

Nov. 29, 1955

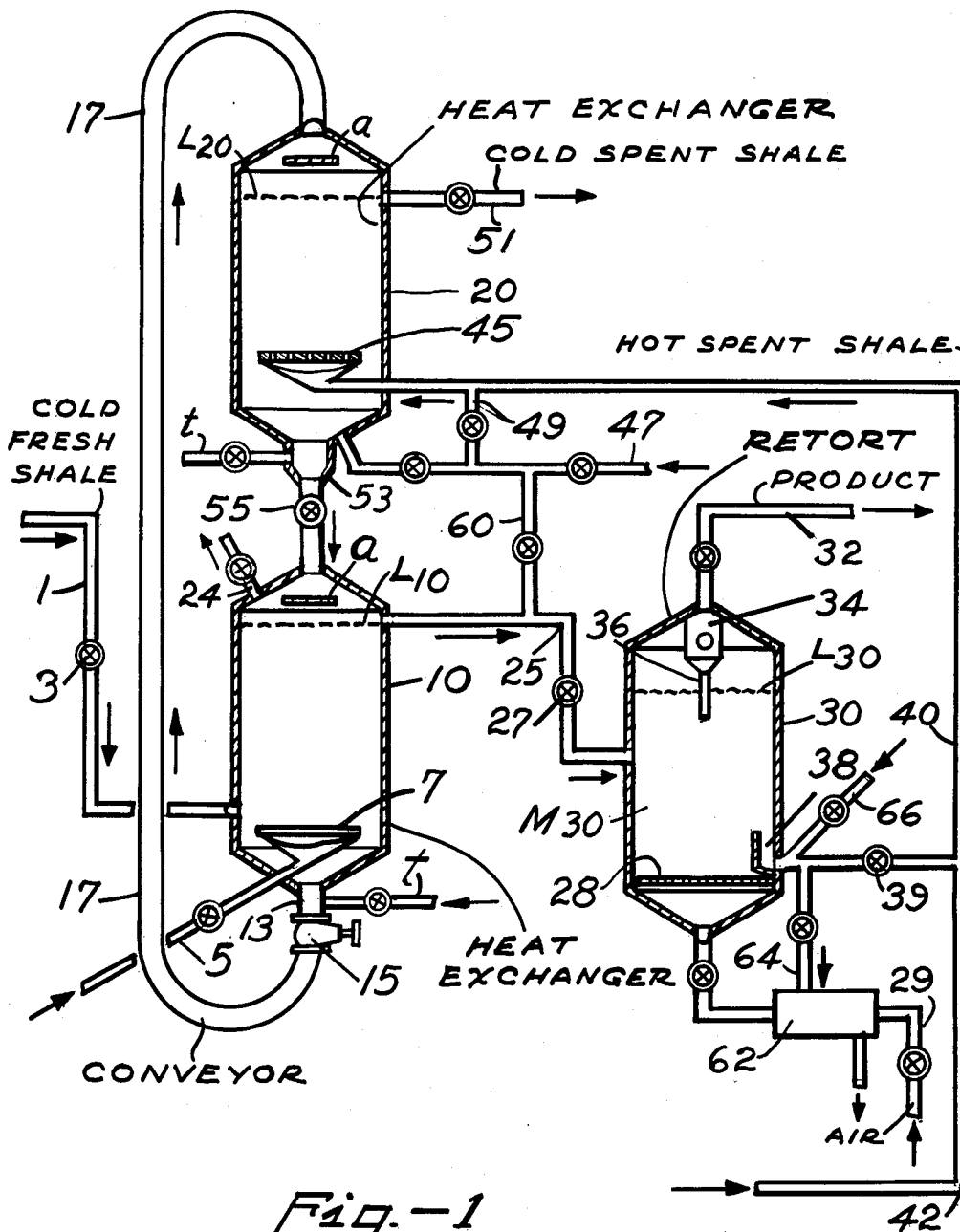
H. Z. MARTIN ET AL

2,725,348

FLUIDIZED DISTILLATION OF OIL-BEARING MINERALS

Filed Dec. 30, 1949

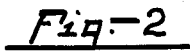
2 Sheets-Sheet 1



Homer Z. Martin Inventors
 Charles W. Tyson
 By J. Cashman Attorney

2,725,348

2 Sheets-Sheet 2



Homer Z. Martin Inventors
Charles W. Tyson
By J. Cashman Attorney

1

2,725,348

FLUIDIZED DISTILLATION OF OIL-BEARING MINERALS

Homer Z. Martin, Cranford, and Charles W. Tyson, Summit, N. J., assignors to Esso Research and Engineering Company, a corporation of Delaware

Application December 30, 1949, Serial No. 135,896

23 Claims. (Cl. 202-14)

The present invention relates to the distillation of oil-bearing minerals of the type of oil shale, oil sands, tar sands, coal, lignite, or the like. More particularly, the present invention pertains to an improved process of distilling oil shale or the like in the fluidized state wherein at least a portion of the heat required for the distillation is supplied by direct heat exchange of the fresh shale with an extraneous heat carrier. The retorted shale, prior to its withdrawal from the distillation system, is cooled substantially below distillation temperature by direct heat exchange with the aforementioned material subsequently used as the heat carrier, all heat exchange taking place in an essentially countercurrent fashion.

It is known that certain types of naturally occurring oil-bearing minerals, such as oil shale and bitumens, 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 1/4 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. Both methods are inherently uneconomical in heat recovery due to the fact that the spent shale leaving the system is at, or very close to, distillation temperature or even combustion temperature. The same is true for the flue gases withdrawn from the burner of the two-vessel system. It is, therefore, necessary to supply heating means very substantially out of proportion to the amount of heat actually required to distill the shale.

The single-vessel system, while simple in design, involves the further disadvantages of product losses by combustion and product dilution with flue gases. The two-vessel system avoids these drawbacks but it may be conducive to shale disintegration and excessive fines entrainment from the distillation zone. In addition, oil yields may be 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.

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, an extraneous heat carrier is circulated through a fluid-type shale distillation system in direct heat exchange with process solids in such a manner that heat from relatively hot fluidized shale is absorbed by the circulating heat carrier in direct and countercurrent heat exchange and the heat so absorbed is transferred to relatively cool fluidized shale, likewise in direct and countercurrent heat ex-

2

change. When operating in this manner, the spent shale may be discharged at a desirably low temperature after heat exchange with the heat carrier and heat for distillation may be generated by combustion of combustible shale constituents and supplied to the raw shale without the circulation of burned shale through the system and, if desired, without any product dilution with flue gases.

The heat carrier, which is preferably solid at the conditions of the process, should be of such specific gravity and/or particle size that it may be passed in particulate form downwardly through upwardly moving fluidized masses of process solids without appreciable back-mixing of heat carrier in a vertical direction. Depending on the quantities of heat to be transferred and the fluidization conditions in the heat exchanging zones involved, the downward flow of heat carrier solids through the fluidized masses within three zones may be so controlled that the heat carrier moves in the form of a dense moving bed of particles whose downward motion is little or not at all affected by the upwardly flowing fluidizing gas, while the process solids are fluidized within the interstices of the heat carrier bed, or the heat carrier particles may be subjected to a limited degree of turbulence or hopping motion within a bed of lesser density, or the heat carrier particles may be permitted to fall more or less freely through the fluidized mass of process solids at a velocity controlled by that of the fluidizing gases. These conditions may be varied, as desired, from heat exchange zone to heat exchange zone and even within the same heat exchange zone in accordance with the heat requirements of the process. In this manner, highest heat transfer flexibility is afforded at constant conditions of heat generation and consumption. It is, however, essential for highest efficiency that excessive back-mixing of fluidized solids in a vertical direction be avoided to enhance the countercurrent character of the heat exchange. For this reason, the density of the heat carrier bed or beds should preferably be high enough to act in the manner of a porous packing which limits downward back-mixing of upwardly moving fluidized solids.

The solid heat carrier is preferably used in the form of balls or pebbles of suitable size and specific gravity. While all types of inexpensive metals, such as iron, steels, aluminum, high-melting lead alloys, etc. may be used, refractories and particularly ceramic materials which have relatively high heat capacities and are not subject to oxidation or reduction are likewise suitable as heat carriers for the purposes of the invention. The particle size of the heat carrier may vary within wide ranges depending on the specific gravity of the material used. If the heat carrier is iron or a metal of similar specific gravity particle sizes of about 100 mesh to 1/2 inch, preferably about 20 mesh to 1/4 inch, may be employed. If ceramic materials are used, particle sizes of about 50 mesh to 1 inch, preferably about 20 mesh to 1/2 inch, are most suitable.

The process of the invention may be applied with equal advantages to single-vessel and two-vessel shale distillation systems of the type mentioned above. When applied to single-vessel operation, the circulating heat carrier may be contacted with hot spent fluidized shale in the countercurrent fashion of the invention so as to be heated to temperatures about 150°-200° F. below distillation temperature which may be about 800°-1200° F., while cooling the spent shale about 500°-1000° F. below distillation temperature prior to its withdrawal. The heat carrier so heated may then be passed in direct countercurrent heat exchange with a fluidized mass of raw shale to preheat the latter to temperatures about 100°-500° F. below distillation temperature. In this manner, the thermal efficiency of the process is greatly increased as compared with conventional single-vessel operation, with the result that smaller quantities of air or oxygen are re-

quired for retorting and the size of the retort may be reduced. In addition, the recovery of light ends is greatly facilitated because product dilution with flue gas is minimized.

In two-vessel systems the heat carrier may either be heated in direct countercurrent heat exchange with a fluidized mass of hot burned shale or combustion of fluidized retorted shale may be carried out in the burner vessel in direct countercurrent heat exchange with the heat carrier. The hot heat carrier may be used either alone or together with circulating burned shale to supply the heat required for preheating and distilling the raw shale by direct countercurrent heat exchange in accordance with the invention. When operating in this manner, burned shale may be withdrawn at temperatures about 600°–1200° F. below burner temperature which may vary between about 900°–1400° F., thus affording similar improvements in the thermal efficiency as described for the single-vessel system.

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

Figure 1 is a schematic illustration of a system principally adapted to carry out the present invention in a system of the single-vessel type; and

Figure 2 is a similar illustration of a system employing the principles of the invention in an operation of the two-vessel type.

Referring now to Figure 1 of the drawing, the system illustrated therein essentially comprises a raw shale preheater 10, a heat exchanger vessel 20 and a distillation vessel or retort 30, the functions and coaction of which will be forthwith described using as an example the distillation of a Colorado-type oil shale assaying about 30 gals. per ton while employing pebbles of ceramic material as the heat carrier in accordance with the present invention. It should be understood, however, that the system may be used for distillation of other oil shales and the application of other heat carriers in a generally analogous manner.

In operation, raw shale ground to a particle size passing 100 mesh is supplied through line 1 provided with a suitable metering device 3 to a lower portion of preheater 10 which may be in the form of a conventional type fluid-solids treating vessel. The raw shale may be fed through line 1 by means of a screw conveyor, an aerated standpipe, or any other suitable solids feeding means known in the art of fluid-solids handling. Preheater 10 contains a relatively dense mass of ceramic pebbles having a particle size of about 30 mesh to 5 mesh continuously supplied from heat exchanger 20 at a temperature of about 700°–900° F. to the top of preheater 10, as will appear more clearly hereinafter, and continuously withdrawn from the bottom of preheater 10 through line 13 at a temperature of about 100°–300° F. A fluidizing gas, such as product tail gas, flue gas, steam or the like, is supplied from line 5 via suitable distributing means such as cone 7 to a point below the feed point of line 1. The superficial linear velocity of the fluidizing gas within preheater 10 is so controlled that the relatively more buoyant raw shale is well fluidized, that is, present in the form of a turbulent pseudo-liquid mass "boiling" within the interstices of the downwardly moving heat-carrying pebbles and having a more or less defined upper interface L₁₀. The apparent density of the fluidized shale mass should be about 10–30 lbs. per cu. ft. as compared to about 15–45 lbs. per cu. ft. of the heat carrier. Linear superficial fluidizing gas velocities within preheater 10 of about 0.5–2.5 ft. per second are generally suitable for these purposes at the particle sizes specified.

Under the influence of the upwardly flowing fluidizing gas and the continuous supply of raw shale to the bottom of preheater 10, the fluidized mass of raw shale moves upwardly through the interstices of the heat carrier and

countercurrently to its downward motion to be preheated from a feed temperature of say, about 100° F. to a temperature of, say, about 400°–800° F. on its way through preheater 10 in countercurrent heat exchange with the heat carrier. A suspension of preheated shale in fluidizing gas is withdrawn from an upper portion of preheater 10 through line 25 substantially at the maximum temperature of preheater 10 of about 700°–900° F. This withdrawal may take place at, or slightly below, level L₁₀ of the fluidized shale mass or from the dilute phase forming above level L₁₀. If desired, suitable screening means may be used to prevent the withdrawal of large sized heat carrier through line 25. Heat carrier withdrawn through line 13 at a rate controlled by star-feeder or similar metering device 15 is returned at the minimum temperature of preheater 10 of about 100°–300° F. by means of a bucket conveyor, fluid lift, or similar transporting means 17 to the top of heat exchanger 20 to be reheated therein as will appear hereinafter.

The suspension of preheated shale in fluidizing gas withdrawn from the top of preheater 10 passes through line 25 to an upper portion of retort 30 at a rate controlled by a valve or other metering device 27. Depending on the point of withdrawal and the density of this suspension, line 25 may have the form of an aerated standpipe, a high velocity transfer line or any other fluid-solids conveying means. Retort 30 may be a conventional fluid-solids treating vessel provided in its bottom portion with a suitable gas distributing means, such as grid 28. A combustion-supporting gas containing free oxygen is supplied from line 29 to retort 30 at a point below grid 28 in amounts sufficient to maintain within retort 30, by means of a limited combustion of combustible shale constituents, a retorting temperature of about 900°–1100° F. Retort 30 is preferably so designed that when this amount of oxygen is supplied as air it establishes, in cooperation with the distillation vapors and flue gases evolved, a linear superficial velocity within retort 30 of about 0.5–2.5 ft. per second, suitable to maintain the shale undergoing distillation and disintegration to a particle size of about 5–200 microns in the form of a highly turbulent fluidized mass M₃₀ having an apparent density of about 20–40 lbs. per cu. ft. and a more or less well defined upper interface L₃₀. The amount of oxygen required for this purpose is only 0.3–0.6 standard cu. ft. (s. c. f.) per lb. of shale as compared with 0.8–1.2 s. c. f. per lb. of shale in conventional single-vessel operation. If desired, the air supplied through line 29 may be enriched with oxygen or diluted with inert gases, such as product gas, steam, nitrogen, etc., if advisable for fluidization considerations.

A mixture of gasiform distillation products and flue gases containing entrained solids fines leaves level L₃₀ overhead and is passed through line 32 to a conventional product recovery system (not shown), preferably after separation of solids fines in a gas-solids separator, such as cyclone 34, from which separated solids may be returned to mass M₃₀ via dip-pipe 36. Hot spent shale may be withdrawn from a lower portion of retort 30 under the pseudo-hydrostatic pressure of mass M₃₀ via a withdrawal well 38 into line 40 to be passed therethrough to a lower portion of heat exchanger 20, at a rate controlled by metering device 39. Depending on the relative positions of retort 30 and heat exchanger 20, line 40 may be either an aerated standpipe or a high velocity transfer line receiving a carrier gas, such as steam, air or product gas as may be found most advantageous, from line 42. Any gas supplied through line 42 may be preheated to about 600°–1000° F. in heat exchange with product withdrawn through line 32, or in any other conventional manner.

Returning now to heat exchanger 20, there is maintained therein a downwardly moving mass of heat carrier pebbles similar to the heat carrier mass of preheater 10. Relatively cool heat carrier solids are supplied from line

17 at a rate controlled by star feeder 15. The hot spent shale supplied by line 40, substantially at the temperature of retort 30, enters a lower portion of this mass via a distributing cone 45 together with any gas added through line 42. The hot spent shale is fluidized within the interstices of the heat carrier to form a "boiling" mass having an apparent density of about 5–20 lbs. per cu. ft. and an upper interface L₂₀ and passing upwardly and countercurrently to the moving heat carrier through heat exchanger 20. If the amount of gas supplied from line 42 is insufficient for this purpose, additional fluidizing gas, such as steam or product tail gas, may be supplied from line 47 to the bottom of heat exchanger 20 and/or via line 49 to cone 45. In general, it may be noted, however, that the linear superficial gas velocity within heat exchanger 20 may be somewhat smaller than that in preheater 10 within the broad range of about 0.1–1 ft. per second, because the particle size of the spent shale is normally substantially smaller than that of the raw shale.

The upflowing hot spent shale gives off most of its heat content to the heat carrier in countercurrent heat exchange. As the result, a suspension of spent shale in fluidizing gas may be withdrawn via line 51 from the top of heat exchanger 20 at a temperature of about 100°–300° F. in a manner similar to the preheated shale withdrawal from vessel 10. Heat carrier solids, on the other hand, may be withdrawn from the bottom of heat exchanger 20 at a temperature of about 700°–900° F. and supplied at this temperature via line 53 to the top of preheater 10 at a rate controlled by star feeder or the like 5, as indicated above.

The following example illustrates specific conditions at which a system of the type described above with reference to Figure 1 may be operated for the type of oil shale specified.

Example I

	Shale	Heat Carrier
Temperatures, ° F.:		
Top Preheater 10.....	550	900
Bottom Preheater 10.....	100	200
Top Heat Exchanger 20.....	300	200
Bottom Heat Exchanger 20.....	1,000	900
Retort 30.....	1,000	-----

Solids flow rates, lb./lb. of raw shale:

Heat carrier through preheater 10 and heat exchanger 20..... 1.0

Spent shale through heat exchanger 20..... 0.85

Bed densities, lbs./cu. ft.:

Heat carrier in preheater 10..... 25

Shale in preheater 10..... 20

Heat carrier in heat exchanger 20..... 25

Spent shale in heat exchanger 20..... 10

Shale in retort 30..... 20

Air requirement, S. C. F. per lb. of raw shale..... 2.5

The system illustrated in Figure 1 permits of various modifications. Additional heat may be generated by carrying out a combustion in heat exchanger 20 and/or in preheater 10. For this purpose, a free oxygen-containing gas, such as air, may be admitted through lines 47 and/or 5 in the desired amounts. The entire distillation may be carried out in this manner in preheater 10, thus eliminating the need for the separate retorting vessel 30. This may be done by the addition of all the air required for heat generation to heat exchanger 20 and the supply of retorted shale from vessel 10 via lines 25, 60, 47 and 49 directly to vessel 20. In this case, only retorted shale is burned and the heat carrier solids may be heated in heat exchanger 20 sufficiently high to supply all the heat required for retorting in vessel 10 as sensible heat of circulating heat carrier, in the general manner of a two-vessel system, thus avoiding product dilution with flue gases. Product vapors may be removed through line 24.

When applying the single-vessel principle as described with reference to Figure 1, the air requirement may be further reduced by preheating the air to temperatures of about 500°–1000° F. in direct heat exchange with hot

spent shale withdrawn from retort 30. For this purpose, the air supplied through line 29 may be contacted with a portion of the spent shale in a conventional direct contact air preheater 62 which may receive hot spent shale from line 40 via line 64. Air preheater 62 may contain suitable baffles to promote countercurrent heat exchange between air and hot spent shale in a manner obvious to those skilled in the art. Shale withdrawn from well 38 may be stripped of adhering product vapors by a suitable gas admitted through line 66. Tail gas, rather than steam, should be used for this purpose to avoid emulsion problems upon condensation.

Heat required for retorting in retort 30 may also be supplied by burning a portion of the retorted shale withdrawn through line 40 in a separate higher temperature burner (not shown) rather than within retort 30 and returning hot solid combustion residue to retort 30 as in a two-vessel system. As a result of the efficient preheating of the shale in accordance with the invention, the solids circulation rate between retort 30 and such a separate burner may be maintained very low, thus holding the above-mentioned drawbacks of the two-vessel system to a minimum.

A further adaption of the invention to the principle of the two-vessel system is illustrated in Figure 2 of the drawing. This system affords additional savings in the air requirements and permits a substantial reduction in the amounts of cooling water required for condensing the products. It involves the use of countercurrent heat carrier-powdered shale retort- and burner-exchangers 210 and 220, respectively, and a cooler-exchanger 250 which serves to cool the distillation products, as will appear more clearly hereinafter.

Referring now in detail to Figure 2 of the drawing, raw shale ground to a particle size passing 100 mesh is supplied from feed hopper 201 via lines 203 and 205 to the bottom of a lower small diameter extension 212 of retort-exchanger 210. The shale feed rate may be controlled by a suitable metering device 204. The raw shale in line 205 is suspended in a substantially inert carrier and fluidizing gas, such as product tail gas, or the like. Line 203 may be any of the shale feeding means described with reference to line 1 of Figure 1. Retort-exchanger 210 and its extension 212 contain a relatively dense mass of pebbles having a particle size of about 20 mesh to ¼ in., continuously supplied from burner-exchanger 220 at a temperature of about 1000°–1300° F. suitable to supply the heat required for retorting in retort-exchanger 210, as will appear hereinafter, and continuously withdrawn from the bottom of extension 212 through line 214 at a temperature of about 100°–300° F. The superficial linear velocity of the fluidizing gas within extension 212 is so controlled that the more buoyant raw shale forms a highly turbulent fluidized mass "boiling" within the interstices of the downwardly moving heat carrier pebbles and, at the same time, moving upwardly within these interstices to assure countercurrent heat exchange between heat carrier and raw shale. Linear superficial fluidizing gas velocities of about 0.5–2.5 ft. per second which will establish apparent shale bed densities of about 10–30 lbs. per cu. ft. and apparent heat carrier bed densities of about 15–45 lbs. per cu. ft. within extension 212 are normally suitable for this purpose, depending on the diameter of extension 212, which may be about ½ to ¾ of that of retort-exchanger 210. The larger diameter of the main section of retort-exchanger 210 compensates for the increase in gas volume due to the evolution of volatile retorting products so that similar fluidization conditions may be maintained therein and the fluidized shale undergoing retorting forms a more or less defined upper interface L₂₁₀. In this manner, distillation may be carried out in the upper portion of retort-exchanger 210 at suitable temperatures of about 900°–1100° F. without any combustion taking place therein.

Retorted shale is withdrawn directly from the fluidized

shale mass at or just below level L₂₁₀ via line 216 and passed into line 218 at a rate controlled by valve 217. The shale in line 218 is suspended in air preferably preheated to about 600°–1000° F. in heat exchange with hot process solids and/or gases in any conventional manner. The suspension of retorted shale in air enters a lower portion of burner-exchanger 220 through a suitable distributing device, such as cone 222. Burner-exchanger 220 contains downwardly moving heat carrier pebbles similar to those in retort-exchange 210, which are supplied from line 214 as will appear hereinafter. The amount of air supplied through line 218 should be sufficient to establish by combustion of retorted shale a heat carrier temperature of about 1000°–1200° F. within burner-exchanger 220 and fluidizing conditions similar to those described with reference to exchanger 20 of Figure 1 so that the burning and burned shale in burner-exchanger 220 forms a fluidized mass within the interstices of the heat carrier, and assumes an upper level L₂₂₀.

Flue gases are removed overhead from level L₂₂₀ through line 224, preferably after separation of entrained solids in cyclone 226 from which separated solids may be returned via dip-pipe 228. The hot flue gas which may have a temperature of about 1000°–1300° F. may be used for heat recovery in heat exchange with process materials or for steam production in any conventional manner. The flow of flue gas through line 224 may be regulated by valve 225. Burned shale passes upwardly through an upper small diameter extension 230 opening below level L₂₂₀ into burner-exchanger 220, in counter-current heat exchange with a downwardly moving mass of heat carrier pebbles in a manner similar to that described with reference to extension 212. Cool heat carrier pebbles are supplied from line 214 via line 232 to the top of extension 230 at a temperature of about 100°–200° F. and at a rate determined by metering device 234. A cool suspension of shale ash in flue gas leaves extension 230 via line 236 at a temperature of about 100°–300° F., while heat carrier pebbles flow from extension 230 into burner-exchanger 220 at a temperature of about 800°–1200° F. By a proper control of valve 225, the level L₂₂₀ may be controlled at a point above the lower end of extension 230. Pressure built up by a control of valve 225 will force fluidized spent shale into and upwardly through extension 230. Other suitable means for controlling level L₂₂₀ and the pressure above it may appear to those skilled in the art. The diameter of extension 230 may be about 1/2 to 1/10 of that of burner-exchanger 220.

Heat carrier pebbles heated to a temperature of about 1000°–1200° F. flow from the bottom of burner-exchanger 220 through a standpipe or similar conveying means 238 into retort-exchanger 210 to supply the heat required therein as described above. A suitable gas, such as steam or product tail gas, may be injected through line 240 into pipe 238 to increase the standpipe pressure and to provide a gas blanket preventing product vapors from rising through pipe 238 into burner-exchanger 220.

Returning now to the bottom of extension 212, the cool heat carrier pebbles withdrawn therefrom via metering device 215 are hoisted by a bucket conveyor or similar means through line 214. A portion of, say about 50–80% of these pebbles is returned via line 232 to the top of extension 230 as described above. The remainder of the heat carrier pebbles is passed to the top of cooler-exchanger 250 via line 242, provided with metering device 244, to form a downwardly moving mass of heat carrier pebbles in cooler-exchanger 250. A mixture of hot distillation vapors and gases and fluidizing gas containing small amounts of entrained solids fines is withdrawn from an upper portion of retort-exchanger 210 and passed through line 246 to a lower portion of cooler-exchanger 250. It is generally desirable to provide gas-solids sepa-

rating means 247 to prevent excessive carry-over of fines into line 246 and exchanger 250.

Cool heat carrier pebbles and hot product vapors exchange heat within cooler-exchanger 250 in a counter-current fashion so that liquid product condenses in the upper portions of cooler-exchanger 250. Troughs 252 may be arranged in this condenser portion, from which liquid product containing a small amount of scrubbed solids fines may be recovered through line 254 to be worked up in any conventional system (not shown). Product tail gas is withdrawn through line 256 at a temperature of about 100°–300° F.

Reheated heat carrier pebbles are withdrawn from the bottom of cooler-exchanger 250 at a temperature of about 800°–1000° F. and may be returned through line 258 to burner-exchanger 220 to be reheated therein to the temperatures required for distillation. For a plant capacity of about 10,000–14,000 tons of raw shale per stream day, the heat exchange elements 212, 230 and 250 may have typical dimensions of 8' inner diameter x 20' high, 8' inner diameter x 20' high, and 1.5' inner diameter x 10' high, respectively.

The operation of a system of the type shown in Figure 2 will be further illustrated by the following specific example.

Example II

	Shale	Product	Heat Carrier
Temperature, ° F.:			
Top Preheater 212.....	885	-----	1,000
Bottom Preheater 212.....	100	-----	200
Top Heat Exchanger 230.....	300	-----	200
Bottom Heat Exchanger 230.....	1,170	-----	1,000
Top Heat Exchanger 250.....	-----	300	200
Bottom Heat Exchanger 250.....	-----	1,000	800
Retort 210.....	1,000	-----	-----
Burner 220.....	1,170	-----	-----
Solids flow rates, lb./lb. of raw shale:			
Heat carrier through preheater 212.....			1.5
Heat carrier through heat exchanger 230.....			1.0
Heat carrier through heat exchanger 250.....			0.5
Spent shale through heat exchanger 230.....			0.85
Product through heat exchanger 250.....			0.13
Bed densities, lbs./cu. ft.:			
Heat carrier in preheater 212.....			25
Shale in preheater 212.....			20
Heat carrier in heat exchanger 230.....			25
Spent shale in heat exchanger 230.....			10
Heat carrier in heat exchanger 250.....			70
Air requirement, S. C. F./lb. of raw shale.....			1.6

The system of Figure 2 permits of various modifications. Most of the retorted shale, say about 50–75% thereof, may be bypassed around the burner-exchanger 220 and sent directly to the upper extension 230 via line 260. This saves the necessity of heating the major portion of the retorted shale from distillation temperature to combustion temperature, and this is a large part of the heat load. This has the further advantage that the small amount of retorted shale which is sent to the burner-exchanger 220 can be burned to nearly 0% carbon content, so that the loss of fines into the flue gas from the lower burner-exchanger 220 is minimized.

The hot pebbles removed at about 800°–1000° F. from cooler-exchanger 250 instead of being charged directly to the burner-exchanger 220 may be charged via line 262 to a location above the burner-exchanger 220 in extension 230, so that they are preheated by shale rather than requiring the use of air for combustion for their preheat. Alternately, part or all of these pebbles may be sent through line 264 to that part of extension 212 where the pebbles are at approximately 800°–1000° F. to obtain a somewhat similar improvement. To facilitate dust collection in the retorting and burner-exchangers 210 and 220, supersonic dust precipitators may be used at any suitable point. The shale withdrawn from retort-exchanger 210 through line 216 may be stripped of adhering distillation products by gas admitted through line 266. To avoid emulsion problems, tail gas rather than steam should be used for this purpose.

In most cases it will be desirable to provide means for separating shale from heat carrier pebbles being removed from the lower ends of vessels 10, 20, 212 and 220, to prevent shale and oil losses. This may be accomplished by introducing stripping gases, such as product tail gas, steam, flue gas, etc., through taps *t* and line 240.

Both systems illustrated in the drawing permit of various further modifications. For example, distributing cones 7, 45 and 222 may be provided with perforated cover plates or they may be replaced by other suitable distributing means, such as perforated plates having openings sufficient and properly designed to permit downward passage of heat carrier pebbles and upward flow of gas. Also a plurality of gas-nozzles properly distributed over the cross-section of the vessels may be substituted. In order to permit uniform distribution of heat carrier pebbles over the entire cross-section of the vessels, suitable baffling means may be provided as it is schematically indicated at (a). Other modifications within the spirit of the invention may appear to those skilled in the art.

While the foregoing description has stressed the application of the invention to the distillation of oil shale and this is the preferred embodiment of the invention, it is noted that certain of the advantages specified above also accrue in an application of the principles set forth to the carbonization and/or gasification of other carbonaceous solids, such as coal. For example, substantial savings in heat and oxygen requirements are obtainable. In addition, equipment size may be greatly reduced.

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. The process of distilling oil-bearing minerals in the form of a highly turbulent, dense, fluidized mass of subdivided solids, which comprises heating an extraneous subdivided solid heat carrier having a gas settling rate higher than that of said subdivided minerals to an elevated temperature by intimately contacting said heat carrier with a mass of hot particulate solid residue of said first mentioned solids, transferring sensible heat of said heated heat carrier to an incoming mass of said minerals by passing said heated heat carrier in a substantially non-turbulent condition downwardly through a substantially vertical contacting zone in direct countercurrent heat exchange with an upwardly moving fluidized mass of said minerals, limiting the free motion of the particles of said mass by maintaining an apparent density of about 15 to 45 pounds per cubic foot of said heat carrier particles and a density of about 10 to 30 pounds per cubic foot of said sub-divided minerals so as to reduce back mixing of said mineral particles in a downward direction, withdrawing heat carrier at a relatively low temperature from a bottom portion of said zone and said materials at a relatively high temperature from an upper portion of said zone, separating vaporized oil from said materials and contacting the hot residue with said low temperature heat carrier to continue the process.

2. The process of claim 1 in which said heat carrier is heated to a temperature not substantially exceeding distillation temperature and said heat exchange takes place in a preheating zone.

3. The process of claim 1 in which said heat carrier is heated to a temperature substantially above distillation temperature and said heat exchange takes place in a distillation zone.

4. The process of claim 1 in which said heat carrier is heated in direct countercurrent heat exchange with fluidized hot solid residue from a combustion of distilled oil-bearing minerals.

5. The process of claim 4 in which said combustion is carried out in direct heat exchange with said heat carrier.

6. The process of claim 1 in which said heat exchange takes place in a zone through which said heat carrier is

passed downwardly in the form of a substantially non-turbulent dense moving bed and said fluidized mass is passed upwardly through the interstices of said bed, the downward motion of said bed being substantially unaffected by the fluidization of said mass.

7. In the process of distilling oil-bearing minerals of the type of oil shale in the form of a highly turbulent, dense, fluidized mass of subdivided solids, the improvement which comprises passing a subdivided solid heat carrier having a gas settling rate higher than that of said subdivided minerals downwardly in a substantially non-turbulent condition through and in direct contact with an upwardly moving fluidized mass of hot solid burned distillation residue in a heat exchange zone so as to heat said heat carrier to an elevated temperature and to cool said residue in direct countercurrent solids-solids heat exchange, limiting the free motion of the particles of said mass by maintaining an apparent density of about 15 to 45 pounds per cubic foot of said heat carrier particles and a density of about 10 to 30 pounds per cubic foot of said sub-divided minerals so as to reduce back mixing of said mineral particles in a downward direction withdrawing heat carrier at a relatively high temperature from a lower portion of said heat exchange zone, withdrawing said residue at a relatively low temperature from an upper portion of said heat exchange zone, passing said heat carrier so heated downwardly in a substantially non-turbulent condition through and in direct contact with an upwardly moving fluidized mass of said minerals in a treating zone so as to transfer to said minerals at least a portion of the heat required for distillation and to cool said heat carrier in direct countercurrent solids-solids heat exchange, limiting the free motion of the particles of said mass by said heat carrier particles so as to reduce back mixing of said mineral particles in a downward direction withdrawing heat carrier at a relatively low temperature from a lower portion of said treating zone, withdrawing said minerals at a relatively high temperature from an upper portion of said treating zone, and returning heat carrier so cooled to an upper portion of said heat exchange zone.

8. The process of claim 7 in which said treating zone is a preheating zone and said withdrawn minerals are subjected to distillation in a separate distillation zone.

9. The process of claim 7 in which said treating zone is a distillation zone.

10. The process of claim 7 in which said residue is derived from a fluid-type distillation zone wherein a portion of the combustible constituents of said minerals is burned to supply heat required for distillation.

11. The process of claim 7 in which said residue is burned in contact with said heat carrier.

12. The process of claim 7 in which said fluidized mass of hot residue flows upwardly through a narrow vertical path in said heat exchange zone countercurrently to, and in direct heat exchange with, said downwardly flowing heat carrier; said path having a relatively high ratio of length to diameter.

13. The process of claim 12 in which said fluidized residue is forced upwardly through said path under the influence of a substantial negative pressure differential between the bottom and top of said path.

14. The process of claim 13 in which said fluidized mass of residue is forced into the bottom of said path by applying a relatively high pressure to the upper level of said mass outside said path, and a relatively low pressure to the top of said path.

15. The process of claim 7 in which said treating zone is a distillation zone and a portion of said cooled heat carrier is passed through a cooling zone in countercurrent direct heat exchange with vapors generated in said distillation zone so as to cool said vapors in said cooling zone, heat carrier being recycled from said cooling zone to said heat exchange zone.

16. Apparatus for the direct countercurrent heat exchange between relatively fine and relatively coarse sub-

11

divided solids which comprises a first substantially vertical and cylindrical vessel closed at the top and bottom, a second substantially vertical and cylindrical vessel the lower portion of which has a diameter substantially smaller and a ratio of height over diameter substantially greater than those of said first vessel, an upper portion of said second vessel being arranged above said first vessel, the bottom of said second vessel having an opening connected with the interior of said first vessel, the arrangement of the vessels being such that relatively fine fluidized solids in said first vessel may flow upwardly into said second vessel, means for supplying subdivided solids and gases to fluidize said fine solids to a lower portion of said first vessel, means for lifting said fluidized fine solids from said first vessel upwardly through said second vessel, means for withdrawing relatively coarse subdivided solids independent of gases from the bottom of said first vessel, means for supplying subdivided solids to the top of said second vessel, means for withdrawing fluidized relatively fine solids from the top of said second vessel and means for withdrawing gases from an upper portion of said first vessel.

17. Apparatus for the direct countercurrent heat exchange between subdivided solids, which comprises a first substantially vertical and cylindrical vessel closed at the top and bottom, a second substantially vertical and cylindrical vessel having a diameter substantially smaller than the diameter of said first vessel and a ratio of height over diameter substantially greater than that of said first vessel, an upper portion of said second vessel being arranged above said first vessel, the bottom of said second vessel having an opening connected with the interior of said first vessel, means for supplying subdivided solids and gases to a lower portion of said first vessel, means for withdrawing subdivided solids independent of gases from the bottom of said first vessel, means for supplying subdivided solids to the top of said second vessel, means for withdrawing fluidized solids from the top of said second vessel, means for withdrawing gases from an upper portion of said first vessel, a third substantially vertical and cylindrical vessel arranged below said first vessel, a lower extension of said first vessel extending from the bottom of said first vessel into the interior of said third vessel and opening thereinto, said extension having a diameter smaller than the diameters of said first and third vessels, a lower substantially vertical extension of said third vessel having a diameter smaller than the diameter of said third vessel and a ratio of height over diameter larger than that of said third vessel, means for supplying subdivided solids and gases to a lower portion of said third vessel extension, means for withdrawing solids from the bottom of said third vessel extension, means for carrying said last-mentioned withdrawn solids to the top of said second vessel, means for withdrawing fluidized solids from said third vessel, and means for withdrawing gasiform materials from an upper portion of said third vessel.

12

18. The apparatus of claim 17 which comprises means for carrying said last-mentioned withdrawn fluidized solids into said first vessel.

19. The apparatus of claim 17 which comprises means for carrying said last-mentioned withdrawn fluidized solids into said second vessel.

20. The process of claim 1 in which said mineral is coal.

21. Apparatus for the direct countercurrent heat exchange between subdivided solids, which comprises a first substantially vertical and cylindrical vessel closed at the top and bottom, a second substantially vertical and cylindrical vessel the lower portion of which has a diameter substantially smaller than the diameter of said first vessel and a ratio of height over diameter substantially greater than that of said first vessel, an upper portion of said second vessel being arranged above said first vessel, the bottom of said second vessel protruding into the space defined by said first vessel and opening into said space, means for supplying relatively finely subdivided solids and gases to fluidize them to a lower portion of said first vessel, means for withdrawing relatively coarse subdivided solids independent of gases from the bottom of said first vessel, means for supplying relatively coarsely subdivided solids to the top of said second vessel, means for withdrawing relatively fine fluidized solids from the top of said second vessel and means for withdrawing gases from an upper portion of said first vessel.

22. The apparatus of claim 16 in which said bottom of said second vessel protrudes into the space defined by said first vessel.

23. The process as defined in claim 1 using a linear superficial gas velocity of 0.5 to 2.5 foot per second.

References Cited in the file of this patent

UNITED STATES PATENTS

1,291,137	Reed	Jan. 14, 1919
2,376,564	Upham et al.	May 22, 1945
2,393,636	Johnson	Jan. 29, 1946
2,396,036	Blanding	Mar. 5, 1946
2,396,709	Lifer	Mar. 19, 1946
2,402,875	Cornell	June 25, 1946
2,420,376	Johansson	May 13, 1947
2,441,170	Rose et al.	May 11, 1948
2,447,306	Bailey	Aug. 17, 1948
2,480,670	Peck	Aug. 30, 1949
2,483,485	Barr	Oct. 4, 1949
2,519,340	Bailey	Aug. 22, 1950
2,538,219	Welty	Jan. 16, 1951
2,573,906	Huff	Nov. 6, 1951

FOREIGN PATENTS

600,326	Great Britain	Apr. 6, 1948
---------	---------------	--------------