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## 2,953,205

## PROCESS FOR INITIATING IN SITU COMBUSTION

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No Drawing. Filed July 28, 1958, Ser. No. 751,578 8 Claims. (Cl. 166—11)

This invention relates to a process for igniting a carbonaceous stratum. An aspect of the invention pertains to a process for initiating in situ combustion in a carbonaceous stratum.

In situ combustion in the recovery of hydrocarbons from underground strata containing carbonaceous material is becoming more prevalent in the petroleum industry. In this technique of production, combustion is initiated in the carbonaceous stratum and the resulting combustion zone is caused to move thru the stratum by either inverse or direct air drive whereby the heat of combustion of a substantial proportion of the hydrocarbon in the stratum drives out and usually upgrades a substantial proportion of the unburned hydrocarbon material.

The ignition of carbonaceous material in a stratum around a borehole therein followed by injection of air thru the ignition borehole and recovery of product hydrocarbons and combustion gas thru another borehole in the stratum is a direct air drive process for effecting in situ combustion and recovery of hydrocarbons from the stratum. In this type of operation the stratum usually plugs in front of the combustion zone because a heavy viscous liquid bank of hydrocarbon collects in the stratum in advance of the combustion zone which prevents movement of air to the combustion process. To overcome this difficulty and to permit the continued progress of the combustion zone thru the stratum, inverse air injection has been resorted to. By this technique, a combustion zone is established around an ignition borehole by any suitable means and air is fed thru the stratum to the combustion zone from one or more surrounding boreholes.

In situ combustion techniques are being applied to tar sands, shale, Athabasca sand, and other strata in virgin state, to lignite, and to other coal veins by fracturing, and to strata partilaly depleted by primary, and even by secondary and tertiary recovery methods.

One of the problems in recovering hydrocarbons from an underground formation containing carbonaceous material is the establishment of a self-sustaining combustion in the stratum. The usual method comprises heating the stratum around an ignition borehole therein and injecting O<sub>2</sub>-containing gas into the hot stratum so as to ignite the carbonaceous material therein. Various methods of heating the stratum to a combustion supporting temperature have been utilized. These methods include utilizing an electrical heater, a downhole gas burner, injected hot gas, burning charcoal adjacent the stratum, etc. In many instances the source of heat overheats the stratum so as to cause fusing of stratum rock, with attendant plugging and or spalling of the walls of the borehole. This reduces the permeability of the area thru which air must be injected or thru which produced hydrocarbons must pass, in the case of inverse air injection, and is generally detrimental to the process.

Another problem lies in heating the stratum to a sufficient depth around the ignition borehole to establish a large enough heat reservoir to permit ignition of the carbonaceous material and propagation of the resulting

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combustion front thru the stratum to other boreholes therein.

It is accordingly an object of the invention to provide an improved process for igniting a carbonaceous stratum and establishing in situ combustion therein. Another object is to control the temperature of the preheating step in establishing in situ combustion and ignition in a carbonaceous stratum so as not to overheat and fuse the sand or other rock material in which the hydrocarbon material is deposited. A further object is to provide a process for preheating a carbonaceous stratum around an ignition bore hole which permits heating to any desirable depth from the borehole. It is also an object of the invention to provide a process for igniting a carbonaceous stratum which is rapid, sure, and efficient. Other objects will become apparent from a consideration of the accompanying disclosure.

A broad aspect of the invention comprises introducing liquid hydrazine into a stratum to be ignited and effecting decomposition of the hydrazine so as to heat the stratum to combustion supporting temperature, and contacting the hot stratum with O<sub>2</sub>-containing gas so as to ignite the carbonaceous material. The hydrazine may be introduced in an anhydrous substantially pure state or it may be admixed with water and/or with ammonia and/or hydrazine nitrate. Hydrazine decomposes at temperatures of about 572° F. and higher in the absence of oxygen. Certain catalysts lower the temperature of decomposition substantially. Such catalysts include molybdenum, chromium, platinum, tungsten, iron, nickel, cobalt, porous asbestos, active carbon, and quartz. Hydrazine decomopses in accordance with the following reactions.

(1) 
$$3N_2H_4 \rightarrow 4NH_3 + N_2 + 80.15$$
 kcal.  
(2)  $4NH_3 \rightarrow 2N_2 + 6H_2 - 44.00$  kcal.

These two reactions proceed at different speeds, the disassociation of NH<sub>3</sub> being slower. However, the net result is the liberation of a substantial amount of heat and this can be controlled by adding ammonia to the hydrazine before introducing the same into the stratum. Another manner of controlling the temperature developed within the stratum in which the hydrazine is positioned is to admix water in limited proportions with the hydrazine, preferably, less than 5% by weight, based on the hydrazine, whereby the heat of decomposition is partially absorbed by vaporization of the water. Under usual circumstances the decomposition of hydrazine does not overheat the stratum with which it is in contact because the decomposition rate is slowed by the heat absorption characteristics of the stratum. The hydrazine is dispersed thru the stratum and does not exist therein in large amounts per unit area because of the low porosity of most oil bearing strata. In fact, in some strata of low permeability it is desirable to increase the rate of decomposition and add to the heat liberated by the decomposition by incorporating in the hydrazine a suitable oxidant such as hydrazine nitrate or nitric acid. Hydrazine nitrate is readily formed by dissolving ammonium nitrate in hydrazine or by adding nitric acid thereto. The thermal stability of a mixture of hydrazine and hydrazine nitrate is much less than that of pure hydrazine but, even when containing as much as 25 weight percent nitric acid, the mixture has been found to be not greatly different from nitromethane and may be handled with sufficient care to be utilizable in igniting a carbonaceous stratum. Adjusting the amount of nitrate in the mixture in the range of 1 to 25 weight percent, calculated as HNO<sub>3</sub>, regulates the amount of heat developed by the decomposition and the reaction between the released oxygen and decomposition products. Such a procedure adapts the mixture to strata of varying permeabilities

and can be utilized to raise the temperature to any appropriate temperature level above the combustion temperature of the in-place carbonaceous material which is usually in the range of about 500 to 700° F.

The pure hydrazine or any desirable mixture thereof with the disclosed additives is injected into a carbonaceous stratum thru an ignition borehole until the stratum is saturated to a predetermined suitable depth, such as several inches to several feet, and decomposition of the hydrazine is then effected in any suitable manner, such as by burning a squib or railroad flare, charcoal, or by heating the walls of the borehole in any other suitable manner. The hydrazine decomposition may also be initiated by the use of ultra violet light directed into the hydrazine in the wall of the borehole. A mercury vapor 15 lamp or any other suitable source of ultra violet light may be lowered into the borehole and utilized for this purpose.

When the hydrazine decomposition is completed or during the latter stages thereof, air is injected into the 20 hot area so as to establish in situ combustion of the inplace carbonaceous material. If direct air injection is to be utilized, the same is injected thru the ignition borehole while in effecting inverse air injection, air, preferably admixed with a small proportion of fuel gas such as 25 natural gas or other normally gaseous hydrocarbons, including propane, usually in the range of about 1 to 5 weight percent of the air, is injected thru one or more surrounding boreholes so that the injected mixture passes to the hot stratum around the ignition bore hole, there- 30 by establishing ignition and inverse movement of the combustion front toward the injection boreholes. As the combustion takes place, a portion of the in-place carbonaceous material is volatilized and is driven out of the stratum with the combustion gas from the burning process 35 either into the ignition borehole, in the case of inverse air injection, or into the surounding boreholes in the case of direct air injection.

One of the important advantages of the invention lies in the fact that hydrazine decomposes gradually and releases heat in the same manner so that released heat is conducted thru the formation before overheating of any particular portion of the formation, contiguous to the decomposing hydrazine, occurs. Use of diluents such as ammonia and water can be utilized to decrease the amount of heat release per unit volume of hydrazine in the stratum in situations where the pore volume or intersticial space is reasonably large or in fractures in a stratum established for the purpose of initiating combustion in a pancake area at one lever and driving the combustion front to fractures in the stratum at another level. In a stratum of low permeability and therefore small intersticial space in a given volume, the use of undiluted

hydrazine, or hydrazine containing nitric acid, increases the amount of heat liberated for a given volume of the mixture to compensate for the low volume of the mixture in a given volume of stratum.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

I claim:

- 1. A process for igniting a carbonaceous stratum which comprises introducing liquid hydrazine into said stratum to saturate a selected area thereof and effecting decomposition of said hydrazine so as to heat said stratum to combustion supporting temperature; and contacting the heated stratum with O<sub>2</sub>-containing gas so as to ignite same.
- 2. The process of claim 1 wherein said hydrazine is in admixture with a minor proportion of ammonia up to about 40 weight percent of the mixture.
- 3. The process of claim 1 wherein said hydrazine is in admixture with water in minor proportion up to about 5 weight percent of the hydrazine.
- 4. The process of claim 1 wherein said hydrazine is admixed with hydrazine nitrate in minor proportion in the range of 1 to 25 weight percent calculated as HNO<sub>3</sub>.
- 5. The process of claim 1 wherein decomposition is aided by incorporating a catalyst in the hydrazine which lowers the temperature of hydrazine decomposition.
- 6. The process of claim 1 wherein decomposition of said hydrazine is initiated by directing ultra violet light into same.
- 7. A process for igniting a carbonaceous stratum which comprises introducing hydrazine into a section of said stratum adjacent an ignition borehole therein to saturate said section; effecting decomposition of said hydrazine so as to heat said stratum to ignition temperature; passing air containing a minor amount of fuel gas up to about 5 weight percent of the mixture through at least one injection borehole spaced from said ignition borehole so as to ignite the hot stratum and cause the resulting combustion zone to move toward said injection borehole.
- 8. The process of claim 1 wherein decomposition of said hydrazine is initiated by heating the hydrazine-containing stratum to an elevated temperature sufficient to initiate the decomposition.

## References Cited in the file of this patent UNITED STATES PATENTS

1,248,689	McVoy	Dec. 4, 1917
1,494,735	Cooper	
2,316,596	Kennedy	
2,841,375	Salomonsson	