METHOD FOR PRODUCING OXYGENATED PRODUCTS FROM OIL SHALE

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FIG. 1

FIG. 2

PRODUCT

GAS

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METHOD FOR PRODUCING OXYGENATED PRODUCTS FROM OIL SHALE

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5 Claims

ABSTRACT OF THE DISCLOSURE

Contacting a hydrocarbon-containing shale with an oxygen-containing fluid at conditions sufficient to promote oxidation without ignition of said hydrocarbons results in an improved method for recovering hydrocarbons from hydrocarbon-yielding formations such as oil shale. This method can be conducted in situ.

This invention relates to the production of hydrocarbons and oxygenated hydrocarbons from hydrocarbon-yielding material found in formations such as oil shale. It further relates to a novel method of producing valuable hydrocarbons from oil shale.

Vast deposits of oil shale are located within the United States and are generally disposed beneath the earth surface in underground formations. The oil shale in such deposits contains hydrocarbon-yielding material known as kerogen. These hydrocarbons cannot be recovered by conventional petroleum producing methods. An efficient and economical process for the recovery of petroleum products from oil shale has long been sought. Because of the high cost of mining the shale for subsequent processing, efforts have been directed in many instances to thermal decomposition of the organic content of the shale in situ. This involves the supplying of decomposing heat from the formation and the conducting of decomposition products from such formation to surface areas. Most of the in situ processes proposed heretofore have relied in whole or in part on the burning of a portion of the hydrocarbonaceous constituent of the shale, for supplying much or all of the decomposing heat required. For this purpose, air or another oxygen-containing gas has been introduced into the formation along with heating means capable of raising the temperature of a portion of the shale to the ignition point.

An object of this invention is to recover hydrocarbons from oil shale. Another object is to produce oxygenated products from hydrocarbons contained in oil shale.

A further object is to provide a more efficient and economic method of recovering hydrocarbons from oil shale.

Other aspects, objects, and the advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawings.

According to the present invention, an improved method for recovering hydrocarbons from oil shales is provided comprising contacting said shale with an oxygen-containing fluid at temperatures and oxygen partial pressure sufficient to produce oxygenated products, without causing spontaneous combustion to occur.

Such treatment or contacting can be carried out while the oil shale remains in its natural location under ground, although it is possible to derive certain advantages of the invention by carrying out the process within a retort. In either instance, the quality of the decomposition products is superior to that of products obtained by previously known processes.

When oil shale is contacted with oxygen, the type of reaction which results depends primarily on oxygen concentration and temperature. Other lesser factors are character of the kerogen, rate of gas injection, and residence time. Spontaneous ignition temperature is relatively independent of total pressure. Therefore, oxygen concentration is directly proportional to oxygen partial pressure. At high concentrations of oxygen and/or high temperatures rapid oxidation known as combustion occurs. At temperatures and oxygen concentrations less than those necessary for ignition, i.e., the beginning of combustion, a different type of oxidation occurs. This different type of oxidation is the oxidative cleavage of the kerogen and/or bitumen which forms from low temperature pyrolysis of the kerogen. Such materials as ketones, aldehydes, alcohols, esters, etc. can be produced from the hydrocarbon-yielding substance found in oil shale by our invention.

There are a variety of workable processes that can be developed by incorporating features of our invention. Low temperature gases from 350°F. to 600°F. with varying oxygen partial pressures from 1 p.s.i.a. to 400 p.s.i.a. are injected through fractures in oil shale to produce oxygenated products. In one embodiment, the oxygenated gases can be injected through alternate fractures with products being recovered through intervening fractures. In another embodiment, higher temperatures can be used initially to establish permeability between fractures vertically. In another embodiment, after a substantial portion of the oil shale has been contacted with oxygen, a sweep of the formation with hot oxygen-free gases can be made to pyrolyze the remaining kerogen and vaporize the remaining oxygenated compounds in pyrolysis products. In another embodiment, oxygen-free fluids and oxygen-containing fluids are injected into alternate fractures at different pressures. As the temperature of the shale is gradually increased, through conduction and permeation of the gases, the oxygen content is decreased, until it is essentially zero, as the kerogen temperature reaches its spontaneous ignition conditions.

At this time a sweep of all the fractures with hot fluids can be made. The process described herein has the advantages that oxygenated compounds are recovered in the presence of oxygen and encourages the breakup of the kerogen and/or low temperature pyrolysis products at lower temperatures than would occur for ordinary pyrolysis. Part of the oxygenated compounds can be vaporized and produced at these low temperatures; however, increasing the temperature and decreasing the oxygen content of the gas will allow more to vaporize.

FIGURE 1 is a schematic view in vertical section through the ground and a strata of oil shale showing injection and production bore holes therein.

FIGURE 2 is another schematic view which in addition shows injection into alternate fractures and recovery through the remaining fractures.

FIGURE 3 is a graph of the ignition temperature of Colorado oil shale as a function of oxygen partial pressure.

FIGURE 4 is a graph of the rate of oxidation of hydrocarbons contained in oil shale as a function of temperature of the shale.

Referring to the drawings: FIGURE 1 shows multiple (two or more) fractures 1, 2, 3, 4 generated and propped between at least two wells, 5 and 6, in the oil shale 7. These fractures may be generated by any suitable means, such as forcing a fluid into the formation under sufficient pressure to rupture the formation. After the injection pressure has been released the fracture produced in the formation tends to close due to the weight of the overburden. In order to keep the fracture open, granular
insoluble solids such as sand are usually suspended in the fracturing medium. The granular solids upon being carried into the fractures act as plugs and hold open the fracture after the injection pressure is released. Although the illustrated fractures are horizontal, fractures of other orientation will also suffice. A small gas permeability in the shale between the fractures can be created by heating the shale by injection of hot gases through well 5 to a low temperature in the 300°F to 700°F range. If this step is not established, the temperature of the shale should be sufficient to produce some oxygenated hydrocarbons at the desired oxygen concentration. Heating at these temperatures causes gases to be evolved, thus creating gas permeability in the shale, since approximately 10 weight percent of the organic material is evolved in the 300 to 700°F range. These figures are for short residence times and a larger amount of evolved gases could be obtained at lower temperatures and longer residence times. Therefore, the lower limit of the temperature range is somewhat arbitrary. The purpose of this step in the process can be accomplished by injection of hot fluids into all fractures. The hot fluids can be combustion gases, super-heated steam, saturated steam, and even oxygen-containing gases provided the oxygen content is below the amount needed for spontaneous ignition of the formation.

When shale temperatures above 600°F. are used to establish the desired permeability, then the temperature of the shale should be allowed to decrease—perhaps by natural losses—below 600°F. before the next step of the process is initiated. Otherwise, the oxygen content of the formation may be sufficient to cause spontaneous combustion. Due to this complication, operating below 600°F. would be most desirable. In this step, hot fluids are not necessarily injected throughout the time for this step. Once the shale has been heated to the desired temperature, then it can be allowed to “soak” for the required residence time to produce sufficient gas permeability.

Referring now to FIGURE 2, after permeability has been established, an oxygen-containing gas can be injected through conduit 9 into alternate fractures. The oxygen content of this gas will be governed by the temperature of the formation and will be maintained at all times below the ignition concentration needed at the shale temperature. Production is through conduit 10 from fractures 2 and 4. Oxygenated compounds and pyrolysis products which are vapors at the shale temperature will be recovered at the second well 6. Alternate fractures are blocked at 11 to force the fluids into the remaining fractures.

In another embodiment, after a substantial portion of the oil shale has been contacted with oxygen, then hot, oxygen-free gases can be injected through all the fractures at temperatures in the 800°F to 1600°F. range to pyrolyze the remaining kerogen and vaporize the remaining oxygenated compounds and pyrolysis products. In this embodiment the hot, oxygen-free gases are injected through all the fractures and are produced from the same fractures.

In yet another embodiment, hot, oxygen-free gases are injected into alternate fractures 2 and 4 at a temperature higher than the shale temperature. The hot, oxygen-free gas temperature is in the 800 to 1600°F. range. The oxygen-containing gases are injected into alternate fractures 1 and 3 at a pressure higher than in fractures 2 and 4. As the temperature of the shale is gradually increased, the oxygen content is decreased, until it is essentially zero, before the shale temperature reaches 600°F. At this time, the formation can be swept through all fractures with hot, oxygen-free gases in the 800 to 1600°F. range until the shale is exhausted.

EXAMPLE

Recent work on differential thermal analysis of oil shale in the presence of oxygen at a partial pressure of 105 p.s.i. of oxygen showed that oxidation begins as low as 104°F. At 105 p.s.i. oxygen partial pressure, the corresponding ignition temperature is slightly above 375°F. These data indicate that oxidation occurs much below the spontaneous combustion point of 375°F, having started at 104°F.

Ignition temperature as a function of oxygen partial pressure for data covering several oxygen concentrations in the gas stream has been reported in volume 59, No. 3, July 1964, of the Quarterly of the Colorado School of Mines, pp. 55–58. This graph has been reproduced in FIGURE 3.

FIGURE 4 is a graph of the rate of oxidation of hydrocarbons contained in oil shale as a function of temperature. This plot was obtained from differential thermal analysis data. Partial oxidation occurs at zero on this curve and continues as the temperature increases from left to right. The upper limit of temperature (the spontaneous ignition temperature) is obtained from FIGURE 3 at some specified oxygen pressure.

Those modifications and equivalents which fall within the spirit of the invention and the scope of the appended claims are to be considered part of the invention.

We claim:

1. A process for producing oil and oxygenated products in situ from a subterranean oil shale stratum containing kerogen, a hydrocarbon-yielding material, penetrated by at least two spaced-apart boreholes comprising the steps of:

(a) fracturing an area in said stratum surrounding said boreholes so as to form artificial cracks or crevices in said stratum connecting said boreholes,

(b) introducing a propping agent into said cracks or crevices to hold same open,

(c) injecting an oxygen-containing fluid having an oxygen partial pressure ranging from 1 p.s.i.a. to 400 p.s.i.a., and having a temperature ranging from 350–600°F., into said stratum through one of said boreholes so as to form oxygenated products from said kerogen without causing spontaneous combustion or ignition of said kerogen to produce oil and oxygenated products including ketones, aldehydes, alcohols, esters, etc., from the hydrocarbon-yielding material present in oil shale,

(d) thereafter injecting an inert gas heated to a temperature in the range 800–1600°F., into said stratum through one of said boreholes to pyrolyze the remaining kerogen and vaporize remaining oxygenated and pyrolysis products and drive same from surrounding stratum to at least one of said boreholes, and

(e) recovering from at least one other of said boreholes oil and oxygenated products driven from said stratum by said heated inert gas.

2. The method of claim 1 wherein the oxygen partial pressure of said oxygen-containing fluid is controlled by decreasing the oxygen content as the temperature of the oil shale stratum is increased until the oxygen content is essentially 0 before the kerogen temperature reaches said spontaneous ignition conditions.

3. The method of claim 2 wherein the oxygen content of said oxygen-containing fluid is reduced to 0 before the kerogen reaches a temperature of 600°F, and further wherein the inert gas used in step (d) is combustion gases or steam.

4. The method of claim 1 further comprising creating permeability between said propped fractures by injecting fluid heated from 300–700°F. into said stratum and further wherein said propping agent is granular insoluble solid.

5. The method of claim 1 wherein said oxygen-containing fluid is injected into alternate fractures and further wherein oxygen-free fluids at a temperature of 800–1600°F. are injected into the remaining fractures at a lower pressure than said oxygen-containing fluid.

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