

# United States Patent

[11] 3,617,471

[72] Inventors **Warren G. Schlinger**  
**Pasadena;**  
**Dale R. Jesse, Hacienda Heights; Joseph P.**  
**Tassoney, Whittier, all of Calif.**

[21] Appl. No. **787,207**

[22] Filed **Dec. 26, 1968**

[45] Patented **Nov. 2, 1971**

[73] Assignee **Texaco Inc.**  
**New York, N.Y.**

2,761,824	9/1956	Eastman et al. ....	201/20
2,989,442	6/1961	Dorsey .....	201/37
3,044,948	7/1962	Eastman et al. ....	208/11
3,074,877	1/1963	Friedman .....	201/32
3,117,072	1/1964	Eastman et al. ....	208/11
3,480,082	11/1969	Gilliland.....	166/266

*Primary Examiner*—Curtis R. Davis  
*Attorneys*—K. E. Kavanagh and Thomas H. Whaley

[54] **HYDROTORTING OF SHALE TO PRODUCE  
 SHALE OIL**  
**8 Claims, No Drawings**

[52] U.S. Cl..... **208/11,**  
 166/266, 201/20, 201/27, 201/29

[51] Int. Cl..... **C10b 53/06**

[50] Field of Search..... **208/11, 8,**  
 10; 201/20, 29, 31, 32, 33, 36, 37, 38; 166/266

[56] **References Cited**  
**UNITED STATES PATENTS**  
 2,694,035 11/1954 Smith et al..... 201/20

**ABSTRACT:** Hydrogen-rich gas, e.g., synthesis gas, and H<sub>2</sub>O are injected into oil shale at a comparatively moderate pressure in the range of about 300 to 1,000 p.s.i.g. and at a temperature in the range of about 850° to 950° F., for producing high-quality shale oil in yields that exceed the Fischer Assay. The addition of H<sub>2</sub>O reduces the hydrogen consumption and heat load required for a given yield of shale oil. The process can be self-sustaining in that the shale oil and water produced may be used for making the synthesis gas used in the hydrogenation and denitrification of the shale oil.

## HYDROTORTING OF SHALE TO PRODUCE SHALE OIL

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention relates to the recovery of oil from oil shale. More specifically it relates to the hydrotorting of raw oil shale with synthesis gas and H<sub>2</sub>O.

## 2. Description of the Prior Art

In most contemporary procedures, crude shale oil is obtained by pyrolysis of the solid insoluble organic part of the raw shale (kerogen). Thus, raw shale is subjected to destructive distillation in a retort at a temperature of about 850° to 950° F. The chemical decomposition of the kerogen which takes place by the action of heat alone yields crude shale oil vapors, together with water, gas, and spent shale containing a carbonaceous residue and mineral matter. The application of hydrogenation to the retorting of oil shale for upgrading shale oil has been previously proposed, for example U.S. Pat. No. 3,117,072 issued to DuBois Eastman and Warren G. Schlinger.

Disadvantages of some proposed retorting schemes include low heat-transfer rates and correspondingly low shale throughput, limited vessel size, poor thermal control and low thermal efficiency, difficult material handling problems, high operating and equipment costs, low yields in comparison with the Fischer Assay, and poor quality of the shale oil, e.g., high nitrogen and sulfur content. For a description of the standard Fischer Assay refer to "Method of Assaying Oil Shale by a Modified Fischer Retort" by K. E. Stanfield and I. C. Frost, R.I. 4477, June 1949, U.S. Dept. of the Interior. Furthermore, hydrogen consumption is generally excessive, pressures are high (1,000 to 20,000 p.s.i.g.), temperatures range up to 1,500° F., relatively long retort periods are necessary (6 to 20 hours), spent shale retains some carbonaceous residue and in comparison with crude petroleum, the shale oil recovered is a very low grade.

In contrast with the prior art, by our hydrotorting process, a hydrogenated shale oil is produced at a comparatively moderate pressure. Furthermore, sulfur and those levels of the shale oil may be reduced to those usually found in crude petroleum, there is minimum degradation in the distillate boiling range, and yields are greater. Such shale oil would then be amenable to further processing by conventional crude refinery technique with high yields for a minimum of treating. Further the spent shale is comparatively free from any organic or carbonaceous residue from the kerogen. By our process, retorting and hydrogenation may be combined in one operation, obviating the delayed coking step or other preliminary treatment commonly used in other processes during refining, and thereby saving costs.

## SUMMARY

We have discovered a process for preparing maximum yields of shale oil of reduced nitrogen and sulfur content from raw shale under relatively reduced pressure. More particularly, the invention relates to the discovery that raw shale can be readily converted to shale oil and relatively kerogen-free dry-powdered shale by treating raw oil shale with a hydrogen rich gas, e.g., synthesis gas, providing about 5,000 to 20,000 s.c.f. of hydrogen per ton of raw shale and H<sub>2</sub>O (about 0.01 to 0.06 tons of H<sub>2</sub>O per ton of raw shale) under a pressure in the range of about 300 to 1,000 p.s.i.g., and preferably at a pressure in the range of about 400 to 600 p.s.i.g., and at a temperature in the range of about 850° to 950° F. Hydrogenation takes place without the addition of a supplementary catalyst. Shale oil is produced having a substantially reduced nitrogen and sulfur content and with yields of greater than 110 percent of the Fischer Assay. The addition of H<sub>2</sub>O reduces the hydrogen consumption and heat load required for a given yield of shale oil. As used in this specification and the ensuing claims, the term "hydrogen-rich gas" is intended to mean a gas containing at least 45 volume percent H<sub>2</sub>, (dry basis).

Substantial savings in the cost of hydrogen for the process are obtained in a specific embodiment by integrating into the system a synthesis gas generator which produces a mixed stream of hot hydrogen and carbon monoxide at a temperature in the range of 1,800°-3,000° F. by the partial oxidation of product shale oil. Thus the unshifted effluent gas stream from the synthesis gas generator is introduced into the reaction zone to supply the necessary hydrogen and heat for hydrotorting the raw oil shale. Further, by the water-gas shift reaction in the reaction zone with spent shale serving as a shift catalyst, the CO in the synthesis gas is simultaneously converted into additional H<sub>2</sub>, liberating heat. Also, portions of the heavy shale oil and the steam produced by the process of our invention may be used as feedstock to the synthesis gas generator. Thus little or no water or fuel from an external source is required and in this respect the process can be self-sustaining.

The principal object of this invention is to recover from raw oil shale increased yields of hydrogenated shale oil of improved product quality.

Another object of this invention is to simultaneously retort raw oil shale and hydrogenate the kerogen and shale oil to produce increased yields of a shale oil with a substantially reduced nitrogen and sulfur content.

A further object of this invention is to provide a process for producing shale oil, water, and spent shale containing essentially no carbonaceous matter from raw oil shale by means of a process having a high thermal efficiency, high oil yield, and a high retorting rate.

A still further object of this invention is to pyrolyze and hydrogenate raw oil shale to produce shale oil and steam using low cost synthesis gas that provides substantially all of the necessary heat, pressure, and hydrogen required in the process; and which process is self-sustaining in that a portion of the shale oil and steam produced may be recycled to the partial oxidation gas generator to produce more of said synthesis gas.

## DESCRIPTION OF THE INVENTION

The present invention involves an improved hydrotorting process for recovering high quality shale oil from raw oil shale at low-pressure and at greater yields than the Fischer Assay. A hydrogen-rich gas containing at least 45 volume percent of H<sub>2</sub> at a pressure in the range of 300 to 1,000 p.s.i.g. and at a temperature in the range of about 850° to 950° F. and H<sub>2</sub>O are injected into raw oil shale in a reaction zone. The quantity of hydrogen in the hydrogen-rich gas which is supplied to the oil shale reaction zone is in the amount of 5,000 to 20,000 s.c.f. of hydrogen per ton of oil shale processed. The water is mixed with the hydrogen or separately injected into the reaction zone in the amount of about 0.01 to 0.6 tons of water per ton of oil shale treated. The oil shale may be dry or slurried with a liquid hydrocarbon fuel oil e.g., shale oil, crude oil. The reaction zone may constitute a fixed or fluidized bed of raw oil shale particles, as described for example in U.S. Pat. No. 3,224,954 issued to Warren G. Schlinger and DuBois Eastman; a tubular retort, as more fully described in the aforementioned U.S. Pat. No. 3,117,072; or a fractured subterranean oil shale stratum as described for example in U.S. Pat. No. 3,084,919 issued to William L. Slater, thereby effecting pyrolysis and hydrogenation in situ. Further, the oil shale reaction zone may be externally heated; or substantially all or part of the heat required for retorting may be supplied by the hydrogen-rich gas and H<sub>2</sub>O.

Injecting water into the oil shale reaction zone was found to have several new, and unobvious results. It was unexpectedly found that when water is added to the oil shale reaction zone, the endothermic decomposition of inorganic carbonates in the shale and the production of CO<sub>2</sub> is repressed. This saves hydrogen, as CO<sub>2</sub> would ordinarily react with H<sub>2</sub> to form H<sub>2</sub>O and CO. Thus by water injection, there is a savings of energy in the form of heat ordinarily consumed by the decomposition

of inorganic carbonates; and further, there is a considerable reduction of hydrogen consumption in the reaction zone. Further, the mass velocity through the oil shale reaction zone, and the heat transfer coefficient of the mixture in the reaction zone are all increased by the addition of H<sub>2</sub>O. Thus, rapid heat transfer is effected which allows conversion of the kerogen to crude shale oil in the oil shale reaction zone at a residence time in the range of about one-fourth minute to 2 hours. Furthermore, vaporization and expansion of water in the oil shale reaction zone tends to disintegrate the shale particles and facilitate the atomization of the shale oil. Also, coking of the shale may be minimized or eliminated at a substantially reduced hydrogen consumption. Other unobvious advantages for injecting the water underpressure into the oil shale during hydrotorting are (1) greater concentrations of shale may be incorporated in pumpable oil-shale slurries, and (2) clogging of the retort tubing is prevented. For example, a portion of the water produced by the process, at a temperature in the range of about 100° to 500° F. may be recycled to and injected into the reaction zone in an amount of about 0.01 to 0.6 ton of water per ton of raw oil shale, and preferably about 0.1 to 0.4 ton of water per ton of raw oil shale. Both the hydrogen-rich gas and the recycle water are supplied to the oil shale reaction zone at a pressure of about 100 to 200 p.s.i.g. greater than the system line pressure. Further, a portion of the water produced by the process may be used to cool the hot effluent gas from the synthesis gas generator from a temperature of about 2,200° F. to about 1,000° F. by recycling the water to the quench zone and quenching the effluent synthesis gas in the manner shown in U.S. Pat. No. 3,232,728 issued to Blake Reynolds. One advantage of this embodiment of the invention is that all of the water required in the retorting step may be picked up by the synthesis gas vaporizing the quench water during cooling.

By the addition of hot hydrogen-rich gas to the raw shale followed by the hydrogenation of the pyrolysis products of the kerogen, the yield of the product shale oil is improved and a greater amount of the desirable middle distillate material is produced. Further, the formation of heavy polymers, unsaturated hydrocarbons and carbonaceous residues, which characterize known processes, are suppressed. The hydrogen in a specified embodiment of our process is obtained from synthesis gas by integrating into the process of our invention a partial oxidation gas generator comprising an unobstructed reaction zone free of solid packing and catalyst as described in U.S. Pat. No. 2,582,938 issued to DuBois Eastman. The feed to the synthesis gas generator preferably comprises substantially pure oxygen (95+ mole percent O<sub>2</sub>) at a temperature in the range of 250° to 350° F., shale oil at a temperature in the range of 300° to 750° F., and steam at a temperature in the range of about 300° to 750° F. A decided economic benefit is obtained in our process by using a portion of the H<sub>2</sub>O and the shale oil which are produced elsewhere in our process. From about 3 to 13 vol. percent of the product oil is sufficient to produce that quantity of synthesis gas which would supply all of the hydrogen required for the process. The lower figure represents about 500 s.c.f. of synthesis gas per barrel of product shale oil and the high figure about 2,300 s.c.f./bbl. Hydrogen consumption is in the range of about 1,000 to 20,000 s.c.f. per ton of oil shale treated. The ratio of atoms of oxygen to atoms of carbon in the hydrocarbon feed to the unpacked synthesis gas generator should be in the range of about 0.80 to 1.5. The relative proportions of steam and oil may vary over a wide range, for example, from about 0.2 to about 3 pounds of steam per pound of shale oil supplied to the reaction zone of the generator, and preferably from 0.5 to 0.9 lbs. of H<sub>2</sub>O per lb. of oil feed. The generator may be operated so as to produce synthesis gas at the line of pressure (300 to 1,000 p.s.i.g.) desired for the retorting of the kerogen in the oil shale reaction zone and the hydrogenation of the shale oil, thereby avoiding the necessity for compressing the product gases. Although recycling a portion of the product shale oil as feed to the synthesis gas generator is a preferred embodiment of the

invention, the hydrogen-rich gas may be produced by almost any hydrocarbonaceous material suitable for charging a synthesis gas generator, e.g., natural gas, propane, butane, reduced crude, whole crude, coal oil, shale oil, tar sand oil. Similarly the oxidizing gas fed to the synthesis gas generator may be selected from the group consisting of air, oxygen (greater than 95 mole percent O<sub>2</sub>), and oxygen-enriched air (greater than 45 mole percent of O<sub>2</sub>).

The water and hydrogen-rich gas are introduced into the oil shale reaction zone at a temperature in the range of about 850° to 950° F. and preferably 900° to 950° F. while at a pressure in the range of from 300 to 1,000 p.s.i.g., and preferably at a pressure range of about 400 to 600 p.s.i.g. It was unexpectedly found that maximum yields of shale oil of improved quality and containing a greater amount of C<sub>6</sub> material are obtained by operating within this pressure range. Oil yields of about 34.3 gallons of 24.0°API gravity oil per ton of raw shale may be expected in comparison with a Fischer Assay of about 31.2 gallons per ton. This represents an increase in yield of about 10 percent and marks an improvement over the yield from contemporary processes. Also, examination of the hydrotorted shale oil produced at this pressure shows it to be of superior quality;

that is, compared with a Fischer Assay of the same shale, the sulfur and nitrogen content of our shale oil are each about 25 to 35 percent lower. Further, the nitrogen and sulfur content of our hydrotorted oil reaches a minimum in this pressure range.

It was unexpectedly found that spent shale acts like a shift catalyst and that simultaneously with the hydrotorting in the oil shale reaction zone the CO supplied by the synthesis gas undergoes an exothermic water-gas shift reaction to produce additional hydrogen gas and CO<sub>2</sub>. Thus the following additional savings are brought about by our improved process, (1) costly pure hydrogen may be replaced by relatively inexpensive synthesis gas containing H<sub>2</sub> to effect denitrogenation and desulfurization of shale oil, (2) additional H<sub>2</sub> is produced by the water-gas shift reaction from CO supplied by low cost synthesis gas, and (3) additional heat is released in the tubular retort during the water-gas shift reaction.

The residence time in the oil shale reaction zone must be long enough to permit disintegration of the raw shale oil. However, excess time in the reaction zone may cause coking and result in degraded shale oil. Thus the residence time is maintained at about one-fourth minute to 2 hours while at the previously mentioned conditions of temperature, pressure and feed.

The gaseous effluent stream leaving the reaction zone comprises vapors of shale oil and water, unreacted hydrogen, NH<sub>3</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>S, CO<sub>2</sub>, and may contain a small amount of entrained spent shale particles (about 250 to 350 mesh). When necessary, the entrained spent shale particles may be separated from the remaining gaseous stream by means of a gas-solids separator that comprises, for example a chamber with a downwardly converging bottom and baffling elements. Otherwise hot gaseous effluent leaving overhead from the reaction zone is cooled below the dew points of the water and the shale oil. In a gas-liquids separator the shale oil and water are separated by gravity from each other and from the uncondensed gases. Depending on the composition of the hydrogen-rich feed gas to the oil shale reaction zone, the uncondensed gases withdrawn from the top of the gas-liquids separator may have the following composition in mole percent dry basis: H<sub>2</sub> 45 to 85, H<sub>2</sub>S 0 to 2.0, CO<sub>2</sub> 1.0 to 15.0, NH<sub>3</sub> 0.05 to 0.50, CO 3.0 to 30.0, and CH<sub>4</sub> 2.0 to 20.0. This gas may be compressed and recycled to the oil shale reaction zone. However, to prevent the buildup of impurities all or a portion of this gas stream may be diverted into a gas purifier. A suitable gas purifier of conventional type utilizing refrigeration and chemical absorption to effect separation of the gases, such as described in U.S. Pat. No. 3,001,373 issued to DuBois Eastman and Warren G. Schlinger may be used. A stream of pure hydrogen is withdrawn from the gas purifier, and may be mixed with the

aforesaid stream of uncondensed gases being recycled to the oil shale reaction zone and makeup hydrogen-rich gas containing more than 45 mole percent  $H_2$ . For example, 21 vol. percent of pure  $H_2$ , 30 vol. percent of the uncondensed gas stream, and 49 vol. percent of makeup hydrogen-rich gas may be mixed and introduced into the oil shale reaction zone.

In summary, by the process of our invention, wherein oil shale is injected with  $H_2O$  and a hot hydrogen-rich gas, e.g., synthesis gas, underpressure and hydrogenation takes place as previously described, the following occurs:

(1) kerogen in oil shale is raised to a high enough temperature to fracture; (2) pyrolysis of the kerogen and hydrogenation of the shale oil produced; (3) the porous structure of the shale is maintained during retorting to enable cracked Kerogen in the interior to quickly escape before being converted to polymeric or gaseous products;

and (4) rapid disintegration of raw oil shale into minute particles free of carbonaceous matter. In our process, shale oil,  $H_2O$ , and hydrogen-rich gas act as heat transfer agents by conducting heat to the surface of the shale particles. The  $H_2O$  also reduces the hydrogen consumption and heat load for a given yield of shale oil. The hydrogen is able to permeate into the shale matrix so that it is available to properly terminate the hydrocarbon fractures before coke is formed plugging the pathway to the surface of the shale particle. By the process of our invention, the higher boiling hydrocarbons are subjected to viscosity breaking with substantially immediate hydrogenation of the molecular fragments and without further brakedown, thereby materially increasing the production of material boiling in the 400°-700° F. range without substantial increase in lower boiling gasoline range materials or the formation of normally gaseous hydrocarbons and heavy tars and coke. Evidence of the success of this method can be seen by the unusually high yield of high quality product shale oil, the production of excess water, and by the finely ground kerogen-free quality of the spent shale. Finally, the self-sustaining features of the process makes it particularly attractive for use in arid lands.

#### EXAMPLE OF THE PREFERRED EMBODIMENT

The following example is offered as a better understanding of the present invention but the invention is not to be construed as limited thereto.

Chunks of Colorado oil shale having a maximum cross-sectional dimension of about 4 inches and having a Fischer Assay of about 31.2 gallons of shale oil per ton of raw oil shale and 2.9 gallons of  $H_2O$  per ton of raw oil shale are charged into a fixed bed vertical oil shale reactor 1 foot in diameter by 40 feet long. The reactor is charged hourly with 2,000 pounds of oil shale per batch. The system is purged of air and 10,170 s.c.f.h. of a hydrogen-rich gas mixture, to be further described, at a temperature of 1,000° F., and 3.6 gallons per hour of  $H_2O$  at a temperature of 900° F. are passed through the oil shale reaction zone maintained at a pressure of about 500 p.s.i.g. The gaseous effluent stream leaving from the top of the oil shale reactor comprises essentially vaporized hydrogenated kerogen products, e.g., shale oil, and water, as well as minor amounts of gases including hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, ammonia, methane, ethane, propane, butane, pentane, and butylenes. The effluent stream is cooled below the dewpoint of the product shale oil and the water, which are liquefied and separated from each other and from the uncondensed hydrogen containing gas mixture by gravity in a gas-liquids separator. The hydrogen containing gas mixture is withdrawn from the top of the gas-liquids separator and recycled to the bottom of the oil shale reactor where it is enriched with about 1,305 s.c.f.h. of makeup synthesis gas, as described below. About 30 lbs./hr. of water is withdrawn from said gas-liquids separator, heated to a temperature of about 900° F., and introduced into the bottom of the oil shale reaction zone as previously described. Another 11.7 lbs./hr. of water and 23.4 lbs./hr. of shale oil are separately removed

from said gas-liquids separator, preheated to a temperature of about 750° F., and introduced into the synthesis gas generator along with 27.5 lbs./hr. of 95+ mole percent of oxygen at a temperature of about 300° F. About 1,305 s.c.f.h. of synthesis gas is produced having the following composition (mole percent dry basis):

$H_2$  46.37, CO 45.35,  $CO_2$  7.07, and  $H_2S$  0.23. The makeup synthesis gas is cooled by means of a waste heat boiler from a temperature of about 2,300° F. to about 1,000° F., mixed with recycle hydrogen containing gas from the gas-liquids separator, and introduced into the bottom of the shale reaction zone as previously described. Once steady state has been reached, the CO concentration in the hydrogenating gas, as it is introduced into the retorting zone, is at least 3.0 vol. percent.

TABLE I

Operating conditions	Run		Fischer assay
	1	2	
Shale reaction zone:			
Pressure, p.s.i.g.	500	500	N
Temperature, ° F.	950	950	N
Retorting period, hours	1	1	N
$H_2O$ injection, lbs./hour	30	None	N
Synthesis gas make-up, s.c.f.h.	1,305	2,028	N
Recycle hydrogen-rich gas, s.c.f.h.	10,170	10,170	N
Consumption of hydrogen (from syn gas), s.c.f./bbl. of shale oil produced	1,590	2,470	N
Recovery, product shale oil:			
Gals./ton of raw shale	34.3	33.5	31.2
Percent Fischer assay	110	107.4	100.0
Gravity, °API	24.0	24.5	24.1
Viscosity, SSU at 122° F.	55	49	50.0
Pour point, ° F.	70	65	75
Sulfur, weight percent	0.65	0.65	0.98
Nitrogen, weight percent	1.65	1.65	1.80
Conradson carbon, weight percent	4.50	4.28	2.3
Characterization factor (K)	11.5	11.5	11.4
ASTM distillation, ° F., percent:			
IBP	165	160	192
10	280	278	336
30	435	430	518
50	575	568	655
70	690	682	705
90			
Water yield:			
Gals./ton of raw shale	3.6	9.7	2.9
Percent Fischer assay	124	334	100
Spent shale:			
Pounds/ton of raw shale	1,633	1,634	1,670
Carbonaceous residue, weight percent	3.60	3.75	5.0

NOTE.—N=Not applicable.

By a comparison of the results in table I, it may be shown that in run 1 with  $H_2O$  injection the consumption of hydrogen (as supplied by the synthesis gas) is less than in run 2 where no  $H_2O$  is supplied. Further, the water yield for run 1 is less than that for run 2. This supports the theory that water injection inhibits the undesirable decomposition of shale carbonate, which reaction absorbs heat and liberates  $CO_2$  that reacts with hydrogen to form water.

The results clearly show that compared with the Fischer Assay (column 3), product shale oil produced by the process of our invention (run 1) is of a greater yield and has superior properties.

The process of the invention has been described generally and by examples with reference to oil shale and synthesis gas of particular compositions for purposes of clarity and illustration only. It will be apparent to those skilled in the art from the foregoing that various modifications of the process and materials disclosed herein can be made without departure from the spirit of the invention.

We claim:

1. A process for producing shale oil comprising introducing into an oil shale reaction zone a hydrogen-rich gas at a temperature in the range of about 850°-1,000° F. and a pressure in the range of about 300 to 1,000 p.s.i.g. and water in the amount of about 0.01 to 0.6 tons of water per ton of oil shale, wherein said hydrogen-rich gas is produced by the partial ox-

idation of at least a portion of the shale oil product and comprises at least 45 mole percent hydrogen, and wherein said hydrogen-rich gas is supplied to said shale reaction zone in an amount that will provide sufficient heat for pyrolyzing the oil shale in said shale reaction zone and for effecting hydrogenation thereby producing a gaseous effluent stream comprising hydrogenated shale oil vapor, H<sub>2</sub>O, H<sub>2</sub>, and carbon oxides, cooling said gaseous effluent stream to liquefy and separate shale oil and water from uncondensed gases, and recycling said separated water to said oil shale reaction zone as at least a portion of said water.

2. The process of claim 1 with the added steps of purifying said uncondensed gases in a gas purification zone to produce a gaseous stream having an increased concentration of hydrogen and introducing said purified gaseous stream into said oil shale reaction zone in admixture with said hydrogen-rich gas to provide a total of about 5,000 to 20,000 s.c.f. of hydrogen per ton of oil shale treated, and wherein the residence time in said oil shale reaction zone is in the range of one-fourth minute to 2 hours.

3. The process of claim 1, wherein said oil shale reaction zone comprises a fractured subterranean oil shale stratum.

4. A process for producing shale oil comprising (1) reacting a hydrocarbonaceous fuel with oxygen and steam in the reaction zone of a free-flow partial oxidation synthesis gas generator at a pressure in the range of about 300 to 1,000 p.s.i.g. to produce at a temperature in the range of about 1,800°-3000° F. a stream of synthesis gas substantially comprising H<sub>2</sub> and CO and containing minor amounts of CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S; (2) introducing into an oil shale reaction zone containing raw oil shale, water in the amount of about 0.1 to 0.6 tons of water per ton of oil shale treated and the synthesis gas stream from (1), wherein said synthesis gas stream is supplied in an amount sufficient to provide 5,000 to 20,000 s.c.f. of hydrogen per ton of oil shale treated and is at a temperature in the range of 850°

to 1,000° F. and a pressure in the range of about 300 to 1,000 p.s.i.g. thereby effecting the pyrolysis of the oil shale in said oil shale reaction zone and the hydrogenation of the shale oil produced;

5 (3) withdrawing from the oil shale reaction zone in (2) an effluent stream comprising hydrogenated shale oil vapor, H<sub>2</sub>O, H<sub>2</sub> and carbon oxides;

(4) cooling and effluent stream of (3) and condensing out and separating shale oil and water from uncondensed gases;

10 (5) passing a portion of the shale oil from step (4) to the synthesis gas generator in step (1) as at least a portion of the hydrocarbonaceous fuel; and

15 (6) passing a first portion of the water from (4) to the oil shale reaction zone of (2) and passing a second portion of said water to the reaction zone of the synthesis gas generator of (1).

20 5. The process of claim 4 with the added steps of purifying said uncondensed gases from step (4) in a gas purification zone to produce a gaseous stream having an increased concentration of hydrogen and recycling said purified gaseous stream into the oil shale reaction zone of (2) in admixture with said synthesis gas.

25 6. The process of claim 4 wherein the stream of synthesis gas in step (1) is produced at a pressure in the range of about 400-600 p.s.i.g. and is introduced into the oil shale reaction zone in step (2) at substantially the same pressure as produced less ordinary line drop.

30 7. The process of claim 4 wherein the oil shale reaction zone of step (2) comprises a fractured subterranean oil shale stratum.

8. The process of claim 4 wherein substantially all of the heat required for the hydrotorting in step (2) is supplied by the sensible heat of the synthesis gas.

\* \* \* \* \*

40

45

50

55

60

65

70

75

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,617,471 Dated November 2, 1971

Inventor(s) WARREN G. SCHLINGER, DALE R. JESSE, JOSEPH P. TASSONEY

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 41      After "and" insert --nitrogen levels  
of the shale oil may be reduced to--

Column 1, line 64      "0.06" should read --0.6--

Column 7, line 31      "01" should read --.01--

Signed and sealed this 24th day of October 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents