March 11, 1952 H. Z. MARTIN ET AL 2,589,109

FLUIDIZED DISTILLATION OF SHALE

Filed Dec. 29, 1945

2 SHEETS—SHEET 1

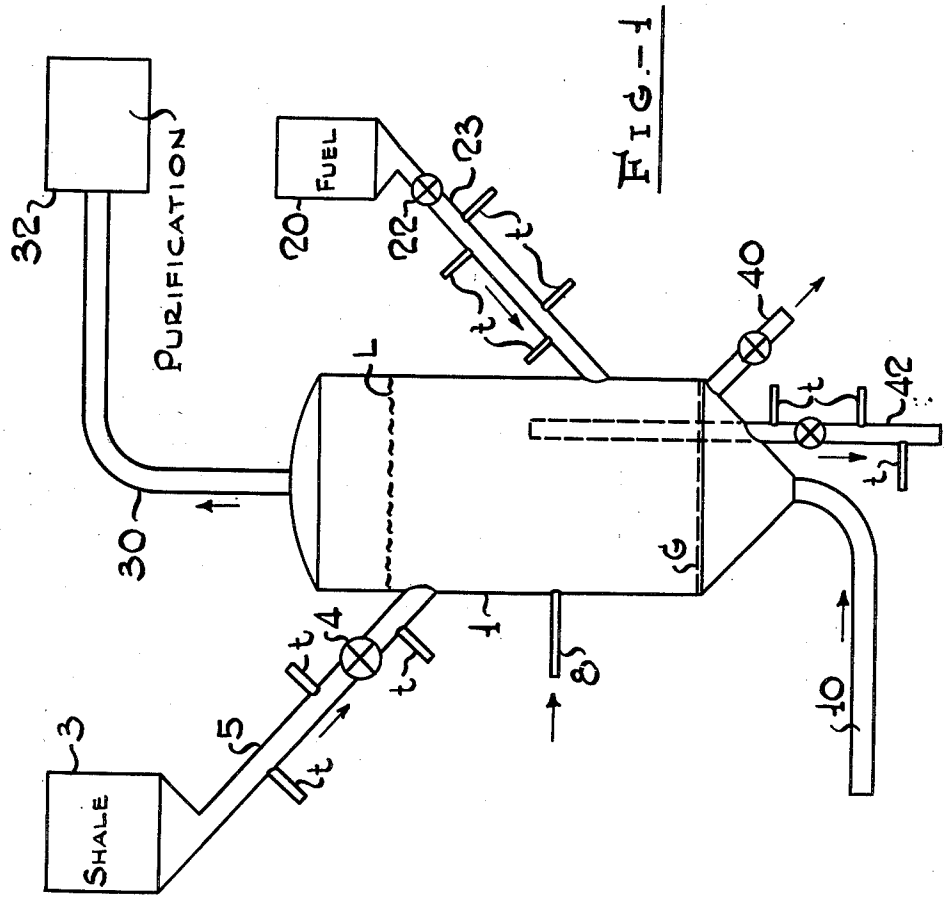


FIG. 1

Homer Z. Martin
Frank T. Barr Inventors

By J. C. Arnall Attorney

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2 SHEETS—SHEET 2

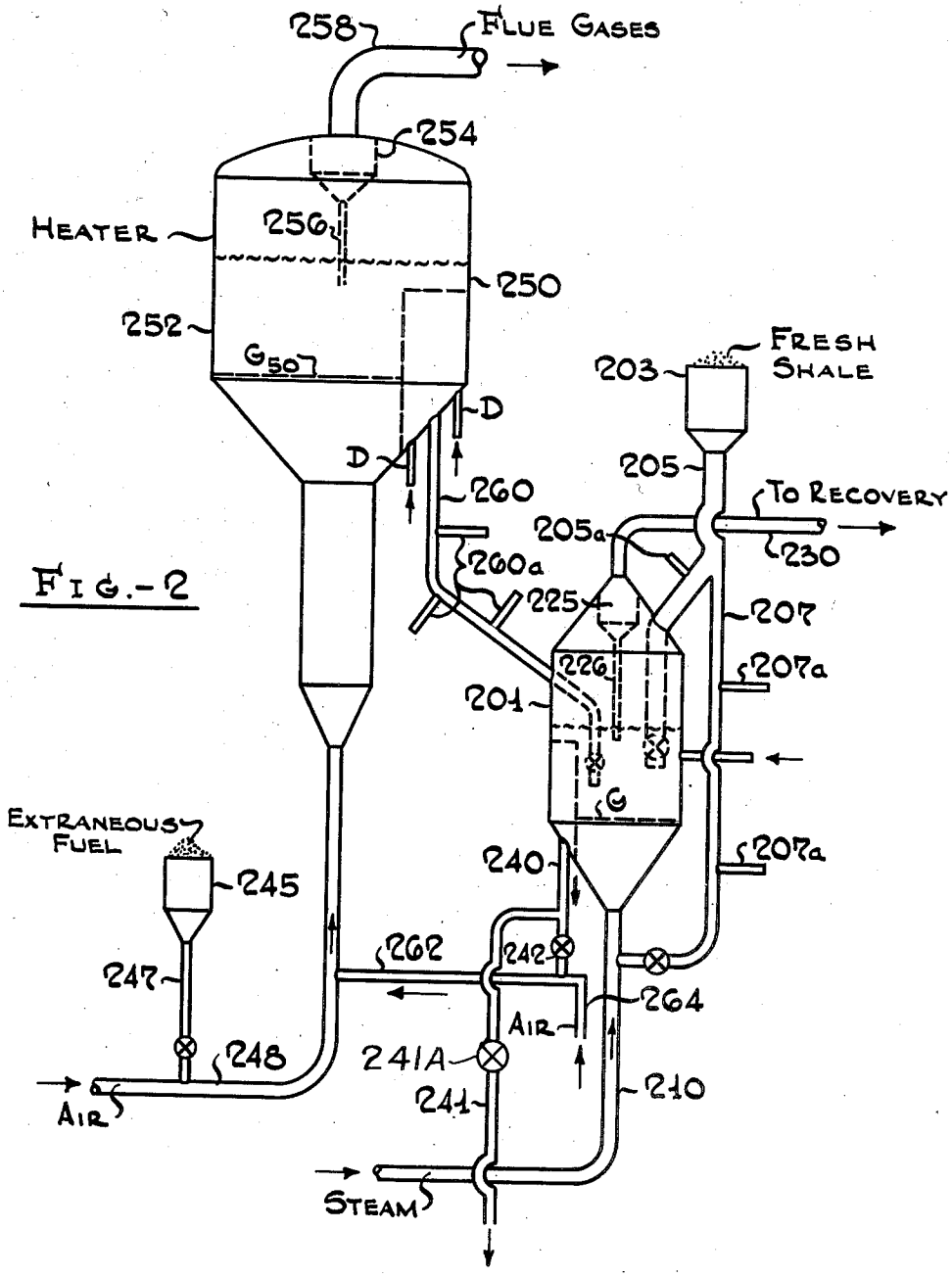


FIG.-2

Homer Z. Martin
Frank T. Barr Inventors

By J. C. Kimball Attorney

Patented Mar. 11, 1952

2,589,109

UNITED STATES PATENT OFFICE

2,589,109

FLUIDIZED DISTILLATION OF SHALE

Homer Z. Martin, Roselle, and Frank T. Barr, Summit, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

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5 Claims. (Cl. 202—6)

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The present invention relates to the novel features hereinafter fully disclosed in the following specification and claims considered in connection with the accompanying drawing.

It is known that certain types of naturally occurring oil-bearing minerals, such as shale or oil sands, contain materials which may be converted by pyrolytic treatment into commercially feasible quantities of hydrocarbon oils, including oils boiling in the gasoline and gas oil range.

Prior to our invention, others proposed carrying out the pyrolytic treatment of the shale while the same was in the form of a powder or rather large aggregates, which may be as large as four mesh, in a fluidized state in a distillation or pyrolytic zone, while supplying the heat necessary for the reaction by combustion, that is, either by burning a portion of the combustibles in the distillation or pyrolytic zone or by burning the spent shale in a separate combustion zone and returning the burnt substantially uncooled shale to the distillation or pyrolytic zone. The former method has the advantage of a simple design, while the latter method permits the production of oil free of gaseous combustion products. However, both methods have marked disadvantages. The heat supplied by burning residual spent or partially spent shale consumes combustible material equivalent to as high as 0.1 to 0.4 barrel of oil per ton of shale, and will actually reduce the oil yield by the amount that truly non-distillable carbonaceous residue cannot supply. Heat supply by combustion within the distillation zone, if not controlled with extreme care, may lead to loss of valuable distillation products which are burned instead of non-distillable residue as a result of the low concentration of the residual carbon available for this purpose. When spent shale is burnt in a separate combustion zone, the combustibles content of this shale is present in high dilution in ash which results in a low rate of combustion. To supply in this manner the heat required for distillation, excessive volumes of spent shale and correspondingly large heater dimensions are required.

The present invention overcomes the aforementioned difficulties and affords various additional advantages. These advantages, the nature of the invention and the manner in which it is performed will be fully understood from the following description thereof read with reference to the drawing which shows semi-diagrammatic views of apparatus particularly adapted to carry out the invention.

The main object of our present invention relates to improvements in the continuous distillation and/or pyrolytic treatment of shale or oil sands wherein the operation is performed in a manner which induces a greater production of valuable hydrocarbon oil per ton of shale.

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A second object of our present invention has to do with supplying the heat necessary for supporting the distillation of naturally occurring shale or oil sands under conditions such that burning of the desired oil in the shale is substantially avoided.

A still further object of our invention concerns the supply of the heat necessary for supporting the distillation of naturally occurring shale or oil sands in the form of a dense turbulent bed of fluidized finely-divided solids under conditions such that burning of the desired oil in the shale is substantially avoided.

Other and further objects and advantages of the present invention will appear from the following more detailed description and claims.

We have found that these objects and advantages may be accomplished by supplying the heat-generating combustion stage of the distillation process with extraneous fuel, that is, fuel other than carbonaceous constituents of the shale or oil sands undergoing distillation. For example, we may add extraneous solid fuel, preferably of a relatively low ignition temperature, such as coal, particularly lignites or bituminous coals, or wood, e. g., sawdust, to the material to be distilled, and supply an oxidizing gas to the distillation zone to generate the heat required for the distillation by a preferred combustion of the added extraneous material. The combustion of the extraneous material may be further favored over that of the shale by charging the former in a particle size different from that of the latter. If the particle size of the extraneous fuel is larger, the combustion takes place in a partially differentiated layer of the total process solids which consists mainly of extraneous fuel. If this particle size is smaller, the larger surface presented favors combustion of the fuel over that of the shale. If desired, spent shale may be circulated to a separate combustion zone or heater, highly heated therein by combustion of residual carbon and returned to the distillation zone to supply additional heat. Depending on the amount of oil to be distilled, the coke content of the spent shale or sand and the type of extraneous fuel employed, the latter may be added in proportions of about 50 to 200 lbs. per ton of oil-bearing solids. One ton of an oil shale containing about 0.4 bbl. of oil, for example, may require about 100 lbs. of a bituminous coal. In this manner, the

loss of otherwise recoverable oil by combustion is substantially completely eliminated.

When applied to a distillation system involving a separate heater, our invention may be practiced to greatest advantage by burning extraneous solid fuel in the heater and feeding hot solid combustion residue to the distillation zone containing the oil-bearing solids to be distilled. If no other inexpensive solid fuels are readily available, fresh shale may be used for this purpose. Other solid fuels such as coal, coke, wood or the like, may be burnt in the heater in the presence of inerts such as ash, spent shale, etc., which are circulated to the distillation zone to supply the heat required therein. In both cases, solid distillation residue, such as spent shale, may be circulated to the heater to serve as heat carrier and/or to contribute combustibles. If this is the case, a combustible gas may be used as an extraneous fuel for the heater. The amount of extraneous fuel supplied to the heater depends on numerous variables, such as the heat requirement in the distillation zone, heat carrier circulation rate, type of extraneous fuel, etc. Broadly, operative amounts may vary from 1000 to 1500 lbs. of shale to be burnt, from 40 to 180 lbs. of coal, and 100 to 800 lbs. of wood per ton of shale containing 0.4 bbl. of oil to be distilled. The use of a separate heater operated by the process of our invention affords a high concentration of combustibles in the heater, thus permitting a considerable reduction in heater size, and allows independent control of heater operation.

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

Fig. 1 is a partly schematic, partly diagrammatic illustration of a system suitable for carrying out the process of our invention by combustion of extraneous fuel in the distillation zone; and

Fig. 2 is a similar illustration of apparatus for carrying out the process of our invention by generating heat in a separate heater.

Referring now in detail to Fig. 1, 1 represents a cylindrical case or reactor having a conical crown piece and base; 1 is also provided with a distributor G which may be in the form of an ordinary grid, the purpose of this being to cause uniform distribution of a fluidized mass which is present in the distillation zone 1, as will be more fully explained hereinafter. 3 represents a shale supply hopper. The shale in the feed hopper 3 need not be in the form of a fine powder, although it can be in that state, but may be in the form of rather large roughly ground aggregates having a size up to one-quarter inch for it has been found that particles of shale of this size may be conveniently fluidized, i. e., maintained in a turbulent and highly mobile condition by causing a gasiform material, for example fixed hydrocarbon gases from the process, to flow upwardly therethrough at a controlled rate of speed. The raw shale discharges through a star feeder 4 and a pipe 5 into the reaction zone 1. Meanwhile, an oxygen-containing gas, such as air for example, is introduced into the bottom of the reaction vessel 1 through line 10 and passes upwardly through the grid G. By controlling the linear velocity of the gas passing upwardly in reactor 1, we may effect the state of fluidization as follows: Depending on the size of the aggregates present in the reactor, the velocity should vary from one-half to 10 to 12 ft. per second, the larger particles of course requiring the higher velocities in order to maintain the shale in a highly fluidized suspension of solid in gasiform material. If the shale has a particle size of, say, 200 mesh the net velocity of the gas in reactor 1 will be of the order of 1 to 2 ft. per second. On the other hand, if the average size of the particles in the reactor is about ¼ inch, then the velocity of the gasiform material should be of the order of 4 to 10 ft. per second.

When the shale enters the reaction zone, which is maintained at a temperature of about 850°–1100° F., certain agglutinants present in the shale become decomposed, thus causing usually physical distintegration of the shale in the case where the particles or aggregates are of appreciable size, say ¼ inch. Thereafter, the distillation of the volatilizable constituents of the shale takes place at an accelerated rate. Simultaneously, the solids in the reaction zone are classified to a certain degree by size and/or specific gravity, heavy particles tending to concentrate in the lower layers of the fluidized bed. The air entering through line 10 contacts the spent shale and consumes the fixed carbon or a substantial portion thereof, thus evolving heat which supports the pyrolytic treatment taking place above the combustion portion of the mass. The pressure in the reaction zone is preferably atmospheric, though slightly reduced pressures or elevated pressures ranging up to about 175 lbs./sq. in. may be used.

Our present invention relates to adding to the shale, preferably in the lower portion thereof or in the vicinity of the grid G, a quantity of extraneous fuel, such as finely-divided coal. To this end, therefore, coal rather than feed may be passed from hopper 20 through star feeder 22 and a pipe 23 into the lower portion of vessel 1. The amount of coal thus added depends on the kind and amount of distillable substances and residual combustibles in the shale, and the temperature and rate of distillation employed, and may vary within broad ranges. For example, many shales containing in the neighborhood of 5% of water and about 0.4 bbl. of oil per ton will require between about 40 and 180 lbs. of coal, say about 80 to 120 lbs. of a 13,000 B. t. u. coal. The shale feed is preferably maintained at about 100–500 lbs. of shale per hour per cubic foot of dense solids phase. At a fresh shale particle size of about ¼ inch, good results are obtained at gas velocities of about 3–5 ft. per second. If desired, the particle size of the coal may be larger than that of the shale so as to favor concentration and combustion of the coal in the lower layers of the dense solids phase before that of any significant quantity of the shale, thereby consuming the oxygen supplied, and conserving the shale oil for recovery.

It is advisable to control the amount of air supplied so as to approximate the oxygen supply theoretically required for the combustion of the coal and any carbonaceous shale residue. Proportions of about 115–200 cu. ft. of air at 60° F. per lb. of coal or about 5,000–40,000 cu. ft. of air per ton of shale are generally operative for that purpose. This amount of air may under certain circumstances not be sufficient to provide proper fluidization of the dense solids phase. If this is the case, it in advisable to feed an additional fluidizing gas, such as stean, or gaseous products of the distillation to the dense phase preferably above the zone in which the main portion

of the combustion takes place, for instance by line 8. Such a procedure has the additional advantage of establishing an aeration differential between top and bottom layers of the dense phase which favors gravitation through the dense phase in a downward direction.

Under the conditions stated, the shale undergoing distillation together with volatile products may be withdrawn through line 30 and passed through a purification and product recovery system 32 for recovery of gasoline, gas oil, heating oil, and other valuable products in a system which need not be illustrated in detail herein, for the skilled petroleum engineer need not have this recovery and purification system explained to him or illustrated in the drawing.

It is pointed out in connection with the grid G that the same may be in the form of a revolving grid driven by a suitable driving means which will cause further agitation of the shale in the region of the grates, thus tending to prevent the formation of relatively large aggregates of slag and/or ash. Also, it may be desirable to continuously withdraw ash by any suitable means from G via a draw-off pipe 40.

Another modification of this embodiment of our invention includes an operation wherein the spent shale is withdrawn from reactor 1 via a draw-off pipe 42. Pipes 23 and 42 are provided with taps *t*, into which a slow current of gas may be continuously injected in order to fluidize the solids flowing therein, thus preventing bridging and plugging of the said pipes and causing the solids to flow freely.

The embodiment of our invention illustrated in Fig. 2, which relies substantially on heat generated outside the distillation zone, essentially comprises a distillation reactor 201 and a combustion zone or heater 250 cooperating, as will be presently described.

Fresh shale or oil sands having a fluidizable particle size, preferably of about ¼ inch on the average, is fed from fresh shale hopper 203 to the distillation reactor 201 to form therein, above distribution plate or grid G, a dense turbulent mass of solids fluidized by a fluidizing gas, such as steam, product gas or flue gas from the process, etc., supplied to reactor 201 through line 210 below grid G. The feed shale may be conveyed from hopper 203 to reactor 201 in any conventional manner, for example by gravity through line 205 or by means of a standpipe 207 feeding the shale to the fluidizing gas line 210 wherein it is picked up by the fluidizing gas, e. g., steam, and passed to the bottom of reactor 201 under the pressure of standpipe 207. The flow of solids through lines 205 and/or 207 is facilitated by the addition of small amounts of fluidizing gas through lines 205*a* and/or 207*a*, respectively. The shale in reactor 201 is maintained at the desired distillation temperature of about 850°–1100° F. by means of hot solid circulated to reactor 201 from heater 250, as will appear more clearly hereinafter.

Volatile distillation products are taken overhead from the dense solids phase in reactor 201, passed, if desired, through a conventional gas-solids separator 225 from which solids may be returned through pipe 226, and thence withdrawn through line 230 to be processed in any conventional manner. Spent shale is withdrawn downwardly through overflow pipe 240 and may be discharged from the system through line 241 having a valve 241A.

The heat required in reactor 201 is generated in heater 250. For this purpose, a finely-divided solid fuel of fluidizable particle size is fed from fuel hopper 245 through a standpipe 247 to line 248 wherein it is suspended in an oxidizing gas, such as air and/or oxygen, and passed to the bottom of heater 250 which has a design similar to that of reactor 201. The fuel suspension enters the combustion zone 252 through grid G_{50} to form thereabove a dense turbulent mass of solids fluidized by the oxidizing gas and the combustion gases produced. While we may burn in heater 250 any type of solid fuel, such as coal, lignite, wood, etc., fresh shale or tar sands which leave a larger amount of non-combustible residue suitable as a heat carrier may also be used if desired. An additional advantage of the use of high-ash solid fuels resides in the fact that the presence of inerts in high concentrations favors the complete combustion of carbon to CO_2 by limiting the heat-consuming reaction between carbon and CO_2 to form CO. The net result is the generation of more heat from the total amount of carbon available by means of smaller amounts of oxygen. The temperature in heater 250 may be controlled by a proper oxygen supply at any desired level within the approximate limits of 1100° and 1800° F.

Flue gases are withdrawn overhead through conventional gas-solids separator 254 provided with solids return line 256, and discharged through line 258 for any desired use, including fluidization of the reactor and standpipes of the process. Solid fluidized combustion residue is withdrawn downwardly from heater 250 substantially at the temperature of zone 252, through overflow-standpipe 260 and fed to reactor 201 in amounts sufficient to supply the heat required therein. The flow of solids through standpipe 260 is facilitated by fluidizing gas admitted through line 260*a*. It will be understood that, instead of suspending the solid fuel in the gases carried by line 248, these solids may be fed directly by gravity or mechanical conveyors to heater 250 at any suitable point, for example in a manner similar to the feed of fresh shale through line 205 to reactor 201. On the other hand, standpipe 260 may lead into fluidizing gas line 210 to supply hot solid combustion residue in the form of a low density suspension through line 210 to the bottom of reactor 201.

In case low-ash solid fuels, such as coal or wood, are employed in heater 250, it might be necessary to add inert solids to heater 250 in order to provide the amount of heat carrier required for the supply of heat to reactor 201. For this purpose, we prefer to use spent shale withdrawn from reactor 201 through overflow pipe 240 and passed through line 262 to feed line 248 of heater 250. If desired, this spent shale may be suspended in air or other oxidizing gas supplied to line 262 through line 264. A substantial portion of the residual carbon on the spent shale will burn in heater 250 and thus contribute to the generation of heat.

The amounts of solid fuel and oxygen supplied to the heater and the rate of heat carrier circulation from heater 250 to reactor 201 may vary within fairly wide ranges, depending on the type of fuel used and the heat requirements in heater 201. For example, when fresh shale containing about 0.4 bbl. of combustibles per ton of shale is used for heat generation and distillation, we may feed per lb. of distillation shale supplied to reactor 201 about 0.8 lb. to 1.0 lb. of fuel shale and about 0.15 lb. to 0.16 lb. of oxygen to heater

250 and circulate about 12 lbs. to 15 lbs. of solid combustion residue from heater 250 to reactor 201 to maintain the distillation temperature at about 1000° F. These figures change when other fuels are used roughly as the B. t. u. content of the fuel changes. The superficial velocities of the feed gases may vary within the wide ranges of 0.5–10 ft. per second, depending on the particle size and specific gravity of the respective solids. Velocities of 1 to 5 ft. per second are generally preferred.

It will be understood that even if fresh shale is used as the fuel, a certain amount of spent shale may be circulated from reactor 201 to heater 250 whereby the consumption of fresh shale per unit of product recovered is reduced. Also, some extraneous fuel may be charged to reactor 201 in the manner outlined in connection with Fig. 1, in order to assist in the heat supply. Other modifications which may occur to those skilled in the art are within the scope of our invention.

The process of our invention may be made fully continuous by continuously charging process materials and continuously withdrawing solid and volatile products in the manner outlined above with reference to Figs. 1 and 2. Any or all of the process materials may be preheated to any desired temperatures, particularly for purposes of starting up the process. Suitable modification of flow quantities will, of course, be necessary to adjust the system for the effect of preheat. The system, particularly the distillation zone, may be operated at elevated pressures, say about 75 lbs. per sq. in. or more, if desired. The gas-solids separators may be located outside the high-temperature chambers, for instance subsequent to waste heat boilers arranged on the gas and vapor withdrawal lines from the high-temperature chambers.

It is noted that there are certain naturally occurring shales which are convertible into substantial quantities of hydrocarbon oils where the heat required for distillation may be supplied by burning the spent shale within the distillation zone and, even if the equivalent of 0.1 to 0.4 barrel of oil is consumed per ton of shale, these processes may be commercially feasible if the amount of oil burnt represents only a small fraction of the oil in the shale. However, for shales of lower oil content, say less than one barrel per ton, which probably constitute the greater proportion of all shales available (particulary in the U. S. A.), this internal fuel requirement represents considerable loss of valuable product. Indeed, many shales which might otherwise be economically processed would give practically no oil yield after fuel requirements were taken care of. Consequently, our improvements are particularly suitable for the processing of shales containing a relatively small quantity of oil.

We have found that low oil content shales can be economically treated by charging either with the shale to be distilled or to a separate heater an amount of extraneous properly sized fuel sufficient to supply fuel requirements for the process. As mentioned before, it is desirable that the fuel charged to the distillation zone have a relatively low ignition temperature, although all coals have ignition temperatures considerably lower than the processing temperature for oil recovery from the shale. Lignites and bitiminous coal are particularly suitable on this account, having ignition temperatures in hot air in the neighborhood of 300°–450° F. In addition, these coals yield in many cases appreciable amounts of valuable low-temperature tar which contributes to the overall economy of the process.

It will be understood that by the term "fluidized," we mean a suspension or mixture of solid and gas in which the solid, although supported by the gas, is permitted by the velocity of the same to undergo a sort of delayed settling. For example, in the reactor 1 the fluidized solid will attain an upper dense phase level at L which may be, say, 20 ft. from G and above L the density or concentration of the solid in gas will be greatly reduced so that the gases and vapors issuing through line 30 will contain only a minimum amount of solids which may be removed by passing through solid-contacting devices, such as centrifugal separators, electrical precipitators, and the like, as shown at 225 and 254 of Fig. 2. The level L may be fixed by controlling the quantity of shale and coal fed to the reactor 1 and the rate of purging of spent shale. Also, the density of the fluidized mass between L and G is fixed by the gas or vapor velocity; ordinarily the density of the fluidized mass is greater than 3 lbs. per cu. ft., usually from 10–25 lbs. per cu. ft. Similar considerations apply to corresponding features of Fig. 2.

Our invention will be further illustrated by the following specific example.

Example

An oil shale distillation system designed to produce about 1000 bbls. of distillate per day from shale containing about 0.4 bbl. of volatile constituents per ton, comprises a distillation zone having an inner diameter of about 6–8 ft. and a separate heater having an inner diameter of about 34–35 ft. The distillation zone is maintained at a temperature of about 1000° F. and the heater at about 1100° F., both at atmospheric pressure. About 2500 tons of shale per day are fed to the distillation chamber and the heater is supplied with about 159 tons of coal having a heating value of about 13,000 B. t. u. per lb. Operation of the heater requires about 25,800 standard cu. ft. of air per minute while the temperature in the distillation zone is maintained at about 1000° F. by circulating about 23 tons of solids per minute, having a temperature of about 1100° F., from the heater to the distillation zone.

If no extraneous coal were used in this procedure and the heat required for distillation were generated by the combustion of carbonaceous constituents of the distilled shale, about 4600 tons of shale would be required to produce 1000 bbls. of distillate per day.

Numerous modifications of our invention will appear to those familiar with the art without departing from the spirit thereof.

We claim:

1. A continuous method of distilling oil shale to produce therefrom volatile constituents containing normally liquid hydrocarbon oils by subjecting the subdivided oil shale to elevated temperatures in the fluidized state, which comprises continuously charging subdivided fresh oil shale to a distillation zone, maintaining said shale in said zone at distillation temperatures in the form of a dense fluidized bed of subdivided solids, adding to said zone subdivided solid carbonaceous materials selected from the group consisting of lignites and bituminous coals and having a particle size substantially different from that of said fresh oil shale, supplying a free oxygen-

containing gas to said zone to generate heat by burning said materials in said zone, continuously supplying throughout the course of the distillation heat so generated to said distillation zone by direct heat exchange between said oil shale and materials directly heated by said burning, said heat being sufficient in amount to support the distillation in said distillation zone, continuously withdrawing from said distillation zone a vapor stream containing normally liquid hydrocarbons and continuously withdrawing a downward stream of said solids from said reaction zone.

2. The method of claim 1 in which said carbonaceous materials have a particle size substantially larger than that of said fresh shale and said carbonaceous materials are concentrated and burned in a fluidized bed of solids concentrated below the fluidized fresh shale in said distillation zone.

3. The method of claim 2 in which said fresh oil shale is supplied directly to said distillation zone and said carbonaceous materials are supplied directly to said lower bed.

4. The method of claim 1 in which an additional fluidizing gas is introduced directly above said lower bed.

5. The method of claim 2 in which said carbonaceous materials have a particle size substantially smaller than that of said fresh shale whereby said carbonaceous materials are burned in contact with, but in preference to, said fresh shale.

HOMER Z. MARTIN.
FRANK T. BARR

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