METHOD OF RECOVERING OIL FROM OIL SHALE

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INVENTOR.

J. W. MARTIN

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METHOD OF RECOVERING OIL FROM OIL SHALE

James W. Martin, Tuckahoe, N. Y., assignor to Carbonic Products, Inc., New York, N. Y., a corporation of New York

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The present invention relates to a method of recovering oil from oil shale in situ, and, more particularly, to an improved method of destructively distilling oil shale in situ by using a combustion-supporting gas containing carbon dioxide and oxygen in a critical ratio.

It is well known that heretofore the conventional method of obtaining oil from oil shale involved the mining of the shale from the ground, its preparation for thermal treatment in retorts and its subsequent destructive distillation in retorts by heat, the recovery of oils and by-products from the vapors and gases distilled from the retorts, and the removal of the residual spent shale from such retorts and its subsequent combustion under the retorts to supply some of the heat. Attempts have been made to replace the conventional destructive distillation of oil shale in surface plants with the usual retort and recovery equipment with processes which attempted to destructively distill the oil shale in situ in the ground. These attempts included heating the oil shale in the ground by electricity and heating the oil shale by hot combustion gases piped down into the shale structure from the surface air burners burned fuel. Other attempts have involved the use of air to burn carbonaceous material of the oil shale under ground, but this attempt has proven unsatisfactory because nitrogen, which constitutes about 80% of the air, tended to dilute the off-coming combustion gases and rendered them unsuitable for proper recovery and commercial use. When attempts were made to use pure oxygen, it was found that it was so concentrated in its oxidizing effect that the temperature of combustion was uncontrollably high and excessive. The problem is to destructively distill the volatile compounds from the oil shale in situ in such a manner as to obtain the maximum amount of the carbon and hydrogen in the oil shale as volatile compounds of these two elements. While attempts have been made to solve the problem and to overcome the shortcomings and disadvantages of the conventional methods, none, as far as I am aware, have been wholly satisfactory in commercial operations.

I have discovered an improved method of destructively distilling oil shale in situ which overcomes the disadvantages of the prior methods and attempts and which provides the art with new results.

It is an object of the present invention to provide a process for the destructive distillation of oil shale in situ by means of low temperature, underground combustion which promotes greater yields of volatile hydrocarbons which lessens the cracking of hydrocarbons and which lessens or prevents slagging of the spent shale and thus permits the cinder to remain porous to the flow of oxidizing and other gases.

Another object of the invention is to provide an improved process for the destructive distillation of oil shale in situ in which gaseous products of combustion (fuel gases) with highest heat content are effectively utilized.

The invention also contemplates providing an improved process for the destructive distillation of oil shale in situ wherein means will be utilized to limit the formation of viscous tar which will be difficult to remove from the shale beds.

It is a further object of the invention to provide an improved process for the destructive distillation of oil shale in situ wherein means will be used to limit the formation of hydrogen and light hydrocarbon gases.

The invention further contemplates providing an improved process for the destructive distillation of oil shale in situ wherein a lessening of the cracking of volatile hydrocarbons will be accomplished.

It is likewise within the contemplation of the invention to provide an improved process for the destructive distillation of oil shale in situ which will cause a fixation and recovery of ammonia, urea, and other similar nitrogen compounds.

It is also an object of the invention to provide a process for the destructive distillation of oil shale in situ to effect an improved recovery of hydrocarbons.

Among the further objects of the present invention is the provision of an improved process for the destructive distillation of oil shale in situ which will prevent relatively high temperatures in the zone of destructive distillation of oil shale, which will maintain relatively low temperatures in the combustion zone, and which will bathe the zone of destructive distillation with carbon dioxide and thus mix carbon dioxide with resultant hydrocarbons, that cracking of these volatile hydrocarbons is kept at a minimum, that the evolution of hydrocarbons is promoted by the permeation action of carbon dioxide, that the formation of more volatile hydrocarbons through combination with carbon dioxide is increased and that ammoniacal compounds are fixed with carbon dioxide to prevent their loss in exit gases from condensers.

Other objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying
drawing which illustrates diagrammatically an oil shale structure and equipment necessary to carry the novel process into practice. Broadly stated, the invention contemplates a solution to the vexatious problem confronting the art by effecting a combustion of fixed carbon of oil shale in situ by a gaseous mixture of oxygen and carbon dioxide in critical proportions. By utilizing this special mixture containing oxygen and carbon dioxide in critical proportions, a relatively low and regulated temperature can be obtained. The temperature in the combustion zone within the oil shale structure is preferably kept below about 1000°C to limit the formation of carbon monoxide. Furthermore, the temperatures in the zones of destructive distillation are controlled to a temperature range above about 400°C and below about 600°C. Such regulation can be effected by controlling the ratio of carbon dioxide to oxygen in the oxidizing gas fed into the combustion zone. The normal reaction of combustion is:

\[ \text{C} + \text{O}_2 = \text{CO}_2 + 14,600 \text{ B. t. u.'s} \]

However, in the presence of an excess amount of carbon dioxide and a temperature in the neighborhood of about 1000°C, the following combustion reaction occurs:

\[ \text{CO}_2 + \text{C} = 2\text{CO} - 5,850 \text{ B. t. u.'s} \]

Thus, in the presence of carbon dioxide, two reactions are possible, one exothermic and the other endothermic. By the use of a predetermined and critical oxygen:carbon dioxide ratio, the temperature can be held relatively uniform across the burning face and the average temperature automatically controlled. The temperature can be further limited and controlled by the diluting effect of the excess carbon dioxide. By such control of oxygen:carbon dioxide ratio not only can the temperature be controlled, but also the carbon monoxide content of the flue gases from the combustion zone can be kept at a minimum.

The regulation of the temperatures in the zone of destructive distillation has a most desirable effect. It has been found that as the temperature of the shale increases above 600°C, carbon to hydrogen linkages tend to be progressively broken down and also as the temperature rises, the average molecular weight of the volatile products tend to decrease and the evolution of hydrogen, carbon monoxide, methane, etc., increase. It has further been found that in the presence of an excess of carbon dioxide (above 80% in the flue gases) the following desirable effects take place:

(a) The carbon dioxide forms loose temporary compounds with the hydrocarbons as they cool and tend to make these compounds more volatile and thus more quickly and completely removed from the shale.

(b) The carbon dioxide under the conditions brought about in the shale structure will permeate even the smallest of interstices in the structure purging the hydrocarbons that have been adsorbed therein. Such interstices may be native to the structure or deformed by heat or by explosions.

(c) The carbon dioxide under the conditions above described tends to preserve carbon to hydrogen linkages.

(d) Carbon dioxide volumetrically having substantially (almost double) higher specific heat (heat content) than carbon monoxide, nitrogen or other common flue gases, carries more of the heat of combustion to the undecomposed oil shale.

Generally speaking, my improved process for the destructive distillation of oil shale in situ includes the following:

1. The maintenance of predetermined, controlled temperatures, such as about from 400°C to about 600°C, in the heating zone of a system for the distillation of hydrocarbons from their underground sources.

2. The use of a fluid chemical, such as carbon dioxide, having the property of preserving the carbon-hydrogen linkages during the process of distillation.

3. The use of a fluid which has the properties of being selectively adsorbed in the porous underground structure so as to replace hydrocarbons already adsorbed.

4. The use of a fluid which has a high heat content to convey heat from combustion zone to zone of distillation.

5. The use of a fluid which will promote the formation of more volatile hydrocarbon compounds.

6. The use of a fluid which is of acid nature so as to fix and render non-volatile at condenser temperatures, the ammoniacal compounds distilled.

In carrying my invention into practice, it is preferred to control the combustion temperature by the use of a predetermined and critical oxygen:carbon dioxide ratio in the oxidizing gas. The use of carbon dioxide in the optimum proportion possible to support combustion (say above 20%) in an oxidizing gas mixture is preferred. In order to convey the maximum heat per cubic foot from a combustion zone to a zone in which the heat is required (reaction zone). The use of carbon dioxide as an additive to hydrocarbons at reactive temperatures tends to preserve carbon-hydrogen linkages. The use of carbon dioxide tends to purge out volatile hydrocarbons adsorbed in the interstices of an underground structure, either natural or deformed. The use of carbon dioxide tends to form unstable compounds with the heavier (large molecule) hydrocarbons under pressure, which compounds are found to be more volatile than the heavier hydrocarbons. The use of carbon dioxide in ammoniacal-hydrocarbon mixtures tends to fix the ammonia gas as compounds that will separate readily from hydrocarbons in any suitable condensing system.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative example is given:

Oxygen from oxygen tower 1 is driven by compressor 2 into pipe 3 along with carbon dioxide from Dry Ice liquefier 4. The mixture is regulated by valves 5 and 6 and its composition shown on indicator 7 and the temperature of combustion shown by thermometer 8. This oxidizing mixture is driven through pipe 3 to the oil shale structure at the bottom of inlet well 9. In combustion chamber or space 10 (made, for example, by prior use of an explosive) ignition is started by electric spark, thermite or any chemical capable of igniting the oil shale. For a short period of time products and distillation exit through the casing of inlet well 9 and are wasted. As soon as ignition is well started sufficient pressure is built up in the combustion chamber space well up in the oil shale structure to outlet well 11 which may be, say, 50 feet from well 9. In passing through the oil shale zone 12 the hot combustion gas distills out of the oil shale the hydrocarbons resulting from its destruction. There re-
mains in the oil shale a large part of this fixed carbon, in the form of coke. This carbon is burned by the oxidizing gases in zone 13 to furnish the hot combustion gases mentioned herebefore. In the system described, the shale sometimes is sufficiently dense that the combustion gases cannot penetrate the outlet well 11. In this case, the structure may be cracked by use of explosives, so as to establish a cracked and permeable zone 11-Z and to permit the passage of these gases from combustion zone 13, to outlet well 11. The process for destructive distillation of the oil shale is accompanied by the products of combustion and the excess carbon dioxide, flow via the open end or port 11-O and via a plurality of perforations in a perforated zone 11-P of well 11 and thence upwardly through well 11 to condenser 14. As is well known, the condenser is provided with a coolant, such as cooling water, which enters coolant inlet 14-I and leaves via coolant outlet 14-O. In addition, condensing water is introduced into the condenser near the top plates thereof via water inlet 14-W and leaves the condenser at an intermediate zone thereof, preferably at a plate located just above the middle thereof, via an outlet 14-RS. In the separate sections or plates of the condenser the heavier hydrocarbons are condensed and are discharged via hydrocarbon outlet 14-H, the water soluble compounds are removed by water via water soluble outlet 14-RS, and the fixed gases are permitted to escape via vent 14-V, as those skilled in the art will readily understand. In some instances, it may be desirable to place some restriction in the outlet gases from the top of the condensing tower as a control valve V-1 or a control valve V-2 in the gas inlet pipe at the bottom of the condenser in order to maintain a back pressure on the burning zone within the oil shale structure. The character of the distillate is somewhat improved by the distillation under pressure. I have found as a result of tests that combustion under pressure is feasible and readily controlled.

The fixed gases may be separated from the carbon dioxide in water under pressure in carbon dioxide separator 8 or by means of chemicals, the remaining gases, mostly combustible, may be either further separated or used for fuel. In some cases where the combustible gases mixed with the carbon dioxide are in relatively small amounts, this latter separation process may be omitted. The carbon dioxide is returned to a compressor 15 where it is compressed and is again cycled and mixed with oxygen to form oxidizing gas described hereinbefore.

It is to be observed that the present invention provides an improved process for the destructive distillation of oil shale in situ involving the following features:

1. The use of carbon dioxide as a diluent of oxygen to reduce and control temperatures of combustion.

2. The use of an oxidizing gas that yields as a flue gas a high concentration of carbon dioxide because of the superior heat carrying capacity per cubic foot of gas of carbon dioxide over the customary flue gases which normally consists of a mixture of gases in which more than 75% is nitrogen. Nitrogen, I find, has volumetrically approximately three-fourths to half of the heat carrying capacity of carbon dioxide.

3. The mixing of the flue gas with the products of combustion.

4. The use of carbon dioxide in such a flue gas to purge out adsorbed hydrocarbons.

5. The use of carbon dioxide in place of the customary sulfuric acid to fix the ammoniacal compounds in the distillation products.

6. Carbon dioxide is one of the few commercial gases which may be readily condensed by increased pressure and reduced temperature so as to separate it from the less condensible gases such as lighter hydrocarbons, nitrogen, monoxide, etc.

Moreover, it is to be appreciated that the present invention provides an improved process for the destructive distillation of oil shale in situ having the following advantageous points:

1. A control of combustion temperatures by varying the percentage of carbon dioxide in the oxidizing gases.

2. The formation of a flue gas that is essentially carbon dioxide and the mixing of such a gas with the products of destructive distillation.

3. The use of a gas substantially carbon dioxide in underground distillation as the conveyer of heat.

4. The use of carbon dioxide to purge out of natural underground structures, hydrocarbons adsorbed therein.

5. In the destructive distillation of oil shale, coal, etc., the introduction of gases rich in carbon dioxide into the reaction zone to prevent cracking and to promote the preservation of carbon-hydrogen linkages.

6. The use of carbon dioxide to promote the formation of more volatile hydrocarbon compounds resulting from a destructive distillation.

7. The use of carbon dioxide in ammonia-hydrocarbon mixtures to promote the separation of ammonia and kindred compounds from hydrocarbon mixtures during the process of condensation.

8. Operations for maintaining a free burning surface by the prevention of the formation of an occluding curtain of slag.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. An improved method of destructively distilling oil shale in situ by using a combustion well and an exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supporting gas containing carbon dioxide and oxygen in a critical ratio which comprises drawing oxygen from an oxygen tower to provide a supply of oxygen, obtaining carbon dioxide from a Dry Ice liquefier to provide a supply of carbon dioxide, forming an oxidizing gas mixture with said oxygen and said carbon dioxide, forcing said oxidizing gas mixture under pressure down into a combustion well extending into an oil shale structure, starting combustion in a combustion zone adjacent to the base of a combustion well in said oil shale struc-
ture, regulating the composition of said gas mixture to provide a special mixture containing oxygen and carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure.

2. An improved method of destructively distilling oil shale in situ by using a combustion-supporting gas containing carbon dioxide and oxygen in a critical ratio which comprises forcing an oxidizing gas mixture containing carbon dioxide and oxygen in a critical ratio which comprises forcing an oxidizing gas mixture containing carbon dioxide and oxygen in a critical ratio at a temperature at a relatively low and regulated temperature by using a critical amount of said hydrocarbons and oxygen in a critical ratio which comprises forcing an oxidizing gas mixture containing carbon dioxide and oxygen in a critical ratio to volatile hydrocarbons from said oil shale, maintaining a controlled temperature below 1000° C in said combustion zone and below at least 1000° C in said combustion zone, and an exhaust well extending from the surface of the earth into an oil shale structure.

3. An improved method of destructively distilling oil shale in situ by using a combustion well and an exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure.

4. An improved method of destructively distilling oil shale in situ by using a combustion well and an exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure.

5. An improved method of destructively distilling oil shale in situ by using a combustion well and an exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supplying gas containing carbon dioxide in critical proportion and subject to said exhaust well extending from the surface of the earth into an oil shale structure.
mixture containing carbon dioxide and oxygen in critical proportions under pressure down into a combustion well located in an oil shale structure, burning oil shale in a combustion zone in the presence of a critical amount of carbon dioxide above 20% at the base of said combustion well with the aid of said oxygen whereby heat is generated at a relatively low and regulated temperature and hot combustion gases are produced containing a critical amount of carbon dioxide, maintaining a critical amount of carbon dioxide in said combustion gases above 80% to provide relatively low and regulated temperatures passing hot combustion gases at relatively low and regulated temperatures through an oil shale structure to destructively distill the same to produce volatilized hydrocarbons in the presence of a critical amount of carbon dioxide whereby the liberation of said hydrocarbons is facilitated, withdrawing said gases containing said hydrocarbons and carbon dioxide in a critical amount above 80% through an exhaust well to the surface of the earth, and recovering hydrocarbons from said gases whereby greater yields of volatile hydrocarbons are recovered from said oil shale while at the same time the spent shale is prevented from slagging and the cinder is maintained porous to said gas mixture.

6. An improved method of destructively distilling oil shale in situ by using a combustion well and an exhaust well extending from the surface of the earth into an oil shale structure and by using a combustion-supporting gas containing carbon dioxide and oxygen in a critical ratio which comprises forcing an oxidizing gas mixture containing carbon dioxide and oxygen under pressure into a combustion well located in an oil shale structure; regulating the composition of said gas mixture to provide sufficient oxygen to support combustion and to provide an excess of carbon dioxide thereby controlling combustion, maintaining a relatively low temperature, facilitating the evolution of hydrocarbons from said oil shale, preventing cracking of said volatilized hydrocarbons and promoting the preservation of carbon-hydrogen linkages; burning oil shale in a combustion zone in the presence of a critical amount of carbon dioxide above 20% at the base of said combustion well with the aid of said oxygen whereby heat is generated at a relatively low and regulated temperature and hot combustion gases are produced containing a minimum amount of carbon monoxide; maintaining a critical amount of carbon dioxide in said oxidizing gas mixture and in said combustion gases; passing said combustion gases at relatively low and regulated temperatures through an oil shale structure to destructively distill the same to produce volatilized hydrocarbons in the presence of a critical amount of carbon dioxide and a minimum amount of carbon monoxide whereby the liberation of said hydrocarbons is facilitated, withdrawing said gases containing said hydrocarbons and carbon dioxide in a critical amount and carbon monoxide in a minimum amount through an exhaust well to the surface of the earth; and recovering hydrocarbons from said gases whereby greater yields of volatile hydrocarbons are recovered from said oil shale while at the same time the spent shale is prevented from slagging and the cinder is maintained porous to said gas mixture.

7. The improved method set forth in claim 1 in which the gases from the exhaust well after the recovery of hydrocarbons are treated to separate carbon dioxide for re-cycling to the combustion well and re-used therein.

JAMES W. MARTIN.

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