

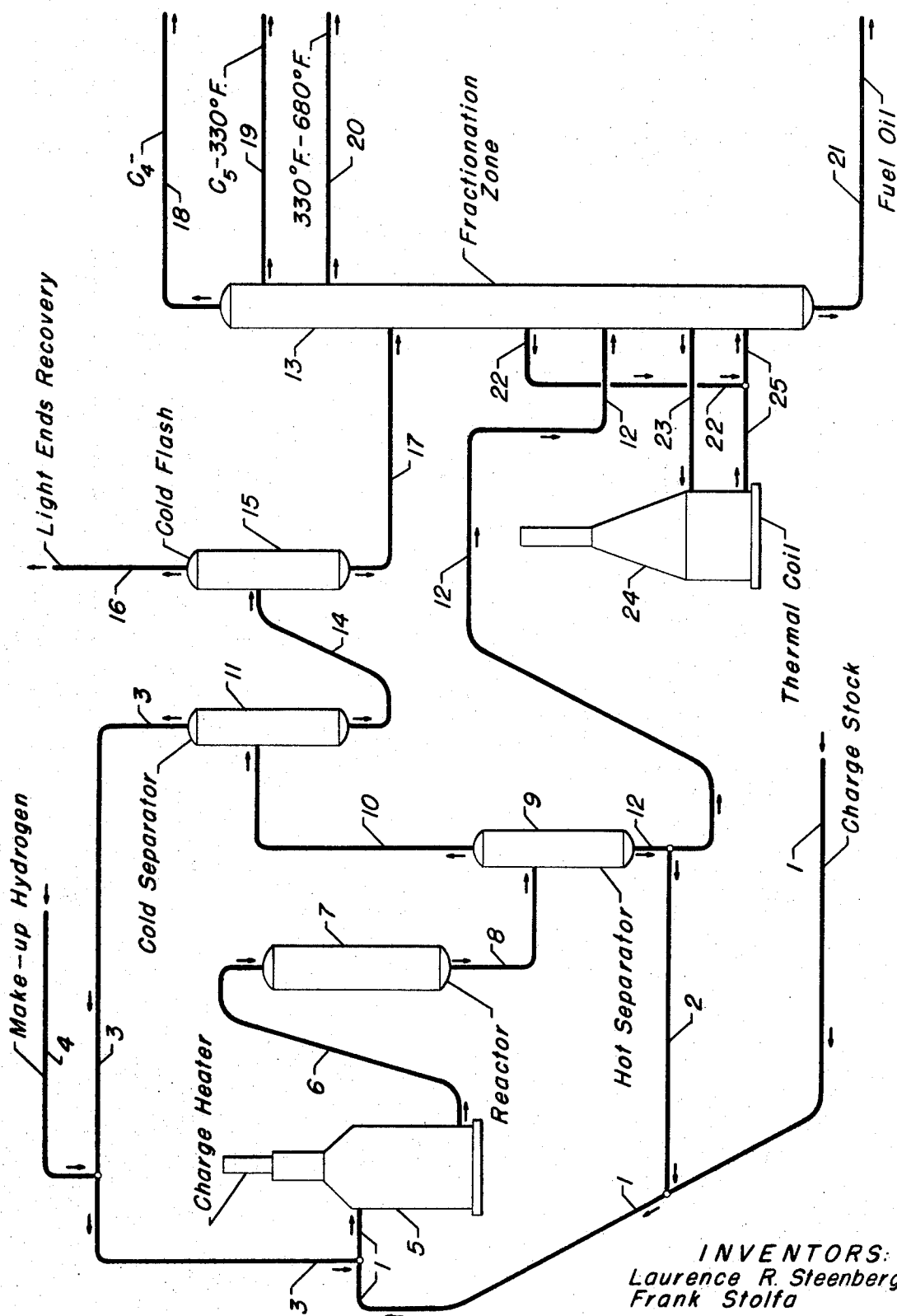
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PRODUCTION OF LOW-SULFUR FUEL OIL

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PRODUCTION OF LOW-SULFUR FUEL OIL

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ABSTRACT OF THE DISCLOSURE

A process for the production of low-sulfur fuel oil from sulfurous, hydrocarbonaceous black oils. The process involves the integration of thermal cracking and fixed-bed catalytic desulfurization, and is especially applicable to those hydrocarbon charge stocks containing less than 150 p.p.m. of metallic contaminants. The charge stock is initially catalytically hydrogenated and desulfurized, and following separation of the catalytic reaction zone product effluent, a high-boiling concentrate is introduced into a thermal reaction zone, or coil. The process affords flexibility with respect to product distribution, and particularly in regard to critical pour point and viscosity fuel oil characteristics where cold climate so demands.

APPLICABILITY OF INVENTION

The process described herein is adaptable to the desulfurization of petroleum crude oil residuals having a relatively low metals content—i.e. containing less than about 150 p.p.m. of total metals. More specifically, the present invention is directed toward a process for converting and reducing the sulfur concentration of hydrocarbonaceous charge stocks, commonly referred to in the art as "black oils," to produce maximum quantities of fuel oil having a low pour point and low viscosity, as well as a sulfur concentration less than about 1.0% by weight.

Petroleum crude oils, and particularly the heavy residuals extracted from tar sands, topped or reduced crudes, vacuum residuals, etc. contain high molecular weight sulfur compounds in exceedingly large quantities, nitrogenous compounds, asphaltic material insoluble in light hydrocarbons such as pentane and/or heptane, and high molecular weight organo-metallic complexes. With respect to the latter, containing nickel and vanadium as the principal metallic components, the wide variety of black oil charge stocks can be classified as (1) "high metals" residuals or (2) "low metals" residuals. The present invention is primarily directed toward the processing of those black oils having a low metals content less than about 150 p.p.m., calculated as if existing as the element. A "black oil" is generally characterized in the petroleum refining art as a heavy carbonaceous material of which more than about 10.0% by volume has a normal boiling point above a temperature of about 1050° F. This high-boiling fraction is further referred to as being non-distillable. Such material generally has a gravity less than about 20.0° API, and is contaminated by sulfur concentrations greater than about 2.0% by weight. Conradson carbon residue factors exceed 1.0% by weight, and a great proportion of black oils indicate a Conradson carbon residue factor above about 10.0.

Exemplary of those sulfurous, hydrocarbonaceous black oils, to the conversion and desulfurization of which our 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, about 85 p.p.m. of total metals and about 11.0% by weight of asphaltic non-distillables. Another typical charge stock is a vacuum column bottoms product derived from a Mid-East crude oil. This vacuum column

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bottoms product indicates a gravity of 6.0° API, an average molecular weight of about 620, an ASTM 20.0% by volume distillation temperature of about 1035° F., and contains about 4,000 p.p.m. of nitrogen, 5.5% by weight of sulfur, 100 p.p.m. of vanadium and nickel and about 6.0% by weight of heptane-insoluble asphaltenes. The present invention affords the conversion of such material into normally liquid hydrocarbon products of lower molecular weight, and further converts a significant quantity of the non-distillables. Additionally, the normally liquid product of the process has been substantially reduced in sulfur content, particularly in order to meet the objective of 1.0% by weight as the preferred maximum allowable in fuel oil of any character.

The principal difficulty, heretofore encountered in an attempt to process black oils, resides in the lack of a significant degree of sulfur stability of catalytic composites when the charge stock is characterized by the presence of large quantities of asphaltic material. The difficulty arises as a consequence of the necessity for effecting the process at operating severities such that non-distillable conversion simultaneously takes place while the high molecular weight sulfurous compounds are being converted into hydrogen sulfide and hydrocarbons. The asphaltic material, dispersed within the charge stock, has the tendency to flocculate and polymerize, whereby the conversion thereof to more valuable oil-soluble products, of acceptable sulfur concentration, is virtually precluded. Furthermore, the sulfur-containing polymerized asphaltic complexes become deposited upon the catalytic composite employed, steadily increasing the rate at which the catalytic composite becomes deactivated.

The present invention is founded upon recognition of the fact that desulfurization of low metals-containing black oils, to a level which more than satisfies the current objective of a maximum 1.0% by weight of sulfur, is possible at relatively mild operating severities which favor extended catalyst life. In order that the process is economically attractive from the standpoint of producing more valuable oil-soluble hydrocarbon products, a feature of our invention resides in the subsequent processing of the reaction product effluent from the fixed-bed catalytic reaction zone. Therefore, as hereinafter set forth in greater detail, the catalytic reaction zone effluent is separated at a temperature which is in the range of about 650° F. to about 800° F., and preferably at a maximum temperature of about 750° F., and at substantially the same pressure imposed upon the catalytic reaction zone, in order to provide a principally liquid phase, at least a portion of which is thereafter subjected to a non-catalytic, thermal cracking reaction zone, or coil.

OBJECTS AND EMBODIMENTS

A principal object of our invention is to provide an economical process for effecting the desulfurization and hydrogenative conversion of low metal black oils. A corollary objective is to produce maximum quantities of kerosene fractions, low pour point, low viscosity fuel oil and diesel fuel, which are significantly reduced in sulfur concentration.

Another object is to extend the period of acceptable, economical catalyst life while desulfurizing and converting hydrocarbonaceous black oils containing less than about 150 p.p.m. of total metals.

Another object is to convert asphaltic-containing hydrocarbon charge stocks into lower-boiling distillable hydrocarbons having a sulfur concentration less than about 1.0% by weight.

Therefore, in a broad embodiment, our invention relates to a process for the desulfurization of a sulfurous, hydrocarbonaceous black oil, which process comprises

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the steps of: (a) heating said black oil to a temperature of from about 500° F. to about 700° F., reacting said black oil with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure greater than about 1000 p.s.i.g.; (b) separating the resulting reaction zone effluent, in a separation zone, at substantially the same pressure imposed upon said catalytic reaction zone, to provide a first liquid phase and a first vapor phase; (c) introducing at least a portion of said first liquid phase into a fractionation zone, and withdrawing a second liquid phase, having a higher normal boiling range than said first liquid phase, from said fractionation zone; (d) cracking at least a portion of said second liquid phase in a non-catalytic reaction zone; (e) introducing the resulting cracked product effluent into said fractionation zone at a locus below that from which said second liquid phase is withdrawn; and (f) recovering a liquid hydrocarbon stream, reduced in sulfur concentration, from said fractionation zone.

Other embodiments of our invention, as hereinafter set forth in greater detail, reside principally in the preferred ranges or process operating variables and in various processing techniques. For example, at least a portion of said first liquid phase is recycled to combine with said black oil to provide a combined liquid feed ratio to said catalytic reaction zone in the range of from about 1.05:1 to about 3.5:1.

Furthermore, the total charge to the fixed-bed catalytic reaction zone, consisting of fresh black oil charge stock, a recycled portion of the first liquid phase, a recycled hydrogen-rich vapor phase and make-up hydrogen, is preferably heated to a temperature of from about 550° F. to about 650° F. The precise temperature, to which the total charge to the 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 highly exothermic, a temperature rise is experienced as the charge stock and hydrogen passes through the catalyst bed. In some instances, a degree of temperature control is made available through the use of quench streams, introduced into the reaction zone at intermediate points thereof. Economically acceptable catalyst life, particularly when the desired object entails maximum production of fuel oils, is achieved when the maximum catalyst temperature, which is virtually the same as that of the product effluent, is maintained at a maximum level below about 800° F.

In a specific embodiment, the present invention affords a process for the conversion of a sulfurous, hydrocarbonaceous black oil, of which at least about 10.0% boils above a temperature of about 1050° F., into lower-boiling, low viscosity fuel oil products of reduced sulfur concentration, which process comprises the step of: (a) heating said black oil to a temperature of from 500° F. to about 700° F., reacting said black oil with hydrogen in a catalytic reaction zone, and in contact with a catalytic composite at a pressure greater than 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 and a first liquid phase; (c) introducing at least a portion of said first liquid phase into a fractionation zone, and withdrawing a second liquid phase, having a higher normal boiling range than said first liquid phase, from said fractionation zone; (d) cracking at least a portion of said second liquid phase in a non-catalytic reaction zone, or coil; (e) introducing the resulting cracked product effluent into said fractionation zone at a locus below that from which said second liquid phase is withdrawn; (f) separating said first vapor phase in a second separation zone, at substantially the same pressure imposed upon said first separation zone, to provide a third liquid phase and a second vapor phase rich in hydrogen, and recycling said second vapor phase to combine with said hydrocarbonaceous black oil; (g) separating said

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third liquid phase in a third separation zone at a pressure lower than that imposed upon said second separation zone, to provide a third vapor phase and a fourth liquid phase; (h) introducing said fourth liquid phase into said fractionation zone at a locus above that from which said second liquid phase is withdrawn; and (i) recovering a liquid hydrocarbon stream of reduced sulfur concentration from said fractionation zone.

A more limited embodiment involves introducing said fourth liquid phase into said fractionation zone at a locus above that through which said first liquid phase is introduced into said fractionation zone. Other objects and embodiments of our 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 served by the present invention is the production of maximum quantities of distillable hydrocarbons, including gasoline, kerosene, fuel oil of low pour point and low viscosity and diesel fuel, all of which have been substantially reduced in sulfur concentration. Thus, our invention affords significant advantages in the production of fuel oils for use in relatively cold climates where pour point and viscosity are critical, and especially where the charge stock is itself highly viscous. Another distinct advantage resides in the available flexibility with respect to the product distribution of gasoline, kerosene, diesel fuel and fuel oil fractions. Of paramount importance, is the extension of the period of time during which the fixed-bed catalytic composite functions in an acceptable manner.

With respect to the processing of "high metals" black oils, being those containing more than about 150 p.p.m. of total metals, it has been found that a successful, economical process involves initially hydrovisbreaking the fresh hydrocarbon charge stock in the presence of limited quantities of hydrogen. While both technical and economical justification exists in support of this processing technique, particularly respecting the attainable catalyst life, there is incurred a yield loss with respect to that quantity of the original non-distillable asphaltics which remain unconverted. The unconverted asphaltics are removed as a heavy residuum prior to subjecting the remainder of the thermally-cracked product effluent to additional conversion in the fixed-bed catalytic hydrogenation/desulfurization reaction zone. In accordance with the present process, primarily applicable to those charge stock of low metals content, the residual 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 separated into a principally vapor phase and a principally liquid phase, at least a portion of the latter, after fractionation, being utilized as the charge to a non-catalytic thermal cracking reaction zone. This particular process affords maximum production of distillable hydrocarbons, accompanied by maximum desulfurization of a black oil charge stock, the metals content of which is less than about 150 p.p.m.

In a preferred embodiment, the total charge to the fixed-bed catalytic reaction zone includes the fresh hydrocarbonaceous black oil, a recycled hydrogen-rich gaseous phase, make-up hydrogen to supplant that consumed within the overall process and to maintain unit pressure, and a recycled diluent, a source of the latter being hereinafter set forth. This mixture is raised to a temperature of from about 500° F. to about 700° F., and preferably from about 550° F. to about 650° 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. The reaction zone will be maintained under an imposed pressure of from about 1000 to about 4000

p.s.i.g. and preferably from about 1500 to about 3000 p.s.i.g. The hydrocarbon charge stock will contact the catalytic composite at a liquid hourly space velocity of from about 0.4 to about 10.0, based upon the fresh black oil, exclusive of any recycled diluent. Liquid hourly space velocity (LHSV) is commonly defined as volumes of fresh liquid hydrocarbon charge stock per hour, per volume of catalyst disposed within the reaction zone. The preferred hydrogen concentration is in the range of from about 5000 to about 50,000 standard cubic feet per barrel, while the combined feed ratio, defined as total volume of liquid charge per volume of fresh black oil charge, is in the range of from about 1.05:1 to about 3.5:1.

The catalytic composite disposed within the fixed-bed catalytic reaction, or conversion zone, can be characterized as comprising 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, or 68.0% by weight of alumina, 10.0% by weight of silica and 22.0% by weight of boron phosphate 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 & Company, 1964. Thus, the catalytic composite may comprise one or more metallic components from the group of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The concentration of the catalytically active metallic component, or components, is primarily dependent upon a particular metal as well as the physical and/or chemical 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 from about 0.1% to about 5.0% by weight, all of which are calculated as if these components existed within the catalytic composite in the elemental state.

Before further summarizing our invention, several definitions are believed necessary in order that a clear understanding be afforded. In the present specification and appended claims, the terms "principally vaporous" and "principally liquid" are intended to describe a particular stream, the major proportion of the components of which is either normally gaseous, or normally liquid at standard conditions. Similarly, the phrase "pressure substantially the same," is intended to connote that the pressure under which a succeeding vessel is maintained is the same as the previous vessel, allowing only for the pressure drop experienced as a result of the flow of fluid through the system. Likewise, the phrase "temperature substantially the same" is utilized to indicate that the only reduction in temperature is that which stems from the normally experienced heat loss due to the flow of material from one piece of equipment to another, or from the conversion of sensible heat to latent heat by "flashing" in which a pressure drop occurs.

The total product effluent, from the first catalytic reaction zone, at a maximum temperature of about 800° F., and preferably at a temperature of about 750° F., is passed into a first separation zone hereinafter referred to as the "hot separator." The principal function served by the hot separator resides in providing recycle to the fixed-bed catalytic reaction zone. Since many black oil conversion processes require the addition of water to the reaction zone, the hot separator further serves to remove

the water in the principally vaporous phase, from which it is separated in the cold separator. The hot separator further provides a principally liquid phase, the greater proportion of which boils above a temperature of about 650° F. to about 750° F. 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 650° F. to about 800° F., and preferably below a level of about 750° F. The principally vaporous 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 from about 60° F. to about 140° F., serves to concentrate the hydrogen in a second principally vaporous phase, and to remove water by way of a dip-leg. This hydrogen-rich vaporous phase, comprising about 83.0 mol percent hydrogen, and only about 2.1 mol percent propane and heavier hydrocarbons, is made available for utilization 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 liquid phase which is introduced into a third separation zone.

The liquid phase from the hot separator is in part recycled to combine with the fresh black oil charge stock, serving as a diluent for the heavier constituents thereof. The quantity of the hot separator liquid phase, diverted in this manner, is such that the combined feed ratio to the catalytic reaction, defined as volumes of total liquid charge per volume of fresh liquid charge, is within the range of from about 1.05:1 to about 3.5:1. The remaining portion of the liquid phase from the hot separator is introduced into a fractionation zone at a locus in the lower portion thereof.

The fractionation zone functions at conditions of temperature and pressure such that a bottoms fuel oil stream, having an initial boiling point of about 680° F., is recovered. This temperature normally defines the initial boiling point of fuel oil as distinguished from jet fuel and diesel fuel, and may be adjusted to either a higher, or lower level, depending upon the particular locality and current marketing demands. It is understood that the specific initial boiling point of the fuel oil fraction is not essential to the present invention.

The condensed liquid phase separated from the cold separator is introduced into a third separation zone, hereinafter referred to as the "cold flash" zone, the latter functioning at substantially the same temperature but at a significant reduced pressure in the range of from about 100 to about 400 p.s.i.g. The principal function served by the cold flash zone is the separation of a gaseous phase principally comprising propane and lighter hydrocarbons, hydrogen, hydrogen sulfide and ammonia, which is introduced into a light ends recovery system. A fourth liquid phase, comprising butanes, pentanes and heavier normally liquid hydrocarbons, is also separated from the cold flash zone, and introduced into the fractionation zone at a locus above that at which the first liquid phase from the hot separator is introduced.

That portion of the first liquid phase from the hot separator, not being diverted as recycled diluent to combine with the black oil charge stock, is introduced into the fractionation zone at a locus above that from which the 680° F.-plus fuel oil fraction is removed. A second liquid phase, having a normal boiling range higher than that of the first liquid phase, is introduced into a thermal cracking reaction zone, or coil, at a pressure of from about 200 to about 400 p.s.i.g. and a temperature of from about 700 to about 750° F. The thermally-cracked product effluent, at a temperature of from about 900° F. to about 950° F., is introduced into the fractionation zone at a locus in the lower portion thereof, and below that

from which the second liquid phase, serving as the charge to the thermal reaction coil, is withdrawn. Temperature control of the reboiler section of the fraction zone is facilitated by withdrawing a heart-cut from an intermediate locus, and combining the same with the thermally-cracked product effluent.

The principal advantage, or benefit, attendant the utilization of our invention, resides in the production of maximum quantities of low viscosity, low pour point fuel oil, diesel fuel, and gasoline and kerosene fractions, all of which are significantly reduced in sulfur concentration. Another, closely related advantage is that the process affords a great degree of flexibility with respect to the quantities of the various fuel oil streams. For example, the operating conditions of the fixed-bed catalytic reaction zone can be adjusted to vary the quantities of jet fuel, diesel fuel and fuel oil to some extent, providing care is exercised to insure that the fuel oil meets the specification of a maximum of 1.0% by weight of sulfur. Similarly, the fractionation zone temperature and pressure can be adjusted to vary the boiling range of the second liquid phase utilized as the charge to the thermal reaction zone, or coil.

Another important advantage, or benefit, resides in an extension of the period of acceptable catalyst life with respect to the fixed-bed catalytic reaction zone. This 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 with the result that the atmosphere within the catalytic reaction zone is not conducive to the formation of sulfur-containing polymer products, otherwise resulting from the presence of hydrocarbon-insoluble asphaltenes. Of further interest is the fact that no vacuum flash column is necessary in order to concentrate the fuel oil boiling above a temperature of about 680° F. This as will be recognized by those having skill in the art of petroleum processing techniques, affords a significant advantage with respect to the overall economics of the process.

DESCRIPTION OF DRAWING

For the purpose of demonstrating the illustrated embodiment, the drawing will be described in connection with the conversion of a vacuum column bottoms, derived from a Middle-East crude oil blend, into maximum quantities of fuel oil. This particular vacuum column bottoms product indicates a gravity of about 16.5° API, an average molecular weight of about 510, an ASTM 50.0% volumetric distillation temperature of about 930° F., and contains about 3.60% by weight of sulfur, 2190 p.p.m. of nitrogen, 54 p.p.m. of vanadium and nickel, has a Conradson carbon residue factor of about 9.0% by weight and contains about 3.0% by weight of heptane-insoluble asphaltenes.

In addition, the description will be directed toward a commercially-scaled unit having a design capacity of about 40,000 barrels per day. In the drawing, the embodiment is presented by means of a simplified flow diagram in which details such as pumps, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as non-essential to an understanding of the invention and the techniques involved. The utilization of such miscellaneous appurtenances, to modify the illustrated process flow, are well within the purview of those skilled in the art. Similarly, it is understood that the charge stock, stream compositions, and boiling ranges, operating conditions, design of fractionators, separators and the like, are illustrative only and may be varied widely without departure from the spirit of our invention, the scope of which is defined by the appended claims.

This particular vacuum column bottoms charge is intended for conversion into high yields of low viscosity, low pour point fuel oil which has an initial boiling point of from 450° F. to 680° F., while maximizing the volu-

metric yields of kerosene and gasoline boiling range fractions. The charge stock is processed in a fixed-bed catalytic conversion zone in admixture with about 10,000 standard cubic feet per barrel of hydrogen, based upon fresh black oil charge stock, at an inlet catalyst temperature of about 650° F. and an inlet pressure of about 2000 p.s.i.g. The liquid hourly space velocity, based upon fresh feed only, is 0.74, and the combined feed ratio, with respect to total liquid feed, is about 1.5:1. With reference now to the drawing, the vacuum column bottoms in an amount of about 41,000 barrels per day, is introduced into the process by way of line 1, is admixed with about 20,500 barrels per day of a hot separator liquid stream in line 2 and a recycled hydrogen-rich gaseous phase, in an amount of about 10,000 standard cubic feet per barrel, in line 3, the mixture continuing through line 1 into heater 5. Not illustrated in the drawing is the technique whereby the total charge to heater 5 is initially heated by way of conventional heat-exchange facilities with various hot effluent streams to a temperature of about 575° F. Heater 5 raises the temperature of the feed mixture to a level of 650° F., the heated mixture passing through line 6 into fixed-bed catalytic reactor 7.

The product effluent, in mixed-phase in line 8, at a temperature of about 750° F., is utilized as a heat-exchange medium in order to lower the temperature to about 700° F., and enters hot separator 9 at a pressure of about 1950 p.s.i.g. A principally vaporous phase is withdrawn from a hot separator 9 by way of line 10 and, after cooling by conventional means, is introduced into cold separator 11 at a temperature of about 100° F. and a pressure of about 1900 p.s.i.g. A hydrogen-rich gaseous phase is removed from cold separator 11 by way of line 3 through the use of compressive means not illustrated in the drawing. After make-up hydrogen is introduced via line 4, the gaseous mixture continues through line 3 to be combined with the liquid feed mixture in line 1. A liquid phase from cold separator 11, comprising principally butanes and heavier normally liquid hydrocarbons, is withdrawn from cold separator 11 by way of line 14, and is introduced into cold flash zone 15.

A principally liquid phase, containing some dissolved hydrogen and light normally gaseous hydrocarbons, is withdrawn from hot separator 9 through line 12, a portion thereof being diverted by way of line 2 as recycled diluent for the fresh charge stock in line 1. The remaining portion of the hot separator liquid stream continues through line 12, being introduced thereby into fractionation zone 13.

Cold flash zone 15 serves to concentrate further butanes and heavier hydrocarbons, as a fourth liquid phase in line 17. Methane, ethane and propane, and hydrogen, hydrogen sulfide, and ammonia are removed from cold flash 15 to a light ends recovery system by way of line 16. The fourth liquid phase in line 17 is introduced into fractionation zone 13 at a locus above that through which the first liquid phase in line 12 is introduced.

A second liquid phase, comprising primarily normally liquid hydrocarbons having a boiling range above about 600° F., is withdrawn from fractionation zone 13 by way of line 23, and introduced therethrough into thermal coil 24 at a temperature of about 700° F., and a pressure of about 400 p.s.i.g. The thermally-cracked product effluent, at a pressure of about 50 p.s.i.g., and a temperature of about 930° F., and in admixture with a side-cut in line 22, is introduced into fractionation zone 13 by way of line 25, and at a locus below that from which the second liquid phase is withdrawn by way of line 23.

As hereinbefore set forth, fractionation zone 13 functions at conditions of temperature and pressure such that an overhead stream consisting primarily of butanes and lighter hydrocarbons is removed via line 18, and a fuel oil fraction comprising hydrocarbonaceous material boil-

ing above a temperature of about 680° F., is removed as a bottoms product by way of line 21. A gasoline boiling range fraction, in the illustration containing pentanes and hydrocarbons boiling up to a temperature of about 330° F., is withdrawn as an intermediate side-cut by way of line 19. In the illustration, the jet fuel fraction, boiling from about 330° F. to about 450° F., and the diesel fuel fraction boiling from about 450° F. to about 680° F., are indicated as being withdrawn as a single side-cut by way of line 20.

In order to further illustrate the process of the present invention, the following Table I indicates the composition of the reaction product effluent from fixed-bed catalytic reaction zone 7, exclusive of any recycle and/or quench streams.

TABLE I.—CATALYTIC REACTION ZONE YIELDS

Component	Wt. percent	Vol. percent
Ammonia.....	0.10	-----
Hydrogen sulfide.....	2.76	-----
Methane.....	0.08	-----
Ethane.....	0.11	-----
Propane.....	0.13	-----
Butanes.....	0.15	0.25
Pentanes.....	0.10	0.15
Hexanes.....	0.07	0.10
Heptane/330° F.....	0.55	0.70
330° F.-450° F.....	1.86	2.19
450° F.-680° F.....	4.39	4.81
680° F.-plus.....	90.53	94.17

In the following Table II, component yields are presented with respect to the overall process, including those component streams removed from fractionator 13, and any normally liquid hydrocarbons which may be recovered in the light ends recovery system which utilizes as the charge thereto, the third vaporous phase in line 16.

TABLE II.—PRODUCT YIELD AND DISTRIBUTION

Component	Wt. percent	Vol. percent	Bbl./day
Ammonia.....	0.10	-----	-----
Hydrogen sulfide.....	2.85	-----	-----
Methane.....	0.24	-----	-----
Ethane.....	0.38	-----	-----
Propane.....	0.74	-----	-----
Butanes.....	0.73	1.21	495
Pentanes.....	0.92	1.40	575
Hexanes-330° F.....	4.61	5.97	2,450
330° F.-450° F.....	5.84	6.99	2,860
450° F.-680° F.....	16.70	18.93	7,750
680° F.-plus.....	67.72	68.77	28,270

The naphtha, or gasoline boiling range fraction, hexanes to 330° F., has a gravity of 60.2° API and contains 0.1% by weight of sulfur. The kerosene cut, 330° F. to 450° F., contains only 0.15% by weight of sulfur, and indicates a gravity of 36.3° API. Of further interest is the fact that the diesel fuel fraction, 450° F. to 680° F., has a gravity of 36.3° API and contains 0.5% by weight of sulfur, while the fuel oil fraction, 680° F. -plus, has a gravity of 18.8° API and contains about 0.95% by weight of sulfur. In order to meet the pour point and viscosity requirement dictated by relatively cold climates, the diesel fuel and fuel oil fractions are blended. The quantities of each fraction, which go to make up the final blend, will vary from one locale to another, as well as from one season to another in any given locale. For illustrative purposes, it will be assumed desirable to blend both fractions en toto. In this manner, 36,020 bbl./day are produced by the present process, and the pour point is about 30° F.-35° F., with the viscosity being about 100 cst. In the situation involving only the fixed-bed catalytic reaction zone, the viscosity would be 200 cst. and the pour point in the range of 45° F.-50° F.

The foregoing specification, and particularly the example integrated into the description of the drawing, indicates the benefits afforded through the utilization of our invention. From a fresh black oil charge of about 41,000 barrels per day, there is produced 42,400 barrels per day of distillable hydrocarbon products, including butanes which have value, for example, as motor fuel blending components. Of further interest is the fact that the chemical consumption of hydrogen, in the overall

process, is only about 0.83% by weight of the total black oil charge stock.

We claim as our invention:

1. A process for the desulfurization of a sulfurous, hydrocarbonaceous black oil which comprises the steps of.

- heating said black oil to a temperature of from 500° F. to about 700° F., reacting said black oil with hydrogen in a catalytic reaction zone, in contact with a catalytic composite and at a pressure greater than about 1000 p.s.i.g.;
- separating the resulting reaction zone effluent, in a separation zone, at substantially the same pressure imposed upon said catalytic reaction zone, to provide a first liquid phase and a first vapor phase;
- introducing at least a portion of said first liquid phase into a fractionation zone, and withdrawing a second liquid phase, having a higher normal boiling range than said first liquid phase from said fractionation zone;
- cracking at least a portion of said second liquid phase in a non-catalytic reaction zone;
- introducing the resulting cracked product effluent into said fractionation zone at a locus below that from which said second liquid phase is withdrawn; and
- recovering a normally liquid hydrocarbon stream, reduced in sulfur concentration, from said fractionation zone.

2. The process of claim 1 further characterized in that at least a portion of said first liquid phase is recycled to combine with said black oil to provide a combined liquid feed ratio to said catalytic reaction zone in the range of from 1.05:1 to about 3.5:1.

3. The process of claim 1 further characterized in that said catalytic reaction zone effluent is introduced into said separation zone at a temperature of from about 700° F. to about 800° F.

4. The process of claim 1 further characterized in that said first vapor phase is separated in a second separation zone at substantially the same pressure imposed upon said first separation zone, to provide a third liquid phase and a second vapor phase rich in hydrogen, and recycling said second vapor phase to combine with said charge stock.

5. A process for the conversion of a sulfurous, hydrocarbonaceous black oil, of which at least about 10.0% boils above a temperature of about 1050° F., into lower-boiling hydrocarbon products of reduced sulfur concentration, which process comprises the steps of:

- heating said black oil to a temperature of from about 500° F. to about 700° F., reacting said black oil with hydrogen in a catalytic reaction zone, and in contact with a catalytic composite at a pressure greater than 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;
- introducing at least a portion of said first liquid phase into a fractionation zone, and withdrawing a second liquid phase, having a higher normal boiling range than said first liquid phase, from said fractionation zone;
- cracking at least a portion of said second liquid phase in a non-catalytic reaction zone;
- introducing the resulting cracked product effluent into said fractionation zone at a locus below that from which said second liquid phase is withdrawn;
- separating said first vapor phase in a second separation zone, at substantially the same pressure imposed upon said first separation zone, to provide a third liquid phase and a second vapor phase rich in hydrogen, and recycling said second vapor phase to combine with said hydrocarbonaceous black oil;

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- (g) separating said third liquid phase in a third separation zone at a pressure lower than that imposed upon said second separation zone, to provide a third vaporous phase and a fourth liquid phase;
 (h) introducing said fourth liquid phase into said fractionation zone at a locus above that from which said second liquid phase is withdrawn; and
 (a) recovering a liquid hydrocarbon stream of reduced sulfur concentration from said fractionation zone.

6. The process of claim 5 further characterized in that said black oil is heated to a temperature of from about 550° F. to about 650° F.

7. The process of claim 5 further characterized in that said fourth liquid phase is introduced into said fractionation zone at a locus above that through which said first liquid phase is introduced into said fractionation zone.

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References Cited

UNITED STATES PATENTS

1,932,174	10/1933	Gaus et al.	196—24
2,282,451	5/1942	Brooks	196—24
2,327,099	8/1943	Eastman	196—49
2,339,918	1/1944	Thomas	196—52
2,355,366	8/1944	Conn	196—24
3,409,538	11/1968	Gleim	208—59

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