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MIXED-PHASE CONVERSION PRODUCT
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The present invention relates to a product separation 10
process, and especially to a mixed-phase conversion prod-
uct separation process. More specifically, the present in-
vention involves a particular scheme for separating a
mixed-phase hydrocarbonaceous product effluent result- 15
ing from the conversion of a heavier-than-gasoline (boil-
ing substantially, completely above a temperature of 400°
F.) hydrocarbon charge stock, which product effluent
contains hydrogen, normally liquid hydrocarbons and
normally gaseous hydrocarbons.

The mixed-phase separation process hereinafter de- 20
scribed in detail, is applicable to a hydrocarbon conver-
sion process which may be classified as hydrogen-consum-
ing, and in which processing techniques dictate the re-
cycle of a hydrogen-rich gaseous phase and, in many in-
stances, the recycle of at least a portion of the normally
liquid product effluent. Such hydrogen-consuming pro- 25
cesses include the hydrotreating, or hydrotreating of kero-
sene fractions, middle-distillate fractions, light and heavy
vacuum gas oils, light and heavy cycle stocks, etc., for the
primary purpose of reducing the concentration of various
contaminating influences contained therein. Another typi- 30
cal hydrogen-consuming hydrocarbon conversion process
is known in the petroleum refining art as "hydrocrack-
ing." Basically, hydrocracking techniques are utilized to
convert relatively heavy hydrocarbonaceous material into
lower-boiling hydrocarbon products such as gasoline and 35
fuel oil. In other instances, the desired end result is the
production of liquefied petroleum gas. Relatively recent
developments in the area of petroleum technology have
indicated that the hydrocracking reactions can be applied
successfully to residual stocks, or so-called "black oils." 40
Exemplary of the material classified as black oils, are at-
mospheric tower bottoms products, vacuum tower bot-
toms products (vacuum residuum), crude oil residuum,
topped crude oils, crude oils extracted from tar sands, etc.
As hereinafter indicated by specific example, and by the
embodiment presented for illustrative purposes in the ac- 45
companying drawing, the utilization of the present prod-
uct separation process affords unusual advantages in a
process effecting the conversion of black oils. It will be
noted, however, that the foregoing brief description of
petroleum processes to which the present separation pro-
cess is adaptable, utilize hydrocarbon charge stocks boiling
above the gasoline boiling range—i.e. having an initial
boiling point above about 400° F.

For the sake of convenience and simplification, and
without the intent of unduly limiting the present inven-
tion beyond the scope and spirit of the appended claims,
the following discussion will be directed to the use of the
present invention in a process for the conversion of heavy
hydrocarbonaceous material broadly classified as black
oils. Black oils, particularly the heavy oils extracted from
tar sands, topped or reduced crudes, and vacuum resid-
uum, etc., contain high molecular weight sulfurous com-
pounds in exceedingly large quantities. In addition, these
black oils contain excessive quantities of nitrogenous
compounds, high molecular weight organo-metallic com-
plexes comprising nickel and vanadium, and a consider-
able amount of asphaltic material. 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 proportion of which has a gravity less than
10.0. This material is generally further characterized by
a boiling range indicating that 10.0% or more, by volume,
boils above a temperature of about 1050° F. Although
the amount is not known accurately, a significant quantity
of the available black oils are further characterized in
that more than 50.0% by volume thereof 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, such as gasoline
and fuel oil, is precluded by present-day refining tech-
niques, due especially to the exceedingly high sulfur and
asphaltic concentrations. The conversion of a portion of
such material into distillable hydrocarbons—i.e. those
boiling below 1050° F.—has hitherto been 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.

Specific examples of the black oils, the conversion of
which utilizes advantageously the present mixed-phase
separation process, include a vacuum tower bottoms prod-
uct having a gravity of 7.1° API at 60° F., and contain-
ing 4.1% by weight of sulfur and 23.7% by weight of 25
asphaltics; a "topped" Middle East Kuwait crude oil,
having a gravity of 11.0° API at 60° F., and contain-
ing 10.1% by weight of asphaltics and about 5.2%
by weight of sulfur; and a vacuum residuum having a
gravity of 8.8° API at 60° F., and containing 3.0% by
weight of sulfur and 4300 p.p.m. of nitrogen, and having
a 20.0% volumetric distillation point at 1055° F. Gener- 30
ally, the asphaltic material is found to be colloiddally dis-
persed within the black oil, and, when subjected to ele-
vated temperatures, has the tendency to flocculate and
polymerize, whereby the conversion thereof to more val-
uable oil-soluble products becomes extremely difficult.
Thus, the heavy bottoms from a crude oil vacuum distil-
lation column indicates a Conradson Carbon Residue fac-
tor 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.

The principal object of the present invention is to pro-
vide an improved process for separating a mixed-phase
hydrocarbonaceous reaction product effluent, which prod-
uct effluent contains hydrogen, normally liquid hydrocar-
bons and normally gaseous hydrocarbons.

Another object of this invention is to afford a mixed-
phase conversion product separation process, which prod-
uct effluent contains hydrogen, normally liquid hydrocar-
bons, a portion of both of which is intended to be
recycled to a conversion process, and normally gaseous
hydrocarbons including methane, ethane, and propane.

Another object is to convert sulfur-contaminated black
oils having a gravity, at 60° F., of less than about 20.0°
API, and a boiling range indicating that a substantial por-
tion thereof is non-distillable, into lower boiling distil-
lable hydrocarbon products of significantly reduced sul-
fur concentration.

These and other objects are achieved by the present in-
vention as more completely described hereinbelow, and
especially with reference to the accompanying drawing
which is a simplified representation of one embodiment.

In a broad embodiment, therefore, the present inven-
tion affords a process for separating a mixed-phase hydro-
carbonaceous reaction product effluent, resulting from the
conversion of a hydrocarbon charge stock boiling above
a temperature of about 400° F., said product effluent con-
taining hydrogen to be recycled, normally liquid hydro-
carbons, and normally gaseous hydrocarbons, which proc-
ess comprises the steps of: (a) separating said effluent

in a first separation zone under substantially the same pressure as said effluent, to provide a first liquid phase and a first vapor phase; (b) cooling said vapor phase to a temperature within the range of from about 60° F. to about 140° F., and separating the cooled vapor phase in a second separation zone at substantially the same pressure as said first separation zone, to provide a hydrogen-rich second vapor phase and a second liquid phase; (c) separating said first liquid phase in a third separation zone at substantially the same temperature as in said first separation zone, and under a substantially reduced pressure, to provide a third liquid phase containing normally liquid hydrocarbons, and a third vapor phase; (d) cooling said third vapor phase and combining it with said second liquid phase, separating the resulting mixture in a fourth separation zone at a temperature of from 60° F. to about 140° F. to provide a fourth vapor phase containing normally gaseous hydrocarbons and a separated fourth liquid phase containing normally liquid hydrocarbons.

Other embodiments of my invention reside in particular operating conditions and in the use of specific internal recycle streams. The latter includes recycle of a portion of said fourth liquid phase to combine with the cooled first vapor phase, prior to separation of the latter in said second separation zone. Also, a portion of said first liquid phase is recycled to combine with the charge stock to the conversion zone. The first separation zone, referred to as a hot separator, is maintained at essentially the same pressure as the reaction product effluent being initially separated therein, and, for the various hydrogen-consuming conversion processes hereinbefore described, such pressure is in the range of from about 1000 p.s.i.g. to about 3000 p.s.i.g. It is further preferred that the temperature of the reaction product effluent, as it enters this hot separator, is below about 750° F. At temperatures above 750° F., the heavier normally liquid hydrocarbons are carried over in the first vapor phase, whereas at temperatures below about 700° F., ammonium salts, resulting from the conversion of nitrogenous compounds contained within the hydrocarbonaceous charge stock, tend to fall into the liquid phase. The second separation zone, although maintained under essentially the same pressure as the reaction product effluent and the hot separator, is at a temperature of from about 60° F. to about 140° F., and is referred to as a cold separator. Although the third and fourth separation zones may be maintained at substantially the same pressure, the pressure therein is substantially reduced from the pressure under which the hot and cold separators are maintained. Thus, although the pressure of the third and fourth separation zones will generally be superatmospheric, the maximum pressure will be about 200 p.s.i.g. The third separation zone, referred to as a hot flash zone, will, however, operate at an elevated temperature somewhat less than the temperature of the first liquid phase emanating from the first separation zone, and generally above about 700° F. On the other hand, the fourth separation zone, referred to as a cold flash zone, will operate at a significantly reduced temperature within the range of about 60° F. to about 140° F.

Through the use of the various embodiments hereinabove set forth, three principal product streams are obtained. A first product stream is essentially a gaseous phase rich in hydrogen, and generally containing at least about 80.0 mol percent thereof, and less than about 0.1% of normally liquid hydrocarbons; it is therefore, extremely well suited as a hydrogen-rich recycle gaseous phase. A second product stream, also essentially a gaseous phase, contains about 97.5 mol percent propane and lighter gaseous components, including substantial quantities of hydrogen sulfide resulting from the conversion of sulfurous compounds. The third product stream consists essentially of normally liquid hydrocarbon products which may be subjected to fractionation for the purpose of obtaining particularly desired selected fractions thereof. For example, as hereinafter specifically indicated, 4.5% by

volume of gasoline boiling range (up to about 380° F.) hydrocarbons are produced, middle-distillate hydrocarbons in an amount of about 10.0% by volume and about 88.0% by volume of a fuel oil containing less than 1.0% by weight of sulfur.

From the foregoing brief description, it will be readily ascertained by those possessing skill in the art of petroleum processing techniques, that the present invention comprises a series of integrated steps for the separation of a mixed-phase reaction product effluent in an easy and economical manner. As hereinbefore set forth, the present invention is uniquely adaptable to processes designed for the conversion of black oils. Those skilled in the art, however, will recognize the fact that the novel mixed-phase separation process of the present invention is equally applicable to various reaction product effluent streams which may be obtained from sources other than the conversion of such hydrocarbon black oils. In describing the present invention for mixed-phase separation of a conversion reaction product effluent, the conversion of the previously described black oils will be employed. The conversion of black oils is intended to accomplish primarily two objects: first, to desulfurize the black oil to the extent dictated by the desired end result, whether maximizing fuel oil, or gasoline boiling range hydrocarbons; secondly, it is intended to produce "distillable hydrocarbons," being those normally liquid hydrocarbons including pentanes, having boiling points below about 1050° F. The conversion conditions are those conditions imposed upon a conversion zone for the purpose of achieving both desulfurization and conversion into lower-boiling hydrocarbon products. It will be noted by those skilled in the art of petroleum refining techniques, that the conversion conditions hereinafter enumerated are significantly less severe than those being currently commercially employed in processing similar charge stocks. The distinct economic advantages, over and above those normally stemming from the production of the more valuable distillable hydrocarbons, will be recognized. The conversion conditions are intended to include temperatures above 700° F., with an upper limit of about 800° F., as measured at the inlet to the fixed-bed of catalyst disposed within the reaction zone. 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 at a level such that the temperature of the reaction product effluent does not exceed 900° F. Hydrogen is admixed with the black oil charge stock, by means of compressive recycle, in an amount usually less than about 10,000 s.c.f./bbl., at the selected operating pressure; the hydrogen is present in the recycle gaseous phase preferably in an amount of about 80.0% or more. A preferred range of the quantity of hydrogen being admixed with the fresh black oil charge stock is from about 3000 to about 6000 s.c.f./bbl. The conversion reaction zone will be maintained at a pressure greater than about 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 point of pressure measurement, for the purpose of the control thereof, is generally either the discharge of the compressive means, the inlet to the catalyst bed, or the pressure in the cold separator. The black oil passes through the catalyst at a liquid hourly space velocity (defined as volumes of liquid hydrocarbon charge per hour, as measured at 60° F., per volume of catalyst disposed within the reaction zone) of from about 0.25 to about 2.0. Notwithstanding that the conversion of black oils may be conducted in a batchwise fashion, it readily lends itself to the more economical continuous processing in an enclosed vessel. When conducted as a continuous process, it is preferred to introduce the hydrogen-hydrocarbon mixture into the vessel in such a manner that the same passes therethrough in downward flow. The internals of the vessel may be constructed in any suitable manner capable of providing the required 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 of inert materials such as particles of granite, porcelain, berl saddles, sand, aluminum or other metal turnings, etc., to facilitate distribution of the charge stock, 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 gaseous phase, 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 available catalytically active sites for the incoming, unconverted hydrocarbon charge stock. In view of the fact that some hydrogenation will be effected, there will be a net consumption of hydrogen; to supplement this, hydrogen must be added to the system from a suitable external source. However, as a result of the incorporation of the present separation process whereby the quantity of hydrogen being removed from the reaction section is considerably decreased, the amount of make-up hydrogen necessarily added is also decreased.

The catalytic composite disposed within the reaction zone can be characterized as comprising a metallic component possessing hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material which may be of either synthetic or natural origin. The precise composition and method of manufacturing the carrier material is not considered to be an essential element of the present process, although a siliceous carrier, such as 88.0% by weight of alumina and 12.0% by weight of silica, or 63.0% alumina and 37% silica, are generally preferred for processes designated to convert black oils. Suitable metallic components, having hydrogenation activity, are those selected from the group consisting of the metals of Group VI-B and VII 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 dictated by the particular metal as well as the physical and chemical characteristics of the black oil charge stock. The metallic components of Group VI-B are generally 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, 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.

Other conditions and preferred operating techniques will be given in conjunction with the following description of one embodiment incorporating the mixed-phase separation process of the present invention. In further describing this process, reference will be made to the ac-

companying figure which is presented for the purpose of illustration. 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 illustrated process flow, are well within the purview of those skilled in the art.

For the purpose of demonstrating the illustrated embodiment, and the utilization therein of the mixed-phase separation process of the present invention, the drawing will be described in connection with the conversion of a Middle East reduced crude oil having a gravity of 16.6° API at 60° F., and an ASTM 65.0% volumetric distillation temperature of 1034° F. The reduced crude oil contains about 3.8% by weight of sulfur, 2032 p.p.m. of nitrogen, 6.5% by weight of pentane-insoluble asphaltics, a Conradson Carbon Residue factor of 8.0 weight percent and about 85 p.p.m. of metals, the latter being principally nickel and vanadium. In addition, the description will be directed toward a commercially-scaled unit having a capacity of 40,000 bbl./day of reduced crude oil. 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 reduced crude oil, having an average molecular weight of about 600, enters the process through line 1. It should be added that this commercially-scaled unit is designed for the primary purpose of maximizing the quantity of distillable fuel oil (boiling above about 650° F.) with the restriction that this product contain less than 1.0% by weight of sulfur. Furthermore, it is intended that this object be accomplished with minimal production of propane and lighter hydrocarbons. That is, with respect to that portion of the conversion product effluent boiling at temperatures below about 650° F., and constituting normally gaseous hydrocarbons, gasoline boiling range hydrocarbons, and middle-distillate hydrocarbons, it is intended that there be minimum production of the light, normally gaseous hydrocarbons, with accompanying maximum production of the normally liquid hydrocarbons.

The 40,000 bbl./day of reduced crude oil, 557,620 lbs./hr., entering the process via line 1, is admixed with makeup hydrogen of about 97.5 mol percent purity in an amount of 9440 lbs./hr., from an external source indicated by line 2. It has been found appropriate in some instances to add water to the reaction zone in admixture with the charge stock. When this is deemed advisable, it takes place via line 3; for the present illustrative purposes, it is presumed that such water addition is not being effected. The hydrogen-crude oil mixture continues through line 1, being further admixed with 159,420 lbs./hr. of a hydrogen-rich recycle gaseous phase (about 80.0 mol percent hydrogen) in line 4, the source of which is hereinafter set forth. The total charge, after suitable heat-exchange with various effluent streams not illustrated, is at a temperature of about 525° F. and a pressure of about 2165 p.s.i.g.

Heater 5 is employed to raise the temperature of the charge to about 705° F., and the heated mixture in line 6 is admixed with 527,190 lbs./hr. of a hot recycle stream (750° F.) in line 7; the reactor charge at 720° F. continues through line 6 into conversion reactor 8 at a pressure of about 2125 p.s.i.g. The catalyst disposed in conversion zone 8 is a composite of 2.0% by weight of nickel, 16.0% by weight of molybdenum and a carrier material of 68.0% by weight of alumina, 22.0% by weight of boron phosphate and 10.0% by weight of silica. The reduced crude oil contacts the catalyst at a liquid hourly space velocity of 0.8, and the combined feed ratio, based

only on normally liquid charge, is 2.0. The total conversion product effluent leaves reactor 8 via line 9, and passes therethrough into hot separator 10. Since the conversion effluent product is at a temperature of about 780° F. and a pressure of 2075 p.s.i.g., it is employed as a heat-exchange medium in order that its temperature be lowered to 750° F., prior to entering hot separator 10. The pressure within hot separator 10 is about 2060 p.s.i.g., lower than reactor 8 inlet pressure due to pressure drop through the system. A first liquid is withdrawn from separator 10 through line 11, in an amount of 975,600 lbs./hr., and of this amount 527,190 lbs./hr. are diverted through line 7 to combine with the heated mixture in line 6. The remaining portion, 448,410 lbs./hr., continues through line 11 into hot flash zone 24.

A first vapor phase in an amount of 278,070 lbs./hr. is removed from hot separator 10 through line 12, passes through condenser 13 whereby the temperature is lowered to 120° F.; at this point, due to pressure drop through the system, the pressure is about 2005 p.s.i.g. The cooled first vapor phase passes through line 14, is admixed with a portion, 275,780 lbs./hr., of a fourth liquid phase in line 23 hereinafter described, and the mixture is introduced into cold separator 15. A second vapor phase containing about 80.0 mol percent hydrogen, in an amount of 159,420 lbs./hr., is removed via line 16, is raised to a pressure of about 2245 p.s.i.g. via compressor 17, and discharges through line 4 to combine with the charge stock and make-up hydrogen in line 1. As hereinbefore set forth, there are some situations in which water is added to the charge stock via line 3; in such situations, the water is removed via line 34 as indicated.

The first liquid phase in line 11 entering hot flash zone 24 is at a temperature of about 745° F. and a substantially reduced pressure of about 220 p.s.i.g. A third liquid phase is removed via line 27 in an amount of 425,610 lbs./hr., to be combined with a fourth liquid phase, hereinafter described, as the major product stream. A third vapor phase is removed through line 25 in an amount of 22,800 lbs./hr., and is cooled to about 105° F. in condenser 26, prior to continuing through line 19 into cold flash separator 20. The cooled third vapor phase is combined with a second liquid phase in line 18 from cold separator 15, the latter in an amount of 393,930 lbs./hr., the total charge to the cold flash zone thus being 416,730 lbs./hr. In the illustrated embodiment, the material entering cold flash separator 20 is at a pressure of about 200 p.s.i.g. and a temperature of 105° F.

A fourth vapor phase, in an amount of 19,450 lbs./hr. (97.5 mol percent, propane and lighter normally gaseous components), is removed from separator 20 through line 21. Since the material contains a considerable quantity of hydrogen sulfide, it is generally subjected to a suitable treating process prior to being vented and/or burned as flue gas. The particular economic aspects to be considered will dictate whether the fourth vapor phase is suitably treated to recover the small quantity of C₄-plus normally liquid hydrocarbons contained therein. A fourth liquid phase, in an amount of 397,280 lbs./hr., is removed from cold flash zone 20 through line 22. Of this amount, 275,780 lbs./hr. is diverted through line 23 to be combined with the cooled first vapor phase in line 14, forming thereby the feed stream to cold separator 15. The remaining 121,500 lbs./hr. is combined with the third liquid phase in line 27, the mixture continuing through line 22 to fractionator heater 28, and through line 29 into fractionator 30. It is understood that the third liquid phase in line 27 is combined with the unrecycled portion of the fourth liquid stream in line 22 for illustrative purposes only. For reasons peculiar to the particular operation involved, these streams may be separately fractionated to recover desired product streams.

Fractionator 30 will be operated at conditions of temperature and pressure, and will be designed in accordance with the desired fractions to be recovered there-

from. With respect to the commercially-scaled unit being described, as previously stated, the primary objective was to maximize the production of fuel-oil (650° F.-plus) having a sulfur concentration not greater than 1.0% by weight. This product, in an amount of 480,550 lbs./hr., is indicated as leaving fractionator 30 via line 33. A second, middle-distillate fraction (380° F.-650° F.) is removed via line 32 in an amount of 42,440 lbs./hr. The gasoline boiling range material, having an end boiling point of 380° F., is removed via line 31 in an amount of 24,120 lbs./hr.

As hereinbefore set forth, many modifications may be made to the illustrated flow without removing the same from the scope of the invention. For example, the ammonia and/or ammonium salts contained in conversion zone 8 effluent, may be removed from the process by being adsorbed in water which is injected into the reaction product effluent before the same is passed into hot separator 10. The water and ammonia are removed with the first vapor phase, introduced into cold separator 15, and subsequently withdrawn via line 34. Where desired, the water may be injected into the first vapor phase leaving hot separator 10.

In further illustration of the present invention, the following tables indicate the various feed streams and separated phases of hot separator 10, cold separator 15, hot flash zone 24 and cold flash zone 20. The following Table I illustrates the composition of the conversion zone effluent (line 9), the first vapor phase (line 12) and the first liquid phase (line 11) prior to diverting a portion to the conversion zone via line 7.

TABLE I.—HOT SEPARATOR STREAM ANALYSES

	Line No.		
	9	12	11
Component, mols/hr.:			
Water.....	19.36	19.36	-----
Ammonia.....	29.47	29.47	-----
Hydrogen Sulfide.....	2,559.27	2,374.70	184.57
Hydrogen.....	19,274.72	18,363.82	910.90
Methane.....	2,634.79	2,492.28	142.51
Ethane.....	206.31	184.75	21.56
Propane.....	176.24	156.55	19.69
Iso-butane.....	31.96	27.80	4.16
N-butane.....	68.82	59.70	9.12
Iso-pentane.....	19.53	16.42	3.11
N-pentane.....	17.88	14.96	2.92
C ₆ -380° F.....	202.97	153.21	49.76
380° F.-650° F.....	359.63	160.94	198.69
650° F.-plus.....	2,299.21	160.37	2,138.84
Totals.....	27,900.16	24,214.33	3,685.83

With respect to the foregoing tabulation, it should be noted that the 19.36 mols/hr. of water in the reaction zone effluent is a consequence of the water of saturation in the recycle gas. As hereinafter indicated, a minor portion of this water finds its way into the hydrogen-rich recycled gaseous phase (line 16 in the drawing). The function of hot separator 10 is indicated by virtue of the fact that 63.3 mol percent of the first liquid phase (line 11) consists of 380° F.-plus hydrocarbons, while the first vapor phase contains 98.6 mol percent of material boiling below about 380° F. However, the first liquid phase comprises about 24.7 mol percent of hydrogen and a total of 36.7% material boiling below about 380° F.

In the following Table II, there is presented the component analyses of the feed stream to cold separator 15 (line 14), the hydrogen-rich recycled gaseous phase (line 16) and the second liquid phase (line 18). The analysis shown for line 14 takes into account the injection of water for ammonia removal and the fact that the material in line 14 is the combined first vapor phase (line 12) and a portion of the fourth liquid phase (line 23 diversion from line 22).

TABLE II.—COMPONENT STREAM ANALYSES; COLD SEPARATOR

Component, mols/hr.:	Line No.		
	14	16	18
Water.....	*991.16	19.36	-----
Ammonia.....	29.47	-----	-----
Hydrogen Sulfide.....	2,653.51	1,957.24	696.27
Hydrogen.....	18,370.63	18,205.54	165.09
Methane.....	2,508.51	2,372.04	136.47
Ethane.....	197.89	157.58	40.31
Propane.....	187.44	127.66	59.78
Iso-butane.....	38.08	21.30	16.78
N-butane.....	87.94	43.51	44.43
Iso-pentane.....	29.63	10.16	19.47
N-pentane.....	28.96	8.53	20.43
C ₆ -380° F.....	452.66	19.74	462.92
380° F.-650° F.....	551.29	0.07	551.22
650° F.-plus.....	601.66	-----	601.66
Totals.....	26,788.83	22,942.73	2,844.83

*971.80 mols/hr. of water injection for ammonia removal. This, along with the 29.47 mols/hr. of ammonia are removed via line 34.

The data presented in Table II illustrates the function of cold separator 15 and the advisability of combining a portion of the fourth liquid phase (line 23) with the charge thereto. As a result, the recycled hydrogen-rich second vapor phase, as one of the three product streams of the present separation process, contains about 80.0 mol percent hydrogen, and is virtually void of the 380° F.-plus hydrocarbonaceous material, while the second liquid phase (line 18) contains 61.3 mol percent of butanes-and-heavier hydrocarbons.

Hot flash zone 24 serves to separate light gaseous material from the normally liquid hydrocarbons ultimately fractionated in fractionator 30. Were these gaseous components not removed at this point, the presence of the same in fractionator 30 would make overhead condensation for reflux purposes extremely difficult, and would unnecessarily adversely affect the recovery of gasoline hydrocarbons. A number of compressive stages and/or absorption zones would be required to fractionate to recover the desired product streams. In the following Table III, the attainment of this objective is clearly illustrated by the component analyses of that portion of the first liquid phase not diverted through line 7, (termed line 11a for convenience in the table), the third vapor phase from the hot flash zone (line 25) and the third liquid phase (line 27).

TABLE III.—COMPONENT STREAM ANALYSES, HOT FLASH ZONE

Component, mols/hr.:	Line No.		
	11a	25	27
Water.....	-----	-----	-----
Ammonia.....	-----	-----	-----
Hydrogen Sulfide.....	84.83	75.81	9.02
Hydrogen.....	418.67	391.23	27.44
Methane.....	65.50	60.91	4.59
Ethane.....	9.91	8.37	1.54
Propane.....	9.05	7.48	1.62
Iso-Butane.....	1.91	1.49	0.42
N-butane.....	4.19	3.25	0.94
Iso-pentane.....	1.43	1.03	0.40
N-pentane.....	1.34	0.96	0.38
C ₆ -380° F.....	22.87	13.82	9.05
380° F.-650° F.....	91.32	24.32	67.00
650° F.-plus.....	983.06	34.02	949.02
Totals.....	1,694.08	622.66	1,071.42

It should be noted from Table III that the third liquid phase (line 27) contains 94.7 mol percent of 380° F.-plus hydrocarbons, and only 2.5 mol percent of hydrogen. Taking into account the C₆-380° F. gasoline portion, the third liquid phase constitutes only 4.3 mol percent of material boiling below hexane.

In the following Table IV, the function of cold flash zone 20 is illustrated by the component analyses of the feed thereto in line 19, being the mixture of the second liquid phase and the cooled third vapor phase, the fourth vapor phase (line 21) and the fourth liquid phase (line 22). For convenience, by way of indicating an end result

of the separation process, Table IV includes the component analysis of the combined third (line 27) and fourth (line 22) liquid phases, after a portion of the latter has been diverted via line 23 to combine with the first vapor phase in line 14. This would be the material continuing through line 22 into heater 28 for product separation in fractionator 30.

TABLE IV.—COMPONENT ANALYSES, COLD FLASH ZONE

Components, mols/hr.:	Line No.			
	19	21	22	22-27
Water.....	-----	-----	-----	-----
Ammonia.....	-----	-----	-----	-----
Hydrogen Sulfide.....	772.08	370.44	122.83	131.85
Hydrogen.....	556.32	546.51	3.00	30.44
Methane.....	197.38	174.00	7.15	11.74
Ethane.....	48.68	29.75	5.79	7.33
Propane.....	67.21	22.71	13.61	15.23
Iso-butane.....	18.27	3.46	4.53	4.95
N-butane.....	47.68	7.00	12.44	13.28
Iso-pentane.....	20.50	1.47	5.82	6.22
N-pentane.....	21.39	1.22	6.17	6.55
C ₆ -380° F.....	476.74	2.15	145.14	154.19
380° F.-650° F.....	605.54	-----	185.19	252.19
650° F.-plus.....	635.70	-----	194.41	1,143.43
Totals.....	3,467.49	1,153.71	706.08	1,777.50

From the data presented in Table IV, it will be immediately ascertained that the combined third and fourth liquid phases comprise about 89.0 mol percent butanes-and-heavier hydrocarbons, and that the fourth vapor phase (line 21) constitutes 97.5 mol percent propane and light gaseous material. It should be further noted that the final separated normally liquid product, ultimately fractionated into the desired product fractions, contains only 1.7 mol percent hydrogen. It will be recognized that this has a significant beneficial effect with respect to the economic design and ease of operation of fractionator 30.

To summarize the foregoing, the following Table V indicates the overall yields on both a volumetric and weight basis. The desired product of the black oil conversion process described, was the maximum quantity of fuel oil (650° F.-plus) having a sulfur content of less than 1.0% by weight. As seen from the following table, this product was obtained in an amount of 87.9% by volume.

TABLE V.—BLACK OIL CONVERSION OVERALL YIELDS

	° API	Bbl./day	Vol. percent	Wt. percent
Reduced Crude.....	16.6	40,000	100.00	100.00
Hydrogen Consumed.....	-----	-----	-----	1.15
Ammonia.....	-----	-----	-----	0.09
Hydrogen Sulfide.....	-----	-----	-----	3.07
Methane.....	-----	-----	-----	0.20
Ethane.....	-----	-----	-----	0.20
Propane.....	-----	266	0.67	0.30
Iso-butane.....	-----	60	0.15	0.09
N-butane.....	-----	139	0.35	0.21
Iso-pentane.....	-----	61	0.15	0.10
N-pentane.....	-----	61	0.15	0.10
C ₆ -380° F.....	54.9	1,510	3.77	3.00
380° F.-650° F.....	33.0	3,998	10.00	9.00
650° F.-plus.....	22.0	35,160	87.90	84.79
Totals.....	-----	41,215	103.04	101.15

Also noted is the fact that the desired product was recovered at the expense of the production of only 0.7% by weight of light gaseous waste products, methane, ethane and propane. Of further significance is the fact that 1510 bbl./day of gasoline boiling range hydrocarbons were produced, and about 4000 bbl./day of middle-distillate, the combined sulfur content of these two streams being only about 0.3% by weight. Also, a butane-pentane concentrate may be recovered, where desired as a motor fuel blending component, in an amount of more than 320 bbl./day.

The foregoing specification and example clearly illustrate the conversion product separation process of the present invention, and indicate the benefits to be afforded through the utilization thereof. The unique application of this mixed-phase separation process to the conversion of black oils has also been demonstrated.

I claim as my invention:

1. A process for separating a mixed phase hydrocarbonaceous reaction product effluent, resulting from the conversion of a hydrocarbon charge stock boiling above a temperature of about 400° F., said product effluent containing hydrogen to be recycled, normally liquid hydrocarbons, and normally gaseous hydrocarbons, which comprises the steps of:

- (a) separating said effluent in a first separation zone under substantially the same pressure as said effluent, to provide a first liquid phase and a first vapor phase;
- (b) cooling said first vapor phase to a temperature within the range of from about 60° F. to about 140° F., and separating the cooled vapor phase in a second separation zone at substantially the same pressure as said first separation zone, to provide a hydrogen-rich second vapor phase and a second liquid phase;
- (c) separating at least a portion of said first liquid phase in a third separation zone at substantially the same temperature as in said first separation zone, under a substantially reduced pressure, to provide a separated third liquid phase, containing normally liquid hydrocarbons, and a third vapor phase;
- (d) cooling said third vapor phase and combining it with said second liquid phase, separating the resulting mixture in a fourth separation zone at a temperature of from 60° F. to about 140° F. to provide a fourth vapor phase containing normally gaseous hydrocarbons and a separated fourth liquid phase containing normally liquid hydrocarbons.

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

3. The process of claim 1 further characterized in that a portion of said fourth liquid phase is combined with said cooled first vapor phase, prior to separation in said second separation zone.

4. The process of claim 1 further characterized in that said product effluent is separated in said first separation zone at a temperature below about 750° F.

5. The process of claim 1 further characterized in that said third and fourth separation zones are maintained at substantially the same pressure.

6. A process for the conversion of an asphaltic hydro-

carbon charge stock of which at least about 10% 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) admixing said charge stock with hydrogen and heating the resulting mixture to a temperature above about 700° F.;
- (b) contacting the resulting heated mixture with a conversion catalyst in a reaction zone under an imposed pressure greater than about 1,000 p.s.i.g.;
- (c) separating the resulting reaction zone effluent in a first separation zone under substantially the same pressure as said effluent and at a temperature not exceeding 750° F., to provide a first liquid phase and a first vapor phase;
- (d) cooling said first vapor phase to a temperature within the range of from about 60° F. to about 140° F., and separating the cooled vapor phase in a second separation zone at substantially the same pressure of said first separation zone, to provide a hydrogen-rich second vapor phase and a second liquid phase, and recycling said second vapor phase to combine with said charge stock;
- (e) recycling a portion of said first liquid phase to combine with said charge stock and separating the remainder in a third separation zone at substantially the same temperature as in said first separation zone, under a substantially reduced pressure to provide a separated third liquid phase containing normally liquid hydrocarbons and a third vapor phase;
- (f) cooling said third vapor phase and combining it with said second liquid phase, separating the resulting mixture in a fourth separation zone at a temperature of from 60° F. to 140° F. to provide a fourth vapor phase containing normally gaseous hydrocarbons and a separated fourth liquid phase containing normally liquid hydrocarbons.

References Cited

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