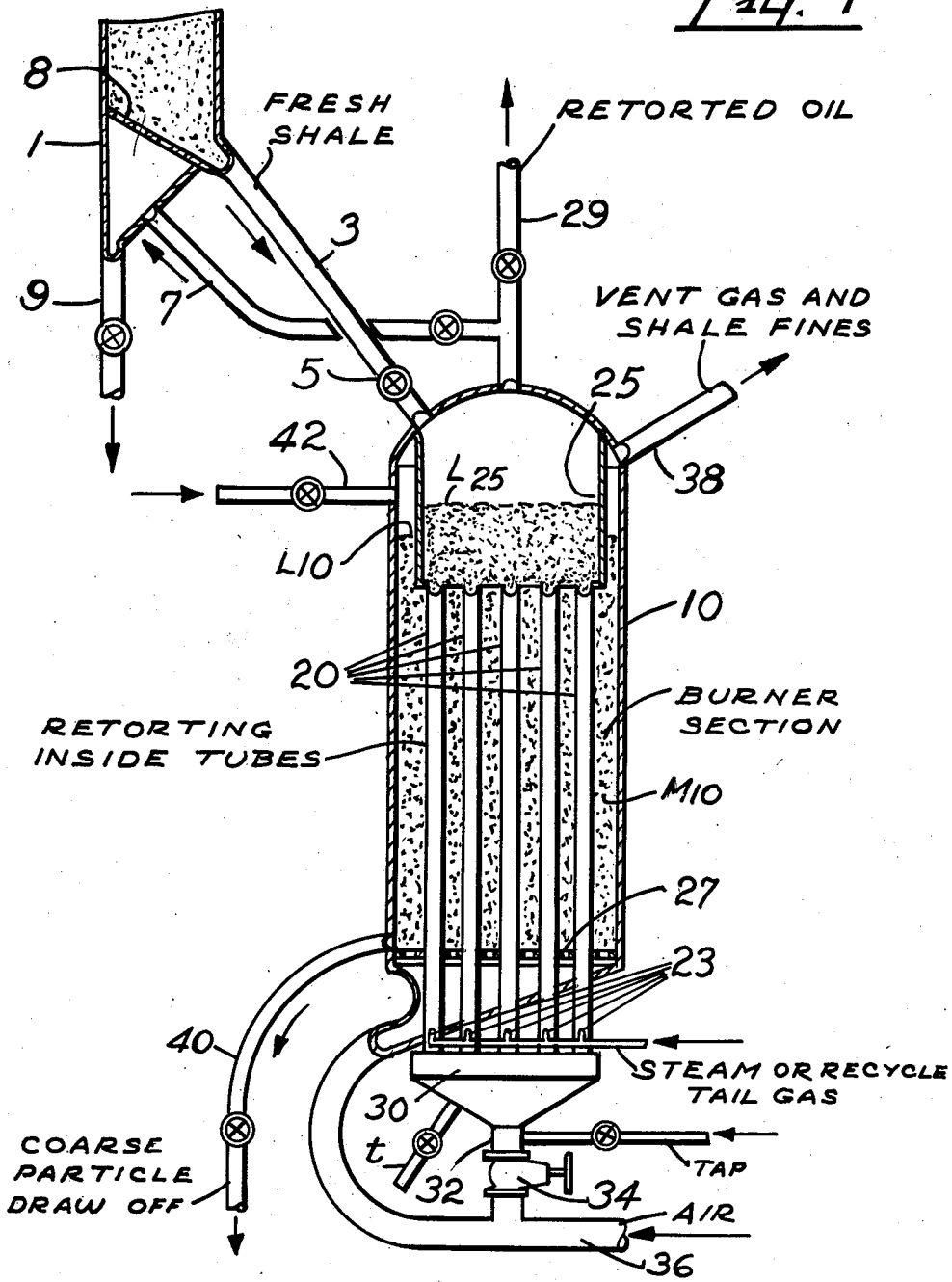
Feb. 8, 1955 C. E. HEMMINGER ET AL 2,701,787

DISTILLATION OF OIL-BEARING MINERALS

Filed Dec. 23, 1949 5 Sheets-Sheet 1

Fig. -1



Charles E. Hemminger, Inventors
Edward W. S. Nicholson
Alexis Voorhies, Jr.
By J. Cashman Attorney

Feb. 8, 1955 C. E. HEMMINGER ET AL 2,701,787

DISTILLATION OF OIL-BEARING MINERALS

Filed Dec. 23, 1949 5 Sheets-Sheet 2

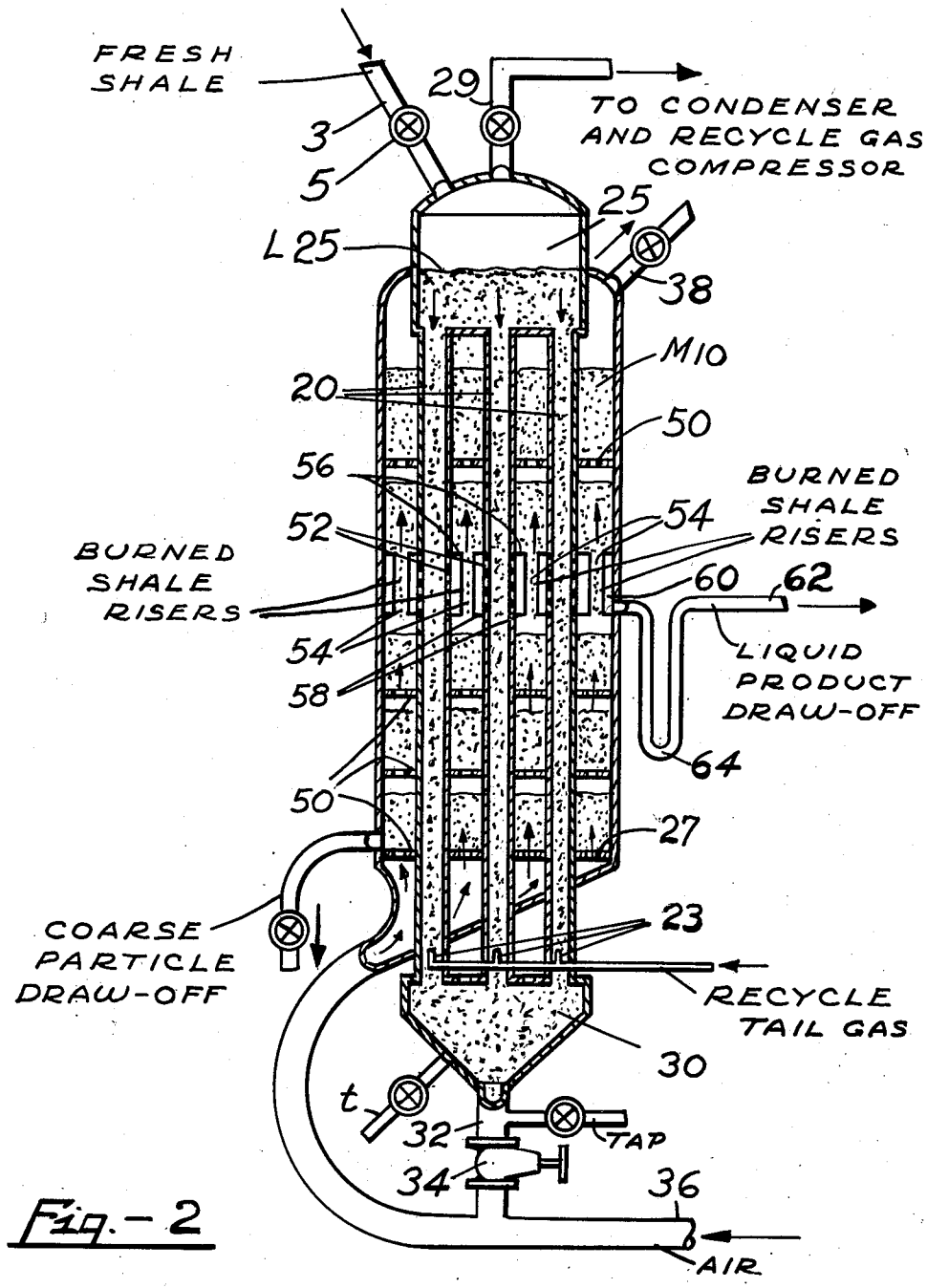


Fig. - 2

Charles E. Hemminger Inventors
Edward W. S. Nicholson
Alexis Voorhies, Jr.
By J. Cashman Attorney

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DISTILLATION OF OIL-BEARING MINERALS

Filed Dec. 23, 1949 5 Sheets-Sheet 3

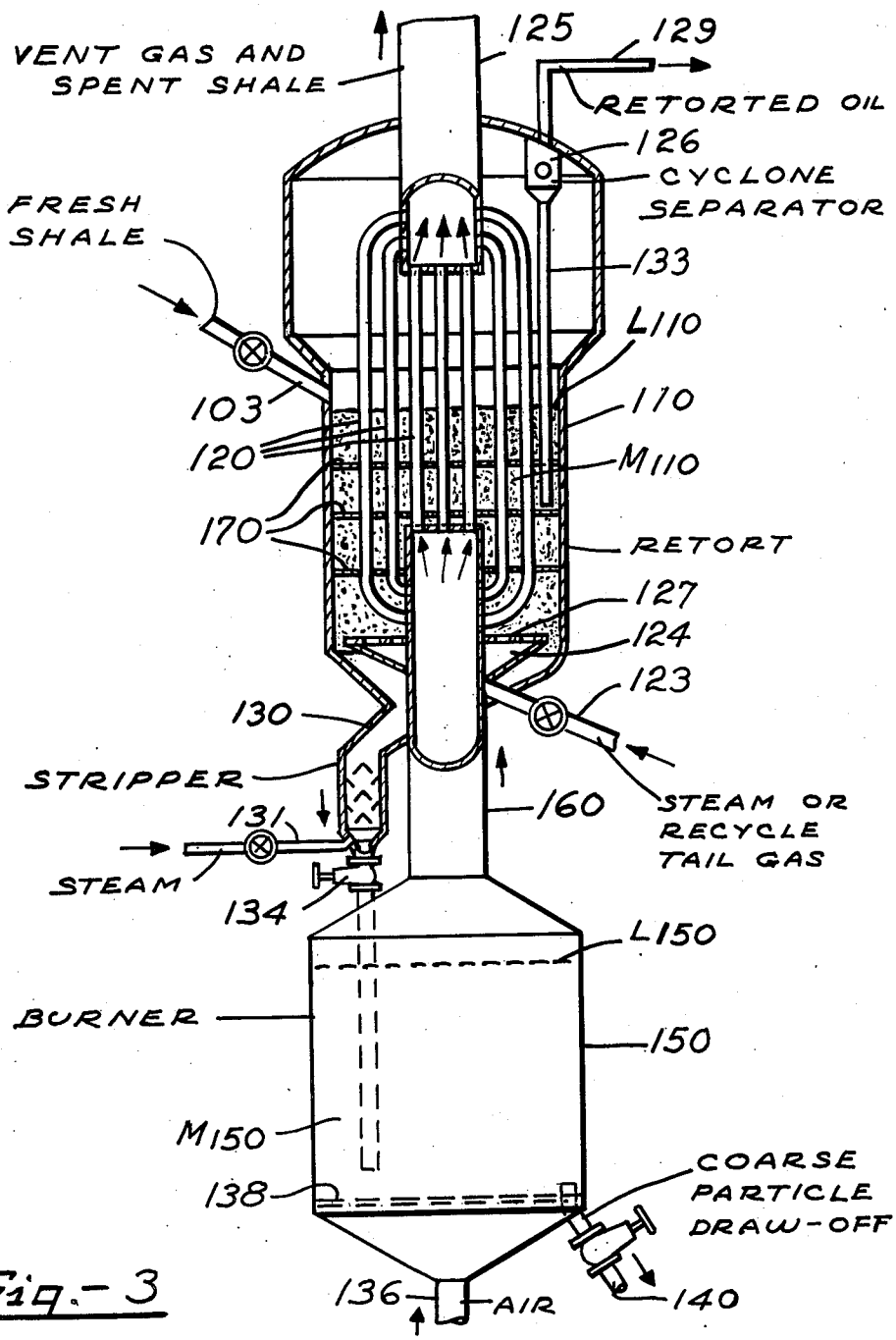


Fig. - 3

Charles E. Hemminger Inventors
Edward W. S. Nicholson
Alexis Voorhies, Jr.
By J. Cashmon Attorney

DISTILLATION OF OIL-BEARING MINERALS

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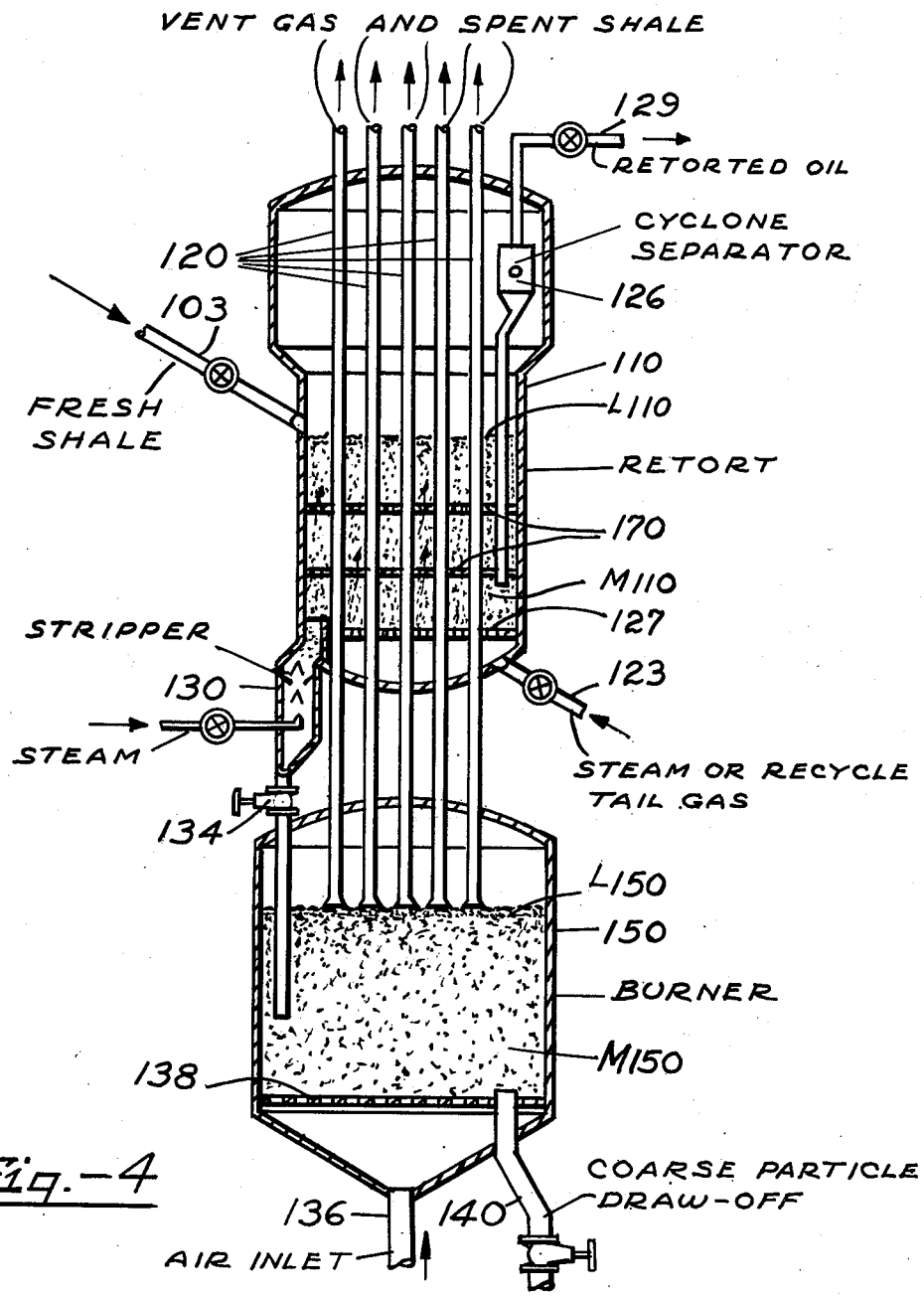


Fig.-4

Charles E. Hemminger Inventors
Edward W. S. Nicholson
Alexis Voorhies, Jr.
By J. Cashman Attorney

Feb. 8, 1955 C. E. HEMMINGER ET AL 2,701,787

DISTILLATION OF OIL-BEARING MINERALS

Filed Dec. 23, 1949 5 Sheets-Sheet 5

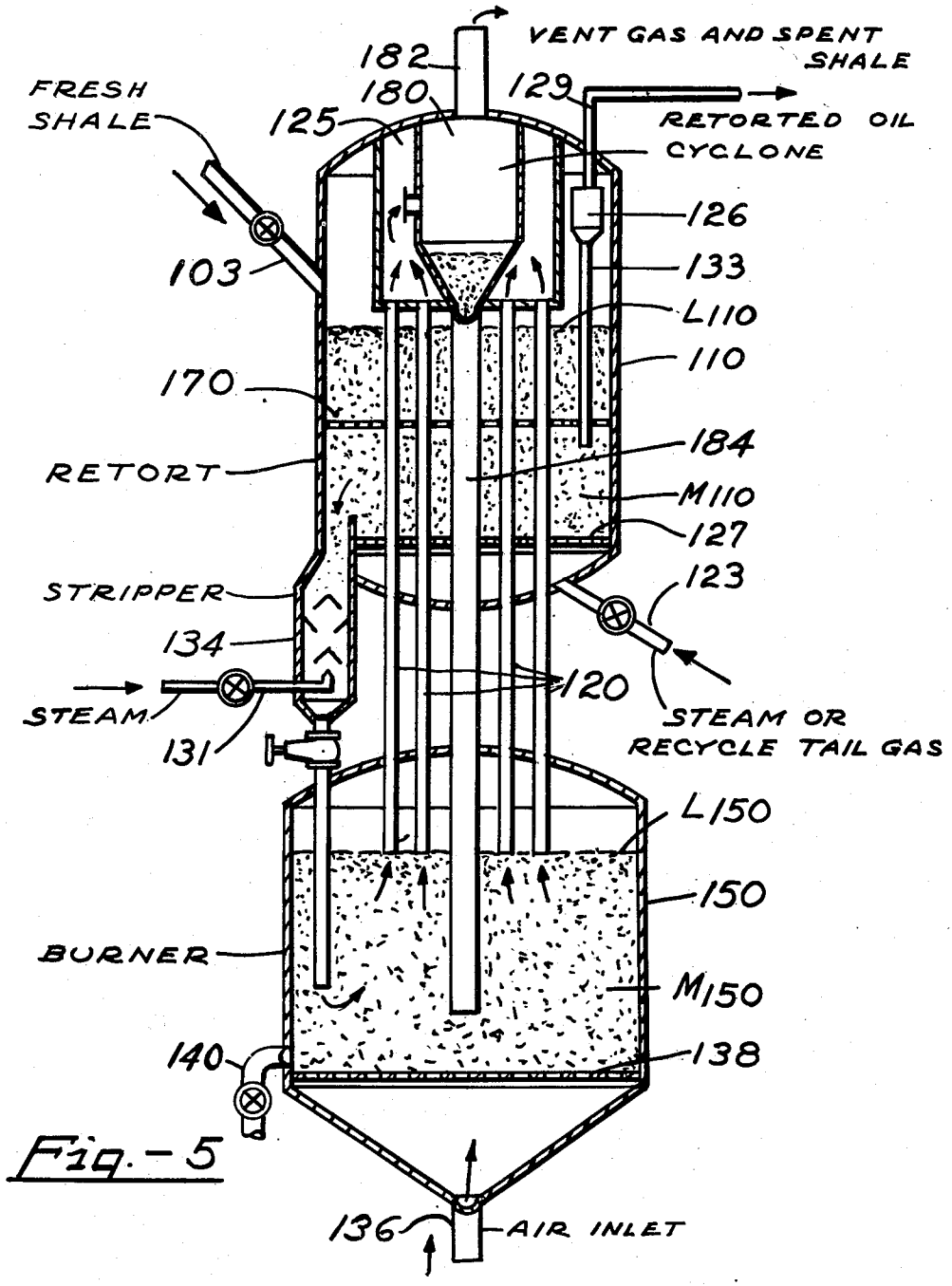


Fig. - 5

Charles E. Hemminger Inventors
Edward W. S. Nicholson
Alexis Voorhies, Jr.
By J. Cashman Attorney

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2,701,787

DISTILLATION OF OIL-BEARING MINERALS

Charles E. Hemminger, Westfield, N. J., and Edward W. S. Nicholson and Alexis Voorhies, Jr., Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

Application December 23, 1949, Serial No. 134,772

2 Claims. (Cl. 202—12)

The present invention relates to the distillation of oil-bearing minerals of the type of oil shale, oil sands, tar sands or the like, which tend to disintegrate upon distillation. More particularly, the present invention relates to an improved process of distilling oil shale wherein the heat required for the distillation is supplied by carrying out the distillation in indirect heat exchange with a fluidized mass of spent shale highly heated by combustion.

It is known that certain types of naturally occurring oil-bearing minerals, such as oil shale contain materials which may be converted by a pyrolytic treatment into hydrocarbon oils in commercially feasible yields. Prior to the present invention, others proposed carrying out the pyrolytic treatment of the shale in the form of a powder or larger aggregates of up to ¼ inch diameter in a highly turbulent state fluidized by an upwardly flowing gas, in a distillation zone, while supplying the heat necessary for the reaction by combustion, that is, either by burning a portion of the combustibles in the distillation zone in a system of the single-vessel type, or by burning the spent shale in a separate combustion zone and returning the burnt substantially uncooled shale to the distillation zone for heat supply in a system of the two-vessel type. The former method while simple in design involves the disadvantages of product losses by combustion and product dilution with flue gases. The latter method avoids these drawbacks but it is conducive to extreme shale disintegration and excessive fines entrainment from the distillation zone. In addition oil yields are seriously affected by the adsorption, in the retort, of retorted oil on the circulated burned shale followed by combustion of the adsorbed oil in the burner. Furthermore, it is difficult to obtain efficient heat utilization in such conventional two-vessel systems because a large part of the total heat generated in the burner is lost with spent shale discarded from the burner and with the flue gases vented from the burner.

The present invention overcomes these difficulties and affords various additional advantages as will appear from the description below wherein reference will be made to the accompanying drawing.

In accordance with the present invention, subdivided oil shale preferably in a dense turbulent fluidized state is retorted in indirect heat exchange with a turbulent fluidized mass of spent shale highly heated by burning the same with a combustion supporting gas so as to generate the heat required for distillation. This method of heat supply affords all the advantages of conventional two-vessel systems of the type mentioned above while avoiding the drawbacks resulting from a direct contact between burned shale and oil products and from the excessive disintegration caused by the extremely high solids circulation rates involved. In addition, excellent overall heat transfer coefficients of the order of 50–100 B. t. u./sq. ft./hr./° F. may be obtained by using fluidized solids phases on both sides of the heat transfer surfaces. Greatest heat efficiency may be obtained when the spent shale is undergoing combustion over a substantial portion of its heat exchange with the shale being retorted, i. e., when the heat generation itself takes place in indirect heat exchange with the shale undergoing distillation. Heat losses may be substantially reduced as compared with conventional operation, by maintaining a generally countercurrent flow of heat-carrying burnt or burning shale and shale undergoing distillation and by transferring at least a portion of the sensible and latent heat of the distillation products to the fresh incoming shale feed.

In accordance with a specific embodiment of the invention, distillation is carried out in a plurality of confined vertical extended fluid-type distillation zones having a relatively high ratio of length over diameter (L/D) of say about 30–100:1 which are imbedded in and separated by suitable heat transfer surfaces from a burning relatively dense fluidized mass of spent shale. Another embodiment of the invention involves maintaining the shale to be retorted in a distillation zone in the form of a dense turbulent fluidized mass surrounding a plurality of confined vertical extended heating zones having a high L/D ratio and containing fluidized turbulent masses of hot burning and/or burnt shale separated by suitable heat transfer surfaces from the shale undergoing distillation. In either embodiment, the heat-carrying spent shale and the fresh shale undergoing distillation are preferably caused to flow in opposite vertical directions through their respective zones so as to effect most efficient countercurrent heat exchange between the two types of fluidized solids masses. This may be readily accomplished for example by feeding fresh shale to the top of the distillation zone or zones, removing spent shale from the bottom of the distillation zone or zones, feeding spent shale to the bottom of the heating zone or zones and withdrawing burned shale from the top of the heating zone or zones while preferably limiting vertical backmixing of solids in the heating and/or distillation zones by suitably spaced non-fluidizable packings or horizontal perforated grids in a manner known per se.

In general, the reaction conditions should be so controlled that the temperature increases over the height of the various fluidized zones, preferably from the top to the bottom of the zones, from a minimum of about 200°–500° F. to a maximum of about 900°–1200° F. with a temperature differential of about 200 to 500° F. between heating and distillation zones over substantially the entire length of these zones. At least a portion of the normally liquid distillation products may be permitted to condense on incoming fresh shale to add preheat thereto. Liquid products may then be withdrawn from an intermediate or lower portion of the distillation zones. Temperature control may be readily accomplished by controlling the feed rate of the combustion air and/or by controlling the vertical circulation rate of the solids in the heating and/or distillation zones.

Having set forth its general nature and objects, the invention will be best understood from the more detailed description hereinafter wherein reference will be made to the accompanying drawing in which

Figure 1 is a semidiagrammatic illustration of a system suitable for carrying out shale distillation in a plurality of distillation zones embedded in a fluidized mass of burning spent shale;

Figure 2 illustrates in a similar manner a modification of the system of Figure 1, wherein countercurrent flow of solids is favored by suitable baffles, and product condensation takes place on the fresh shale charge within the distillation zones;

Figures 3, 4 and 5 illustrate the heat transfer between fresh shale and hot burned shale circulating in heating zones imbedded in the fluidized fresh shale, in accordance with three modifications of this embodiment of the invention.

Referring now to Figure 1 of the drawing, the system illustrated therein consists essentially of a vertical heat-exchanger type treating vessel **10** containing a plurality of retorting tubes **20** topped by a header-type enlarged hopper **25**. The lower ends of tubes **20** penetrate a perforated grid or similar distributing means **27** arranged in the lower portion of vessel **10** and lead into a second header-type hopper **30**. A standpipe **32** provided with a slide valve **34** connects zone **30** with a pipe **36** which leads into the bottom of vessel **10** at a point below grid **27**. Tubes **20** may have a diameter of about 3–10 inches and an L/D ratio of about 30–100:1. They are preferably made of a suitable heat resisting alloy steel such as one containing about 18% chromium and 8% nickel. The walls of vessel **10** may be lined with refractory material and heat insulated.

In operation, the fresh shale crushed to a particle size passing about a 4 mesh screen is supplied from a feed hopper **1** through line **3** provided with a metering device such as star feeder **5** to hopper **25** enclosed in the top of

vessel 10. If desired, the fresh shale in hopper 1 may be preheated to a temperature of about 200°–400° F. by hot product vapors introduced through line 7 and screen 8 into a lower portion of hopper 1. Condensed oil products may be recovered from hopper 1 through line 9.

The fresh shale supplied to hopper 25 flows down tubes 20. Simultaneously, a fluidizing gas such as steam, product tail gas or the like is introduced through lines 23 into the lower ends of tubes 20 at a rate sufficient to maintain a superficial linear gas velocity within tubes 20 and hopper 25 of about 0.5–3 ft. per second, suitable to maintain the solids in tubes 20 and hopper 25 in the form of a turbulent fluidized mass having an apparent density of about 10–50 lbs. per cu. ft. and forming a well defined upper level L25 in hopper 25. The fresh shale in hopper 25 and tubes 20 is heated on its downward path to distillation temperatures of about 800°–1400° F. by heat transferred from a fluidized bed M10 of burning spent shale maintained in vessel 10 as will appear hereinafter. A mixture of distillation vapors and fluidizing gas is withdrawn overhead from level L25 and may be passed through line 29 to conventional product recovery equipment, preferably after separation of entrained solids fines in any conventional manner (not shown). Part or all of the products in line 29 may be passed to hopper 1 via line 7 to preheat the fresh shale as previously described.

Hot retorted shale which has been stripped of adhering distillation vapors by the gas introduced through lines 23 collects in hopper 30 wherein it may be aerated and maintained in a free flowing condition by small amounts of fluidizing gas introduced through one or more taps into standpipe 32 and/or the bottom of hopper 30. The shale collected in hopper 30 is withdrawn through standpipe 32 at a rate controlled by slide valve 34. This withdrawal rate controls in turn the flow rate of the shale through tubes 20, which is preferably such as will permit a shale residence time within tubes 20 of about 2–10 minutes at distillation temperatures.

The hot retorted shale passing valve 34 flows into pipe 36 where it is picked up by air to form a dilute solids-in-gas suspension which is carried through grid 27 into vessel 10. Sufficient air should be supplied to maintain by the combustion of residual carbon on the spent shale the heat required for the distillation in tubes 20 and simultaneously to convert the solids introduced into vessel 10 through grid 27 into a turbulent fluidized mass M10 similar to that within tubes 20 and hopper 25. The temperature within mass M10 may be controlled at about 1100°–1600° F. by adjusting the oxygen and inerts content of the air supplied to line 36. About 2 to 5 cu. ft. of air per pound of raw shale fed are generally suitable for this purpose. The absolute amount of gas so supplied should be maintained at the level required for proper fluidization, that is, at a level conducive to superficial gas velocities of about 0.5–1.5 ft. per second in mass M10. Flue gases containing entrained burned shale fines are withdrawn overhead from level L10 of mass M10 through line 38 to be used for heat recovery in any conventional manner if desired after a suitable separation of entrained solids (not shown). Very coarse burnt shale particles which are not entrained in the upflowing gases may be withdrawn through line 40 from the bottom of vessel 10.

Variations of the gas velocity in mass M10 and/or variations in the burnt shale withdrawal rate through line 40 may be used to adjust the level L10 of mass M10 as desired. If combustion within mass M10 is incomplete and the flue gases contain appreciable portions of combustible gases, secondary air may be introduced through line 42 into an upper portion of vessel 10 preferably at a point above level L10 to generate additional heat.

When operating as described with reference to Figure 1, the fresh oil shale is heated much more slowly to distillation temperatures on its path downwardly through tubes 20 than is the case when fresh shale is dropped directly into a fluidized bed of hot retorted shale. Some shales when heated slowly go through a plastic or "sticky" stage which is conducive to particle agglomeration and fluidization difficulties. This difficulty is avoided in the system of Figure 1 because whenever the shale tends to become "sticky," which would reduce or interrupt the flow through any of the tubes 20, the tube wall temperature at that point will increase rapidly, the fresh shale will be heated quickly to a temperature above those at which stickiness can occur and flow through the tubes 20 will be reestablished automatically.

As a result of the high L/D ratio of tubes 20 coupled with the fact that the major portion of the combustion takes place in pipe 36 and the lower portion of vessel 10, countercurrent-type heat exchange is accomplished to an appreciable extent in the system of Figure 1. This effect may be substantially enhanced by carrying out the process of the invention in a system of the type illustrated in Figure 2.

Referring now to Figure 2 the equipment shown is generally similar to that of Figure 1, like elements being identified by like reference characters. The essential difference between the two systems resides in the fact that vessel 10 is provided with a plurality of spaced perforated grids 50 which are penetrated by tubes 20 and which limit vertical back-mixing of solids in vessel 10. The perforations of grids 50 should be large enough to permit the free passage of entrained solids particles which are —200 microns size. Grid openings having diameters of about ⅜ to 1.5 inches are suitable for this purpose. A further modification resides in the arrangement of liquid product drawoff means in an intermediate section of tubes 20. For this purpose tubes 20 have a perforated or screened section 52. The perforations of these sections are of such size that only very fine shale particles of smaller than about 325 mesh size may penetrate. At the same location, vessel 10 is provided with narrow vertical risers 54 through which burned shale and gases pass upwardly through the perforated tube sections 52. The cross-sectional area of vessel 10, not occupied by tubes 20 or risers 54 is closed by metal plates 56 and 58 at the top and bottom of perforated sections 52, thus forming an oil-collecting space 60 from which oil seeping through perforated sections 54 may be withdrawn from line 62 preferably via a liquid seal 64. Operation of the system of Figure 2 is generally similar to that of Figure 1. Indirect heat exchange is employed, with the fresh shale being retorted flowing down through tubes 20 arranged inside vessel 10 wherein residual carbon is burned from the retorted shale to provide the heat of retorting. Tubes 20 discharge into hopper 30 and the rate of flow of shale through tubes 20 is controlled by the rate of withdrawal of retorted shale from hopper 30 through valve 34. Retorted shale is picked up by air in line 36 and passed to vessel 10 surrounding tubes 20. Tail gas from the retorting operation is recycled and introduced at the bottom of tubes 20 through lines 23 to provide for stripping of retorted shale and fluidization of the shale being retorted.

Vessel 10 is staged by grids 50 as pointed out above. This staging greatly enhances the countercurrent character of the heat exchange between the incoming fresh shale and the hot burned shale. Sufficient air is provided to burn carbon on the retorted shale and to heat this shale to temperatures in the range of 1100°–1600° F. As this hot shale is carried vertically through succeeding fluidized beds formed on grids 50, it transfers its heat to the fresh shale being retorted in tubes 20, and the burned shale is correspondingly lowered in temperature. The burned shale may leave the top of vessel 10 through line 38 at a temperature in the range of 300°–600° F. The bulk of the sensible heat of the burned shale and the flue gases has thus been transferred to the fresh shale.

The fresh shale falling through tubes 20 is simultaneously being heated to retorting temperature, reaching retorting temperature in the lower part of tubes 20. Oil is being retorted from the shale during its passage through tubes 20 and vapors tend to rise up through the tubes with the fluidizing gas. In the upper part of tubes 20, however, which is maintained at low temperatures, oil vapors condense and the liquid falls back down into the tubes. Liquid oil is drawn through the perforations of section 52 and collected in intermediate section 60 of the vessel. This oil is drawn off through liquid seal 64 to prevent release of tail gas at this point. The burned shale and the gases in vessel 10 pass through vertical risers 54 and then through the remaining fluidized beds in the upper part of vessel 10.

It will be seen that, with this system, no extraneous heat and very little extraneous cooling of streams is required. The fresh oil and air enter the system at atmospheric temperature. The spent shale and vent gases from

the burner leave at relatively low temperatures and with relatively little useful heat content. Liquid product may be drawn off from intermediate section **60** at around 300°–600° F. at which temperature it can be conveniently filtered. No special means for condensation of this liquid product and relatively little cooling are required. The gases leaving the top of hopper **25** through line **29** may be cooled further to recover light hydrocarbons, but very little cooling is required and in many cases it may be possible to eliminate this cooling step entirely.

Rather than burning retorted shale in a fluidized solid mass surrounding the distillation tubes as shown in Figures 1 and 2, hot burned shale may be carried in fluidized form through tubes embedded in a fluidized mass of fresh shale being retorted. Systems of this type are illustrated in Figures 3–5.

Referring now to Figure 3 the system shown therein essentially comprises a fluid type distillation retort **110** provided with vertical heat exchange tubes **120** topped by a header pipe **125**, and a burner vessel **150** arranged below retort **110** and communicating through a header pipe **160** with the lower ends of tubes **120**. The bottom portion of retort **110** is connected via a pipe **130** with burner **150**.

In operation, raw oil shale of the particle size specified above is supplied through line **103** to an upper portion of retort **110**. Simultaneously, a fluidizing gas such as product tail gas or the like is admitted through line **123** and a distributing cone having a perforated top **127**, into the lower portion of retort **110**. The cross-sectional area of cone **124** is slightly smaller than that of retort **110** to permit the withdrawal of fluidized solids from retort **110** around cone **124**. The fluidizing gas passes upwardly through retort **110** at a velocity suitable to convert the fresh shale into a dense turbulent fluidized mass M**110** of solids having an upper level L**110**, similarly as described in connection with mass M**10** of Figure 1. Mass M**110** is maintained at distillation temperatures of about 800°–1000° F. by hot burned shale passing upwardly through tubes **120** as will appear hereinafter.

Retorted shale is withdrawn from the bottom portion of retort **110** and passed through a stripper pipe **130** wherein entrained distillation products are removed by stripping with steam admitted through line **131**. The stripped shale maintained in a readily flowing condition by the stripping steam passes through a metering device such as slide valve **134** into a lower portion of burner **150**. Air is introduced through line **136** and a distributing grid **138** to the bottom of burner **150** at a rate adequate to burn residual carbon on the retorted shale, and to fluidize and heat the solids in burner **150** to temperatures of about 1600°–1900° F. About 3 to 6 cu. ft. of air per pound of raw shale may be supplied for this purpose preferably at a superficial linear velocity within mass M**150** of about 1 to 3 ft./sec. Hot shale entrained in flue gases passes overhead from level L**150** through header pipe **160** into and upwardly through heat exchange tubes **120** at an apparent density of about 5 to 20 lbs. per cu. ft. and in a highly turbulent condition, to transfer most of its sensible heat to the surrounding shale bed M**110** undergoing distillation. The suspension of spent shale in flue gases may be vented through header pipe **125**. Any coarse spent shale particles not carried overhead from M**150** and accumulating in burner **150** may be withdrawn through line **140** from the bottom of burner **150**. Retorted oil vapors and fluidizing gas are withdrawn from an upper, preferably enlarged section of retort **110** through line **129**, and passed to suitable product recovery equipment (not shown) preferably after separation of solids fines in a separator such as cyclone **126** from which separated solids may be returned to mass M**110** through dip pipe **133**.

Another modification of this embodiment of the invention is illustrated in Figure 4. The system of Figure 4 is generally similar to that of Figure 3, like elements being identified by like reference characters. The main difference between the two systems is that tubes **120** communicate directly with the dense bed M**150** in burner **150**. Distributing cone **124** is replaced by a grid plate **127** penetrated by tubes **120**. Operation of the system of Figure 4 is likewise similar to that described above with reference to Figure 3, except that the burned shale from burner **150** passes directly from the dense phase M**150** into tubes **120** and up to a height above the top of retort **110**.

The arrangement of Figure 4 affords several important advantages. Burned shale from the burner dense bed passes directly into the tubes without having to traverse a dispersed phase, and thus essentially all the burned shale can be used to transfer heat to the retort. Where the burned shale must pass through a dispersed phase, very coarse particles may not be entrained, and a larger proportion may have to be drawn off the bed at the bottom. This results in a loss of heat utilization. By having individual tubes, the discharge ends of which are visible at the top of the retort, it is possible to determine easily by visual observation if any of the tubes are plugged or are not functioning properly. Cleaning of these tubes is very easy inasmuch as tube cleaners can readily be inserted at the tops of tubes **120**. It is even possible to clean the tubes during operation if desired.

In the systems shown in Figures 3 and 4, the burned shale is heated to 1600°–1900° F. in order to provide, on a once-through basis, the heat necessary for bringing the fresh shale to retort temperature. In Figure 5, a modification is shown wherein at least part of the burned shale which has passed through the tubes in the retort is recirculated back to the burner. By this means, the temperature level required in the burner may be lowered appreciably.

Referring now to Figure 5, the arrangement shown is similar to those of Figures 3 and 4, like elements being identified by like reference characters. However, the system is modified by the provision of a gas-solids separator **180** within a header space **125** topping tubes **120** and of a dip pipe **184** leading from separator **180** to a lower portion of burner **150**.

Shale distillation takes place in retort **110** substantially as described with reference to Figures 3 and 4. The burned shale from burner **150** is carried upwardly through tubes **120** as shown in Figure 4 and withdrawn from tubes **120** into a header space **125** confined within the top portion of retort **110**. The suspension of burned shale in flue gases entering header **125** from tubes **120** rather than being directly vented as shown in Figure 3 enters cyclone separator **180** wherein most of the entrained shale particles are separated to release flue gases substantially free of entrained solids through line **182**. Burned shale separated in separator **180** is returned through dip pipe **184** to the bottom of burner **150**. In this manner, the circulation rate of hot burned shale through heat exchange tubes **120** may be held at a multiple of the feed rate of the fresh shale say at about 2 to 10 times the fresh shale feed rate so that the temperature of the circulating hot shale may be reduced to about 1100 to 1400° F.

In order to enhance the countercurrent character of the heat exchange in the systems of Figures 3–5, the flow of the fresh shale through retort **110** may be staged by the arrangement of a plurality of spaced perforated plates or similar baffles **170** which permit upward flow of gases and downward percolation of fluidized solids thus limiting solids back-mixing in a vertical direction, all in a manner known per se in the art of fluid solids handling. Other modifications of the systems of the drawing may appear to the expert without deviating from the spirit of the invention.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. In the method of distilling oil-bearing minerals of the type of oil shale in the form of a dense turbulent bed of subdivided solids fluidized in a distillation zone by an upwardly flowing gas wherein the heat required for distillation is generated by a combustion of retorted shale in the form of a turbulent solids-in-gas suspension maintained in a separate combustion zone, the improvement which comprises passing said fluidized solids in the absence of solid combustion residue downwardly through a plurality of substantially parallel vertical elongated distillation zones having a ratio of length-to-diameter between about 30:1 and 100:1, passing spent oil-bearing minerals highly heated by said combustion upwardly through a series of vertically spaced heating zones in each of which spent shale is maintained in the form of a dense fluidized turbulent mass above which exists a dilute phase separating said dense mass from the next higher dense mass, said vertical distillation zones being imbedded in said series of heating zones, thereby supplying substantially all of said required heat to said solids in the distillation zones by indirect countercurrent heat exchange

with said heated spent oil-bearing minerals, maintaining said solids at a relatively low temperature in the portions of said distillation zones adjacent to the feed point of fresh oil-bearing minerals, and maintaining said solids at a relatively high temperature in the bottom portions of said distillation zones adjacent to the discharge point of spent oil-bearing minerals from said distillation zones.

2. A process according to claim 1 wherein liberated oil vapors are condensed at an intermediate height of said distillation zones and the resulting liquid condensate is withdrawn from said distillation zones at said intermediate height while forming a liquid seal against the escape of uncondensed vapors.

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