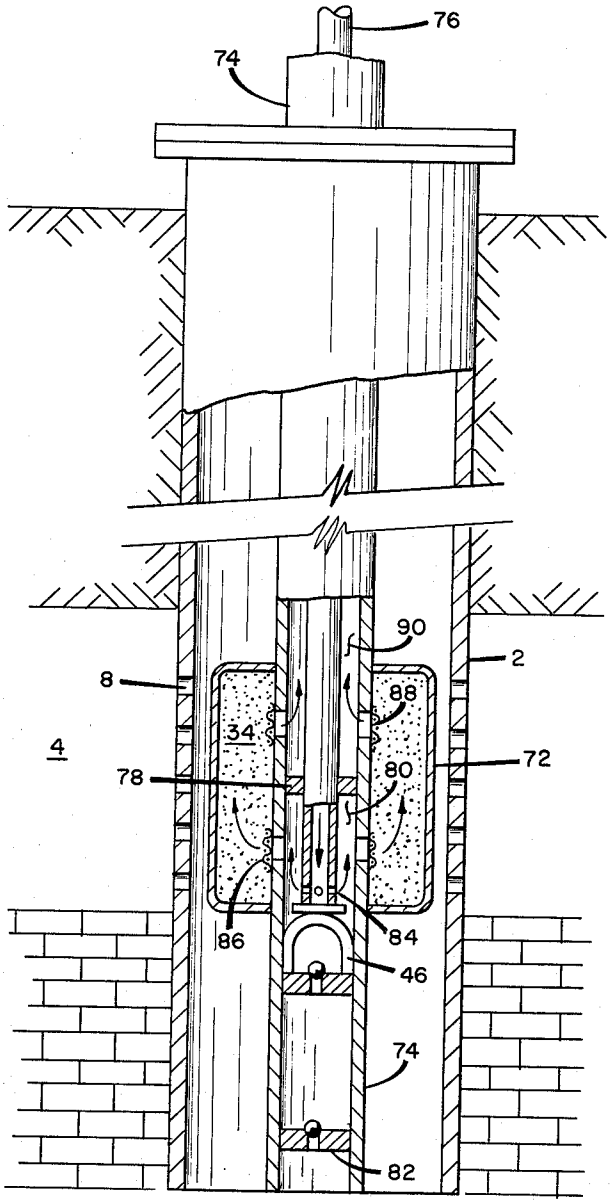

FIG. - 10

HOWARD GREKEL
KAROL L. HUJSAK
INVENTORS.

BY Arthur McElroy

ATTORNEY.

METHOD FOR CATALYTICALLY HEATING OIL BEARING FORMATIONS

Filed April 9, 1963 4 Sheets-Sheet 4

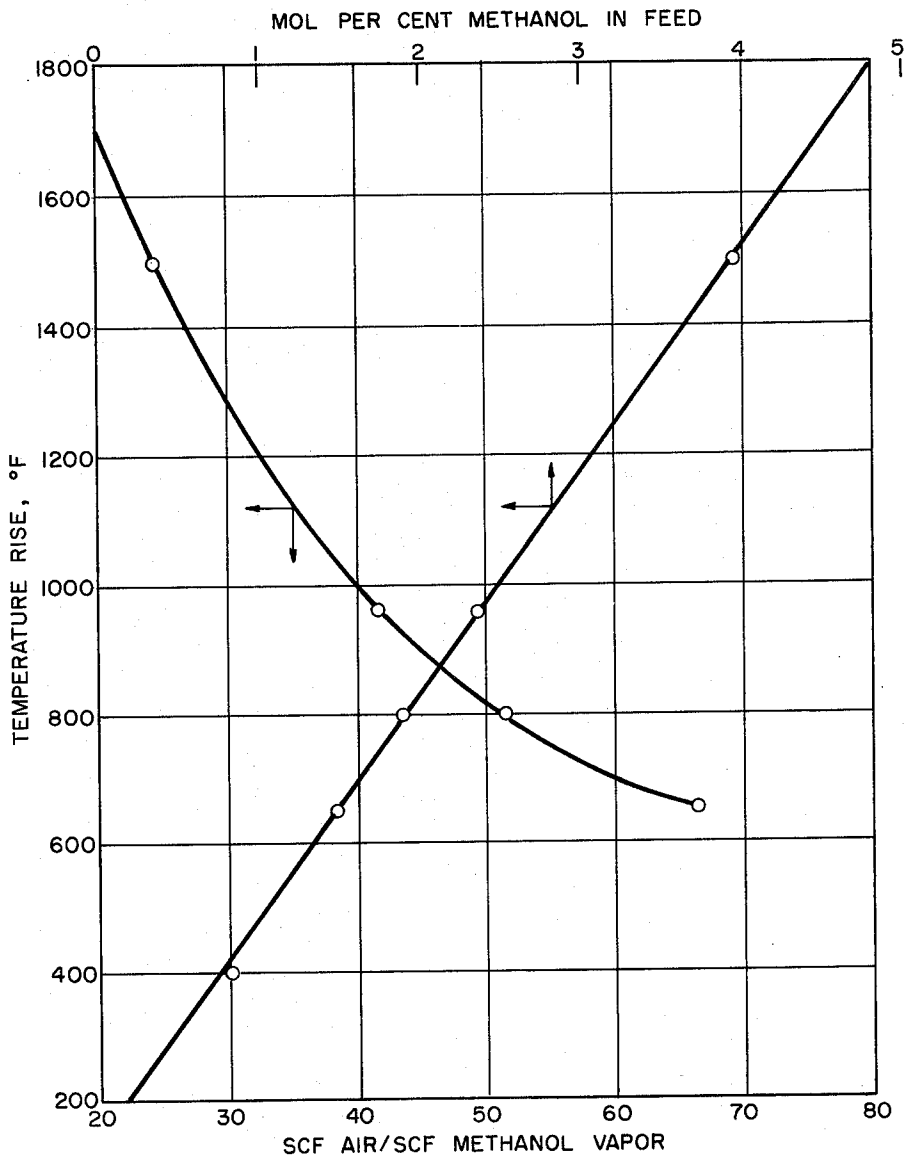

FIG. -11

HOWARD GREKEL
KAROL L. HUJSAK
INVENTORS.

BY Arthur McElroy

ATTORNEY.

United States Patent Office 3,244,231 Patented Apr. 5, 1966

3,244,231

METHOD FOR CATALYTICALLY HEATING OIL BEARING FORMATIONS

Howard Grekel and Karol L. Hujsak, Tulsa, Okla., assignors to Pan American Petroleum Corporation, Tulsa, Okla., a corporation of Delaware

Filed Apr. 9, 1963, Ser. No. 271,664
13 Claims. (Cl. 166—38)

The present invention relates to a method for heating and stimulating oil wells. More particularly, it is concerned with a method suitable for heating oil bearing or similar formations to a temperature sufficient either for stimulating the flow of oil therefrom or for igniting such formation to recover oil by means of combustion.

Briefly, our invention contemplates supplying heat to an oil bearing zone through the use of a catalytic heater especially adapted for the generation of heat by catalytic oxidation of any of a number of different fuels.

Many methods have been employed in the prior art for heating oil wells, e.g., by electrical means, by injecting heat transfer agents into the well such as steam, hot oil, etc., and by burning natural gas in the well bore. Considerable difficulty has been encountered in the application of electric well heating owing to the highly corrosive nature of oil field brine, sulfur compounds, and other components of the fluids produced through the well bore. These fluids penetrate the innermost parts of the well heater, and even traces of moisture cause short-circuiting of the apparatus necessitating shutdown, removal and repair. These difficulties materially reduce the operating efficiency of such heating processes. Well bore liquids also penetrate and permeate the customary insulating materials rendering them practically useless. These problems are peculiar to the well heating art and are not generally encountered in other applications of electrical heating.

One of the principal drawbacks of the gas or liquid fueled heaters is that it is extremely difficult to avoid damage to the casing and any well equipment present in the area where heat is being applied. This is due to the fact that the temperature at which heaters of this kind operate cannot be maintained at levels which such equipment can withstand. One of the difficulties with electrical heaters is their tendency to short out owing to hot spots developing through poor heat exchange, generally resulting from coke formation on the surface. With increasing thickness of the coke layer on the exterior of the heater, the temperature tends to build up until it exceeds the melting point of the heating elements causing the latter to fail.

It is another object of our invention to provide a method for heating oil bearing zones that permits easy and effective temperature control at reasonable operating costs. It is a further object of our invention to provide a method for stimulating the flow of oil from an underground deposit thereof by the use of heat without the formation of coke in objectionable amounts.

In the accompanying drawings a number of embodiments of our invention are illustrated:

FIGURE 1 shows an over-all, partly sectional, view of one embodiment of the apparatus used in accordance with our invention to heat an oil bearing zone by means of catalytic oxidation.

FIGURE 2 is a modification of the design shown in FIGURE 1 in which the effluent from the catalyst bed travels back up the annulus formed by the concentric arrangement of tubing thereby allowing further control of the heater skin temperature which, in turn, aids materially in preventing excessive deposition of coke on the unit.

FIGURE 3 is a detailed design, in section, of a catalytic bottom hole heater or igniter which can be operated on a wire line and hung from tubing. The base of the heater is composed of a heavy stainless steel screen to permit passage of gases while still supporting the catalyst bed.

FIGURE 4 is a plan view of the top of heater shown in FIGURE 3, having suitable cross-pieces for attachment to the wire line.

FIGURE 5 is an elevational view, partly in section, showing an adaptation of our invention wherein the heater is in operation while the well is being pumped.

FIGURE 6 is a detailed design of one form of catalytice bottom hole heater mounted on tubing as contemplated by our invention.

FIGURE 7 is a cross-section of FIGURE 6 taken along line 6—6, showing in somewhat more detail the structure of the apparatus displayed in FIGURE 6.

FIGURE 8 is still another variation of the catalytic bottom hole heater mountable on tubing, as contemplated by our invention.

FIGURE 9 is a modification of the upper portion of the heater design shown in FIGURES 6 and 8.

FIGURE 10 is another sectional view illustrating a design of our invention wherein heating of the formation and simultaneous pumping of the well are effected with the use of a single string of tubing.

FIGURE 11 is a plot showing the volume ratio of air to fuel (methanol in this case) required to produce a given gas effluent temperature from the catalyst bed; it also shows the concentration of methanol in the feed in terms of mole percent to generate a given temperature.

Referring now to FIGURE 1, a protective casing **2** is shown extending from the earth's surface down to an oil-bearing zone **4** which communicates with the casing via perforations **8**. Within casing **2** is a string of production tubing **10** which may extend above, below or substantially within the vertical distance covered by perforations **8**. Concentrically disposed in tubing **10** is a second tubing **12** which may or may not extend into the well to the depth of perforations **8**. At the base of tubing **12** is a seating nipple **14** into which catalytic heater **16** is lowered on wire line **18** and seated. A fuel-air mixture having a composition outside the explosive limit and in proper proportions for generating gas effluent temperatures from heater **16** of from about 500° to about 1000° F. is introduced into tubing **12** via valved flow line **20**. On contacting the catalyst in heater **16** with the aforesaid mixture, the oxidation of the fuel creates combustion products having a temperature within the above-stated range. The combustion products, including excess air, are produced either through casing or through the annulus between tubing **12** and tubing **10** and out line **22** along with the produced oil. When the combustion products are produced with the oil, the amount of air used is regulated such that there is no possibility of developing explosive mixtures or excessive temperatures if it reacts with the produced oil.

In the case where it is desired to heat formation **4** to ignition temperature, i.e., preferably of the order of 800° to 1000° F., prior to conducting a combustion process, production tubing **10** is omitted. Well fluids are forced back into the formation by means of gas pressure until they have dropped to a level in the well below perforations **8**. The hot combustion gases are then directed into formation **4** via perforations **8**, or casing **2** may be landed near the top of formation **4** in which case the hot gases from heater **16** are directed to the walls of the open hole extending into said formation. In this heating step the well head and valved line **22** is closed, of course, so that the hot gases are directed to all of the formation **4**. This same procedure may be used where it is desired merely

to heat up the formation within a radius of 10 to 15 feet, for example, from the well bore in order to stimulate the flow of oil. It will also be appreciated, of course, that this technique may be employed in open hole preparatory to combustion operations. It should be pointed out that in case it is found desirable to preheat the fuel-air mixture in tubing 12, valved line 22 may be left open slightly so that a small stream of hot oxidation products flows up the annulus, thereby furnishing heat to said mixture.

If the aforesaid heating step is carried out for the purpose of initiating a combustion process, heater 16, after the formation ignition temperature is reached, is removed from the well and the latter becomes either a producing or an injection well, depending on whether it is being used in a reverse or forward combustion drive. If the well is employed as a producer, oil is produced through line 22, and if it is used as an injection well, air is introduced into the formation via line 20.

In FIGURE 2, heater 16 may be either in the form as shown in FIGURES 1 or 3, i.e., all of the fuel-air mixture flows through only a portion of the catalyst bed or said mixture may flow through the entire bed.

Where it is desired to employ a bottom hole heater for the purpose of preventing accumulation of paraffin at or near the face of the formation and in the tubing, an arrangement such as that shown in FIGURE 5 may be used. In this case, tubing 24, carrying heater 26, is secured to well head 28. Heater 26 is threadedly or otherwise removably mounted to tubing 24 at 30. The necessary fuel-air mixture is supplied to the heater via valved line 32. The structure of heater 26 is shown in further detail in FIGURES 6 and 7 in which an elongated cylindrical vessel 33, measuring usually 10 to 20 feet in length and about 2 inches O.D., is filled with a suitable oxidation catalyst 34. The catalyst is supported at a level near the base of the heater by means of a stainless steel screen 36. At the mouth of heater 26 fuel line 32 extends into vessel 33 for a short distance above the top of catalyst 34. Line 32 is held in alignment with the mouth of vessel 33 by means of metal seal 38. Tubes 40 fit snugly against the exterior of vessel 33 and place into communication the space below screen 36 with the open area just above seal 38 in tubing 24. The total cross-sectional area of tubes 40 should be large enough, in proportion to that of vessel 33, to avoid excessive pressure drop.

Production tubing 42 is equipped at the lower end with a check or standing valve 44 which permits flow of oil from formation 4 into tubing 42 but prevents reverse flow. The flow of oil through the system is maintained by the reciprocal motion of pump 46 connected to sucker rod 48 extending upwardly to the surface through tubing 42 to suitable power means (not shown) located at the surface. Oil pumped from the well in this fashion is removed by means of flow line 50.

The heater shown in FIGURE 8 can be substituted for the one illustrated in FIGURE 5, shown in more detail in FIGURE 6. The device in FIGURE 8 is somewhat simpler in design and includes an elongated metal case 52 holding a bed of catalyst 34 supported at the base by a grate or screen 54. Screen 54 is secured both to the interior of case 52 and to the base of tubing 32. A similar structure 57 is placed at the top of the bed to prevent entrainment of the catalyst with the fluids flowing upwardly into the annulus between tubing strings 24 and 56. The upper portion of case 52 is engaged to tubing 24 at threaded connection 30.

In operation of an assembly such as that shown in FIGURE 5, a suitable fuel-air mixture is forced down line 32 into contact with the catalyst as shown in the heater of FIGURE 5. Rapid oxidation of the hydrocarbon or oxygenated organic compound in the feed occurs, generating temperatures of the order of from 400° to 800° or 1000° F. The hot products of combustion flow through catalyst 34 down to the base of the heater and then flow upwardly through tubes 40. Heat in these tubes, as well as in vessel 33, is extracted therefrom and transferred to surrounding well fluids which, in turn, release this heat to formation 4. After the heat has been largely removed from the gaseous products in tubes 40, said products flow, as indicated, into tubing 24 where the remainder of the heat is transferred to the fresh fuel-air mixture flowing downwardly in line 32 to catalyst 34.

In substituting the heater shown in FIGURE 8 for the one in FIGURES 5 and 6, the gas flow is somewhat different in that the fuel-air mixture passes through tubing 32 the full length of catalyst bed 34, then flows upwardly through the catalyst, and heat is generated by oxidation of the fuel. At the top of catalyst bed 34, the resulting combustion products are conducted up the well and out of the system via the annulus between tubing 32 and tubing 24. It will be appreciated, of course, that the fluid flow can be reversed, i.e., the fuel-air mixture passed down the annulus between tubing strings 24 and 32 and back up through tubing 24. In the event the temperature in the vicinity of tubing 24 becomes excessive, i.e., the fuel-air mixture is preheated to too high a temperature before contacting the catalyst bed, suitable insulation can be placed about tubing 24, thereby avoiding such undesirably high temperatures.

The apparatus shown in FIGURE 9 may be used with any type of heater of the general design illustrated in FIGURES 6 and 8. The modification shown in FIGURE 9 comprising tubing 62, has metal seal 64, holding pipe 66 and maintains the latter substantially concentric with tubing 62 at or near the juncture of seal 64 with pipe 66 or perforations 68. This entire assembly may be attached at the lower end thereof to a heater such as shown in FIGURE 5. The modification in tubing arrangement, as shown in FIGURE 9 may be safely used where the combustible gas production from the oil is low enough that there will be no danger of formation of an explosive mixture in the casing. Thus, the fuel-air mixture flows downwardly to the heater via tubing 62 until it reaches seal 64 located, for example, 4 or 5 feet above the catalyst bed. The entire flow is then directed into pipe 66 where it continues on its way and comes in contact with the oxidation catalyst, as previously described. Combustion or oxidation products are conducted away from the heater via annulus 70 and then leave the latter through perforations 68, traveling upwardly inside the casing and are then removed from the well.

The heat contained in the combustion products generated in the various ways mentioned above is transferred through the well fluids to formation 4, heating the oil therein and preventing paraffin or materials of a similar nature from solidifying at or near the formation face. The hot oil thus produced into the well and lifted to the surface via tubing 42, likewise, tends to prevent the deposition of paraffin in said tubing as well as in flow line 50.

The modification shown in FIGURE 10 eliminates the dual tubing arrangement used in the previously illustrated embodiment and is suitable for simultaneously pumping oil and heating an oil-containing formation penetrated by a well. In this particular embodiment the assembly illustrated may replace the equipment shown in FIGURE 5. A heater 72 containing catalyst 34 is mounted on tubing 74 and located opposite perforations 8 and oil-bearing formation 4. Inside tubing 74 is hollow sucker rod 76 carrying pump 46. A seal 78 is placed substantially midway of heater 72 to prevent flow of fluids upwardly through annulus 80. At the base of tubing 74 is standing valve 82 which allows hot produced oil to flow into the variable volume chamber defined by said valve and pump 46. Near the lower end of hollow sucker rod 76 are ports 84 which permit the fuel air mixture to flow out of the rod and into lower ports 86 in heater 72. After the temperature of catalyst bed 34 has reached the desired level, air alone is sent down sucker rod 76 and the produced crude used as the fuel for heating. The

air rate is regulated to obtain substantially complete consumption of air in the catalyst bed to avoid burning or possible formation of explosive mixtures on the way to the surface. Produced oil flows into and through heater 72 and out upper ports 88 along with oxidation products formed when the mixture of oil and air comes in contact with catalyst 34. The produced oil and combustion products are then removed from the well via annulus 90.

The fuel portion of the feed which is to be contacted with the catalyst in accordance with our invention may be selected from a wide variety of substances, such as, for example, light hydrocarbons, typically natural gas, propane, butane and unsaturated derivatives thereof, kerosene, crude oil, oxygenated organic chemicals, such as the lower molecular weight alcohols, for example, methanol, and the like. Mixtures, of course, of two or more of the foregoing materials may be used—in gaseous or liquid form—as the fuel component of the feed. In general, we prefer to employ air or oxygen-rich fuel mixtures, however, our invention also contemplates the use of fuel-rich mixtures. Tests using feed mixtures of propane and air and propylene and air were carried out under the conditions outlined below.

Table I

Conditions	Run No. 1	Run No. 2
Catalyst	(1)	(1)
Fuel	(2)	(3)
Mol Percent Fuel in Air Feed	0.45	0.61
Pressure, p.s.i.g.	50	50
Space Velocity, s.c.f. total feed/hr./c.f. catalyst	25,400	25,400
Preheat Temperature, ° F.	635	402
Outlet Temperature	942	882
Hydrocarbon Conversion, percent	49	100

[1] Platinum Oxide on Alumina.
[2] Propane.
[3] Propylene.

The above results, translated in terms of field requirements, show that to generate one million B.t.u./day, a total of 12 gallons of hydrocarbon and 87,000 s.c.f.d. of air are needed. To handle this feed mixture, approximately 0.14 cubic foot of catalyst is used. This corresponds to a column of catalyst 6 feet long in a 2-inch I.D. pipe.

The space velocities employed will vary with the nature of the fuel employed. Generally speaking, when methanol is used as the fuel, space velocities as high as 100,000 s.c.f.h. per cubic foot of catalyst may be employed. With fuels less readily oxidized, the space velocities ordinarily will be in the range of from about 10,000 to about 25,000 s.c.f.h. per cubic foot of catalyst. These figures, in both instances, refer to the combined fuel-air mixture.

The table below illustrates the temperature rise produced by contacting varying methane-air and propane-air mixtures with a supported platinum oxide catalyst so as to effect complete combustion of the fuel in an adiabatic system.

Table II

Volume Ratio s.c.f.-Air/CH	Temperature Rise, ° F.	Volume Ratio s.c.f.-Air/ Propane	Temperature Rise, ° F.
		100	1,220
30	1,500	130	970
40	1,200	170	770
50	1,000	200	660
60	900		
70	750		
128	400		

Preferred volume ratios of air to methane and air to propane (s.c.f.) are from about 25 to 130 and from about 60 to about 200, respectively.

The effluent temperature from the catalyst bed can also be regulated by limiting the contact time of the fuel-air mixture with the catalyst so as to limit the amount of

reaction obtained. Ordinarily, temperatures in excess of about 1500° F should not be employed.

The catalysts used may be selected from a wide list of materials and form no part of our invention. Typically, catalysts suitable for oxidation of the feeds contemplated herein include the oxides of platinum, palladium, rhodium, etc. These oxides are preferably used in very dilute concentrations, e.g., 0.05 to about 0.5 weight percent, and may be supported on materials having a large surface area, such as pumice, aluminum oxide, metal wool, for example, stainless steel wool, and the like. Supported platinum oxide catalyst suitable for this purpose is manufactured by the Chemetron Corporation of Louisville, Ky., and is identified as catalyst G–43. In operation, the portion of catalyst apparently entering into the oxidation reaction is that with which the feed mixture first comes in contact.

It is to be understood that while our invention is particularly applicable to the recovery of hydrocarbons from liquid petroleum reservoirs, it is equally suited to the recovery of valuable products from other sub-surface combustible materials such as, for example, oil shale, tar sand, coal and the like.

We claim:

1. A method for heating a subsurface formation containing combustible material, said formation being penetrated by a well, which comprises placing a body of an oxidation catalyst in said well at the approximate level of said formation, thereafter conducting a fuel-air mixture through said catalyst, said mixture being outside the explosive range, and passing the resulting hot oxidation products in heat exchange relation with said formation, said products having a temperature of from about 500° to about 1100° F.

2. The method of claim 1 in which the fuel component of said mixture is a light hydrocarbon.

3. The method of claim 1 in which the fuel component of said mixture is methanol.

4. The method of claim 1 in which the fuel component of said mixture is propane.

5. The method of claim 1 in which the fuel component of said mixture is propylene.

6. The method of claim 1 in which the fuel component of said mixture is natural gas.

7. The method of claim 1 in which the combustible material is a heavy viscous crude.

8. The method of claim 7 in which said catalyst is in the form of a confined mass and the temperature of the oxidation products ranges from about 500° to about 1000° F.

9. In a process for recovering crude oil from a pumping well penetrating an oil-bearing formation and wherein production of said oil is hindered by the deposition of solid solid materials from said oil on the face of said formation, the improvement which comprises placing a body of oxidation catalyst in said well and near the face of said formation, thereafter contacting a fuel-air mixture with said catalyst, said mixture being outside the explosive range, passing the resultant products of oxidation having a temperature of from about 500° to about 1100° F. in direct heat exchange relation with said formation whereby said deposition of materials is at least minimized, and recovering the heated oil via said well from said formation.

10. The process of claim 9 in which the oil from said formation is employed as the fuel.

11. In a process for recovering crude oil from a pumping well penetrating an oil bearing formation and wherein production of said oil is hindered by the deposition of solid materials from said oil on the face of said formation, the improvement which comprises placing a confined mass of oxidation catalyst in said well and at the approximate level of said formation, thereafter contacting said catalyst with a fuel-oxygen-containing gas mixture having a composition sufficient to produce oxidation products hav-

ing a temperature range from about 500° to about 1100° F., said mixture being outside of the explosive range, thereafter passing said products in heat exchange relationship with said formation, and recovering the heated oil via said well from said formation.

12. A method for treating an oil-bearing formation to promote the flow of oil therefrom, said formation being penetrated by a well, which comprises placing a confined body of an oxidation catalyst in said well and near the face of said formation, thereafter conducting a fuel-oxygen-containing gas mixture upwardly through said catalyst to produce oxidation products having a temperature of from about 500° to about 1100° F., said mixture being outside of the explosive range, and bringing said products into indirect heat exchange with said mixture and with said formation.

13. In a method for heating to ignition temperature an underground formation containing a combustible material, said formation being penetrated by a well, the improvement which comprises placing a confined body of an oxidation catalyst opposite said formation, thereafter conducting a fuel-oxygen-containing gas mixture through said catalyst in the absence of liquid in said well at the level of said body of catalyst, said mixture being outside the explosive range, and passing the resulting hot oxidation products in direct heat exchange with said formation until the latter has been heated to said ignition temperature.

References Cited by the Examiner

UNITED STATES PATENTS

1,678,592	7/1928	Garner et al.	166—59
2,675,081	4/1954	Nowak	166—59 X
2,847,071	8/1958	De Priester	166—39
2,890,755	6/1959	Eurenius et al.	166—59
2,997,105	8/1961	Campion et al.	166—59
3,010,516	11/1961	Schleicher	166—59
3,026,937	3/1962	Simm	166—39
3,055,427	9/1962	Pryor et al.	166—59
3,070,178	12/1962	Graham et al.	175—17
3,107,728	10/1963	Kehn	166—39 X
3,113,623	12/1963	Krueger	166—59
3,127,935	4/1964	Poettman et al.	166—11

OTHER REFERENCES

Haslam and Russell: Fuels and Their Combustion, 1st edition, McGraw-Hill Book Co., New York, 1926 (pages 304 and 305) TP 318.H3.

Hackh's Chemical Dictionary, 3rd edition (1944), The Blakiston Co., Phila., Pa., page 532.

The Condensed Chemical Dictionary, 6th edition, Reinhold Publishing Corporation, New York, 1961, pages 51, 52 and 794.

CHARLES E. O'CONNELL, *Primary Examiner.*

BENJAMIN HERSH, *Examiner.*