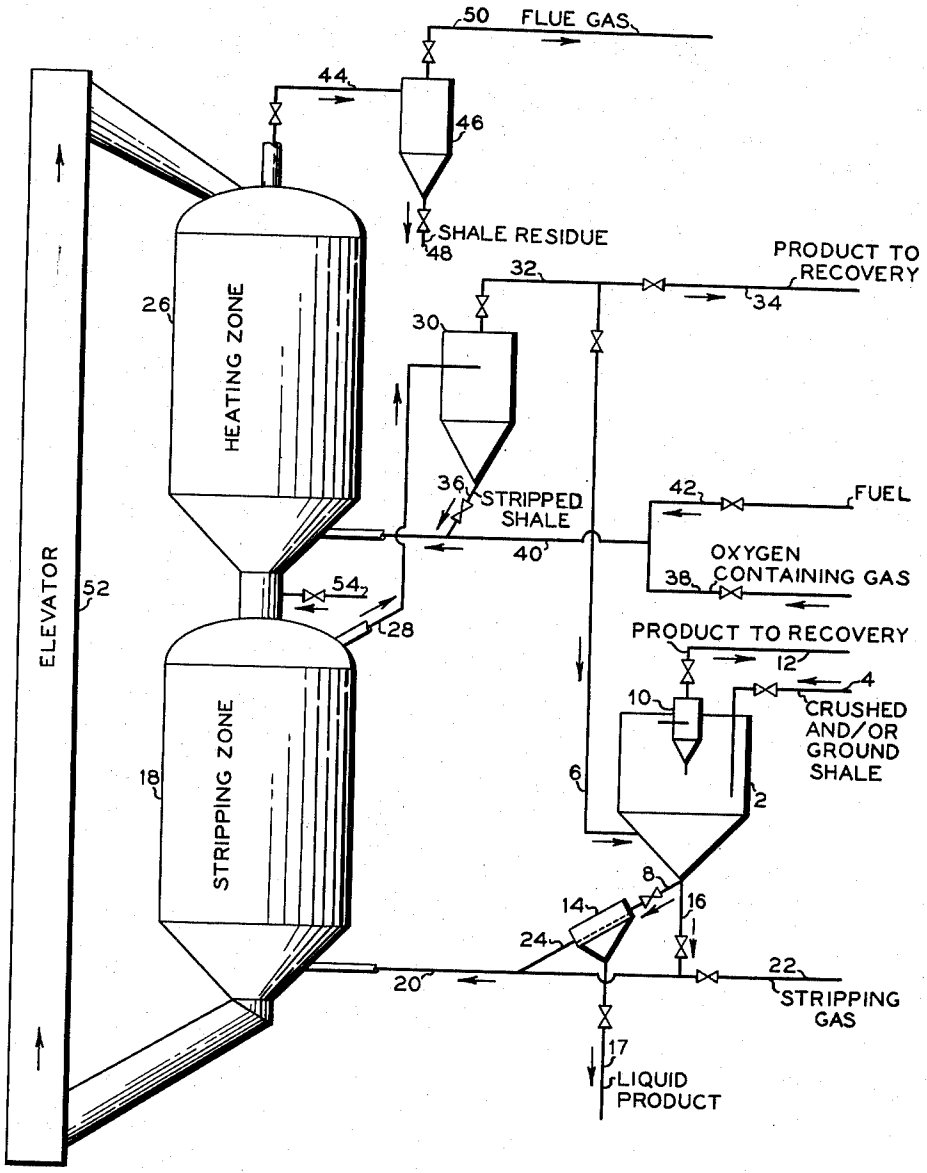
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PROCESS FOR DESTRUCTIVE DISTILLATION OF SOLID CARBONACEOUS MATERIALS

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PROCESS FOR DESTRUCTIVE DISTILLATION OF SOLID CARBONACEOUS MATERIALS

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This invention relates to destructive distillation. In one of its more specific aspects it relates to destructive distillation of solid carbonaceous material which is characterized by containing carbon available for producing heat by burning said carbon in the presence of an oxygen-containing gas subsequent to destructive distillation. In yet another of its more specific aspects it relates to the recovery of shale oil from oil shale.

Destructive distillation of solid carbonaceous materials, such as coal, wood, oat hulls, oil shale, etc., to recover useful, valuable products of such distillation has been long known in the art. Generally, destructive distillation has been carried out by heating carbonaceous material to drive off vaporous products which are condensed to be used as desired, such as separation and recovery of individual chemical components contained therein. Since oil shale is a typical example of a carbonaceous material which may be destructively distilled to convert kerogen contained in the oil shale into recoverable liquids and vapors, and since the process of my invention can be readily applied to the destructive distillation of oil shale, in this disclosure I will discuss the prior art relating to the destructive distillation of oil shale, usually referred to as retorting or stripping the oil shale, and the advantages over prior art processes which the process of my invention offers. However, as will be evident to one skilled in the art, the process of my invention is applicable to the destructive distillation of any solid carbonaceous material, and most of the advantages which the process of my invention has over prior art oil shale retorting processes can be realized in applying the process of my invention to the destructive distillation of any solid carbonaceous material.

In prior art practices oil shale has been stripped or retorted in batch fixed-bed processes using steam or flue gas, produced in the stripping chamber or produced outside and passed into the stripping chamber, as the stripping gas. These batch retorting processes are not efficient and capacity is low. Oil shale has been stripped in contiguous moving bed processes using steam or internally produced flue gas as the stripping gas. Some processors have stripped oil shale using hot spent shale, that is, shale heated by burning the residual carbon remaining after stripping, to furnish heat to convert the kerogen contained in the oil shale into shale oil. Fluidized shale retorting processes are known in the prior art, for instance, a process wherein hot spent

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oil shale heated by burning residual carbon is used to furnish heat for stripping shale oil from fresh untreated oil shale. One major disadvantage of known contiguous moving bed and fluidized processes which are carried out in conventional equipment is the formation of clinker aggregates which plug up moving beds of oil shale and disadvantageously affect the fluidization of oil shale, and, in addition, such clinker formation also presents a difficult removal problem. All of the processes of the prior art have disadvantages which I believe I have overcome by the process of my invention. The advantages which my process has over those processes of the prior art will appear to one skilled in the art hereinafter.

I have invented a process for destructively distilling solid carbonaceous material. In the process of my invention the solid carbonaceous material to be destructively distilled is finely divided so that destructive distillation can be carried out while the carbonaceous material is in fluidized suspension. By the process of my invention finely divided solid carbonaceous material is introduced into a destructive distillation zone wherein it is fluidized with a destructive distillation gas passed into said zone and wherein it is heated by directly contacting the fluidized carbonaceous material with a moving bed of hot refractory material which is passed into the destructive distillation zone. Heat is furnished by the hot refractory material to destructively distill the carbonaceous material, and resulting products of destructive distillation in admixture with destructively distilled carbonaceous material and destructive distillation gas are withdrawn from the destructive distillation zone. In an important modification to the process of my invention residual carbon remaining after destructive distillation is burned in the presence of an oxygen-containing gas in a refractory material heating zone. The heat resulting from the burning of the carbon is used to heat refractory material which is passed into the destructive distillation zone. I prefer to carry on the refractory material heating in much the same manner as I carry on destructive distillation, that is, burning the residual carbon from the destructively distilled carbonaceous material while it is fluidized in the refractory material heating zone and in direct contact with the refractory material to be heated. As will appear hereinafter, the process of my invention is particularly adaptable to the recovery of shale oil from oil shale. In retorting or stripping oil shale I prefer to use

steam and/or gaseous shale oil products as the stripping or retorting gas, referred to in the above discussion as the destructive distillation gas.

I find that the process of my invention has many advantages over the processes of the prior art. During stripping or retorting the motion of the refractory material, such as refractory pebbles which are extremely hard, prevents the formation of clinker aggregates. This advantage is very valuable since it prevents plugging of retorting equipment and eliminates the difficult problem of removal of clinkers which are formed in most shale retorting processes. I find that by the process of my invention oil shale can be retorted using short contact times, making it possible to use relatively high temperatures of from 1600 to 2000° F. for lightly cracking the oil shale organic material resulting from stripping the oil shale. At these relatively high temperatures, which are above the usual retorting temperatures of 825 to 1050° F., I find that some catalytic cracking is obtained from minerals contained in the shale. In comparison to other shale retorting processes, the capacity of suitable equipment in operating by my process is very high, and I find that my process is easy to operate giving little difficulty and high efficiency.

It is an object of this invention to provide a process for carrying on destructive distillation of solid materials.

It is another object of this invention to provide a process for destructively distilling solid carbonaceous material which is characterized by containing carbon available for producing heat by burning residual carbon in the presence of any oxygen-containing gas subsequent to destructive distillation.

Still another object of this invention is to provide a process for carrying on destructive distillation of solid carbonaceous material, such as oil shale, coal, wood, oat hulls, etc., which is easier to operate and more efficient than the processes known in the prior art.

Yet another object of this invention is to provide a process for recovering shale oil from oil shale.

Other objects and advantages of my invention will become apparent, to one skilled in the art, upon reading this disclosure.

The drawing, which accompanies and which is a part of this disclosure, is a diagrammatic flow sheet setting forth an arrangement of apparatus for practicing a preferred specific embodiment of the process of my invention in which the process of my invention is used to recover shale oil from oil shale. In this preferred specific embodiment of the process of my invention pebble heater apparatus, utilizing a contiguous moving bed of refractory pebbles, is used. The refractory pebbles are heated in an upper heating zone and are introduced into a lower stripping zone wherein the hot refractory pebbles furnish the heat necessary for stripping shale oil from the oil shale. The refractory pebbles are continuously circulated, being withdrawn from the stripping zone and elevated back into the heating zone. As will be apparent to one skilled in the art, the system which the diagrammatic flow sheet sets forth is applicable to the destructive distillation of any solid carbonaceous material.

I find that the process of my invention can be carried on in conventional pebble heater apparatus, utilizing a contiguous moving bed of refractory pebbles. Two zones or chambers are used. The upper chamber is used to heat refractory pebbles and the lower chamber is used to retort or strip shale oil from fluidized oil shale. The term "pebble" as used herein denotes any solid refractory material of flowable form, size, and strength which is suitable to carry large amounts of heat from a pebble heating chamber to the stripping or retorting chamber. Pebbles conventionally used in pebble heater apparatus are substantially spherical in shape and are about one-eighth inch to about one inch in diameter. Usually, in a high temperature process, pebbles having a diameter of between about one-fourth inch to three-eighths inch are preferred. In carrying on the process of my invention to strip or retort oil shale, that is, destructively distilling at from 825 to 1050° F., I prefer to use pebbles having a diameter of from one-fourth inch to one inch, while in carrying on the process of my invention to obtain some cracking of the shale oil products as well as retorting or stripping, I prefer that the pebbles be somewhat smaller, in the range of from one-fourth to five-eighths inch in diameter. In my process it is necessary that there be enough free flowing space to allow the fluidized oil shale to flow upwardly through the downwardly moving bed of pebbles.

The pebbles must be formed of a refractory material which will withstand temperatures at least as high as the highest temperature obtained in the pebble heating chamber. The pebbles must also be capable of withstanding temperature changes within the apparatus. Refractory materials, such as a metal alloy, ceramic, or other satisfactory material, may be utilized to form such pebbles. Satisfactory pebbles may be formed of silicon carbide, alumina, periclase, berryllia, Stellite, zirconia, and mullite in admixture with each other or with other materials. Pebbles formed of such materials, when properly fired, serve very well at high temperatures, some withstanding temperatures up to about 3500° F. If it is desired, catalytic pebbles can be used to catalytically crack shale oil products which have been stripped from the oil shale.

In the following I will discuss the process of my invention as applied to the recovery of shale oil from oil shale. Reference is made to the accompanying drawing which sets forth schematically a desired method of treating oil shale to recover shale oil products. It is to be understood that the following discussion setting forth materials, flow schemes, heat recovery schemes, compositions, etc., is an example of one specific embodiment of my invention, and should not be construed to limit unduly the scope of my invention. Crushed and/or ground shale in finely divided form is passed into a preheating zone 2 via line 4 wherein it is preheated and fluidized to form a fluidized bed by directly contacting the crushed and/or ground oil shale with hot gaseous shale oil product vapors passed into the lower portion of preheating zone 2 via line 6. These hot gaseous shale oil product vapors are produced as hereinafter set forth and are in admixture with stripping gas. For instance, if gaseous shale oil product vapors, resulting from condensing and separating liquid shale oil products, are used as the stripping gas in the oil shale retorting step of the process of my invention, they will be present with shale oil product vapors. In preheating zone 2 the finely divided oil shale is heated, preferably to a temperature not exceeding 450° F., so that no stripping or retorting occurs in this zone. In this preheating operation a portion of the gaseous shale oil products

are condensed and are withdrawn with preheated oil shale via line 8. Separation means 10, which can conveniently be a cyclone separator, a Cottrell precipitator, or a supersonic separator, is used to separate finely divided oil shale from the shale oil product vapors which are withdrawn via line 12 to be used as desired, usually to a product recovery system. Oil shale is returned to the fluidized bed within preheating zone 2 from separation means 10.

Preheated oil shale is passed to a separation means 14 wherein condensed shale oil products and preheated oil shale are separated, the liquid shale oil products being withdrawn via line 17. Separation means 14 is conveniently an oscillating or reciprocating screen separator but any suitable separation means can be used. If no condensation of shale oil product vapors occurs in preheating zone 2, the preheated oil shale is withdrawn from preheating zone 2 via line 16. In either case the preheated oil shale is passed in concurrent and direct contact with a stripping gas into the lower portion of stripping zone 18 via line 20. The stripping gas is introduced into the system via line 22 and picks up the preheated oil shale from either lines 16 or 24, which can conveniently be standpipes. The stripping gas is desirably either steam, gaseous shale oil products, a flue gas, and/or a portion of gaseous shale oil products resulting from stripping the oil shale, and preferably resulting from condensing and separating liquid shale oil products. As will be clear to one skilled in the art, if steam is used as the stripping gas or is present in admixture with other stripping gases, it is possible that some of it will be condensed in preheating zone 2, usually necessitating its removal from the preheated oil shale in separation means 14.

Preheated oil shale in contact with stripping gas is fluidized in stripping zone 18 and is directly contacted with a moving bed of hot refractory pebbles which is introduced into stripping zone 18 from heating zone 26. As the oil shale is passed upwardly in fluidized form through stripping zone 18, it is heated to retorting temperature, or temperatures higher than retorting temperatures if cracking is desired, and the kerogen in the oil shale is converted to shale oil vapors.

Shale oil product vapors in admixture with stripped oil shale and stripping gas are withdrawn from the upper portion of stripping zone 18 via line 28 and are passed into a separation zone 30 which can conveniently be a cyclone separator, a Cottrell precipitator, or a supersonic separator. Therein stripped oil shale is separated from the shale oil product vapors and stripping gas. The shale oil product vapors and stripping gas are withdrawn from separation zone 30 via line 32. These withdrawn vapors are passed into preheating zone 2 via line 6, as hereinbefore set forth, or they are passed via line 34 to a product recovery system. In normal operation I find that it is desirable to pass as much of the vapors as possible into preheating zone 2 to recover heat, that is, as much of the vapors as possible without preheating the fresh oil shale to retorting temperatures, and preferably no higher than 450° F. since at this temperature and lower temperatures the formation of clinker aggregates in preheating zone 2 is avoided. My process can be operated without this preheating operation but I find that it is a particularly good heat saving scheme.

Hot stripped shale is withdrawn from separation zone 30 via line 36, which is conveniently a standpipe, and is passed in direct and concurrent contact with an oxygen-containing gas supplied via line 38 into heating zone 26 via line 40. Fuel gas may be supplied, if desired, via line 42 if additional heat is necessary to heat the refractory pebbles in heating zone 26. Stripped oil shale and oxygen-containing gas are introduced into the lower portion of heating zone 26 and therein the stripped shale is fluidized and the residual carbon is burned. Flue gas produced from said burning and hot spent oil shale directly and countercurrently contact the refractory pebbles and heat them prior to their introduction into stripping zone 18. Flue gas and spent oil shale are withdrawn from the upper portion of heating zone 26 via line 44 and are passed into separation zone 46, which can conveniently be a cyclone separator, a Cottrell precipitator or a supersonic separator. In separation zone 46 spent oil shale is separated from flue gas. Spent oil shale residue is withdrawn via line 48 and flue gas is withdrawn via line 50. While I find it desirable to heat the refractory pebbles in this manner I find that other methods can be used, such as burning residual carbon from the stripped oil shale and passing resulting flue gases into heating zone 26.

Refractory pebbles are withdrawn from the lower portion of stripping zone 18 and are passed by elevation means 52 into the upper portion of heating zone 26 for recycling.

In order to prevent vapors from entering heating zone 26 from stripping zone 18, I find it desirable to introduce sealing steam or other sealing gas into the conduit between heating zone 26 and stripping zone 18. This sealing gas may be introduced via line 54. This is desirable since product vapors entering heating zone 26 are burned, thus lowering the amount of recovery and efficiency of my process.

As will be evident to one skilled in the art, other heat recovery schemes can be used within the scope of the process of my invention. For instance, the oxygen-containing gas, such as air, used to burn residual carbon from the stripped oil shale can be preheated by the spent oil shale residue withdrawn from separation zone 46 via line 48. And, while I prefer to use steam or gaseous shale oil products as the stripping gas, I find that flue gas can be used, if desired, as the stripping gas. However, since flue gas, unlike steam, cannot be separated from the shale oil product vapors in a relatively simple condensation and separation operation, I find that it is not too desirable to use flue gas. Dilution of the shale oil product vapors with flue gas is not desirable and it is advantageous to use steam or product vapors as the stripping gas.

If difficulty is encountered in separating preheated oil shale from condensed shale oil products in separation means 24, as can be the case when tars and other heavy products are condensed, I find that partial condensation of shale oil products resulting from stripping, and separation of condensed products from the resulting vapors can be used, the resulting vapors are then passed into preheating zone 2 to preheat oil shale.

I find that the process of my invention can be used to strip shale oil from oil shale of a wide range of richness, containing from 10 to 90 gallons of shale oil per ton, without encountering any difficulty with clinker formation. In my process, any size of oil shale particles which

can be fluidized can be used. It is desirable that the particle size not exceed one-eighth inch, and I find that it is preferable to use oil shale of a particle size of 40 mesh and smaller.

In destructively distilling carbonaceous materials which do not contain an appreciable quantity of inert material subsequent to burning residual carbon, the residual carbon resulting from the destructive distillation can be substantially completely burned in heating zone **26**, in many cases eliminating separation zone **46**. Also, I find that in destructively distilling some carbonaceous materials, such as oat hulls, high grade coal, wood, etc., the degree of destructive distillation can be controlled so as to provide the necessary residual carbon to provide heat to heat the refractory pebbles or materials. Many times it is necessary to do this, since many carbonaceous materials can be substantially completely destructively distilled leaving little carbon available to produce heat. As the result of destructively distilling oil shale, more heat is usually available from the residual carbon than is necessary to heat the refractory materials, but it is a relatively easy operation to provide fuel gas if additional heat is found to be necessary.

The above set forth preferred specific embodiment of the process of my invention, and the drawing which accompanies and is a part of this disclosure, will serve as examples of the operations to which the process of my invention can be applied. However, such preferred specific embodiment and drawing are not to limit unduly the scope of the process of my invention.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of this disclosure and discussion, without departing from the spirit or scope of this disclosure or from the scope of the claims.

I claim:

1. A process for separating and recovering shale oil from oil shale which comprises: introducing finely divided oil shale having a particle size no greater than 40 mesh and containing from 10 to 90 gallons of shale oil per ton into a preheating zone and therein forming a fluidized oil shale bed and preheating said oil shale by directly contacting said oil shale with a gaseous mixture of stripping gas and shale oil product withdrawn from a separation zone as hereinafter set forth and introduced into the lower portion of said preheating zone, thereby preheating said oil shale to a temperature no greater than 450° F. and cooling and condensing a portion of said gaseous mixture of stripping gas and shale oil product introduced into said preheating zone; withdrawing resulting gaseous shale oil product and stripping gas from the upper portion of said preheating zone as a product of the process; withdrawing resulting preheated oil shale and condensed shale oil product from the lower portion of said preheating zone, separating resulting preheated oil shale from resulting condensed shale oil product and withdrawing resulting condensed shale oil product as a product of the process; passing resulting preheated oil shale in direct concurrent contact with a stripping gas into the lower portion of a stripping zone and therein fluidizing said resulting preheated oil shale; therein heating said resulting preheated oil shale to a temperature in the range from 825 to 1050° F. by directly and countercurrently contacting same with a moving bed of hot refractory pebbles having a diameter of from one-fourth inch to one inch passed into the upper portion of said stripping zone and heated as hereinafter set forth in a pebble heating zone, thereby stripping shale oil from said resulting preheated oil shale; withdrawing resulting products of said stripping in admixture with stripping gas and stripped oil shale from the upper portion of said stripping zone and passing same into a separation zone and therein separating said stripped oil shale from said stripping gas and shale oil products; passing a portion of a resulting gaseous mixture of shale oil products and stripping gas into said preheating zone as hereinbefore set forth; removing resulting stripped oil shale from said separation zone and passing same in direct and concurrent contact with an oxygen-containing gas into the lower portion of a pebble heating zone, thereby fluidizing said stripped oil shale, burning residual carbon from said stripped oil shale and heating a moving bed of refractory pebbles by directly contacting same with a resulting mixture of hot flue gases and spent oil shale; withdrawing resulting hot refractory pebbles from said pebble heating zone and passing same into said stripping zone as hereinbefore set forth; and withdrawing spent oil shale and flue gases from the upper portion of said pebble heating zone.

2. The process of claim 1 wherein said stripping gas is shale oil products resulting from stripping said oil shale.

3. The process of claim 1 wherein said preheated oil shale is stripped at a temperature of from 1600 to 2000° F. in said stripping zone.

4. A process for separating and recovering shale oil from oil shale which comprises: introducing finely divided oil shale into a preheating zone and therein forming a fluidized oil shale bed and preheating said oil shale by directly contacting said oil shale with a gaseous mixture of stripping gas and shale oil product withdrawn from a separation zone as hereinafter set forth and introduced into the lower portion of said preheating zone, thereby preheating said oil shale and cooling and condensing a portion of said gaseous mixture of stripping gas and shale oil product introduced into said preheating zone; withdrawing resulting gaseous shale oil product and stripping gas from the upper portion of said preheating zone as a product of the process; withdrawing resulting preheated oil shale and condensed shale oil product from the lower portion of said preheating zone, separating resulting preheated oil shale from resulting condensed shale oil product and withdrawing resulting condensed shale oil product as a product of the process; passing resulting preheated oil shale in direct concurrent contact with a stripping gas into the lower portion of a stripping zone and therein fluidizing said resulting preheated oil shale; therein heating said resulting preheated oil shale by directly and countercurrently contacting same with a moving bed of hot refractory pebbles passed into the upper portion of said stripping zone and heated as hereinafter set forth in a pebble heating zone, thereby stripping shale oil from said resulting preheated oil shale; withdrawing resulting products of said stripping in admixture with stripping gas and stripped oil shale from the upper portion of said stripping zone and passing same into a separation zone and therein separating said stripped oil shale from said stripping gas and shale oil products; passing a portion of a resulting gaseous mixture of shale oil products and stripping gas into said preheating zone as hereinbefore set forth; re-

moving resulting stripped oil shale from said separation zone and passing same in direct and concurrent contact with an oxygen-containing gas into the lower portion of a pebble heating zone, therein fluidizing said stripped oil shale, burning residual carbon from said stripped oil shale and heating a moving bed of refractory pebbles by directly contacting same with resulting mixture of hot flue gases and spent oil shale; withdrawing resulting hot refractory pebbles from said pebble heating zone and passing same into said stripping zone as hereinbefore set forth; and withdrawing spent oil shale and flue gas from the upper portion of said pebble heating zone.

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