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**METHOD FOR RECOVERING OIL
 FROM OIL SHALE**

Louis D. Friedman and Leon P. Gaucher, Beacon, N.Y.,
 assignors to Texaco Inc., New York, N.Y., a corpora-
 tion of Delaware

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 1 Claim. (Cl. 208—11)

This invention relates to an improved process for the
 recovery of oil from oil shale.

In carrying out the process of this invention, oil shale
 particles are subjected to treatment with steam at a pres-
 sure in the range of 1000 to 3000 pounds per square inch
 gauge and a temperature in the range of 700 to 900° F.,
 for a period of time within the range of about 20 minutes
 to 6 hours. In a preferred operation, shale particles are
 mixed with sufficient water to form a pumpable mixture
 and the mixture passed under pressure through an elon-
 gated heating zone of restricted cross-sectional area in
 which the water is vaporized, entraining the shale parti-
 cles in steam, and the mixture heated to the desired
 temperature; the heated mixture is discharged into a soak-
 ing zone of large volume wherein the oil shale is sub-
 jected to the stripping and heating action of steam for the
 required period and from which recovered oil from the
 oil shale is withdrawn in vapor form admixed with said
 steam. Oil yields of more than 100 percent in compari-
 son with the standard Fischer assay, are obtained from
 commercial grade oil shales. The quality of the recov-
 ered oil is comparable with that obtained by other
 methods of retorting.

It is known that kerogens contained in oil shale may
 be converted to hydrocarbon oil by the application of
 heat. Various methods have been proposed for the re-
 covery of hydrocarbon oil from oil shales. For example,
 it has been proposed heretofore to recover shale oil from
 oil shale by contacting the shale with steam at tempera-
 tures above 850° F. and at substantially atmospheric
 pressure. It has also been proposed to hydrate oil shales
 with liquid water at 500 to 700° F. under elevated pres-
 sures of the order of about 1,000 to about 3,000 pounds
 per square inch gauge.

The present process has a distinct advantage over such
 prior proposals. The yields of hydrocarbon oil are ex-
 ceptionally high as compared with low pressure steam
 distillation operations of the prior art. As compared
 with hydration with water in liquid phase, the present
 process has the advantage of requiring very little pro-
 cess water and of permitting the recovery of the shale oil
 directly. In the liquid phase hydration process, the clayey
 pulp resulting from hydration must be further treated,
 e.g. with a hydrocarbon solvent, to recover the oil there-
 from. Condensate water from the present process may
 be recirculated to the slurry feed preparation step. Rel-
 atively small amounts of make-up water are required.
 This is a definite advantage in arid regions, for example,
 the western part of the United States where many com-
 mercial shale beds are located.

The process of this invention provides a method for
 direct recovery of oil in high yield from oil shales by
 retorting with steam at a pressure above 1,000 pounds
 per square inch gauge and at relatively low temperature
 in the range of 700 to 900° F. The relatively mild tem-
 perature employed in the present process largely prevents
 decomposition of carbonates contained in the shale. A
 large part of the heat required in conventional shale re-
 torting processes is required for decomposition of car-
 bonates. Carbon dioxide liberated from the carbonates
 generally serves no useful purpose in the retorting process.

The process of this invention will be more readily
 understood from the following detailed description, taken

in conjunction with the accompanying drawing. The FIG-
 URE illustrates diagrammatically an arrangement of ap-
 paratus suitable for carrying out the present process.

With reference to the figure, oil shale crushed to a
 particle size not larger than about ¼ inch diameter is
 charged to mixer 1 wherein it is admixed with sufficient
 water to form a pumpable mixture or slurry. A mini-
 mum of about 35 percent water by weight of the final
 slurry is generally required; usually approximately equal
 parts of water and shale by weight are preferred.

We have found, as indicated in the examples herein-
 after, that particles smaller than about ¼ inch in average
 diameter are not particularly advantageous insofar as the
 recovery of shale oil from the oil shale is concerned.
 Smaller particles are, however, somewhat more readily
 handled as a suspension or slurry and are preferred for
 this reason. Usually it is desirable to crush the oil shale
 only to the extent necessary to permit the shale particles
 to pass through a sieve or screen having openings of
 about ¼ inch and to utilize the unclassified material
 passing through the screen as feed to the process.

To prevent the formation of scale in subsequent heat-
 ing operations it is desirable to add an alkali metal hy-
 droxide, preferably sodium hydroxide, to the slurry. An
 alkali metal carbonate may also be added to the slurry
 to supplement the action of alkali metal hydroxide. The
 preferred treatment involves addition of both alkali metal
 carbonate and alkali metal hydroxide. The amount of
 additive required to prevent scale formation in the heater
 will depend upon the chemical composition of the oil
 shale, but may be determined for any given shale by
 simple tests. Trouble free operation is obtained when
 the pH of the slurry is between 9 and 10, and the hard-
 ness, expressed as calcium carbonate, is between 0 and 2
 parts per million.

To determine the amounts, for example, of sodium hy-
 droxide and sodium carbonate, required to produce a
 slurry which will not cause scale deposits to form on
 heated surfaces, sodium hydroxide is added to the slurry
 until the pH is between 9 and 10. The hardness, ex-
 pressed as calcium carbonate, is then determined and an
 amount of sodium carbonate added which is sufficient to
 precipitate calcium remaining in the solution in the slurry
 water. The calcium is precipitated as insoluble calcium
 carbonate which is deposited on the solid shale particles
 and passes through the heating coil with the solid particles
 without depositing on the walls of the tubular heater.

Slurry is withdrawn from mixer 1 to a pump 2 from
 which it is passed into and through the initial portion of
 a heater tube at a rate sufficient to prevent separation
 of the solid particles from the aqueous carrier, generally
 at a linear velocity within the range of ½ to 10 feet per
 second, suitably about 1 to 2 feet per second. Heat may
 be supplied to the tube 3 from any suitable source, for
 example, an oil-fired furnace 4. The slurry is heated
 in the initial or vaporizing section 3a of the tubular
 heater by an amount at least sufficient to vaporize the
 water to steam. When the water is vaporized from the
 moving stream of slurry, the resulting steam entrains the
 particles of solid shale in steam flowing at relatively high
 velocity, generally 4 to 50 feet per second, through a
 second portion, or high velocity section 3b, of the tubular
 heater 3. From the high velocity section of the heater,
 the dispersion is passed into a low velocity section 3c
 the heating coil containing tubing of larger diameter than
 that in said vaporizing and high velocity sections of the
 heater where the entrained shale is further heated to a
 temperature in the range of 800 to 1000° F.

The tubular heater can have any desired shape, such
 as single or double helical coils, parallel straight pipe
 lengths connected by return bends, sinusoidal or other
 suitable configuration, or even a long straight length of

pipe. The various sections indicated, i.e. the vaporizing, high velocity, and low velocity sections, may be each located in one or more separate heating furnaces.

The dispersion is discharged through line 8 into soaking zone 9. The soaking zone is designed to maintain the shale in contact with steam from heater 4 for a period of time within the range of about 20 minutes to about 3 hours. Some of the retorting or liberation of oil from the oil shale by conversion of the kerogen in the oil shale to hydrocarbon oil is accomplished in the heater and the remainder takes place in soaking zone 9. The soaking zone is maintained at a temperature within the range of about 700 to 900° F. Preferably the temperature in the soaking zone is in the range of 800 to 900° F. and the residence time in the coil and soaking zone of the individual shale particles is of the order of 30 minutes to 2 hours. Oil shale and steam are heated in the low velocity section of heater 4 to a temperature in the range of about 800 to 1,000° F. sufficient to maintain the desired temperature in soaking zone 9. All of the heat required for distillation and stripping of the oil from the oil shale in soaking zone 9 is derived from heater 4.

The soaking zone or vessel 9 is designed so that the velocity of the steam upwardly through the particles of oil shale contained therein is sufficient to impart some motion or jiggling to the shale oil particles contained therein without the violent agitation characteristic of fluid bed reaction chambers and without substantial carryover of particles from the soaking zone. With shale particles ranging in size from a fine powder (smaller than 300 mesh) to particles ¼ inch diameter, the linear superficial velocity of steam in the soaking zone required to produce jiggling of the particles in the bed is generally within the range of 0.1 to 3.0 feet per second, usually 0.3 to 1.0 foot per second. The linear superficial velocity may be defined as the velocity which the gas, or in this case, steam, passing upwardly through the vessel would attain if there were no solids present in the vessel.

Steam and oil vapors liberated from the oil shale in soaking zone 9 are discharged through line 11 to a separator 12. Vapors from line 11 contain some solid particles entrained therein which are removed from the vapor stream by separator 12, suitably a cyclone type separator.

As illustrated the soaking zone is operated with a bed level somewhat below the top of the vessel and below outlet line 11 so that only the finest particles of the oil shale are entrained in the vapors and discharged through line 11. Alternatively, and without departing from the spirit of this invention, the soaking zone may be operated completely filled with solid particles so that all of residual solid is discharged through line 11 entrained in the vapor stream. In this latter case, all of the residue passes to separator 12 wherein it is separated from the steam and oil vapors.

The solid residue from separator 12 is discharged through line 13. The steam and oil vapors pass through line 14 to a condenser 15 where they are condensed and resulting condensate passed through line 16 to a condensate receiver 17. In the condensate receiver, the oil and water separate into immiscible layers; oil is withdrawn through line 18 and the water discharged through line 19. Water from line 19 may be recirculated to mixer 1 for use in the preparation of slurry feed to the process.

Treated shale withdrawn from the top of the bed in soaking zone 9 passes through line 21 to shale receiver 22. Water is introduced into shale receiver 22 through line 23 to displace residual oil from the spent oil shale and to assist in further handling of the residual shale under pressure. To facilitate the separation between the residual oil and water, it is preferable to introduce a light hydrocarbon suitably a hydrocarbon within the distillate boiling range, e.g. kerosene or gas oil, into contact with the spent shale in line 21. The hydrocarbon is preferably added through line 24. Line 26 permits gases dis-

placed from the spent shale in shale receiver 22 to return to the soaking zone and discharge through line 11.

The mixture of oil, water and shale from receiver 22, maintained at elevated pressure, is discharged into a separator 31 wherein the hydrocarbon is separated from the water and residual solids. As illustrated in the drawings, the residual solid suspended in liquid is discharged from receiver 22 through valve 27 into a lock hopper 28 from which the liquid-solid mixture is discharged through valve 29 to separator 31. Separator 31 may be at substantially atmospheric pressure. By alternately opening and closing valves 27 and 29, shale may be removed from the high pressure shale receiver 22 without danger of permitting steam and gases to escape. In separator 31, the oil and water form immiscible layers, the shale residue remaining in the water layer. Oil from the shale, together with added hydrocarbon, is withdrawn from separator 31 through line 32, while the water and residual shale particles are discharged through line 33.

The process of this invention is further illustrated in the following examples reporting data from runs demonstrating the effect of steam at high pressures on shale oil recovery.

Colorado oil shale having a Fischer assay of 28.3 gallons per ton was crushed to a particle size smaller than ¼ inch and treated with steam at a temperature and pressure as indicated. The results of these tests in comparison with the standard Fischer assay are shown in the following table. The standard Fischer assay method is described in U.S. Bureau of Mines, R.I. 3977 (October 1946). Gas analysis is reported in volume percent, or mol percent, on a water-free and air-free basis. Oil analysis is in weight percent.

	Fischer Assay	Example 1	Example 2
Temp., ° F.....	932	700	900
Time, hrs.....	a 1	6	0-1-6
Pressure, p.s.i.g.....	0	3,000	3,000
Percent "Organic" Carbon Removed ^b	84.2	84.5	86.2
Percent Carbon Removed.....	55.6	69.7	61.9
Percent Organic Carbon Removed.....	80.3	85.7	83.2
Gas Analysis:			
Hydrogen.....		3.8	
Methane.....		4.1	
C ₂ Hydrocarbons.....		1.3	
C ₃ +Hydrocarbons.....		2.1	
Carbon dioxide.....		81.6	
Nitrogen and Argon.....		6.6	
Hydrogen sulfide.....		0.5	
Oil Analysis:			
Carbon.....		84.0	84.4
Hydrogen.....		11.2	11.9
Nitrogen.....		1.46	1.74
Sulfur.....		0.36	0.80

a Total heating time.

b Includes nitrogen, sulfur and oxygen.

c No appreciable time effect observed after 1 hour at 900° F.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claim.

We claim:

A method for recovery of oil from oil shale which comprises forming a flowable mixture of particles of oil shale in water, introducing said mixture as a flowing stream at a velocity in the range of 1 to 10 feet per second to an elongated tubular heating zone at a pressure above about 1000 pounds per square inch gauge, heating said mixture in said heating zone as it flows therethrough to a temperature in the range of 800 to 1000° F. completely vaporizing said water to steam and forming a dispersion of shale particles in steam moving at a velocity in the range of about 4 to 50 feet per second, discharging said dispersion of heated shale particles in steam into the lowermost portion of a vertically extended soaking zone of relatively large cross-sectional area containing a bed of said heated shale particles, passing said steam up-

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wardly through said soaking zone in contact with said shale particles in said bed at a velocity sufficient to impart motion to said shale particles contained therein but insufficient to produce a fluid bed of said particles in said zone, maintaining said particles in said bed in contact with steam at a pressure within the range of 1000 to 3000 pounds per square inch gauge and a temperature within the range of 800 to 900° F. for a period of 20 minutes to 3 hours, continuously removing treated shale particles from the uppermost portion of said bed, withdrawing steam and oil vapors substantially free from shale particles from said soaking zone at a point above the uppermost portion of said bed, and recovering oil from said effluent stream of steam and oil vapors.

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