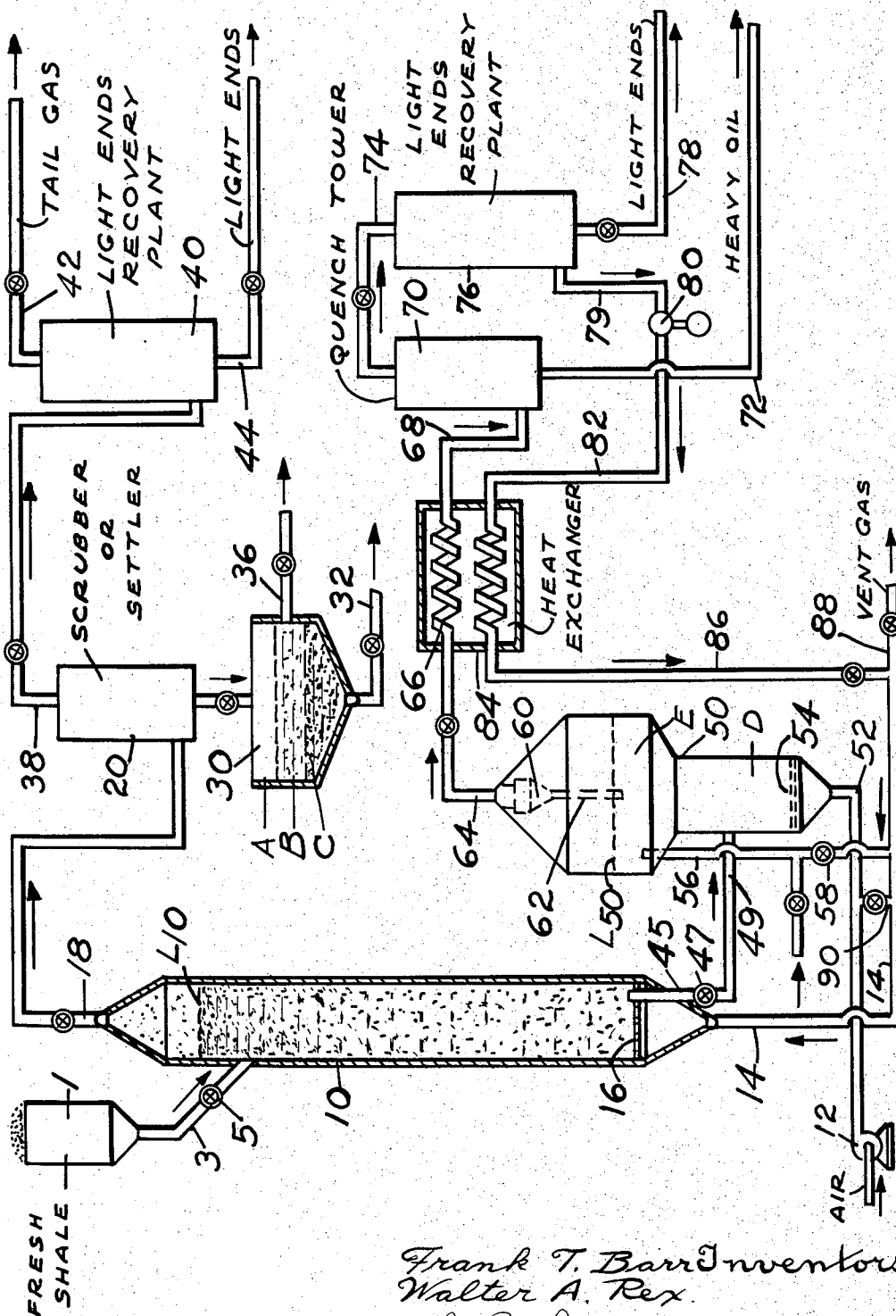


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PREHEATING OF OIL-SHALE

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PREHEATING OF OIL-SHALE

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The present invention relates to a process of distilling oil shale. More specifically, the invention is concerned with an improved method of preheating subdivided oil shale in a "fluidized" preheating zone by a countercurrent direct contact with hot spent shale fines formed in the course of the distillation process.

It is known that certain types of naturally occurring oil-bearing minerals, such as oil shale, contain constituents which may be converted by pyrolytic treatment into commercially feasible quantities of hydrocarbon oils, including oils boiling in the gasoline and gas oil range. It has also been proposed, prior to the present invention, to carry out the pyrolytic treatment of the shale in the form of a powder or larger aggregates up to $\frac{1}{4}$ inch in diameter or larger, in a "fluidized" state in a distillation zone, while supplying the heat necessary for the distillation by combustion, that is either by burning a portion of the combustibles of the shale in the distillation zone or by burning the spent shale in a separate combustion zone and returning the burnt substantially uncooled shale to the distillation zone.

While various practical shale retorting processes have been developed on this basis, the oil yields and/or heat economies accomplished generally have fallen short of those theoretically obtainable on the basis of the chemical composition of the shales. The present invention affords considerable improvements in this respect as will appear from the following description in which reference will be made to the accompanying drawing.

In the retorting of oil shale, which must be carried out at temperatures of 800°-1000° F. (although the present invention is adapted to operation over a still wider range), the major heat load is that required for raising the cold shale feed to retorting temperatures. It has also been observed that the oil yields of the shale distillation are detrimentally affected by inefficient preheating procedures which involve excessive heating times of the shale at, and even substantially below, distillation temperature. It will be appreciated, therefore, that a proper preheating procedure is essential for a commercially feasible shale distillation process.

Prior to the present invention it has been suggested to preheat the shale feed in separate preheating zones by direct or indirect heat exchange with outgoing oil products and/or flue gases carrying small amounts of suspended shale fines. However, the amount of heat carried by such gases or dilute suspensions is relatively small

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and only limited preheat can thus be obtained. Other suggestions for preheating the raw shale with hot spent shale as such, whereby the net heat load would be significantly reduced, have in general required the use of complicated and expensive equipment. The present invention overcomes these difficulties and affords various additional advantages.

In accordance with the present invention, raw oil shale of relatively large particle size, preferably about 0.5 to 1.5 inches in diameter is charged to an upper portion of a vertical treating zone having a relatively high ratio of length: diameter (L/D) of at least 3:1 and preferably greater than 5:1, say about 5-20:1 or the equivalent thereof, in which the coarse shale passes downwardly in direct contact with, and counter-currently to, upflowing distillation products and flue gases and hot spent shale fines of a particle size small enough to permit their elutriation from the coarse raw shale, e. g., of less than 100-200 microns size. The material in the vessel is maintained in a "fluidized" state by a gas supplied to a lower portion of the vessel and passed upwardly therethrough at a superficial linear velocity adequate for fluidization and for the effective overhead elutriation of the shale fines. Suitable linear superficial gas velocities may fall within the wide range of about 0.5-5 ft. per second but are preferably maintained at about 1-2 ft. per second, depending on the specific size of the coarse shale feed and of the size to which the shale must disintegrate before giving up the desired amount of oil. Independent of the gas velocity, the level of the fluidized mass will build up to a point at which carry-over in the outlet gas stream is just sufficient to maintain the level constant. By using a high L/D vessel, or its equivalent, top to bottom mixing of materials in the fluidized solids bed is avoided and relatively direct passage of the fresh large shale particles downwardly and of spent shale fines upwardly in the bed is accomplished.

Operation in accordance with the invention is facilitated by the fact that oil shale upon retorting and loss of its kerogen content disintegrates to form fines of the size specified above which may be easily elutriated from the coarse fresh shale feed. The solids fines used for preheating are, therefore, available at the desired temperature as a by-product of the distillation process itself. They are used in relatively large amounts and have a heat content many times greater than heating gases or dilute solids-in-gas suspensions. It will be appreciated, therefore,

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that the invention provides a preheating scheme which combines most efficient heat utilization with substantial equipment economies.

It has been noted that the shale fines are removed overhead at a temperature about 25°-100° F. higher than that at which the raw shale is introduced. Because of this low temperature which contributes to the high thermal efficiency, any product liberated in the lower portion of the column will be condensed and will be absorbed by the shale fines. For separation of this oil from the shale fines steam stripping and water stripping are preferred. Steam stripping using low pressure steam may be used to remove the volatile constituents of the oil but recovery of the non-volatile materials without resorting to temperatures higher than those at which cheap low pressure steam can easily be supplied, say 250° F. maximum, must be achieved by water stripping. Water stripping at temperatures from atmospheric to 200° F. may be carried out satisfactorily by simple mixing of the shale fines with sufficient water to form a satisfactorily fluid phase, especially if the carbon content of the shale has been reduced to a sufficiently low level. If desirable, wetting agents may be added to the stripping water to cause the water to replace the oil in the shale fines and to allow recovery of the oil as a solids-free layer. Another suitable stripping method comprises the use of light solvents as the stripping means, which may then be vaporized from the shale at economically low temperatures.

In accordance with the preferred embodiment of the invention the preheating step and the distillation step proper are carried out in separate stages and using the fines produced in the distillation stage for preheating the raw shale in the preheating stage substantially as described above while recovering oil products substantially exclusively from the distillation stage. In this manner, the necessity for removing oil products from cold shale fines discharged from the system may be greatly reduced or even completely eliminated.

For this purpose, raw shale in relatively large particles, say $\frac{1}{2}$ in. to $1\frac{1}{2}$ in. size, is charged to the top of a high L/D fluid solids vessel of the type described above and allowed to move downward in this vessel through rising retorted shale fines. A fluidizing gas which preferably contains no free oxygen, such as product tail gas, flue gas, steam, or the like, is used to accomplish this at the flow velocities described above. Material from the bottom of this vessel is introduced into a separate fluid solids vessel to which the heat required for retorting is supplied by internal combustion or any other suitable means and which is fluidized by an upflowing gas having a linear superficial velocity of about 0.5-3 ft. per second. This second vessel includes an enlarged upper section in which the superficial gas velocity is reduced to the point where an insignificant amount of fines is carried overhead, say to about .05-.05 ft. per second. The fines are withdrawn from this low velocity section of the vessel and returned to the first vessel for heat exchange with entering shale and final overhead disposal. The low velocity section of the second vessel may be fitted with entrainment reducing equipment, such as cyclone separators, or the like. The vapors overhead from this vessel, which comprise fluidizing gas and practically all the oil products and which are substantially free of solids fines, may be conducted directly to suitable product recovery facilities.

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It will normally be desirable to have the second vessel operating on shale which has been preheated in the first vessel as high as feasible without driving off an excessive amount of products. This will ordinarily be in the range of 700°-800° F., although temperatures lower or higher than this range may be required depending upon the characteristics of the shale charged to the system and of the oil produced therefrom. If relatively high temperatures can be used near the bottom of the first vessel, no additional countercurrent flow portion of the second vessel is necessary and the shale withdrawn from the first may be introduced directly into the low velocity bed in the second or the second vessel may be operated throughout as a low velocity zone. This will ordinarily not be possible, however, and a relatively high velocity section in the second vessel beneath the low velocity bed will usually be required, as mentioned above. This permits increasing the temperature of the shale sufficiently to drive off the major portion of the oil in the second vessel so that the oil will be discharged and separated from the shale fines in the low velocity section. For this purpose, maximum temperatures in the second vessel may run from 25°-300° F. higher than in the bottom of the first vessel. The high velocity zone in the second vessel has an additional advantage in that it insures adequate velocity for fluidization of any shale particle that may not have broken down in size.

By virtue of the decrease in temperature of the product stream before it is separated from the spent shale fines in the low velocity section of the second vessel, some of the heavier portions of the product may be condensed on the shale fines. The operation in accordance with the present invention, however, permits a considerable recycling of the shale fines from the bottom of the first vessel through the second vessel. In this manner, the time during which the heavy portions of the shale oil is subjected to temperatures in the neighborhood of, say, 1000° F. is increased. As a result of this increase in residence time at high temperatures, considerable cracking and conversion of the heavy ends into lighter, more valuable products occur, and these products are easily taken overhead from the low velocity fines separating section of the second vessel.

When operating in accordance with this embodiment of the invention, the first vessel acts simply as a preheating zone for the fresh shale with simultaneous cooling of the spent shale. No oil recovery equipment operating on the gas from this section is required and the fines-bearing cooled fluidizing gas may be disposed of directly. Some shales may release a significant portion of their oil content at temperatures lower than those required at the bottom of the first vessel. These products, however, will largely be light materials which do not condense in the overhead gas from the first reactor. Such product vapors together with the fluidizing gas may be separated from the shale fines using simple liquid scrubbing or dry settling techniques, and the oil may then be recovered from the tail gas in a light ends recovery plant. This plant may be combined with the light ends recovery plant operating on the overhead gas from the low velocity section of the second vessel.

If shales are used from which oil is released over an extremely wide temperature range so that an excessive amount of oil is carried out of the top of the first vessel, an additional vessel

having a low velocity section may be employed. This third vessel may be inserted in the lower or middle portion of the high L/D preheating vessel in such a manner that together with the lower portion of the high L/D vessel, which now forms the bottom of the intermediate vessel, the system comprises two secondary type vessels in tandem with the primary high L/D preheater type vessel receiving the fresh oil shale. The intermediate secondary vessel with low velocity separator top may be advantageously operated in the range of 500°–800° F. in the low velocity section.

While combustion of combustible shale constituents within the distillation zone has been referred to above as the principal means of heat supply, it is noted that any other conventional means of heat generation and supply may be used. For example, in all embodiments of the invention described above, combustion of the retorted shale may be carried out in a separate fluid-type combustion zone and the heat so generated may be supplied to the distillation zone as sensible heat of hot burned shale circulated to the distillation zone all in a manner known per se. Other suitable heating means include indirect heat supply, use of extraneous heat carriers in direct contact with the shale, etc.

Having set forth its objects and general nature, the invention will be best understood from the subsequent more specific description wherein reference will be made to the accompanying drawing which is a semi-diagrammatic illustration of a system in which preheating and distilling are carried out in separate vessels.

Referring now in detail to the drawing, the system illustrated therein essentially comprises a vertical fluid-type shale preheating vessel 10, a vertical fluid type retorting vessel 50, and product recovery equipment 20, 30 and 40, the functions and cooperation of which will be forthwith described using the retorting of a Colorado type oil shale having a Fischer assay of 30 gals./ton as an example. It will be understood, however, that other types of oil shale may be treated in a substantially analogous manner.

In operation coarse fresh shale having a particle size of about 1 to 1.5 in. diameter is charged from hopper 1 through line 3 to the top of vessel 10 at a rate determined by metering device 5. Vessel 10 may have a relatively high L/D of, say, about 10:1. The fresh shale is allowed to move downwardly in vessel 10, countercurrently to a fluidizing gas and retorted shale fines substantially at the gas flow and fluidization conditions described in connection with vessel 10 of Figure 1. Fluidizing gas, such as product tail gas which may be admixed with air, is supplied through line 14 as will appear more clearly hereinafter, via grid 16 to the bottom of vessel 10 in amounts sufficient to establish the desired linear superficial velocity of about 0.5–3 ft. per second within vessel 10 and the apparent densities previously referred to.

Solids are withdrawn from a lower portion of vessel 10 via line 45 provided with control valve 47 and passed through line 49 to a lower portion of vessel 50. As indicated, vessel 50 comprises a lower section D of relatively small diameter and an upper section E of relatively large diameter. A combustion-supporting gas which, for the purposes of the present example, is assumed to be air is introduced by blower 12 through line 52 to the bottom of vessel 50 to enter section D through a distributing grid 54. The air feed rate through grid 54 is preferably so controlled that sufficient

oxygen is supplied to generate by combustion the heat required to maintain in the lower portion of section D a temperature of about 850°–1000° F. and simultaneously to establish a total linear superficial gas velocity within section D of about 1.0–5.0 ft. per second and in section E of about 0.1–1.0 ft. per second. At these conditions, an efficient segregation of coarse shale from shale fines takes place in section D. Coarse shale tends to remain in the lower portion of section D while shale fines of the size of, say, less than about 50–200 microns concentrate in section E wherein they are permitted to form a relatively dense phase having a well defined interface L₅₀. Distillation takes place over substantially the entire height of vessel 50 at a temperature of about 850°–1000° F. Vessel 50 may be readily so designed that these conditions may be maintained at an air supply of about 1,000–4,000 standard cu. ft. per ton of fresh shale charged.

Shale fines are withdrawn from section E and passed via standpipe 56 provided with control valve 58 into line 14 wherein they are suspended in the fluidizing gas of vessel 10 and passed substantially at the temperature of vessel 50 to the lower portion of vessel 10 to supply the desired preheat to the coarse fresh shale. Normally, all fines produced in vessel 50 will be returned to vessel 10 in this way, the flow of fines being controlled by valve 58 to maintain the desired level L₅₀. Shale preheat temperatures of about 700°–800° F. may thus be attained in vessel 10.

At the conditions specified, only insignificant distillation of shale takes place in vessel 10. The gases and entrained solids fines rising upwardly through the coarse shale in vessel 10 are cooled to a temperature of about 100°–200° F. when they reach interface L₁₀. While the dilute suspension of solids-in-gases passing overhead from interface L₁₀ is substantially free of product vapors, the entrained solids may contain small proportions of oil adsorbed on the shale fines in vessel 50. In order to recover such adsorbed oil and any light ends liberated in vessel 10, the solids-in-gas suspension withdrawn from the top of vessel 10 through line 18 may be worked up in scrubbing means 20, settling means 30 and light ends recovery means 40.

The dilute suspension of spent shale fines in gases and vapors is withdrawn overhead from vessel 10 through line 18 and may be passed at a temperature of about 100°–200° F. to a lower portion of a water scrubber 20 wherein it passes upwardly countercurrently to water introduced through line 22 into the top of scrubber 20. It is the purpose of scrubber 20 to condense substantially completely the normally liquid distillation products and simultaneously to wash out the entrained solids from the residual gas. About 4–10 gals. of water having an inlet temperature of about 75°–100° F. are sufficient per pound of raw shale fed to accomplish this purpose.

A suspension of shale fines in a mixture of water and liquid oil products may be withdrawn from scrubber 20 through line 24 and passed to a settler 30. The contents of settler 30 are permitted to stratify into a lower aqueous layer A containing substantially all of the shale fines, and an upper oil layer B. Layer A is preferably permitted to further stratify to form a lower sludge layer C leaving the remainder of layer A substantially free of solids. Water overlying sludge layer C may be recirculated by pump 33 via line 22 to scrubber 20. Makeup water may be fed through line 34. A sludge of spent shale suspended in

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water may be withdrawn from the bottom layer A through line 32. Product oil may be recovered from oil layer B and passed through line 36 to conventional oil refining equipment.

A mixture of product light ends and flue gases substantially free of entrained shale fines may be withdrawn overhead from scrubber 20 and passed through line 38 to a light ends recovery plant 40 which may have the form of conventional low temperature fractionation, oil absorption or solid absorption equipment. Residual gas may be vented through line 42 while light ends may be recovered through line 44.

As previously pointed out, suitable wetting agents or detergents, such as the sodium alkyl aryl sulfonates, oleates, stearates, etc., may be added to the water supplied to scrubber 20 in concentrations of about 0.02-0.5%. Also, light solvents, such as a 150°-200° F. naphtha may be used in scrubber 20 in place of water. In this case, layers A and B in settler 30 will comprise essentially a single phase which may be withdrawn, the solvent separated by simple distillation (not shown) and recycled by pump 23 through line 22 to scrubber 20, and the recovered oil obtained as bottoms from the distillation. Product in the solvent boiling range may be withdrawn from the solvent stream as necessary to avoid its build-up. Solvent may be recovered from the spent shale sludge by pressing, by indirect heating, or preferably by stripping with steam at a temperature of 175°-225° F. For optimum recovery of shale oil, solvent circulation should be about 0.25-2.0 gals. per lb. of shale treated.

Returning now to vessel 50, a dilute suspension of spent shale fines in a mixture of flue gases and product vapors and gases having an apparent density of about 0.002-0.05 lb. per cu. ft. may be withdrawn overhead from interface L₅₀ and passed through a conventional gas-solids separator, such as cyclone 60, from which separated solids fines may be returned through dip-pipe 62 to the dense solids phase in section E. Gases and vapors now substantially free of entrained solids may be passed from cyclone 60 through line 64 to a heat exchanger 66 wherein they are cooled to a temperature of about 200°-400° F. in heat exchange with product tail gas. The cooled gaseous mixture then may be supplied via line 68 to a conventional quenching tower 70 wherein its temperature may be reduced to atmospheric temperature by indirect cooling or direct contact with countercurrently flowing cold product oil in a manner known per se. Normally liquid product oil may be recovered through line 72. A mixture of product light ends and flue gas may be passed from tower 70 through line 74 to a light end recovery plant 76 of the type of plant 40 described in connection with the overhead scrubber 20. Product light ends may be recovered through line 78.

Tail gas stripped of substantially all recoverable distillation products may be withdrawn from plant 76 through line 79 and passed by means of blower 80 via line 82, heat exchanger 84 and line 86 to line 14 at a temperature of about 500-900° F. to be used as the fluidizing gas in vessel 10 as previously described. Excess tail gas may be vented through line 88. If desired, small amounts of air may be supplied from blower 12 via line 90 to line 14 and vessel 10 in order to balance and control the gas velocity and temperature in vessel 10.

The embodiment of the invention described with reference to the drawing permits of various

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modifications. For example, the overall height of vessel 10 may be reduced without sacrificing countercurrent contact and residence time of the solids and gases therein by arranging suitable vertical or horizontal baffles within vessel 10 which either divide vessel 10 into a plurality of vertical sections of small diameter and/or which prescribe a tortuous path for gases and solids, all in a manner known per se. Baffles of the conventional disc and doughnut type are likewise suitable for this purpose. As previously pointed out, other heating means than internal combustion within the distillation and preheating zone may be used to supply the heat required. A system wherein the heat is generated in a separate combustion vessel wherein retorted shale is burned to be circulated to the distillation zone as a solid heat carrier may be used to particular advantage. This type of heat supply to shale distillation zones is well known in the art (see for instance U. S. 2,480,670) and need not be described in greater detail for a proper understanding by those skilled in the art. When applied to a system as illustrated in the drawing, a substantially inert fluidizing gas may then be supplied both to vessels 10 and 50, withdrawing retorted shale from a lower portion of section D of vessel 50, passing the withdrawn shale to a separate combustion vessel and returning burned shale of relatively fine particle size from the combustion vessel to a lower portion of section D.

Other modifications obvious to those skilled in the art are within the scope of the invention.

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

What is claimed is:

1. In the distillation of oil shale in the form of a dense turbulent mass of subdivided solid particles fluidized by an upwardly flowing gas, the improvement which comprises supplying coarse fresh shale particles ranging in size from about 0.5 to 1.5 inches at substantially atmospheric temperature to the top of a substantially vertical preheating column of finely divided shale having a column ratio of length-to-diameter of at least 3:1, introducing hot spent shale fines into the bottom portion of said preheating column at a rate sufficient to maintain said bottom portion at a preheating temperature of about 700 to 800° F. and conducive to only insignificant shale distillation, said shale fines having a particle size elutriatable from said coarse shale particles, passing a fluidizing gas upwardly through said column at a linear superficial velocity of about 0.5 to 3 ft. per second so as to fluidize the fines while permitting the said coarse shale particles to settle downwardly through said column, passing the fluidized shale fines upwardly through said column in direct counter-current contact with said downwardly moving coarse shale particles, said column being high enough to establish a substantial temperature gradient over the height of said column, withdrawing a dilute suspension of shale fines in said fluidizing gas from the top of said column at a temperature of about 100 to 200° F., withdrawing a mixture of relatively coarse shale particles and shale fines from said bottom portion substantially at said preheating temperature and at a rate preventing appreciable shale distillation in said bottom portion, supplying said mixture to a separate distillation zone, fluidizing said

mixture in said distillation zone by an upwardly flowing gas at a temperature of about 850 to 1000° F. until the shale oil is substantially completely distilled from the shale, concentrating retorted shale fines in an upper portion of said distillation zone in the form of a relatively dense fluidized mass, recovering distillation vapors upwardly from said last named mass through a disengaging zone, and separately withdrawing hot shale fines from said last named mass for return substantially at said distillation temperature to said bottom portion of said preheating column.

2. The process according to claim 1 wherein the linear superficial gas velocity in said distillation zone is maintained at about 1 to 5 ft. per second in the lower portion thereof and at about 0.1 to 1 ft. per second in the upper portion thereof whereby relatively coarse shale particles tend to remain in the said lower portion.

3. The process of claim 1 in which heat is supplied to said distillation zone by burning combustible shale constituents with an oxygen containing gas in a lower portion of said distillation zone.

4. The process of claim 1 in which said gas flowing upwardly through said column comprises product tail gas remaining after separation of normally non-gaseous distillation products.

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