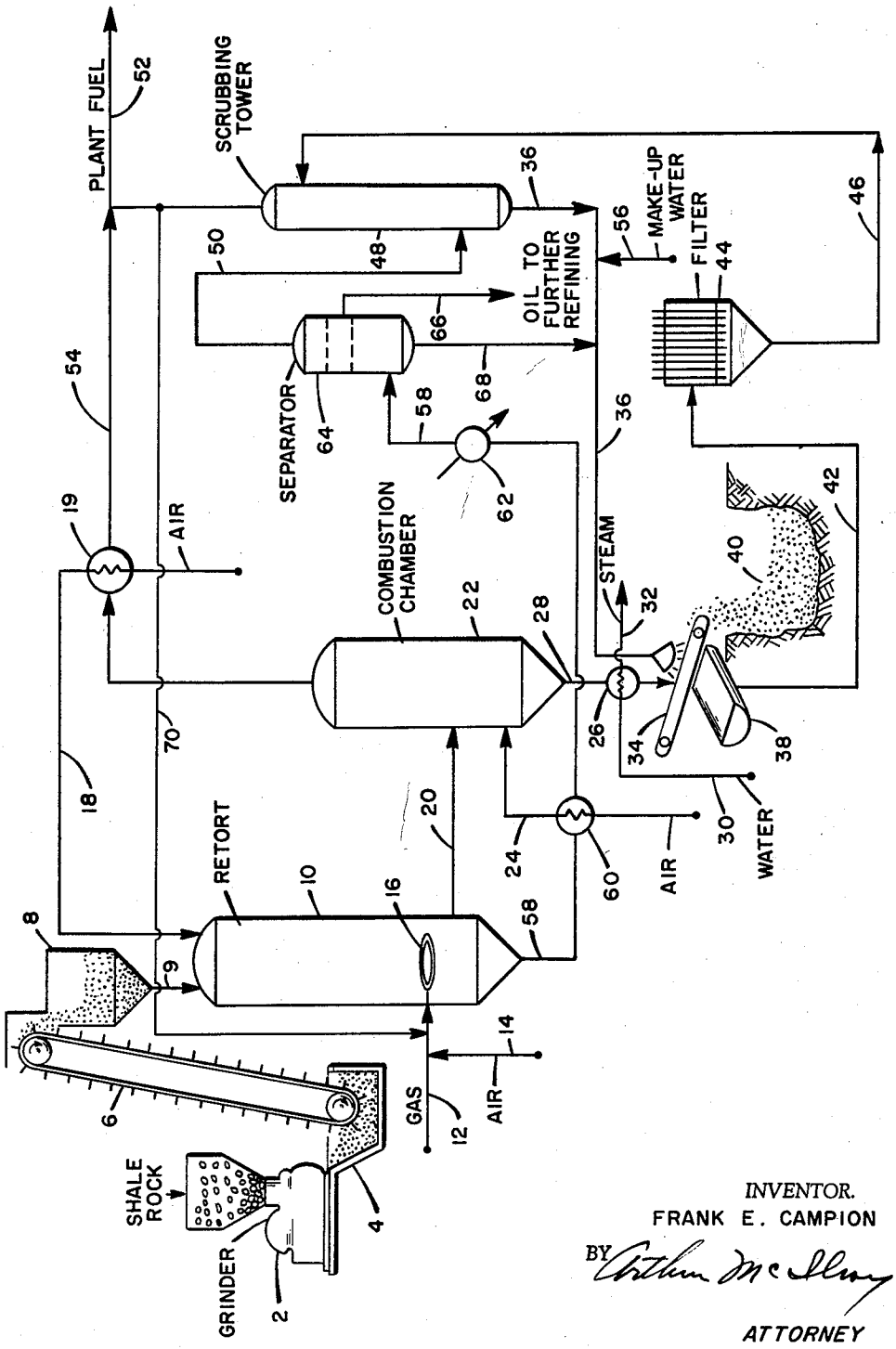
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PROCESS FOR RECOVERING HYDROCARBONS FROM SOLID MATERIALS

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# PROCESS FOR RECOVERING HYDROCARBONS FROM SOLID MATERIALS

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The present invention relates to the recovery of hydrocarbon oils from solid materials. More particularly it is concerned with the treatment of bituminous materials such as oil shale and the like.

The recovery of oil from oil shale requires the retorting of crushed shale at temperatures which may vary from about 800° to about 2,000° F. As will be recognized, oil shale ordinarily does not contain oil as such but has in it a solid bituminous material known as kerogen which, when heated, decomposes into gases, liquid hydrocarbons and free carbon. The oil produced in this operation is a mixture of higher molecular weight hydrocarbons, including waxes, and is extremely viscous. In general this liquid product is unfit for transmission by pipe-line and must be subjected to a vis-breaking or coking operation in order to obtain an oil of suitable viscosity for pipe-line transport or for further refining operations. The coking operation is carried out in a unit separate from the oil shale retort. Commercial shale retorting operations previously used generally have been cumbersome and expensive involving large equipment and high operating costs per unit of shale. One factor contributing to the undesirable economics of such operation has been poor heat recovery in the retorting system.

Accordingly, it is an object of my invention to provide a method for the recovery of hydrocarbons from oil bearing minerals under conditions such that the liberation of hydrocarbons from said minerals and subsequent coking of the liberated oil can be effected in a single operation. It is another object of my invention to provide a method for the recovery of hydrocarbons from the aforementioned oil bearing minerals in accordance with the procedure whereby full utilization can be made of the heat derivable from the coke and highly volatile hydrocarbon fractions produced. A further object of my invention is to provide a practicable and convenient method for treating shale ash to remove harmful alkaline impurities therefrom which might otherwise be leached out from spent shale piles and eventually contaminate streams into which such leachings drain.

One embodiment of my invention is directed to an improved process for the retorting of hydrocarbon yielding materials such as oil shale under conditions such that the retorting and coking operations are both effected within the same vessel or unit. In such an operation, oil shale and an oxidizing gas such as air, are concurrently introduced into a suitable retort. A zone of combustion is established within the retort at a level determined by the rates of injection of shale and air or oxygen and the temperature of the shale and oxidizing gas. Oil produced from the shale passes through the combustion zone where it is thermally cracked into lower weight molecular hydrocarbons. In this manner the coking process, ordinarily effected in a separate unit, is accomplished in the retort thus eliminating the cost of constructing and operating individual coking units. The oil thus produced is of suitable viscosity for pipe-line transmission or, if desired, may be further refined at the retorting site.

My invention may be further illustrated by reference to the accompanying flow diagram. Mined shale rock is fed to a grinding unit 2 where it is converted to a particle size sufficiently fine to render the material free flowing.



Usually particle sizes of from about one quarter to about one inch in diameter are satisfactory. Crushed shale in larger sizes may be employed in my invention, however, handling and oil recovery efficiencies are ordinarily not as good as with the more finely divided material. The ground shale is taken from a bin 4 by means of endless belt conveyer 6 and added to hopper 8. Retort 10 is first filled with ground shale flowing through line 9, after which the addition of shale is temporarily discontinued. Gas in line 12 and air in line 14 are then mixed and burned in spray type burner 16 to cause the shale in contact therewith to burn. After a burning zone has been established, air heated to about 300°–1,000° F., by passage through exchanger 19, is introduced into the top of retort 10 via line 18. The temperature of the air, generally speaking, should be adjusted to the particular case under consideration. For example, air temperatures as high as 1,000° F. may be used but will depend largely on the particle size of the shale charged to the retort. In the case of finely divided shale, heat is rather rapidly transferred from the air into the matrix of the rock and results in the creation of a "hot spot" in the top of the retort which may even ignite and burn. This condition, of course, would be undesirable. However, if the shale particles charged to the retort are comparable to golf balls in size, high air temperatures may be tolerated since the diffusion of heat into the shale matrix is slower. The higher this air temperature can be made without causing ignition of the incoming shale, the more desirable it is since less heat will be required in the combustion zone to maintain the desired temperature level and less oil will be consumed as fuel.

Under some instances it may be desirable, where the oil content of the shale is low, to inject part of the scrubbed gaseous hydrocarbon stream, making up the plant fuel product, back into the retort to provide additional fuel. Also, owing to the inert gas content of this plant fuel product stream, the latter may be injected into the combustion zone as a means for controlling the temperature in said zone.

As the air added to the system through line 18 contacts the burning zone in the lower part of retort 10, the burning front of the zone tends to move upwardly toward the air source. Flow of gas and air through lines 12 and 14, respectively, is then shut off since the necessary combustion can be sustained and controlled by injection of air through line 18. Introduction of air only at the top of retort 10 is ordinarily continued until the burning zone reaches an intermediate level in the retort, preferably from about one-third to about half-way up the column of shale in the retort. When this condition is reached both shale and air are added concurrently through lines 9 and 18 respectively, to the top of retort 10.

For best operating efficiency the flow of enriched air or oxygen into the retort should be regulated with the flow of shale. The amount of air or oxygen needed in a given case generally does not depend significantly on the quantity of carbonaceous material in the shale. For example, with a retort having a volume of 100 cubic feet and designed to process 100 tons of shale (having an oil content of about 30 gal./ton) per day, air should be added to the top of the retort at the rate of about 18,240 s.c.f.h. to maintain steady state conditions.

The retort may be operated at atmospheric pressure although higher pressures such as, for example, 400 to 500 p.s.i. may be employed.

One of the advantages of the process of my invention is the fact that it can readily be carried out at relatively low temperatures, i.e., about 800 to about 1,000° F., thus aiding in the prevention of excessive clinker formation in the retort. In some commercial shale retorting proc-

esses, temperatures as high as about 2,000° F. are reached. To avoid shutdown and other difficulties due to sintering and clinkering of the shale, large spiral steel plows are kept moving in the retort bed. The economic advantages in operating without such elaborate auxiliary equipment are apparent.

During the retorting operation approximately ten to twelve percent of the hydrocarbons in the average grade of oil shale is burned to sustain the operation. The remainder of the liquid kerogen decomposition products passes downwardly through the burned shale bed in retort 10 and is extensively cracked owing to prolonged contact with the hot spent shale as the latter travels toward the base of the retort. It will thus be seen that the level at which the burning zone is to be maintained in the bed will be at least partially dependent upon the degree of cracking desired and the nature of the hydrocarbon fractions liberated from the oil shale. Selection of a proper level for the burning zone in the shale bed for any given set of circumstances can be readily determined by simple experimentation.

The spent shale is withdrawn through line 20 and transferred to combustion chamber 22. The shale at this stage of the process contains an appreciable amount of coke representing substantial quantities of heat as well as fuel gas which can be secured from controlled burning of the coke. Accordingly, in carrying out the combustion of the coke and other combustible components present on the retorted shale, an important factor is the temperature at which the shale tends to sinter or form clinkers in combustion chamber 22. The amount of coke adhering to the retorted shale will, of course, vary. However, in the process contemplated by my invention, the coke residue on the shale ash should not ordinarily exceed about ten percent and for the most part would generally be in the neighborhood of five percent. In general, clinker formation will be avoided as long as the temperature is held below about 1,200°–1,300° F. Air at 400°–600° F. is introduced into combustion chamber 22 via line 24, preferably at a rate such that coke and other carbonaceous material present is only partially burned resulting in gaseous products rich in carbon monoxide. Temperatures required to produce gaseous products rich in carbon monoxide are in the range normally used in the well-known methods for making producer gas, i.e. 850°–1,350° F. With some oil shales, clinkering does not occur until temperatures of 1,500°–1,600 F. are reached. In case of shale of this type, temperatures as high as high as about 1,300° to about 1,400° F. may be used in the partial combustion step.

Further economies in the process can be realized by generation of steam in heat exchanger 26 through absorption of heat from spent shale withdrawn through line 23. The steam resulting from the conversion of water in line 30 is transferred through line 32 and may be used for the generation of plant power. The cooled spent shale or ash is transferred to a vibrating screen 34 and leached by water flowing through line 36. This operation removes the major portion of the alkaline components present in the ash resulting in an aqueous alkaline solution and a suspension of fine particles passing through screen 34 into an open tank 38. The bulk of the ash discharged from line 28 on to screen 34, is dumped into a suitable disposal pit 40. From tank 38 the aqueous alkaline mixture is taken through line 42 and the solid material removed in filter 44. The filtrate is then transferred through line 46 and used to scrub uncondensed product gases fed to the bottom of tower 48 through line 50. Scrubbed gas is taken off through line 52, combined, if desired, with other gases from combustion chamber 22, contained in line 54 and used for plant fuel. For example, a portion of the scrubbed gas may be taken off through line 70 and combined with the fuel-air mixture in line 12 used to feed the burning zone in retort 10. The scrubbing water from tower 48 is removed via line 56, filtered if necessary and then used as leaching water to remove alkali from spent shale as previously described. Make-up water is added to the system through line 56 as needed.

Cracked retort oil of substantially reduced viscosity is removed from retort 10 via line 58 and heat exchanged in exchanger 60 with cold air in line 24. This product stream is further cooled in condenser 62 before it is sent to separator 64. Oil is taken off through line 66 and sent to further processing while the lower water layer is run off through line 68 and combined with the scrubbings in line 36.

From the foregoing description it will be apparent that my invention not only affords a substantial savings in heat but also it provides a method for producing in one step a relatively low viscosity shale oil without the use of a separate coking unit. While I have shown the retorting unit to be in a vertical position with reactants flowing concurrently from top to bottom, comparable results can be obtained with a generally horizontal retort, appropriate modifications being made for the removal of liquid hydrocarbons therefrom. Also the air and shale can be injected concurrently from the bottom of the retort with ash and products being taken off at the top thereof. Orientation of the retort in effecting my invention is not necessarily important. The essential feature of my invention is the establishment of a burning zone in one end of the shale bed and maintaining such burning zone at a desired position in the bed by controlled concurrent introduction of air or oxygen and oil shale at the end of the retort opposite that in which the burning operation was initiated. Under such condition the liberated hydrocarbons remain in contact with the hot shale ash for a time sufficient to effect appreciable cracking of the normally viscous product into a material of substantially reduced viscosity.

It will likewise be apparent that the process of my invention is not limited to the treatment of oil shale to recover valuable hydrocarbon fractions therefrom, but applies equally well to bituminous materials having characteristics generally similar to oil shale such as, for example, torbanite or cannel coal.

I claim:

1. In a process for the recovery of liquid hydrocarbons from a solid hydrocarbonaceous material involving retorting said material in a confined reaction chamber filled therewith, the improvement comprising establishing a burning zone in said material at one end of said chamber, thereafter supplying from the end of said chamber opposite said burning zone the oxygen required to sustain the burning of said material, continuing the introduction of oxygen until said burning zone has travelled to an intermediate point in said chamber, next adding concurrently from said opposite end oxygen and said material in an amount and in a ratio such that said burning zone remains substantially at said intermediate point, and the portion of said material moving through said chamber between said opposite end and said burning zone remains unburned, whereby the hydrocarbons thus liberated are permitted to remain in contact with the resulting ash for an appreciable period of time to effect thermal cracking of said hydrocarbons, and withdrawing ash and liquid hydrocarbons from the end of said chamber opposite that into which said material and oxygen are concurrently introduced.

2. In a process for the recovery of liquid hydrocarbons from a solid hydrocarbonaceous material involving retorting said material in a confined reaction chamber filled therewith, the improvement comprising establishing a burning zone in said material at one end of said chamber, thereafter supplying from the end of said chamber opposite said burning zone the oxygen required to sustain the burning of said material, continuing the introduction of oxygen until said burning zone has travelled to an intermediate point in said chamber, next adding concurrently from said opposite end oxygen and said material in an amount and in a ratio such that said burning zone is maintained at a temperature of from about 800° to about 1,000° F. and remains substantially at said intermediate

point, and the portion of said material moving through said chamber between said opposite end and said burning zone remains unburned, whereby the hydrocarbons thus liberated are permitted to remain in contact with the resulting ash for an appreciable period of time to effect thermal cracking of said hydrocarbons, and withdrawing ash and liquid hydrocarbons from the end of said chamber opposite that into which said material and oxygen are concurrently introduced.

3. The process of claim 2 in which the solid hydrocarbonaceous material used is oil shale.

4. In a process for the recovery of liquid hydrocarbons from oil shale involving retorting said shale in a confined reaction chamber filled therewith, the improvement comprising establishing a burning zone in said shale at one end of said chamber, thereafter supplying from the end of said chamber opposite said burning zone the oxygen required to sustain the burning of said shale, continuing the introduction of said oxygen until said burning zone has travelled to an intermediate point in said chamber, next adding concurrently from said opposite end oxygen and said shale in an amount and in a ratio such that said burning zone remains substantially at said intermediate point, and the portion of said material moving through said chamber between said opposite end and said burning zone remains unburned, whereby the hydrocarbons thus liberated are permitted to remain in contact with the resulting hot spent shale for an appreciable period of time to effect thermal cracking of said hydrocarbons, separately withdrawing spent shale and a product stream containing gaseous and liquid hydrocarbons, scrubbing said gaseous hydrocarbons with water, thereafter employing the resulting aqueous scrubbing to leach the alkaline components from said spent shale, filtering the resulting leach water and repeating this cycle by using said leach water in said scrubbing step.

5. In a process for the recovery of liquid hydrocarbons from shale oil involving retorting said shale in a confined vertical chamber filled therewith, the improvement comprising establishing a burning zone in said shale at the base of said chamber, thereafter supplying from the top of said chamber the oxygen required to sustain the burning of said shale, continuing the introduction of said oxygen until said burning zone has travelled upwardly to a level of from about one-third to about one-half the height of said chamber, next concurrently introducing crushed shale and oxygen into the top of said chamber in an amount and in a ratio such that said burning zone remains substantially at said level, and the portion of said material moving through said chamber between said opposite end and said burning zone remains unburned, whereby the hydrocarbons thus liberated are permitted to remain in contact with the spent shale passing slowly and downwardly through said chamber to effect thermal cracking of said hydrocarbons, and separately withdrawing spent shale and liquid hydrocarbons from the base of said chamber.

6. In a process for the recovery of liquid hydrocarbons from oil shale involving retorting said shale in a confined reaction chamber filled therewith, the improvement comprising establishing a burning zone in said shale at one end of said chamber, thereafter supplying from the end of said chamber opposite said burning zone the oxygen required to sustain the burning of said shale, continuing the introduction of said oxygen until said burning zone has travelled to an intermediate point in said chamber, next adding concurrently from said opposite end oxygen and said shale in amounts sufficient to maintain combustion, and the portion of said material moving through said chamber between said opposite end and said burning zone remains unburned, whereby the hydrocarbons thus liberated are permitted to remain in contact with the resulting hot spent shale for an appreciable period of time to effect thermal cracking of said hydrocarbons, withdrawing spent shale and a product stream containing gaseous and liquid hydrocarbons, scrubbing said gaseous hydrocarbons with water and thereafter returning a portion of the resulting scrubbed gaseous hydrocarbons to said burning zone in an amount and at a temperature such that said burning zone remains substantially at said intermediate point.

7. A process for removing oil from oil-bearing mineral solids which comprises feeding oil-bearing mineral solids to an elongated upright confined retorting zone, creating a confined combustion zone within said upright zone by igniting combustible substances on said solids passing said solids downwardly as a moving bed through said combustion zone, introducing a stream of oxygen-containing gas into said upright zone above said combustion zone to support combustion processes in said combustion zone and at a rate to force combustion products from said combustion zone and educted oil products from the solids above said combustion zone to pass downwardly through said combustion zone and downwardly through hot, oil-free solids in a direction which is concurrent with the direction of movement of said bed in said upright zone, removing a stream of said combustion products and said oil products at a level below said combustion zone and removing a stream of oil-free solids at the bottom of said upright zone at a rate to maintain said combustion zone at a substantially constant position within said upright zone.

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