Dec. 30, 1969 K. L. BERRY 3,487,004

# CATALYTIC OXIDATION IN OIL SHALE RETORTING

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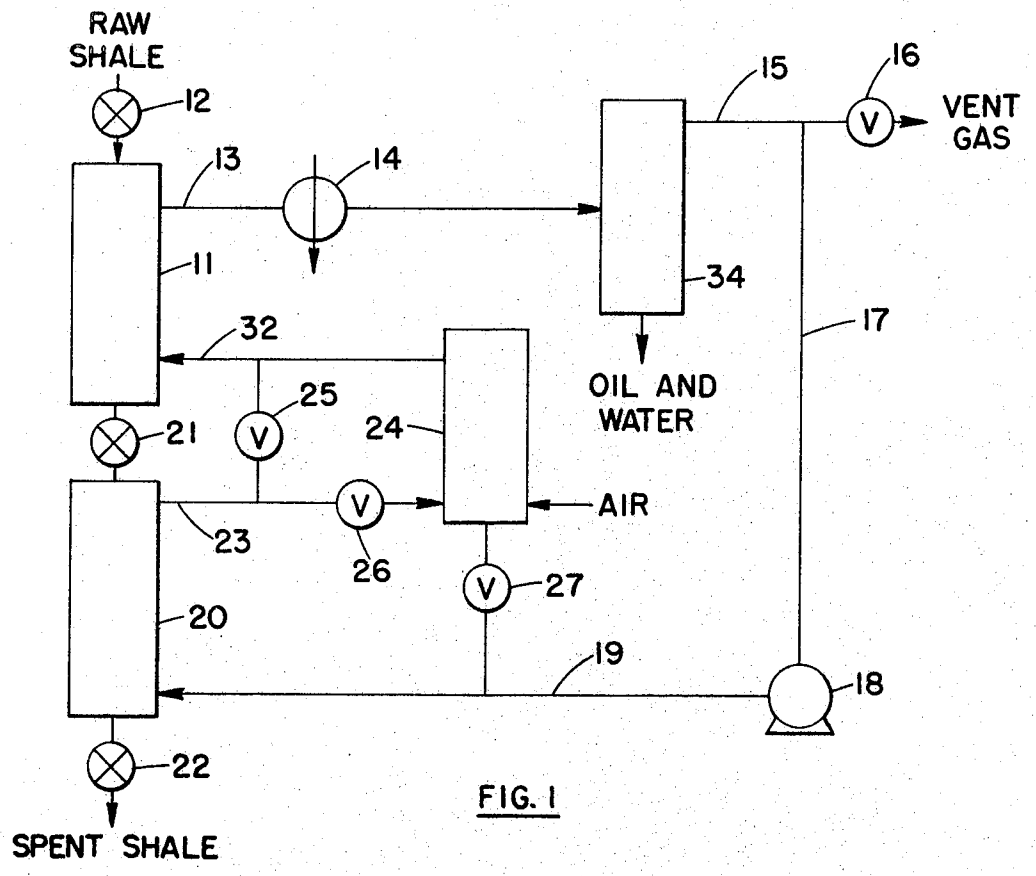



FIG. 1

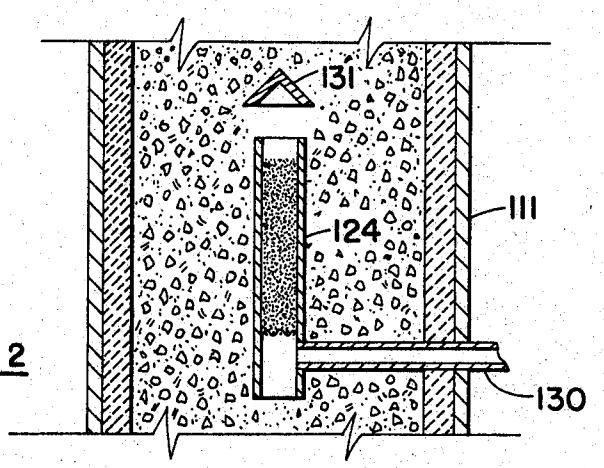



FIG. 2

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# CATALYTIC OXIDATION IN OIL SHALE RETORTING

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## ABSTRACT OF THE DISCLOSURE

In a retort for the recovery of oil from oil shale, hot gases for the retorting are prepared by controlled oxidation of recycled product gases. The oxidation is confined to burners within the retort by the placing of an oxidation catalyst within the burners and the limiting of air introduced into the burners. Retorting temperature is thus maintained between 800° F and 1,300° F.

Several ways have been proposed for heating oil shale to produce oil. In one method, a combustion zone is maintained in a moving bed of oil shale. Air is fed to this combustion zone. The air burns part of the carbonaceous materials in the oil shale to provide the necessary heat.

There have been two principal difficulties with such combustion processes. First, about 25 percent of the condensable oil vapors remains in the gas when the products from the retort are cooled to a temperature of about 100° F. Second, in spite of this large loss of oil vapors in the product gases, the heating value of the gases is normally only about 100 to 150 B.t.u. per cubic foot. Sometimes the heating value is even less.

The explanation of the apparently anomalous difficulties is the presence of large volumes of nitrogen, carbon dioxide and carbon monoxide in the product gases. A large amount of air must be introduced to maintain combustion temperatures in the retort. This introduces a large volume of nitrogen. The combustion of the large volume of air with carbonaceous materials produces large volumes of carbon dioxide and carbon monoxide. The high combustion temperatures of 2,500° F. or higher causes endothermic inorganic reactions, such as decomposition of calcium carbonate, thus producing additional carbon dioxide. Considerable additional quantities of heat are required to decompose inorganic carbonates, drive off water of crystallization, etc. This further increases the amount of air which must be introduced to provide the necessary additional heat. The high combustion temperature also causes inordinate cracking of any exposed organic material producing more low molecular weight hydrocarbons which are more difficult to recover.

An object of this invention is to provide a combustion process to generate retorting temperatures without the use of large volumes of air. Another object is to decrease the retorting temperature to reduce the formation of carbon dioxide from the decomposition of inorganic carbonates, and thus reduce the amount of air required to provide the heat of decomposition, and to decrease the decomposition of higher molecular weight compounds into methane, ethane, and the like. Still other objects will be apparent to those skilled in the art from the following description and claims.

In general, I accomplish the objects of my invention by burning recycled product gases to provide retorting heat, the combustion being carried out in the presence of an oxidation catalyst, so that the combustion can occur at low temperatures.

In the drawing, FIGURE 1 is a flow diagram of the preferred embodiment of my invention in which the



combustion operation is carried out in a burner outside the retort. FIGURE 2 is a view in cross-section of a portion of a retort with the burner inside the retort.

Considering FIGURE 1 in more detail, a preferred operating procedure will first be described. Raw shale is fed to retort **11** by feeding mechanism **12**, such as a star feeder. The raw shale moves downwardly in the retort countercurrent to upwardly rising hot gases introduced through line **32**. The gas heats the shale to release oil vapors which are swept out of the retort through line **13**, cooler **14**, and on to separator **34**. Oil and water are withdrawn from the bottom of separator **34**.

Product gases are withdrawn from the top of separator **34** through line **15**. Gases not required for recirculation to the retort are withdrawn through valve **16**. Recycled gases pass through line **17** to blower, compressor, or pump **18**. This pump forces the recycled gases through line **19** into the bottom of heat recovery vessel **20**. Here, the recycled gases are heated by downwardly moving hot shale from retort **11**. Feeder mechanism **21** transfers hot shale from retort **11** to heat recovery vessel **20**. Feeder mechanism **22** removes the cooled, spent shale from vessel **20**.

The heated recycled gases are withdrawn from vessel **20** through line **23** through which they flow to burner **24**. Burner **24** is filled with an oxidation catalyst such as platinum, vanadium pentoxide, molybdenum trioxide, or the like. The nature of the catalyst forms no part of this invention, many suitable catalysts being known in the art. For a more detailed description, see, for example, Catalysis VII—Oxidation, Hydration, Cracking Catalysts, by Paul H. Emmett, Reinhold Publishing Corporation, 1960 ed. These catalytic materials are preferably supported in low concentration on the surfaces of particles of porous solids, such as alumina, pumice, or the like. The catalyst concentration on the supporting material may be on the order of 0.05 percent to 0.5 percent by weight of the supporting solid, for example.

Air is introduced into burner 24. Low temperature combustion takes place between the air and hydrocarbons in the presence of the catalyst. The amount of air is controlled to provide an exit gas temperature of at least about 800° F. but not more than about 1,300° F., and preferably between about 950° F. and 1,150° F. This hot gas passes through line **32** to retort **11** as previously described. One example of apparatus, except for the burner, suitable for my purposes, is shown in U.S. Patent 2,812,288 Lankford et al.

Since the heat requirements are reduced, air requirements are less and there is a resulting decrease in nitrogen and carbon dioxide in product gases. Methane and ethane and lower molecular weight oil vapors production are also less due to the lower temperatures. Decomposition of inorganic carbonates is essentially eliminated by operating at temperatures below 1,300° F. Consequently, carbon dioxide production is further reduced. In addition, the heat of decomposition of inorganic carbonates need not be added, so even less air is required. The over-all result is that organic materials are present in much higher concentrations in product gases leaving the retort. These higher concentrations, in turn, faciltate recovery of a larger percentage of the kerogen decomposition products as a liquid product. A smaller percentage of kerogen decomposition products appears in the vent gas from the separator.

It is true that the heating value of produced gas from the separator is not much higher than in the prior art processes. The quantity of gas, however, is decreased. In addition, in my process at least a part of this gas is used internally in the process to provide the restoring heat. Burning of organic vapors, including some normally liquid ones, in the retort is avoided, thus even further increasing

the quantity of liquid hydrocarbons recoverable from a given weight of shale.

When the gases are partially burned in catalytic burner **24** of FIGURE 1, some coke formation can be expected. For this reason, it is generally advisable to provide two burners so one can be operating while the carbon is burned off the catalyst in the other one.

Several alternate methods of operation should now be considered. Valve **25** may be opened allowing at least part of the recycled gases to bypass burner **24** and flow directly from heat recovery vessel **20** to retort **11**. The remainder of the gas passes through valve **26** to burner **24**. Hot gases from the burner are then mixed with cooler gases coming through valve **25**. The amounts of air and gas fed to burner **24** are controlled to provide the desired temperature in the total mixture of gases fed through line **32** to retort **11**. If desired valve **26** can be closed and cool gas can be taken through valve **27** to the burner. The advantage of feeding cool gas to the burner is that the combustible materials in the gas passing to the burner can be more completely burned than if hot gases are fed to the burner. More heat is required to raise the temperature of the cool gases to the required temperature. Due to the more complete combustion, there is less coke formation in the burner. It is also possible to adjust the ratio of gases bypassing the burner to those passing through the burner in order to permit more complete combustion of hydrocarbons in the bases flowing through the burner. When bypass valve **25** is open, the burner is operated to provide hot gases with a temperature somewhat above that required in the retort. If desired, valve **25** can be used as a control valve to adjust the temperature of gas entering the retort to exactly the desired temperature.

In FIGURE 2, burner **124** is placed within retort **111**. Air is introduced through line **130**. Gases enter the open bottom of the burner and rise upwardly with the air through the burner. A guard cap **131** is preferably spaced above the open top of the burner to direct the downwardly moving shale away from the open top of the burner. Preferably, several burners are used in the retort. In the arrangement of FIGURE 2, the remainder of the apparatus may be as shown, as for example, in U.S. Patent 2,813,823 Putman.

In operating the apparatus of FIGURE 2, much of the recycled gas moving upwardly through the retort passes around the burners rather than through them. Therefore, it is necessary to operate the burners to produce a gas at a somewhat higher temperature than the retorting temperature desired. This hotter gas then mixes with the cooler gas rising around the outside of the burners to provide a total mixed retorting gas having a temperature of not more than about 1,300° F. Several variations and modifications of my process have been described above. These are given by way of example only. Others will be apparent to those skilled in the art. For example, the shale may move up, down or horizontally in vertical, horizontal or even diagonal retorts as long as it moves countercurrent to the hot retorting gases. The same is true of the heat recovery chamber, if this is separated from the retort. Such systems are described, for example, in U.S. Patents 1,523,942 and 2,640,019. I do not wish to be limited to the examples given above, but only by the following claims.

I claim:

**1.** In a process for retorting oil shale in which the oil shale moves countercurrent to recycled gases in a retort, the gases being heated sufficiently to release normally liquid organic materials from the shale, the heat being provided by contact of the gases with hot spent shale and by at least one burner chamber positioned within said retort so that gases flow from the retort, through the burner chamber and back into the retort and air is introduced into said burner to burn combustible materials in the gases flowing through said burner, the improvement comprising placing an oxidation catalyst in said burner so oxidation can take place at a low temperature and introducing sufficient air into the burner to raise the temperature of the total hot gases contacting the shale in said retort to a temperature of at least about 800° F. but not more than about 1,300° F., the amount of air being sufficiently limited to substantially avoid burning of organic vapors in the retort outside the burner.

**2.** The process of claim **1** in which the temperature of said total hot gases is between about 950° F. and about 1,150° F.

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U.S. Cl. X.R.

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