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USE OF PROPYNOL IN CHEMICAL IGNITION

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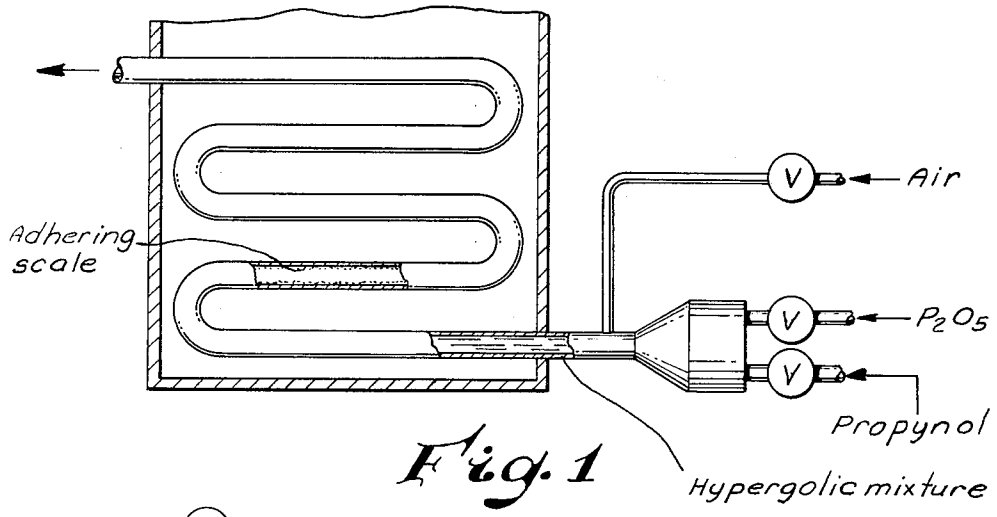


Fig. 1

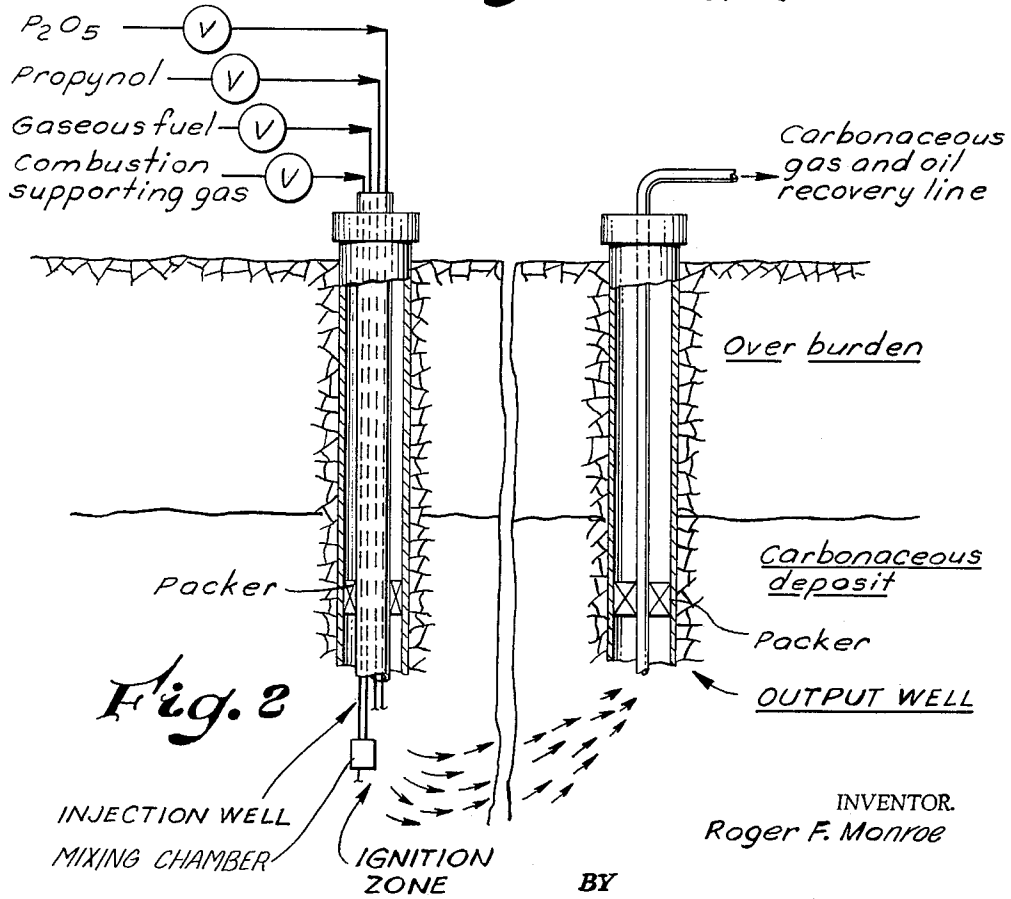


Fig. 2

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USE OF PROPYNOL IN CHEMICAL IGNITION

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The invention pertains to chemical ignition of fuels. It has application to in situ combustion of hydrocarbons, e.g., petroleum and oil shale, and to the removal by combustion of adhering carbonaceous deposits from surfaces, e.g., from petroleum refining fractionating towers, petroleum cracking units, and petroleum transfer, storage, and treating units. The term "carbonaceous" is used herein to refer to an organic carbon-containing substance consisting largely of carbon or of chemically combined carbon and hydrogen (i.e., hydrocarbons) with trace amounts of chemically combined metals, oxygen, nitrogen, sulfur, silicon, and the like and usually containing small amounts of inorganic materials.

In situ combustion is a technique employed in the production of petroleum and shale oil from a carbonaceous deposit thereof in an underground stratum comprising initiating a combustion zone in the vicinity of an injection hole or well penetrating an underground stratum, supplying oxygen or air to the zone so initiated, and causing the zone to advance into the stratum by supplying a gaseous force, usually that provided by the air or oxygen, whereby the heat of combustion of a substantial portion of the burning carbonaceous material is forced out into contiguous portions of the stratum, sweeping or driving fluid carbonaceous materials toward one or more output or production wells making possible the recovery of large amounts of commercially valuable hydrocarbons and also usually in upgrading the carbonaceous material remaining in the treated stratum. In situ combustion has been found to be an effective way of carrying out secondary recovery of petroleum, the heat of the combustion serving as the driving force (instead of more widely employed water, natural gas, or air). Such practice, commonly called fire flooding or thermal recovery of oil in place, has been found more effective in many instances than other methods of secondary recovery.

Ignition of the stratum to establish the incipient combustion zone has been usually effectuated by positioning an electric heater or an electric spark-ignited gas-fired heater, torch, or nozzle in contact with some part of the stratum, providing a flow of oxygen and illuminating gas thereto, igniting the gas by means of the heater and burning the gas until the ignition temperature of the carbonaceous material in situ is reached whereupon the flow of illuminating gas is usually discontinued. Heaters, which are of suitable design and size for lowering into the injection hole and which are equipped with illuminating gas and oxygen feed lines are commercially available from oil well supply companies for use in situ combustion purposes.

The use of fire flooding in petroleum production is definitely increasing. Most of the producers engaged in the practice prefer a gas-fired heater to initiate the combustion but have raised a number of objections to the use of an electric spark as the ignition technique. A definite demand for a more improved method of igniting the carbonaceous material in situ has arisen.

The removal of adhering carbonaceous deposits from the surfaces of equipment, particularly those with which petroleum at advanced temperatures is brought in contact, has long been a persistent problem. An expeditious procedure for its removal, where conditions permit, has been to burn such deposits in situ. Ignition of such deposits under many circumstances, e.g., in difficultly accessible coils and conduits, however, has presented an unusual problem. A need therefore, has also arisen for an improved ignition technique for use in removing adhering combustible deposits from equipment.

The invention is predicated on the discovery that when P_2O_5 and propynol are brought into contact with each other, either in the presence of air or in a CO_2 or nitrogen gas atmosphere, ignition is spontaneous and continuous until the propynol is oxidized. When such ignition is carried out in the presence of a combustion-supporting gas such as air, either at atmospheric pressures or somewhat less but preferably greater, combustible materials in contact therewith ignite during the oxidation of the propynol and continue to burn thereafter until substantially burned.

The invention, accordingly, provides a method of igniting a carbonaceous deposit of incrustations and scale, such as form on surfaces contacted by such materials, and of naturally occurring strata thereof in underground formations consisting of bringing into contact with the deposit propynol (also known as propargyl alcohol) and phosphorus pentoxide, i.e., P_2O_5.

FIGURE 1 illustrates one embodiment of the invention whereby accumulated carbonaceous deposits and scale are removed according to the invention. FIGURE 2 illustrates an embodiment of the invention whereby carbonaceous deposits in a subterranean formation are recovered by in situ combustion according to the invention.

FIGURE 1 shows P_2O_5, preferably as a pulverulent powder, entering a tube having tenaceously adhering scale, on the inner surface thereof (as shown in a broken away portion) to be removed. The P_2O_5 may be fluidized in air, if desired, at a velocity sufficient to enter the tube, but to collect near the entrance thereof on the scale-coated surface. Propynol is shown entering the same tube to come into contact with the P_2O_5 in the tube (as shown in a broken away portion) whereby a mixture is formed which spontaneously ignites and, in the presence of the combustion-supporting gas, shown also entering the tube, ignites the carbonaceous scale. Thereafter, the P_2O_5 and propynol being introduced may be greatly lessened in velocity or shut off entirely (in the case of more combustible deposits) while combustion of the thus ignited scale continues. If preferred, the air may be introduced entirely through the same inlet as the P_2O_5, or if preferred but one inlet may be used, passing successively therethrough air-borne P_2O_5, propynol, and thereafter, only the combustion-supporting gas.

FIGURE 2 shows carbonaceous subterranean mineral being recovered by the practice of the invention. P_2O_5 and propynol are being injected, either successively or simultaneously, down individual tubes located in a cased well, designated injection well, to a level below the casing, into a carbonaceous mineral deposit, e.g. oil shale or liquid petroleum. There is thereby produced a hypergolic mixture. Air or oxygen, as a combustion-supporting gas, is injected down a third tube and a gaseous fuel, e.g., illuminating gas such as natural gas or coke-oven gas. The mixture of the combustion-supporting gas and the combustible gaseous fuel are ignited by the hypergolic mixture and burn. The illuminating gas, as aforesaid, is then cut back or shut off and the combustion-supporting gas continued so that the combustion zone is moved toward the cased well designated output well. The carbonaceous deposit in the vicinity of the combustion zone is heated, at least partially liquefied and/or volatilized, and, by the aid of the injected combustion-supporting gas and heat is swept toward and up the production well. Subsequent treatment of the gas and liquid carbonaceous fluids so produced may be carried out according to known separtion and refinement techniques (not shown).

The relative amounts of the propynol and P_2O_5 are not highly critical, so long as at least about 1 part by weight

of the P_2O_5 is present per 100 parts of propynol. It is preferable to employ between about 5 and 50 parts of propynol per 100 parts of P_2O_5. When as little as 0.1 part by weight of propynol is contacted with as much as 10.0 parts by weight of P_2O_5, ignition occurs but will last only until the propynol has been oxidized. Therefore, it is suggested that a higher proportion of propynol be employed than 0.1 part per 10 parts of P_2O_5, both because a larger proportion of propynol insures a longer ignition period and because such high proportion of P_2O_5 is unjustified economically. For in situ combustion, suggested amounts to employ are from 2 to 10 pounds of P_2O_5, usually conveniently in the form of pellets, and from 2 to 10 gallons of propynol. Up to a total of about 10 percent by weight of the propynol, of diluents such as alkyl monoalcohols, hydrocarbon liquids such as kerosene, diesel fuel, and gas oils, and/or water may be employed without objectionably detracting from the efficacy of the invention.

The preferred mode of carrying out the invention is first to place pellets of P_2O_5 in contact with the deposit to be burned and thereafter add the propynol thereto. To illustrate the embodiment of the invention directed to in situ combustion of a subterranean stratum of oil or oil shale, an injection hole and at least one output hole penetrating the stratum are provided. A suitable amount of P_2O_5 pellets are lowered down the injection hole and into contact with the stratum. Thereafter, the propynol is injected down the injection hole into contact with the P_2O_5. When such contact is brought about, spontaneous combustion occurs. A supply of air or oxygen is then supplied. It is preferred, but usually unnecessary, that a supply of illuminating gas, usually natural gas, be also provided. The heat from the P_2O_5 and propynol reaction ignites the illuminating gas, if present, and then the oil or oil shale, or the oil or oil shale directly, in the absence of the gas, and in situ combustion takes place. Recovery of the products of such combustion from the output well or wells is carried out in known ways, e.g., as described in U.S. Patent 3,032,102.

A convenient and economical way of igniting oil or the like in situ according to the invention is to lower a commercially available heater provided with a nozzle and designed for underground use but without employing the accompanying means for providing electric spark. Natural gas and oxygen or air are then fed to the heater. P_2O_5, followed by the propynol, is injected into the hole in the vicinity of the nozzle of the heater. The mixture so produced ignites spontaneously and in turn ignites the oxygen-natural gas mixture at the nozzle of the heater which subsequently starts the contacting stratum on fire. The gas feed may then be discontinued. The oxygen or air flow is continued to support combustion of the oil or the like in situ and also to sweep the heat outwardly from the injection well and into the stratum in the direction of one or more output wells. Since the rate of combustion may become too great, it is sometimes advisable to provide a supply of steam or of nitrogen or other non-combustion supporting gas to supplement the sweeping action of the oxygen or air and also to dampen the combustion and maintain the desired rate of burning.

To remove adhering carbonaceous deposits such as scale or incrustations from surfaces, it is recommended that the P_2O_5 be placed in contact with the deposit and thereafter be followed by the propynol. Self ignition results immediately and, in the presence of air or oxygen, the fire propagates along the scale or incrustation until it is substantially all converted to the gaseous products of combustion and a small amount of inorganic ash. It is usually expedient and conducive to best results to force air or oxygen into the vessel or conduit at the locus where combustion is desired.

For the purpose of evaluating the efficacy of the invention, comparative tests were made as follows:

A number of chemicals were employed with P_2O_5 instead of propynol for the purpose of observing their operability for attainment of the objectives of the invention. Among those tried were 1–17 carbon atom alkyl, and alkenyl mono-alcohols and dialkyl ethers containing 1 to 8 carbon atoms per alkyl group, hydrocarbon liquids, and various aldehydes, ketones, and organic acids. Although a number of the reactants so employed as a substitute for the propynol resulted in the evolution of heat, none of them could be used for ignition purposes in accordance with the invention.

However, it was found that, if desired, the propynol could be diluted, up to about 10 percent by weight thereof, of the following liquids without objectionably adversely affecting the process of the invention: alkyl and alkenyl mono-alcohols containing from 1 to 10 carbon atoms per molecule, dialkyl ethers containing from 1 to 8 carbon atoms per alkyl group; alkanes and alkenes containing from 5 to 17 carbon atoms per molecule; naphthenes and single ring cyclodienes; single ring aromatic hydrocarbons and alkyl, alkenyl, nitro, and amino substituted derivatives thereof, and water.

Having described my invention, what I claim and desire to protect by Letters Patent is:

1. The method of igniting a carbonaceous substance by bringing P_2O_5 and propynol into contact with each other and with said substance in the presence of a combustion-supporting gas at any ambient temperature at which the propynol is a liquid.

2. The method of claim 1 wherein the P_2O_5 and propynol are employed in amounts of between about 1 and about 50 parts by weight of P_2O_5 per 100 parts of propynol.

3. The method of recovering a carbonaceous substance from an underground stratum thereof having at least two holes penetrating said stratum comprising positioning a conduit, provided with an outlet for carrying a combustion-supporting gas down one of said holes so that said outlet is in the vicinity of the stratum; placing P_2O_5 in contact with the stratum at said outlet for the combustion-supporting gas; bringing propynol into contact with the P_2O_5 to effect spontaneous ignition of the P_2O_5-propynol mixture; feeding the combustion-supporting gas through said outlet to effect combustion in situ of the carbonaceous substance and to sweep fluid hydrocarbons from the contacting zone into the stratum in the direction of and to at least one other hole penetrating the stratum; and recovering fluid hydrocarbons at said other hole.

4. The method of claim 3 wherein up to 10 percent by weight of the propynol is selected from the class consisting of alkyl and alkenyl mono-alcohols containing from 1 to 17 carbon atoms per molecule; dialkyl ethers containing 1 to 8 carbon atoms per alkyl group; alkanes and alkenes containing from 5 to 17 carbon atoms per molecule; naphthalenes and single ring cyclodienes; single ring aromatic hydrocarbons and alkyl, alkenyl, nitro, and amino substituted derivatives thereof; and water.

5. The method of recovering carbonaceous substances from an underground stratum thereof penetrated by an injection well and at least one output well comprising lowering a gas-mixing nozzle, provided with feed lines for supplying an illuminating gas and a gas containing free oxygen down the injection well to the level of said stratum; starting a flow of illuminating gas and gas containing free oxygen out of said nozzle; dropping P_2O_5 down the injection well into the vicinity of the nozzle; injecting propynol down the injection well and into contact with the P_2O_5 in an amount sufficient to provide about 100 parts by weight thereof per 1 to 50 parts of P_2O_5 to effect spontaneous ignition thereof, thereby igniting the mixture of illuminating gas and gas containing free oxygen issuing from the nozzle which in turn ignites carbonaceous substances in the stratum, thereafter; discontinuing any substantial flow of illuminating gas and continuing the flow

of gas containing free oxygen; and recovering fluid hydrocarbons at said output well.

6. The method of oxidizing a carbonaceous deposit adhering to the surface of equipment comprising bringing P_2O_5 into contact with said deposit, bringing propynol into contact with the P_2O_5 to ignite spontaneously while in contact with the deposit; introducing a gas containing free oxygen to effect ignition and combustion of the deposit and create a combustion zone; continuing to supply a gas containing free oxygen to the combustion zone to support combustion and to cause the combustion zone to propagate along said deposit until the deposit is substantially all converted to combustion gases and inorganic ash.

7. The method of initiating in situ combustion of a carbonaceous underground stratum, having a borehole penetrating said stratum, comprising injecting successively down the borehole, out of contact with each other in

the borehole during injection, and into contact with each other in the stratum, propynol and P_2O_5 at the temperature existing in the stratum.

8. The method according to claim 7 wherein P_2O_5 and propynol are employed in amounts of between about 1 and 50 parts by weight of P_2O_5 per 100 parts of propynol.

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