

May 16, 1961

T. D. NEVENS ET AL

2,984,602

METHOD AND APPARATUS FOR STRIPPING OIL FROM OIL SHALE

Filed Dec. 11, 1957

4 Sheets-Sheet 1

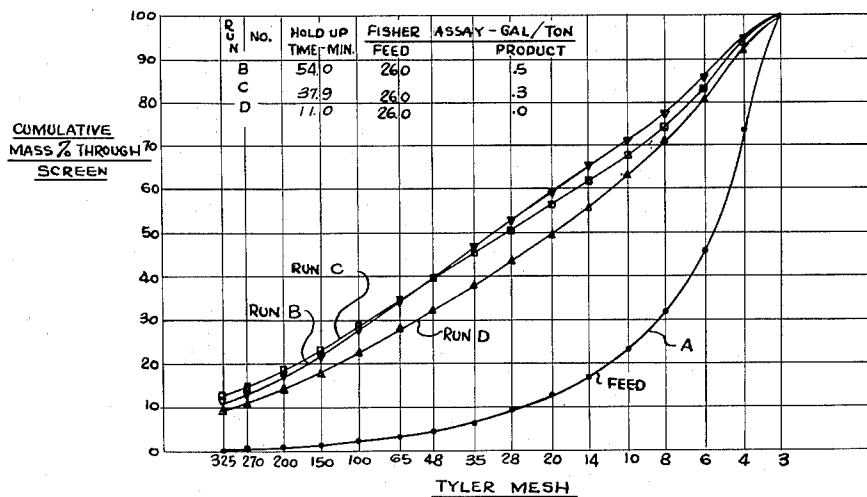


Fig. 2

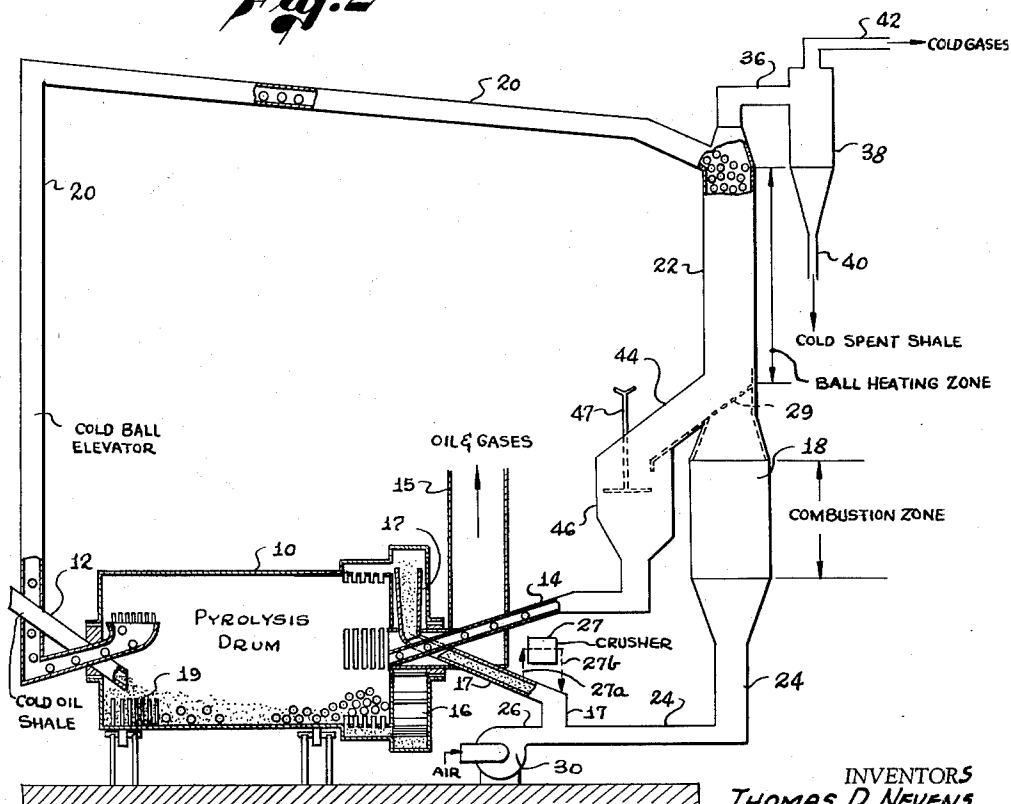


Fig. 1

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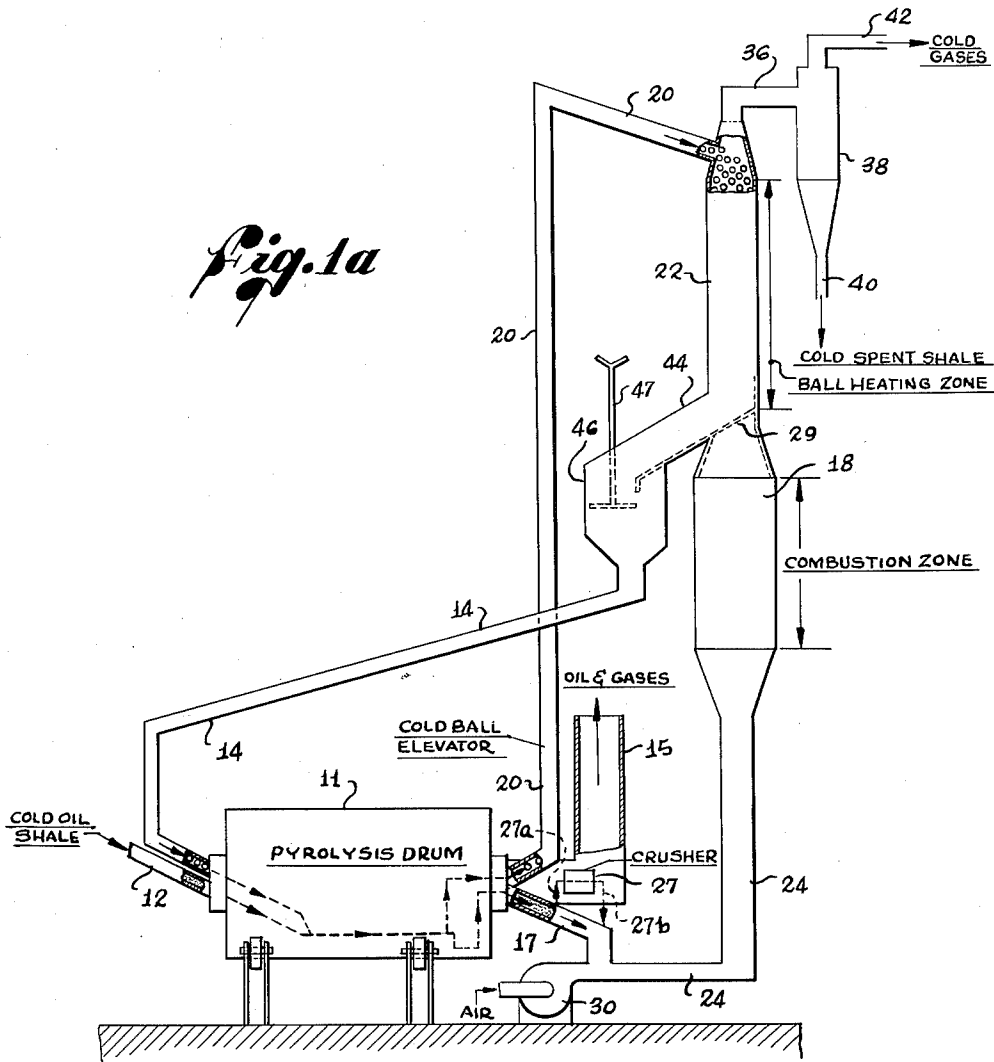
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4 Sheets-Sheet 3

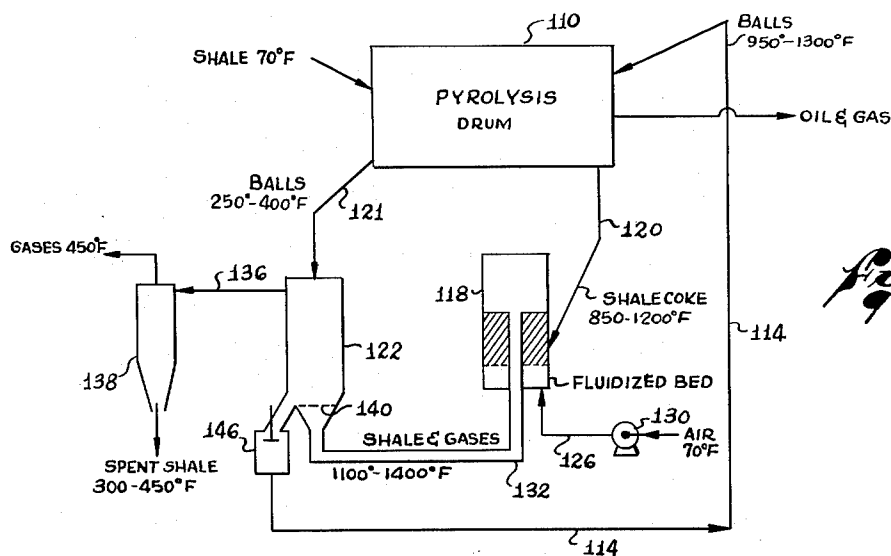


Fig. 3

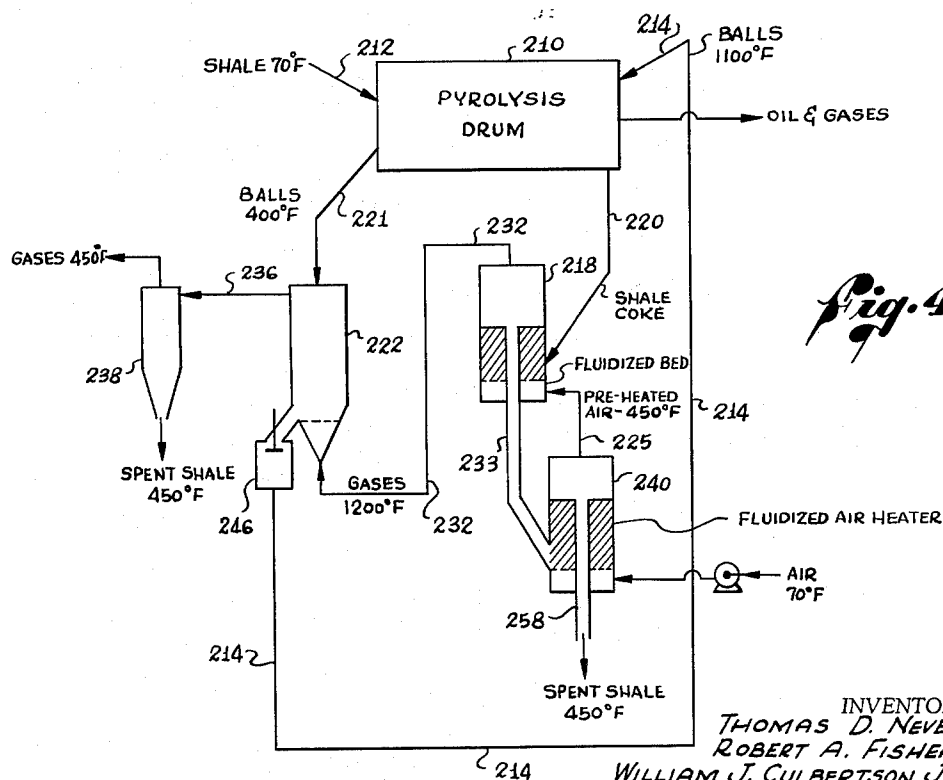


Fig. 4

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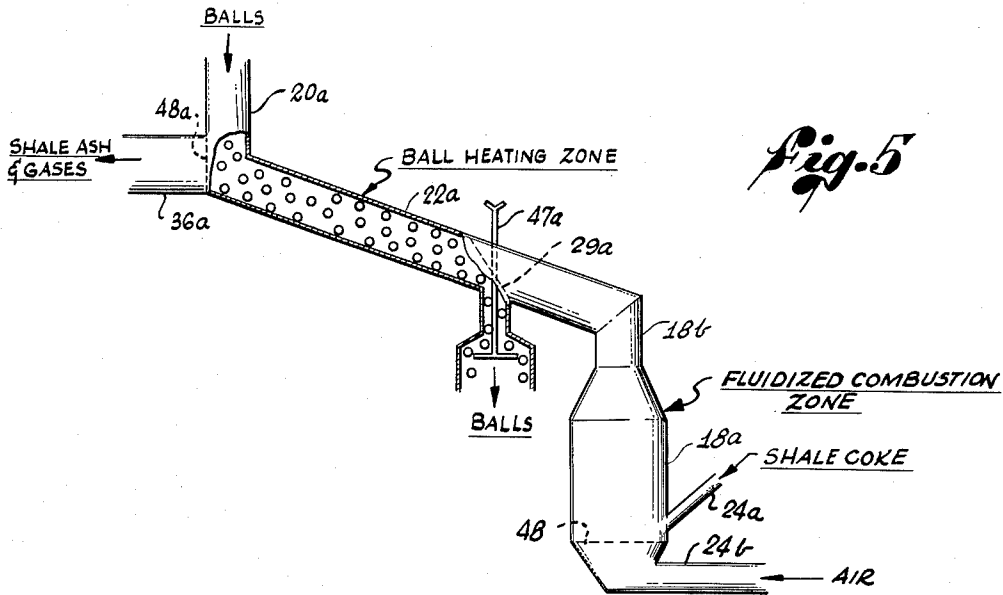


Fig. 5

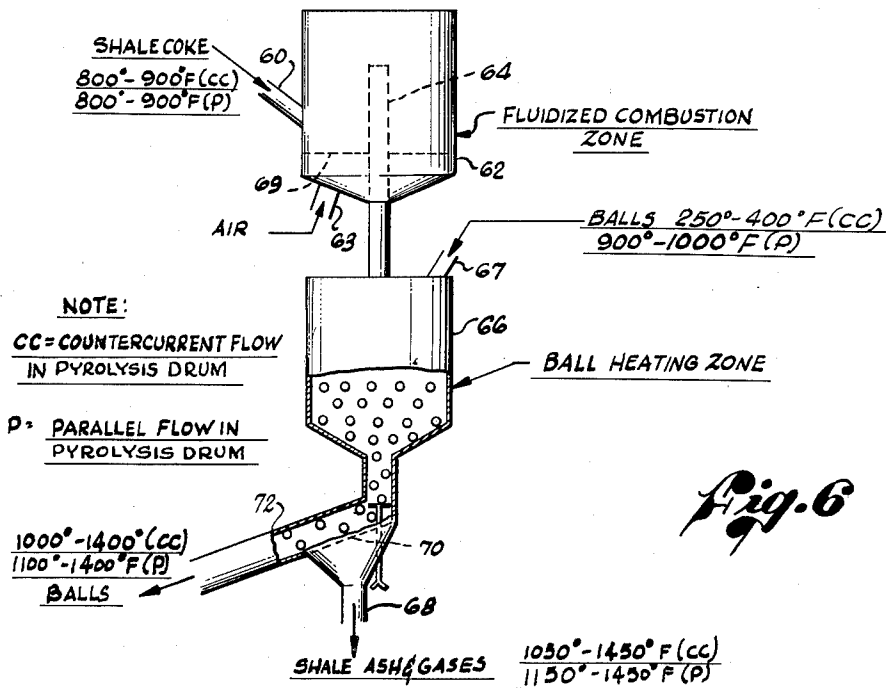


Fig. 6

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METHOD AND APPARATUS FOR STRIPPING OIL FROM OIL SHALE

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Filed Dec. 11, 1957, Ser. No. 702,150

27 Claims. (Cl. 202—14)

This invention relates to a process for the treatment of solid-pieced material, and relates especially to the pyrolysis of oil-bearing solid materials which leaves a carbonaceous residue after distillation. More specifically, this invention relates to the recovery of shale oil from oil shale, wherein the oil shale is pyrolyzed, leaving a carbonaceous or combustible residue, the combustible residue then being burned with a combustion-supporting gas to provide heat for the pyrolysis phase of the process.

The term "pyrolysis" as referred to hereinafter, denotes the actual conversion of kerogen or organic matter in the oil shale to oil or oil vapors and gas. Included within the term "pyrolysis" is the process of separation of oil from other oil-bearing materials, such as bituminous sands (e.g. tar sands, oil sands). The pyrolyzed carbon-containing residue is referred to hereinafter as "shale coke" and the combusted shale coke is referred to hereinafter as "shale ash."

In the past, many processes for the destructive distillation or pyrolysis of solid carbonaceous fuel, such as oil shale, have employed fixed bed or moving bed processes in which steam or flue gas is the pyrolyzing gas. Fluidized bed processes have also been used in the pyrolysis step, the fluidizing gas acting as the pyrolyzing gas as well. However, gas as a pyrolyzing medium is not advantageous for the reasons given below.

In the distillation processes of the type under consideration, it is important that the shale oil produced be either substantially uncracked, or, at most, lightly cracked, in order that the maximum oil yield be obtained. To this end, a close temperature control during the pyrolysis stage of the process is essential. Because the heat capacity per unit volume of pyrolyzing gas is substantially lower than the heat capacity of solid heat-transfer bodies such as metal or ceramic balls, substantially larger flow rates of gas per unit of heat input to the pyrolysis zone are necessarily employed in comparison to the through-put heat-transfer bodies. The accurate control of large volumes of gas is substantially more difficult than the control of the smaller volume of solid bodies, and, correspondingly, the control of temperature within the pyrolyzing zone is relatively more difficult with gas as the pyrolyzing material. It is thus found that the most satisfactory method of providing the required temperature control is to employ a purely solid-to-solid heat transfer during the pyrolyzing stage between the raw oil shale and solid heat-transfer bodies, rather than by employing a process wherein the heat is transferred from gas to solid; and thence from solid to solid.

In addition to the large volumes of gas necessarily employed during pyrolysis by gas, and the consequent difficulty in temperature control, there is another inherent disadvantage in employing gas as the pyrolyzing material. As mentioned, the heat capacity per unit volume of gas is relatively low compared with the heat capacity of solid heat-transfer bodies, such as metal balls, and for this reason, the pyrolyzing gas must be introduced at a considerably higher temperature than the optimum

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pyrolysis temperature in order to heat the oil shale to the required point. In such a gas, local overheating of the oil shale takes place. To avoid such overheating, large flow rates of gas may be employed, in which case considerable loss of carbonaceous fine particles may be encountered. Of course, both overheating and loss of carbonaceous fines by entrainment are highly disadvantageous and are to be avoided.

Further, another major disadvantage of gas-to-solid heat transfer is that the non-condensable gases produced during the pyrolysis step are diluted with the gases used for heat transfer purposes thus causing a low heating value non-condensable gas to result rather than a high heating value non-condensable gas. For example, in a gas-to-solid pyrolysis process, the resulting heating value of the gas produced is of the order of 100 B.t.u. per cubic foot, whereas if a solid-to-solid heat transfer is employed, a non-condensable gas having a heat value of between 700 and 1000 B.t.u. per cubic foot will result.

The conditions stated herein of accurate temperature control and absence of overheating and production of gas of high heating value in the pyrolysis zone can be met if the required heat is added by means of preheated heat-transfer bodies. Since these bodies have a small volume in relation to heat capacity, the temperature drop of the heating medium within the pyrolysis zone need not be as great as when employing gas, even if the through-put volume per unit of time of the gas is kept within reasonable limits. For these reasons, we employ, in the pyrolysis phase of our process, solid heat-exchange bodies having a high heat conductivity which are directly intermixed with raw shale for the pyrolysis of the oil thereby. Such a pyrolysis process is fully disclosed in the co-pending application of Olof Erik August Aspegren and Anders Josef Eklund, both of Stockholm, Sweden, in their application for U.S. patent Serial No. 645,139, entitled "Method for the Treatment of a Fuel."

Generally speaking, in one form of the Aspegren-Eklund or Aspeco pyrolysis process, a horizontal rotating kiln is employed, to one end of which is fed inert, hot, heat-carrying bodies and to the opposite end of which is fed relatively cool raw shale which has been coarsely crushed to a size smaller than that of the incoming heat-carrying bodies. For example, the average size of the raw shale may be from one-quarter inch to one-half inch and the balls may be one inch in diameter. In the rotating pyrolysis kiln, the heated heat-carrying bodies or balls intimately contact and are intermixed with the cooler raw shale, in countercurrent fashion, thereby pyrolyzing the oil therefrom. The rate of heat exchange in such a process is extremely high, being of the order of 100 B.t.u./(hr.)(ft.²)(° F.). The particular process just described enables a higher shale through-put rate for a given retort volume and also prevents coking and agglomeration of the heat transfer bodies fed to the revolving drum.

In addition to the just-enumerated advantages of the revolving pyrolysis drum, the heat-carrying bodies which are extremely wear-resistant and heat-resistant (being usually made of such materials as metal, ceramic or alumina) grind the shale during the pyrolysis process to thereby effect a considerable size reduction. Thus, for example, it is found, after complete pyrolysis thereof, that approximately 90% of the residues (shale coke) pass a 10 mesh screen.

While the above description of the Aspeco process is made with reference to counterflow of balls and shale, the same process advantages are present when parallel or co-flow of balls and shale is employed. In certain instances to be described, the parallel flow is preferred.

Because of the high heat recovery due to the solid-to-

solid heat exchange in the pyrolysis drum, the above-identified United States patent application discloses a second rotating drum employing solid-to-solid heat exchange, wherein the shale coke produced during the pyrolysis step passes countercurrently to cool heat-carrying bodies, the shale coke being simultaneously combusted with combustion-supporting gases during its countercurrent passage through the heat-carrying bodies. Substantial heat recoveries were indeed obtained in experiments conducted by us; however, certain difficulties were sometimes met in the operation of the rotating combustion drum which brought about changes in apparatus and process. These difficulties stemmed mainly from the fact that considerable size reduction of the shale occurred during the pyrolysis step.

Because of the large extent of size reduction of the shale coke, channelling of the combustion-supporting gases through the shale coke in the combustion drum sometimes occurs resulting in inadequate combustion. During channelling, a large amount of the shale coke fines are blown out of the bed of shale coke charge thereby resulting in a substantial part of the combustion taking place above the charge. This fine material burns rapidly and at higher temperatures than that of the charge because it is not associated with the large mass of cooler balls intermixed therein. The higher temperatures produced cause substantial decomposition of calcium and magnesium carbonates in the shale coke, and, inasmuch as the decomposition of carbonates is an endothermic reaction, a substantial heat loss takes place. Also, heat released from the combustion of fines in the space above the charge is unavailable for transfer to the cooler balls. For all these reasons, the heat transfer to the balls in the combustion drum is not, under certain conditions of operation, as high as was originally contemplated.

Bearing in mind the foregoing facts, it is a major object of the present invention to provide a process for the pyrolysis, or stripping (that is, extraction generally) of volatiles from solid material by means of heat-carrying bodies wherein improved heat transfer to the heat-carrying bodies is obtained during the combustion of combustible residue remaining after the pyrolysis of the solid material.

It is another major object of the present invention to provide a process for the pyrolysis of solid material wherein a substantial amount of crushing, grinding and/or attrition of the solids occurs during the pyrolysis step, the residues thus produced being of a small size suitable for fluidization, and thereafter combusting the small sized solids by fluidization methods to obtain an optimum amount of heat transfer for the pyrolysis process.

By way of definition, by the term "fluidization" we mean an operation in which the solid material undergoing treatment is maintained in a dense suspension by controlling the velocity of a gasiform material flowing there-through at a sufficiently low value that the solid material forms a dense, turbulent, mobile mass of solid in gas resembling a boiling liquid.

Another object of the present invention is to provide a process for the pyrolysis of oil shale by means of hot heat-carrying balls, whereby to simultaneously pyrolyze and grind the oil shale, the shale coke thus produced being rendered fluidizable and being combusted in a fluidized state, the products of combustion giving up a substantial portion of their heat by direct heat transfer to the heat-carrying balls which are then re-used in the pyrolysis of oil shale in the pyrolysis zone.

Still a further object of the present invention is to provide a process for the pyrolysis of oil shale wherein hot heat-transfer bodies are intermixed with raw oil shale in co-flow or counterflow to pyrolyze oil from said oil shale and produce also particulate shale coke, the shale coke being then fluidized and combusted by means of a combustion-supporting gas, the hot combusted gases and

shale ash thereby produced imparting a substantial portion of their heat to heat-transfer bodies for use in the pyrolysis of oil from fresh oil shale.

It is yet another object of the present invention to provide a process for the pyrolysis of oil shale wherein excess carbon present in the shale coke produced during the pyrolysis step is employed for the generation of steam or the heating of the other liquid or solid materials in an improved manner.

Yet another object of the present invention is to provide a process for the pyrolysis of oil shale wherein the combustion-supporting gas employed in the combustion of shale coke is preheated by heat exchange with fluidized hot shale ash produced in the combustion zone.

It is still a further object of the present invention to provide a simplified and economical apparatus and process for the combustion of shale coke whereby high heat recoveries can be obtained.

It is another object of the present invention to provide a simple and economical plant for the pyrolysis of oil shale which includes a rotating ball furnace in combination with an improved fluidized combustion and ball-heating apparatus.

These and other objects of the present invention will become more clearly understood by referring to the following description, and to the accompanying drawings, in which:

Figures 1 and 1a are schematic flow diagrams of preferred forms of the process of our invention;

Figure 2 is a graph of inlet and outlet sizes of raw shale and shale coke respectively associated with the rotating ball furnace of Figure 1a operated under a particular set of conditions;

Figures 3 and 4 are schematic flow diagrams of modifications of the process of our invention; and

Figures 5 and 6 are schematic flow sheets of two modified forms of our invention.

In general, our process for pyrolyzing solid-pieced material such as oil shale comprises first, pyrolyzing fresh coarsely ground oil shale in a rotating drum in which larger inert wear-resistant heat-carrying bodies or balls are intermixed countercurrently or in parallel flow with the oil shale at a temperature sufficiently high to cause pyrolysis of the oil shale to produce oil and gases therefrom. The inert balls are generally of ceramic, alumina, or metal composition. During the pyrolysis of the oil shale by means of the inert balls, a considerable amount of grinding takes place and the oil shale residue, i.e., the shale coke produced in the pyrolysis drum, generally is rendered of such a size that it can be readily directly fluidized. Shale coke is therefore sent directly to a combustion zone where it is fluidized by an oxygen-containing gas and its combustion takes place with said oxygen-containing gas.

The hot combusted gases thus produced are made to flow at an increased velocity thereby entraining the burnt shale or shale ash, both the shale ash and hot gases containing substantially all the heat of combustion. These products of combustion are passed upwardly in a countercurrent direction to downwardly moving cooler balls taken from the pyrolysis zone after they have been cooled in the pyrolysis step. The cooled balls are heated by direct heat transfer with the hot gases and entrained shale ash particles therein, the heated balls being then recycled to the pyrolysis drum for the pyrolysis of additional fresh incoming oil shale.

Referring now to Figures 1 and 1a, these figures are identical except that Figure 1 shows the preferred process in conjunction with counterflow in the pyrolysis drum and Figure 1a shows the preferred form schematically in conjunction with parallel flow in the pyrolysis drum. The process will be now described first with specific reference to Figure 1. Fresh oil shale which has been ground, for the most part, to a size larger than 10 mesh, enters a rotating kiln 10 along stationary inlet pipe 12.

The rotating pyrolysis drum or kiln is preferably of the type described in U.S. Patent No. 2,592,783, although any drum which enables intimate mixing and ready separation of differently sized material to take place can be employed. Hot heat-carrying balls enter the pyrolysis drum along the stationary pipe 14 at temperatures ranging from about 100 to 300 degrees higher than the desired pyrolysis temperature within the pyrolysis drum 10; the pyrolysis temperature itself generally ranges between 850° to 1100° F., depending upon the nature of the oil shale introduced and the type of volatile product desired.

In the rotating kiln or drum 10, the hot heat-carrying bodies or balls are countercurrently intermixed with the coarsely ground oil shale to cause the pyrolysis thereof (the oil and gas produced leaving the drum 10 along the outlet line 15). At the same time, the balls cause a considerable amount of grinding to take place. In either co-flow or counterflow, the amount of grinding done in the pyrolysis drum 10 is substantially greater than one would expect, because, as the oil and gas are released by pyrolysis from the oil shale, the remaining shale coke becomes substantially more friable than the fresh shale, the net result being that it is much more susceptible to the grinding action of the balls. It is believed that the shale coke is substantially easier to grind than the raw shale because the oil or organic matter within the raw shale acts as a binder binding the remaining mineral matter in the shale coke together. Thus, as the oil is removed, the mineral shale coke becomes more friable.

Referring specifically to Figures 1 and 2, the curve of the sieve analysis of the inlet oil shale feed to Figure 1 is designated by the letter A. It will be noted that over 75% of the inlet oil shale feed is larger than 10 mesh. The other three curves of Figure 2 denote the sieve analysis of the outgoing shale coke for three different runs and are designated by the letters B, C, and D. These three curves show approximately the same sieve analyses even though the oil shale hold-up or residence times within the pyrolysis drum 10 varied considerably. The residence or hold-up time is that length of time in which the shale passes through the drum 10. As summarized in the legend in the left hand upper corner of the figure, the hold-up time for run B was 54.0 minutes, and the amount of oil remaining in the shale coke was 0.5 gallon/ton, the amount remaining being less than 2% of the total initial volatile content. Run No. C shows that for a hold-up time of a shorter period, 37.9 minutes, approximately the same amount and percentage of oil was retained in the outgoing shale coke as in run No. B, and, further, the outgoing sieve analysis was approximately that of run No. B. In run No. D no oil was left in the outgoing shale coke and the hold-up time was short, being of the order of 11.0 minutes. The sieve analysis of the shale coke in run No. D was approximately equal to that of the runs B and C.

It is believed that the amount of size reduction in the pyrolysis drum 10 is dependent to a greater extent upon the degree of pyrolysis of the oil shale within the drum 10 than upon the residence time of the oil shale there-within. Thus, while the residence time of oil shale may be reduced by means of a greater ball/coke ratio or higher temperature differential between the balls and the oil shale feed, size reductions approaching runs B, C and D are obtained so long as substantially complete pyrolysis takes place within the drum 10.

It will be noted upon a study of Figure 2 that the amount of size reduction is such that almost 65% of the outgoing shale coke has a mesh size smaller than -10 mesh, whereas the original feed had 75% of larger than 10 mesh size particles.

It will be understood that the sieve analysis of the shale coke shown in Figure 2 could be considerably finer or coarser depending upon operating conditions of the pyrolysis drum 10.

The shale coke, being pulverized to the sizes above described by the heat-carrying balls, leaves the pyrolysis drum 10 by means of any appropriate sieve and elevating mechanism, designated generally by the numeral 16. For example, the mechanism described in the Aspengren patent above mentioned is suitable. The shale coke is then deposited in an outlet pipe 17 for transport to a combustion zone 18 to be described.

The cooled balls leave the pyrolysis drum 10 by means of an elevating mechanism 19 within the drum 10, thence entering pipe 20 mounted at the end of the drum opposite the exit end of the shale coke. The cooled balls are then sent to a ball-heating zone 22, to be described, by any suitable elevator means (not shown).

The pulverized shale coke, usually containing from 3 to 8% organic carbon, leaving the pipe 17 is generally passed directly into a pipe 24 and thence transported to a vertical shaft combustion zone 18 by means of a fluidizing combustion-supporting gas, such as air. The air is blown into the pipe 24 by means of an appropriate air blower 30 via the pipe 26. It should be noted that the bulk of the shale coke particles leaving the drum 10 have a size range below 10 mesh, as shown by the curves B, C, and D in Figure 2, this size being found to be the largest practical size that can be passed through one-inch diameter balls in the ball tower 22, to be described. That shale coke which lies above 10 mesh can be sent from pipe 17 along dotted line 27a to an auxiliary crusher 27 for crushing to -10 mesh, and thence sent back into the main stream 17 along line 27b.

In the parallel flow pyrolysis shown schematically in Figure 1a, the numerals affixed to apparatus and materials identify the same items as in Figure 1 except that the pyrolysis drum of Figure 1a is designated by the numeral 11. During the pyrolysis, a fine mesh material is produced, which is fluidizable in the combustion zone 18. Under appropriate conditions in the ball tower 22, the ash particles are also entrained.

Referring now specifically to both Figures 1 and 1a, the velocity of air required for fluidization and combustion of the shale coke in the combustion zone 18 is determined by such factors as the depth of the shale coke combustion bed, particle size of the shale coke, bed temperature required, residence time of the shale coke required for optimum combustion thereof, enthalpy requirements of the shale coke, and other factors which are well known in the art.

Depending upon the feed size and the carbon content of the shale coke, it is found that the residence time of the shale coke in the fluidized bed should be between three and fifteen minutes for substantially complete combustion, and the air mass velocity at which the fluidized bed should be operated lies between about 50 lbs./hr. ft.² and 450 lbs./hr. ft.² depending upon the feed particle size, the carbon content, bed depth, and bed temperature required.

Inasmuch as the ignition temperature of the shale coke is approximately 1100° F., the combustion of the coke is usually operated at temperatures above 1100° F. However, the combustion temperature is generally kept below 1400° F., because at this temperature a considerable amount of carbonate in the shale will decompose, the carbonate decomposition being an endothermic reaction which increases the heat losses in the combustion zone. However, where the parallel flow pyrolysis drum 11 is employed, the fluidized bed 18 may be maintained at temperatures of the order of 1500-1600° F., notwithstanding the carbonate decomposition, because of other advantages attributable to parallel flow pyrolysis such as increased simplicity of separating mechanisms for the balls and material.

The shale coke residence time in most conventional shale combustion units lies generally between one and four hours. With such long residence times, the extent of carbonate decomposition of the coke is substantial. In our process, the carbonate decomposition is kept to

a minimum by control of bed temperature, air rate, shale coke feed particle size, and residence time.

The fluidized combustion zone 18 reaches equilibrium temperatures rapidly and is quite flexible in that it may be easily controlled over a relatively wide range of conditions. For example, a temperature between 1100° F. (the ignition point) and 2000° F. (the temperature of shale ash fusion) can be maintained within the combustion zone by controlling the air/shale coke feed ratio, the particle size of the coke, and the residence time in the combustion bed. The combustion zone 18 as well as the other units are usually insulated so that the amount of heat loss from the system is small.

As another example of the flexibility of the fluidized zone 18, it has been found that even though the air for combustion is sent to the combustion zone without preheating, the desired temperature within the above-mentioned range can be readily obtained. It has also been found that bed densities in the zone 18 can be varied within wide limits ranging from that of a packed bed to that just below the density of an entrained solids mixture where extremely long or short residence times, respectively, are required. The fluidized bed can also be used to burn shale coke having a range of carbon content from 1 to 15%, even though the usual organic carbon content of the shale coke lies within the 3 to 8% range.

After the fluidized shale coke has been substantially completely burned in the combustion zone 18 at temperatures preferably ranging from 1100° to 1400° F., it is blown upwardly with the combusted hot gases through a ball-heating zone or tower 22 to countercurrently contact a downwardly flowing bed of cooled heat-carrying balls entering the zone 22 from pipe 20. Simultaneous handling of shale ash and gases is thus obtained, thereby enabling an extremely simple form of equipment to be utilized. Also, by passing entrained shale ash solids having high sensible heat along with the hot combusted gases in direct countercurrent contact with the balls, extremely high heat-transfer coefficients governing the heat transfer to the balls are obtained. It has been found that the presence of the fine ash solids in the hot combusted gases is capable of raising the heat-transfer coefficient to values ranging from 10 to 100 B.t.u./(hr.)(ft.²)(° F.), as compared with values of the order of 1.0 to 5 generally prevailing without entrained particles. (See D. F. Othmer, "Fluidization." Reinhold Publishing Co., New York 1956.)

A grate member 29 separates the ball-heating zone 22 from the combustion zone 18, the grate member having a sufficiently small mesh to prevent the downwardly flowing balls from passing into the combustion zone 18, while allowing the smaller shale ash particles to pass upwardly therethrough. The linear gas velocity required to entrain the ash solids into the ball-heating zone 22 is considerably greater than that required to maintain the fluidized condition in the combustion zone 18, and to this end, the ball-heating zone is made substantially smaller in diameter than the combustion zone. As an illustration of the increased velocity required, shale coke particle sizes ranging from —10 mesh to approximately 200 mesh which have a carbon content of approximately 8.3% carbon requires an optimum air rate of approximately 250 lbs./hr. ft.², whereas for entrainment of the ash produced during combustion, a gas velocity of approximately 500 lbs./hr. ft.² is required in the ball-heating zone 22. The ball-heating zone 22 therefore has a cross-sectional area approximately 30 to 70% that of the combustion zone cross section.

The entrained hot shale ash and the hot combusted gases thus pass upwardly through the ball-heating zone 22 at an increased velocity transferring heat to the downwardly flowing balls, the effluent gases and entrained shale ash passing along overhead pipe 36 to any appropriate separating means such as a cyclone separator 38. The

cooled spent shale leaves the separator 38 along the pipe 40, the relatively cool combusted gases passing overhead via the pipe line 42.

The heated balls, which preferably have a temperature between 950° and 1400° F., pass from the ball-heating zone 22 along a lateral outlet conduit 44 and into a ball hopper 46 having a suitable regulating device 47 controlling the inflow of the balls to the pipe line 14. The hot balls in pipe 14 then enter the pyrolysis drum 10 and meet incoming fresh shale to pyrolyze the same.

In one form of operation of our process as applied, for example, to Colorado oil shale, the pyrolysis drum 10 of Figure 1 was charged with cold oil shale at approximately 70° F., and met hot incoming one-inch diameter ceramic balls from pipe 14, the balls being at a temperature of approximately 1100° F. The residence time of the oil shale in the drum 10 was eleven minutes, which corresponded to essentially 100% pyrolyzing of the oil from the oil shale. The size reduction associated with the stripping treatment was substantial, the shale coke outlet corresponding to the curve of run D in Figure 1. Auxiliary crushing at 27 was employed for the 20+ % of coarse shale coke.

The product oil and gas leave the pyrolysis drum 10 along conduit 15 at a temperature of approximately 900° F., and were sent directly to a condenser although they could be first passed through a heat exchange step, as, for example, to preheat incoming fresh oil shale.

The balls, after imparting their heat to the oil shale in the pyrolysis drum 10, were elevated to the outlet line 20 at a temperature of approximately 450° F., and are sent to the ball-heating zone 22 for reheating to the pyrolyzing temperature. The finely ground shale coke leaving the drum along line 17 at a temperature of 900° F. was blown along the line 24 into the combustion zone 18 to form a fluidized bed therein. The inlet combustion air enters the duct 26 cold and was blown into line 24 and the combustion zone 18 by means of the blower 30.

A bed temperature of 1225° F. was maintained in the zone 18; the density of the fluidized bed was 1.08 grams per cc., the mean shale residence time being 3.92 minutes and the bed depth being 8 inches. The ratio of air rate to shale coke feed rate was 1.37, over 85% of the organic carbon in the shale coke being combusted.

The only heat losses are due to radiation, conduction, and to carbonate disassociation, the total of these losses being approximately 20% of the total heat of combustion. The remaining 80% of the heat of combustion passes into the ball-heating zone 22 as sensible heat in the ash and in the flue gas. The sensible heat in the ash represents 40% of the total heat in the products of the combustion, and it can thus be seen to be a very substantial contributor to the heat available for transfer to the balls in the ball-heating zone 22.

The balls, entering the ball-heating zone 22 at a temperature of approximately 450° F., form a downwardly moving packed bed, the individual balls being heated to a pyrolysis temperature of approximately 1100° F. by the upward passage of effluent hot ash and gases. The heated balls are then sent directly to hoppers 46 and ball inlet line 14 for the pyrolysis of fresh oil shale. In order to insure entrainment of the hot ash through the balls, the gas rate within the ball-heating tower 22 is increased, due to the restriction in diameter thereof, to approximately 500 lbs./hr. ft.², at which rate —10 mesh ash is entrained through the packed bed of balls.

The outlet temperature of the cool gases and spent shale is approximately 450° F., and it will thus be seen that the major portion of the heat in the effluent ash and gases has been transferred to the balls in the ball-heating zone 22.

An alternate method for the design of a fluidized combustion bed and entrained solids system is shown in Figure 3. According to this modification, shale coke leaving the pyrolysis drum 110 at a temperature of 900°

F. is passed into a separate fluidized combustion zone 118 along the line 120. Air at 70° F. is blown into the bottom of combustion zone 118 along line 126 by blower 130. Fluidized combusted shale residue (ash) overflows into a bottom standpipe 132 in the center of the fluidized bed in zone 18 and is blown into the bottom of the ball-heating zone 122 through a grate 140 by the hot combusted gases. The hot ash and gases passing along the pipe 132 have a temperature of approximately 1100° to 1450° F., and are passed upwardly through a downwardly moving bed of balls which have an entrance temperature of approximately 250° to 400° F., the balls entering the zone 122 via line 121.

The gases and shale ash, after imparting the bulk of their heat content to the balls, pass from the ball-heating zone 122 along the line 136, the shale ash being separated from the cooled gases by means of a cyclone separator 138. The effluent gases and shale ash are at temperatures generally of from 300° to 450° F., as they pass from the separator 138.

The balls heated in the zone 122 pass to the ball-hopper 146 at a temperature of approximately 950° to 1300° F., and are sent along the line 114 through the pyrolysis drum 110.

It will be noted that the chief difference between the process shown and described in Figures 1 and 1a and the process just described in Figure 3 is that in Figures 1 and 1a a top take-off standpipe for the removal of combusted gases and the entrained shale ash is employed, and in Figure 3 a bottom take-off standpipe is used. While the apparatus shown in Figure 2 is simpler than that of Figure 3, it is sometimes necessary to employ the conventional bottom standpipe of unit 118 if the shale ash is not readily entrained from the combustion zone 18 of Figure 3.

A second alternate method for heat recovery is shown in Figure 4 which employs a pyrolysis drum of the type described previously, in combination with a plurality of fluidized beds. A first fluidized combustion unit is employed as described in the process of Figures 1 and 1a; however, instead of entraining hot ash and combustion gases through the ball-heating tower, the hot ash produced in the combustion zone is sent to a second fluidized bed for the purpose of preheating the air used in combustion.

Referring specifically to the flowsheet of Figure 4, fresh oil shale enters the pyrolysis drum 210 along the line 212 at a temperature of approximately 70° F., and is intimately mixed with countercurrently moving hot balls which enter the pyrolysis drum along the line 214 at a temperature of approximately 1100° F. The balls, after giving up their heat to the shale, leave the pyrolysis drum 210 at a temperature of approximately 400° F., along the line 221 and are sent to the ball-heating zone 222 similar to that described with reference to Figures 1 and 1a.

Shale coke, being pulverized, as described previously with reference to Figure 1, to a considerably smaller mesh size, leaves the pyrolysis drum 210 along the line 220 and is sent to a fluidized combustion zone 218 where it is fluidized by incoming preheated air at 450° F.

The air enters the bottom of the combustion zone 218 along the line 225 and, due to the combustion thereof, leaves the top of the zone 218 at a temperature of approximately 1200° F., being then sent to the ball-heating zone 222 along the line 232.

The balls entering zone 222 move downwardly therein and are heated to a temperature of approximately 1100° F., by the hot gases, being then recycled to the pyrolysis drum via hopper 246 and line 214. The spent gases and any entrained shale therein leave the ball-heating zone 222 along line 236 at a temperature of approximately 450° F., the ash being separated from the gases by means of cyclone separator 238.

The bulk of the shale ash produced in the combustion zone 218 is taken off from the bottom standpipe 233

and is sent to a fluidized air heating zone 240 where it preheats incoming air (entering at an inlet temperature of approximately 70° F.) to a temperature of approximately 450° F. The cooled shale ash leaves the fluidized air heating zone along the standpipe 258 at a temperature of approximately 450° F.

The heat recovery from the hot ash by means of the second fluidization unit 240 is somewhat less efficient than the methods shown and described in Figures 1, 1a and 3, and, of course, the additional fluidization unit is also required. However, possible clogging of the ball-heating zone is eliminated. Further, the coarser particles in the shale coke produced in the pyrolysis drum need not be ground in auxiliary grinders, such as shown at 27 in Figure 1. Thus, in some cases, it is economically feasible to send the ash through a fluidized air heater 218 and 240 rather than through a ball-heating tower.

It will be noted that in Figure 1 the ball-heating zone 22 is placed directly over the fluidized combustion zone 18. The grating or screen 29 must be sufficiently small so as not to permit broken pieces of the balls to fall into the fluidized zone 18. The use of the screen might possibly, in some cases, result in a high pressure drop. In these cases, it is preferable to offset the ball-heating zone 22 from the fluidized zone 18 with a trap between to collect broken pieces of balls or to employ a horizontal or sloping ball-heating zone 18, in conjunction with the combustion zone 22.

Referring now specifically to Figure 5, the crushed shale coke enters the combustion zone 18a along the line 24a, and moves upwardly therein by means of a stream of air entering the zone 18a along the line 24b. The cooled balls from the pyrolysis drum 10, or 11, enter the sloping ball-heating tower or zone 22a along the line 20a and pass countercurrently to the entrained hot shale ash particles being blown through the ball-heating zone. These particles, along with the air, leave the zone 22a along the line 36a.

In order to prevent the broken pieces of balls from being deposited in the combustion zone 18a, a screen or grate 29a is disposed at an angle so that the possibility of broken pieces of balls falling into the outlet section 18b of zone 18a is minimized.

As mentioned with reference to Figure 1, an inlet ball flow control 47a is employed. A fine screen 48 is also placed at the bottom of the combustion zone 18a to prevent shale coke particles from escaping into the air line 24b. Another screen 48a is disposed at the ball inlet end of the zone 22a to prevent balls from entering line 36a.

Hitherto, counterflow of shale ash and/or coke with the balls has been considered in the combustion and ball-heating zones. However, parallel flow of these materials would be advantageous mechanically because (1) such a process would completely eliminate the possibility of clogging the combustion zone with broken pieces of balls; (2) decrease the pressure drop of the gases across the ball heating tower; (3) allow larger particles to be entrained; and (4) simplify construction. Probably the main disadvantage is the reduction in amount of heat transferred per given amount of balls.

A schematic parallel flow combustion and ball-heating apparatus is shown in Figure 6, having the above described advantages. The crushed shale coke leaving the pyrolysis drum 10, or 11, passes into the line 60, thence entering the fluidized combustion zone 62. Air enters the zone 62 along line 63 and fluidizes the incoming shale coke, the hot shale ash and hot gases leaving zone 62 through the standpipe 64 to enter the ball-heating zone 66, in co-flow with balls entering along the line 67. A screen 69 placed in zone 62 prevents any shale coke from escaping.

The shale ash and gases, after giving up a substantial part of their heat to the balls, leave the bottom of the ball-heating zone 66 via line 68. The balls are prevented

from leaving via line 68 by an appropriately sized screen 70 and pass into outlet line 72 to be recycled to the stripping drum 10.

As a specific example, and still referring to parallel flow in the combustion zone 62 and ball-heating zone 66, the shale coke enters the combustion zone 62 at a temperature of 800°–900° F. If the pyrolysis has been conducted in parallel flow, the incoming air is preferably preheated to approximately 650° F., for example, by recycling a portion of the hot gases leaving the ball-heating zone 66 through a heat exchanger (not shown) to heat the air ultimately entering line 63.

The shale ash and gases then meet the balls, which enter at 900°–1000° F., and the balls are reheated by the substantially hotter shale ash and gases to a temperature of between 1100° to 1400° F. The shale ash and gases leave along line 68 at a temperature of 1150° to 1450° F., much of this heat being recuperated by preheating the air for combustion.

If the pyrolysis has been conducted in counterflow, the shale coke, entering at an 800°–900° F. temperature, may be combusted with cold air, inasmuch as a lower ball rate is usually employed with countercurrent flow in the retort. The balls will then be heated to a temperature of between 1000°–1400° F., upon passage through the ball heating zone 66. The exit temperature of the shale ash and gases lies between 1050°–1450° F.

Attention is drawn to the fact that power requirements for all the fluidized combustion and ball-heating systems are extremely low, the power costs being approximately 0.6 to 1 cent/ton at current power rates.

Attention is also drawn to the fact that should there be excess carbon, i.e., more carbon in the shale coke than is needed for the heating of the balls, superheater coils or boiler tubes can be installed in the fluidized combustion bed to be either used for the production of process steam or for power generation. The low power requirements are thereby further reduced for the following reasons: in order to keep the temperature within the fluidization bed 18, 118, or 218 between preferred ranges of temperature, i.e., between 1100° and 1400° F., 75 to 150% excess air is normally introduced to keep the temperature down. By continuously producing steam or heating other liquid or solid materials in the coils or tubes mounted in the combustion bed, the temperature of the bed is lowered and lower air rates can therefore be employed with consequent reduction in requirements for the air blowers.

While several embodiments of the apparatus and process for producing oil from oil shale have been described, it will readily be seen by those skilled in the art that substantial changes and modifications may be made that lie within the scope of this invention. Therefore, we do not wish to be limited by the specific embodiments herein shown and described, but only by the appended claims.

We claim:

1. A process for the pyrolysis of a coarsely ground solid, said solid upon being pyrolyzed leaving a combustible residue, which comprises the steps of: substantially completely pyrolyzing and simultaneously grinding said solid by means of inert heat-carrying bodies in a pyrolysis zone, thereby rendering the bulk of the combustible residues produced directly fluidizable, the bulk of the combustible residues produced having a mesh size smaller than said heat-carrying bodies; transferring said fluidizable combustible residue to a combustion zone; fluidizing said combustible residue in said combustion zone by means of a fluidizing combustion-supporting gas to thereby produce heat; removing the heat-carrying bodies from the pyrolysis zone and imparting a substantial portion of the heat produced in said combustion zone to said heat-carrying bodies; and recycling said heated heat-carrying bodies to said pyrolysis zone to pyrolyze additional fresh incoming solids.

2. The method of claim 1 in which the solids are

particulate oil shale, and the combustible residue is particulate shale coke.

3. The method of claim 2 in which the pyrolysis zone comprises a generally horizontal rotating drum in which the heat-carrying bodies are continuously countercurrently intermixed with fresh solids, said heat-carrying bodies being inert, generally spherical, and wear and heat-resistant.

4. The method of claim 1 in which the pyrolysis zone comprises a generally horizontal rotating drum in which the heat-carrying bodies are continuously intermixed with fresh solids, in parallel flow, said heat-carrying bodies being inert, generally spherical, and wear and heat-resistant.

5. A process for the pyrolysis of coarsely ground solid material containing organic matter, which upon pyrolysis leaves a combustible residue, including the steps of: pyrolyzing said solid material by direct contact with hot, inert, heat-carrying bodies; simultaneously grinding said material during the pyrolysis thereof whereby to render the bulk of the combustible residue produced fluidizable; fluidizing and combusting said finely ground residue by means of a combustion-supporting gas to thereby substantially raise the temperature of the effluent combusted residue and hot gases; separating said heat-carrying bodies from said combustible residue and transferring a substantial portion of the heat of said combusted residue to said bodies; and recycling said heated heat-carrying bodies to pyrolyze fresh incoming solid material.

6. The method of claim 5 wherein the majority of the coarsely ground inlet feed has a size substantially larger than 10 mesh, and the majority of the combustible residue produced is substantially below 10 mesh.

7. The process of claim 5 wherein the temperature during the pyrolysis is maintained between approximately 900° and 1100° F., the temperature in the combustion zone is between approximately 1100° and 1600° F., and the temperature of the heat-carrying bodies entering the pyrolysis zone is approximately between 1000° and 1400° F.

8. The method of claim 5 wherein excess carbon burnt in the fluidized combustion zone, above the requirements necessary for ball heating, heats liquid materials passing through said fluidized combustion zone.

9. The method of claim 5 wherein the solid material is oil shale, the combustible residue is shale coke, and the effluent combusted residue is shale ash.

10. The method of claim 9 wherein the combustion-supporting gas employed in the combustion of shale coke is preheated by heat exchange with fluidized hot shale ash produced in the combustion zone.

11. The process of claim 9 wherein the temperature of pyrolysis lies approximately between 900° and 1100° F., and the temperature in the fluidized combustion zone lies approximately between 1100° and 1600° F.

12. A process for the pyrolysis of oil shale, which includes the steps of: substantially completely pyrolyzing fresh, coarsely ground oil shale by intermixing with larger, inert, wear-resistant, heat-carrying bodies, these bodies being at a temperature sufficiently high to cause the pyrolysis of said oil shale to produce oil and gas, the heat-carrying bodies being cooled during said pyrolysis; simultaneously grinding said oil shale during the pyrolysis thereof by means of said bodies, the size of the shale coke produced being such that it can be readily directly fluidized in a combustion zone; transferring the bulk of the finely ground shale coke directly to said combustion zone where it is fluidized by a combustion-supporting gas and combusted by means of said gas to produce effluent hot combusted gases and effluent shale ash; increasing the velocity of said effluent gases to thereby entrain the shale ash therein; separating said cooled heat-carrying bodies from said shale coke and passing said effluent hot gases and entrained ash in direct contact with said cooled heat-carrying bodies, to thereby heat said bodies; and recycling said heated balls for the pyrolysis of additional fresh incoming shale.

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13. A plant for the pyrolysis of oil shale by means of hot balls, which includes: rotatable ball furnace apparatus for heating oil shale having inlet and outlet means for oil shale and shale coke, respectively, and having inlet and outlet means for hot and cool balls, respectively; a fluidized combustion chamber having inlet means connected to said shale coke outlet means and having outlet means for the products of combustion; a ball-heating chamber having ball inlet means connected to said ball outlet means in said shale-heating apparatus, and having a second inlet means for the products of combustion fluid-connected to the combustion products outlet means in said combustion chamber, said ball inlet means associated with said ball-heating chamber and said combustion product inlet means being positioned so that said balls and combustion products intimately contact each other; and ball outlet means in said ball-heating chamber connected to said ball inlet means of said shale-heating apparatus.

14. The plant of claim 13 wherein the ball inlet means and combustion product inlet means of said ball-heating chamber are positioned so that said balls and combustion products contact each other in counterflow.

15. The plant of claim 13 wherein the ball inlet means and combustion product inlet means are positioned so that said balls and combustion products contact each other in parallel flow.

16. The plant of claim 13 wherein said combustion chamber has a diameter substantially larger than the diameter of said ball-heating chamber, and said ball-heating chamber has a screen of mesh size smaller than the diameter of said balls in said ball-heating zone, said screen separating said ball-heating chamber from said combustion chamber.

17. A plant for the pyrolysis of oil shale which includes: rotatable ball furnace apparatus for heating oil shale having inlet ball means and inlet oil shale means, and outlet ball means and outlet shale coke means; a first fluidized combustion chamber having inlet shale coke means connected to said outlet shale coke means in said ball furnace apparatus, and inlet means for fluidizing combustion-supporting gases whereby to fluidize and combust said incoming shale coke; outlet means in communication with said first fluidized combustion chamber for passing the combusted residues from the first fluidized combustion chamber to a second fluidized bed chamber; gas inlet means in said second fluidized chamber whereby to fluidize said combusted residues from said first fluidizing chamber and preheat said combustion-supporting gases; outlet means for passing said preheated combustion-supporting gases to said gas inlet means of said first fluidization chamber; a ball-heating chamber having ball inlet means connected to the ball outlet means of said rotatable ball furnace apparatus; gas inlet means in said ball-heating chamber connected to a gas outlet means in said first fluidization chamber, the ball inlet means and said gas inlet means being positioned at the upper and lower ends of said ball-heating chamber; and a ball outlet means in said ball-heating chamber connected to the ball inlet means of said rotatable ball furnace apparatus.

18. An improved fluidized combustion and ball-heating apparatus which comprises: a combustion zone having bottom and top openings; a ball-heating zone having a smaller cross-sectional area than said combustion zone, and having bottom and top openings, one of said openings of said combustion zone being fluid-connected with the bottom opening of said ball-heating zone; and a screen separating said combustion zone from said ball-heating zone having a mesh size smaller than the balls employed in said ball-heating zone, thereby preventing their passage to said combustion zone.

19. An improved fluidized combustion and ball-heating apparatus which comprises: a vertical, substantially cylindrical combustion chamber having bottom and top

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openings; a substantially smaller-diametered vertical ball-heating chamber having bottom inlet and top inlet means, one of said openings of said combustion chamber being fluid-connected to the bottom opening of said ball-heating chamber; and a screen separating said combustion chamber from said ball-heating chamber having a mesh size smaller than the balls employed in said ball-heating chamber, thereby preventing their passage to said combustion chamber.

20. A method for the continuous pyrolysis of a solid material, said solids upon being pyrolyzed leaving a combustible residue, which comprises the steps of: contacting fresh solids with substantially hotter heat-carrying bodies in a pyrolysis zone to cause the pyrolysis of said solids, to cause a substantial reduction in size of the bulk of said solids to a size below 10 mesh, and to cause cooling of said bodies; transferring the combustible residue formed in said pyrolysis zone to a combustion zone; fluidizing and combusting said combustible residue in said combustion zone to thereby substantially increase the temperature of effluent gas and effluent combusted residue thereby produced; removing said heat-carrying bodies from said pyrolysis zone and transferring at least a portion of the heat of said effluent to said cooled heat-carrying bodies; and recycling said heated heat-carrying bodies to said pyrolysis zone to pyrolyze additional fresh incoming solids.

21. A process for the pyrolysis of a coarsely ground solid, said solid upon being pyrolyzed leaving a combustible residue, which comprises the steps of: heating and simultaneously grinding said solid by means of hotter heat-carrying bodies in a heating and grinding zone, thereby rendering the bulk of the combustible residues produced directly fluidizable and of a mesh size below 10 mesh; transferring said fluidizable combustible residue to a combustion zone; fluidizing said combustible residue in said combustion zone by means of a fluidizing combustion-supporting gas to thereby produce heat; removing said heat-carrying bodies from said pyrolysis zone; imparting a substantial portion of the heat produced in said combustion zone to said heat-carrying bodies; and thereafter returning said heated heat-carrying bodies to said heating and grinding zone to heat additional fresh incoming solids.

22. The method of claim 21 in which the solids are particulate oil shale, and the combustible residue is particulate shale coke.

23. The method of claim 21 in which the pyrolysis zone comprises a generally horizontal rotating drum in which the heat-carrying bodies are continuously counter-currently intermixed with fresh solids, said heat-carrying bodies being inert, generally spherical, and wear-and-heat-resistant.

24. The method of claim 21 in which the pyrolysis zone comprises a generally horizontal rotating drum in which the heat-carrying bodies are continuously intermixed with fresh solids, in parallel flow, said heat-carrying bodies being inert, generally spherical, and wear-and-heat-resistant.

25. A process for the pyrolysis of coarsely ground solid material containing organic matter which upon pyrolysis leaves a combustible residue, including the steps of: pyrolyzing said solid material by direct contact with hot, inert, heat-carrying bodies in a pyrolysis zone; simultaneously grinding said material during the pyrolysis thereof whereby to render the bulk of the combustible residue produced fluidizable; removing said heat-carrying bodies and said combustible residue from said pyrolysis zone and separating said heat-carrying bodies from said combustible residue; fluidizing and combusting said finely ground residue by means of a combustion supporting gas in the absence of said heat-carrying bodies to thereby substantially raise the temperature of the effluent combusted residue and hot gases; transferring a substantial portion of the heat of said combusted residue to

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said bodies; and recycling said heated heat-carrying bodies to heat and pyrolyze fresh incoming solid material.

26. The method of claim 25 wherein the majority of the coarsely ground inlet feed has a size substantially larger than 10 mesh, and the majority of the combustible residue produced is substantially below 10 mesh.

27. The method of claim 25 wherein the solid material is oil shale, the combustible residue is shale coke, and the effluent combusted residue is shale ash.

References Cited in the file of this patent

UNITED STATES PATENTS

1,712,083 Koppers ----- May 7, 1929

2,420,376
2,441,386
2,654,698
2,664,389
2,673,177
2,725,348
2,788,313
2,794,724

10

541,571
305,106
633,648

16

Johansson ----- May 13, 1947
Berg ----- May 11, 1948
Phinney ----- Oct. 6, 1953
Rex et al. ----- Dec. 29, 1953
Buell ----- Mar. 23, 1954
Martin et al. ----- Nov. 29, 1955
Aspegren ----- Apr. 9, 1957
Mayland ----- June 4, 1957

FOREIGN PATENTS

Canada ----- May 28, 1957
Great Britain ----- Jan. 28, 1929
Great Britain ----- Dec. 19, 1949

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,984,602

May 16, 1961

Thomas D. Nevens et al.

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

Column 6, line 39, for "Figuers" read -- Figures --;
column 12, line 3, for the claim reference numeral "2" read
-- 1 --.

Signed and sealed this 10th day of October 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

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Commissioner of Patents

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