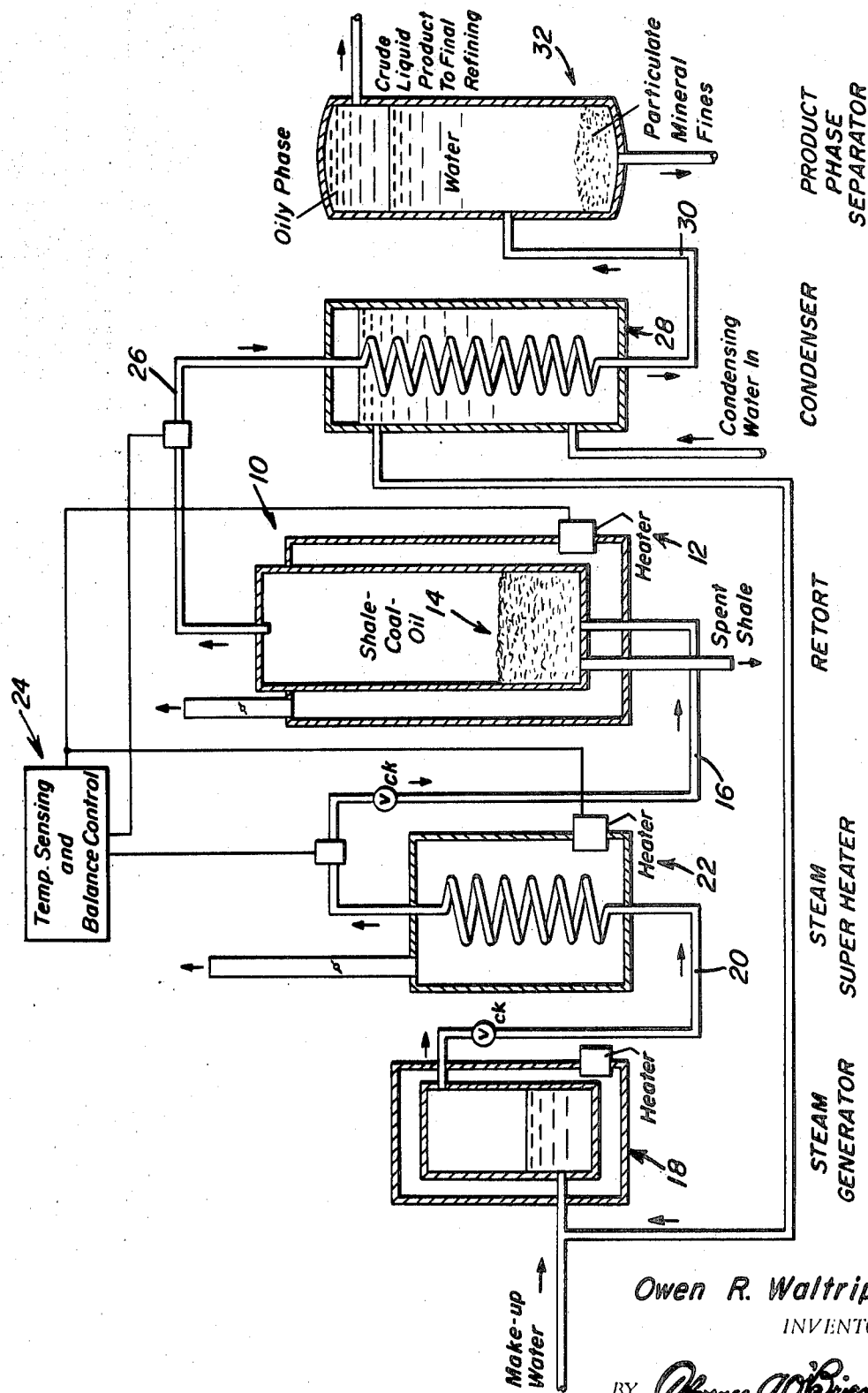


March 2, 1971

O. R. WALTRIP
OIL RECOVERY PROCESS
Filed Nov. 21, 1968

3,567,622



Owen R. Waltrip
INVENTOR.

BY *Lawrence A. O'Brien*
and Harvey B. Jacobson
Attorneys

1

3,567,622

OIL RECOVERY PROCESS

Owen R. Waltrip, Roseville, Calif., assignor to Coleman D. Stephens, Jr., Sacramento, Calif.; John Konsonlas and Owen R. Waltrip, both of Roseville, Calif.; and Noel E. Adams, Oklahoma City, Okla., fractional part interest to each

Filed Nov. 21, 1968, Ser. No. 777,613

Int. Cl. C10g 1/02

U.S. Cl. 208—11

8 Claims

ABSTRACT OF THE DISCLOSURE

A noncombustive, atmospheric pressure, retorting process for the production of high grade crude petroleum and petrochemicals from carbonaceous solids wherein superheated steam comprises a system carrier fluid and hydrogen donor and the retorting is carried out in the presence of a minor proportion of a middle fraction hydrocarbon oil selectively commingled with the carbonaceous solid in the retort zone or injected into the retort zone with the carrier fluid.

This invention relates generally to a process for the treatment of oil-containing or oil-producing solids for the extraction and/or production of liquid and gaseous products therefrom. More particularly, this invention relates to a new and improved process for the noncombustive retorting of oil shale, bituminous sands, and the like, to increase the yield and quality of the petroleum and petrochemicals which can be produced therefrom.

Inasmuch as the reserves of solid carbonaceous materials, oil shale, bituminous sands, coal, etc., and more particularly the liquid hydrocarbons to be derived therefrom, greatly exceed the known reserves of liquid hydrocarbons, a substantial amount of both private and government financed research has gone into an attempt to develop processes for the distillation of oil shales and other oil bearing minerals such as oil sands, to enable such oil bearing minerals to be economically processed on a commercial scale for the recovery of hydrocarbon oil therefrom. Prior art processes resulting from such research in addition to contemplating both combusive and noncombustive retorting of oil shale, bituminous sands, etc., have suggested the utilization of commingled carbonaceous solids and liquids, as exemplified by coal and hydrocarbon oil for example, with the oil bearing minerals being retorted to enhance both the yield and quality of hydrocarbon product derived from the retorting thereof.

Furthermore, in some instances, it has been suggested to optionally add steam to the retort to increase the gas production during the retorting. However, the aforementioned prior art processes do not adequately take into consideration the criticality of the pressure and temperature parameters in the retort zone.

Accordingly, it will be appreciated that it is an object of the present invention to provide a noncombustive retorting process for the production of high grade crude petroleum and petrochemicals from oil bearing minerals by maintaining heretofore unrecognized particular pressure and temperature parameters in the retort zone of the apparatus utilized for carrying forth the process.

Another object of the present invention is to provide an improved process for the noncombustive, atmospheric pressure, retorting of oil bearing minerals wherein the process parameters effect autogenous hydrofining of the

2

organic volatile matter in the oil bearing minerals which results in the production of aromatics necessary for the production of a relatively high ° API gravity, crude petroleum characterized by a relatively low viscosity.

Still another object of the present invention is to provide an improved process for the noncombustive, atmospheric pressure, retorting of oil shale, bituminous sands, and the like, wherein a middle fraction hydrocarbon oil is vaporized within the retort in the presence of superheated steam, or supplied in vapor form to the retort zone together with superheated steam, effects simultaneous recovery and hydrofining of the hydrocarbons from the oil bearing minerals.

Still another object of the present invention is to provide an improved noncombustive, atmospheric pressure, retorting process wherein a controlled amount of superheated steam within a critical temperature range is introduced into the retort zone, maintained at a temperature within a critical range for the production of crude shale oil of a quality level that can be used in existing refinery units.

Still another object of the present invention is to provide an improved noncombustive, atmospheric pressure, retorting process for the production of synthetic crude oils from hydrogen-deficient hydrocarbon bearing solid materials wherein the hydrogen-deficient hydrocarbons are retorted in the presence of a relatively low temperature hydrogen donor-system carrier fluid having a vaporous middle fraction hydrocarbon oil enrichment.

Other objects and aspects of the present invention will become apparent from the following discussion, reference being had to the accompanying single figure which comprises a semischematic diagram of an exemplary apparatus suitable for carrying forth an exemplary batch-processing embodiment of the process comprising the present invention.

The carbonaceous materials contemplated for treatment by the process of the present invention comprise any solid carbonaceous materials containing hydrocarbon values which can be recovered by a thermal treatment of the solid materials. The recovery of the hydrocarbon values is generally accompanied by the production of a solid residue, normally comprising combustible carbon, such as in the case of oil shale, and in the case of the treatment of certain tar sands, comprising a relatively clean silica sand. Solid materials which suitably may be treated by the process of the present invention include, oil shale, bituminous sand, coal, etc.

The hydrocarbon oil utilized in conjunction with the noncombustive retorting of the carbonaceous materials comprises a middle fraction, either from an external source or a fraction recycled from the process product, which may be characterized as a No. 2 fuel oil having a boiling point range from about 440° F. to 675° F.

The hydrogen donor-carrier fluid utilized in the present noncombustive retorting process comprises superheated steam supplied to the retort zone in a controlled amount at a temperature within the critical range of about 460° F. to about 1,000° F. and wherein the initial flow of steam is at a temperature within the range of about 460° F. to about 800° F. Steam at a temperature within the aforementioned critical temperature range is not introduced into the noncombustive retort zone until the carbonaceous materials being processed have been heated by external means to a minimum temperature of about 550° F. and wherein the temperature of the carbonaceous materials being retorted are not permitted to exceed about 750° F. during retorting thereof.

The hydrocarbon oil necessary for carrying forth the present process can, in carrying forth the process in a batch manner, be commingled with the particulate carbonaceous material within the batch retort by wetting of the particulate carbonaceous material with the hydrocarbon oil on the basis of about 2% to 5% by weight of the material to be retorted. In the batch processing of particulate carbonaceous materials, oil shale, tar sands, coal, etc., or mixtures thereof, i.e., 95% particulate oil shale or tar sands and 5% particulate bituminous coal, preferably lump coal, it is necessary that the middle fraction hydrocarbon oil be added within the retort to insure that a significant proportion of the oil is present in the retort in a vapor state before injection of superheated steam into the retort is initiated. Alternatively, when carrying forth the process of the present invention in a continuous manner, wherein raw particulate carbonaceous material is continuously introduced into a continuous feed retort, subjected to noncombustive retorting at atmospheric pressure, and continuously discharged as "spent" residue, thus necessitating the continuous introduction of superheated steam, it is necessary to insure that vaporized hydrocarbon oil be available. Thus, in an exemplary embodiment of the present invention comprising continuous retorting of particulate carbonaceous material the necessary minor proportion of hydrocarbon oil is injected into the superheated steam, prior to introduction of the steam into the continuous retort, whereby it will be assured that the hydrocarbon oil is substantially vaporized at such time as the superheated steam contacts the preheated particulate carbonaceous material. As with batch retorting, in the continuous process the particulate carbonaceous material being retorted is not permitted to exceed a temperature of about 750° F.

The hydrocarbon product effluent from the retort, be it a batch or continuous retort, is then selectively cooled to effect condensing of the condensable gases therein and the condensate directed to a phase separator for separation of the oily phase from the condensed carrier fluid, i.e., water. The water will be understood to have entrained therein mineral fines resulting from the physical breakdown of the finer particles of the carbonaceous material being treated, and various synthols resulting from a Fisher-Tropsch type reaction occurring to a limited extent in the retorting zone. It will be appreciated that it is also desirable to make provision for the recovery of noncondensable gases resulting from the retorting procedure. Alternatively, the effluent of the retort can be directed to a conventional fractionator, i.e., a vacuum fractional distillation column, for suitable fractionation and wherein a suitable middle hydrocarbon oil fraction derived as a result thereof can be recycled for supplying the necessary hydrocarbon oil for contact with the particulate carbonaceous material being treated.

Referring now to the single figure in greater detail, an exemplary embodiment of the carrying forth of the process of the present invention in a batch manner will be described, keeping in mind of course, that the salient aspect of the process of the present invention resides in the noncombustive retorting of particulate carbonaceous material preheated to within a critical temperature range of about 550° F. to 750° F. wherein the carbonaceous material is contacted with superheated steam at a temperature greater than 460° F. to about 800° F., when the carbonaceous material has reached the aforementioned lower preheat temperature of 550 F. in the presence of a vaporized middle fraction hydrocarbon oil and wherein the steam-carbonaceous material contact is made at substantially atmospheric pressure in the presence of a hydrocarbon oil fraction having a boiling point range of about 440° F. to 675° F. In addition during subsequent introduction of steam the temperature thereof is not permitted to be above about 1000° F. Furthermore, and as indicated heretofore, since the retort temperature range is not sufficient for complete dissociation of the steam, i.e.,

as would occur in a water-gas shift type reaction, it will be appreciated that a volume of steam greatly in excess of that required for supplying hydrogen necessary in the retort will be supplied. In this regard, steam is supplied to the retort in a controlled amount so as to provide the equivalent of about 40 gallons of water per ton of carbonaceous material being processed.

The exemplary apparatus schematically illustrated comprises a noncombustive retort indicated generally at 10 maintained substantially at atmospheric pressure and externally heated by a heater means indicated generally at 12 deriving its energy source from any suitable means, even including utilization of process gas subsequent to the initial start-up of the system by the utilization of externally derived fuel. As indicated generally at 14 the batch retort 10 is shown to be charged with particulate carbonaceous material, i.e., oil shale 14 having a particle size between 0 and 6 inches for example, wetted with about 2% to 5% by weight of No. 2 fuel oil.

Steam for introduction into the retort 10 through the conduit 16 is supplied from a wet steam generator 18 provided with a heater means deriving its energy from any suitable source, and wherein water for the steam generator 18 may comprise fresh make-up water or recycle water derived in conjunction with the condensing or fractionating of the product of the process. Wet steam generated within the steam generator 18 is directed through the conduit 20 to a steam superheater means indicated at 22 provided with a heater means, suitably energized, and wherein the superheated steam delivered therefrom through the conduit 16 is continuously monitored to insure that the superheated steam is within the critical temperature range of about 460° F. to 1,000° F.

As indicated, the forward movement of the hydrogen donor-carried fluid, i.e., superheated steam, within the process apparatus is assured by check valves suitably disposed in the conduits 16 and 20. In addition, a temperature sensing and balance control means 24 sensing the temperature of the superheated steam in the conduit 16 as well as the effluent of the retort 10 discharging through the conduit 26, as schematically shown, selectively and automatically controls the heater means of both the steam superheater 22 and retort 10 to insure that superheated steam, within the prescribed temperature range, is not admitted to the retort 10 until such time as the particulate shale has been heated to the aforesaid minimum temperature of 550° F. In addition, the temperature of the shale 14, which may be sequentially raised in a stepwise fashion for the off-take of various product fractions, is not permitted to rise above about the aforesaid 750° F.

The effluent discharging from the noncombustive retort 10 through the conduit 26 is directed to a condenser means 28 wherein the condensibles are liquefied, such as by being placed in indirect heat-exchange relation with condensing water, and the condensate directed through conduit 30 to a product phase separator indicated generally at 32 wherein the product separates into a plurality of distinct phases such as exemplified by the oil oily phase comprising the crude petroleum derived from the shale 14, and including synthesis products derived from the hydrogenation of hydrogen-deficient hydrocarbons therein. The water phase includes a number of water-soluble oxygenated organic compounds and may be treated for the separate recovery thereof by suitable conventional means with recycle of the water per se for generation of additional amounts of steam for the treatment of additional carbonaceous material. In addition, means is provided for withdrawal of any particulate mineral fines, i.e., asbestos fines, that may be carried over from the retort 10 by the carrier fluid. The following table is included to specifically show a number of the properties of Rifle, Colorado oil shale, Utah tar sands and Price, Utah oil shale noncombustibly retorted in accordance with the invention such as by the exemplary batch process as discussed hereinbefore.

TABLE I

	Rifle, Colorado oil shale	Utah tar sands	Price, Utah oil shale
Gravity, ° API at 60° F.	23.3	35.6	31.0
Sulfur, wt. percent.	.24	1.01	.12
Nitrogen, wt. percent.	1.44	.073	.083
Viscosity, CST at 100° F.	7.8	2.5	3.82
ASTM distillation:			
I.B.P., ° F.	152	150	350
10% 360	360	356	390
20% 424	424	404	410
30% 468	468	418	424
50% 500	500	446	450
70% (1)		486	507
80% 618		518	604
90% 610		610	
Percent distilled.	67	90	70
Percent volatiles plus residue.	33	10	30

¹ E.P. 634 (at 67%).

From the foregoing table it will be seen that the carrying forth of the process of this invention results in the production, for example, of a high grade crude petroleum characterized by a relatively high ° API gravity and a relatively low viscosity.

What is claimed as new is as follows:

1. A retorting process for the production of high grade crude petroleum and petrochemicals from carbonaceous solids which comprises the steps of:

(a) noncombustively heating particulate carbonaceous material in a retort to preheat the material to a temperature range of about 550° F. to 750° F. under substantially atmospheric pressure conditions;

(b) contacting the preheated carbonaceous material with superheated steam at a temperature within the range of no less than about 460° F. to no more than about 1,000° F. in the presence of a vaporized middle fraction hydrocarbon oil having a boiling point range of about 440° F. to 675° F.; and

(c) collecting the effluent from the retort for separate recovery of the condensible and noncondensable fractions thereof.

2. The process of claim 1 wherein in step (b) the hydrocarbon bearing solid minerals are contacted with superheated steam initially introduced at a temperature in the range of no less than about 460° F. to no more than about 800° F.

3. A process for the noncombustive, atmospheric pressure retorting of oil bearing minerals to effect autogeneous hydrofining of the organic volatile matter of the oil bearing minerals for the production of high gravity, low viscosity crude petroleum and petrochemicals which comprises the steps of:

(a) noncombustively heating particulate solid oil bearing minerals in a retort maintained at substantially atmospheric pressure to preheat the minerals to a temperature of at least about 550° F.;

(b) contacting the preheated oil bearing minerals with a hydrogen donor system carrier fluid stream of superheated steam at a temperature of no less than about 460° F. to no more than about 1,000° F. in the presence of a vaporized middle fraction hydrocarbon oil having a boiling point range of about 440° F. to about 675° F. while maintaining the temperature of the oil bearing minerals in a temperature range of no less than about 550° F. and no more than about 1,000° F.; and

(c) collecting the system carrier fluid-volatile matter effluent from the retort for separate recovery of the condensible and noncondensable fractions thereof.

4. The process of claim 3 wherein in step (b) the hydrocarbon bearing solid minerals are contacted with superheated steam initially introduced at a temperature in the range of no less than about 460° F. to no more than about 800° F.

5. A noncombustive atmospheric pressure retorting

process for the production of synthetic crude petroleum and petrochemicals from hydrogen-deficient hydrocarbon bearing solid minerals which comprises the steps of:

(a) preheating hydrogen-deficient hydrocarbon bearing solid minerals in a retort means by noncombustive means at substantially atmospheric pressure to a temperature of no less than about 550° F.;

(b) contacting the preheated hydrogen-deficient hydrocarbon bearing solid minerals with a hydrogen donor system carrier fluid stream of superheated steam at a temperature of no less than about 460° F. to no more than about 1,000° F. in the presence of a vaporized middle fraction hydrocarbon oil having a boiling point range of about 440° F. to about 675° F. while maintaining the temperature of the oil bearing minerals in a temperature range of no less than about 550° F. and no more than about 1,000° F.; and

(c) collecting the system carrier fluid-volatile matter effluent from the retort for separate recovery of the condensible and noncondensable fractions thereof.

6. The process of claim 5 wherein in step (b) the hydrocarbon bearing solid minerals are contacted with superheated steam initially introduced at a temperature in the range of no less than about 460° F. to no more than about 800° F.

7. A noncombustible atmospheric pressure retorting process for the production of high grade low viscosity petroleum and petrochemicals from hydrogen-deficient hydrocarbon bearing solid minerals which comprises the steps of:

(a) charging an admixture of about 95% particulate hydrocarbon bearing solid mineral selected from the group consisting of oil shale and tar sands and about 5% bituminous coal in the presence of about 2% to about 5% by weight of said admixture of a middle fraction hydrocarbon oil having a boiling point range of about 440° F. to about 675° F. into an externally heated retort means;

(b) preheating the charge of (a) at substantially atmospheric pressure to a temperature of no less than about 550° F.;

(c) contacting the preheated charge with a hydrogen donor system carrier fluid stream of superheated steam at a temperature of no less than about 460° F. to no more than about 1,000° F. while maintaining the temperature of the charge in a temperature range of no less than about 550° F. and no more than about 1,000° F. said steam being introduced at a rate to provide about 40 gallons of water per ton of solid mineral being processed; and

(d) collecting the system carrier fluid-volatile matter effluent from the retort for separate recovery of the condensible and noncondensable fractions thereof.

8. The process of claim 7 wherein in step (c) the hydrocarbon bearing solid minerals are contacted with superheated steam initially introduced at a temperature in the range of no less than about 460° F. to no more than about 800° F.

References Cited

UNITED STATES PATENTS

2,814,587	11/1957	Van Dijck	201—29
2,832,725	4/1958	Scott	201—31
2,694,035	11/1954	Smith et al.	201—20
3,044,948	7/1962	Eastman et al.	208—11
3,349,022	10/1967	Mitchell et al.	208—11

CURTIS R. DAVIS, Primary Examiner

U.S. Cl. X.R.

201—20, 23; 208—8