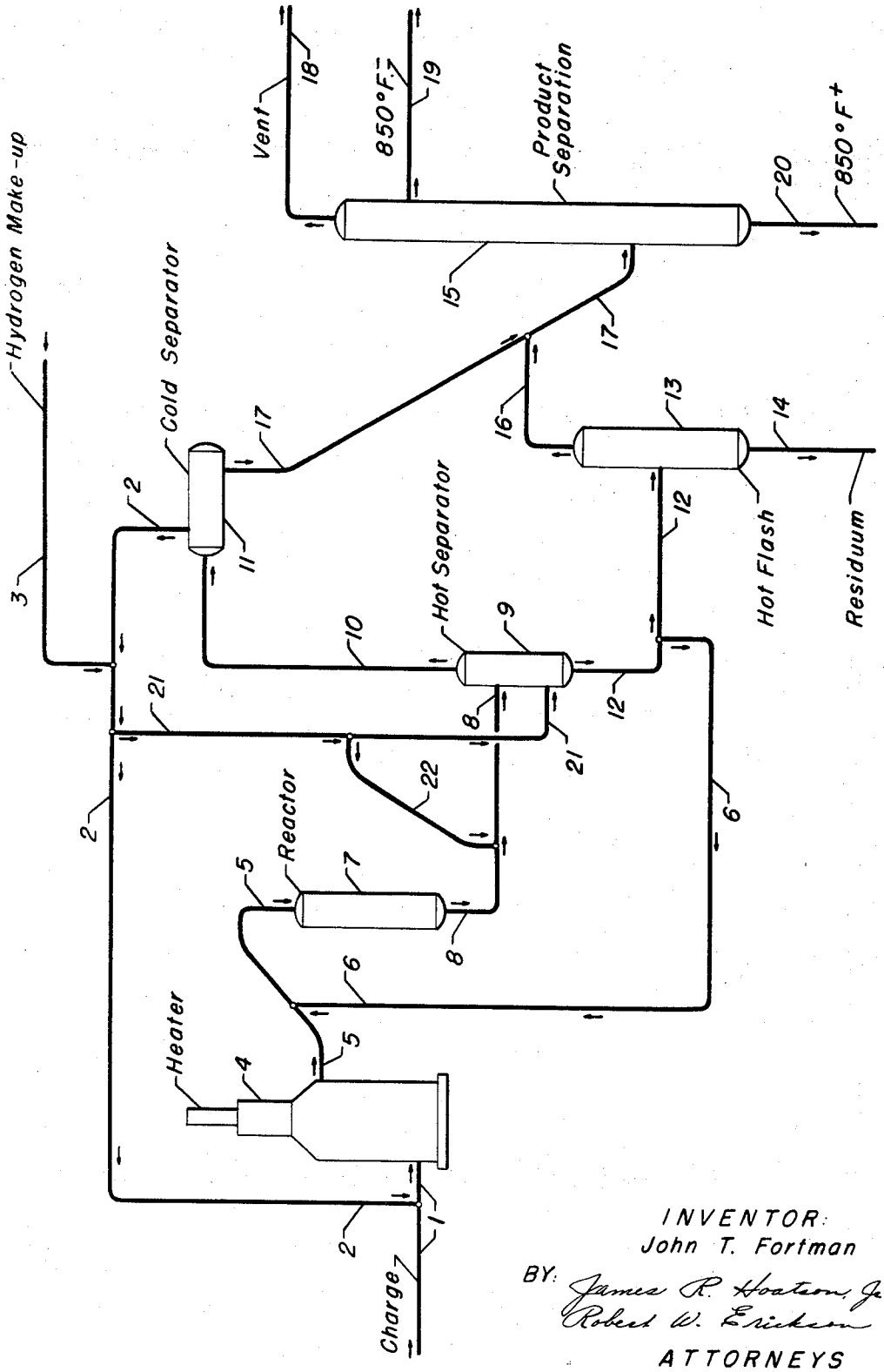
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BLACK OIL CONVERSION PROCESS

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BLACK OIL CONVERSION PROCESS

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ABSTRACT OF THE DISCLOSURE

A process for the conversion of contaminated, heavy hydrocarbonaceous material commonly referred to in the art as "black oil." Hydrogen is recycled within the process to combine with the charge to the conversion zone and with the conversion zone effluent. The quantity of "distillables" produced in the vaporous phase from the initial separation of the product effluent is increased.

APPLICABILITY OF INVENTION

The invention described herein is adaptable to a process for the conversion of petroleum crude oil into lower boiling hydrocarbon products. More specifically, the present invention is directed toward a process for converting atmospheric tower bottoms products, vacuum tower bottoms products, crude oil residuum, topped crude oils, crude oils extracted from tar sands, etc., which are sometimes referred to as "black oils," and which contain a significant quantity of asphaltic material.

Petroleum crude oils, particularly the heavy oils extracted from tar sands, topped or reduced crudes, and vacuum residuum etc., contain high molecular weight sulfurous compounds in exceedingly large quantities. In addition, such crude, or black oils contain excessive quantities of nitrogenous compounds, high molecular weight organo-metallic complexes principally comprising nickel and vanadium, and asphaltic material. Currently, an abundant supply of such hydrocarbonaceous material exists, most of which has a gravity less than 20.0° API at 60° F., and a significant proportion of which has a gravity less than 10.0. This material is generally further characterized by a boiling range indicating that 10% or more, by volume boils above a temperature of about 1050° F. The conversion of at least a portion of the material into distillable hydrocarbons—i.e. those boiling below about 1050° F.—has hitherto been considered nonfeasible from an economic standpoint. Yet, the abundant supply thereof virtually demands such conversion, especially for the purpose of satisfying the ever-increasing need for greater volumes of the lower boiling distillables.

The present invention is particularly adaptable to the catalytic conversion of black oils into distillable hydrocarbons. Specific examples of the black oils to which the present scheme is uniquely applicable, include a vacuum tower bottoms product having a gravity of 7.1° API at 60° F. containing 4.05% by weight of sulfur and 23.7% by weight of asphaltics; a "topped" Middle-East Kuwait crude oil, having a gravity of 11.0° API at 60° F., containing 10.1% by weight of asphaltenes and 5.20% by weight of sulfur; and, a vacuum residuum having a gravity of 8.8° API at 60° F., containing 3.0% by weight of sulfur and 4300 p.p.m. of nitrogen and having a 20.0% volumetric distillation point of 1055° F The principal difficulties, attendant the conversion of black oils, stem from the presence of the asphaltic material. This asphaltic material consists primarily of high molecular weight, nondistillable coke precursors, insoluble in light hydrocarbons such as pentane or heptane, and which are often found to be complexed with nitrogen, metals and especially sulfur.

Generally, the asphatic material is found to be colloidally dispersed within the crude oil, and, when subjected to elevated temperatures, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult.

PRIOR ART

While it must be acknowledged that the literature abounds with processes of various types, designed to effect the hydrorefining of black oils, while simultaneously hydrocracking to produce lower boiling hydrocarbons, a perusal of the art reveals little with respect to fixed-bed catalytic processing. Thus, many literature references and/or publications might be found which disclose propane deasphalting followed by cracking of the resulting normally liquid product, desalting followed by halogen hydride treatment to coagulate the metallic-containing asphalts, etc. It is noteworthy that such processing schemes are unconcerned with catalytic processing of black oils.

With respect to this area of catalytic processing, two principal approaches have been advanced: liquid-phase hydrogenation and vapor-phase hydrocracking. In the former, liquid phase oil is passed (generally upwardly), in admixture with hydrogen, into a fixed-fluidized bed of catalyst particles. Although perhaps effective in converting at least a portion of the oil-soluble metallic complexes, this type process is relatively ineffective with respect to asphaltics dispersed in the charge, since the probability of effecting simultaneous contact between the catalyst particle and the asphaltic molecule is remote. Furthermore, since the hydrogenation reaction zone is generally maintained at an elevated temperature of at least about 500° C. (932° F.), the retention of unconverted asphaltics suspended in a free liquid phase oil for an extended period of time, results in further flocculation and agglomeration, making conversion thereof substantially more difficult. The efficiency of hydrogen to oil contact obtainable by bubbling hydrogen through an extensive liquid body is relatively low. Some processes have been described which rely extensively upon thermal cracking in the presence of hydrogen; any catalyst present rapidly succumbs to deactivation as a result of the deposition of coke thereon. This type process requires an attendant high capacity regeneration system in order to implement the process on a continuous basis. Furthermore, such processes are unable to effect the conversion of asphaltic material. Briefly, the present invention is directed toward a process whereby the asphaltic material is maintained in a dispersed state in a liquid phase rich in hydrogen. This material comes into intimate contact with a fixed-bed of catalyst capable of effecting reaction between the hydrogen and asphaltic material; the liquid phase is itself dispersed in a hydrogen-rich gas phase so that the dissolved hydrogen is continually replenished. The two-fold dispersion and rapid, intimate contacting with the catalytic surface overcomes the difficulties encountered in previous processes whereby excessive residence times and depletion of localized hydrogen supply permit agglomeration of asphaltics and other high molecular weight species. Such agglomerates are even less available to hydrogen and are not, therefore, susceptible to catalytic reaction. They eventually form coke which becomes deposited on the catalyst, thereby further reducing catalytic activity within the system.

A principal object of the present invention is to enhance the economic advantages attendant a fixed-bed catalytic hydrorefining/hydrocracking process.

A corollary objective is to offer an improvement for integration into a process for the conversion of hydrocarbonaceous asphaltic black oils. Specifically, it is an object of my invention to provide a more efficient and

economical method for effecting the separation of the bizarre conversion product effluent into the desired product fractions.

SUMMARY OF INVENTION

In one embodiment, therefore, the present invention relates to a process for the conversion of hydrocarbonaceous black oil into lower boiling hydrocarbon products, which process comprises the steps of: (a) admixing said black oil with hydrogen and heating the resulting mixture to a temperature above about 700° F.; (d) contacting the heated mixture with a catalytic composite in a conversion zone maintained under an imposed pressure above about 1000 p.s.i.g.; (c) admixing the resulting conversion zone effluent with additional hydrogen in a first separation zone at a temperature above about 700° F., and separating said effluent to provide a first vapor phase and a first liquid phase; (d) further separating said first vapor phase, in a second separation zone at a temperature of from about 60° F. to about 130° F. to provide a hydrogen-rich second vapor phase and a second liquid phase; (e) further separating said first liquid phase, in a third separation zone at a pressure of from subatmospheric to about 100 p.s.i.g. and at a temperature in the range of from about 550° F. to about 900° F., to provide a residuum fraction and a third vapor phase; and, (f) combining said third vapor phase, or liquid condensed therefrom, with said second liquid phase, and separating the resultant mixture to provide a normally gaseous phase and a normally liquid hydrocarbon product containing said lower boiling hydrocarbons.

Other embodiments of my invention reside in particular operating conditions and the use of specific internal recycle streams. The latter include recycle of the hydrogen-rich second vapor phase in part to combine with the fresh charge stock prior to reacting the same in the conversion zone and in part to combine with said conversion zone effluent. In the specific example which follows, this this second vapor phase constitutes more than 80.0% hydrogen, by volume. In a preferred embodiment, the hydrogen is separately introduced into the first separation zone at a locus below that at which said effluent is introduced. At least a part of the first liquid phase is diverted and combined with the heated charge and hydrogen mixture, and serves as a solvent stream to keep the asphaltics dispersed and available to both hydrogen and catalyst in the reaction zone. In a preferred embodiment, a second portion of the first liquid phase is cooled and recycled to the inlet of the first separation zone to serve as a quench of the reaction zone effluent such that the temperature in said first separation zone is at a maximum level of 750° F. Thus, the first separation zone is controlled at a temperature within the range of from about 700° F. to about 750° F. A lower temperature permits ammonium salts, resulting from the conversion of nitrogenous compounds, to fall into the liquid phase, whereas a higher temperature permits the heavier hydrocarbons to be carried over in the vapor phase.

A second separation zone, herein referred to as a cold separator, serves to provide the hydrogen-rich recycle gas stream which is preferably combined with the charge stock. Thus, the cold separator operates at essentially the same pressure imposed on the conversion reaction zone, but at a signficantly lower temperature of from about 60° F. to about 130° F. In commercial practice, the temperature of the cold separator is generally controlled at about 115° F. to about 125° F.

Since the hot oil from the conversion reaction zone, containing unconverted asphaltenes, can give rise to serious emulsification problems, as a result of the co-production of water, a hot flash zone is employed to keep the unconverted asphaltics from the reminder of the process. The hot flash zone functions at a significantly reduced pressure of from sub-atmospheric to about 100 p.s.i.g., and may comprise a low-pressure—i.e. about 60 p.s.i.g.—

flash zone in combination with a vacuum column contained at about 50–60 mm. of Hg absolute. The hot flash system serves to eliminate the emulsification problem by providing a residuum fraction containing the unconverted asphaltic material, and to simplify greatly the subsequent separation of distillable products. A third, principally vaporous fraction is combined with the normally liquid stream from the cold separator, and the mixture subjected to distillation and/or fractionation to recover the desired product fractions.

Before describing my invention with reference to the accompanying drawing, and by way of illustrating the manner in which it facilitates the separation of the product effluent, several definitions are believed necessary in order that a clear understanding is afforded. In the present specification and the appended claims, the phase "pressure substantially the same as," is intended to connote that pressure under which a downstream vessel is maintained, allowing only for the pressure drop experienced as a result of the flow of fluids through the system. For example, where the conversion zone pressure, measured at the inlet thereof is 2650 p.s.i.g., the hot separator will function at about 2530 p.s.i.g., and the cold separator at a pressure of about 2490 p.s.i.g. That is, no specific, intentional means will be employed to reduce the pressure. Similarly, unless otherwise specified, the phrase, "temperature substantially the same as," is used to indicate that the only reduction in temperature stems from the normal loss due to flow from one piece of equipment to another.

Likewise, a "black oil" is intended to connote a hydrocarbonaceous mixture of which at least about 10.0% boils above a temperature of about 1050° F., and which has a gravity, °API at 60° F., of 20.0, or less. "Distillable hydrocarbons" are those normally liquid hydrocarbons, including pentanes, having boiling points below about 1050° F. Conversion conditions are intended to be those conditions imposed upon the conversion zone in order to convert a substantial portion of the black oil to distillable hydrocarbons. As will be readily noted by those skilled in the art of petroleum refining techniques, the conversion conditions hereinafter enumerated are significantly less severe than being currently commercially employed. The distinct economic advantages, over and above those inherent in producing the more valuable distillable hydrocarbons, will become immediately recognized. The conversion conditions are intended to include temperatures above about 700° F., with an upper limit of about 800° F., measured at the inlet to the catalyst bed. Since the bulk of the reactions are exothermic, the reaction zone effluent will be at a higher temperature. In order that catalyst stability be preserved, it is preferred to control the inlet temperature such that the effluent temperature does not exceed about 900° F. Hydrogen is admixed with the black oil charge stock, by means of compressive recycle, in an amount generally less than about 10,000 s.c.f./bbl., at the selected operating pressure, and preferably in an amount of from about 3000 to about 6000 s.c.f./bbl. The operating pressure will be greater than 1000 p.s.i.g., and generally in the range of about 1500 p.s.i.g. to about 4000 p.s.i.g. The black oil passes through the catalyst at a liquid hourly space velocity defined as volumes of liquid hydrocarbon charge per hour, measured at 60° F, per volume of catalyst disposed in the reaction zone, of from about 0.25 to about 2.0. When conducted as a continuous process, it is particularly preferred to introduce the mixture into the vessel in such a manner that the same passes through the vessel in downward flow. The internals of the vessel may be constructed in any suitable manner capable of providing the required intimate contact between the liquid charge stock, the gaseous mixture and the catalyst. In some instances it may be desirable to provide the reaction zone with a packed bed or beds of inert material such as particles of granite, porcelain, berl saddles, sand, aluminum or other metal turnings, etc., to facilitate distribution of the charge or to

employ perforated trays or special mechanical means for this purpose.

As hereinbefore set forth, hydrogen is employed in admixture with the charge stock, and preferably in an amount of from about 3000 to about 6000 s.c.f./bbl. The hydrogen-containing gas stream, herein sometimes designated as "recycle hydrogen," since it is conveniently recycled externally of the hydrorefining zone, fulfills a number of various functions: it serves as a hydrogenating agent, a heat carrier, and particularly a means for stripping converted material from the catalytic composite, thereby creating still more available catalytically active sites for the incoming, unconverted hydrocarbon charge stock. Since some hydrogenation will be effected, there will be a net consumption of hydrogen; to supplement this, make-up hydrogen is added to the system from any suitable external source.

The catalytic composite disposed within the reaction zone can be characterized as comprising a metallic component having hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material of either synthetic of natural origin. The precise composition and method of manufacturing the carrier material is not considered essential to the present process, although a siliceous carrier, such as 88.0% alumina and 12.0% silica, or 63.0% alumina and 37.0% silica, are generally preferred. Suitable metallic components having hydrogenation activity are those selected from the goup consisting of the metals of Group VI–B and VIII of the Periodic Table, as indicated in the Periodic Chart of the Elements, Fisher Scientific Company, (1953). Thus, the catalytic composite may comprise one or more metallic components from the group of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The concentration of the catalytically active metallic component, or components, is primarily dependent upon the particular metal as well as the characteristics of the charge stock. For example, the metallic components of Group VI–B are preferably present in an amount within the range of about 1.0% to about 20.0% by weight, the iron-group metals in an amount within the range of about 0.2% to about 10.0% by weight, whereas the platinum-group metals are preferably present in an amount within the range of about 0.1% to about 5.0% by weight, all of which are calculated as if the components existed within the finished catalytic composite as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, and mixtures of the two or more including silica-alumina, alumina-silica-boron phosphate, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, silica-alumina-boria, etc. It is preferred to utilize a carrier material containing at least a portion of silica, and preferably a composite of alumina and silica with alumina being in the greater proportion.

In accordance with my inventive concept, the product effluent from the conversion zone is admixed with additional hydrogen in the first separation zone. As hereinafter indicated with reference to the accompanying figure, the hydrogen may be added to the effluent just prior to entering the hot separator; it may be added separately and directly into the hot separator, but at a locus thereof which is below that at which the conversion zone effluent enters; or, the hydrogen may be added both directly into the hot separator, and in admixture with the conversion product effluent. The particularly preferred embodiment involves the addition of the hydrogen directly into the hot separator, separately from the conversion product effluent.

In any event, the added hydrogen is in an amount of from about 550 to about 2500 s.c.f./bbl., computed on the basis of the fresh hydrocarbonaceous charge stock. In a preferred operation, the amount of hydrogen thus added is that amount, or slightly more, which is consumed in the process and removed from the reaction section by way of so-called "solution loss." The effect upon the operation of the hot separator is to cause additional normally liquid distillables to be carried out in the first principally vapor phase. This in turn increases the quantity of distillables which are removed as the liquid phase from the cold separator which can be further treated catalytically without refractionation. Furthermore, since a greater quantity of distillables is removed in the vapor phase from the hot separator, less material will have to be vaporized in subsequent fractionation and/or separation of the hot separator liquid phase.

Other operating conditions and preferred operating techniques will be given in conjunction with the following description of the present process. In further describing this process, reference will be made to the accompanying figure which illustrates one specific embodiment of my invention.

EXAMPLE

In the drawing, the embodiment is presented by means of a simplified flow diagram in which such details as pumps, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as being non-essential to an understanding of the techniques involved. The use of such miscellaneous appurtenances, to modify the process, are well within the purview of one skilled in the art.

For the purpose of demonstrating the illustrated embodiment, the drawing will be described in connection with the conversion of a vacuum residuum in a commercially scaled unit. It is to be understood that the charge stock, stream compositions, operating conditions, design of fractionators, separators and the like, are exemplary only, and may be varied widely without departure from the spirit of my invention, the scope of which is defined by the appended claims. With reference now to the drawing, a vacuum residuum having the properties set forth in Table I, is introduced into the process via line 1:

TABLE I. VACUUM RESIDUUM PROPERTIES

Gravity, ° API at 60° F.	8.8
Sulfur, wt. percent	3.0
Nitrogen, p.p.m.	4,300
Conradson carbon residue, wt. percent	16.0
Heptane-insoluble asphaltenes, wt. percent	6.5
Distillation, ASTM D1160 ° F.:	
IBP	690
2%	860
5%	950
10%	1000
20%	1055
Molecular weight (est.)	600
Total metals, p.p.m.	100

After appropriate heat-exchange with various hot effluent streams, the charge stock, in an amount of 147,000 lbs./hr. at a temperature of 625° F. and under a pressure of about 2,730 p.s.i.g., is admixed with 31,830 lbs./hr. of a hydrogen-rich gaseous phase in line 2. The recycle hydrogen-containing stream results in part from a vaporous phase provided by cold separator 11, and in part by a hydrogen make-up stream introduced via line 3. In this particular illustration, the hydrogen-rich phase from separator 11 is about 82.4% hydrogen (on a mol basis), and is in an amount of 32,075 lbs./hr. Of this, as hereinafter further described, 4,175 lbs./hr. are diverted from line 2 through line 21, while the remaining 27,900 lbs./hr. and 3,930 lbs./hr. of make-up hydrogen continues through line 2 and line 1 into heater 4. The mixture enters heater 4 at a temperature of about 625° F., which temperature is raised to a level of about 830° F. The thus-heated mixture is combined with a hot sepa-

rator liquid phase recycle stream in line **6**, in an amount of 134,000 lbs./hr. Since this recycled stream is at a temperature of 750° F., the temperature of the total charge to reactor **7**, via line **5**, is 800° F., and the pressure is about 2685 p.s.i.g.

Reactor **7** has disposed therein a catalytic composite of 16.0% by weight of molybdenum and 2.0% by weight of nickel, calculated as the elements, and based upon the total composite. The carrier material consists of 68.0% by weight of alumina, 12.0% by weight of silica and 22.0% by weight of boron phosphate. The fresh charge rate in line **1** is such that the liquid hourly space velocity (of the fresh feed) is 0.5, the quality of hot separator recycle in line **6** being such that the combined feed ratio is 2.0. With respect to the latter, combined feed ratios of from about 1.25 to about 3.0 are well suited for use in the present process.

The hot effluent (about 875° F.), at a pressure of about 2535 p.s.i.g., is combined with 835 lbs./hr. of a hydrogen-rich stream in line **22**, and continues through line **8** into hot separator **9**. In a preferred operation, not illustrated, the material in line **8** is admixed with a portion of the hot separator liquid effluent being diverted from line **12** through line **6**, and cooled by suitable heat-exchange, in order to reduce the temperature of the material introduced to hot separator **9** to a level of 750° F. It should be noted that the pressure has been reduced thus far only to the extent of the normal pressure drop through the system.

In accordance with the present invention, 4,175 lbs./hr. of the hydrogen-rich gas is diverted from line **2** through line **21** as hereinabove set forth. In the illustrated embodiment, 835 lbs./hr. are further diverted through line **22** to combined with the reactor **7** effluent, the remaining 3,340 lbs./hr. continue through line **21** into the lower portion of hot separator **9** at a locus below that at which the product effluent enters. In this regard, it is preferred that at least 65.0% of the additional hydrogen continue through line **21** into the bottom of separator **9**. It is recognized that several modifications may be made to the illustrated embodiment, such that the general flow pattern becomes somewhat changed. It is not believed, however, that such modifications are sufficient to remove the resulting flow beyond the scope and spirit of the appended claims. For example, the make-up hydrogen now shown by line **3**, may be introduced to the system via line **21**, in which case the amount diverted originally by line **21** is correspondingly decreased. Thus, if the hydrogen make-up in the illustration is 3,930 lbs./hr., only 245 lbs./hr. is withdrawn from line **2** via line **21**. Also recognizable by those having expertise in the art, is the fact that separator **9** may be provided with internal modifications to facilitate mixing the ascending added hydrogen and the descending normally liquid hydrocarbons—i.e. separator **9** may be provided with side-to-side pans, etc.

A vapor phase is withdrawn from hot separator **9** via line **10** and passes therethrough into cold separator **11**. The latter is maintained at substantially the same pressure, again allowing only for the normal pressure drop through the system, but at a significantly lower temperature in the range of 60° F. to about 130° F.; in the scheme illustrated, cold separator **11** is under a pressure of about 2485 p.s.i.g. and a temperature of about 120° F. Thus, it will be noted that the reactor manifolding, including heater **4**, and the hot and cold separators, are maintained under substantially the same pressure. In commercial practice, the pressure at the inlet of reactor **7** would be the critical point, and it may be controlled by any suitable means such as by adjusting the quantity of make-up hydrogen in line **3** or by venting a small quantity of gas from cold separator **11**. As hereinbefore stated, this pressure is at least about 1000 p.s.i.g., and preferably within the range of from 1500 p.s.i.g. to about 4000 p.s.i.g.

The vapor phase from hot separator **9** (the material in line **10**) is in an amount of 73,120 lbs./hr., of which 32,075 lbs./hr. are removed as the hydrogen-rich gaseous phase via line **2**, from cold separator **11**. Make-up hydrogen is introduced via line **3** in an amount of 3,930 lbs./hr., for a total of 36,005 lbs./hr. Of this, 4,175 lbs./hr. are diverted through line **21**, and the remaining 31,830 lbs./hr. continue through line **2** to combine with the charge stock in line **1**, shown entering thereby into heater **4**. As hereinbefore set forth, 835 lbs./hr. of the gaseous phase in line **21** is diverted through line **22**, while the remaining portion continues through line **21** into the lower portion of hot separator **9**.

The net hot separator liquid phase, in an amount of 110,055 lbs./hr., continues through line **12** into hot flash zone **13**. Although shown as a single vessel, it is understood, and will be so recognized by those having expertise in the field of petroleum technology, that hot flash zone **13** may consist of multiple vessels. For example, the material in line **12** may first be flashed at substantially the same temperature at which it leaves hot separator **12**—in the instant case, about 750° F.—and at a super-atmospheric pressure of about 100 p.s.i.g.; the temperature after flashing will, of course, be reduced due to the conversion of some sensible heat into latent heat of vaporization. The liquid phase from this initial flash can then be heated to an elevated temperature, and passed into a vacuum column at a subatmospheric pressure of from 50–60 mm. of Hg, the elevated temperature being as high as about 900° F.; such lower effective pressure may be achieved by the addition of inert gas such as steam, hydrogen or nitrogen. In any event, the liquid phase from hot separator **9** is further separated in a suitable hot flash zone **13** at a pressure from subatmospheric to about 100 p.s.i.g. and a temperature of from 750° F. to about 900° F., to provide a residuum fraction in line **14**, containing the unconverted high molecular weight asphaltics, and a vapor fraction which may be removed through line **16**, as a vapor or after condensation. The residuum fraction in the instant illustration is in an amount of 29,400 lbs./hr., or 19.0% by volume of the fresh charge stock. The material from the vapor phase, in line **16**, is in an amount of 80,655 lbs./hr., and is admixed with the 41,045 lbs./hr of liquid phase from the cold separator **11**, the mixture continuing through line **17** into product separation zone **15**.

For the sake of simplicity, product separation is illustrated by a single-vessel zone **15**, from which three product streams are removed. A vent gas stream, in an amount of about 10,940 lbs./hr. (of which 3,230 lbs. represents hydrogen sulfide) is removed via line **18**. This stream consists principally of hydrogen, hydrogen sulfide, light paraffinic hydrocarbons and minor quantities of butanes, pentanes, hexanes, and heptane to 400° F. gasoline. Where desired, this stream can be further treated to recover any one or a number of these components in substantially pure state. A liquid stream, containing that portion of the lower-boiling product boiling up to about 850° F., is removed via line **19**. This stream consists principally of liquid hydrocarbons, including some butanes, and higher boiling material up to 850° F. and is in an amount of about 55,160 lbs./hr. As hereinafter indicated, a component analysis of the liquid stream in line **19** shows the same to be composed in the main of hydrocarbons boiling from about 400° F. to about 850° F., with only a minor quantity boiling at a temperature above 850° F. The bottoms stream, leaving product separation zone **15** via line **20**, consists primarily of those distillable hydrocarbons boiling between 800° F. and 1000° F., and is recovered in an amount of 55,500 lbs./hr. In an actual commercial operation, the split between the liquid streams indicated as leaving via lines **19** and **20** is made such that the lighter stream in line **19** contains a minimal quantity of hydrocarbons boiling above 800° F., while the material in line **20**, which may be referred to as a heavy vacuum gas oil, will consist of about 10.0% by volume

of hydrocarbons boiling between temperatures of from 700° F. to 800° F. Various aspects normally considered in a commercial operation will dictate the exact separations of the liquid product streams, and the indicated separation into the two normally liquid streams, discounting the vent gas stream in line **18**, is presented solely for the purpose of illustration.

Based upon the indicated charge rate of 147,000 lbs./hr., or 10,000 bbl./day, the yields of the major streams are presented in the following Table II:

TABLE II.—PRODUCT YIELDS

Component	° API	Bbl./day	Vol. percent	Wt. percent
Fresh Charge	8.8	10,000	100.0	100.0
Residuum	2.0	1,900	19.0	20.0
Heavy Gas Oil	17.5	4,000	40.0	37.8
850° F	40.5	4,600	46.0	37.9
Vent Gas		*4.74		4.9
Hydrogen Sulfide		*0.86		2.2

*Millions of s.c.f./day.

It should be noted that the weight percent yields given in the foregoing Table II take into account the 2.8% by weight of make-up hydrogen supplied to the process to supplement for the hydrogen consumed, and for that "lost" by solution. Of interest is the fact that approximately 73.0% by weight of the original sulfur has been converted into hydrogen sulfide and removed from the process by way of a vent gas stream. Of the remaining 27.0%, the greater share is in the residuum stream (line **14**); thus, the product streams are recovered substantially reduced in sulfur concentration.

The component analysis of the principal streams in the illustrated flow scheme are given in the following tables, being presented on a mols per hour basis. The fresh charge rate is 245 mols per hour, and the hydrogen make-up rate is 1651 mols per hour, of which 1610 mols is hydrogen, 39 mols is methane and 2 mols is nitrogen. Of the 245 mols/hr. of vacuum residuum charge stock, 6.5% by volume boils at temperatures in the range of 800° F. to 900° F.; 11.4% from 900° F. to 1000° F.; 24.5% from 1000° F. to 1100° F.; and, 5716% at temperatures above 1100° F.

In the following Table III, component analyses are presented for the reaction zone effiuent (line **8**), inclusive of the hot separator recycle in line **6** and the amount of hydrogen-rich vapor diverted from line **3** via line **21**; the hot separator vapor phase (line **10**); and, the hot separator liquid phase (line **12**), after the hot recycle is withdrawn through line **6**.

TABLE III.—HOT SEPARATOR STREAM ANALYSES

Stream	Line 8	Line 10	Line 12
Component:			
Ammonia	17	17	
Nitrogen	33	32	1.0
Hydrogen Sulfide	247	221	9.7
Hydrogen	5,881	5,540	160.0
Methane	635	600	6.4
Ethane	129	115	2.8
Propane	110	99	2.5
Butanes	68	58	3.2
Pentanes	31	25	1.4
Hexane	32	25	2.2
200° F.-300° F	65	44	9.2
300° F.-400° F	51	30	9.1
400° F.-500° F	51	23	11.7
500° F.-600° F	82	27	23.4
600° F.-700° F	82	17	26.7
700° F.-800° F	87	12	31.2
800° F.-900° F	78	2	34.9
900° F.-1,000° F	75		35.0
1,000° F.-1,100° F	68		32.3
1,100° F.-plus	96		45.2
Total	7,918	6,887	447.9

The values presented in the foregoing Table III indicated the separation effected in hot separator **9** as a result of the incorporation of the present invention. In the following Table IV, the component analyses are given for an operation conducted without the addition of hydrogen into the hot separator.

TABLE IV.—STREAM ANALYSES WITHOUT HYDROGEN ADDITION

Stream	Line 8	Line 10	Line 12
Component:			
Ammonia	17	17	
Nitrogen	31	29	1.0
Hydrogen Sulfide	247	217	13.7
Hydrogen	4,175	3,834	160.0
Methane	594	539	26.4
Ethane	129	108	9.8
Propane	110	93	8.5
Butanes	68	55	6.2
Pentanes	31	23	3.4
Hexane	32	23	4.2
200° F.-300° F	65	42	11.2
300° F.-400° F	51	28	11.1
400° F.-500° F	51	21	13.7
500° F.-600° F	82	22	28.4
600° F.-700° F	82	10	33.7
700° F.-800° F	87	4	39.2
800° F.-900° F	78	1	35.9
900° F.-1,000° F	75		35.0
1,000° F.-1,100° F	68		32.3
1,100° F.-plus	96		45.2
Total	6,152	5,049	518.9

A comparison of the data shown in Tables III and IV readily indicates the benefits afforded the use of my invention. The quantity of "distillables" in line **12**, being introduced into hot flash zone **13**, is 86.5% by volume of the amount subjected to hot flashing in the absence of hydrogen addition to hot separator **9**. This in turn provides for more liquid hydrocarbons separated in cold separator **11** and leaving via line **17**. It will become readily recognized that lesser quantities of hydrocarbons will necessarily be vaporized in hot flash zone **13** in order to recover the maximum quantity thereof while concentrating the non-distillables in the residuum fraction (line **14**).

In order to complete the illustration of black oil processing, utilizing the present invention, and by way of the simplified fracturiation scheme in the drawing, the following Table V indicates the stream analyses for the total material entering product separation zone **15** (line **17**); the vaporous vent stream (line **18**); the full boiling range gas oil (line **19**); and, the heavy vacuum gas oil (line **20**). The residuum recovered from hot flash zone **13**, via line **14**, is substantially free from "distillables," and consists of 45.2 mols per hour of 1100° F.-plus boiling range material.

TABLE V.—STREAM ANALYSES, MOLS PER HOUR

Stream	Line 17	Line 18	Line 19	Line 20
Component:				
Nitrogen	1.5	2.5		
Hydrogen Sulfide	81.1	81.1		
Hydrogen	134.0	292.4		
Methane	85.9	112.0		
Ethane	34.1	43.6		
Propane	34.8	24.0		
Butanes	24.4	1.8	6.3	
Pentanes	14.4	0.6	15.8	
Hexane-200° F	18.0	0.3	21.1	
200° F.-300° F	40.0		51.4	
300° F.-400° F	27.5		38.7	
400° F.-500° F	20.9		34.8	
500° F.-600° F	21.8		50.7	
600° F.-700° F	10.5		44.3	
700° F.-800° F	3.7		28.9	14.3
800° F.-900° F	0.7		3.5	33.1
900° F.-1,000° F			0.5	34.5
1,000° F.-1,100° F			0.1	32.2
1,100° F.-plus				
Total	553.3	614.8	295.6	114.1

The composition analyses presented in the foregoing tables are intended to be illustrative only, and may vary widely depending upon the precise characteristics of the charge stock, the flow rates and other operating variables, including the particular desired product separation. It should be further pointed out that the three product streams, represented by lines **18**, **19** and **20**, are well suited either for further processing, or separation to recover particularly desired components. For example, the heavy vacuum gas oil recovered through line **20** may be used directly as fuel oil, or subjected to catalytic hydrocracking to produce addi-

tional boiling hydrocarbons. The vent gas stream recovered through line **18** can be scrubbed to remove the hydrogen sulfide, and subsequently further separated to recover, for example, substantially pure hydrogen and/or butane-plus hydrocarbon fraction. With respect to the 850° F. stream recovered in line **19**, one scheme for further utilization is a separation at about 400° F., accompanied by catalytic hydrocracking of the light fraction for LPG (Liquefied Petroleum Gas) production, and hydrocracking for the heavier, 400° F.-plus fraction to produce additional gasoline boiling range hydrocarbons. Of major interest is the fact that the 850° F.-fraction in line **19** comprises 133.3 mols/hr. of gasoline boiling range hydrocarbons—i.e. butanes to 400° F. end boiling point. These, as well as other processing schemes will become evident to those skilled in the art.

I claim as my invention:

1. A process for the conversion of hydrocarbonaceous black oil into lower boiling hydrocarbon products, which process comprises the steps of:

(a) admixing said black oil with hydrogen and heating the resulting mixture to a temperature above about 700° F.;

(b) contacting the heated mixture with a catalytic composite in a conversion zone maintained under an imposed pressure above about 1000 p.s.i.g.;

(c) admixing the resulting total conversion zone effluent with hydrogen in a first catalyst free separation zone at a temperature above about 700° F., and separating said effluent to provide a first vapor phase and a first liquid phase, said hydrogen separately introduced into said zone at a locus below that at which said effluent is introduced;

(d) further separating said first vapor phase, in a second separation zone at a temperature of from about 60° F. to about 130° F., to provide a hydrogen-rich second vapor phase and a second liquid phase;

(e) further separating said first liquid phase, in a third separation zone at a pressure of from subatmospheric to about 100 p.s.i.g. and at a temperature in the range of from about 550° F. to about 900° F., to provide a residuum fraction and a third vapor phase; and

(f) combining said third vapor phase with said second liquid phase, and separating the resultant mixture to provide a normally gaseous phase and a normally liquid hydrocarbon product containing said lower boiling hydrocarbons.

2. The process of claim **1** further characterized in that said hydrogen-rich second vapor phase is recycled in part to combine with said charge stock, and in part to combine with said conversion zone effluent.

3. The process of claim **1** further characterized in that said first liquid phase is in part recycled to combine with the heated mixture of said charge stock and hydrogen.

4. The process of claim **1** further characterized in that said first separation zone is maintained at a temperature less than said conversion zone effluent.

5. The process of claim **4** further characterized in that said first separation zone is maintained at a maximum temperature of about 750° F.

6. The process of claim **1** further characterized in that at least a portion of said first liquid phase is combined with said conversion zone effluent prior to separation in said first separation zone.

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