

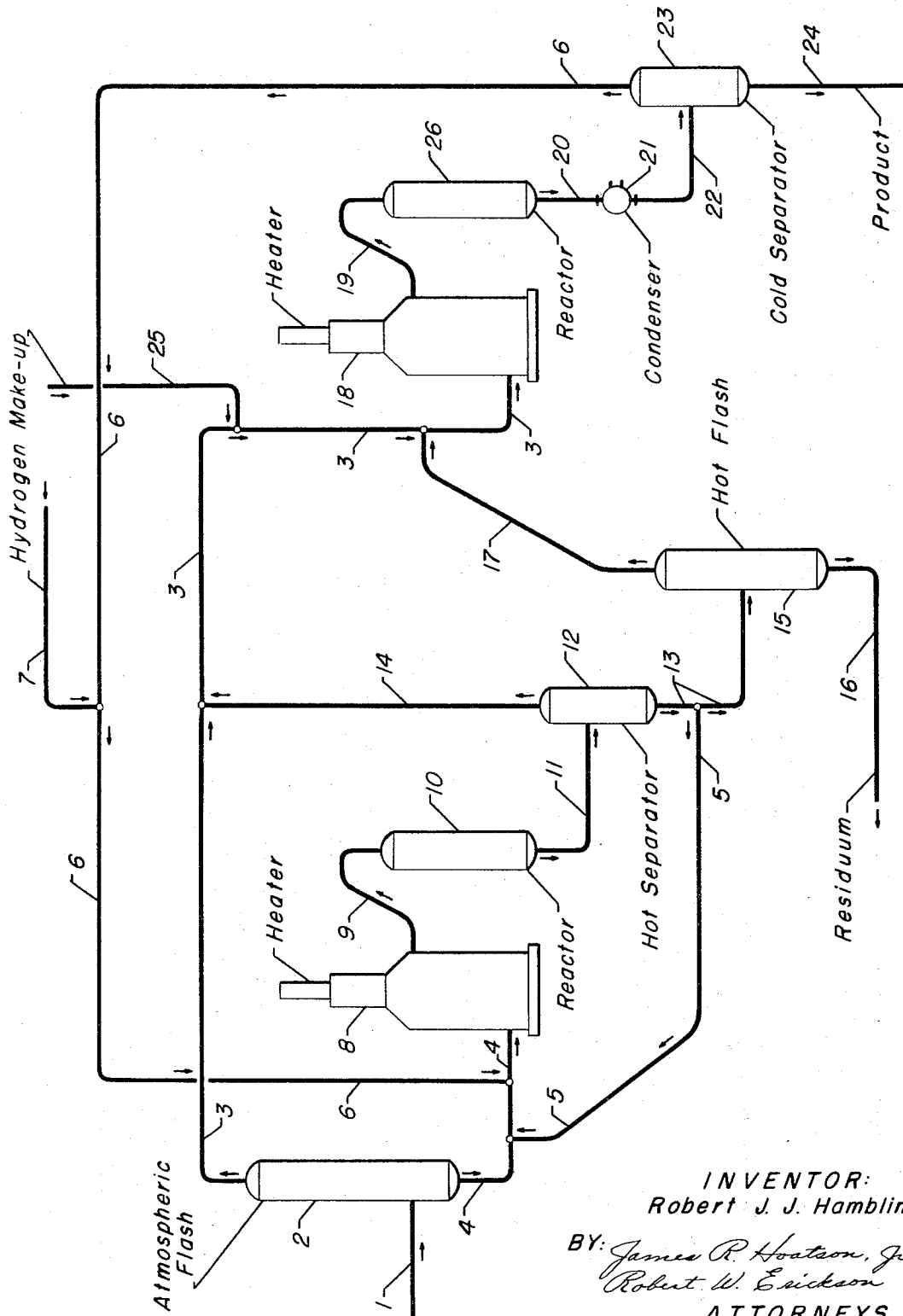
Jan. 16, 1968

R. J. J. HAMBLIN

3,364,134

BLACK OIL CONVERSION AND DESULFURIZATION PROCESS

Filed Nov. 30, 1966



INVENTOR:
Robert J. J. Hamblin

BY: *James R. Hoatson, Jr.*
Robert W. Esickson
ATTORNEYS

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**BLACK OIL CONVERSION AND
DESULFURIZATION PROCESS****Robert J. J. Hamblin, Deerfield, Ill., assignor to Universal
Oil Products Company, Des Plaines, Ill., a corporation
of Delaware****Filed Nov. 30, 1966, Ser. No. 597,935
5 Claims. (Cl. 208-93)**

The invention described herein is applicable to a process for the conversion of petroleum crude oil and the heavier fractions derived therefrom, 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 commonly referred to as "black oils," and which contain a significant quantity of asphaltic material and high concentrations of sulfur.

Petroleum crude oils, particularly heavy oils extracted from tar sands, topped or reduced crudes, and vacuum residuum, contain high molecular weight sulfurous compounds in exceedingly large quantities, nitrogenous compounds, high molecular weight organo-metallic complexes containing principally 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 metallic contaminants. In this regard, "black oils" differ considerably from heavy gas oils which are not so severely contaminated, and which normally do not have as high a boiling range. A black oil can be characterized as a heavy hydrocarbonaceous material of which more than 10.0% (by volume) boils above a temperature of 1050° F., having a gravity, ° API at 60° F., of less than 20.0. Sulfur concentrations are exceedingly high, more than 1.0% by weight, and are often in excess of 3.0% 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. There exists currently an abundant supply of such hydrocarbonaceous material, most of which has a gravity less than 10.0° API at 60° F., and which is characterized by a boiling range indicating that 30.0% or more boils above a temperature of about 1050° F. The utilization of these highly contaminated black oils as a source of more valuable liquid hydrocarbon products is precluded by present-day techniques unless the sulfur and asphaltic content is sharply reduced, and a significant proportion of the material can be converted into distillable hydrocarbons—i.e. those boiling below about 1050° F. (as determined by the ASTM Method D-1160).

The process encompassed by the present invention is particularly directed toward the catalytic conversion of black oils into distillable hydrocarbons in yields which may be as high as 80.0% by volume, and sometimes higher. Specific examples of the crude oils to which the present scheme is uniquely 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 Kuwait crude oil, having a gravity of 11.0° API and containing 10.1% by weight of asphalts and 5.2% by weight of sulfur; a vacuum residuum having a gravity of 8.8° API and containing 3.0% sulfur and 4300 p.p.m. (by weight) of nitrogen; vacuum bottoms having a gravity of 5.4° API, and containing 6.15% sulfur 233 p.p.m. (by weight) of metals and 12.8% by weight of heptane-insoluble asphaltic material; and, a reduced crude having a gravity of 11.5° API,

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and containing 4.2% sulfur, 3400 p.p.m. nitrogen, 166 p.p.m. of metals and 8.6% by weight of heptane-insolubles.

The present invention affords the conversion of up to 80.0% by volume of such material into distillable hydrocarbons, heretofore having been considered impossible to achieve, especially on an economically feasible basis. The principal difficulty resides in the lack of sulfur stability of many catalytic composites employed in current processes, and primarily from the presence of large quantities of asphaltic material and other non-distillables. This asphaltic material comprises high molecular weight coke precursors, insoluble in pentane and/or heptane, and which are usually complexed with nitrogen, metals and especially sulfur. Generally, the asphaltic material is found to be dispersed within the black oil, and when subjected to heat, as in a vacuum distillation process, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-insoluble products becomes extremely difficult. Thus, the heavy bottoms from a crude oil vacuum distillation column (vacuum residuum), indicates a Conradson Carbon Residue factor of 16.0% by weight. Such a material is generally 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 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-bed or slurry of sub-divided catalyst; although perhaps effective in removing at least a portion of the organo-metallic complexes, this type process is relatively ineffective with respect to insoluble asphalts which are dispersed within the charge, with the consequence that the probability of effecting simultaneous contact between the catalyst particle and the asphaltic material in the presence of sufficient hydrogen is remote. Furthermore, since the reaction zone is generally maintained at an elevated temperature of at least about 500° C. (932° F.), the retention of unconverted asphalts, suspended in a free liquid phase oil for an extended period of time, will result in flocculation, 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 reactions in the presence of hydrogen; any particular catalytic composite present succumbs rapidly to deactivation as a result of the deposition of coke thereon. Such a process requires an attendant high capacity catalyst regeneration system in order to implement the process on a continuous basis. Furthermore, such processes are unable to effect substantial conversion of asphaltic material.

Briefly, the present invention embodies a method whereby the asphaltic material is maintained in a dispersed state in a liquid phase which is rich in hydrogen. This material comes into intimate contact with a catalyst which is 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. This two-fold dispersion and rapid, intimate contacting with the catalytic surfaces overcomes the difficulties encountered in previous processes whereby excessive residence times and depletion of localized hydrogen supply permit agglomeration of asphalts 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 the desulfurization and conversion of black oils into distillable hydrocarbons for lower molecular weight and boiling range. As hereinafter indicated by a specific example, the practice of the present process results in a distillable hydrocarbon product in an amount of about 80.0% by volume of the black oil 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.

Another object of my invention is to provide a process for desulfurizing and converting black oils having a gravity, °API at 60° F., less than about 20.0, and to produce distillable hydrocarbons boiling below 800° F. from charge stocks, or select portions thereof having a °API gravity less than about 10.0.

Another object is to effect the conversion and desulfurization of black oils with minimum yield loss to asphalt and/or residuum.

In a broad embodiment, therefore, the present invention affords a process for the conversion of a hydrocarbon charge stock, of which at least about 10.0% by volume boils above a temperature of about 1050° F., and which contains at least about 1.0% by weight of sulfur, into lower boiling distillable hydrocarbon products, which process comprises the steps of: (a) separating said charge stock, in a first separation zone, into a light fraction having an end boiling point of from about 650° F. to about 850° F. and a heavy fraction having an initial boiling point above about 650° F.; (b) admixing said heavy fraction with hydrogen and heating the resulting mixture to a temperature above about 700° F.; (c) contacting the heated mixture with a catalytic composite in a first conversion zone maintained under an imposed pressure greater than 1000 p.s.i.g.; (d) separating the resulting conversion zone effluent, in a second separation zone, at substantially the same pressure imposed upon said first conversion zone, and at a temperature above about 700° F. to provide a first vapor phase and a first liquid phase; (e) further separating at least a portion of said first liquid phase, in a third separation zone, at a pressure of from subatmospheric to about 100 p.s.i.g. and at a temperature in the range of about 550° F. to about 900° F., to provide a residuum fraction and a second vapor phase; (f) combining said second vapor phase, or liquid condensed therefrom, said first vapor phase and said light fraction, and contacting the resulting mixture with a catalytic composite in a second reaction zone, with or without the addition of a hydrogen-rich gaseous stream, at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons; and (g) separating the second reaction zone effluent, in a fourth separation zone, at a temperature of from about 60° F. to about 130° F. to provide a hydrogen-rich vapor phase and a normally liquid hydrocarbon product.

Other embodiments of my invention reside in particular operating conditions and internal recycle streams. The latter include recycle of the hydrogen-rich third vapor phase to combine with the heavy fraction, resulting from the initial separation, prior to reacting the same in the first conversion zone. In the specific example which follows, this third vapor phase constitutes more than about 80.0% hydrogen. At least a portion of the first liquid phase from the second separation zone is diverted and combined with the heavy fraction and hydrogen, and serves as a type of solvent stream to maintain the asphaltics dispersed and available to both hydrogen and catalyst in the conversion zone. The diverted portion may, in some situations, be combined with the fresh charge stock, prior to its initial separation, or may be in part

combined with the heated mixture of hydrogen and said heavy fraction. When processing variables demand, the first liquid phase can be combined with all of the fresh charge, the heated mixture of heavy fraction and hydrogen, and the unheated mixture thereof. In a preferred embodiment, a second portion of the first liquid phase is cooled and recycled to the inlet to this second separation zone to serve therein as a quench of the reaction zone effluent such that the temperature within the zone is at a maximum level of 750° F. Thus, the first separation zone is temperature controlled to function within the range of from about 700° F. to about 750° F. Lower temperatures permit ammonium salts, resulting from the conversion of nitrogenous compounds, to fall into the liquid phase, thereby effecting serious plugging problems around the heater, whereas higher temperatures cause heavier hydrocarbons containing unconverted asphaltics to be carried over in the vapor phase.

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 temperature of the reaction zone effluent; as 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 be obtained. In the present specification and appended claims, a "pressure substantially the same as," or a "temperature substantially the same as," is intended to connote the pressure or temperature on a downstream vessel, allowing only for the normal pressure drop due to fluid flow, and the normal temperature loss due to transfer of material from one zone to another. Thus, where the conversion zone is at a pressure of about 2650 p.s.i.g., and the temperature of the effluent is about 875° F., the first separation zone (hot separator) will function at a pressure of about 2530 p.s.i.g.; as previously set forth, it is preferred to quench this stream to about 750° F. Similarly, the second separation zone will function at a significantly reduced pressure less than 100 p.s.i.g., but at a temperature of about 750° F., subject to temperature loss due to flash evaporation at constant enthalpy.

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 contains more than 1.0% by weight of sulfur; and, "distillable hydrocarbons" are those normally liquid hydrocarbons, including pentanes, having boiling points below about 1050° F. Many of the black oils which may be desulfurized and converted by the process of this invention, are considered completely non-distillable—i.e. the total "liquid" boils above 1050° F. Still others are those of which from 10.0% to 60.0% by volume boils above 1050° F. Conversion conditions are intended to be those conditions imposed upon the conversion zone to convert a substantial portion of the black oil into distillable hydrocarbons. As will be readily noted by those skilled in the art of petroleum refining techniques, the conversion con-

ditions hereinafter enumerated, are significantly less severe than those being currently commercially employed. The distinct economic advantages, over and above those inherent in the resulting catalyst stability, will become immediately recognized. The first conversion zone conditions are intended to include temperatures above about 700° F., with an upper limit of about 800° F., as measured at the inlet to the catalyst bed. Since the bulk of the reactions being effected are exothermic, the reaction zone effluent will be at a higher temperature. In order that catalyst stability be preserved, it is preferred to control the inlet temperature such that the effluent temperature does not exceed a maximum limit of about 900° F. Hydrogen is admixed with the black oil charge stock by way of compressive recycle, in an amount generally less than about 10,000 s.c.f./bbl., at the selected operating pressure, and preferably in an amount of from about 3000 to about 6000 s.c.f./bbl. The operating pressure will be greater than 1000 p.s.i.g., and generally in the range of about 1500 p.s.i.g. to about 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. The present process readily lends itself to 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 conversion zone 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 many instances it may be desirable to provide the reaction zone with a segment or beds of inert material such as particles of granite, porcelain, berl saddles, sand, aluminum or other metal turnings, etc., or to supply perforated trays in order to facilitate distribution of the charge.

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 conversion zone, fulfills a number of various functions: it serves as a hydrogenating agent, a heat carrier, and particularly a means for stripping converted material from the catalytic composite, thereby creating still more catalytically active sites available 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 reaction zone can be characterized as comprising a metallic component having hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material of either synthetic 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 charac-

teristics of the charge stock. For example, the metallic components of Group VI-B are preferably present in amounts within the range of about 1.0% to about 2.0% 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, 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.

As hereinbefore stated, the light fraction, initially separated from the fresh charge stock, by-passes the first conversion zone, and is admixed with the vapor phases, or liquids condensed therefrom, from the second and third separation zones for conversion as a mixture in the second reaction zone. Generally, therefore, the charge to the second 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 1100° F. or less, the greater volume thereof being in the range of 650° F. to 1100° F., although a significant amount will be butanes-400° F. With respect to this second reaction zone, 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 reactor will be maintained at a temperature of about 500° F., to about 1000° F. and under an imposed pressure within the range of about 500 to about 3000 p.s.i.g. In this reaction zone, the hydrocarbon charge stock contacts the catalytic composite at a liquid hourly space velocity of from about 0.5 to about 10.0.

The catalyst disposed in the second reaction zone serves the dual function of further converting sulfurous and nitrogenous compounds, and converting those hydrocarbons boiling above about 700° F. to 800° F. into lower boiling hydrocarbons. 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. 1.0% to about 6.0% by weight of nickel. As previously set forth with respect to the first conversion zone, the precise make-up of the catalyst, as well as its method of manufacture, is neither essential to, nor limiting upon the present invention.

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 illustrated by means of 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 crude oil in a commercially scaled unit. It is to be understood that charge stocks, 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, 205,530 lbs./hr. of a crude oil, of which about 15.0% boils above a temperature of 1050° F., having a gravity of 19.0° API at 60° F., and an average molecular weight of about 346, enters the process via line 1. The contaminating influences, characteristic of this crude oil, include 3.25% by weight of sulfur, 2400 p.p.m. of nitrogen, about 170 p.p.m. of metals and slightly more than about 8.0% by weight of heptane-insoluble asphaltics. Following suitable heat-exchange with various hot process streams, the material in line 1 is at a temperature of about 725° F. as it enters a first separation zone, conveniently termed atmospheric flash column 2. Although the initial separation of the fresh charge stock may be effected in any suitable manner which produces a light fraction containing the greater share of distillable hydrocarbons in the feed, the use of an essentially atmospheric pressure flash zone is selected considering the ease of separation at the selected cut point as well as the economic aspects.

A light principally vaporous fraction is removed overhead in line 3, in the amount of 62,763 lbs./hr., and has an average molecular weight of about 188. A heavy fraction, comprising 142,768 lbs./hr., having a molecular weight of about 548, is removed via line 4. This heavy fraction, at a temperature of about 720° F., is admixed with 133,734 lbs./hr. of a hot separator bottoms recycle stream in line 5, the source of which is hereafter described, and a recycle hydrogen stream, in an amount of 80,771 lbs./hr., in line 3. This hydrogen-rich stream is approximately 81.5 mol percent hydrogen, of which 2,840 lbs./hr. is make-up hydrogen from an external source in line 7. The total mixture enters heater 8, wherein the temperature is increased to a level of about 835° F. The heated charge continues through line 9 into reaction, or conversion zone 10 which is under an imposed pressure (at the inlet thereto) of about 2,650 p.s.i.g.

The conversion zone effluent leaves reactor 10 via line 11 at a temperature of about 875° F., and at a pressure of about 2600 p.s.i.g. After its use as a heat-exchange medium, the effluent is passed into hot separator 12 at a temperature of 750° F. and a slightly lower pressure, resulting from fluid flow through the system, of about 2590 p.s.i.g. It should be noted that the pressure in this initial section of the process is substantially the same throughout, the lower pressures naturally resulting from the normal pressure drop due to fluid flow.

A principally vaporous phase is withdrawn from the separator 12 through line 14, in an amount of 149,539 lbs./hr. A liquid phase is withdrawn from separator 12 through line 13, and a portion is diverted through line 5 to be combined with the heavy fraction in line 4. The liquid phase effluent in line 13 (leaving separator 12) is in a total amount of 207,734 lbs./hr. and of this, 133,734 lbs./hr. is diverted via line 5. The remaining portion continues through line 13, and enters hot flash zone 15 at a temperature of about 730° F. In the illustrated embodiment, hot flash zone 15 functions at a pressure of about 75 p.s.i.g. The quantity of material diverted through line 5 from the hot separator effluent in line 13, will be dependent primarily on the degree of contamination of the charge stock. Generally, however, the amount will be such that the combined feed ratio to reactor 10 is within the range of 1.25 to about 3.0.

A residuum fraction, having a molecular weight of about 880, is withdrawn from hot flash zone 15 via line 16 in an amount of about 15,846 lbs./hr. A vaporous fraction, in an amount of 58,154 lbs./hr. is removed via line 17, and is admixed in line 3 with the light fraction from separation zone 2; also admixed with the light fraction is the principally vaporous phase from separator 12.

The mixture continues through line 3, in a total amount of 273,238 lbs./hr., into heater 18, wherein the temperature is increased to about 825° F. In the illustrated embodiment, 2,783 lbs./hr. of make-up hydrogen is added to this charge by way of line 25. The heated charge passes through line 19 into reactor 26 maintained at a pressure of about 2600 p.s.i.g. by compressive means not shown. The effluent from reactor 26, leaving via line 20, is at a temperature of about 875° F.; after passing through condenser 21 and line 22, the effluent enters cold separator 23 at a temperature of about 120° F. A hydrogen-rich gaseous phase is removed from separator 23 through line 6, in the amount of 77,931 lbs./hr. and is recycled thereby to be combined with the heavy fraction in line 4. The normally liquid product is removed from separator 23 through line 24.

Although not illustrated in the drawing, it will be readily recognized that the product stream in line 24 may be subjected to a variety of subsequent separations and/or fractionations to recover any desired boiling range mixture or mixtures, or substantially pure component streams. Significantly, the normally liquid hydrocarbons boiling below about 700° F., in the total product stream in line 24, contain less than 0.001% by weight of sulfur (less than 10.0 p.p.m.).

As herebefore stated, the drawing was described in relation to a commercially scaled unit. The figures presented are those which stem from a unit designed to process 15,000 bbl./day of the crude oil, to produce maximum middle-distillate hydrocarbons. On this basis, the heavy fraction in line 4 is in an amount of 9,900 bbl./day having a gravity of 11.5° API; the light fraction in line 3 is in an amount of 5,100 bbl./day having a gravity of 36.0° API. The residuum fraction in line 16 has a gravity of 1.2° API, and is produced in an amount of 1,020 bbl./day. In the case where the product stream in line 24 is further separated to concentrate the normally liquid hydrocarbons and to provide a gaseous stream intended to be treated in order to recover hydrogen and additional liquid hydrocarbons, the former is recovered in an amount of 15,985 bbl./day and the latter in an amount of 4.8 millions of s.c.f./day. A component analysis, on a mols./hour basis, of the two streams recovered from the product in line 24 is presented in the following Table I:

TABLE I.—PRODUCT ANALYSES

Component	Gaseous Phase	Liquid Stream
Hydrogen Sulfide.....	83.9	119.1
Hydrogen.....	247.4	4.5
Methane.....	135.4	28.1
Ethane.....	26.1	25.2
Propane.....	14.9	40.6
C ₄ -hydrocarbons.....	6.9	45.8
C ₅ -hydrocarbons.....	2.3	36.6
C ₆ -hydrocarbons.....	1.7	63.4
C ₇ -400° F.....	0.7	346.5
400° F.-700° F.....		600.7

It should be noted that a considerable quantity of gasoline boiling range hydrocarbons—i.e. those boiling up to 400° F. and including butanes—are produced. Of the 1310.5 mols./hr. of the liquid stream in Table I, 510.3 mols are in the gasoline boiling range.

With respect to the heavier liquid fraction, containing those hydrocarbons boiling in the 400° F.-700° F. range, one scheme for subsequent use would be as a charge stock to a hydrocracking process to produce additional gasoline boiling range hydrocarbons. Similarly, the butane-400° F. portion might be subjected to catalytic reforming for the production of aromatic hydrocarbons and LPG (liquefied petroleum gas). These, as well as other processing schemes will become evident to those skilled in the art of petroleum refining techniques.

Component analyses of the major streams in the illustrated flow scheme are given in the following tables, and are presented on the basis of mols./hour. The fresh feed

charge rate, to atmospheric flash chamber 2 is 594 mols/hr., of which 334 mols/hr. is taken overhead; for convenience, this stream is hereafter referred to in Table III as a gas oil. The remaining 260 mols/hr. is combined with the various recycle streams as hereinbefore described, and is charged to the first conversion zone. The total hydrogen make-up rate is 2309 mols/hr., of which 60 mols/hr. constitutes methane. In Table II, analyses are presented for the total charge to the first conversion zone 10 (line 9), the total conversion zone effluent (line 11) and the net hot separator liquid to the hot flash zone (line 13), after a portion has been diverted through line 5 as hot recycle.

TABLE II.—STREAM ANALYSES
[Mols/hr.]

Line Number	9	11	20
Component:			
Hydrogen Sulfide	443	591	9.1
Hydrogen	11,314	10,294	112.5
Methane	1,788	1,866	23.4
Ethane	192	228	5.3
Propane	112	145	3.5
Butanes	55	77	2.2
Pentanes	19	33	1.2
Hexanes	11	32	1.4
C ₇ -400° F.	17	102	6.2
400° F.-650° F.	72	302	39.9
650° F.-725° F.	88	79	22.8
725° F.-775° F.	82	81	24.7
775° F.-825° F.	82	82	26.3
825° F.-900° F.	81	81	27.6
900° F.-1,050° F.	76	75	26.4
1,050° F.-plus	116	51	18.0

The 18.0 mols/hr. of the 1050° F.-plus material is that which is removed from hot flash zone 15 as the residuum fraction in line 16.

In the following Table III, component analyses are given for the hot separator vapor phase (line 14), the total charge to second reaction zone 26 (line 19) and the reaction zone total effluent (line 20).

TABLE III.—STREAM ANALYSES
[Mols/hr.]

Line Number	14	19	20
Component:			
Hydrogen Sulfide	556	650.8	758.5
Hydrogen	9,980	12,960.0	13,317.6
Methane	1,801	2,159.6	2,399.6
Ethane	213	250.5	287.2
Propane	135	157.9	192.4
Butanes	71	82.8	117.1
Pentanes	29	33.9	60.4
Hexanes	29	33.4	78.7
C ₇ -400° F.	85	98.3	355.1
400° F.-650° F.	190	229.9	-----
650° F.-725° F.	15	37.8	-----
725° F.-775° F.	11	35.7	-----
775° F.-825° F.	8	34.3	-----
825° F.-900° F.	3	30.6	-----
900° F.-1,050° F.	1	27.4	-----
400° F.-700° F.	-----	-----	600.7
Gas Oil*	-----	334	-----

*The heavy fraction initially separated from the total fresh charge stock in line 4.

To summarize the foregoing, the following Table VI is presented to illustrate overall the yields of various hydrocarbon components from the crude oil charge stock. As hereinbefore stated, the object of this commercially-scaled unit is to maximize the yield of substantially sulfur-free liquid hydrocarbons boiling below about 700° F.

TABLE IV.—OVERALL PRODUCT YIELDS

	°API	Bbl./day	Vol. percent	Wt. percent
5				
Crude Oil	19.0	15,000	100.00	109.00
Hydrogen Consumed	-----	-----	-----	1.95
Ammonia	-----	-----	-----	0.26
Hydrogen Sulfide	-----	-----	-----	3.36
Methane	-----	-----	-----	0.74
Ethane	-----	-----	-----	0.75
Propane	-----	-----	-----	1.19
10				
Iso-butane	-----	110	0.73	0.45
n-Butane	-----	254	1.69	1.04
Iso-pentane	-----	153	1.02	0.68
n-Pentane	-----	154	1.03	0.69
Hexanes	-----	554	3.69	2.73
C ₇ -400° F.	54.4	3,722	24.81	20.07
400° F.-700° F.	33.3	10,264	68.43	62.28
15				
Residuum	1.2	1,020	6.80	7.71

The foregoing specification and example clearly illustrate the method of conducting the present process for the conversion and desulfurization of black oils, and indicate the benefits to be afforded through the utilization thereof.

I claim as my invention:

1. A process for the conversion of a hydrocarbon charge stock of which at least about 10.0% by volume boils above about 1050° F., and which contains at least about 1.0% by weight of sulfur, which process comprises the steps of:

(a) separating said charge stock, in a first separation zone, into a light fraction having an end boiling point of from about 650° F. to about 850° F. and a heavy fraction having an initial boiling point above about 650° F.;

(b) admixing said heavy fraction with hydrogen, and heating the resulting mixture to a temperature above about 700° F.;

(c) contacting the resulting heated mixture with a catalytic composite in a first conversion zone maintained under an imposed pressure greater than about 1000 p.s.i.g.;

(d) separating the resulting conversion zone effluent, in a second separation zone, at substantially the same pressure imposed upon said conversion zone, and at a temperature above about 700° F., to provide a first vapor phase and a first liquid phase;

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

(f) combining said second vapor phase, said first vapor phase and said light fraction, and contacting the resulting mixture with a catalytic composite in a second conversion zone at conditions selected to convert sulfurous compounds into hydrogen sulfide and hydrocarbons; and,

(g) separating the second conversion zone effluent, in a fourth separation zone, at a temperature of from about 60° F. to about 130° F. to provide a hydrogen-rich third vapor phase and a normally liquid hydrocarbon product.

2. The process of claim 1 further characterized in that said hydrogen-rich third vapor phase is recycled to combine with said heavy fraction.

3. The process of claim 1 further characterized in that said first liquid phase is part recycled to combine with said heavy fraction and said hydrogen-rich third vapor phase.

4. The process of claim 1 further characterized in that said second separation zone is maintained at a temperature below about 750° F.

5. The process of claim 1 further characterized in that at least a portion of said first liquid phase is recycled to combine with said charge stock.

No references cited.

HERBERT LEVINE, *Primary Examiner*.