Dec. 21, 1965 W. G. SCHLINGER ET AL 3,224,954

RECOVERY OF OIL FROM OIL SHALE AND THE LIKE

Original Filed May 29, 1959 2 Sheets-Sheet 1

Fig. 1.

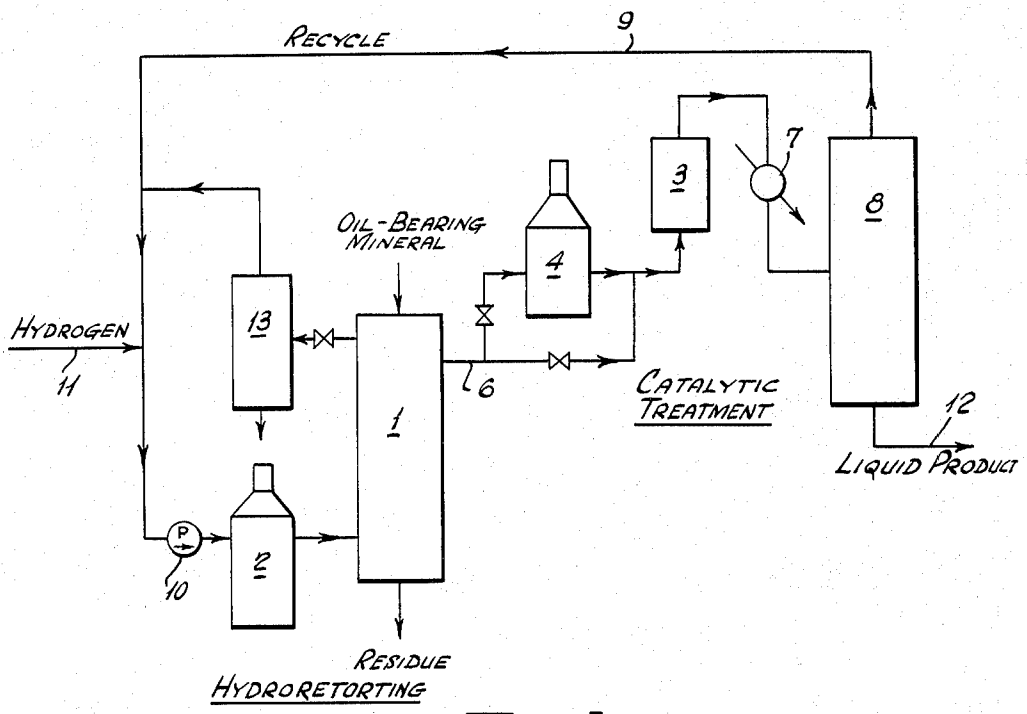
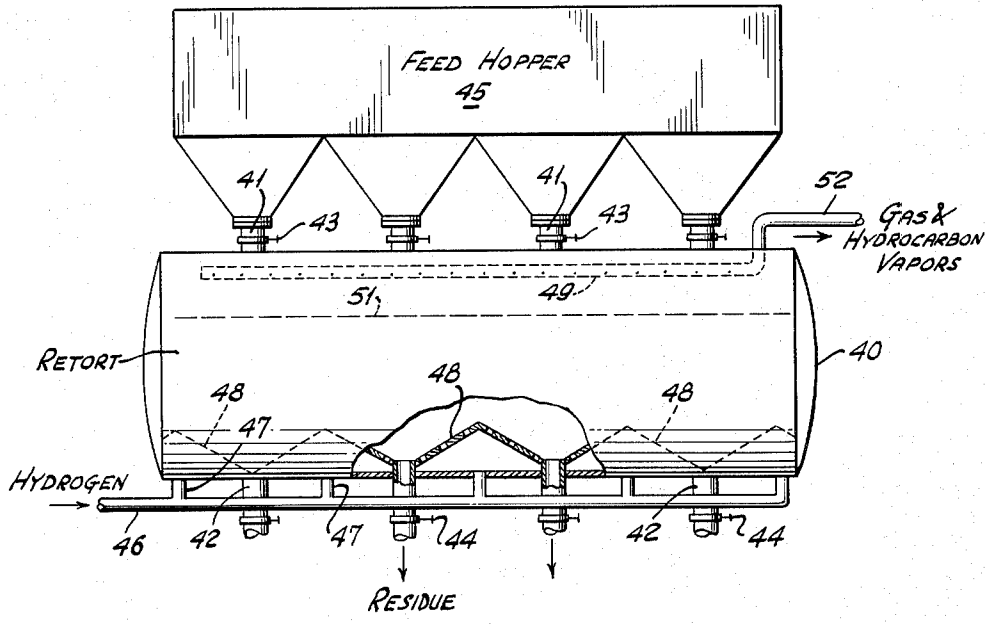


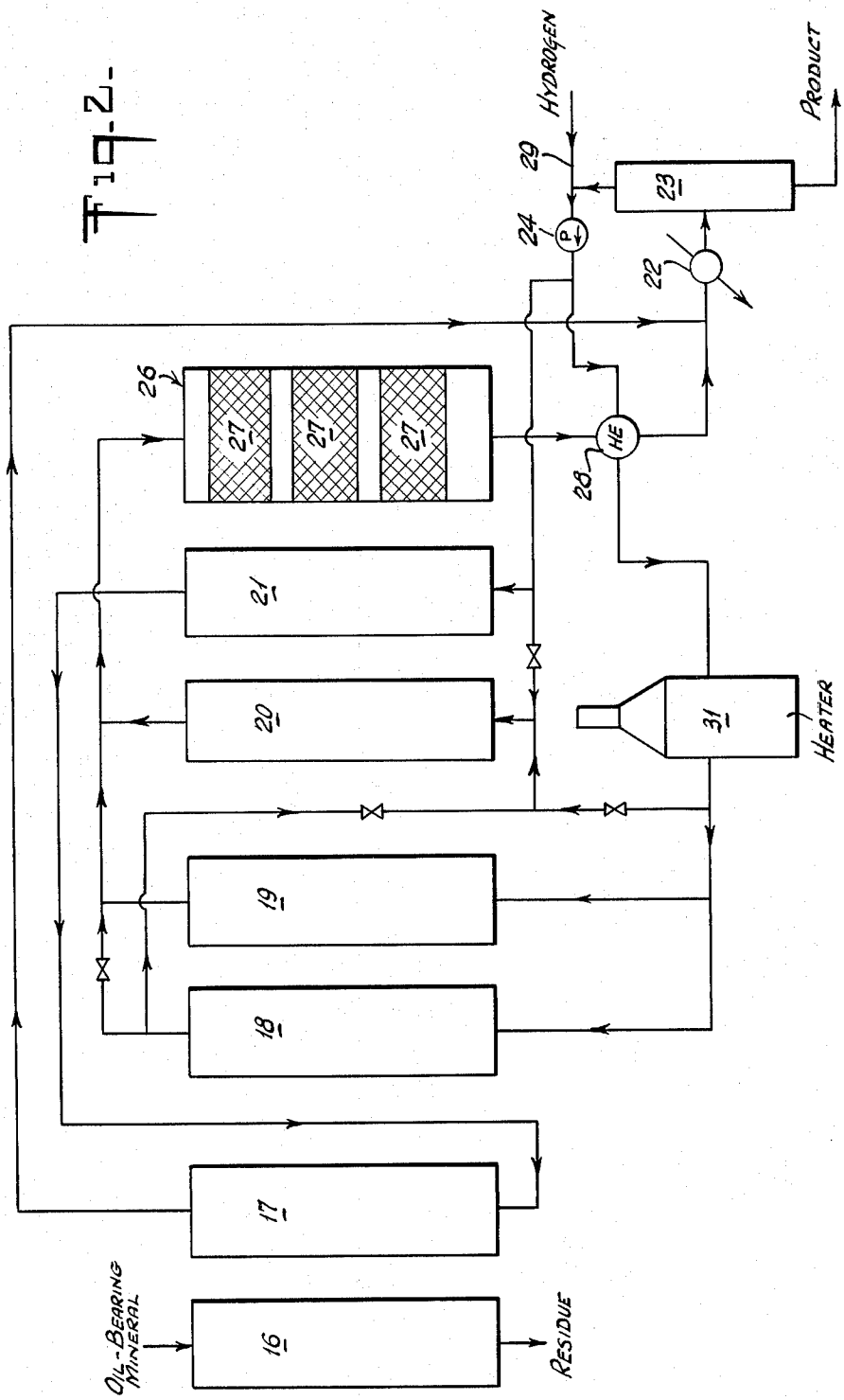
Fig. 3.



RECOVERY OF OIL FROM OIL SHALE AND THE LIKE

Original Filed May 29, 1959 2 Sheets-Sheet 2

Fig. 2.



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3,224,954

RECOVERY OF OIL FROM OIL SHALE AND THE LIKE

Warren G. Schlinger, Pasadena, Calif., and Du Bois Eastman, deceased, late of Whittier, Calif., by Security First National Bank of Los Angeles, Calif., executor, assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

Continuation of application Ser. No. 816,755, May 29, 1959. This application Feb. 3, 1964, Ser. No. 342,852
7 Claims. (Cl. 208—11)

This application is a continuation of our copending patent application, Serial Number 816,755 now abandoned, filed May 29, 1959.

The present invention relates to the production of oil from oil-bearing minerals. The process of this invention involves recovery of oil from oil-bearing minerals, for example, oil shale, oil sand, and tar sand, and simultaneous treatment of said recovered oil with hydrogen. The process results in the production of recovered oil in high yield having relatively low viscosity, low sulfur content, and good refinability, particularly in comparison with oil recovered from these same oil-bearing materials by conventional retorting or by extraction with solvents.

In carrying out the process of this invention, an oil-bearing mineral is subjected to treatment with hydrogen containing gas at a pressure in the range of 1000 to 2500 pounds per square inch gauge and at a temperature in the range of about 800 to 950° F. for a period of about 20 minutes to 5 hours, preferably not more than 2 hours. High oil yields are obtained. Oil yields of more than 100 percent, and typically 125 to 135 percent, by volume, in comparison with the standard Fischer Assay, are obtained from commercial grade oil shales. The quantity of oil remaining in the residue is too small to support combustion. In addition, the recovered oil has lower viscosity, lower specific gravity and lower carbon residue than oils recovered by conventional retorting procedures.

It is known that certain oil-bearing minerals, called oil shales, contain certain substances known as kerogens which may be converted to hydrocarbon oil by the application of heat. Other oil-bearing minerals, such as oil sands or tar sands, contain hydrocarbons which may be distilled or extracted from the mineral residue, or displaced by means of liquids, particularly at elevated temperatures. As is well known, however, oil recovered from oil shale and tar sands, is generally of poor quality as compared with most crude petroleum oils. In particular, the oil from such oil-bearing minerals generally is of low API gravity and contains relatively little material boiling in the distillate boiling range. In addition, the oil has a relatively high content of organic sulfur and organic nitrogen compounds. Yields of motor fuels from these oils by conventional petroleum refining process are comparatively poor. Extensive treating and refining operations are necessary to remove nitrogen and sulfur and to obtain maximum yields of commercially desirable products from the crude oil.

The process of this invention provides a method for direct recovery of oil of improved product quality from oil shales and tar sands by hydroretorting, a combination hydrogenation and heat treatment, under carefully controlled conditions of time, temperature and pressure. In addition, some ammonia is produced which may be recovered as a valuable by-product.

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We are aware of the fact that it has been proposed heretofore to upgrade crude oil recovered from oil shale or tar sand by treatment with hydrogen, either catalytically or non-catalytically, for the express purpose of improving product quality. We are also aware that it has been proposed heretofore to retort oil shale in the presence of hydrogen. Usually such processes are carried out at pressures below about 1000 p.s.i.g. at relatively mild temperatures, e.g. below about 1000° F., or at higher temperature and pressure. We have found that much improved results may be obtained by retorting the oil shale under relatively mild temperatures of 800 to 950° F. in the presence of hydrogen at a pressure above about 1000 p.s.i.g. and in the range of 1000 to 2500 p.s.i.g.

One major disadvantage of prior processes for treating oil-bearing minerals with hydrogen is the large volume-time relationship required in such processes. For example, the time required for treatment of a batch of oil shale by conventional processes ranges from about 6 to 24 hours, thus requiring extensive installations of retorts capable of holding a large volume of material for a period of several hours. When it is appreciated that the oil contents of commercial oil shales range from about 15 to about 40 gallons per ton, the immense investment in equipment required for a plant designed to produce, for example, 10,000 barrels of crude shale oil per day becomes immediately apparent.

As pointed out above, the time required for processing oil-bearing minerals by the process of this invention is short in comparison with other processes. In general, it is only necessary to raise the temperature of the material to 800° F. or above by heat exchange with the hot gas and hold the particles at a temperature in the range of 800 to 950° F. in the presence of the high pressure hydrogen for a period of about 20 minutes to two hours. The external heat required for the hydroretorting operation is comparatively low and is easily supplied by the hot hydrogen stream itself without the necessity for supplemental heating by heat exchange through the walls of the vessel or by means of a heated circulating solid. The relatively mild temperature prevents decomposition of the carbonate, primarily calcium carbonate, in oil shale. A large part of the heat required in conventional shale retorting processes is required for decomposition of the carbonates, liberating carbon dioxide which generally serves no useful purpose in the process, and is actually detrimental.

The extent of recovery of hydrocarbon from oil shale by the process of this invention is such that there is not sufficient fuel value in the residual shale to support combustion. This is in sharp contrast with conventional processes which burn the residual shale. Shale residue obtained in a number of test runs was largely in the form of an impalpable powder or soft lumps easily disintegrated to powder. These residues appear to be suitable as raw material for the production of Portland cement.

In accordance with a preferred embodiment of the present invention, tar sand, or oil shale lumps or pieces having a maximum size of about 1½ to 2 inches, is charged into a pressure vessel, preferably a series of such vessels. and contacted with a hydrogen-rich gas stream which is passed upwardly through said vessel under a pressure within the range of 1000 to 2500 p.s.i.g. and a temperature within the range of 800 to 950° F. It is not necessary to preheat the mineral prior to contact with hydrogen. As the hydrogen passes up through the re-

tort, a fairly sharp temperature profile is observed, above which the temperature is less than retorting temperature, probably as a result of condensation of oil vapors on the cooler material. Oil is entrained in the hydrogen-rich gas passing through the mineral and carried from the vessel where it is recovered by conventional methods, e.g. condensation and/or adsorption. Following recovery of the oil from the effluent gas, the hydrogen-rich gas is recirculated to the retorting vessel. The recirculated gas may be processed for recovery of ammonia and for removal of sulfur-containing gas, e.g. hydrogen sulfide, contained therein but this is not essential to the operation. It is not essential that the gas pass upward through the retort; horizontal flow (cross flow) or down flow may be used with suitable retorts.

Hydrogen feed rates of the order of 25,000 to 150,000 standard cubic feet (60° F. and atmospheric pressure) per ton of mineral per hour may be employed. Generally the hydrogen consumption is within the range of about 500 to about 3,000 standard cubic feet per barrel of oil produced. Hydrogen preferably is supplied in relatively pure form, e.g. 90 volume percent or higher, but may be supplied as a gas mixture having a hydrogen concentration in the range of from about 25 to about 99 percent hydrogen by volume. The hydrogen pressure in the system preferably is at least 1000 p.s.i.g. and preferably within the range of 1500 to 2000 p.s.i.g. Treating time may range from about 20 minutes to 5 hours, although generally satisfactory recovery may be obtained within 30 minutes at reaction temperatures above 800° F. The holding time in the reaction vessel may be somewhat longer, depending upon the size of the vessel and the gas feed rate.

A preferred embodiment of the present invention involves the combination of hydroretorting the mineral under specified pressure-time-temperature conditions followed by passing the total effluent from the hydroretorting reactor in vapor phase directed over a hydrogenation catalyst, for example, a cobalt-molybdenum hydrogenation catalyst. Catalysts which are effective for use in the present process are those which promote hydrogenation of hydrocarbons. In general, the oxides of the Group VI metals and of the first transition series of Group VIII of the Periodic Table of the Elements are effective catlysts. Solid catalyst, such as oxides or sulfides of molybdenum, tungsten, zirconium, chromium, vandium, iron, cobalt or nickel on a suitable carrier material, for example, silica, magnesia, alumina, bauxite, alumiunm silicate or clay, are suitable known hydrogenation catalysts. A preferred catalyst comprises 1.5 to 5 weight percent cobalt oxide and 7 to 14 weight percent molybdenum oxide on an alumina support. Preferably, the vaporous products of the hydroretorting operation are passed directly into contact with one or more beds of solid catalytic material, for example, cobalt molybdate on a suitable support.

The hydrocarbon products are suitably recovered from the fixed gases by condensation, absorption or a combination thereof. The remaining gases may be recycled to the process as desired, together with fresh feed hydrogen from a suitable source.

The fresh feed hydrogen may be produced economically by partial oxidation of a portion of the gas or oil product of the process. Partial oxidation of carbonaceous fuels to carbon monoxide has recently been developed commercially. Gaseous, liquid or solid carbonaceous fuels may be converted to carbon monoxide and hydrogen by reaction at elevated temperature and pressure with free oxygen in a compact reaction zone free from catalyst and packing. The resulting carbon monoxide may be converted to hydrogen by reaction with steam in the water gas shift reaction to produce carbon dioxide and hydrogen. Removal of carbon dioxide from the resulting gas stream yields relatively pure hydrogen. From about 3 to about 13 percent of the recovered oil is sufficient to supply all the hydrogen required for the process, the lower figure corresponding to hydrogen consumption of about 600 s.c.f. per barrel, and the higher, to about 2600 s.c.f. per barrel.

The process of this invention will be more readily understood from the following detailed description taken in conjunction with the attached drawing.

FIG. 1 illustrates diagrammatically an arrangement of apparatus suitable for carrying out the present process.

FIG. 2 illustrates schematically an arrangement of apparatus wherein a plurality of retorts are employed.

FIG. 3 illustrates diagrammatically, a retorting vessel suitable for carrying out the process of this invention on a commercial scale.

With reference to FIG. 1 of the drawing, oil shale crushed to a particle size not greater than 2 inches in diameter is charged into a retort 1 in the form of a pressure vessel, wherein it is contacted with hydrogen-rich gas at elevated pressure and temperature, hereinafter specified, for a period of time sufficient to effect substantially complete recovery of hydrocarbons from the oil shale. The shale in the retort is maintained in a settled bed condition, as distinguished from a fluid bed or a suspension or entrainment operation. The shale may be processed batchwise in a stationary bed or continuously in a downwardly moving bed or in an upwardly moving bed.

In a continuous processing operation, shale is introduced continuously or intermittently into the upper portion of retort 1 while residue is removed continuously or intermittently from its lower portion. The rate of introduction of oil shale and withdrawal of residue is regulated so that the time of contact between the hydrogen-rich gas and the oil shale is within the range of about 20 minutes to 5 hours and sufficient to effect substantially complete recovery of hydrocarbons from the shale. The incoming oil shale may be preheated to about 700° F. or higher, suitably by contact with a hot gas substantially inert with respect to the oil shale and its hydrocarbon content, for example nitrogen, steam, or flue gas although preheating of the shale is not essential.

Hydrogen-rich gas is preheated in heater 2 to a temperature in the range of about 850 to 1,000° F. and introduced into the retort. The hydrogen-rich gas passes upwardly through the particles of oil shale in the retort at a velocity below that required to expand the bed of shale, or fluidize the particles, and insufficient to entrain more than a minor amount of solid particles in the gas stream. Hydrogen-rich gas containing recovered hydrocarbons from the oil shale is passed to catalyst chamber 3 containing a hydrogenation catalyst effective for hydrogenation of hydrocarbons in vapor phase.

Heater unit 4 may be provided to maintain the temperature of the gases and vapors reaching the catalyst chamber within the desired operating range for optimum improvement of the retorted oil by the vapor phase hydrogenation reaction taking place in catalyst chamber 3. Generally, in batch operations, it is desirable to pass the gases and oil vapors through heater 4, at least during that period of the cycle in which oil vapors carried over from the retort in the gas stream in appreciable amounts are at a temperature below about 700° F. When the retort is operated in a continuous manner, heater 4 may be used or not depending upon the temperature of the gas stream containing oil vapors leaving the upper portion of the retort. Since the temperature of the effluent stream from the retort is dependent to a large extent upon the temperature of the shale at the gas outlet from chamber 1, it will be evident that by preheating the incoming oil shale the temperature of the oil at the gas outlet point may be maintained sufficiently high that heater 4 is unnecessary. In latter case, the hydrogen-rich gas and accompanying oil vapors may be passed directly to catalyst chamber 3 via line 6.

The unit 4 may take the form of a turbulent-flow hy-

drogenation unit in which the oil and hydrogen are subjected to highly turbulent flow in a conduit at a temperature in the range of 800 to 1500° F. and a pressure in the range of 1000 to 2500 pounds per square inch gauge for a reaction time of at last five seconds. Turbulent flow hydrogenation is described in my copending application, Serial No. 740,138, filed June 5, 1958. In turbulent flow hydrogenation, the flow rate of hydrogen and oil are correlated with conduit diameter and reaction temperature and pressure to give the desired turbulence level. It has been found that the ratio

$$\frac{\overline{E}_m}{\mu}$$

of average apparent viscosity of the flowing stream, $\overline{E}_m$, to the molecular or kinematic viscosity μ should be at least 25 and preferably in the range of 50 to 1000. $\overline{E}_m$ may be defined in terms which may be determined by physical measurements by the following equation:

$$\overline{E}_m = \frac{r_0}{15}\sqrt{\frac{r_0 g}{2\sigma}\cdot\frac{dp}{dx}}$$

Wherein dp/dx is the pressure drop in pounds per square foot per foot of conduit length; g is the acceleration of gravity in feet per second; r_0 is the radius of the conduit in feet; and σ is the specific weight of the flowing fluid in pounds per cubic foot.

The gases and vapors from the catalyst chamber **3** are passed to cooler **7** for condensation of the readily liquefiable hydrocarbon from the gas stream. Gas and liquid are separated from one another in separator **8**. The gas is recycled via line **9** to compressor **10** where it is returned to heater **2** and to retort **1**. Hydrogen required for the process is supplied from a suitable source through line **11**. Liquid is withdrawn through line **12**.

If desired, catalyst chamber **3** and cooler **7** may be bypassed. Thus in batch processing oil shale, effluent gases from the retort may be passed through line **6** directly to separator **8** and recycled without cooling during a portion of the cycle. If desired, gases from retort **1** may be drawn through a suitable guard separator **13**, to effect removal of solid particles and entrained liquid, directly to recycle line **9**. This latter procedure may be desirable in batchwise processing of the oil shale during the preheating period, i.e. during the period in which the charge of oil shale in the retort is being heated up to a temperature of about 600° F.

In the continuous processing of oil shale, as outlined hereinabove, it may also sometimes be desirable to withdraw a portion of the gaseous effluent from retort **1** from a point above the point of product withdrawal, e.g. via separator **13** for direct recycle. By this means the temperature of the effluent stream withdrawn through line **6** may be maintained at the temperature level desirable in catalyst chamber **3** without the necessity for preheating the incoming oil shale or alternatively the use of heater **4**. When gases are withdrawn to separator **13**, readily condensable hydrocarbons contained in the gas stream are condensed on the relatively cool oil shale, serving to preheat the shale. Hydrocarbons so condensed are revaporized at a lower point in the retort and recovered through product line **6**.

In batch processing operations a series of retorts may be used with suitable switching arrangements to permit the retorting vessels to be connected with various inlet and outlet lines in sequence to preheat the shale, retort the shale, and cool the residue.

FIG. 2 of the drawing illustrates diagrammatically an arrangement of apparatus for carrying out a batchwise hydroretorting of oil shale in a series of retorts in accordance with the present invention. As illustrated, pressure vessels **16**, **17**, **18**, **19**, **20** and **21** are arranged for treatment in sequence in the order illustrated. The piping is arranged so that the various pressure vessels may be connected in a cyclic manner to provide the flow pattern illustrated in the figure. It is to be understood that neither of the specific arrangements illustrated nor the specific number of vessels is to be taken as limiting our invention.

In operation, retort **16** is charged or recharged, while the remaining retorts are connected for gas circulation. Residue from a previous retorting opeation is discharged from retort **16** and fresh oil shale in the form of particle no larger than 2 inches in average diameter is charged to the retort. Numeral **17** designates a pressure vessel which has been charged with fresh shale and is undergoing preheating. Preheating of the fresh shale may be accomplished in a number of ways. In the specific embodiment illustrated in FIG. 2, the preheating is accomplished by means of circulating hydrogen-rich gas preheated by contact with hot residual shale resulting from the hydroretorting operation. In this particular example, hydrogen-rich gas is passed through spent or residual shale in retort **21** where it is heated to a temperature, of the order of 500° F. for example, and then passed over the fresh shale in retort **17** to preheat the fresh shale. Gas discharged from retort **17** is passed to cooler **22**, then through separator **23** to compressor **24** for recirculation.

Following preheat of the oil shale (as illustrated, in retort **17**), the shale is preheated further and retorting started by passing hot hydrogen-rich gas, for example, at a temperature of the order of 900° F., over the shale particles. Effluent gas from retort **18** may be processed directly for recovery of oil or passed through a second retort **20** from which a considerable portion of the hydrocarbons have been retorted, depending upon the temperature and hydrocarbon content of the effluent. The retorting is completed in retort **20** to which heated gas or cold recycle gas may be supplied as required. In retort **20**, retorting is completed and the residual shale is cooled moderately, e.g. to a temperature of the order of 500 to 600° F. Effluent gas containing hydrocarbon vapors from retort **20** passed to catalyst reactor **26** in which the hydrocarbons recovered from the oil shale are subjected to catalytic treatment with hydrogen at reactor pressure and a temperature above 800° F. Some vapor phase hydrogenation of the hydrocarbons takes place in reactor **26** in which the catalyst preferably is disposed in a series of beds **27**.

Hydrogen-rich gas and hydrocarbon leaving the catalyst chamber **26** pass through heat exchanger **28**, wherein they are cooled by heat exchange with cold hydrogen-rich gas, and through cooler **22** for further cooling sufficient to effect condensation of readily condensible hydrocarbons, and are then passed to separator **23** maintained at substantially retort pressure. In separator **23**, condensed liquid is separated from residual gases comprising hydrogen and gaseous hydrocarbons recovered from the oil shale. The gases pass to compressor **24** and are recirculated to the retorts.

Hydrogen from a suitable source, preferably in relatively pure form, is introduced to the system as required through line **29**. From compressor **24**, a part of the hydrogen-rich gas is passed to retort **21** as previously mentioned. A further portion of the hydrogen-rich gas passes through heat exchanger **28** where it is heated by indirect heat exchange with the product from catalytic reactor **26**, for example, to a temperature of the order of 600 to 700° F. and then passed through heater **31** wherein it is heated to a temperature in the range of 800 to 950° F. A part of the gas from heater **31** is passed to retort **18** in which recovery of hydrocarbons from the shale is initiated and further portion of the heated gas is passed to retort **19** in which recovery of hydrocarbons from previously heated and partially retorted shale is continued. Gaseous effluent from retort **19** containing hydrocarbon vapors is passed to catalytic reactor **26**. The mixture of shale oil vapors and hydrogen from the retorts may be subjected to turbulent flow hydrogenation (not

illustrated) as described hereinabove in connection with FIG. 1.

In the sequence illustrated, a period of time for each operation in the range of 15 to 45 minutes is usually adequate. It will be appreciated that the time requirements will depend to some extent on the particle sizes of the oil shale and the depth of the shale bed in each of the retorts. It will be evident that the larger particle sizes require longer heating times than do the smaller particles. The minimum time requirement, therefore, is largely dependent upon the time required to process the largest shale particles in the charge to the retorts. As previously indicated, a period of two hours above 800° F. is generally adequate for pieces up to 2 inches in diameter. During the retorting periods proper, i.e. the period following the preheat, during which hydrocarbons are vaporized from the shale particles, the bed depth has considerable effect upon the time required for retorting a given amount of shale. The results of a number of trial runs, data for which are reported in the following examples, indicate that it is possible to recover the hydrocarbon from oil shale substantially completely in about 20 minutes at a temperature in the range of 800 to 950° F. with hydrogen at a pressure in the range of 1,000 to 2,500 p.s.i.g. It will be appreciated however that in a bed several feet in depth, the zone of actual retorting extends over only a portion of the entire shale bed. For example, in retort **19** of FIG. 2, shale in the lowermost portion of the vessel is completely retorted. As the hot gas from the heater ascends through the portion of the shale bed in which retorting is complete, the temperature of the hot gases remains essentially constant and the residual shale particles are substantially inert with respect to the processing gas stream. At a somewhat higher level in the bed, hydrocarbons liberated from the oil shale are undergoing vaporization from the shale and simultaneous reaction with hydrogen contained in the processing gas stream. The net effect of these reactions is an endothermic one. Consequently, the temperature of the gas stream beings to fall as it ascends through that portion of the bed in which hydrocarbon vapors are liberated from the shale. In this connection it should be noted that the liquid product from the oil shale has an atmospheric boiling range of from about 140 to about 725° F. (Example 1). As the processing gas containing these hydrocarbon vapors ascends to a still higher level in the shale bed, a part of the oil vapor is condensed by contact with the cooler shale in the upper portion of the retort. The high temperature retorting zone moves slowly up through the bed of oil shale. It will be apparent that the depth of the bed has an appreciable effect on the length of time required for retorting. The superficial linear gas velocity in the retorts generally is in the range of 0.005 to 0.5 feet per second, preferably 0.01 to 0.25 feet per second. Low gas velocities prevent entrainment of fine particles of residue in the processing gas stream. At the same time, the temperature of the processing gas stream is limited to a maximum of about 950° F. Consequently, relatively shallow large beds of shale are preferred for retorting. A preferred retort is illustrated in FIG. 3.

With reference to FIG. 3, the numeral **40** designates a pressure vessel shell adapted to withstand operating pressure and provided with a liner of refractory insulating material. The preferred form of retort is a horizontal cylinder as illustrated with a plurality of loading nozzles **41** along its topmost surface and a plurality of ash discharge nozzles **42** along its lowermost surface. Nozzles **41** and **42** are provided with suitable valves **43** and **44** to permit the flow of crushed shale into the retort and the withdrawal of residue from the retort and to effectively seal the nozzles against pressure during the retorting operation. Crushed oil shale of a suitable size for retorting is applied to nozzle **41** from feed hopper **45**. Hydrogen-rich gas is introduced to the retort through line **46** and nozzles **47** and distributed throughout the shale bed by perforated plates **48**. Processing gas and hydrocarbon vapors are collected by a perforated header **49** in the upper portion of the retort above the normal level, indicated by dashed line **51**, of the oil shale during the retorting operations. Effluent gas and hydrocarbon vapors from the retorts are discharged through line **52** for further processing, for example as illustrated in FIG. 2.

The process of this invention is further illustrated in the following examples reporting data from a number of runs made in accordance with the above described process.

EXAMPLE 1

Colorado oil shale having a Fischer Assay of about 43.5 gallons per ton was crushed to 1½ inch maximum size and treated with hydrogen in a vertical reactor 6 inches in diameter by 12 feet long. Runs A and B, reported in Table 1 below, represent composite data from several batches of shale. The reactor was charged with 100 to 150 pounds shale per batch, pressured with hydrogen, and circulation established. The gas at a rate of about 7,000 s.c.f.h., was passed through a preheater, up through the reactor, through a cooler and a condensate separator and back to the heater. Makeup hydrogen was added as required to maintain pressure. The temperature of the hydrogen was then raised to 800 to 900° F. and circulation continued 3 to 4 hours. When the temperature of the gas stream at the top of the reactor reached 800° F., circulation of the gas stream was continued for two hours. Inspection of the residual shale from the reactor showed no apparent difference from top of the reactor to the hydrogen inlet, evidencing that shale treated for the minimum period of time (at the top of the reactor) was as effectively extracted as that treated for the entire period.

Operating conditions and results are shown in Table 1, in comparison with the standard Fischer Assay described in U.S. Bureau of Mines, R.I. 3977 (October 1946). Each run represents several batches of shale processed in the reactor. The characterization factor, K.V., an index of the type hydrocarbon recovered, is described by Watson, Nelson, and Murphy, Ind. Eng. Chem. 25,880 (1933); 27, 1460 (1935).

These data show the substantial increase in oil yields over the Fischer Assay and improvement in API Gravity, pour point and yield of distillate, as compared with oil from the Fischer Assay.

EXAMPLE 2

A series of runs were made with the same oil shale and retorting apparatus as was used for Runs A and B of Example 1. Substantially pure hydrogen was used as the retorting gas in each case. The total effluent from the shale was passed without condensation or separation of vapors, into direct contact with a hydrogenation catalyst in the form of ⅛ inch pellets comprising 3.1 weight percent cobalt oxide and 8.5 weight percent molybdenum oxide on alumina. In Run C, 15 pounds of catalyst was placed in the reactor, directly above the shale bed. The catalyst bed was approximately 15 inches in depth. In Runs D and E the actalyst was contained in a separate vessel, four feet long and three inches inside diameter filled with the catalyst (a total of about 12 pounds). The total effluent from the hydroretorting reactor was passed directly to the catalyst chamber without heating or cooling. In Run F, the total effluent from the retort was heated before contacting the catalyst in the catalyst vessel. Runs E and F illustrate the effect of the temperature of the catalytic treatment of the hydrocarbon vapors on product quality. In each case, the bulk of the oil vapors from each batch of shale passed over the catalyst in a relatively short period of time (estimated at about 15 minutes) so that the space velocity of oil vapors over the catalyst was relatively high. Operating conditions and results are shown in Table 2.

Table 1

	Fischer Assay		Run A	Run B
Retorting Gas	None	None	H_2	H_2
Retorting Period, Hrs./Batch	(1)	(2)	4	3
Operating Conditions:				
Pressure, p.s.i.g.			1,802	1,803
Temperature, ° F.				
Preheater Outlet			875	915
Overhead			642	662
Gas Flow, s.c.f.h.			7,000	7,000
Yields, Product, Lbs.:				
Ash			570	329
Oil			133.1	86.0
Water			16.0	4.7
Gas			3.7	3.3
Loss			16.7	16.0
Total Shale Charged, Lbs.			739.5	439.0
Recovery, Wt. Percent			97.7	96.4
Oil:				
Gals./Ton		43.29	48.17	52.85
Percent Fischer Assay		100.0	[3] 111	[3] 122
Water:				
Gals./Ton		3.50	5.19	2.55
Percent Fischer Assay		100.0	[3] 148	[3] 73
Hydrogen Consumption, s.c.f./bbl. (Est.)			600–800	600–800
Product Oil:				
Gravity, °API	25.2	24.5	25.9	27.1
Viscosity, SSU at 122° F.	58.0	54.2	80.0	59.4
Carbon Residue, Wt. Percent	2.48	2.23	1.10	1.05
Sulfur, Wt. Percent	0.88	0.92	0.63	0.88
Nitrogen, Wt. Percent	1.65	1.94	1.42	1.26
Pour Point, ° F.	75	80	90	85
Distillation, ° F.—				
IBP	170		153	140
10%	370		397	358
50%	650		676	664
90%	700 (80%)		724	715
EP				
K.V.	11.6	11.51	11.78	11.77
Recovery, Percent	80		92.5	93.0
Residue			7.5	7.0
Ash, Carbon Content, Wt. Percent	~5	4–5	2.00	0.83

[1] Composite from Fischer Assays.
[2] Typical Fischer Assay—10 Samples.
[3] Based on Typical Fischer Assay (2).

Table 2

	Run C	Run D	Run E	Run F
Retorting Gas	H_2	H_2	H_2	H_2
Retorting Period, Hr.	3	~5	4	3
Catalyst	Cobalt Molybdate	Cobalt Molybdate	Cobalt Molybdate	Cobalt Molybdate
Operating Conditions:				
Pressure, p.s.i.g.	1,800	~2,000	1,900	2,000
Temperature, °F.—				
Preheater Outlet, Avg.	900	920	910	930
Overhead, Avg.	670	660	720	730
Catalyst Chamber Inlet			685	825
Gas Flow, s.c.f.h., Avg.	7,000		6,450	6,000
Yields: Product, Lbs.—				
Ash	591.8	1,628.5	305.5	288.0
Oil	153.2	407.1	81.3	71.6
Water	25.3	82.8	9.2	16.9
Gas	11.3	35.3	4.2	7.2
Loss	6.4	11.8	10.8	22.8
Total Shale Charged, Lbs.	788.0	2,165.5	411.0	406.5
Recovery, Wt. Percent	92.2	99.5	97.5	94.4
Oil:				
Gals./Ton	54.11	52.94		
Percent Fischer Assay	[1] 125	[2] 134	[3] 128	[3] 120
Water:				
Gals./Ton	7.72	9.18	7.53	
Percent Fischer Assay	[1] 220	[2] 223	[3] 128	[3] 239
Hydrogen Consumption, s.c.f./bbl. (Est.)	1,000–1,400	2,500	2,700	4,000
Product Oil:				
Gravity, ° API	32.3	34.5	32.2	39.4
Viscosity, SSU at 122° F.	40.9	41.2	47.3	33.7
Carbon Residue, Wt. Percent	0.37	0.03	Trace	0.06
Sulfur, Wt. Percent	0.43	0.12	0.13	0.06
Nitrogen, Wt. Percent	0.60	0.77	1.20	0.49
Pour, ° F.	80	80	90	45
Distillation, ° F.:				
IBP	152	166	144	126
10%	316	359	358	256
50%	704	710 (80%)	728 (70%)	640 (80%)
EP				
K.V.	11.8	11.9	12.0	11.7
Recovery, Percent	91.0			94.0
Residue	9.0			6.0
Ash, Carbon Content, Wt. Percent	0.95	0.86	1.07	0.57

[1] Based on Typical Fischer Assay (2), Example 1.
[2] Based on Fischer Assay avg. of 7 runs.
[3] Based on Fischer Assay of 42.86 and 4.19 lbs. oil and H_2O, respectively.

In all of the runs in this example, preheated hydrogen is passed up through the retorting vessel. Circulation was continued for a period of two hours after the temperature at the top of the shale bed reached 800° F. From one half to one hour was required to bring this temperature up to 800° F. At the conclusion of the two-hour period, the fire in the preheater was cut out and the cool hydrogen circulated through the reactor until the temperature of the effluent gases from the reactor had dropped to less than 150° F.

EXAMPLE 3

Runs were made with the same oil shale as in the foregoing examples using mixtures of hydrogen and carbon monoxide, and hydrogen and carbon dioxide as stripping gases. In each of the following runs, the procedure was the same as in Run F of Example 2. In Run G, the composition of gas initially supplied to the reactor and added as make up gas in the processing of each batch contained 69 mole percent hydrogen and 30 mole percent carbon dioxide. In Run H, the gas supplied to the reactor contained 57 mole percent hydrogen and 42 mole percent carbon monoxide. Operating conditions and results are shown in Table 3.

Table 3

	Run G	Run H
Retorting Gas	H_2+CO_2	H_2+CO
Retorting Period, Hrs	3 to 4	~2
Catalyst	Cobalt Molybdate	Cobalt Molybdate
Operating Conditions:		
Pressure, p.s.i.g	1,935	1,930
Temperature, ° F.—		
Preheater Outlet	926	930
Overhead		
Catalyst Chamber Inlet	699	740
Gas Flow, s.c.f.h	>5,000	>5,000
Yields, Product, Lbs.:		
Ash	197.5	411
Oil	53.5	96.6
Water	44.5	39.4
Gas	5.6	15.8
Total Shale Charged, Lbs		
Oil:		
Gals./Ton	55.39	48.69
Percent Fischer Assay	[1] 129	[1] 114
Water:		
Gals./Ton	40.58	17.60
Percent Fischer Assay	[1] 968	[1] 420
Hydrogen Consumption, s.c.f./bbl. (est.)	6,550	6,500
Product Oil:		
Gravity, ° API	28.8	29.6
Viscosity, SSU at 122° F	49.7	45.2
Carbon Residue, Wt. Percent	0.38	0.65
Sulfur, Wt. Percent	0.32	0.46
Nitrogen, Wt. Percent	1.46	1.44
Pour Point, ° F	85	85
Distillation, ° F.:		
IBP	170	168
10%	384	360
50%	675	628
90%	719 (70%)	700 (80%)
EP		
K.V.	11.8	11.7
Recovery, Percent	71.5	65.5
Ash, Carbon Content—Wt. Percent	1.01	1.38

[1] Based on Fischer Assay of 42.86 and 4.19 Lbs. Oil and H_2O, respectively.

It will be noted from the above data that there is a considerable increase in the relative quantity of gas and water produced. This indicates reaction between the carbon oxides and hydrogen. Hydrogen consumption in these runs was exceptionally high as compared with Runs C, D and E, of Example 2. The increase in water yield is particularly noticeable in the case of the carbon dioxide-hydrogen mixture. Water production is generally undesirable since it represents a direct loss of hydrogen to no useful product. The quality of the oil from Runs G and H was not as high as that from Runs C, D and E. Run H however, shows a considerable increase in gas yield as compared with Runs C, D and E. Where gas is a desired product, e.g. for heating gas, operation as illustrated by Run H may be desirable.

While the process of this invention has been described and illustrated with specific reference to the treatment of oil shale, it is to be understood that it is equally effective for the processing of tar sands or oil sands.

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 claims.

We claim:

1. A continuous process for the production of hydrocarbon oils from oil shale by retorting with hydrogen which comprises maintaining a downwardly moving settled bed of oil shale particles in a vertically extended retorting zone, introducing hydrogen into the lower portion of said zone and passing hydrogen at a temperature within the range of from about 800 to about 950° F. at a rate of from about 25,000 to about 150,000 standard cubic feet per ton of shale per hour at a pressure within the range of about 1,000 to about 2,500 pounds per square inch gauge upwardly through said bed effecting retorting of hydrocarbons from said shale, withdrawing said hydrocarbons solely in vapor phase in admixture with unreacted hydrogen from said zone at an intermediate point below the top of said bed and passing resulting mixture at a temperature above about 700° F. directly from said retorting zone into contact with a bed of solid catalyst effective for promoting vapor phase hydrogenation of said hydrocarbons, recovering resulting hydrocarbons from the vaporous effluent of said bed of catalyst, recyling unconverted hydrogen to said process, withdrawing residual oil shale substantially free from carbon from the lower end of said retorting zone, introducing cold raw shale in particle form into the upper end of said zone as said residual shale is withdrawn from said zone to maintain said bed of shale particles therein, withdrawing hydrogen-rich gas substantially free from readily condensible hydrocarbon vapors from the upper portion of said zone above the point of withdrawal of said hydrocarbons in vapor phase, and recycling said hydrogen-rich gas to the lower portion of said zone.

2. A process for the production of hydrocarbon oils from the oil shale by retorting with hydrogen in a settled bed of oil shale particles in a vertically extended retorting zone, which comprises introducing hydrogen into the lower portion of said zone and passing said hydrogen at a temperature in the range of 800° F. to 950° F. and at a pressure within the range of about 1,000 to about 2,500 pounds per square inch gauge upwardly through said bed at a rate of from about 25,000 to about 150,000 standard cubic feet per ton of oil shale per hour for a period of time within the range of 20 minutes to 5 hours effecting retorting of hydrocarbons from said shale as hydrocarbon vapors mixed with said hydrogen, and passing said mixture solely in vapor phase at a temperature above 700° F. over a bed of solid catalyst effective for promoting vapor phase hydrogenation of said hydrocarbons, recovering resulting hydrocarbons from the vaporous effluent of said catalyst, recycling unconverted hydrogen to said process, and discharging residual oil shale substantially free from carbon from said retorting zone.

3. A process according to claim 2 wherein said catalyst is selected from the group consisting of the oxides and sulfides of molybdenum, tungsten, zirconium, chromium, vanadium, iron, cobalt and nickel.

4. A process according to claim 2 wherein said catalyst is cobalt molybdate.

5. A process according to claim 2 wherein said catalyst comprises 1.5 to 5 weight percent cobalt oxide and 7 to 14 weight percent molybdenum oxide on alumina.

6. A process according to claim 2 wherein said catalyst comprises molybdenum sulfide.

7. A process according to claim 1 wherein said cata-

lyst consists essentially of oxides of cobalt and molybdenum.

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PAUL M. COUGHLAN, *Primary Examiner.*

ALPHONSO D. SULLIVAN, *Examiner.*