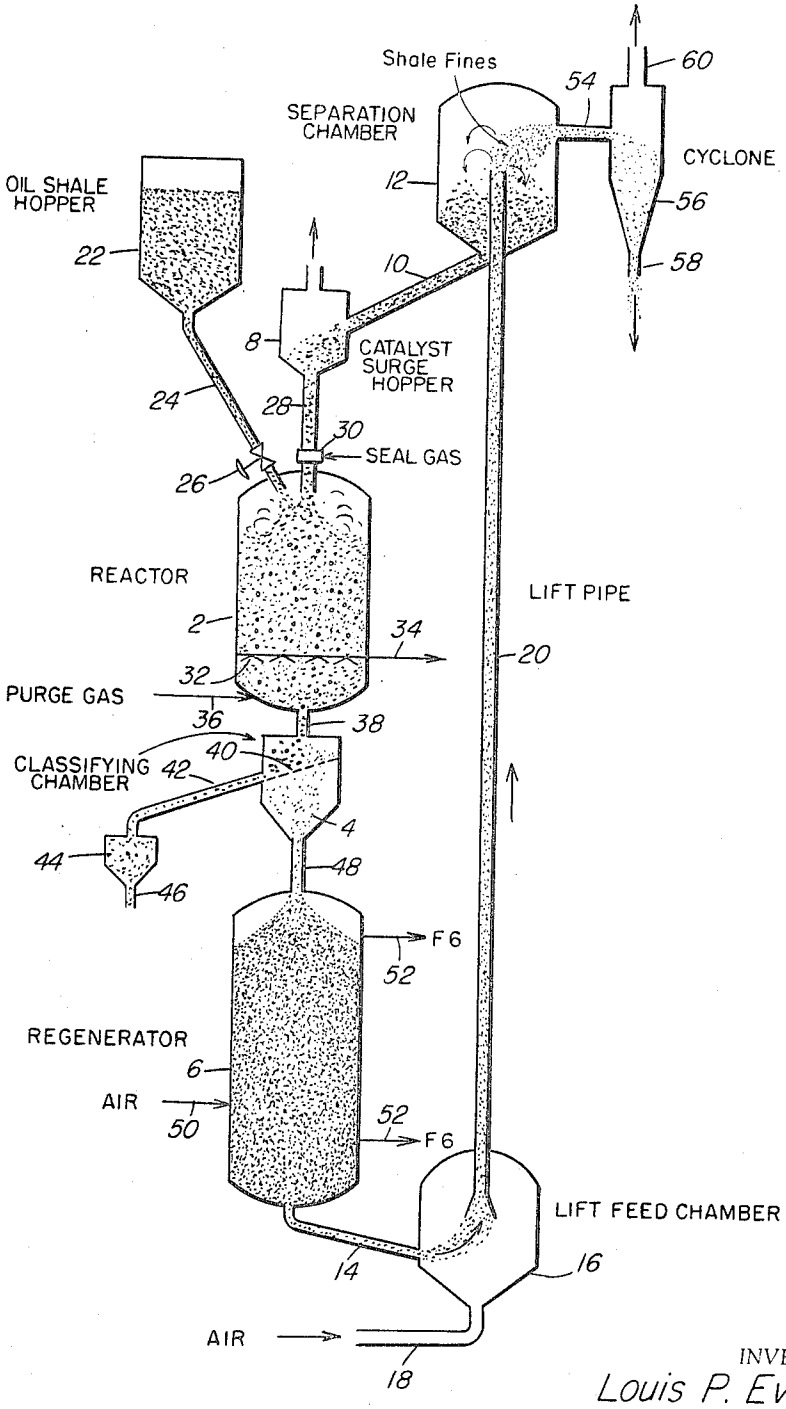
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SEPARATING AND CRACKING OF SHALE OIL FROM OIL SHALE

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INVENTOR.
Louis P. Evans
BY
Paul D. Furnsworth
AGENT

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SEPARATING AND CRACKING OF SHALE OIL FROM OIL SHALE

Louis P. Evans, Woodbury, N.J., assignor to Mobil Oil Corporation, a corporation of New York

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This invention relates to a method for recovering hydrocarbons from hydrocarbonaceous solids such as oil shale and the like. More particularly, the invention relates to the method and means for effecting simultaneously the separation and catalytic cracking of shale oil from crushed shale.

Various methods have been utilized to achieve the separation of valuable hydrocarbon products from hydrocarbonaceous solids such as oil shale. For example, oil can be recovered from tar sands by hot and cold water processes; however, such methods are not completely desirable because separation of the hydrocarbon products from large quantities of water is required. Similarly, the distillation of oil from shale by contact with hot gaseous streams, for example, by burning a portion of the recovered oil, is also undesirable in that an ultimate separation of the flue gases from the hydrocarbon products cannot be avoided. Furthermore, the above processes yield a hydrocarbon product which is characteristically highly viscous and which would require further treatment, such as thermal or catalytic cracking, to be amenable to economic transport from an oil shale region to a refinery or market area.

It is an object of the present invention to effect the recovery of shale oil from oil shale and the catalytic conversion thereof to more useful products.

It is a further object o fthe present invention to effect the simultaneous recovery and conversion of the shale oil within a single zone in order to recover directly therefrom a product amenable to fluid transfer.

It is a further object of the present invention to effect a substantially complete separation of the retorted shale from the cracking catalyst before catalyst regeneration, in order that the creation of shale fines as a contaminant of the oil product, which readily proceeds under catalyst regeneration conditions, and the consequent loss of heat from the system by such endothermic shale decomposition, shall be beneficially avoided.

It is a further object of the present invention to provide at least a major portion of the endothermic heat of recovery and conversion of shale oil by the cracking catalyst—heated in a regeneration zone by burning of carbon deposited on the catalyst—in order that process heat requirements shall be decreased.

Other objects and advantages of the present invention will become more apparent to those skilled in the art from the following detailed description and drawing.

Briefly, the essential steps of the present invention consist of separating and catalytically cracking shale oil by commingling crushed shale particles with heated catalyst particles and of classifying the resulting organically deplated shale particles and catalyst particles. Thereafter the catalyst particles may be reheated and recycled.

Briefly, the method of the present invention comprises utilizing functionally integrated zones, including a retorting-cracking zone, a solids classifying zone, a catalyst regeneration zone, and a shale fine separation zone. Within the retorting-cracking zone shale oil is separated from crushed shale particles upon being commingled with heated catalyst particles, and the resulting separated shale oil is cracked catalytically to more desired products. During this simultaneous retorting and cracking step organic matter is distilled from the shale particles; concurrently the cracking reaction deposits carbonaceous matter upon the solid catalyst particles and thereby reduces catalyst activity. Separation of organically depleted shale particles from the deactivated catalyst is effected in the solids classifying zone. Thereafter carbonaceous matter is burned from the catalyst in the regeneration zone; the catalyst is thereby heated and reactivated. After removal of entrained shale fines in the shale fine separation zone, the heated catalyst is recycled to the retorting and cracking zone for reuse therein as described above.

Accordingly, this invention is directed to an improved and novel method for providing efficient recovery of hydrocarbon oil from solids containing hydroconbonaceous material, the product being in a condition amenable to fluid transfer. The method of this invention, under varied operating conditions, may be applied to the converting of the many varieties of oil shale and other solids bearing hydrocarbonaceous matter to oily products.

Oil shales occur as a finely laminated inorganic-organic structure. The inorganic material is a magnesium marlstone and its effect is discussed below. The organic material, consisting of carbon, hydrogen, nitrogen, sulfur and oxygen, is largely a complex solid termed "kerogen" which upon heating is decomposed into gas, liquid and solid reside.

This disclosure is directed primarily to the recovery of shale oil from Green River oil shales, found in northwestern Colorado, due to their richness and extent and to the large amount of related technical information made available by the Bureau of Mines research. It should be understood, however, that the method of this invention is not hereby limited and may be applied similarly to the recovery of oil from other shales and hydrocarbonaceous solids.

Upon the heating of shale of the Green River formation, the conversion rate becomes appreciable at about 660° F. and the kerogen decomposes to gas, oil, water and a solid, coke-like residue. At increased temperatures the decomposition proceeds more rapidly; the liquid products become vaporized and may be recovered from the retort or charge vessel, while the coke-like residue deposits on the spent shale and retort internals. In a continuous retort, such as a moving- or fluidized-bed system, it is desirable that the shale be relatively lean so that the shale particles spent of kerogen may retain their original shape. Rich shales, assaying over 40 gallons of oil per ton upon conversion become plastic and foam, thus causing an undesirable agglomeration of spent shale, which can restrict the flow of shale through the retort. Such a deleterious conversion is substantially avoided by the use of shales assaying about 25 gallons per ton or less.

The inorganic material found in Green River shales consists largely of calcium carbonate, which decomposes about 1200° F., and magnesium carbonate, which decomposes rapidly above 850° F., in about a 2:1 ratio. The carbonate decomposition is endothermic and produces exceedingly fine shale particles, largely in a 0–70 micron size range. Such decomposition is to be avoided since the original shape of the shale particles is destroyed and efficient classification techniques discussed below are precluded, the heat of decomposition increases the energy requirements of the process, and the resulting shale fines contaminate the oil product by forming an oil-water-fines emulsion that is difficult to break.

Raw shale oil is highly viscous and readily cannot be pumped under atmospheric conditions. Since, usually, the oil must be transported great distances to refinery areas, a coking or cracking of the shale oil is generally employed before transport to obtain a product amenable to fluid transfer. In the method of this invention, the necessary cracking is done catalytically within the retorting vessel. Crushed shale particles and heated catalyst particles are commingled within the upper portion of a re-

torting-cracking zone and pass through the zone as a downwardly moving bed. Separation of oil from the shale and catalytic cracking of separated oil occur substantially simultaneously and under conditions so that the spent shale largely retains its original shape, i.e. the plasticizing of rich shale and the decomposition of carbonates is avoided, as hereinabove mentioned. During this retorting-cracking operation effected at a temperature below carbonate decomposition temperatures, coke-like residue is deposited upon the shale and catalyst particles which are removed together as commingled discrete particles from a lower portion of the retorting-cracking zone. A purge gas, such as steam is introduced into a lower portion of the retorting-cracking zone adjacent to the solids exit to preclude the entrainment of hydrocarbon vapors with the spent solids.

The retorting-cracking zone is maintained at a temperature between about 660° F. and about 950° F., the exact limits depending on shale characteristics, desired product, etc., under which conditions shale oil separation and cracking is effected appreciably and shale decomposition as hereinabove described is avoided. In the method of this invention, the process heat requirements are provided preferably in major proportions by the heated or regenerated catalyst particles which are passed to the retorting-cracking zone at a temperature in excess of about 1100° F. Additional sources of heat may be provided, for example, the raw shale may be preheated by exchange with burned spent shale or by any other suitable means. Heat is required in the retorting-cracking zone to effect:

(1) The heating of raw crushed shale to conversion temperatures,

(2) The pyrolysis of kerogen,
(3) The vaporizing of shale oil, and
(4) The catalytic cracking of retorted shale oil.

Thus, the quantity of catalyst charged with the raw shale is determined primarily by the heat requirements of the retorting and cracking process and is dependent in part upon the oil content of the shale, the extent of shale degradation, the particular products desired and the inlet temperature of the shale and catalyst particles. In a typical embodiment of this invention, catalyst particles at about 1200° F. and shale particles at about 50° F. in about a 5–10:1 ratio are commingled and equilibrate to about 850° F. near the top of a downwardly-moving particle bed. As the compact mass descends, the endothermic pyrolysis, cracking and decomposition reactions, occur, thus decreasing the bed temperature. Cracked shale oil is removed in a lower portion of the retorting-cracking zone at about 650° F., while the spent shale and catalyst particles are purged with steam and removed from the bottom by gravity flow at a slightly lower temperature.

The solids passing from the bottom of the retorting-cracking zone consist of catalyst and spent shale particles covered with a coke-like residue as described above. Under the controlled conditions of the retorting-cracking zone as mentioned hereinabove, the spent shale discharge largely comprises discrete particles of their original shape, with a minor portion of smaller attrited particles and decomposed fines. The coke-like material deposited on the catalyst is burned in a catalyst regenerator to provide heat for the retorting and cracking hereinabove mentioned. It is desired, however, that the catalyst be essentially free of spent shale in the regenerator since at regeneration temperatures the endothermic decomposition of the shale carbonates:

(1) Proceeds rapidly and reduces substantially the heat generated, and

(2) Produces undesirable shale fines which, if not removed, contaminate the oil product as hereinabove discussed.

Consequently, in the method and system of this invention, spent shale particles preferably are separated from catalyst particles in a classifying zone intermediate between the retorting-craking zone and the regeneration zone. It is proposed to employ in the system herein described a mechanical separating device, such as a screen or vibrating grate or shaker table, although a fluid solid elutriation process or a combined elutriation-mechanical-separation process may be employed.

The coke-like material deposited on the catalyst particles and entrained shale fines discharged from the classifying zone is burned by contact with an oxygen-bearing gas in a regeneration zone to provide at least in part but preferably a major portion of the heat requirement of the retorting and cracking zone. Additional heat, if required, may be provided, for example, by suitable gas burners using methane or shale gas as a combustible material, by burning some of the hot, spent shale, or by any other suitable means. According to the method of this invention, it is preferable that the heat requirements be supplied in the regeneration zone since:

(1) There is present a minimum amount of shale which decomposes endothermically to fines at combustion temperatures, and

(2) Flue gases generated thereby cannot directly contaminate the product oil and gas.

In a typical embodiment of this invention catalyst particles and entrained shale fines discharged from the classifying zone at about 600° F. pass through a regeneration zone as a downwardly moving bed of solids. A combustion-supporting gas such as air is introduced into the regeneration zone wherein the coke-like residue on the catalyst is burned as the bed descends. Concurrently, the entrained shale is decomposed into fines and the catalyst particles are heated to a temperature of at least 1100° F. Hot flue gas is removed from the regeneration zone with decomposed shale fines entrained therewith. Further steps may effect energy recovery therefrom.

According to the method of this invention, preferably the heated catalyst discharged from the regeneration zone is recycled to the retorting-cracking zone with a minimum heat loss. Additionally, it is desirable that the entrained shale fines be removed prior to retorting and cracking since the fines tend to form an emulsion with the product shale oil as hereinabove mentioned. In a typical embodiment of this invention, catalyst particles with entrained shale fines at about 1300° F. are passed by gravity flow from the regeneration zone into a catalyst lift chamber. A suitable lift gas such as air at a temperature of about 1200-1300° F. lifts the solids to a separation chamber elevated above the retorting-cracking zone under conditions to allow a minimal loss of heat from the catalyst particles. The more buoyant shale fines are carried from the top of the separation chamber with the hot lift gas and are subsequently collected, while the heavier catalyst particles fall by gravity to the lower portion of the separation chamber. The hot catalyst particles pass by gravity feed into the retorting-cracking zone at a temperature in excess of about 1100° F. after having been purged of oxidizing gas by a suitable seal gas such as hot steam. The catalyst particles at an elevated temperature provide a major portion of the energy required in the retorting-cracking zone upon commingling with raw crushed shale particles as hereinabove described.

The method of the present invention is enhanced by effecting separation of spent shale particles from catalyst particles in the classifying zone and of shale fines from heated catalyst particles in the separation chamber. Preferably, therefore, the catalyst utilized is of a substantially uniform particle size intermediate to that of the raw shale particles and that of the decomposed shale fines. Many of the common beaded cracking catalysts, such as superfiltrol or other catalysts which meet the required physical characteristics, can be employed herein. It has been found that favorable retorting conditions can be achieved utilizing shale particles of about ¼ to 1-inch diameter. In order to maintain moderately uniform heat flow to the shale and to provide effective separation

from the catalyst particles, preferably shale of substantially uniform ¼ to 1-inch or larger particles size is charged to the retorting-cracking zone. Precedent thereto, in a shale crushing operation, preferably shale fines are discarded. Catalyst of a 1/16–⅛ inch particle size can be effectively separated in the present invention both from ¼ to 1-inch shale particles and from the 0–70 micron shale fines.

The figure is a typical schematic embodiment of the present invention shown diagrammatically in an elevation. Referring now to the figure by way of example there is shown a reactor **2** supported in a elevated position above a classifying chamber **4**. Said reactor **2** and classifying chamber **4** are positioned above regenerator **6** to permit gravity flow of solids thereto. Positioned above a catalyst surge hopper **8** and connected thereto by a gravity feed leg **10** is a separation chamber **12** into which lift gas and catalyst are discharged as explained more fully hereinafter. A withdrawal conduit for standpipe **14** leads from the bottom of regenerator **6** to a lift feed chamber **16**. A suitable lift gas inlet conduit **18** connects with the lift chamber **16** and an open-ended lift pipe **20** extends substantially vertically upward from a location within the lift chamber into the upper portion of the elevated separation chamber **12**.

In the method of this invention employing the means described above, raw crushed shale particles, passed from oil shale hopper **22** by way of gravity feed leg **24** provided with flow control valve **26**, are commingled with hot regenerated catalyst particles passed from an elevated catalyst surge hopper **8** by gravity feed leg **28** into reactor **2**. The commingled mixture of catalyst and shale is passed through reactor **2** as a relatively dense, downwardly moving bed of particles. A suitable seal gas is introduced into gravity feed leg **28** or seal chamber **30** provided therewith by means not shown to maintain a seal pressure at the base of the feed leg **28** elevated sufficiently to permit flow of catalyst therefrom into reactor **2**. Oil shale and hot regenerated catalyst contact is effected within reactor **2** under conditions and in a manner which accomplishes a separation or distillation of hydrocarbonaceous material from the oil shale and a catalytic cracking of separated hydrocarbonaceous material to provide useful products of a more desired nature. The endothermic heat required for effecting the above separation of hydrocarbonaceous material and the catalytic cracking thereof is supplied at least in part by recycled regenerated catalyst particles. The ratio of hot catalyst to cold shale is controlled to allow heating of the shale upon commingling with the catalyst particles to a temperature of about 850–950° F. at the top of the bed. The separated hydrocarbonaceous material flows concurrently with the relatively dense, downwardly moving bed in reactor **2**, is cracked simultaneously to more useful constituents and emerges from reactor **2** by vapor outlets **32** through conduit **34** to a shale oil recovery section not here shown. The deactivated catalyst and organically depleted shale particles are purged free of hydrocarbonaceous vapors by means of a suitable inert purge gas supplied through conduit **36**. The spent catalyst and shale particles then pass by gravity flow via conduit **38** into classifying chamber **4**.

The mixture of spent catalyst and shale particles is separated in classifying chamber **4** by means of a suitable separating device **40**, such as a grate, vibrating screen, shaker table, or other classifier. As hereinbefore mentioned, preferably a catalyst is used in the method of this invention which is of a substantially different particle size from that of the spent shale particles, to allow an effective physical separation of the spent shale. A major portion of the spent shale particles is separated from the main catalyst stream and removed from classifying chamber **4** through conduit **42** into a coarse spent shale hopper **44** and discarded through conduit **46**. If economics warrant, the spent shale may undergo heat recovery before discarding. The deactivated catalyst particles and entrained small shale particles then pass by gravity flow via conduit **48** into regenerator **6**.

The catalyst and small shale particles pass through regenerator **6** as a relatively dense, downwardly moving bed being contacted with air or other oxygen-bearing gas introduced via conduit **50**. Carbonaceous deposits are burned from the catalyst and shale particles under conditions to heat the catalyst particles to a temperature of at least 1100–1200° F. Under such conditions the entrained shale is rapidly disintegrated into fines. Gaseous combustion products are withdrawn from regenerator **6** via conduits **52**. Hot regenerated catalyst and disintegrated shale fines pass by gravity flow via conduit **14** into lift feed chamber **16**. A suitable lift gas is introduced via conduit **18** at a temperature sufficiently elevated to preclude any significant cooling of the regenerated catalyst particles and at a velocity sufficient to elevate the regenerated catalyst particles and shale fines via lift pipe **20** to the separation chamber **12**. Regenerated catalyst particles fall by gravity to the bottom of separation chamber **12** and are removed by gravity flow via conduit **10** to catalyst surge hopper **8**. Virtually all of the buoyant shale fines are removed overhead by the lift gas from separation chamber **12** via conduit **54** into cyclone **56** wherein the shale fines are separated from the lift gas and removed by gravity flow via conduit **58** while the lift gas is removed overhead via conduit **60**. As hereinbefore mentioned, preferably a catalyst is used which is of a substantially different particle size and density from that of the spent shale fines so that an economically minimum quantity of catalyst is carried overhead with the spent shale fines from the separation chamber **12**.

As hereinabove mentioned, this disclosure is directed primarily to the recovery of shale oil from Green River oil shales significantly because of the amount of technical information pertaining to such shales. The limitations of temperature, particle size, etc. are directed above to define conditions suitable for the conversion of Green River shale, but it should be understood that the method of this invention is not thereby limited and may be applied as well to the recovery of oil from other shales and hydrocarbonaceous solids. Therefore, operating conditions and limitations suitable for the conversion of oil from other shales and hydrocarbonaceous solids, but outside the ranges suitable for Green River shale as hereinabove disclosed, are also considered fairly to be within the purview and scope of the present invention. Preferably, however, the retorting-cracking zone is maintained at a temperature of between about 500° F. and about 1000° F. and the regeneration zone is maintained at a temperature of between about 1000° F. and about 1400° F.

I claim:

1. A continuous method for simultaneously distilling and catalytically cracking shale oil from crushed particles of oil shale, which comprises commingling oil shale particles and heated catalyst particles in an elevated retorting-cracking zone, both particles being granular and said catalyst particles being largely of a smaller size than said oil shale particles, said catalyst particles being of the order of at least about 1/16 inch in size and being heated in a regeneration zone to a temperature of about 1100°–1400° F. and being of a quantity relative to said oil shale particles sufficient to effect a rise in temperature of said oil shale particles upon commingling in said retorting-cracking zone to about 850° F.–950° F.; passing the commingled particles through said zone as a dense descending moving bed at a temperature of about 650° F.–950° F. at which temperatures disintegration of said shale particles substantially is prevented, effecting the distillation of hydrocarbon vapors from said shale particles and effecting catalytic cracking thereof simultaneously while said hydrocarbon vapors move downwardly through said dense descending moving bed, consequently depositing carbonaceous matter on said catalyst particles; removing said shale and catalyst particles downwardly from the bot-

tom of said descending bed in a continuous gravity flow condition to a classification zone, effecting a separation of at least a major portion of said shale particles from said smaller catalyst particles and small shale particles; removing said catalyst particles and entrained small shale particles in a continuous gravity flow condition to a regeneration zone, passing said particles through said zone as a descending moving bed to a temperature of about 600° F.–1400° F.; effecting burning, with a combustion-supporting gas, of carbonaceous matter deposited on said catalyst particles to a temperature of about 1100° F.–1400° F. and to effect disintegration of entrained small shale particles into shale fines of size smaller than the catalyst particles; lifting said heated catalyst particles and shale fines to a separation zone elevated above the hereinbefore mentioned retorting-cracking zone, effecting therein a separation of substantially all said shale fines from said heated catalyst particles, and recycling said heated catalyst particles in a continuous gravity flow condition to said retorting-cracking zone, whereby substantially no shale fines are recycled to said retorting-cracking zone.

2. The method of claim 1 wherein the hydrocarbon vapors passing downward concurrently with said descending bed are removed therefrom at a point spaced above the bottom thereof, and an inert purging medium is introduced to flow countercurrently from a point nearer the bottom of said descending bed and is withdrawn therefrom together with the hydrocarbon vapors.

3. The method of claim 1 wherein the mix of regenerated catalyst particles and distintegrated shale fines withdrawn from the bottom of the regenerator is passed into a lift chamber and entrained therein into a gaseous lift stream to pass upwardly to a separating zone in which catalyst particles are separated from lift gas and distintegrated shale fines, and the regenerated catalyst particles substantially free of shale component are passed by gravity flow to a catalyst storage and subsequently to admixture with incoming shale particles.

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DANIEL E. WYMAN, *Primary Examiner.*

ALPHONSO D. SULLIVAN, *Examiner.*

H. LEVINE, P. E. KONOPKA, *Assistant Examiners.*