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RECOVERY BY COMBUSTION OF PETROLEUM OIL FROM PARTIALLY DEPLETED SUBTERRANEAN RESERVOIRS

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This invention relates to secondary recovery of petroleum oil from subterranean reservoirs and relates more particularly to the method involving combustion of petroleum oil remaining in partially depleted subterranean reservoirs to assist in recovery of a portion of such remaining oil.

Petroleum oil is usually recovered from subterranean reservoirs initially as a result of gas pressure, rock pressure, or natural water drive which forces the oil from the oil-bearing formation or reservoir through the producing well to the surface. As recovery of oil from the reservoir continues, the reservoir energy gradually decreases and finally becomes insufficient to force the oil to the surface, although a major portion of the original quantity of the oil remains in the reservoir. To increase the ultimate recovery of the oil, pumping is then employed, but when the rate of recovery by pumping falls to an uneconomically low level, a further increase in the ultimate recovery of the oil may still be economically effected by the employment of secondary recovery methods such as gas drive or water drive. It has recently been proposed to increase the ultimate recovery of the oil by a subterranean combustion process.

In the subterranean combustion process, an oxidizing gas, which may be air, oxygen, oxygen-enriched air, air admixed with inert gas to reduce the proportion of oxygen, oxygen admixed with inert gas, or any other suitable oxidizing gas or mixture which will support combustion within the subterranean reservoir, is passed, as by pumping, through an input well or input wells to the reservoir in which the combustion process is to be effected and combustion within the reservoir is initiated by suitable means. The flow of oxidizing gas to the reservoir is continued and combustion gases, oil, and distillation and viscosity breaking products of the oil are carried in front of the combustion zone to an output well or wells from which the fluids are removed and thereafter treated for recovery of the desired valuable constituents. The heated fluids migrating in front of the combustion zone strip the oil-bearing sand of the greater portion of the oil leaving behind within the sand a carbonaceous hydrocarbon deposit and the carbonaceous deposit essentially is the fuel consumed in the process.

In this process, where the amount of carbonaceous deposit left behind on the sand is about 2 per cent or more by weight of the sand, combustion tends to proceed satisfactorily. However, where the amount of carbonaceous deposit is less than about 2 per cent by weight of the sand, combustion proceeds at a slow rate and at a comparatively low temperature irrespective of the rate of passage to the reservoir of the oxidizing gas and its concentration of oxidizing constituent. Further, in the combustion process, for combustion to be initiated, the reservoir must be heated at the combustion zone to the ignition temperature. This requires heating of the oxidizing gas to at least the ignition temperature prior to passage to the input well or, by suitable ignition means within the input well, after

passage thereto. Additionally, combustion occasionally ceases, as, for example, when the supply of oxidizing gas is interrupted because of mechanical breakdown of pumps, or otherwise, with consequent cooling of the reservoir at the previously established combustion front. Re-ignition can be effected upon re-establishment of the passage of oxidizing gas to the reservoir if cooling has not progressed to the extent that the reservoir temperature at the previously established combustion front has fallen below the ignition temperature. However, if the reservoir temperature has fallen below the ignition temperature, heating of the oxidizing gas above the ignition temperature is required to start combustion which involves the expenditure of large amounts of heat since the entire reservoir from the input well to the previously established combustion front will be of necessity heated to the temperature of the oxidizing gas.

It is an object of this invention to increase the rate of combustion within a partially depleted petroleum oil reservoir where combustion is effected for recovery of a portion of the petroleum oil therein. It is another object of this invention to increase the temperature of combustion within a subterranean petroleum oil reservoir treated by the combustion recovery process. It is another object of this invention to reduce the temperature at which combustion may be initiated in a subterranean petroleum oil reservoir. It is another object of this invention to reduce the amount of heat required to be added to the oxidizing gas in order to effect re-ignition in a subterranean petroleum oil reservoir. These and further objects of this invention will become apparent from the following description thereof.

In accordance with the invention, to the oxidizing gas passed to a partially depleted subterranean oil reservoir wherein recovery of a portion of the petroleum oil contained therein is to be effected by the combustion process there is added a catalyst comprising a saturated aliphatic ether or aldehyde containing no more than five carbon atoms.

I have discovered that the addition of a saturated aliphatic ether or aldehyde containing no more than five carbon atoms to the air or other oxidizing gas passed to a subterranean reservoir causes an increase in the rate and temperature of combustion. Further, the addition of the catalyst to the oxidizing gas permits initiation of combustion at a lower temperature, which may be of the order of 350° F. to 400° F. By addition of the catalyst, also, re-ignition of a previously established combustion front may be effected at a lower temperature whereby a longer period of shutdown, or non-combustion, may be tolerated with re-ignition thereafter in the absence of heating of the oxidizing gas or, where cooling has progressed below the ignition temperature, with re-ignition thereafter involving heating of the oxidizing gas to a lesser extent. By the process of the invention therefore, a more effective recovery of petroleum hydrocarbon by the combustion process is obtained and, where re-ignition is required, the heat that must be supplied to the oxidizing gas is minimized.

Any of the saturated aliphatic ethers and aldehydes containing no more than five carbon atoms may be employed. Included among these compounds are formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, normal valeraldehyde, isovaleraldehyde, dimethyl ether, diethyl ether, methyl ethyl ether, methyl propyl ether, methyl isopropyl ether, ethyl propyl ether, ethyl isopropyl ether, methyl butyl ether, and methyl isobutyl ether. Preferably, formaldehyde is employed in view of its effectiveness as well as its availability and economy. Of the other aldehydes, acetaldehyde and propionaldehyde are to be preferred. Dimethyl ether and diethyl ether are

particularly effective where it is desired to re-ignite the reservoir since re-ignition is effected at a lower temperature where these compounds are employed.

The saturated aliphatic aldehydes and ethers employed in the process of the invention are gaseous or liquid at atmospheric conditions of temperature and pressure and, accordingly, may be added in the liquid phase or the gaseous phase to the oxidizing gas passed to the reservoir undergoing combustion. Preferably, however, the catalyst is admixed in the gaseous phase. Where the catalyst is in the liquid phase, a convenient method for effecting admixture in the gaseous phase is to pass the oxidizing gas or, preferably, a portion of the oxidizing gas, through a bath of the liquid catalyst prior to passage to the input well whereby the oxidizing gas will vaporize a portion of the liquid catalyst carrying the vaporized portion along with it to the input well. Proportioning of the oxidizing gas and liquid phase catalyst may be effected by any desired means. A simple means of proportioning involves passing a known portion of the oxidizing gas through a bath of the liquid phase catalyst at a known temperature whereby the proportion of catalyst vaporizing in the oxidizing gas will be equal to the ratio of the vapor pressure of the catalyst at the known temperature to the total pressure of the oxidizing gas after admixture with the catalyst. Where the catalyst is in the gaseous phase, the gaseous catalyst may simply be admixed in the proper proportion with the oxidizing gas and, for this purpose, any suitable conventional means for gas proportioning may be employed.

The rate and temperature of combustion within the reservoir and the temperature required for re-ignition depends within limits upon the concentration of catalyst employed in the oxidizing gas. Concentrations of at least 0.5 percent by volume of catalyst in the gaseous phase in the oxidizing gas may be employed although it is preferred to employ concentrations of at least 0.8 percent by volume in the gaseous phase. Higher concentrations may be employed as desired although satisfactory results are obtainable with concentrations not greater than about 5 percent by volume in the gaseous phase.

Where a saturated aliphatic ether or aldehyde containing no more than five carbon atoms is added to the oxidizing gas passed to the reservoir undergoing combustion, the fluids recovered from an output well will retain to an appreciable extent with respect to combustion the catalytic activity of the ether or aldehyde. In accordance with one aspect of the invention, fluids, either liquids or gases, recovered from a subterranean reservoir in which combustion, with the addition of an aliphatic ether or aldehyde containing no more than five carbon atoms to the oxidizing gas, has been effected to increase the ultimate recovery of petroleum oil therefrom, are admixed with the oxidizing gas passed to the input well or to another input well leading to the same or another subterranean reservoir being treated by the combustion process. In carrying out this procedure, a portion of the fluids from the output well, without any treatment for recovery and removal of any of the constituents thereof, may be admixed with the oxidizing gas, or the fluids or a portion thereof from the output well after treatment for removal and recovery of petroleum hydrocarbons, may be admixed with the oxidizing gas. By recycle of fluid from an output well to an inlet well leading to the same reservoir or to another reservoir, a saving in the amount of catalyst employed is effected since the amount of catalyst added to the oxidizing gas is reduced in proportion to the amount and the activity of the catalytically acting constituent in the fluid from the output well added to the oxidizing gas.

In the practice of the invention, the catalyst may be added to the oxidizing gas at the time combustion within the reservoir is initiated whereby the temperature at which combustion is initiated will be reduced considerably. For example, it is possible to reduce the ignition temperature

of a reservoir from about 1000° F. to about 350° F. to 400° F. by the process of the invention. Thereafter, catalyst may be added continually or at regular intervals during the combustion process with the result that the combustion temperature is increased and the combustion rate accelerated. The addition of the catalyst to the oxidizing gas during the combustion process is particularly indicated where the amount of carbonaceous deposit left behind on the sand is less than about 2 percent by weight of the sand since, with this amount of carbonaceous deposit in the sand, combustion is slow and at a low temperature. Further, where the amount of carbonaceous deposit is sufficiently below about 2 percent by weight of the sand to prevent maintenance of combustion, the addition of the catalyst to the oxidizing gas permits combustion where otherwise combustion would be impossible. In the event combustion has ceased, because of cessation of the supply of oxidizing gas, for example, re-ignition is effected by supplying oxidizing gas containing catalyst to the reservoir whereby re-ignition will occur at a lower temperature than would occur in the absence of the catalyst. By addition of catalyst, it is not necessary to preheat the oxidizing gas with consequent saving in heating costs where the reservoir temperature has remained at or above the ignition temperature obtainable with catalyst. However, in the event the reservoir has cooled below the ignition temperature obtainable with catalyst, the oxidizing gas containing the catalyst is heated before passage to the reservoir to a temperature equal to, but preferably in excess of, the ignition temperature, but even in this case a saving of heat is effected since the oxidizing gas need not be heated to the high ignition temperature required where catalyst is not employed.

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

I claim:

1. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products and combustion products from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir.

2. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir in a concentration in the gaseous phase of at least 0.5% by volume of said oxidizing gas.

3. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products and combustion products from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir in a concentration in the gaseous phase of at least 0.8% by volume of said oxidizing gas.

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4. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products and combustion products from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir in a concentration in the gaseous phase between about 0.8 and 5.0% by volume of said oxidizing gas.

5. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom, combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir, and petroleum products and combustion products are withdrawn from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir and admixing at least a portion of the fluid products withdrawn through said output well from said reservoir with oxidizing gas passed to a subterranean petroleum oil reservoir undergoing combustion for recovery of petroleum oil therefrom.

6. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom, combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir, and petroleum products and combustion products are withdrawn from said reservoir through said output well, the improvement comprising adding formaldehyde to said oxidizing gas passed to said reservoir and recycling at least a portion of the fluid products withdrawn through said output well from said reservoir to said input well for admixture with oxidizing gas passed therein.

7. In a process for the recovery of petroleum oil from

a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products and combustion products from said reservoir through said output well, the method of initiating combustion within said reservoir comprising passing to said reservoir oxidizing gas admixed with formaldehyde, said mixture of said oxidizing gas and said formaldehyde being upon entry into said reservoir at a temperature such that combustion of combustible material within said reservoir will be effected.

8. In a process for the recovery of petroleum oil from a partially depleted subterranean petroleum oil reservoir wherein an oxidizing gas is passed to said reservoir through an input well leading thereto and forced through said reservoir to an output well leading therefrom and combustion of a portion of the petroleum oil contained in said reservoir is maintained within said reservoir for the purpose of withdrawing petroleum products and combustion products from said reservoir through said output well, the method of re-igniting combustible material within said reservoir where combustion has ceased comprising passing to said reservoir oxidizing gas admixed with formaldehyde, said mixture of said oxidizing gas and said formaldehyde being upon arrival at the previously established combustion front at a temperature such that combustion of combustible material within said reservoir will be effected.

References Cited in the file of this patent

UNITED STATES PATENTS

1,473,348	Howard	Nov. 6, 1923
1,806,499	Ranney et al.	May 19, 1931
1,979,841	Pier et al.	Nov. 6, 1934
2,217,749	Hewitt	Oct. 15, 1940
2,221,839	Lipkin	Nov. 19, 1940
2,382,471	Frey	Aug. 14, 1945
2,496,444	Cook	Feb. 7, 1950