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CONVERSION OF BLACK OILS TO MAXIMIZE GASOLINE PRODUCTION

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The invention described herein is adaptable to a process for the conversion of petroleum crude oil into lower boiling hydrocarbon products. More specifically, the present invention is directed toward a process for converting atmospheric tower bottoms products, vacuum tower bottoms products (vacuum residuum), crude oil residuum, topped crude oils, crude oils extracted from tar sands, etc., all of which are sometimes referred to as "black oils," and which contain a significant quantity of asphaltic material. In particular, the process herein defined affords the maximum possible production of gasoline boiling range hydrocarbons from such material.

Petroleum crude oils, particularly the heavy oils extracted from tar sands, topped or reduced crudes, and vacuum residuum, etc., contain high molecular weight sulfurous compounds in exceedingly large quantities. In addition, such crude, or black oils contain excessive quantities of nitrogenous compounds, high molecular weight organo-metallic complexes principally nickel and vanadium, and asphaltic material. The high molecular weight asphaltic material is generally found to be complexed, or linked with sulfur and, to a certain extent, with the organo-metallic contaminants. Currently, an abundant supply of such hydrocarbonaceous material exists, most of which has a gravity less than 20.0° API at 60° F., and a significant quantity of which has a gravity less than 10.0° API. This material is generally further characterized by a boiling range indicating that 10% by volume, and generally more, boils above a temperature of about 1050° F. The utilization of these high molecular weight black oils, as a source of more valuable liquid hydrocarbon products, is precluded by present-day refining techniques, due especially to the exceedingly high sulfur and asphaltic concentrations. The conversion of a significant proportion of the charge stock into distillable hydrocarbons—i.e. those boiling below about 1050° F.—has hitherto been totally nonfeasible from an economic standpoint. Yet, the abundant supply virtually demands such conversion, especially as a means for satisfying the ever increasing need for greater volumes of the lower boiling distillables.

The process of the present invention is particularly directed toward the catalytic conversion of black oils into distillable hydrocarbons boiling in the gasoline boiling range in volumetric yields of 100.0% or more, based upon volumes of charge stock. Specific examples of the black oils, illustrative of those to which the present scheme is especially applicable, include a vacuum tower bottoms product having a gravity of 7.1° API at 60° F., containing 4.05% by weight of sulfur and 23.7% by weight of asphaltics; a "topped" Middle East Kuwait crude oil, having a gravity of 11.0° API at 60° F., containing 10.1% by weight of asphaltenes and 5.20% by weight of sulfur; and, a vacuum residuum having a gravity of 8.8° API at 60° F., containing 3.0% by weight of sulfur and 4300 ppm. of nitrogen and having a 20.0%

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volumetric distillation point of 1055° F. The present invention affords the conversion of the majority of such material into gasoline boiling range distillable hydrocarbons, heretofore having been considered virtually impossible to achieve on an economically feasible basis. The principal difficulty resides in the lack of a suitable technique which would afford many catalytic composites a degree of sulfur stability, while simultaneously producing lower boiling products substantially free from sulfur, and from the presence of the asphaltic material. This asphaltic material consists primarily of high molecular weight, non-distillable coke precursors, insoluble in light hydrocarbons such as pentane or heptane, which are often found to be complexed with nitrogen, metals and sulfur. Generally, the asphaltic material is dispersed within the crude oil, and, when subjected to elevated temperatures, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult. Thus, the heavy bottoms from a crude oil vacuum distillation column (vacuum residuum), indicates a Conradson Carbon Residue factor of, for instance, 16.0% by weight. Such a material is useful only as road asphalt, or as an extremely low grade fuel when cut-back with distillate hydrocarbons such as kerosene, light gas oil, etc.

Heretofore, in the field 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, liquid phase oil is passed upwardly, in admixture with hydrogen, into a fixed-fluidized catalyst bed, or slurry of sub-divided catalyst. Although perhaps effective in converting at least a portion of the oil-soluble organo-metallic complexes, this type process is relatively ineffective with respect to asphaltics which are dispersed within the charge, with the consequence that the probability of effecting simultaneous contact between the catalyst particle, the hydrogen necessary for prevention of coke formation and the asphaltic molecule is remote. Furthermore, since the hydrogenation reaction zone is generally maintained at an elevated temperature of at least about 500° C. (932° F.), the retention of unconverted asphaltics, suspended in a free liquid phase oil for an extended period of time, results in additional flocculation and agglomeration, making 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 thermal cracking in the presence of hydrogen; any catalyst present rapidly succumbs to deactivation as a result of the deposition of coke thereon. This type process requires an attendant high capacity regeneration system in order to implement the process on a continuous basis. Furthermore, such processes are unable to effect the conversion of asphaltic material. Briefly, the present invention embodies a method whereby the asphaltic material is maintained in a dispersed state within a liquid phase which is rich in hydrogen. This material comes into intimate contact with a catalyst capable of effecting reaction between the hydrogen and asphaltic material; the liquid phase is itself dispersed in a hydrogen-rich gas phase so that the dissolved hydrogen is continually replenished. The two-fold dispersion and rapid, intimate contacting with the catalytic surface over-

comes the difficulties encountered in previous processes whereby excessive residence times and depletion of localized hydrogen supply permit agglomeration of asphaltics and other high molecular weight species. Such agglomerates are even less available to hydrogen and are not, therefore, susceptible to catalytic reaction. They eventually form coke which becomes deposited on the catalyst, thereby further reducing catalytic activity within the system.

The principal object of the present invention is to provide an economically feasible catalytic process for converting black oils into distillable hydrocarbons of lower molecular weight and boiling range. A corollary objective is to maximize the production of gasoline boiling hydrocarbons from black oils boiling above the normal gasoline boiling range.

Another object is to convert sulfur-contaminated heavy hydrocarbon charge stocks, the greater proportion of which exhibits a boiling range above a temperature of 1050° F., into lower-boiling distillable hydrocarbon products of significantly reduced sulfur concentration.

Another object of my invention is to provide a process to convert black oils having a gravity, °API at 60° F., less than about 20.0, and especially to produce distillable hydrocarbons from charge stocks, or portions thereof, having an °API gravity less than about 10.0.

Still another object is to provide a multiple-stage catalytic process for the conversion of black oils into gasoline boiling range hydrocarbons in volumetric yields greater than 100.0%, based upon the fresh charge stock.

Therefore, in a broad embodiment, the present invention involves a process for the conversion of a hydrocarbon charge stock of which at least about 10.0% boils above a temperature of about 1050° F., and which contains more than about 1.0% by weight of sulfur, into lower boiling, substantially sulfur-free hydrocarbon products, which process comprises the steps of: (a) admixing said charge stock with hydrogen, heating the resulting mixture to a temperature above about 700° F. and contacting the heated mixture with a catalytic composite in a first reaction zone maintained under an imposed 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 and at a temperature above about 700° F., to provide a first vapor phase and a first liquid phase; (c) combining at least a portion of said first liquid phase with said charge stock and hydrogen, and separating the remainder of said first liquid phase in a second separation zone at a substantially reduced pressure to provide a residuum fraction and a second vapor phase; (d) combining said first and second vapor phases, or liquid condensed therefrom, and reacting the resulting mixture in a second reaction zone at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons, and to produce lower molecular weight normally liquid hydrocarbons; (e) separating the resulting second reaction zone effluent in a third separating zone into a hydrogen-rich gaseous phase and a second liquid phase, fractionating the latter to provide at least a first lighter fraction having an end boiling point of from about 350° F. to about 450° F. and a second heavier fraction having an initial boiling point above about 350° F.; (f) admixing said second heavier fraction with hydrogen and reacting the resulting mixture in a third reaction zone at hydrocracking conditions, and in contact with a hydrocracking catalyst, selected to convert a portion of said second fraction into lower-boiling hydrocarbons; and, (g) separating the third reaction zone effluent, in a fourth separation zone, into a second hydrogen-rich gaseous phase and a third liquid phase, recycling said second hydrogen-rich gaseous phase to combine with said second heavier fraction, and combining said third liquid phase with said second liquid phase prior to fractionating the latter as aforesaid.

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

Since the hot heavy oil from the conversion zone can give rise to serious emulsification problems as a result of the co-production of water, this hot separator is also employed to separate the heavy oil as a liquid phase from a vapor phase containing lighter hydrocarbons, hydrogen and water. This hot separator is maintained at essentially the same pressure as the reaction zone and at essentially the same pressure as the reaction zone and at essentially the temperature of the reaction zone effluent; as above set forth, in a preferred embodiment, the temperature is controlled in the range of about 700° F. to about 750° F.

A second hot flash zone functions at a significantly reduced pressure of from subatmospheric to about 100 p.s.i.g., and may comprise a low-pressure flash zone—i.e. about 60 p.s.i.g.—in combination with a vacuum column maintained at about 50–60 mm. of Hg absolute. The hot flash system serves to eliminate further the difficulties stemming from emulsification problems by providing a residuum fraction containing the unconverted asphaltics and a significant amount of those sulfurous compounds not converted in the first reaction zone. Furthermore, subsequent separations and/or distillations are greatly simplified.

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

The phrase, "hydrocarbons boiling within the gasoline boiling range," or "gasoline boiling range hydrocarbons," is intended to connote those hydrocarbons boiling at tem-

peratures up to about 400° F. or 450° F. including C₅-hydrocarbons, and, in some localities, C₄-hydrocarbons. As will be recognized, iso-butane and normal butane are often included in this category. However, for the purpose of more clearly defining the component yields of the present process, "gasoline" will allude to a C₅-400° F. hydrocarbon fraction, notwithstanding that commercially-scaled units in various locales will raise or lower the end boiling point as dictated by the then current requirements.

Likewise, a "black oil" is intended to connote a hydrocarbonaceous mixture of which at least about 10.0% boils above a temperature of about 1050° F., and which has a gravity, ° API at 60° F., of 20.0 or less. The greater proportion of such black oils contains 60.0% or more of material boiling above 1050° F., and in many instances, the material is considered totally "non-distilled." "Distillable hydrocarbons" are those normally liquid hydrocarbons, including pentanes, having boiling points below about 1050° F. Conversion conditions are intended to be those conditions imposed upon the first conversion zone in order to convert a substantial portion of the black oil to distillable hydrocarbons. As will be readily noted by those skilled in the art of petroleum refining techniques the conversion conditions hereinafter enumerated are significantly less severe than those being currently commercially employed. The distinct economic advantages, over and above those inherent in producing the more valuable distillable hydrocarbons, will become immediately recongnized. The conversion conditions, within this first conversion zone, are intended to include temperatures above about 700° F., with an upper limit of about 800° F., measured at the inlet to the catalyst bed. Since the bulk of the reactions are exothermic, the temperature increases through the catalyst bed, and the reaction zone effluent will be at a temperature higher than the inlet. In order that catalyst stability be preserved, it is preferred to control the inlet temperature such that the effluent temperature does not exceed about 900° F. Hydrogen is admixed with the black oil charge stock, by means of compressive recycle, in an amount less than about 10,000 s.c.f./bbl., at the selected operating pressure, and preferably in an amount of from about 3000 to about 6000 s.c.f./bbl. The operating pressure will be greater than 1000 p.s.i.g., and generally in the range of about 1500 p.s.i.g. to about 3000 p.s.i.g. The crude oil passes through the catalyst at a liquid hourly space velocity (defined as volumes of liquid hydrocarbon charge per hour, measured at 60° F., per volume of catalyst disposed in the reaction zone) of from about 0.25 to about 2.0. Although the present process may be conducted in a batch-wise fashion, it readily lends itself to the more economical continuous processing in an enclosed vessel, through which the mixture of hydrocarbon charge stock and hydrogen is passed. When conducted as a continuous process, it is particularly preferred to introduce the mixture into the vessel in such a manner that the same passes through the vessel in downward flow. The internals of the vessel may be constructed in any suitable manner capable of providing the required intimate contact between the liquid charge stock, the gaseous mixture and the catalyst. In some instances it may be desirable to provide the reaction zone with a packed bed or beds of inert material such as particles of granite, porcelain, berl saddles, sand, aluminum or other metal turnings, etc., to facilitate distribution of the charge, or to employ perforated trays or special mechanical means for this purpose.

As hereinbefore set forth, hydrogen is employed in admixture with the charge stock, and preferably in an amount of from about 3000 to about 6000 s.c.f./bbl. The hydrogen-containing gas stream, herein sometimes designated as "recycle hydrogen," since it is conveniently recycled externally of the hydrorefining zone, fulfills a number of various functions: it serves as a hydrogenating agent, a heat carrier, and particularly a means for strip-

ping converted material from the catalytic composite, thereby creating still more available catalytically active sites for the incoming, unconverted hydrocarbon charge stock. Since some hydrogenation will be effected, there will be a net consumption of hydrogen; to supplement this, hydrogen is added to the system from any suitable external source.

The catalytic composite disposed within the first 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 process, although a siliceous carrier, such as 88.0% alumina and 12.0% silica, or 63.0% alumina and 37.0% silica, are generally preferred. Suitable metallic components having hydrogenation activity are those selected from the 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. For example, the metallic components of Group VI-B are preferably present in an amount within the range of about 1.0% to about 20.0% by weight, the iron-group metals in an amount within the range of about 0.2% to about 10.0% by weight, whereas the platinum-group metals are preferably present in an amount within the range of about 0.1% to about 5.0% by weight, all of which are calculated as if the components existed within the finished catalytic composite as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, and mixtures of two or more including silica-alumina, alumina-silica-boron phosphate, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silic-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, silica and boron phosphate with alumina being in the greater proportion.

Similarly, the catalytic composites disposed within the second and third reaction zones, will comprise metallic components from the metals of Group VI-B and VIII of the Periodic Table, and compounds thereof, which components are composited with one or more of the refractory inorganic oxides previously set forth. However, since the catalytic composites in these two subsequent zones are intended to fulfill different functions, the second and third zones will, in most situations, make use of different catalysts. The applicability of the present process, particularly regarding the integration therein of the second and third reaction zones, is illustrated by a two-stage process, the charge stock to which is the mixture of the first and second vapor phases as hereinbefore described. The function of the first reaction zone is essentially twofold; it serves to concentrate a residuum fraction containing sulfur while simultaneously producing distillable hydrocarbons. The quantity of sulfur remaining in the distillable fraction will, of course, be dependent upon the characteristics of the fresh black oil charge stock. However, most of this remaining sulfur is concentrated in the middle-distillate and gas oil ranges—from about 450° F. to about 650° F.—along with residual nitrogenous compounds. In order to produce maximum yields of

gasoline, it is necessary to remove these residual contaminants.

With such as charge stock, the second reaction zone is employed for the primary purpose of effecting the virtually complete removal of the nitrogenous compounds by converting the same into ammonia and normally liquid hydrocarbons, while simultaneously converting most of the residual sulfurous compounds into hydrogen sulfide and liquid hydrocarbons. Generally speaking, the overall process is enhanced by virtue of the fact that some hydrogenation and hydrocracking of the higher-boiling middle-distillate and gas oil components also takes place. Following the removal of the ammonia, hydrogen sulfide and minor quantities of light paraffinic hydrocarbons including methane, ethane and propane, the normally liquid product effluent from this first reaction zone is generally subjected to separation to remove a lower-boiling gasoline fraction containing hydrocarbons boiling below a temperature, as previously stated, of about 400° F. to about 450° F. The remainder of the normally liquid portion of the first reaction zone effluent is then passed into the third reaction zone, the primary purpose of which to maximize the conversion into lower-boiling, gasoline range products.

Since the functions to be served within the second and third reaction zone are different, most applications of the present invention will involve different operating conditions and different catalysts. Thus, the charge to the second reaction zone, in admixture with hydrogen in an amount of about 1000 to about 8000 s.c.f./bbl. of liquid hydrocarbon charge, is raised to a desired operating temperature within the range of about 500° F. to about 1000° F., prior to contacting the catalytic composite. The reactions are effected under an imposed pressure of about 100 pounds to about 3000 pounds per square inch, the hydrocarbon charge stock contacting the catalytic composite at a liquid hourly space velocity (defined as volumes of liquid charge per hour per volume of catalyst disposed within the reaction zone), within the range of from about 0.5 to about 10.0. In addition to the effective clean-up of the hydrocarbon charge stock, a significant degree of hydrocarbon conversion occurs whereby the heavier molecular weight hydrocarbons, boiling at a temperature of from about 700° F. to about 1050° F., and including the higher-boiling nitrogenous compounds, are converted, by highly selective cracking reactions into lower boiling hydrocarbons, from which the nitrogen is more readily removed. The conversion reactions are such that very little light, straight-chain paraffinic hydrocarbons are produced.

The catalyst disposed within the second reaction zone serves a dual function; that is, the catalyst is non-sensitive to the presence of both nitrogenous compounds and sulfurous compounds, while at the same time is capable of effecting the destructive removal thereof, and, as hereinabove set forth, the conversion of at least a portion of those hydrocarbons boiling at a temperature above about 700° F. A catalyst comprising comparatively large quantities of molybdenum, calculated as the element, composited with the carrier material of silica and from about 60.0% to about 78.0% by weight of alumina, is very efficient in carrying out the desired operation. A preferred catalytic composite, for utilization in this reaction zone, comprises from about 4.0% to about 45.0% by weight of molybdenum. In addition to minor amounts of nickel, from about 0.2% to about 10.0% by weight, like quantities of cobalt and/or iron may be employed in combination with the relatively large amounts of molybdenum.

The gaseous ammonia and hydrogen sulfide, resulting from the destructive removal of nitrogenous and sulfurous compounds, and light paraffinic hydrocarbons, are removed from the total effluent from the second reaction zone in any suitable manner. For example, the effluent

may be admixed with water, and thereafter subjected to separation such that the ammonia is absorbed in the water-phase. Hydrogen sulfide and light paraffinic hydrocarbons may be removed by introducing the effluent into a low-temperature flash chamber, the normally liquid hydrocarbons from which are passed into a fractionating column for the purpose of removing those hydrocarbons boiling within the gasoline boiling range.

The remaining portion of the essentially nitrogen-free effluent from the hydrorefining reaction zone, comprising those hydrocarbons boiling above a temperature of from about 400° F. to about 450° F., in admixture with hydrogen in an amount of from about 1000 to about 6000 s.c.f./bbl., of liquid hydrocarbons, is raised to a temperature within the range of about 500° F. to about 950° F. Due to the characteristics of the charge stock to the third reaction zone, the operating conditions within the same are relatively mild. Therefore, the operating temperature at which the catalyst is maintained within the subsequent hydrocracking reaction zones, may be at least about 50° F. less than the temperature employed in the second reaction zone. The third reaction zone is maintained under an imposed pressure within the range of about 100 to about 3000 p.s.i.g., and the rate of hydrocarbon charge will be within the range of from about 0.5 to about 15.0 liquid hourly space velocity. Catalytic composites which comprise at least one metallic component selected from Groups VI-B and VIII of the Periodic Table, and a composite of silica and from about 12.0% to about 30.0% by weight of alumina, constitute hydrocracking catalysts for use in the conversion of the nitrogen-free charge stock into lower boiling hydrocarbon products. The total quantity of catalytically active metallic components is within the range of from 0.1% to about 20.0% by weight of the total catalyst. The Group VI-B metal, such as chromium, molybdenum, or tungsten, is usually present within the range of from about 0.5% to about 10.0% by weight of the catalyst. The Group VIII metals, which may be divided into two sub-groups, are present in an amount of from 0.1% to about 10.0% by weight of the total catalyst. When an iron sub-group metal such as iron, cobalt, or nickel, is employed, it is present in an amount of from about 0.2% to about 10.0% by weight, while, if a noble metal such as platinum, palladium, iridium, etc., is employed, it is present within an amount within the range of from about 0.1% to about 5.0% by weight of the total catalyst. Suitable catalysts, for utilization within the hydrocracking reaction zone, include, but are not limited to the following: 6.0% by weight of nickel and 0.2% by weight of molybdenum; 6.0% by weight of nickel; 0.4% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of platinum, etc.

The total effluent from the third reaction zone is passed through a suitable high-pressure, low-temperature separation zone from which a hydrogen-rich gas stream is withdrawn and recycled. The normally liquid hydrocarbons, containing some light paraffinic hydrocarbons and butanes, are combined with normally liquid hydrocarbons resulting from the separating means employed with respect to the second reaction zone, to remove therefrom those hydrocarbons boiling within the gasoline boiling range.

Other conditions and preferred operating techniques will be given in conjunction with the following description of the present process. In further describing this process, reference will be made to the accompanying figure which illustrates one specific embodiment. In the drawing, the embodiment is presented by means of a simplified flow diagram in which such details as pumps, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as being non-essential to an understanding of the techniques involved. The use of such

miscellaneous appurtenances, to modify the process, are well within the purview of one skilled in the art.

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

TABLE I.—CHARGE STOCK PROPERTIES

Gravity, ° API at 60° F. -----	8.4
Sulfur, wt. percent -----	7.0
Nitrogen, p.p.m. -----	4,400
Conradson Carbon Residue, wt. percent -----	16.5
Total metals, p.p.m. -----	270

An ASTM D1160 distillation of this black oil charge stock indicates that only 10.0% by volume of distillable hydrocarbons are available—i.e. those boiling below a temperature of about 1050° F. The unit is designed to process 15,000 bbl./day of this material at a combined feed ratio of about 1.8. Thus, the charge in line 1 is admixed with 12,000 bbl./day of a hot separator bottoms recycle stream from line 2, the source of which is hereafter described. Combined feed ratios in the range of about 1.25 to about 3.0, are well suited for use in this process. Based upon the fresh charge stock, a recycle hydrogen-rich gaseous phase, in line 3, in an amount of 10,000 s.c.f./bbl., is admixed with the total liquid in line 1.

The resulting mixture, following suitable heat exchange with various effluent streams, not illustrated, continues through line 1 into heater 5 wherein the temperature is increased to a level such that the reactor 7 inlet temperature is about 775° F. The heated mixture leaves heater 5 via line 6, and enters first reaction zone 7 at an LHSV of 0.6, based upon fresh charge only. Reaction zone 7 is maintained under an imposed pressure of about 2,850 p.s.i.g. The reaction product effluent, at a temperature of about 875° F., is withdrawn via line 8, and is passed thereby into hot separation zone 9 at a pressure of about 2800 p.s.i.g., the drop in pressure being due solely to fluid flow through the system. After its use as a heat-exchange medium, the effluent is at a temperature of 750° F. as it enters separator 9. A principally vaporous phase is withdrawn from the hot separator 9 through line 11, and a liquid phase is withdrawn via line 10. A portion of this liquid phase, in this instance 12,000 bbl./day, is diverted via line 2 to combine with the charge stock in line 1. The remaining portion continues through line 10 into a hot flash zone 12. The greater proportion of the vapor phase in line 11 consists of hydrocarbonaceous material boiling below about 700° F., while the liquid phase in line 10 is principally 700° F.-plus hydrocarbonaceous material.

In the illustrated embodiment, the material in line 10 enters the hot flash zone 12 at a temperature of about 730° F., the zone being under a pressure of about 75 p.s.i.g. A residuum fraction, having an average molecular weight above 850, is removed via line 14 in an amount of about 20.0 wt. percent of the fresh hydrocarbon charge (about 18.1% by volume). A second principally vaporous fraction is removed through line 13, being combined with the first vapor phase, from hot separator 9, in line 11. A component analysis of the reactor 7 effluent, exclusive of recycled material, if any, or a combination of the streams in lines 14, 11 and 13, is presented in the following Table II:

TABLE II.—ANALYSIS, REACTION ZONE 7 EFFLUENT

Component:	Vol. percent ¹
Ammonia -----	0.2
Hydrogen sulfide -----	5.1
Methane -----	0.7
Ethane -----	0.7
Propane -----	1.0
Butanes -----	1.6
Pentanes -----	1.1
Hexanes -----	1.9
C ₇ -400° F. -----	8.9
400° F.-650° F. -----	21.4
650° F.-1050° F. -----	48.0
Residuum -----	18.2

¹The values for the propane and lighter components is given in weight percent.

With respect to hot flash zone 12, although this is indicated as being a single vessel, it will be recognized by those possessing expertise in the area of petroleum technology, that zone 12 may consist of multiple vessels. For example, the material in line 10 may be flashed at substantially the same temperature at which it leaves hot separator 9, and at a substantially reduced pressure below about 100 p.s.i.g.; the temperature after flashing will, of course, be reduced due to the conversion of some sensible heat into latent heat of vaporization. The liquid phase from this initial flash can then be heated to an elevated temperature, and passed into a vacuum column at a sub-atmospheric pressure of from 50-60 mm. of Hg, the elevated temperature being as high as about 900° F.; it is understood that such lower partial pressure may be achieved by the addition of inert gas such as steam, hydrogen or nitrogen.

With reference once again to the drawing, the combined first and second vapor phases continue through line 11 into a second reaction zone 15, after being heated to a temperature such that the inlet to the catalyst bed is about 825° F. Reactor 15 is under an imposed pressure of about 2700 p.s.i.g. The effluent is removed via line 16 at a temperature of about 875° F.; after passing through condenser 17 and line 18, the effluent enters cold separator 19 at a temperature of about 110° F. A hydrogen-rich vapor phase is removed via line 3, and is recycled thereby to combine with the charge stock in line 1. In order to compensate for the hydrogen consumed in the process, as well as solution losses, make-up hydrogen from a suitable external source is supplied through line 4. A principally liquid phase is removed from cold separator 19, through line 20, and passes into product separation zone 21.

It is understood that various modifications may be made to the portion of the present process thus far discussed. Such modifications might include engineering techniques such as, introducing a portion of the make-up hydrogen from line 4 directly into reactor 15 by way of line 11; treating the vapor phase from cold separator 19 to remove hydrogen sulfide prior to recycling said vapor phase; adding water to the effluent from reactor 15 to absorb ammonia; and, condensing the vapor phases from lines 11 and 13 for the purpose of venting light paraffins and lighter gases. These and many changes may be made by those skilled in the art; they are not considered sufficient to remove the resulting flow scheme from the scope and spirit of the appended claims.

A component analysis of the product effluent from reactor 15, as shown in the following Table III, indicates that the remainder of the sulfurous compounds have been converted into hydrocarbons and hydrogen sulfide, and, more significantly, that a substantial amount of the heavier hydrocarbons have been converted into lower boiling products.

TABLE III.—ANALYSIS, REACTOR 15 EFFLUENT

Component:	Vol. percent ¹
Ammonia	0.4
Hydrogen sulfide	6.5
Methane	0.8
Ethane	0.8
Propane	1.3
Butanes	2.4
Pentanes	1.8
Hexanes	2.6
C ₇ -400° F.	17.6
400° F.-650° F.	65.5
650° F.-1050° F.	Nil

¹The values for the propane and lighter constituents are in weight percent.

The liquid phase from cold separator 19, passing into product separation zone 21 is first combined with the liquid portion of reactor 29 effluent as hereinafter described. Although shown as a single column, it is obvious that product separation 21 can take the form of multiple fractionations and/or distillations for the purpose of recovering one or more selected components in a substantially pure state. In the sake of simplicity, product separation 21 is illustrated as a single fractionator from which propane and lighter normally gaseous components are removed via line 22, butanes from line 23, pentanes and hexanes from line 24, C₇-400° F. gasoline boiling range hydrocarbons through line 25 and, through line 26, those middle distillate hydrocarbons boiling above 400° F.

After being admixed with a hydrogen-rich recycle gaseous phase in line 35, the middle-distillate hydrocarbons in line 26 continue into heater 27, wherein the temperature is increased to about 700° F., and via line 28 into reaction zone 29. The pressure imposed upon third reaction zone 29 is about 1500 p.s.i.g., and the liquid hourly space velocity is about 1.5. The effluent is withdrawn through line 30 into condenser 31, and continues through line 32 at a temperature of about 115° F. into cold separator 33. A hydrogen-rich recycle gas phase is combined, via line 35, with the normally liquid charge to reactor 29. Although not illustrated in the drawing, the pressure being maintained on reactor 29 may be controlled by alternate schemes including venting a portion of the gaseous phase in line 35, and by controlling the amount of hydrogen make-up supplied to the reactor to compensate for that consumed. The normally liquid hydrocarbons are removed from separator 33 through line 34, and are combined with the liquid phase in line 20, prior to separation in product separation zone 21.

To summarize the results, the overall product distribution is presented in the following Table IV, taking into account all the product streams from separation zone 21 and the residuum fraction removed via line 14:

TABLE IV.—OVERALL PRODUCT DISTRIBUTION

Component	Wt. Percent	Vol. Percent
Ammonia	0.4	-----
Hydrogen Sulfide	6.5	-----
Methane	0.8	-----
Ethane	0.9	-----
Propane	2.7	-----
Butanes	8.1	14.3
Pentanes	7.8	12.6
Hexanes	8.5	12.3
C ₇ -400° F.	49.0	64.1
400° F.-650° F.	-----	-----
650° F.-1,050° F.	-----	-----
Residuum	20.0	18.2

The product distribution values presented in Table IV are based upon 100.0% by volume of the black oil charge stock and a hydrogen consumption rate of 4.7% by weight of the charge stock.

It should be noted that the volumetric yield of gasoline boiling range hydrocarbons, including butanes, is 103.3%. Of further interest is the fact that of the butane concentrate, 65.0% are iso-butanes, while 85.0% of the pentanes are iso-pentanes. Furthermore, the octane rating F-1 clear, of the pentane-hexane portion is 85.7, the leaded value (3 cc. TEL.) is 98.6; this will be readily recognized as an excellent motor fuel blending component. The gasoline boiling range, C₇-400° F., hydrocarbons analyze to show 37.8% by volume paraffins, 50.4% naphthenes and 11.8% aromatics, forming an excellent charge stock for further up-grading by a suitable catalytic reforming process. Since the latter is known as a hydrogen-producing process, its integration with the present process affords a valuable petroleum refining tool.

The following example is presented in further illustration of the process of the present invention and the benefits afforded through the use thereof in maximizing the yield of gasoline boiling range hydrocarbons from the conversion of black oils. The charge stock is a South American crude oil of which 58.2% by volume boils above 1050° F. In this respect, this charge is not considered as difficult as the black oil described in conjunction with the accompanying drawing of which only 10.0% was considered as distillable. Additionally, the charge stock contains 7,200 p.p.m. of nitrogen, 4.1% by weight of sulfur, 11.9% by weight of heptane-insoluble asphaltics and 616 p.p.m. of total metals, principally nickel and vanadium.

EXAMPLE

The charge stock is processed in the manner presented in the accompanying drawing with some exceptions as to operating conditions. The desired object is to produce the maximum yield of hydrocarbons boiling up to about 375° F., and including pentane. The crude oil, in an amount of 34,368 bbl./day, enters the first reaction zone at an LHSV of 0.5, and a combined feed ratio of 2.0, as a result of hot separator recycle. A hydrogen-rich gas stream is admixed with the charge in an amount of 10,000 s.c.f./bbl. of fresh feed. The temperature to the inlet of the reactor is 775° F. and the pressure is about 2600 p.s.i.g. The reaction zone effluent, at a temperature of 875° F. is passed into a hot separator at 750° F., the liquid phase from which is subjected to two-stage hot flashing at 75 p.s.i.g. and then under 55 mm. of Hg. The vapor phases from the hot separator and hot flash zones are combined and charged to the second reaction zone. A residuum fraction is removed from the hot flash zone in an amount of 15.0% by weight of the charge stock, and contains 3.02% by weight of sulfur. The net first reaction zone effluent has the component analysis shown in the following Table V:

TABLE V.—ANALYSIS OF FIRST REACTOR EFFLUENT

Component	Wt. percent	Vol. percent
Ammonia	0.35	-----
Hydrogen Sulfide	3.20	-----
Methane	0.61	-----
Ethane	0.63	-----
Propane	0.83	-----
Butanes	0.78	1.36
Pentanes	0.56	0.90
Hexanes	1.05	1.53
C ₇ -375° F.	8.28	10.85
375° F.-1,050° F.	70.30	77.21
Residuum	15.0	14.21

The second reaction zone is operated at an inlet temperature of 775° F., a pressure of 2500 p.s.i.g. and an LHSV of 1.2. The effluent, at a temperature of 850° F., is cooled to about 110° F. and separated to provide a normally liquid stream and a hydrogen-rich vapor phase. The latter is treated to remove hydrogen sulfide and a hydrogen-rich stream containing light hydrocarbon gases which is recycled (80.0% purity) to combine with the fresh charge stock. The second reaction zone effluent has

the component analysis presented in the following Table VI:

TABLE VI.—ANALYSIS, SECOND ZONE EFFLUENT

Component	Wt. percent	Vol. percent
Ammonia.....	0.61	-----
Hydrogen Sulfide.....	3.80	-----
Methane.....	0.71	-----
Ethane.....	0.80	-----
Propane.....	1.17	-----
Butanes.....	1.53	2.68
Pentanes.....	1.18	1.91
Hexanes.....	1.80	2.62
C ₇ -375° F.....	15.39	20.17
375° F.-1,050° F.....	61.06	73.70

This effluent is separated to provide a portion of the 375° F.-1050° F. charge to the third reaction zone being maintained at 2000 p.s.i.g. and an inlet temperature of 750° F. The reaction product effluent, at a temperature of 800° F., is cooled to about 105° F. and separated to provide a gaseous phase, in part recycled to this third reaction zone, and a normally liquid phase. The latter is combined with the normally liquid effluent from the second reaction zone, and the mixture is subjected to fractionation to separate the 375° F.-plus fraction (for charge to the third reaction zone), and to provide a butane concentrate, a pentane concentrate, a hexane concentrate and a C₇-375° F. concentrate. The overall product distribution is given in the following Table VII, being principally the streams recovered from the fractionation column, but including the components in various vent gas streams.

TABLE VII.—OVERALL PRODUCT DISTRIBUTION AND YIELDS

Component	Wt. Percent	Vol. Percent
Ammonia.....	0.61	-----
Hydrogen Sulfide.....	3.80	-----
Methane.....	0.71	-----
Ethane.....	0.88	-----
Propane.....	2.84	-----
Butanes.....	9.60	17.04
Pentanes.....	9.25	14.98
Hexanes.....	9.94	14.49
C ₇ -375° F.....	51.64	72.37
375° F.-1,050° F.....	-----	-----
Residuum.....	15.00	14.21

The yields are based upon 100.0% by weight of the fresh charge stock and include about 4.3% by weight of hydrogen consumed in the process. It should be noted that the total volumetric yield was 133.09%, and the butane-375° F. gasoline boiling range yield was 118.88% by volume.

Further analyses show that the sulfur concentration in the residuum fraction is 3.02% by weight and the nitrogen content thereof is 1.29% by weight. The mixture of pentanes and hexanes has an F-1 clear octane rating of 85.6 and a leaded (3 cc. TEL.) value of 98.5, indicating that this would be a valuable motor fuel blending component. With respect to the C₇-375° F. naphtha fraction, analysis indicates negligible olefin content (nil), 11.4% by volume of aromatics, 57.1% naphthenes and 31.5% by volume of aromatics. As such, and it will be so recognized, this material is well suited as charge stock for a catalytic reforming process. In some instances, particularly in foreign marketing areas, the C₇-375° F. fraction can be subjected to selective hydrocracking for the production of LPG (liquified petroleum gas).

The foregoing specification and examples indicate the method by which the present process is effected, and illustrate some of the benefits afforded through the utilization thereof. The present process has been shown to be a valuable tool to petroleum refining in its ability to convert black oils into more valuable distillable hydrocarbon products.

I claim as my invention:

1. A process for the conversion of a hydrocarbon charge stock of which at least about 10.0% boils above about 1050° F., and which contains more than about 1.0% by weight of sulfur, into lower boiling, substantially sulfur-free hydrocarbon products, which process comprises the steps of:

- (a) admixing said charge stock with hydrogen, heating the resulting mixture to a temperature above about 700° F. and contacting the heated mixture with a catalytic composite in a first reaction zone maintained under an imposed 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 and at a temperature above about 700° F., to provide a first vapor phase and a first liquid phase;
 - (c) combining at least a portion of said first liquid phase with said charge stock and hydrogen, and separating the remainder of said first liquid phase in a second separation zone at a substantially reduced pressure to provide a residuum fraction and a second vapor phase;
 - (d) combining said first and second vapor phases, and reacting the resulting mixture in a second reaction zone at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons, and to produce lower molecular weight normally liquid hydrocarbons;
 - (e) separating the resulting second reaction zone effluent in a third separating zone into a first hydrogen-rich gaseous phase and a second liquid phase, fractionating the latter to provide at least a first lighter fraction having an end boiling point of from about 300° F. to about 450° F. and a second heavier fraction having an initial boiling point above about 300° F.;
 - (f) admixing said second heavier fraction with hydrogen and reacting the resulting mixture in a third reaction zone at hydrocracking conditions, and in contact with a hydrocracking catalyst, selected to convert a portion of said second fraction into lower-boiling hydrocarbons; and
 - (g) separating the third reaction zone effluent, in a fourth separation zone, into a second hydrogen-rich gaseous phase and a third liquid phase, recycling said second hydrogen-rich gaseous phase to combine with said second heavier fraction, and combining said third liquid phase with said second liquid phase prior to fractionating the latter as aforesaid.
2. The process of claim 1 further characterized in that said first hydrogen-rich gaseous phase is recycled to combine with said charge stock.
3. The process of claim 1 further characterized in that said second separation zone is maintained at a pressure of from subatmospheric to about 100 p.s.i.g.
4. The process of claim 1 further characterized in that said third and fourth separation zones are maintained at a temperature within the range of from about 60° F. to about 130° F. and at a pressure substantially the same as that imposed upon said second and third reaction zones respectively.
5. The process of claim 1 further characterized in that said second separation zone is maintained at a pressure of from subatmospheric to about 100 p.s.i.g.

References Cited

UNITED STATES PATENTS

3,026,260 3/1962 Watkins ----- 208—59

HERBERT LEVINE, Primary Examiner.