

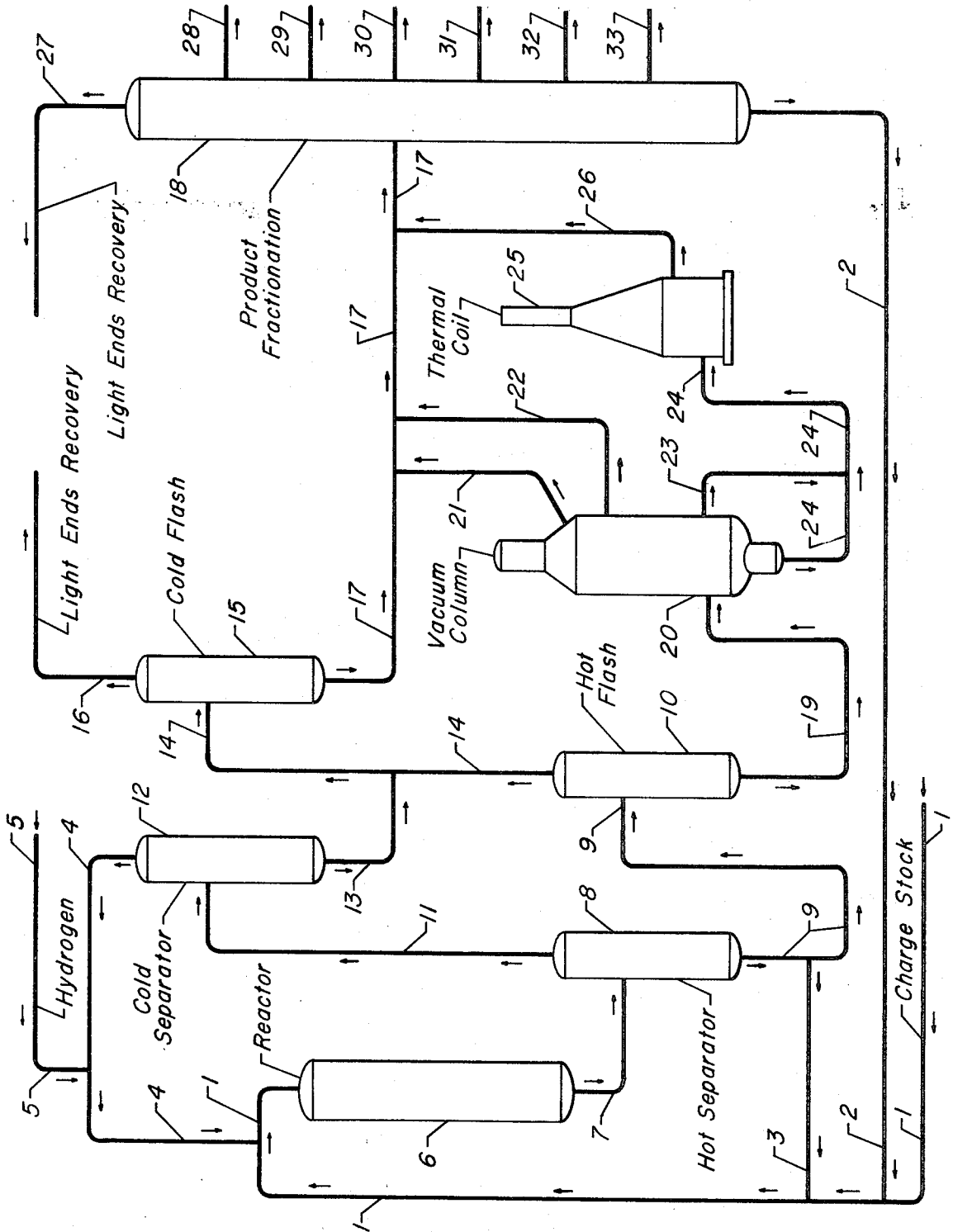
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DESULFURIZATION AND CONVERSION OF HYDROCARBONACEOUS
BLACK OILS WITH MAXIMUM PRODUCTION OF
DISTILLABLE HYDROCARBONS

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**DESULFURIZATION AND CONVERSION OF
HYDROCARBONACEOUS BLACK OILS WITH
MAXIMUM PRODUCTION OF DISTILLABLE
HYDROCARBONS**

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ABSTRACT OF THE DISCLOSURE

A process for converting asphaltene-containing hydrocarbonaceous black oils into lower-boiling, normally liquid hydrocarbon products without substantial yield loss to asphaltic residuum. The process involves the integration of a thermal cracking coil and fixed-bed catalytic hydrogenation and desulfurization, and is especially applicable to sulfurous charge stocks containing less than 150 p.p.m. of metallic contaminants, and more than about 10.0% by volume of non-distillables. The charge stock is initially subjected to fixed-bed catalytic desulfurization and hydrogenation. A high-boiling concentrate is then subjected to a non-catalytic, thermal cracking reaction zone or coil, and unconverted asphaltics are recycled to the fixed-bed reaction zone for hydrogenation.

APPLICABILITY OF INVENTION

The process described herein is primarily adaptable to the desulfurization of petroleum crude oil residuals having relatively low metals content—i.e. containing less than 150 p.p.m. of total metals. More specifically, the present invention is directed toward a combination process for hydrogenating, desulfurizing and converting heavy hydrocarbonaceous charge stocks which are commonly referred to as "black oils." Petroleum crude oils, and particularly the heavy residuals extracted from tar sands, topped or reduced crudes, and vacuum residuals, contain high molecular weight sulfurous compounds in exceedingly large quantities, nitrogenous compounds, asphaltic material insoluble in light hydrocarbons such as pentane and/or heptane, and high molecular weight organometallic complexes. With respect to the metallic complexes, containing nickel and vanadium as the principal metallic components, the various black oil charge stocks can be classified as (1) "high metals" residuals, or (2) "low metals" residuals. The present invention is primarily directed to the processing of those hydrocarbonaceous black oils having low metals content—i.e. less than about 150 p.p.m. of total metals, computed as if existing in the elemental state. A black oil charge stock is generally characterized as a heavy carbonaceous material of which more than about 10.0% by volume boils above a temperature of 1050° F. (referred to as non-distillables). Such material has a gravity less than about 20.0° API, sulfur concentrations greater than about 2.0% by weight and Conradson Carbon Residue factors exceeding 1.0% by weight. Exemplary of those black oils, to the conversion and desulfurization of which the present invention is directed, include a crude tower bottoms product having a gravity of about 14.3° API and contaminated by about 3.0% by weight of sulfur, 3830 p.p.m. of total nitrogen, 85 p.p.m. of total metals, about 11.0% by weight of insoluble asphaltenes, and about 41.0% non-distillables. The present invention affords the conversion of such charge stocks into lower-boiling, normally liquid hydrocarbon products, and further converts substantially all of the non-distillables. Additionally, the normally liquid

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product effluent is desulfurized to a level less than about 1.0% by weight.

The present invention is founded upon recognition of the fact that (1) acceptable desulfurization of low metals-containing black oils is possible at relatively mild operating severities which favor extended catalyst life, and (2) unconverted asphaltics can be hydrogenated in the presence of a high-boiling hydrocarbon, thereby becoming less refractory with respect to cracking conditions. The hydrogenation reactions are enhanced at lower severities, particularly in regard to temperature, this being an added advantage. In order that the process becomes economically attractive from the standpoint of producing lower-boiling, normally liquid hydrocarbon products, an essential feature of the present invention resides in the subsequent processing of the hydrogenated and desulfurized product effluent from the fixed-bed catalytic reaction zone. As hereinafter set forth in greater detail, the catalytic reaction effluent is separated to produce a hydrocarbon stream boiling substantially completely above the gas oil boiling range, which hydrocarbon stream is subsequently introduced into a non-catalytic thermal reaction zone or coil.

OBJECTS AND EMBODIMENTS

A principal object of my invention is to provide an economical process for effecting the desulfurization and conversion of asphaltene-containing black oils to distillable hydrocarbons of lower molecular weight. A corollary objective is to extend the period of acceptable, economical catalyst life while desulfurizing and hydrogenating hydrocarbonaceous black oils containing less than about 150 p.p.m. of total metals.

Another object is to convert a sulfurous hydrocarbon charge stock, a significant quantity of which exhibits a boiling range above a temperature of 1050° F., into lower-boiling distillable hydrocarbons in yields of at least about 95.0% by weight, said distillable hydrocarbons having a sulfur concentration less than about 1.0% by weight.

Therefore, in a broad embodiment, my invention encompasses a process for the conversion of a sulfurous, hydrocarbonaceous charge stock, containing non-distillable asphaltics, into desulfurized, lower-boiling hydrocarbon products, without substantial yield loss to asphaltic residuum, which process comprises the steps of: (a) heating said charge stock to a temperature of from 500° F. to about 775° F., reacting said charge stock with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure above about 1000 p.s.i.g.; (b) separating the resulting reaction zone effluent, in a first separation zone, at substantially the same pressure imposed upon said first reaction zone, to provide a first vapor phase and a first liquid phase; (c) further separating at least a portion of said first liquid phase in a second separation zone, at a reduced pressure, to provide a second vapor phase and a second liquid phase containing asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F.; (d) cracking at least a portion of said second liquid phase in a non-catalytic, thermal reaction zone; (e) separating the resulting thermally-cracked product effluent in a third separation zone, at conditions of temperature and pressure to provide a third vapor phase, and a third liquid phase containing unconverted asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F.; and, (f) recycling said third liquid phase to combine with said charge stock.

A specific embodiment of the present invention affords a process for converting a sulfurous, asphaltene-containing hydrocarbonaceous charge stock into lower-boiling, desulfurized hydrocarbon products, without substantial yield loss to an asphaltic residuum, which process comprises

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the steps of: (a) heating said charge stock to a temperature of from about 500° F. to about 775° F., reacting the heated charge with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure above about 1000 p.s.i.g.; (b) separating the resulting reaction zone effluent in a first separation zone at substantially the same pressure and at a temperature below about 800° F., to provide a first vapor phase and a first liquid phase; (c) separating said first vapor phase in a second separation zone, at substantially the same pressure and at a lower temperature in the range of about 60° F. to about 140° F., to provide a hydrogen-rich second vapor phase and a second liquid phase; (d) recycling a portion of said first liquid phase to combine with said charge stock and further separating the remainder in a third separation zone, at substantially the same temperature and at a reduced pressure below about 300 p.s.i.g., to provide a third vapor phase and a third liquid phase comprising primarily hydrocarbons boiling above about 650° F.; (e) combining said second liquid phase and said third vapor phase, separating the resulting mixture in a fourth separation zone at a temperature of about 60° F. to about 140° F. and a pressure below about 200 p.s.i.g., to separate and recover a fourth vapor phase principally comprising propane and lighter gaseous hydrocarbons, and to provide a fourth liquid phase principally comprising butanes and heavier liquid hydrocarbons; (f) further separating said third liquid phase in a fifth separation zone, at substantially the same temperature and at a subatmospheric pressure to provide a fifth vapor phase and a 980° F.-plus fifth liquid phase; (g) cracking said fifth liquid phase in a non-catalytic thermal reaction zone; (h) separating the resulting thermally-cracked product effluent, said fourth liquid phase and said fifth vapor phase, in a sixth separation zone to provide a sixth vapor phase principally comprising propane and lighter gaseous hydrocarbons and a sixth liquid phase containing unconverted asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F.; and (i) recycling said sixth liquid phase to combine with said charge stock.

Other embodiments of my invention, as hereinafter set forth in greater detail, reside primarily in preferred ranges for process variables and in various processing techniques. For example, in another embodiment, a portion of said sixth liquid phase is recycled to combine with said fifth liquid phase, to provide a combined feed ratio to said thermal reaction zone of from about 1.1:1 to about 4.5:1. In a particularly preferred embodiment, the fifth separation zone is a vacuum column which serves to concentrate the unconverted asphaltic residuum and to provide at least a heavy vacuum gas oil, a light vacuum gas oil and a slop-wax cut. The latter, with or without a portion of the heavy vacuum gas oil, is subjected to the thermal cracking coil in admixture with the unconverted asphaltic residuum.

The total charge to the first, fixed-bed catalytic hydrogenation zone, including hydrogen recycle and make-up hydrogen required to maintain pressure and supplant that which is consumed within the overall process, is heated to a temperature above about 500° F., and preferably within the range of from about 650° F. to about 775° F. The precise temperature, to which the charge to the catalytic reaction zone is heated, is controlled within the aforesaid range by monitoring the temperature of the reaction zone product effluent. Since the principal reactions being effected are exothermic, a temperature rise is experienced as the charge and hydrogen pass through the catalyst bed. Economically acceptable catalyst life is achieved when the maximum catalyst temperature, which is virtually the same as that of the product effluent, is maintained at a maximum level of about 800° F. In another embodiment, the first reaction zone effluent, being introduced into the first separation zone, is at a temperature of from about 700° F. to about 775° F. in order that the heavier con-

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stituents are not carried over into the principally vaporous phase. Other objects and embodiments of my invention will be evident from the following, more detailed description of the process encompassed thereby.

SUMMARY OF INVENTION

As hereinbefore set forth, the principal function of the present invention resides in the production of maximum quantities of distillable hydrocarbons, without substantial yield loss by way of an asphaltic residuum. Through the utilization of the present combination process, this function is accomplished while simultaneously avoiding the difficulties of currently-practiced processing techniques. In addition to yields greater than 95.0% by weight, paramount is the extension of the period of time during which the fixed-bed of the solid catalytic composite functions in an acceptable manner.

In accordance with the present process, primarily applicable to those charge stocks of low metals content, the black oil is catalytically desulfurized and hydrogenated, and at least partially converted, at relatively mild hydrogenation severities which favor extended catalyst life. The catalytically converted product effluent is subjected to a series of separation steps in order to provide a liquid phase substantially free from distillable hydrocarbons boiling below a temperature of 980° F. This liquid phase constitutes the charge to the thermal reaction zone, or coil, and although containing a relatively minor quantity of gas oil boiling range hydrocarbons, is primarily a slop-wax cut containing the treated, but unconverted asphaltics. The latter is presently separately recovered as a residuum fraction, for use only as a low-grade bunker fuel when cut-back with more valuable middle-distillates. In accordance with the present invention, the thermally-cracked product effluent is subjected to separation, and the residual refractory asphaltics are recycled to the catalytic reaction zone for hydrogenation therein.

As hereinafter indicated, in a specific example integrated into the description of the accompanying drawing, this particular process offers production of distillable hydrocarbons without substantial yield loss to an asphaltic residuum. A "substantial yield loss" is intended to connote more than 5.0% by weight of the quantity of charge stock. In many applications of my invention, 100.0% by weight of the charge stock is converted and accounted for in the product distribution of normally gaseous material, including ammonia and hydrogen sulfide, and normally liquid hydrocarbons, including butanes, distillable at temperatures below 980° F. In those situations involving extremely heavy charge stocks—i.e. containing more than about 80.0% by volume non-distillables—up to about 5.0% by weight of the charge stock may be removed as an asphaltic residuum drag stream.

In a preferred embodiment, the total charge to the fixed-bed catalytic reaction zone is raised to a temperature above about 500° F., and preferably in the range of 650° F. to about 775° F., as measured at the inlet to the catalyst bed. In order to preserve catalyst stability, the inlet temperature is controlled at a level such that the temperature of the reaction product effluent, or the maximum catalyst bed temperature, does not exceed about 800° F. A certain measure of temperature control, within the fixed-bed of catalyst, is afforded through the conventional utilization of either a quench hydrogen stream, or quench liquid, or both, introduced at one or more intermediate loci of the catalyst bed. The catalytic reaction zone is maintained under an imposed pressure of from about 1000 to about 4000 p.s.i.g., and the hydrocarbon charge stock contacts the catalyst at a liquid hourly space velocity (LHSV) of from about 0.5 to 10.0, based upon the fresh hydrocarbon charge stock exclusive of recycled diluent and/or any quench streams employed for temperature control. The hydrogen concentration will be in the range of from about 5000 to about 50,000 standard cubic feet per barrel, while the combined

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feed ratio, defined as total volume of liquid charge per volume of fresh hydrocarbon charge, is in the range from about 1.5:1 to about 4.0:1.

The catalytic composite disposed within the fixed-bed catalytic reaction, or conversion zone, can be characterized as a metallic component having hydrogenation activity, which component is combined with a suitable refractory inorganic oxide carrier material of either synthetic, or natural origin. The precise composition and method of manufacturing the carrier material is not considered essential to the present invention, although a siliceous carrier, such as 88.0% by weight of alumina and 12.0% by weight of silica, or 63.0% by weight of alumina and 37.0% by weight of silica are generally preferred. Suitable metallic components having hydrogenation activity are those selected from the group consisting of the metals of Groups VI-B and VIII of the Periodic Table, as set forth in the Periodic Table of The Elements, E. H. Sargent & Co., 1964. Thus, the catalytic composite may comprise one or more metallic components selected from the group of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, iridium, osmium, rhodium, ruthenium, and mixtures and compounds thereof. The concentration of the catalytic 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 generally present in an amount within the range of from 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 noble metals of Group VIII 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 existing within the catalytic composite in the elemental state.

Before further summarizing my invention, several definitions are believed necessary in order that a clear understanding be afforded. In the present specification and the appended claims, the phrase "pressure substantially the same as" is intended to connote the pressure under which a succeeding 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 catalytic first reaction zone is maintained at a pressure of about 2900 p.s.i.g., the first separation zone, or "hot separator" will function at about 2780 p.s.i.g. Similarly, the phrase "temperature substantially the same as" is employed to indicate that the only reduction in temperature stems from normally experienced loss due to the flow of material from one piece of equipment to another, or from the conversion of sensible to latent heat by "flashing."

In the present specification, as well as the appended claims, reference to a "principally vaporous phase" and "principally liquid phase," is intended to allude to a given separated stream, the greater share of the components of which exist in the vapor state or liquid state at normal conditions. An exception concerns the stream withdrawn from the vacuum column separate from the slop-wax and asphaltics. This stream is herein referred to as being "principally vaporous," notwithstanding that it comprises virtually 100.0% normally liquid hydrocarbons. It is believed, however, that this exception avoids confusion, and promotes a clearer understanding of the techniques involved.

The total product effluent from the catalytic reaction zone, at a maximum temperature of about 800° F., is passed into a first separation zone hereinafter referred to as the "hot separator." The principal function served by the hot separator is to separate the mixed-phase rich in hydrogen and a principally liquid phase containing some dissolved hydrogen. In a preferred embodiment, the total reaction product effluent is utilized as a heat-exchange medium in order to lower the temperature thereof to a level in the range of from about 700° F. to about 775° F., and preferably below the level of 750° F. The vaporous

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phase from the hot separator is introduced into a second separation zone hereinafter referred to as the "cold separator." The cold separator, operating at substantially the same pressure as the hot separator, but at a significantly lower temperature in the range of about 60° F. to about 140° F., serves to concentrate the hydrogen in a second principally vaporous phase. The hydrogen-rich vapor phase is made available for use as a recycle stream to be combined with the fresh black oil charge stock. Butanes and heavier hydrocarbons are condensed in the cold separator, and removed therefrom as a second principally liquid phase.

The liquid phase from the hot separator is in part recycled to combine with the fresh hydrocarbon charge stock to serve as a diluent for the heavier constituents thereof. The quantity of the liquid phase diverted in this manner is such that the combined liquid feed ratio to the catalytic reaction zone, being defined as total volumes of liquid charge per volume of fresh liquid charge, and inclusive of the slop-wax recycle as hereafter described, is within the range of from about 1.5:1 to about 4.0:1. The remaining portion of the principally liquid phase from the hot separator is introduced into a third separation zone hereinafter referred to as the "hot flash zone." The hot flash zone functions at about the same temperature as the liquid phase withdrawn from the hot separator, but at a significantly reduced pressure of from about 100 p.s.i.g. to about 300 p.s.i.g. The principally vaporous phase from the hot flash zone comprises primarily hydrocarbons boiling below a temperature of about 650° F., and containing a relatively minor quantity of hydrocarbons normally considered to be within the heavy gas oil boiling range. This principally vaporous stream may be combined with the liquid stream from the cold separator, and the mixture introduced into a cold flash zone at a pressure of from atmospheric to about 200 p.s.i.g. and a temperature of from 60° F. to about 140° F.

The principally liquid phase withdrawn from the hot flash zone is introduced into a vacuum column at substantially the same temperature, but at a reduced, sub-atmospheric pressure of 25-60 mm. of Hg absolute. The primary function of the vacuum column is to concentrate the treated, but unconverted asphaltic residuum. In most applications of the present invention, gas oil streams are recovered from the vacuum column as a separate light vacuum gas oil (LVGO), having a boiling range approximately 320° F. to about 750° F., and a heavy vacuum gas oil (HVGO) boiling up to about 980° F. A preferred technique involves combining these gas oil streams with the liquid phase from the cold flash separation zone for ultimate separation in a suitable fractionation system. In any given situation, the disposition of the gas oil streams will generally be determined by various refinery and/or marketing demands.

Although the slop-wax cut, 980° F.-plus distillables, and the unconverted asphaltic residuum may be separated from the vacuum column as a single product stream, all of which serve as the charge to the thermal reaction coil, a preferable technique involves the individual withdrawal of these streams. In this manner, a portion of the asphaltic residuum may be removed from the process when processing considerations so dictate. The quantity removed from the process is less than 5.0% by weight, based upon the quantity of fresh charge stock, the remainder then being combined with the slop-wax cut and charged to the thermal reaction zone, or coil, at substantially the same temperature, and at a pressure of from about 150 p.s.i.g. to about 350 p.s.i.g. The thermally-cracked product effluent, at a temperature of from about 875° F. to about 950° F., and a pressure of from about 40 p.s.i.g. to about 100 p.s.i.g., is combined with the aforesaid fourth principally liquid phase and the light and heavy gas oils. The resulting mixture is further

separated—i.e. by way of a fractionation system—to provide the desired product streams.

The fractionation system functions under conditions of pressure and temperature which provide a bottoms stream comprising a slop-wax cut and the treated, but unconverted asphaltic residuum. This bottoms fraction is combined en toto with the fresh black oil charge stock, and the asphaltic residuum undergoes hydrogenation in the fixed-bed catalytic reaction zone. With respect to native asphaltenes, being those present in the fresh hydrocarbon charge stock, it has been found that the hydrogen/carbon atomic ratio approximates 1.0:1. The treated, unconverted asphaltenes in the thermally-cracked product effluent have a hydrogen/carbon atomic ratio of about 0.75:1, indicating that these asphalts are structurally dissimilar from the native asphaltenes. They are characterized by a more highly condensed ring configuration, and are, therefore, significantly less susceptible to further reaction. For this reason, it is not feasible to recycle the slop-wax/asphalt fraction to the thermal coil. However, when the unconverted asphaltics are recycled to the catalytic reaction zone in the presence of the slop-wax distillables, they become hydrogenated to the extent that the hydrogen/carbon atomic ratio again approximates 1.0:1. Since they are, as a result, structurally similar to the native asphaltenes, they are more readily convertible to distillable hydrocarbons.

Some of the principal advantages, or benefits, attendant the utilization of my invention, reside in (1) an extension of acceptable catalyst life with respect to the fixed-bed catalytic reaction zone, which stems primarily from the fact that desulfurization, to a level less than about 1.0% by weight, is effected at a relatively low severity of operation; (2) a significant reduction in the required size of the vacuum flash column, as a result of its particular location in the process flow; (3) increased yields of the more valuable gas oils boiling in the range of about 450° F. to 980° F.; and (4) increased overall yield of distillable hydrocarbons as a direct result of the virtually complete elimination of the asphaltic residuum as a by-product stream.

DESCRIPTION OF DRAWING

For the purpose of demonstrating the illustrated embodiment, the accompanying drawing will be described in connection with the conversion of a vacuum column bottoms product having a gravity of 6.0° API and an ASTM 20.0% volumetric distillation temperature of about 1055° F. In addition, the charge stock contains 4000 p.p.m. of nitrogen, 5.5% by weight of sulfur, 100 p.p.m. of nickel and vanadium, 6.0% by weight of heptane-insoluble asphaltenes and has a Conradson carbon residue factor of 21.0% by weight. The description will be directed toward a commercially-scaled unit having a capacity of about 10,000 barrels per stream day. 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; these are considered non-essential to an understanding of the techniques involved. The use of such miscellaneous appurtenances, to modify the illustrated process flow, are well within the purview of those skilled in the art. Similarly, it is further 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.

It is intended that the charge stock be converted into maximum distillable hydrocarbons which are recoverable by ordinary distillation techniques in commonly utilized fractionation systems. The charge stock is processed in a fixed-bed catalytic desulfurization and hydrogenation zone, in admixture with about 10,000 s.c.f./bbl. of hydrogen, based upon fresh feed exclusive of recycle

streams, at a catalyst bed inlet temperature of about 700° F., and a pressure of about 3105 p.s.i.g. The liquid hourly space velocity, based upon fresh feed only, is about 0.5, and it is intended that the combined liquid feed ratio be about 2.0:1.

With respect now to the drawing, the charge stock, in an amount 10,000 bbl./day, is introduced into the system by way of line 1, and, following heat-exchange with various hot effluent streams, is passed into a heater in admixture with a recycled hydrogen-rich stream from line 4, a hot separator bottoms liquid recycle in line 3 and a slop-wax/residuum fraction in line 2. Make-up hydrogen, from a suitable external source, to maintain plant pressure, and to replace that hydrogen consumed in the overall process, is introduced by way of line 5. The total charge to the heater is at a temperature of about 500° F.; this is increased to a level of about 700° F., as measured at the inlet to the catalyst bed. The thus-heated total charge continues through line 1 into fixed-bed catalytic reaction zone 6. The catalyst disposed in reactor 6 is a composite of 88.0% by weight of an alumina and 12.0% by weight of silica, with which is combined 2.0% by weight of nickel and about 16.0% by weight of molybdenum, calculated as elemental metals.

The total charge to reactor 6, exclusive of recycle and make-up hydrogen, consists of the following: (1) 10,000 bbl./day of fresh black oil charge stock, (2) 7,790 bbl./day of hot separator bottoms recycle and (3) 2,210 bbl./day of a slop-wax/residuum recycle. With respect to the latter, the volumetric composition approximates 20.0% of slop-wax (980° F.-plus distillables) and 80.0% cracked, but unconverted asphaltic residuum.

The catalytic reaction zone effluent has the component analyses indicated in the following Table I which reflects a hydrogen consumption of about 1,618 s.c.f./bbl. of fresh black oil charge stock.

TABLE I.—REACTOR 6 PRODUCT EFFLUENT

Component:	Weight percent	Volume percent
Ammonia	0.19	-----
Hydrogen sulfide	4.66	-----
Methane	0.80	-----
Ethane	0.70	-----
Propane	0.90	-----
Butanes	0.90	1.60
Pentanes	0.65	1.06
Hexanes	1.05	1.55
Heptanes-400° F.	7.00	9.34
400° F.-650° F.	14.13	16.90
650° F.-980° F.	32.21	35.14
Slop-wax	7.64	8.00
Residuum	31.54	32.00
Totals	102.37	105.59

The conversion product effluent, in mixed phase in line 7, at a temperature of about 800° F., is utilized as a heat-exchange medium, and is introduced into hot separator 8 at a temperature of 775° F. and a pressure of about 3,040 p.s.i.g. A principally vaporous phase is withdrawn by way of line 11 and a principally liquid phase via line 9. At least a portion of the liquid phase, withdrawn from hot separator 8, is diverted via line 3 to combine with the fresh hydrocarbon charge stock and the slop-wax/residuum recycle in line 2, serving as a diluent for the heavier constituents thereof. The quantity of this recycle stream is 7,790 bbl./day.

The material in line 11 is approximately 75.5 mol percent hydrogen, and comprises only about 1.35 mol percent pentanes and heavier normally liquid hydrocarbons. It is therefore, a principally vaporous phase. Likewise, the stream in line 9 comprises about 19.9 mol percent butanes and lighter material, exclusive of hydrogen which is dissolved in the heavier hydrocarbons, and is considered, therefore, a principally liquid phase.

That portion of the hot separator bottoms stream not diverted through line 3, continues through line 9 into hot flash zone 10. A reduction in pressure is effected by means of a reducing valve not indicated in the drawing, and

the stream enters hot flash zone 10 at a pressure of about 250 p.s.i.g. and a temperature of about 768° F. As hereinafter set forth, the principal function of flash zone 10 is to concentrate the gas oils and heavier components in a liquid phase which serves as the charge to vacuum column 20. The vaporous phase in line 14 comprises about 89.2 mol percent of material boiling below about 520° F. exclusive of hydrogen, while the liquid stream in line 19 comprises about 6.3 mol percent, exclusive of hydrogen.

The principally vaporous phase withdrawn from hot separator 8 through line 11, is cooled to a temperature of about 120° F., and is introduced into cold separator 12 at a pressure of about 3000 p.s.i.g. A hydrogen-rich gaseous phase is withdrawn through line 4, and is recycled therethrough to combine with the fresh hydrocarbon charge stock in line 1. A principally liquid phase is withdrawn from cold separator 12 through line 13. The separation effected in cold separator 12, exclusive of make-up hydrogen, is such that the vaporous phase in line 4 comprises about 0.4 mol percent butanes and heavier hydrocarbons, while the liquid phase in line 13 comprises about 32.0 mol percent butanes-plus, having about 46.9 mol percent hydrogen and hydrogen sulfide dissolved therein. This stream is combined with the vaporous phase from hot flash zone 10, and the mixture is passed into cold flash zone 15 by way of line 14. Cold flash zone 15 functions at about 110° F., and at a reduced pressure of about 150 p.s.i.g., in order to concentrate normally liquid hydrocarbons in line 17, and to provide a principally vaporous phase in line 16; the latter may be introduced into a light-ends recovery system in order to separate out approximately 4.1 mol percent butanes and heavier hydrocarbons. The liquid phase in line 17, subjected to further separation via fractionation, comprises about 23.3 mol percent propane and normally gaseous material, including about 14.4 mol percent hydrogen sulfide.

Vacuum flash column 20 serves to concentrate the asphaltic residuum and slop-wax (980° F.-plus distillables) in lines 24 and 23 respectively. As hereinbefore stated, these streams may be separated as a single stream to be charged to thermal coil 25. However, with some of the heavier black oils, up to about 5.0% by weight of the residuum fraction (based upon the quantity of fresh black oil charge stock) will be removed from the process, and it is, therefore, preferred to withdraw the streams separately as illustrated in the drawing. A light vacuum gas oil, boiling from about 520° F. to 750° F., is removed by line 21, and a heavy vacuum gas oil, 750° F. to 980° F., by way of line 22. Material boiling below about 320° F. is removed from vacuum column 20 by the jets which are not illustrated in the drawing.

In the illustrated embodiment, a drag stream of the residuum in line 24 is not removed from the process; the slop-wax cut in line 23 is combined with the residuum, and the mixture continues through line 24 into thermal coil 25. The temperature of the material charged to the thermal coil is about 750° F., and that of the cracked product effluent in line 26 is about 930° F. The conversion effected in thermal coil 25 is shown in the following Table II.

TABLE II.—THERMAL COIL PRODUCT EFFLUENT

Component:	Weight percent*	Volume percent*
Ammonia.....	0.04	0.04
Hydrogen sulfide.....	0.11	0.11
Methane.....	0.17	0.17
Ethane.....	0.37	0.37
Propane.....	0.33	0.59
Butanes.....	0.26	0.43
Pentanes.....	0.29	0.43
Hexanes.....	2.35	3.16
Heptane-400° F.....	3.74	4.45
400° F.-650° F.....	8.60	9.45
650° F.-980° F.....	22.92	22.10
Slop-wax.....		
Residuum.....		
Total.....	39.18	40.61

*Values based upon fresh charge stock.

For the purpose of illustrating this embodiment, the thermally-cracked product effluent in line 26, the heavy vacuum gas oil in line 22 and the light vacuum gas oil in line 21 are combined with the liquid phase in line 17 from cold flash zone 15, the mixture being introduced through line 17 into product fractionation system 18. The separation is effected at conditions of temperature and pressure such that the 980° F.-plus slop-wax and unconverted residuum is concentrated as a bottoms stream (line 2), and butanes and lighter material is removed as an overhead product via line 27 for transfer to a light ends recovery system. The bottoms stream, in an amount of about 2,210 bbl./day, is recycled through line 2 to combine with the fresh charge in line 1. Intermediate side-cuts, the composition of which depends primarily upon the particularly desired product distribution, are removed from fractionation system 18 by way of lines 28, 29, 30, 31, 32 and 33. These are, respectively a C₅/C₆ motor fuel blending component, a C₇-320° F. gasoline, a 320° F.-520° F. kerosene fraction, a 520° F.-650° F. middle-distillate, a 650° F.-750° F. light gas oil and a 750° F.-980° F. heavy gas oil.

The overall product yields, exclusive of normally gaseous material, but inclusive of butanes and the normally liquid hydrocarbons recoverable from the vacuum jets and light ends recovery (lines 16 and 27), are presented in the following Table III.

TABLE III.—PRODUCT DISTRIBUTION AND YIELDS

Component:	Weight percent	Volume percent	Bbl./day
Ammonia.....	0.19		
Hydrogen sulfide.....	4.70		
Methane.....	1.18		
Ethane.....	1.13		
Propane.....	1.65		
Butanes.....	1.59	2.82	282
Pentanes.....	1.18	1.93	193
Hexanes.....	1.74	2.57	257
Heptane-400° F.....	12.31	16.46	1,646
400° F.-650° F.....	23.51	28.00	2,089
650° F.-980° F.....	53.19	58.35	5,835
Slop-wax.....			
Residuum.....			
Totals.....	102.37	110.22	

The foregoing specification, and especially the example integrated within the description of the drawing, clearly illustrates the process of my invention and indicates the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the conversion of a sulfurous, hydrocarbonaceous charge stock, containing non-distillable asphaltics, into desulfurized, lower-boiling hydrocarbon products, without substantial yield loss to asphaltic residuum, which process comprises the steps of:

- heating said charge stock to a temperature of from 500° F. to about 775° F., reacting said charge stock with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure above about 1000 p.s.i.g.;
- separating the resulting reaction zone effluent, in a first separation zone, at substantially the same pressure imposed upon said first reaction zone, to provide a first vapor phase and a first liquid phase;
- further separating at least a portion of said first liquid phase in a second separation zone, at a substantially reduced pressure sufficient to provide a second vapor phase and a second liquid phase containing asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F. and substantially free from distillable hydrocarbons boiling below 980° F.;
- cracking at least a portion of said second liquid phase in a non-catalytic, thermal reaction zone;
- separating the resulting thermally-cracked product

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effluent in a third separation zone, at conditions of temperature and pressure to provide a third vapor-ous phase, and a third liquid phase containing un-converted asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F.; and

(f) recycling said third liquid phase to combine with said charge stock.

2. The process of claim 1 further characterized in that said first liquid phase is in part recycled to combine with said charge stock to provide a combined feed ratio to said catalytic reaction zone in the range of from about 1.5:1 to about 4.0:1.

3. The process of claim 1 further characterized in that said charge stock is heated to a temperature in the range of from about 650° F. to about 775° F.

4. The process of claim 1 further characterized in that said first reaction zone effluent is introduced into said first separation zone at a temperature of from about 700° F. to about 775° F.

5. A process for converting a sulfurous, asphaltene-containing hydrocarbonaceous charge stock into lower-boiling, desulfurized hydrocarbon products, without substantial yield loss to an asphaltic residuum, which process comprises the steps of:

(a) heating said charge stock to a temperature of from about 500° F. to about 775° F., reacting the heated charge with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure above about 1,000 p.s.i.g.;

(b) separating the resulting reaction zone effluent in a first separation zone at substantially the same pressure and at a temperature below about 800° F., to provide a first principally vapor phase and a first liquid phase;

(c) separating said first vapor phase in a second separation zone, at substantially the same pressure and at a lower temperature in the range of about 60° F. to about 140° F., to provide a hydrogen-rich second vapor phase and a second liquid phase;

(d) recycling a portion of said first liquid phase to combine with said charge stock and further separating the remainder in a third separation zone, at substantially the same temperature and at a reduced pressure below about 300 p.s.i.g., to provide a third

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vapor phase and a third liquid phase comprising primarily hydrocarbons boiling above about 650° F.;

(e) combining said second liquid phase and said third vapor phase, separating the resulting mixture in a fourth separation zone at a temperature of about 60° F. to about 140° F. and a pressure below about 200 p.s.i.g., to separate and recover a fourth vapor phase principally comprising propane and lighter gaseous hydrocarbons, and to provide a fourth liquid phase principally comprising butanes and heavier liquid hydrocarbons;

(f) further separating said third liquid phase in a fifth separation zone, at substantially the same temperature and at a subatmospheric pressure, to provide a fifth vapor phase and a 980° F.-plus fifth liquid phase;

(g) cracking said fifth liquid phase in a non-catalytic thermal reaction zone;

(h) separating the resulting thermally-cracked product effluent, said fourth liquid phase and said fifth vapor phase, in a sixth separation zone to provide a sixth vapor phase principally comprising propane and lighter gaseous hydrocarbons and a sixth liquid phase containing unconverted asphaltics and distillable hydrocarbons boiling above a temperature of about 980° F.; and

(i) recycling said sixth liquid phase to combine with said charge stock.

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