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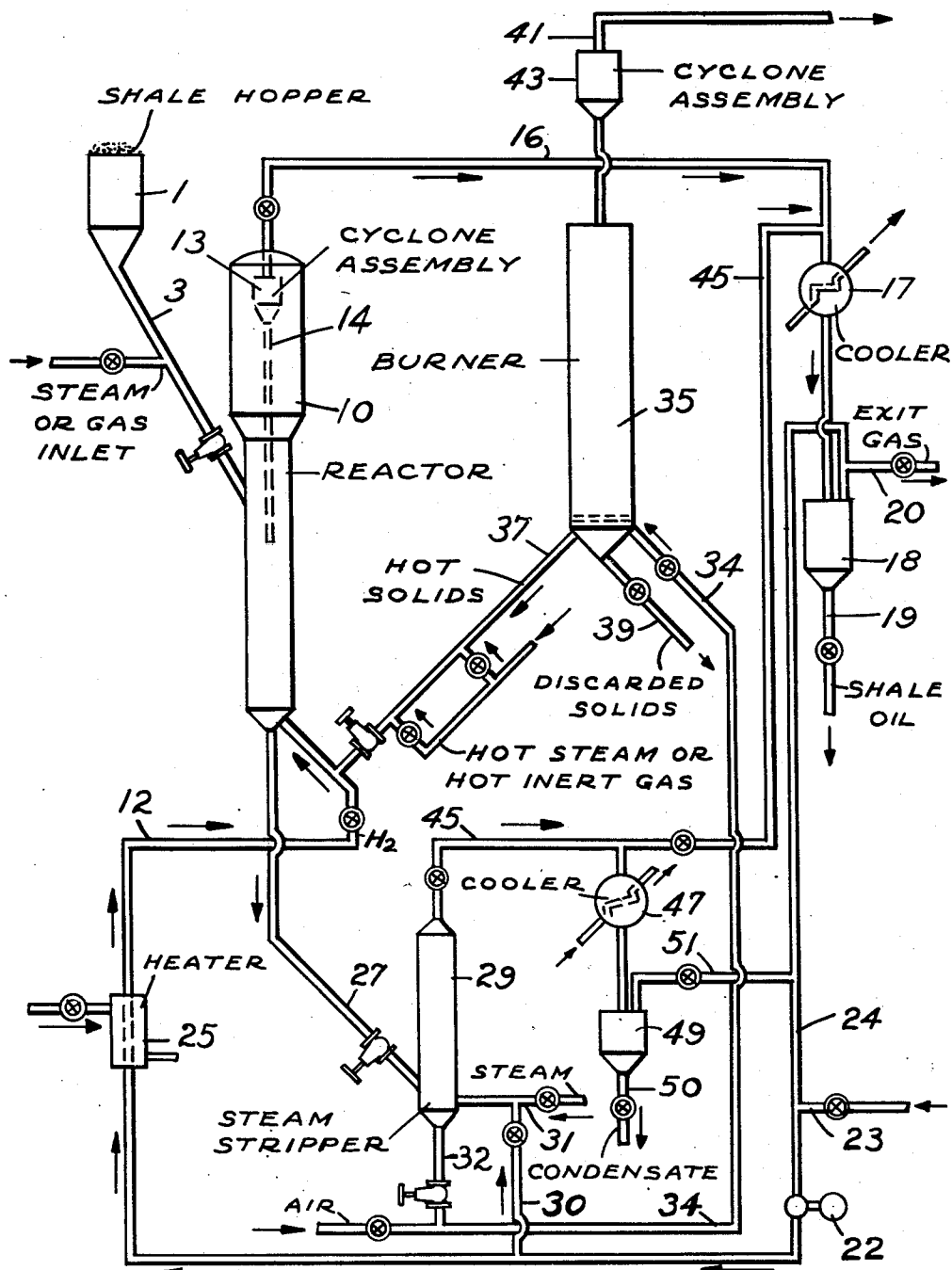


Fig. -2

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DISTILLATION OF OIL-BEARING MINERALS IN TWO STAGES IN THE PRESENCE OF HYDROGEN

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The present invention relates to the art of distilling oil-bearing minerals. More particularly, the present invention pertains to a novel process for the recovery of valuable volatile fuels, such as combustible gases, motor fuels, heating and fuel oils from oil-bearing minerals such as oil shale, oil sand, tar sands and the like, by retorting such minerals in the presence of extraneous hydrogen.

It is known that certain types of naturally occurring oil-bearing minerals, such as oil shales, contain materials which may be converted by a pyrolytic treatment into hydrocarbon oils in commercially feasible yields. Various techniques have been employed in commercial and experimental shale retorting processes including batch-type fixed bed operations and continuous procedures wherein the shale is passed in the form of a dense moving bed, a highly turbulent relatively dense fluidized bed or a dilute solids in-gas suspension through a retorting zone at suitable retorting conditions. Among these techniques, fluid operation has outstanding advantages because it combines continuity of operation with perfect uniformity of temperature and excellent heat transfer characteristics and thus affords the greatest output per unit volume of reactor space and highest oil yields per weight unit of shale charged.

However, in spite of this considerable procedural advance the shale retorting art is still confronted with the serious problem of product quality. The kerogen of the shale, that is its hydrocarbonaceous constituent which is converted into hydrocarbon oils and gas in the course of the retorting process, is very rich in organic sulfur and nitrogen which enter the product oil and complicate considerably its utilization for various fuel purposes. In addition, the crude oil produced is extremely heavy and yields only small amounts of straight run motor fuel range hydrocarbon oils. Extensive and expensive refining operations are, therefore, required to remove nitrogen and sulfur and to improve the motor fuel yield by destructive hydrogenation and/or cracking of the heavy crude. A substantial improvement of the quality of the crude oil product without loss of normally liquid product is, therefore, urgently needed.

For these reasons, it has been suggested prior to the present invention to carry out the shale distillation in the presence of steam and hydrogen at extremely short contact times and at conditions conducive to a reaction of the steam with the shale coke to form hydrogen and carbon oxides and to a hydrogenation of the shale oil by the hydrogen produced. While this procedure may increase the proportion of low boiling hydrocarbons and reduce the amount of sulfur and nitrogen in the oil removed, the extreme temperatures required are conducive to excessive cracking and gas formation whereby the total oil yield is seriously affected.

The present invention overcomes these difficulties and affords various additional advantages as will appear from the description below wherein reference will be made to the accompanying drawing.

In accordance with the present invention, the distillation of oil shale is carried out in the presence of extraneous hydrogen at relatively mild temperatures not exceeding about 1100° F. and preferably within a range of about 700°–900° F. at elevated pressures and for contact times sufficient to cause at least a substantial reduction of the sulfur and nitrogen content of the product oil. While pressures varying within the wide range of

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from about 500 to 10,000 p. s. i. g. may be used, it has been found that pressures even substantially below 1000 p. s. i. g. and particularly within the range of about 600–800 p. s. i. g. give excellent and normally superior results with respect to total oil yield, product gravity, as well as sulfur and nitrogen content so that substantial savings in equipment cost may be realized as compared with prior art procedures requiring pressures substantially in excess of 1000 p. s. i. g. Hydrogen feed rates of, say, about 5,000–15,000 normal cu. ft. per ton of shale per hour may be used, feed rates of about 6,000–10,000 normal cu. ft. per ton of shale per hour being preferred.

The contact time, i. e., the time for which the shale should be exposed to hydrogen at the above condition depends largely on the contacting technique employed. Fixed and moving bed operations, due to their poor heat transfer characteristics and inefficient gas-solids contact, require relatively the longest contact times averaging about 5–15 hours. Relatively short contact times may be employed in fluid-type operation which is the preferred technique for carrying out the process of the present invention. However, even when employing the preferred embodiment of the invention, contact times of at least 1 minute and preferably about 1 to 4 minutes should be used.

It has also been found that the hydrogen treatment of the invention may be employed with excellent results in stages involving a hydrogen-soaking stage carried out at relatively low temperatures of, say, about 650°–750° F. preceding the distillation stage proper carried out in the presence of hydrogen at temperatures of about 800°–950° F. The soaking stage may amount to about 5–15 hours followed by retorting for about another 1–5 hours, in fixed bed batch operation.

The hydrogen may be supplied in substantially pure form or in the form of suitable gas mixtures rich in hydrogen. In this respect, it is interesting to note that experimental data indicate a beneficial influence of the presence of carbon monoxide in addition to hydrogen. Ratios of carbon monoxide to hydrogen up to 1 and even higher than 1 may be successfully used with frequently improved results with respect to total oil yield. Relatively inexpensive hydrogen-containing gases, such as water gas, synthesis gas, or the like, are, therefore, particularly suitable for the purposes of the present invention.

A further embodiment of the invention involves the addition of small amounts of inorganic polar compounds, such as water, sodium hydroxide, calcium chloride and the like, to the shale undergoing the hydrogenating-retorting treatment in accordance with the invention. Additions of this type amounting to as little as about 2–10 lbs. per ton of shale have been found to be conducive to appreciable improvements with respect to oil yield and/or product quality.

All embodiments of the invention may be carried out in the presence of suitable hydrogenation and/or cracking catalysts to improve product quality and permit the use of milder reaction conditions. Particular advantages are secured when catalysts volatile at the reaction conditions are used which may be readily added to the feed gases of the process in desirable proportions of about 50–300 lbs. per ton of shale. Preferred hydrogenation catalysts of this type are the carbonyls of iron, cobalt and nickel. Volatile cracking catalysts suitable for the purposes of the invention include the halides of hydrogen, aluminum, zinc, boron and phosphorus.

Many of the advantages of the invention may be realized independently of the specific retorting technique employed and practically all conventional procedures may be readily adapted for the purposes of the invention. Two examples of such adaptations are illustrated in the attached drawing wherein

Figure 1 is a schematical flow plan of a fixed bed batch-type procedure suitable to carry out an embodiment of the invention; and

Figure 2 illustrates in similar but more detailed fashion the adaptation of the fluid-type retorting technique to the process of the invention.

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These systems will be briefly described hereinafter for a fuller understanding of the invention.

Referring now to Figure 1 of the drawing, the system shown essentially comprises a series of pressure-resistant fixed bed treating zones 1, 2, 3, 4, 5 and 6 which are operated in cyclic rotation for the purposes of discharging, gas preheating, carbon burning, retorting, product cooling and shale charging, as indicated in the drawing, to provide a substantially continuous flow of product oil. A typical complete cycle is about as follows:

A series of at least four vessels are in active use. In vessel 2 product tail gas may be preheated and cracked by hot burnt shale to produce hydrogen at temperatures of about 1200°–1500° F. Steam may be added at this point to produce CO and additional hydrogen by a reaction of the steam with residual shale carbon. Unreacted steam and the CO formed have a beneficial effect in the subsequent distillation, as previously pointed out. In vessel 3 retorted shale may be heated to about 1500°–2000° F. by burning residual carbon with air with or without recirculation of flue gas to control the temperature in the bed, that is, to avoid flame fronts. Steam may also be added to the air for this purpose and to produce combustible gas from the carbon left on the shale. In vessel 4 fresh shale is subjected to distillation temperatures in the order of 800°–1000° F. in the presence of hydrogen. In vessel 5 the hot product gases and vapors are contacted with fresh shale and a large portion of the distilled oil is condensed onto the shale and drips out of the bottom of the vessel. Of course, two or more vessels may be used in each of these functional steps. As the shale is exhausted during retorting in the original vessel, the valves are changed, say, after a period of about 12 hours, so that the vessels change places, that is, the spent shale is subjected to burning and the burnt shale from the previous operation is used to preheat the gas and product H₂. The raw shale which was being preheated by condensation and cooling of the retorting gas now is subjected to higher temperatures so that distillation takes place. A new vessel with raw shale is then introduced to cool the gases. The cooled shale from the first of the above series of vessels is discharged. Separate vessels 1 and 6 may be provided for the stages of charging fresh shale and discharging cool spent shale. Subsequent cycles are exemplified by the tabulation below:

Cycle	A Vessel	B Vessel	C Vessel
Discharge.....	2	3	4
Preheat.....	3	4	5
Burning.....	4	5	6
Retorting.....	5	6	1
Cooling.....	6	1	2
Charging.....	1	2	3

The recirculating gas for this operation is the fixed hydrocarbon gases from the operation which has been passed through gas recovery equipment, such as a condenser 8 and an absorber 10, to remove most of the light hydrocarbons. An important element of the design is that this gas is subjected to temperatures in the order of 1200°–1500° F. in the vessel containing the burnt shale. Thus, the gases entering the retort are sufficiently hot to heat the shale therein and part of the lighter hydrocarbons, as ethane and propane, left in the gas after the gas recovery plant are cracked to produce hydrogen. This hydrogen is then available to react with the compounds in the shale so that a higher grade crude oil results than otherwise would result from the retorting of the shale. The pressures in the vessels may be of the order of 300–700 p. s. i. g. This pressure decreases the size of the vessels and increases the hydrogenation effect. No large compression plant is necessary to attain this pressure because the recirculating gas is maintained at this pressure throughout the system.

While the above procedure has certain advantages in that it avoids problems connected with shale disintegration and mechanical handling of the shale, a fully continuous system of the fluidized solids type is preferred for the purposes of the invention from the point of view of capacity and yields. An example for this type of operation is illustrated in Figure 2 and will now be briefly described with reference thereto.

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Referring now to Figure 2, the system shown therein is essentially of the conventional so-called two-vessel type comprising a fluid-type retort 10 and a separate fluid-type burner 35, both of conventional design. In operation, raw coarse shale is fed from a pressurized lock hopper 1 through line 3 to an upper portion of retort 10. Hot burned shale from burner 35 is supplied via line 37 to a lower portion of retort 10 to maintain suitable distillation temperatures of about 800°–950° F. in retort 10, all in a manner known per se. A gas rich in hydrogen, such as substantially pure H₂ or suitable mixtures of H₂ and CO is fed from line 12 to the bottom of retort 10 at a rate sufficient to hydrogenate and fluidize the shale which disintegrates upon retorting to a readily fluidizable particle size so that a highly turbulent solids phase is formed having an apparent density of about 10–40 lbs. per cu. ft.

Volatile retorting products and excess feed gas are withdrawn through line 16, preferably via a gas-solids separator 13 from which separated solids may be returned to retort 10 through dip-pipe 14. The hot retort effluent is passed through a condenser 17 to a separator 18 wherein liquid product is separated from tail gas. Product oil is recovered through line 19 for further treatment. A portion of the tail gas may be vented through line 20. The remainder of the tail gas may be passed through a conventional absorber for light hydrocarbons (not shown) and then returned by means of pump 22 via line 24 and a preheater 25 to line 12 and retort 10. Make-up feed gas, such as H₂ or H₂+CO may be supplied through line 23.

Shale retorted in retort 10 is withdrawn through line 27 from the bottom of retort 10 and passed to a fluidized stripper 29 similar in construction to retort 10. Superheated steam and/or hydrogen gas from line 24 may be introduced to the bottom of stripper 29 via lines 30 and 31 to strip adhering distillation products from the shale. Stripper 29 may also be operated as a second retorting stage operated at a temperature higher than retort 10 when the latter is used as a hydrogen-soaking zone operated at a relatively low temperature, as previously described.

Completely retorted and stripped shale is passed through line 32 into line 34 wherein it is picked up by combustion air and passed to burner 35 to form a dense fluidized mass of burning shale therein. The air feed rate is so controlled that the burner temperature is maintained by about 50°–200° F. higher than the temperature of retort 10. Hot recycle shale is returned to retort 10 through line 37 as described above at a rate of about 5–20 lbs. per lb. of fresh shale charged. Excess solids may be discarded via line 39. The gases are withdrawn overhead from burner 35 through line 41, if desired, via a gas-solids separator 43.

Off-gases from stripper 29 may be passed through line 45 either to a separate condenser 47 and settler 49 or via line 16 to cooler 17 and separator 18. Liquid separated in separator 49 may be recovered through line 50 and off-gas may be returned via line 51 to recycle line 24.

In both systems illustrated, additional materials such as polar inorganic compounds and volatile catalysts may be supplied either with the fresh shale or to the gas feed lines of the distillation retorts in a manner obvious to those skilled in the art. Various modifications of these systems are within the skill of the expert.

The advantages afforded by the present invention will be further demonstrated by the experimental data reported below.

Example I

Various batches of a Colorado oil shale assaying about 30 gallons of oil per ton of shale were retorted in an autoclave having a capacity of about 3 liters by placing the charge under hydrogen pressure, heating by means of an external heater to retorting temperature for the desired hydrogen retorting time, cooling and depressurizing the autoclave and then submitting the hydrogen-soaked shale charge to a conventional Fischer assay distillation which consists in retorting the shale at atmospheric pressure and temperatures of 900°–1000° F. The Fischer assay or Fischer yield test is mentioned in "The Science of Petroleum" by Dunstan et al. (Oxford, 1938), page 3108, and is described in detail in Zeitschrift Angewandte Chemie, vol. 33 (1920), pp. 172–175. Various addition agents were added by impregnation of the raw shale. For comparison, another batch of the same raw shale

was subjected to a conventional Fischer assay test. The conditions and results of these tests are tabulated below:

Added Component	Fischer Assay Test of Raw Shale	None	None	H ₂ O	NaOH	CaCl ₂
Method of Addition				(1)	(2)	(2)
Soaking Gas		H ₂	H ₂	H ₂	H ₂	H ₂
Pressure, p. s. i. g.		750	2,900	2,800	750	750
Soaking Temp., ° F.		700	700	700	700	700
Hours of Soaking Run		12	12	12	12	12
Total Recovery, Wt. Percent.		98	98	97	98	99
Fischer Retorting of Oil Shale:						
Oil Yield, Gal./Ton	30.2	32.4	31.4	31.2	28.6	33.5
Oil Gravity, ° API	21.5	27.4	24.4	32.1	28.9	25.9
Sulfur in Oil, Wt. Percent	0.7	0.301	0.301		0.270	
Nitrogen in Oil, Wt. Percent	2	1.85	1.93		1.99	

¹ 5% of Shale Direct to Autoclave.

² Impregnation of Shale with 5% Solution and Dried.

The above data demonstrate the beneficial influence of hydrogen retorting in accordance with the invention with respect to total oil yield and product quality showing a substantial drop in sulfur and nitrogen and an appreciable increase in the API gravity. The addition of water further favored API gravity while the addition of CaCl₂ resulted in a further increase of the total yield. The somewhat lower yield in presence of sodium hydroxide is offset by the increase in API gravity and decreased sulfur content of the product.

Example II

Various 5-liter batches of the raw shale specified in Example I were charged to a pressure resistant reactor through which hydrogen-containing gas was continuously passed at retorting conditions of temperature and pressure, heat being supplied by external heating. Water was added to the gas feed in some of the tests. Fischer assay retortings were used for comparison. The detailed conditions and results of these experiments are tabulated below:

	Fischer Assay Raw Shale	Treated Product	A	Fischer Assay Treated Shale	Treated Product	B	Fischer Assay Treated Product	C		D		E	
Run Hours			1-12			1-12		1-4	7-12	1-4 H ₂ O	7-12 H ₂ O	1-4	7-12
Extraneous Feed										0.99	1.1		
Rate, Gals./Ton/Hr.								H ₂	H ₂	H ₂	H ₂	1:1 H ₂ +CO	
Gas Feed			H ₂			H ₂							
Rate, cu. ft./Ton/Hr.			8,200			7,930		8,000	6,950	7,360	8,030	8,400	9,100
Pressure, p. s. i. g.	15		750			750		750	750	750	750	750	750
Temperature, ° F.	900-1000		720			909		706	899	724	883	750	750
Material Bal., Percent.			99			91		101		95		98	883
								Treated Product	Treated Product	Treated Product	Treated Product	Treated Product	Treated Product
Oil Product:							0						
Yield, Gals./Ton...	23.9	22.1		9.5	19.3			7.1	28.7	7.8	29.3	8.0	28.3
Gravity, A. P. I.	19.4	20.1		23.1	24			26.1	26.7	26	24.3	26.8	26.8
Sulfur, Wt. Percent.	0.79	0.47		0.23	0.3			0.74	0.31		0.30	0.72	0.31
Nitrogen, Wt. Percent.				2.54	1.95								
cent.	2.60							1.69	2.79	1.86	2.44	1.66	
Total Oil Yield...	23.9		31.6		19.3			35.8		37.1		36.3	2.57

The above data demonstrate the beneficial influence of two-stage operation (see runs C and E) and the improvement afforded by the use of water in combination with H₂ (see run D) with respect to total yield and sulfur content. Also some decrease in nitrogen content was obtained and it has tentatively been established that the nitrogen content of the hydro stripped oil is more amenable to removal by acid washing than that remaining in the retorted oil.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. The process of producing oil from subdivided oil shale which comprises first soaking said shale at 650° to 750° F. in a gas containing substantial proportions of hydrogen, amounting to 6000 to 10,000 cubic feet of hydrogen under standard conditions per ton of shale, for a period of about 5 to 15 hours to obtain incipient pro-

duction of oil, and thereafter retorting said hydrogen treated shale also in presence of hydrogen, at a tem-

perature of 800° to 950° F. for a further period of 1 to 5 hours, to obtain a substantially greater total oil production from said shale than is obtained by the standard Fischer assay, both said soaking and said retorting being conducted under elevated pressure below about 1000 p. s. i. g.

2. The process of claim 1 in which a minor proportion, based on shale, of an inorganic polar compound is added to said retorting zone.

3. The process of claim 2 in which said compound is water.

4. The method of claim 2 in which said compound is NaOH.

5. The method of claim 2 in which said compound is CaCl₂.

6. The process of claim 1 in which said oil shale is present in said retorting zone in the form of a turbulent, dense fluidized mass of subdivided solids and at least a substantial portion of said heat is supplied in the form of sensible heat of hot shale distillation residue burned and heated to a temperature higher than said first-named

temperature in a separate combustion zone and supplied to said retorting zone at said higher temperature.

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