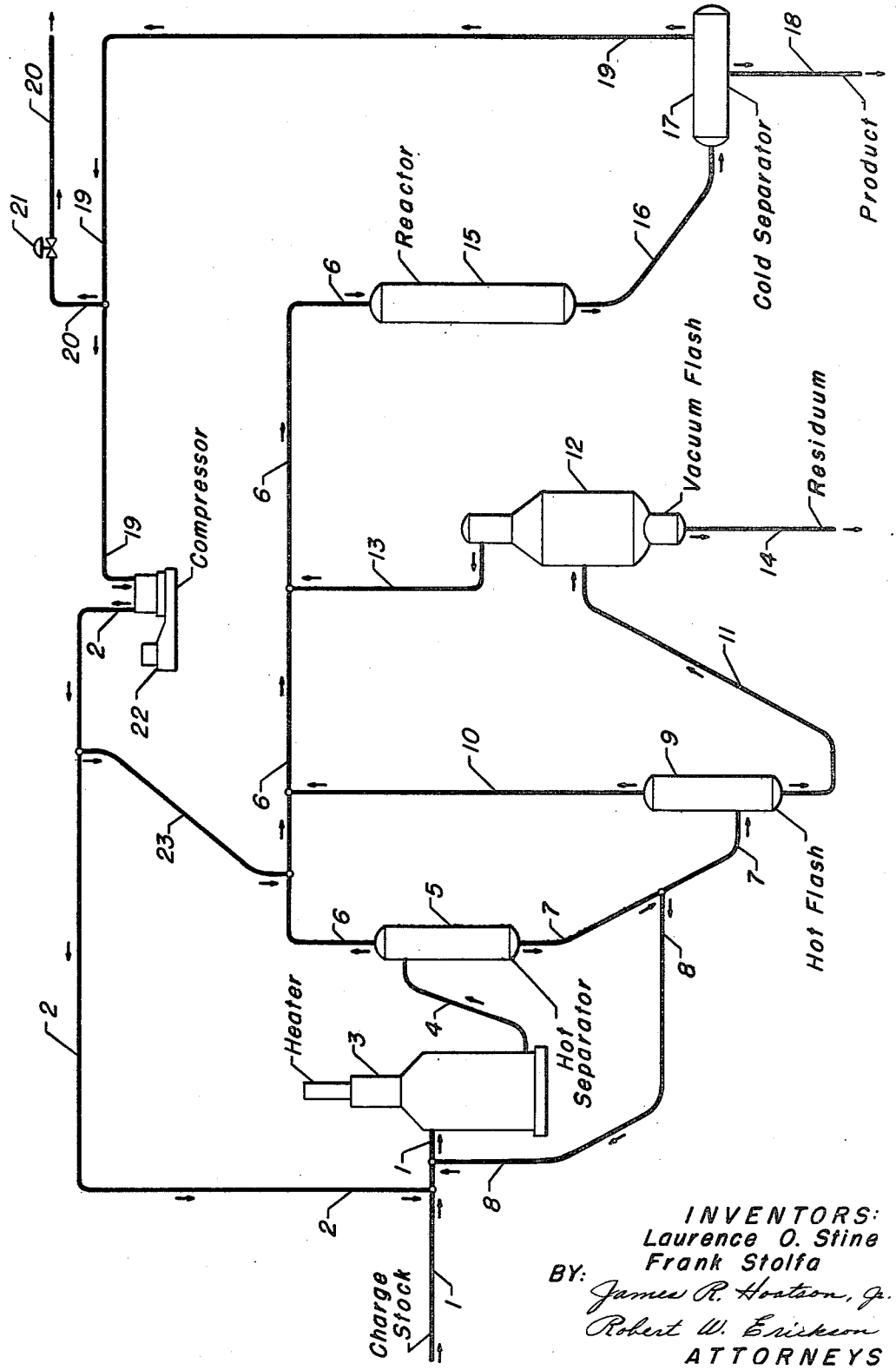
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DESULFURIZATION OF HIGH METAL BLACK OILS

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INVENTORS:
Laurence O. Stine
Frank Stolfa
BY: James R. Hoatson, Jr.
Robert W. Erickson
ATTORNEYS

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DESULFURIZATION OF HIGH METAL BLACK OILS

Laurence O. Stine, Western Springs, and Frank Stolfa, Park Ridge, Ill., assignors to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

A combination process for desulfurizing high metals containing petroleum fractions to produce fuel oil conforming to specifications regarding sulfur concentration. The process involves the integration of hydrogenative cracking and catalytic desulfurization, and is especially applicable to those charge stocks characterized as being more than 10.0% by volume non-distillable, and containing more than about 150 p.p.m. of metals. The fresh charge stock is admixed with a portion of a thermally-cracked product effluent to provide a combined feed ratio greater than 1.4:1, and hydrogen is admixed therewith in an amount less than about 4,000 s.c.f./bbl. of combined liquid feed. In a preferred embodiment, the hydrogen is employ in an amount of from 500 to about 2,500 s.c.f./bbl., and is substantially hydrogen sulfide-free.

Applicability of invention

The combination process described herein is adaptable to the desulfurization of petroleum crude oil residuals with high metals content. More specifically, the present invention is directed toward a combination process for the desulfurization of hydrocarbonaceous residuals including atmospheric tower bottoms product, vacuum tower bottoms product, crude oil residuum, topped and/or reduced crude oils, coal oil extracts, crude oils extracted from tar sands, etc., all of which are commonly referred to in the art as "black oils."

Petroleum crude oils, and particularly the heavy residuals extracted from tar sands, topped or reduced crudes, and vacuum residuum, contain high molecular weight sulfurous compounds in exceedingly large quanties, nitrogenous compounds, high molecular weight organo-metallic complexes, principally comprising nickel and vanadium as the metal component, and heptane-insoluble asphaltic material. The latter is generally found to be complexed with, or linked to, sulfur and, to a certain extent, with the metallic contaminants. A black oil can be generally characterized as a heavy hydrocarbonaceous material of which more than 10.0% (by volume) boils above a temperature of 1050° F. (referred to as non-distillable), and having a gravity, ° API at 60° F., of less than 20.0. Sulfur concentrations are exceedingly high, most often greater than 2.0% by weight, and may range as high as 5.0% by weight. Conradson Carbon Residue factors exceed 1.0 weight percent, and a great proportion of black oils exhibit a Conradson Carbon Residue factor above 10.0. An abundant supply of such hydrocarbonaceous material currently exists, most of which has a gravity less than 10.0° API, and which is characterized by a boiling range indicating that 30.0% or more boils above a temperature of about 1050° F.

The combination process encompassed by the present invention is praticularly directed toward the desulfurization of black oils severely contaminated by a high metals content—i.e. containing more than 150 p.p.m. thereof. Specific examples of the charge stocks to which the present scheme is adaptable, include a vacuum tower bottoms

product having a gravity of 7.1° API at 60° F., and containing 4.05% by weight of sulfur and 23.7% by weight of asphalts; a "topped" Middle-east Gach Saran crude oil having a gravity of 11.0° API and containing 10.1% by weight of asphaltenes and 5.2% by weight of sulfur; and, a vacuum residuum having a gravity of 8.8° API, containing 3.0% sulfur and 4300 p.p.m. (by weight) of nitrogen. Other charge stocks, exemplary of those having high metals content, include a vacuum residuum having a gravity of 8.7° API and containing 4.31% by weight of sulfur, 6,100 p.p.m. of nitrogen, a Conradson Carbon factor of 13.57% by weight, 9.3% by weight of heptane-insolubles and about 626 p.p.m. of total metals.

The present invention affords the conversion of such material into distillable hydrocarbons, heretofore having been considered virtually impossible to achieve on a reasonably continuing basis with an acceptable catalyst life, while simultaneously effecting desulfurization to a level of 1.0% or less. The principal difficulty, heretofore encountered, resides in the lack of sulfur stability of many catalytic composites in the presence of such relatively large quantities of metals—i.e. from 150 p.p.m. to as high as 700 p.p.m., computed as the element—and further from the presence of large quantities of asphaltic material and other non-distillables. The asphaltic material comprises high molecular weight coke precursors, insoluble in light hydrocarbons such as pentane and/or heptane. Generally, the asphaltic material is found to be dispersed within the black oil, and, when subjected to elevated temperature, has the tendency to fluocculate and polymerize whereby the conversion thereof to more valuable oil-insoluble products becomes extremely difficult.

Prior art

Heretofore, in the area of catalytic processing of such hydrocarbonaceous material, two principal approaches have been advanced: liquid-phase hydrogenation and vapor-phase hydrocracking. In the former type of process, oil in liquid phase is generally passed upwardly, in admixture with hydrogen, into a fixed-bed or slurry of subdivided catalyst; although perhaps effective in removing at least a portion of the metallic complexes, this type process is relatively ineffective with respect to desulfurization and insoluble asphaltenes which are dispersed within the charge. Furthermore, since the reaction zone is generally maintained at an elevated temperature, the retention of unconverted asphalts, suspended in a free liquid-phase oil for an extended period of time, results in flocculation, thereby making efficient conversion thereof substantially more difficult. Furthermore, 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 cracking reactions in the presence of hydrogen; any particular catalytic composite present succumbs rapidly to deactivation as a result of the deposition of metals and metal-containing coke thereon. Such a process requires an attendant high capacity catalyst regeneration system in order to implement the process on a continuous basis.

Before describing processes which are exemplary of those known in present-day petroleum technology, our invention will be set forth in brief. The invention, encompassing the combination process described herein, is founded upon several concepts. Of these, paramount is the fact that a highly sulfurous charge stock containing metals in a concentration ranging from about 150 to about 700 p.p.m. (computed as if existing in the elemental state), precludes catalytic processing, whether fixed-bed, or fluidized, where the catalyst comprises metals on the usual metal oxide carrier material. The metals deposit

upon the catalyst particles from the outset of the process, with the result that any catalyst rapidly loses its desired activity for conversion, as well as its intended selectivity. The deposition of coke upon the catalytic composite further aggravates this situation. In utilizing hydrogenative cracking, in the absence of a catalytic composite, the quantity of hydrogen being admixed with the charge stock attains a certain degree of criticality. In accordance with our invention, the hydrogen concentration is less than 4,000 s.c.f./bbl., based on total liquid feed. This avoids severe plugging of the reaction coil, or tubes, otherwise resulting from the formation of coke due to the high level of vaporization within the reaction coil. As hereinafter set forth, one embodiment involves utilizing substantially hydrogen sulfide-free hydrogen in an amount of from 500 to 2,500 s.c.f./bbl.

A series of separation zones is employed to separate the thermal-cracked effluent into distillable hydrocarbons and a residuum fraction containing substantially all the metals originally in the fresh charge stock. The distillable hydrocarbons, substantially free from metals—i.e. containing less than about 20 p.p.m. thereof—and reduced in high molecular weight sulfur compounds, are admixed with additional hydrogen and subjected to catalytic desulfurization in a fixed-bed system.

Candor compels recognition of the fact that published literature is replete with many types of thermal cracking processes designed to effect the conversion of hydrocarbon mixtures akin to those hereinafter described. Furthermore, it must be acknowledged that "hydrogenative cracking," or "hydroconversion" thermal processes are described in combination with hydrogenation and/or desulfurization units. No attempt will be made herein to describe exhaustively these prior art processes; it will suffice to discuss briefly those of more recent vintage.

United States Patent No. 2,989,459 discloses a hydroconversion process wherein the liquid portion of the effluent is quenched to precipitate solid particulate asphalts. The inventive concept appears to reside in the combination of (1) turbulent flow according to a particular formula and (2) rapid quenching of the liquid product. There is no recognition of the difficulties attendant sulfurous charge stocks of high metals content, nor of the technique of the present invention to decrease the risk of hot spots developing in the reaction coil. As will be noted, there is no such rapid quenching of the hydroconversion product effluent in the combination process described herein. Similar processes are described in United States Patents No. 2,989,460 and No. 2,989,461. In the former, the hydroconversion liquid product is in part employed in a water-gas shift reaction to produce hydrogen for use in the hydroconversion reaction coil. The latter is directed only to the turbulence level at which the hydroconversion is effected.

A more recent United States Patent, No. 3,017,345, involves a combination process in which hydroconversion at highly turbulent flow is coupled with catalytic desulfurization of at least a portion of the liquid product. Similar process form the subject matter of United States Patents 3,089,843 and 3,228,871.

While a casual perusal would seem to indicate some pertinency of the foregoing prior art processes, and particularly the last three, it should be noted that there is no awareness of the necessity for hydrogen in an amount less than 4,000 s.c.f./bbl., based upon combined liquid feed, in the hydroconversion reaction coil, or heater.

Objects and embodiments

The principal object of the present invention is to provide an economically feasible catalytic process for the desulfurization and conversion of black oils into distillable hydrocarbons of lower molecular weight. A corollary objective is to prevent localized coking in heater coils employed in hydrogenative cracking to a minimum residuum containing metallic contaminants originating in the hydrocarbon charge stock.

Another object is to convert heavy hydrocarbon charge stocks, a significant amount of which exhibits a boiling range above a temperature of 1050° F.—i.e. at least about 10.0% boils above this temperature, and often more than 30.0%—into lower boiling distillable hydrocarbons, having a sulfur concentration less than 1.0% by weight.

Another object of our invention is to provide a process for desulfurizing and converting black oils having a gravity, °API at 60° F., less than about 20.0.

Another object is to effect the conversion and desulfurization of black oils with minimum yield loss to light normally gaseous hydrocarbons, while producing high yields of fuel oil containing less than 1.0% by weight of sulfur.

In one embodiment, therefore, the present invention encompasses a combination process for the conversion of a sulfurous, metals-containing hydrocarbonaceous charge stock, of which at least about 10.0% boils above a temperature of 1050° F., into lower boiling hydrocarbon products of decreased sulfur content, which process comprises the steps of: (a) thermally cracking a mixture of said charge stock, hydrogen and a portion of a previously thermally-cracked product effluent, said hydrogen being in an amount less than 4,000 s.c.f./bbl. of combined liquid feed, at a reaction temperature above about 800° F. and at superatmospheric pressure; (b) separating the resulting cracked product effluent, in a first separation zone, at substantially the same temperature and pressure, to provide a first vapor phase and a first liquid phase; (c) recycling at least a portion of said first liquid phase to combine with said charge stock in a combined feed ratio greater than about 1.4:1; (d) separating the remainder of said first liquid phase in a second separation zone at substantially the same temperature, and a pressure in the range of from subatmospheric to about 100 p.s.i.g., to provide a second vapor phase and a metals-containing residuum fraction; (e) combining said first and second vapor phases and reactingt the resultant mixture in a catalytic conversion zone in contact with a catalytic composite and at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons; (f) separating the resultant catalytic conversion zone effluent in a third separation zone at a temperature of from about 60° F. to about 140° F. to provide a hydrogen-rich third vapor phase and a normally liquid hydrocarbon product; and, (g) recycling at least a portion of said third vapor phase to combine with said charge stock.

Other embodiments of our invention, as hereinafter set forth in greater detail, reside primarily in particularly desirable process variables and processing techniques. For example, where separate heaters are employed, the liquid charge stock is heated to a temperature below that at which thermal cracking reactions are effected, and generally within the range of from about 700° F. to about 800° F. The hydrogen is, however, heated to a temperature above the temperature at which thermal cracking is effected—i.e. above about 900° F. The precise levels to which the individual streams are heated is, of course, dependent upon the sulfur and metal characteristics of the charge stock as well as the relative concentrations of charge stock and hydrogen; however, the temperature of the charge stock-hydrogen mixture, introduced into a reaction chamber, is within the range of from about 825° F. to about 1000° F.

Other objects and embodiments of our invention will be evident from the following, more detailed description of the present combination process.

Summary of invention

As hereinbefore set forth, the principal function of the present invention resides in the production of maximum quantities of fuel oil containing less than 1.0% by weight of sulfur. Through the utilization of our combination

process, this is accomplished in a relatively simple manner, in a highly economically attractive fashion and while avoiding the difficulties and pitfalls of currently known schemes. Paramount is the virtually complete elimination of localized coking in thermal cracking heaters, or reaction coils, through the expediency of maintaining the hydrogen supplied by internal recycle from the catalytic desulfurization zone, and make-up hydrogen, to a level less than 4,000 s.c.f./bbl. of combined liquid feed, in order that vaporization within the reaction coil, or heater tubes, be maintained at a minimum. In order to further inhibit polymerization and condensation reactions, the quantity of hydrogen may be lowered to a level within the range of from about 500 to about 2,500 s.c.f./bbl. In this embodiment, however, the hydrogen stream entering the reaction coil is substantially free from hydrogen sulfide. Substantially hydrogen sulfide-free is intended herein to connote that the concentration thereof is below a level of 15.0 grains per 100 s.c.f. of hydrogen, and preferably below 5.0 grains per 100 s.c.f. In any event, an essential feature resides in maintaining a hydrogen rate of less than 4,000 s.c.f./bbl. of combined liquid charge.

When, in accordance with one particular embodiment, separate heaters are employed to raise the temperature of the liquid charge stock and the hydrogen, the liquid feed, inclusive of a comparatively heavy aromatic recycle fraction from a hot separator, is separately heated to a temperature below that at which thermal cracking of hydrocarbons is effected. The first, or combined feed heater, raises the liquid charge to a temperature level below about 800° F., and preferably to a temperature within the range of about 700° F. to about 800° F. In a separate heater, the hydrogen stream, in an amount of from 500 to less than about 4,000 s.c.f./bbl. (based upon total hydrocarbon charge inclusive of recycle) is heated to a temperature above that at which thermal cracking of hydrocarbons is effected. Therefore, the hydrogen will be separately heated to a temperature within the range of about 900° F. to about 1000° F. or higher. The thus-heated streams are then admixed prior to introduction into a reaction chamber. In a preferred technique, the separately heated streams are introduced into a common header wherein sufficient turbulence is generated to assure thorough contact and complete heat exchange between the streams prior to introduction into the reaction chamber. The reaction chamber or reaction coil will be maintained under an imposed pressure within the range of about 1000 to about 3000 p.s.i.g.

The effluent from the reaction coil, or reaction chamber when separate heaters are employed, is introduced into a hot separator serving as a first separation zone to provide a first vaporous phase and a first liquid phase. At least a portion of this first liquid phase from the hot separator is diverted and combined with the heavy fresh charge stock of hydrogen, serving as a highly aromatic solvent stream to maintain the asphaltics dispersed and in solution, and thus available to hydrogen. A second portion of the first liquid phase may be cooled and recycled to the inlet of this separation zone such that the overhead temperature within the hot separator is at a maximum level of about 850° F. Thus, the first separation zone is temperature controlled to function within the range of from about 800° F. to about 850° F. Lower temperatures permit ammonium salts, resulting from the conversion of nitrogenous compounds, to fall into the liquid phase, thereby effecting serious plugging problems, whereas higher temperatures cause heavier hydrocarbons containing unconverted asphaltics to be carried over in the vapor phase.

The first liquid phase from the hot separator is recycled to combine with the fresh, heavy black oil charge stock in an amount which results in a combined feed ratio to the reaction coil greater than about 1.4:1. Combined feed ratio (CFR) is herein defined as the volumes of total liquid charge per volume of fresh liquid feed. Although combined feed ratios up to about 10.0:1 may be suitably employed, lower ratios are preferred, and are in the range of from 1.4:1 to about 3.5:1. This hot separator is maintained at essentially the same pressure and at essentially the temperature of the reaction zone effluent; as above set forth, however, the temperature is controlled in the range of about 800° F. to about 850° F.

A hot flash zone functions at a significants reduced pressure of from subatmospheric to about 100 p.s.i.g., and may comprise a low-pressure hot flash zone—i.e. about 60 p.s.i.g.—in combination with a vacuum column maintained at about 35–60 mm. of Hg absolute. The hot flash system serves to eliminate further the difficulties stemming from emulsification problems, and to provide a residuum fraction containing the unconverted asphaltics, extremely high molecular weight sulfurous compounds and substantially all the metals originally present in the fresh hydrocarbon charge stock.

The first and second vapor phases, from the hot separator and flash system, are combined, admixed with additional hydrogen, where necessary, and introduced into a catalytic desulfurization zone. This reaction zone is maintained under an imposed pressure of from 500 to about 5000 p.s.i.g., and preferably from about 1000 to about 3000 p.s.i.g. Economics of the overall process are further enhanced in those instances where the catalytic reaction zone is maintained at the same pressure as the hydroconversion chamber, or reaction coil, or slightly lower, allowing only for the normally experienced pressure drop due to the flow of materials through the system.

The catalytic composite disposed within the catalytic reaction, or conversion 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 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% 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 group consisting of the metals of Groups 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. The metallic components of Group VI–B are preferably present in amounts within the range of about 1.0% to about 50.0% 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 as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, etc., and mixtures of two or more including silica-alumina, silica-zirconia, silica-magnesia, silica - titania, alumina - zirconia, silica - alumina - boron phosphate, 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.

Generally, the charge to the catalytic reaction zone

will contain both light and heavy normally liquid hydrocarbons, gaseous components including light hydrocarbon gases, hydrogen, hydrogen sulfide, etc. Usually, the end boiling point of this material will be 1050° F. or less, the greater volume thereof being in the 650° F. to 1050° F. boiling range, although a significant amount will be in the butanes—400° F. range. The operating conditions will be dependent to a great extent upon the characteristics of the total charge thereto, and upon the desired product quality and quantity. Generally, however, the temperature within the reactor will be maintained by controlling the temperature of the hydrocarbon-hydrogen feed mixture within the range of from about 650° F., to about 850° F.; an imposed pressure within the range of about 1000 to about 3000 p.s.i.g. is employed. The hydrocarbon charge stock contacts the catalytic composite at a liquid hourly space velocity of from about 0.5 to about 10.0. The hydrogen concentration will be in the range of from about 5,000 to 50,000 s.c.f./bbl. The catalyst disposed in the reaction zone serves the principal function of converting sulfurous compounds. A particularly suitable catalyst comprises relatively large quantities of a Group VI–B metal—i.e. from 6.0% to 45.0% by weight of molybdenum—and lesser quantities of an iron-group metal—i.e. about 1.0% to about 6.0% by weight of nickel.

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 embodiment of the present invention.

Description of the drawing

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

In demonstrating the illustrated embodiment, the drawing will be described in connection with a unit designed to effect the desulfurization of a La Guna reduced crude oil. This charge stock is the previously described Venezuelan crude containing 2.61% sulfur and about 730 p.p.m. of metals, principally nickel and vanadium. It is 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 our invention, the scope of which is defined by the appended claims. With reference now to the drawing the reduced crude is introduced into the process via line **1**, being admixed therein with a hydrogen-rich recycled stream in line **2**, the source of which is hereafter described. Following suitable heat-exchange with various hot effluent streams, which engineering technique is not illustrated, the mixture continues through line **1**, and is further admixed with a highly aromatic, heavy recycle stream in line **8**. The combined charge continues further in line **1** into heater **3**, wherein the temperature is increased to a level of from 825° F. to about 1000° F. The concentaration of hydrogen, in admixture with the reduced crude and heavy highly aromatic recycle, is about 3,850 s.c.f./bbl., based upon the combined liquid feed, the latter being at a CFR of about 2.0.

On one particular embodiment, the reduced crude and heavy recycle mixture is heated, in the absence of hydrogen, to a temperature level in the range of 700° F. to about 800° F. The hydrogen stream is separately heated to a temperature above thermal cracking temperature, and in the range of 900° F. to about 1200° F. The thus-heated two streams can be introduced through a common header into the upper portion of a reaction zone, or chamber. This scheme further insures against excessive coke formation, since the hydrocarbons are brought to reaction temperatures in the absence of the excessive skin temperatures normally generated in a fired heater.

The mixed-phase cracked product effluent is withdrawn via line **4**, and, following its use as a heat-exchange medium, whereby the temperature is lowered to a level below about 850° F., is introduced into hot separator **5**. This vessel is maintained at essentially the same pressure as heater, or reaction coil **3**, allowing only for pressure drop due to fluid flow through the system. A principally vaporous phase is withdrawn from hot separator **5** through line **6**, and a principally liquid phase is withdrawn through line **7**. The greater proportion of the hydrocarbonaceous vapor phase in line **6** consists of material boiling below about 850° F., while the principally liquid phase in line **7** is primarily 800° F.-plus hydrocarbons.

The liquid phase in line **7** is introduced into hot flash zone **9**, entering therein at a temperature of about 835° F. As preciously stated, a portion of the hot separator liquid phase in line **7** is diverted through line **8** to combine with the fresh charge stock in line **1**; still another portion may be recycled, with or without heat-exchange, to combine with the cracked effluent in line **4** as a means of controlling the temperature of the mixture entering hot separator **5** in the range of 800° F. to 850° F. Hot flash zone **9** functions at a reduced pressure of from about 50 to about 100 p.s.i.g., and at a slightly lower temperature than hot separator **5**. This vessel serves principally to concentrate the 400° F.-plus hydrocarbons in a liquid phase in line **11**, while producing a vaporous phase substantially free from the 1050° F.-plus material and containing only a minor amount of 650° F.–1050° F. hydrocarbons; the latter is shown leaving vessel **9** by way of line **10**.

The principally 400° F.-plus liquid phase is introduced into vacuum flash zone **12** by way of line **11**. This zone is maintained at about 35 mm. of Hg absolute to separate and concentrate the uncoverted non-distillables as a residuum in line **14**, and which contains substantially all the metals originally present in the reduced crude. Analyses indicate that this residuum, or pitch, has a gravity of from 0.5 to 2.0° API and an average molecular weight from 600 to about 800, or higher. Another principally vaporous fraction is removed from vacuum flash zone **12** via line **13**. The first principally vaporous phase from hot separator **5** continues through line **6**, in admixture with hydrogen from line **23**, and is further admixed with the vaporous phases in lines **10** and **13**, from hot flash zone **9** and vacuum flash zone **12**, respectively. The resulting mixture continues through line **6** into reactor **15** which contains a fixed-bed of a catalytic composite of the type hereinbefore described, for example, 1.8% by weight of nickel and 16.0% by weight of molybdenum (calculated as if in the elemental state), which are composited with a carrier material of 12.0% by weight of silica and 88.0% by weight of alumina.

The principal function of reactor **15** resides in the maximum production of a 650° F.-plus fuel oil containing less than 1.0% sulfur. The inlet temperature of the catalyst bed in reactor **15** is about 700° F. (resulting in a maximum catalyst bed temperature of about 800° F., as a result of the exothermicity of the reactions being effected), the pressure is about 1500 p.s.i.g., and the liquid hourly space velocity, exclusive of any liquid recycle, is is 0.93. In the event liquid recycle to reactor **15** is utilized as an operating technique, the combined liquid feed ratio is preferably in the range of 1.5 to 3.5. The use of such technique is dependent primarily upon the overall characteristics of the liquid charge to reactor **15**, as well as the specifications imposed upon product quality.

Reactor **15** effluent, following use as a heat-exchange medium, is cooled to about 80° F., and passes into cold

separator **17** via line **16**. The normally liquid portion of the reactor product effluent, pentanes and heavier hydrocarbons, including some butanes, is removed as a product stream via line **18**. Normally gaseous hydrocarbons, hydrogen and hydrogen sulfide resulting from the conversion of sulfurous compounds are withdrawn from cold separator **17** by way of line **19**. Cold separator **17** serves also as the focal point for pressure control of the system; there is provided, therefore, line **20** containing control valve **21** for the purpose of venting a quantity of the gaseous phase in line **19**. The remainder continues via line **19** into compressor **22**. Since hydrogen is consumed within the overall process, and at least a minor portion suffers solution loss, it is necessary to supplant the consumed hydrogen with make-up hydrogen from some suitable external source—i.e. a catalytic reforming unit. Make-up hydrogen may be introduced into the system at any suitable point; however, the operation is facilitated by introducing the make-up hydrogen on the suction side of compressor **22**. Compressor **22** discharges into line **2** from which a portion of the hydrogen recycle stream is diverted, as necessary for pressure control, by way of line **23** to combine with the charge in line **6** to catalytic reactor **15**.

Example

The following example is presented for the purpose of further illustrating the process of the present invention, and to indicate the benefits afforded the utilization thereof in maximizing the production of fuel oil containing less than 1.0% by weight of sulfur. For the purpose of demonstrating the embodiment illustrated, the drawing will be further described in connection with a comercially-scaled unit having a fresh stock charge rate of about 25,000 bbl./day (for the purposes of the example, the charge rate is 24,800 bbl./day). It is understood that the charge stock, stream compositions, operating conditions, vessel designs, separators, catalyst, and the like are exemplary only, and may be varied widely without departure from our invention, the scope and spirit of which is defined by the appended claims. The charge stock, for which the commercial unit is designed, is a Venezuelan crude oil (La Guna), having the properties set forth in the following Table I.

TABLE I.—REDUCED CRUDE CHARGE STOCK PROPERTIES

Gravity, °API @ 60° F.	14.4
Distillation, D1160, ° F.:	
Initial boiling point	480
5.0%	610
10.0%	650
30.0%	850
50.0%	[1] 1045
Nitrogen, p.p.m.	3500
Sulfur, wt. percent	2.61
Conradson Carbon, wt. percent	11.84
Heptane-insolubles, wt. percent	7.33
Metals, p.p.m. (approx.)	[2] 730

[1] At a distillation temperature of 1050° F., 55.0% by volume was distilled.
[2] Nickel and vanadium only.

The charge stock, in an amount of 351,003 lbs./hr. (691 mols/hr.), at a temperature of about 405° F., following heat-exchange with various hot product streams, is admixed with 66,541 lbs./hr. of a hydrogen-rich recycled gaseous phase, 85.0 mol. percent of which is hydrogen. Of the remainder, 4.0 mol. percent is hydrogen sulfide and 11.0% is C_1–C_3 normally gaseous paraffins, primarily methane. The charge stock is further admixed with about 24,800 bbl./day of a hot separator liquid phase to provide a combined feed ratio of 2.0:1. The total charge of the hydroconversion zone is at a temperature of about 450° F. and a pressure of about 1700 p.s.i.g.

The hydroconverted effluent, at a temperature of 875° F. and a reaction coil outlet pressure of about 1500 p.s.i.g., is introduced into a hot separator. A vacuum gas oil stream, in an amount of 31,900 lbs./hr. is introduced into the hot separator at a locus in the upper portion in order to maintain the temperature of the vaporous stream withdrawn from the top of the hot separator at about 840° F. The charge to the hot separator, exclusive of liquid recycle streams, being the hydroconversion zone effluent, has the composition indicated in the following Table II. In the table, this stream is designated by line number **4**, as it appears in the figure; similarly, the compositions of the hot separator vapor phase (line **6**) and liquid phase (line **7**) are presented. For convenience the quantities of the various components are given in terms of mols./hr.

TABLE II.—HOT SEPARATOR STREAM ANALYSES

Line number	4	6	7
Component:			
Hydrogen sulfide	579.1	573.3	5.8
Hydrogen	10,412.5	10,332.4	80.1
Methane	1,596.4	1,582.6	13.8
Ethane	55.7	54.6	1.1
Propane	67.7	66.3	1.4
Butanes	50.7	49.6	1.1
C_5–400° F.	231.6	221.2	10.4
400° F.–650° F.	294.9	261.1	33.8
650° F.–1050° F.	534.8	231.5	303.3
Residuum*	135.2	3.5	131.7

*Residuum containing substantially all the metals originally contained in the reduced crude.

It should be noted that the above balances do not account for various recycle and/or heat exchange streams as would be employed by those having skill in petroleum technology. In the foregoing table, no distinction is made between paraffins and olefins in a given hydrocarbon class—i.e. "butanes" are inclusive of all hydrocarbons having four carbon atoms, including isobutanes and butenes.

The principally liquid bottoms stream from the hot separator, at a temperature of 850° F. and a pressure of about 1495 p.s.i.g., is introduced into a hot flash system. The commercially designed unit utilizes a low pressure flash at a pressure of about 35 p.s.i.g., and a vacuum flash at a subatmospheric pressure of 35 mm. of Hg. Pitch is recovered from the hot flash system in an amount of 68,516 lbs./hr., of which about 2.75% by weight is sulfur. The remainder of the material from the hot flash system is combined with the principally vaporous phase from the hot separator, the mixture being employed as the charge to the catalytic desulfurization zone (reactor **15** in the drawing).

The total charge to reactor **15** is, of course, the mixture of the component in lines **6**, **10**, and **13**, being the principally vaporous phases from the hot separator and hot flash system. The 70,000 lbs./hr. of pitch (approximately 4,500 bbl./day) contains about 2.75% by weight of sulfur; as hereinafter set forth, the pitch is blended with a portion of the normally liquid desulfurized effluent to increase the quantity of fuel oil produced. Since the pitch also contains substantially all the metals originally present in the reduced crude (the normally liquid charge to reactor **15** contains only about 12.0 p.p.m. of metals), efficient operation of reactor **15** can be effected over a prolonged period of time. Reactor **15** contains a catalytic composite of 16.0% by weight of molybdenum and 1.8% by weight of nickel (computed on the basis of the elemental metals) impregnated on a carrier material of 12.0% by weight silica and 88.0% by weight of alumina. Reactor **15** is maintained at a pressure of about 1400 p.s.i.g. and a temperature, at the inlet to the catalyst bed of 650° F. Since the reactions being effected are primarily exothermic, the temperature is controlled to provide a maximum of 750° F. at the reactor outlet. The catalytic composite is employed in an amount such that the liquid hourly space velocity therethrough is 2.0.

In the commercially-designed unit, the second principally vaporous phase, line **10** in the drawing, is passed into a cold separation zone functioning at a temperature of about 120° F. and a pressure of about 35 p.s.i.g. Ap-

proximately 701 lbs./hr. of the material in line **10** is removed as an overhead stream to a gas concentration unit. This stream comprises 655 lbs./hr. of butanes and lighter normally gaseous material, and 46 lbs./hr. of normally liquid C_5–400° F. hydrocarbons. Thus, the total feed to reactor **15**, being the mixture of the material in lines **6**, **10** and **13** (all indicated as being combined in line **6** entering reactor **15**) is decreased by the quantity of the overhead stream.

In the following Table III, analyses are presented for the charge to reactor **15** and the reactor effluent (line **16**) which is introduced into cold separator **17**. Also presented is the component analysis for the cold separator liquid product (line **18**). Again the values are in mols/hr. for convenience.

TABLE III.—REACTOR 15 ANALYSES

Line Number	6	16	18
Component:			
Hydrogen sulfide	573.5	660.3	110.5
Hydrogen	10,332.4	9,358.0	121.5
Methane	1,582.7	1,588.6	76.8
Ethane	54.6	59.4	59.4
Propane	66.5	70.6	70.6
Butanes	49.8	55.8	55.8
C_5–400° F.	228.0	283.1	283.1
400° F.–650° F.	294.9	495.8	495.8
650° F.–1050° F.	534.8	360.5	360.5
Residuum	3.6	2.7	2.7

The product stream in line **18** is fractioned to remove 44,365 lbs./hr. of material boiling below 400° F., and to provide a heavier material to blend with the pitch (residuum removed from the vacuum flash via line **14**) to form the fuel oil containing less than 1.0% by weight of sulfur. To complete this illustrative example, the components of the blend, and analyses thereof, are presented in the following Table IV.

TABLE IV.—FUEL OIL BLENDED PRODUCT

Component	°API	Mols/hr.	Wt. percent S	Bbl./day
400° F.–650° F.	35.2	495.8	0.05	8,206
650° F.–1,050° F.	22.5	360.5	0.20	10,353
Residuum	0.5	134.3	2.75	4,485
Fuel oil blend	21.7	990.6	0.73	23,044

The foregoing specification and illustrative example clearly indicate the means by which the persent combination process is effected, and the benefits afforded through the utilization thereof. From the total charge of 24,800 bbl./day, fuel oil, having a sulfur content of 0.73% by weight, was produced in an amount of 23,044 bbl./day, or about 92.0% by volume.

We claim as our invention:

1. A combination process for the conversion of a sulfurous, metals-containing hydrocarbonaceous charge stock, of which at least about 10.0% boils above a temperature of 1050° F., into lower boiling hydrocarbon products of decreased sulfur content, which process comprises the steps of:

(a) thermally cracking a mixture of said charge stock, hydrogen and a portion of a previously thermally-cracked product effluent, said hydrogen being in an amount less than 4,000 s.c.f./bbl. of combined liquid feed, at a reaction temperature above about 800° F. and at superatmospheric pressure;

(b) separating the resulting cracked product effluent, in a first separation zone, at substantially the same temperature and pressure, to provide a first vapor phase and a first liquid phase;

(c) recycling at least a portion of said first liquid phase to combine with said charge stock in a combined feed ratio greater than about 1.4:1;

(d) separating the remainder of said first liquid phase in a second separation zone at substantially the same temperature and a pressure in the range of from subatmospheric to about 100 p.s.i.g., to provide a second vapor phase and a metals-containing residuum fraction;

(e) combining said first and second vapor phases and reacting the resultant mixture in a catalytic conversion zone in contact with a catalytic composite and at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons;

(f) separating the resultant catalytic conversion zone effluent in a third separation zone at a temperature of from about 60° F. to about 140° F. to provide a hydrogen-rich third vapor phase and a normally liquid hydrocarbon product; and,

(g) recycling at least a portion of said third vapor phase to combine with said charge stock.

2. The process of claim **1** further characterized in that said charge stock, thermally-cracked effluent and hydrogen are admixed and the resulting mixture is heated to a reaction temperature above about 800° F.

3. The process of claim **1** further characterized in that said charge stock and thermally-cracked product effluent are heated to a temperature below about 800° F., said hydrogen is separately heated to a temperature above 900° F., and the thus-heated effluents are admixed and introduced into a thermal reaction chamber under an imposed pressure of from 500 to about 5000 p.s.i.g.

4. The process of claim **1** further characterized in that the mixture of said first and second vapor phases is introduced into said catalytic conversion zone at a temperature within the range of from about 650° F. to about 850° F.

5. The process of claim **1** further characterized in that said hydrogen is present in an amount of from 500 to about 2,500 s.c.f./bbl.

6. The process of claim **5** further characterized in that said hydrogen is substantially hydrogen sulfide-free.

7. The process of claim **1** further characterized in that said combined feed ratio is within the range of from about 1.4:1 to about 10.0:1.

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HERBERT LEVINE, Primary Examiner

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