

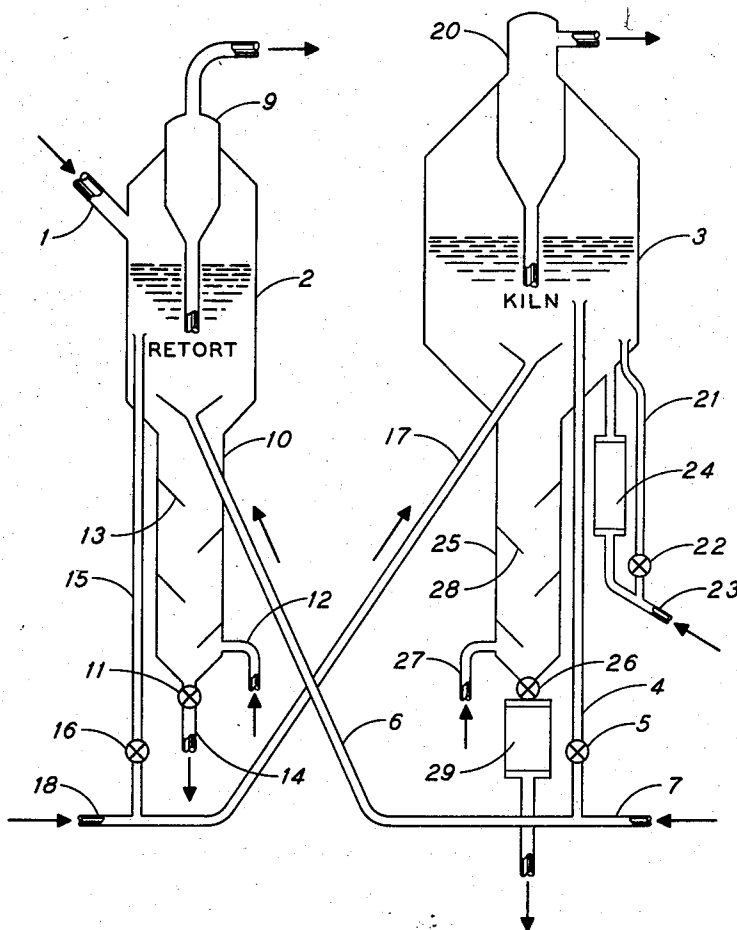
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J. W. SCOTT, JR., ET AL

2,844,525

FLUID RETORTING PROCESS

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FLUID RETORTING PROCESS

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This invention relates to an improved method of the solids fluidization type for retorting oil-bearing minerals, of the type of diatomaceous shale, oil and tar sands, oil-bearing sandstones and the like, including coal, to recover valuable materials therefrom. In a more specific aspect, the invention has to do with an improved fluidization process for the recovery of valuable materials, including motor fuels and oils, from oil-bearing mineral, involving a retorting or distillation zone and a burning zone for the burning of carbon and combustibles from the retorted mineral, wherein the mineral is maintained in a fluidized stable mass or bed by the controlled removal or elutriation of mineral particles, the presence of which would adversely affect the fluid mass, such as by causing channeling, slugging, etc.

A conventional system for retorting oil-bearing minerals is a two-zone or two-vessel system described, for example, in British Patent No. 586,992, involving a continuous operation in which the oil-bearing mineral is subjected to high temperatures in a retorting zone while suspended as a dense phase of highly turbulent particles, or fluidized solid mass, by an inert gas such as steam. The operation is further characterized by the feature that the spent mineral withdrawn from the retorting zone, but still containing residual combustible material on the non-combustible mineral support, is burned, or calcined, in a kiln in the fluidized state while suspended by air and the combustion products, the burned mineral being recycled, at least in part, to the retorting zone where it serves to supply the necessary heat for retorting the fresh oil-bearing mineral. In some cases the necessary heat is supplied, at least in part, either as sensible heat of preheated process materials or by indirect heat exchange of the fluidized bed with suitable heating means or by combustion of combustible mineral constituents within the retorting zone, or by various combinations of any of the above means. Also customarily involved is the transport of solids in dilute phase, namely, spent oil-bearing mineral, the calcined mineral, and sometimes also the ground and sized fresh mineral. Thus, the calcined mineral is picked up in dense phase from a standpipe, which serves as a seal leg, connected to the kiln, and is transported to the retort in dilute phase by means of an inert gas, such as steam; likewise, the retorted mineral is transported to the kiln in dilute phase from a standpipe on the retort by means of air or oxygen-containing gas.

A problem surrounding the recovery of valuable hydrocarbons from oil-bearing minerals arises in connection with the necessity of grinding and sizing the mineral to particles of small dimensions to permit adequate fluidization at gas velocities sufficiently low to minimize size of blower equipment, to reduce vessel height for a given solids inventory and erosion of equipment, as well as to realize fully the high heat transfer and reaction rates intrinsic in the fluid process.

Another problem resides in the nature of the hydrocarbon material and of the non-hydrocarbon mineral sup-

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port constituting the oil-bearing mineral. For example, in the case of the true oil shales, which consist of a kerogen or resinous hydrocarbonaceous substance disposed on a mineral support, great difficulty is encountered as the result of the strong tendency of the shale to disintegrate rapidly in the course of the retorting to particles having an extremely small size, about 0-20 microns, that is, the unit particle size of the shale silt. As a result, serious losses of valuable carbonaceous material are incurred, these being removed from the retorting zone with the fines. Moreover, liquid product recovery is seriously complicated due to heavy slurry formation resulting from heavy carry-over of fines, and the stability of the fluidized bed is so seriously affected that it may not be possible to retain it within the retort unless costly precautions are taken.

Another class of oil-bearing materials are the non-kerogenic type, such as the diatomaceous shales, the tar sandstones, and coal. When the temperature of a diatomaceous shale is raised, the contained heavy viscous oil exudes from the pores of the diatomaceous absorbent, and the individual particles of the diatomaceous shale develop a tacky surface so that agglomeration occurs and prohibitive clinkering results. A similar semiplastic stage occurs in the fluid carbonization of bituminous materials, such as coal. With the true oil sands the support is a non-diatomaceous material from which the contained oil more readily vaporizes without formation of tacky surfaces. A difficulty with some of the oil-bearing minerals of the non-kerogenic type is agglomeration or clinkering of the fluidized particles.

Accordingly, an object of the invention is to provide a process of recovering hydrocarbons from oil-bearing minerals, including coal, in a continuous fluidized operation in which operating difficulties due to agglomeration or clinker formation are substantially eliminated.

Another object of the invention is to provide a method of avoiding excessive grinding of the fresh feed to a system for fluidized retorting, while at the same time maintaining adequate particles size and size distribution in the retort zone and in the kiln zone, whereby stable, smooth fluidization is maintained, without channeling and slugging, at gas velocities sufficiently low to minimize abrasion of equipment and attrition of the particles.

Broadly, the present invention contemplates a process which comprises subjecting a fluidized solids mass or bed of oil-bearing mineral particles, e. g., diatomaceous shale, in a retorting zone to retorting temperatures. In the retorting zone hydrocarbon vapors are distilled from the oil-bearing material, thus leaving spent oil-bearing material ("retorted bing"), having carbon and other combustibles associated therewith. The larger particles of this retorted bing, the presence of which would impede smooth fluidization in the retorting zone, are withdrawn from the zone by elutriation. The remainder of the retorted bing, or spent oil-bearing mineral, is then discharged into a combustion zone or kiln. Passed along with this bing is an oxygen-containing gas which serves to fluidize the retorted bing in the combustion zone and to ensure proper solids fluidization and to burn the combustibles associated therewith. In the combustion or kilning zone the carbon and other combustibles are burned off to give flue gases and hot "burned bing." As in the retorting zone, the larger burned bing particles are withdrawn from the kiln by elutriation in order to ensure smooth solids fluidization and to maintain the desired solids inventory in the system, i. e., in the retorting and burning zones. The remainder of the hot burned bing is then returned to the retorting zone along with a fluidizing gas, preferably an inert gas, e. g., steam, to supply the heat of retorting in the retorting zone and to

maintain or improve smooth solids fluidization in the retorting zone.

More specifically, in carrying out the invention a finely divided oil-bearing mineral, such as diatomaceous shale, which has been broken and sized with a grinder to pass, say, about a 4 to 9 mesh screen, is very rapidly heated to the temperature of volatilization of its hydrocarbon component by and in the presence of a large excess of finely divided burned or kilned "bing" obtained from the shale. The term "retorted bing," as hereinabove indicated, is employed to designate the solid residue of the shale after its hydrocarbon content has been removed by heating to an elevated temperature to effect volatilization of the hydrocarbons, usually to about 1000° F. This bing, usually has a carbon content amounting to about 5% to 10% by weight. Bing from which the carbon has been substantially removed by combustion is referred to as "burned bing," as already indicated. The mixture of finely divided shale and burned bing is maintained in a fluidized bed by passing an inert gas, such as steam, through the mixture of solids at a rate sufficient to produce a turbulent boiling action in the solids. The mixture of burned bing and shale maintained in the bed has a high ratio of burned bing to fresh diatomaceous shale, usually above 3 to 1 and preferably around 4-4.5 to 1 by weight. The burned bing is at an elevated temperature, in excess of 1000 and as high as 1500° F., usually at about 1400° F., at the time of mixing it with the finely divided fresh shale for introduction into the retort where the fluidized bed is maintained. Substantially all of the heat required to bring the bed to the operating temperature, about 1000° F., and to volatilize the hydrocarbon components of the shale can be supplied by the hot burned bing. The volatilized hydrocarbons are taken overhead from the retort and recovered. Further in accordance with the invention, a portion of the mixture of burned bing and retorted bing is withdrawn through an elutriation leg on the retort and elutriated with steam to eject a portion of the bing larger than a predetermined size, preferably, about 15 mesh, from the retort, and to return a substantial fraction of bing smaller than, say, about 15 mesh to the retort. Removal of large bing has a beneficial effect upon fluid bed stability and permits tolerance in the fresh feed of larger particles than are readily transportable or fluidizable by fluid solids technique. Elutriation at this point also offers an exit from the system of any incipient agglomerates formed as the fresh shale passes through the semiplastic stage in being brought up to retort temperature.

The remainder of the mixture of burned bing and retorted bing is withdrawn from the retort and transferred to a kiln. The fixed carbon on the retorted bing is burned with air or oxygen-containing gas, and a portion of the resultant burned bing, superheated, say, to about 1400° F., is returned to the retort for use as already described. The remainder of the burned bing, except for fines, usually 40 to 60 mesh and smaller, lost overhead from the kiln in the combustion and hydrocarbon products, is withdrawn through an elutriation leg on the kiln and elutriated with air or steam to return a fraction of all particles smaller than a predetermined size, preferably about 30 mesh, to the kiln and to reject the remainder, including particles larger than about 30 mesh, from the system. As a result of retention within the kiln of the smaller particles of the burned bing, and of the high ratio of burned bing to fresh shale in the retort, the average size distribution of particles in the kiln and in the retort is markedly smaller and more readily fluidizable and at lower gas velocities than the fresh, finely divided shale, and, as a result, a coarser and more economical grinding of the shale is tolerable. Lower gas velocities give resultant decreases in required blower capacity, vessel height for a given solids inventory, abrasion of equipment and attrition of particles.

The presence of a larger proportion of fine burned bings in the retort assists in preventing agglomeration and clinkering of diatomaceous shale particles during the semiplastic state which these particles pass through in coming up to temperature in the retort.

Oil-bearing mineral of a type particularly adapted to the present process is well exemplified by deposits found in the vicinity of Casmalia, California. This deposit is a diatomaceous earth or shale saturated with organic material having the appearance of a heavy crude oil or petroleum tar. It occurs in massive formation, is softer than true or kerogen-containing shales, being comparable to a hard chalk in hardness, is a brownish gray color and is readily crushed. It has the appearance of ordinary dry rock. The oil can be removed from this material by extraction with solvents and accordingly, it is often referred to as a "tar sand" to distinguish it from true oil shale from which the oil cannot be removed by solvents, although it is markedly different from an oil or tar-saturated sandstone in appearance and character. The residual diatomaceous solid material from which the oil has been removed has a large surface area and apparently much of the oil is adsorbed on it. The Casmalia deposits have long been regarded as a promising petroleum source, but many commercial scale attempts to recover this oil by various retorting methods have failed because of the tendency of the crushed diatomaceous shale to form large clinker-like masses which cannot be removed from the equipment by means designed to handle crushed rock. In the process of the present invention the diatomaceous shale particles are brought up to retorting temperature in the presence of a large excess of calcined shale particles containing a proportion of finely divided particles greater than that of the fresh feed. This gives controlled temperatures, lack of hot spots in the equipment, and, when the shale goes through a tacky state as retorting progresses, the presence of large amounts of fine calcined bing prevents agglomeration and clinkering.

For additional understanding of the invention reference is now made to the accompanying drawing illustrating suitable apparatus and process flow of a two-vessel system suitable for carrying out a preferred embodiment of the invention.

Oil-bearing diatomaceous shale, ground to pass, say, 7 mesh, such as the Casmalia tar sand hereinabove described, and hereinafter referred to as "shale," is introduced via line 1 into retort 2. Hot burned bing from kiln 3 passes through standpipe 4 controlled by valve 5 into line 6 provided with a flared discharge end, and is carried in fluidized condition by means of steam introduced at 7 into retort 2. The burned bing is at an elevated temperature, usually about 1200-1400° F., and the ratio of bing to fresh shale introduced to the retort 2 can range upward from about 3 to 1, preferably about 4.5 to 1. Higher ratios permit reductions in burned bing temperatures for a given retorting temperature. These may be advantageous with a particularly low-melting shale, or one which tends to decompose with the absorption of heat, as in carbonate decomposition. In retort 2 the hydrocarbon components are volatilized and cracked. All the heat required to volatilize the hydrocarbon of the shale, to bring the fresh shale up to retorting temperature and to crack the hydrocarbon is supplied by the hot burned bing. The hydrocarbon product and fluidizing steam are withdrawn through cyclone separator 9 which returns suspended solid material to the fluidized bed in retort 2. The hydrocarbon vapors and steam are cooled, condensed, and separated by means not shown. A portion of the bing in retort 2 is withdrawn through elutriation leg 10, controlled by valve 11 where, by means of steam introduced through line 12, about 0.05 to 0.15 pound of 7 to 14 mesh bing per pound of fresh shale feed (oil and water-free basis) are separated and rejected from the retort through line 14. As

already indicated, elutriation is effected in elutriation leg 10 by the introduction of an inert aerating gas, e. g., steam, through line 12, as a result of which classification of the particles occurs, i. e., settling of the larger particles at the bottom of the zone. In addition, elutriation leg 10 is provided with baffles, represented by 13, which by obstructing solids mixing aids in the classification of the particles. The remainder of the bing is withdrawn from retort 2 through standpipe 15 controlled by valve 16 and passed into line 17. Preheated air is introduced into line 17 through line 18 and carries the bing via line 17 into kiln 3. A fluidized bed of bing is maintained in kiln 3 which constitutes a combustion zone where residual carbon on the bing is burned. Flue gas is withdrawn from kiln 3 through cyclone separator 20 which separates and returns suspended solids to the fluidized bed in the kiln. In the event an undue accumulation of fine particles occurs, the fine particles may be removed by having the cyclone discharge externally, rather than back into the bed. Solid material from the fluidized bed in kiln 3 passes through standpipe 21 controlled by valve 22 into line 23. Air is introduced into line 23 to carry this solid material through heat exchanger 24 back into kiln 3. The temperature in kiln 3 is preferably maintained at about 1400° F. A portion of the burned bing in kiln 3 is withdrawn through elutriation leg 25, provided by

Characteristics of the oil recovered and the residual burned bings are shown below:

Oil—API gravity	20.8
SSU viscosity at 100° F.	48.9
Distillation at 760 mm., ° F.—	
5%	170
10%	330
20%	434
40%	585
50%	624
75%	632
Analysis—Carbon, wt. percent	84.3
Hydrogen, wt. percent	10.6
Sulfur, wt. percent	3.64
Nitrogen, wt. percent	0.20
Retorted bing ¹ —	
Carbon, wt. percent	7.32
Hydrogen, wt. percent	0.37

¹ The remainder of the retorted bing was silicon oxide together with small amounts of aluminum, iron, calcium, and magnesium oxides. When freed from carbon and hydrogen the residue had a surface area of 50–70 sq. meters/gram and did not fuse at 1800° F.

In order to further illustrate the invention, the following table shows the particle size distribution in a typical case in the feed, the recycle, in the kiln and retort, and in the net solid streams withdrawn from the system:

Table

	Solids Streams				Average Size Distribution	
	Feed	Removed from Kiln	Removed from Retort	Overhead from Cyclones	Retort	Kiln
	(1)	(2)	(3)	(4)	(5)	(6)
Lb./Lb. Feed, Oil and Water-Free Basis	1.0	0.928	0.062	0.010		
Mesh Size:						
7-9	5.6	1.1	75.0		0.9	0.2
9-14	6.6	5.3	25.0		1.1	0.8
14-20	20.1	21.4	0		20.3	20.4
20-30	22.2	23.6	0		25.3	25.4
30-40	22.9	24.4			25.7	26.1
40-60						
60-100						
100-200	7.6	8.1		(20)	9.1	9.2
200-	7.6	8.1		(40)	8.9	9.2
	7.4	7.8		(40)	8.7	8.8
Weight, percent	100.0	100.0	100.0	100.0	100.0	100.0

baffles, as represented by numeral 28, controlled by valve 26, where, by means of air introduced into line 27, a portion of all material smaller than, preferably, about 30 mesh in size is restored to the kiln and an amount of burned bing is discharged from the system through exchanger 29, the amount discharged being regulated to maintain solids inventory in the retort and kiln system, generally, about 0.85 to 0.95 lb. of burned bing per pound of shale (oil- and water-free basis). The remainder of the burned bing is withdrawn through standpipe 4 and recycled to the retort 2 through line 6 as described hereinabove.

A set of conditions for processing Casmalia diatomaceous shale in an apparatus conforming essentially to that shown in the appended drawing are as follows:

Charge—lb./hr./sq. ft. of retort cross-section	1570
Mesh size of charge	17–60
Recycled Bing—lb./hr./sq. ft. of retort cross-section	7000
Retort temperature	° F. 950–1050
Kiln temperature	° F. 1340–1430
Steam to retort—lb./hr./sq. ft.	15.6
Air to kiln—lb./hr./sq. ft.	153
Oil recovered—gal./ton of sand	29.8

¹ The major portion of the charge was in this range of particle size.

From inspection of the table it will be noted that the feed composition, column 1 contains substantial quantities of coarse feed, i. e., about 12% of the feed is within the size range 7–14 mesh. As the feed stands it is unfluidizable and would give an unstable fluid bed, that is, would give rise to channeling or bumping, notwithstanding the use of a wide range of fluidizable gas velocities. On the other hand, in columns 5 and 6, the particle size distribution in the system is such that the feed can be fluidized at a minimum gas velocity of 0.5 ft. per second. The nature and amounts of material elutriated to give the size particle distribution in columns 5 and 6 are indicated in columns 2, 3 and 4, column 4 indicating the amount of fines lost from the kiln through the cyclone.

Operation according to the process of this invention provides a convenient and continuous means of controlling particle size and size distribution within the system independently of the size distribution of the feed. It is well known that the energy requirement and other costs of crushing and grinding rock and other materials increases very rapidly as the mesh size of the desired product decreases. On the other hand, successful fluidization, that is, production of a dense phase fluid bed of solid particles which is in uniform high turbulence with good mixing and heat transfer and thus substantially free from channeling and slugging of the fluidizing gas through the bed, requires

careful control of both average particle size and particle size distribution for a given gas velocity. The process of the present invention permits use of a relatively coarsely ground, and hence, inexpensive feed, which is only very difficultly fluidizable or not at all at desirable low gas velocities, and at the same time by means of the elutriation steps described hereinabove a particle size distribution is maintained in the retorting and calcining zones which ensures good fluidization at low gas velocities by returning small particles to the system.

We claim:

1. In a process for retorting particulate oil-bearing solids to recover therefrom valuable hydrocarbons vapors by subjecting said solids to retorting temperatures in a dense, turbulent bed of solids stably fluidized by an upwardly flowing gas in a retorting zone, the steps comprising feeding solid particles of raw oil-bearing minerals to said zone, said feed containing appreciable members of particles of such size that they are incapable by themselves of being stably fluidized at the gas rate employed in said zone; separately withdrawing the larger retorted bing particles from an elutriation section of said retorting zone; withdrawing the remaining retorted bing from said retorting zone and passing it along with an oxygen-containing gas into a combustion zone, said oxygen-containing gas being introduced into the latter zone at a rate sufficient to maintain the retorted bing in a stable fluidized condition within said combustion zone; burning the combustibles associated with the retorted bing in said combustion zone to produce hot burned bing solids; separately withdrawing the larger burned bing solids from an elutriation section of said combustion zone so as to reduce the average particle size in said combustion zone; recycling a substantial portion of the remaining

hot burned bing along with a fluidizing gas to the retorting zone to supply the heat of retorting, said burned bing-containing gas stream being introduced into said retorting zone at a rate sufficient to stably fluidize the incoming feed particles in the presence of the recycled burned bing; and recovering hydrocarbon vapors from said retorting zone as a product.

2. The process of claim 1 wherein the oil-bearing solids are of the non-kerogenic type.

3. The process of claim 1 wherein the oil-bearing solids are Casmalia tar sands.

4. The process of claim 1 wherein the larger retorted bing particles separately withdrawn from the elutriation section of the retorting zone and which are incapable of being stably fluidized in said zone at the gas rate employed are larger than about 14 mesh in size.

5. The process of claim 1 wherein the larger burned bing solids separately withdrawn from the elutriation section of the combustion zone so as to reduce the average particle size in said zone are larger than about 30 mesh in size.

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CERTIFICATE OF CORRECTION

Patent No. 2,844,525

July 22, 1958

John W. Scott, Jr., et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 18, for "members" read ~~--numbers--~~.

Signed and sealed this 14th day of October 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents