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[56]

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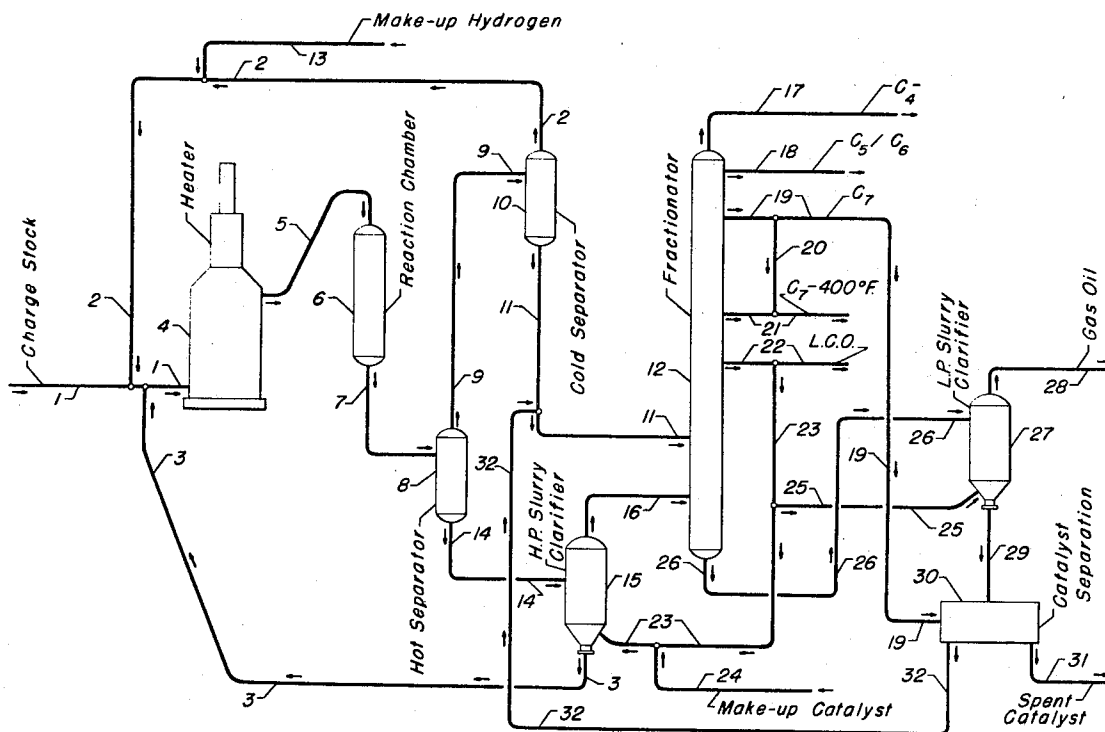
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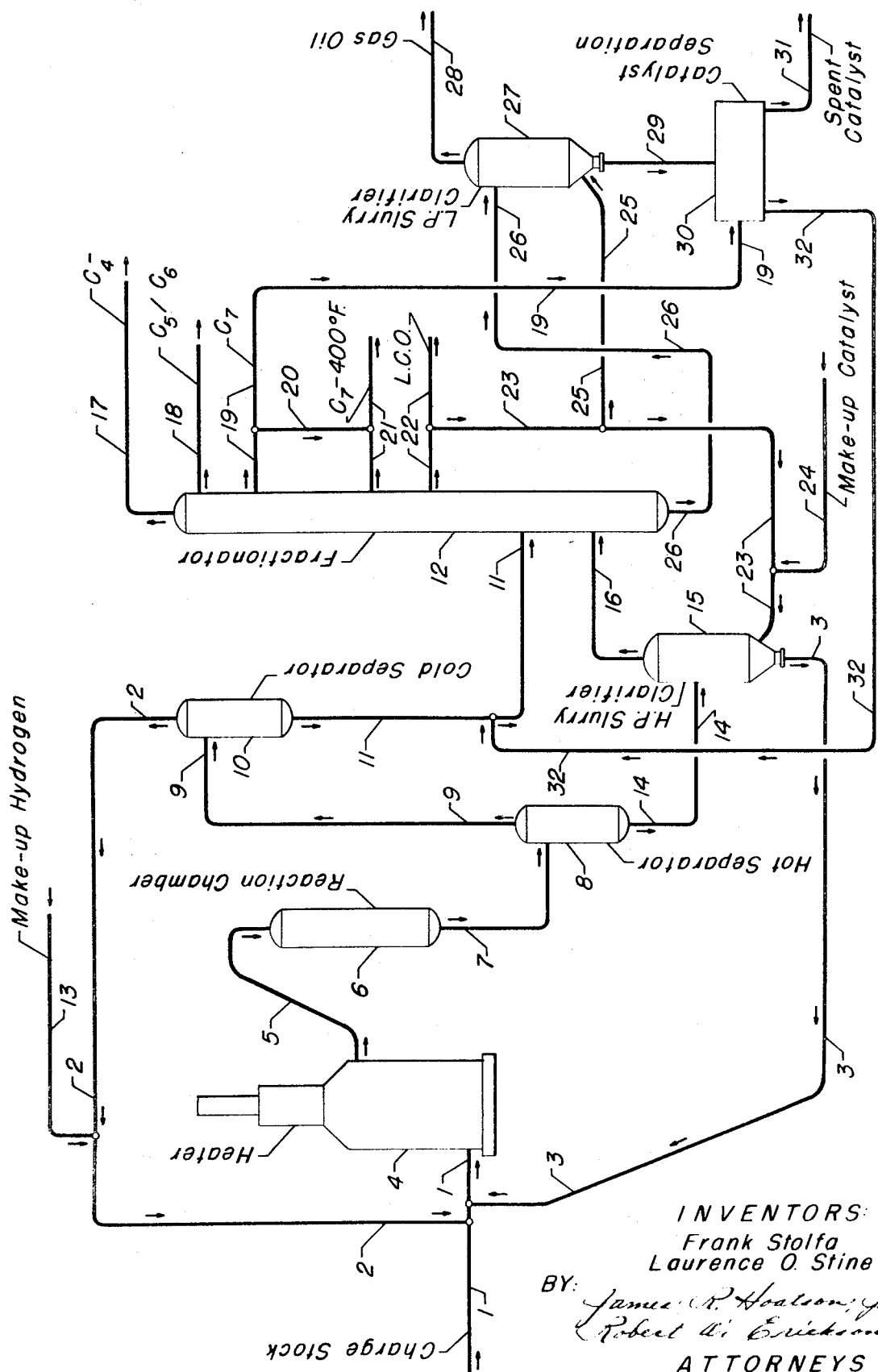
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[54] **SLURRY PROCESSING FOR BLACK OIL
 CONVERSION**
 7 Claims, 1 Drawing Fig.

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ABSTRACT: A catalytic slurry process for effecting the conversion of a hydrocarbonaceous charge stock containing asphaltenes and metallic contaminants. The slurry constitutes the charge stock, hydrogen, a portion of the previously produced product effluent and from about 1.0 to about 25.0 percent by weight of finely divided catalyst particles. Preferred catalysts are the unsupported sulfides of the metals from Groups V-B, VI-B and VIII. A series of product separation steps facilitates catalyst circulation, catalyst withdrawal, and recovery of a substantially catalyst-free product.





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SLURRY PROCESSING FOR BLACK OIL CONVERSION

APPLICABILITY OF INVENTION

The process described herein is applicable to the conversion of petroleum crude oil residuals having a high metals content and comprising a hydrocarbon-insoluble asphaltene fraction. More specifically, our invention is directed toward a method for effecting a catalytic slurry process, in the presence of hydrogen, in order to convert atmospheric tower bottoms, vacuum column bottoms, crude oil residuals, topped and/or reduced crude oils, coal oil extracts, crude oils extracted from tar sands, etc., all of which are commonly referred to in the art as "black oils."

Petroleum crude oils, and particularly the heavy residuals obtain therefrom, contain sulfurous compounds in exceedingly large quantities, nitrogenous compounds, high molecular weight organometallic complexes principally comprising nickel and vanadium as the metallic component, and hydrocarbon-insoluble asphaltenic material. The latter is generally found to be complexed with sulfur, and, to a certain extent, with the metallic contaminants. A black oil is generally characterized in petroleum technology as a heavy hydrocarbonaceous material of which more than about 10.0 percent (by volume) boils above a temperature of about 1,050° F. (referred to as nondistillables) and which further has a gravity less than 20.0° API. Sulfur concentrations are exceedingly high, most often in the range of about 2.0 percent to about 6.0 percent by weight. Conradson carbon residue factors generally exceed 1.0 percent by weight and the concentration of metals can range from as low as 20 p.p.m. to as high as about 750 p.p.m. by weight.

The process encompassed by the present invention is particularly directed toward the conversion of those black oils contaminated by large quantities of insoluble asphaltenes and a high metals content—i.e. containing more than about 150 p.p.m. by weight. Specific examples of the charge stocks to which the present technique is adaptable, include a vacuum tower bottoms product having a gravity of 7.1° API and containing 4.1 percent by weight of sulfur and 23.7 percent by weight of heptane-insoluble materials; a "topped" Middle East crude oil having a gravity of 11.0° API and containing about 10.1 percent by weight of asphaltenes and 5.2 percent by weight of sulfur; and, a vacuum residuum having a gravity of 8.8° API, containing 3.0 percent by weight of sulfur and 4,300 p.p.m. by weight of nitrogen.

The utilization of our invention affords the conversion of such material into distillable hydrocarbons, heretofore having been considered virtually impossible to achieve on a continuous basis with an acceptable catalyst life. The principal difficulty, heretofore encountered in a fixed-bed catalytic system, resides in the lack of sufficient stability of the catalyst in the presence of such relatively large quantities of metals—i.e. from about 150 p.p.m. to as high as 750 p.p.m., computed as the elements— and additionally from the presence of large quantities of asphaltenic material and other nondistillables. The asphaltic material comprises high molecular weight coke precursors, insoluble in light normally liquid hydrocarbons such as pentane and/or heptane. The asphaltic material is generally found to be disbursed within the black oil, and, when subjected to elevated temperature, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult.

Candor compels recognition of the many slurry-type processes which have heretofore been proposed. Regardless of the various operating and processing techniques, the principal difficulty resides in the separation of the reaction product effluent to provide substantially catalyst-free distillable product, internal catalyst circulation and "spent" catalyst withdrawal. Success has been achieved only through the use of intricate equipment at prohibitively high costs. An obvious alternative is to utilize the black oil as the charge to a coking unit for the production of coke and distillable hydrocarbons. In view of the steadily increasing demand for distillable

hydrocarbons, particularly motor fuels, jet fuels and stocks for conversion into liquefied petroleum gas, coking is no longer suitable because of its relatively low yield of distillable hydrocarbons. Our invention provides a slurry process having a series of separation steps integrated therein. There is afforded, thereby, a more economical and less difficult process from the standpoint of the desired product recovery, internal catalyst recirculation and catalyst withdrawal.

OBJECTS AND EMBODIMENTS

A principal object of our invention is to convert nondistillable hydrocarbonaceous material into lower boiling distillable hydrocarbons. A corollary objective is to provide a catalytic slurry process for the hydrogenative conversion of an asphaltene-containing black oil charge stock.

Another object is to convert a black oil charge stock into distillable hydrocarbons with minimum yield loss to unconventable asphaltic residuum.

Still another object of our invention is to provide a catalytic slurry process which facilitates separation of the cracked product effluent, internal catalyst circulation and catalyst withdrawal.

Therefore, in one embodiment, our invention provides a process for converting an asphaltene-containing hydrocarbonaceous charge stock which comprises the steps of:

a. forming a reactive slurry of said charge stock, hydrogen and a finely-divided catalyst containing at least one metal component from the metals Groups V-B, VI-B, and VIII;

b. reacting said slurry in a reaction chamber at cracking conditions including a pressure above about 1,000 p.s.i.g. and a temperature above about 800° F.;

c. separating the resulting cracked product effluent in first separation zone, at substantially the same pressure and a temperature below about 900° F., to provide a first vaporous phase and a first-catalyst containing liquid phase;

d. separating said first vaporous phase in a second separation zone, at substantially the same pressure and a lower temperature of from 60° to about 140° F., to provide a second liquid phase and a second vapor phase, recycling at least a portion of the latter to combine with said charge stock and catalyst;

e. separating said first liquid phase in a third separation zone, at substantially the same pressure and a lower temperature of from 500° to about 850° F., to provide a third liquid phase and a catalyst-containing fourth liquid phase;

f. separating said second and third liquid phases, in a fourth separation zone at conditions of temperature and pressure to provide a heptane concentrate, a light cycle oil concentrate and a catalyst-containing fifth liquid phase;

g. separating said fifth liquid phase and at least a portion of said light cycle oil in a fifth separation zone, to provide a sixth liquid phase substantially free from said catalyst and catalyst-containing seventh liquid phase; and,

h. removing the catalyst from said seventh liquid phase in a sixth separation zone.

Other embodiments of our invention are directed toward particular operating techniques and preferred ranges of operating variables and conditions. Thus, the process is further characterized in that the catalyst-containing fourth liquid phase is recycled to combine with the charge stock. The catalyst concentration, within the slurry being introduced into the reaction chamber, is in the range of from about 1.0 to about 25.0 percent by weight, based upon fresh feed charge stock, and preferably from 2.0 to about 15.0 percent.

SUMMARY OF INVENTION

The particular finely divided, solid catalyst utilized in the present slurry process, is not considered to be essential. However, it must be recognized that preferred catalytically active metallic components possess both cracking and hydrogenation activity. In most applications of our invention, the catalytically active metallic component, or components, will be

selected from the metals of Groups V-B, VI-B and VIII of the Periodic Table. Thus, in accordance with *The Periodic Table of the Elements*, E. H. Sargent and Company, 1964, the preferred metallic components are vanadium, chromium, iron, cobalt, nickel, niobium, molybdenum, tantalum and/or tungsten. The noble metals of Group VIII, namely ruthenium, rhodium, palladium, osmium, iridium, and platinum, are not generally considered use in a slurry-type process in view of the economic considerations involved with these relatively expensive metals. The foregoing metallic components may be combined with a refractory inorganic oxide carrier material, including alumina, silica, zirconia, magnesia, titania, mixtures of two or more, etc., the final composite being reduced to a finely divided state. In such a composite, the active metallic components may exist in some combined form such as the oxide, sulfide, sulfate, carbonate, etc. However, recent investigations and developments in catalytic slurry processing of heavy hydrocarbon charge stocks have indicated that the sulfides of the foregoing metals, and particularly those of Group V-B, offer advantageous results. Furthermore, the process appears to be facilitated when the sulfide of the metal is unsupported, as contrasted to being combined with a refractory inorganic oxide carrier material. For this reason, the preferred unsupported catalyst for use in the process of the present invention, comprises tantalum, niobium or vanadium sulfides, the latter being particularly preferred. In the interest of brevity, the following discussion will be limited to the use of vanadium sulfides, in an amount of about 1.0 to about 25.0 percent by weight, as the catalyst in the present slurry process.

Regardless of the character of the catalyst, it may be prepared in any suitable, convenient manner, the precise method not being essential to the present invention. For example, vanadium sulfides may be prepared by reducing vanadium pentoxide with sulfuric acid, sulfur dioxide and water to yield a solid hydrate or vanadyl sulfate. The latter is treated with hydrogen sulfide at a temperature of about 300° C. to form vanadium tetrasulfide. Reducing the vanadium tetrasulfide in hydrogen, at a temperature above about 300° C., produces the vanadium sulfide slurried into the system. As hereinbefore set forth, the concentration of vanadium sulfide is preferably within the range of about 2.0 to about 15.0 percent by weight, calculated as the elemental metal. Excessive concentrations do not appear to enhance the results, even with extremely contaminated charge stock having exceedingly high asphaltene contents.

DESCRIPTION OF DRAWING

In the accompanying drawing, illustrating one embodiment of the present invention, a simplified flow diagram is utilized. Details such as pumps, instrumentation and controls, heat exchange and heat recovery circuits, valving, startup lines and similar hardware have been omitted; these are considered nonessential 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. Similarly, it is understood that the charge stock, stream compositions, operating conditions, catalyst, design of fractionators, separators and the like are exemplary only, and may be varied widely without departure from the spirit of our invention, the scope of which is defined by the appended claims.

The drawing will be described in connection with a Laguna reduced crude having a gravity of about 9.8° API, and initial boiling point of 560° F., a 10.0 percent volumetric distillation temperature of 700° F., a 30.0 percent volumetric distillation temperature of 851° F. and a 50.0 percent volumetric distillation temperature of 1,000° F. Contaminating influences include nitrogen in an amount of 5,190 p.p.m. by weight, 9.55 percent by weight of heptane-insoluble material, 2.80 percent by weight of sulfur, about 438 p.p.m. by weight of vanadium and about 74 p.p.m. by weight of nickel. The crude oil indicates an average molecular weight of 598 and carbon/hydrogen atomic ratio of about 7.95.

With reference now to the drawing, the reduced crude is introduced into the process by a way of line 1, and is admixed with a hydrogen-rich recycle vaporous phase in line 2 and a catalyst-containing liquid phase from line 3. Following heat exchange with hot effluent streams, which technique is not illustrated, the mixture continues through line 1 into heater 4. With respect to the total charge mixture, the hydrogen concentration is in the range of about 1,000 to about 50,000 s.c.f./bbl. of fresh charge stock, and preferably from about 5,000 to about 20,000 s.c.f./bbl., and the catalyst concentration is in the range of about 2.0 to about 15.0 percent by weight of vanadium sulfide, calculated as elemental vanadium. Heater 4 increases the temperature of the mixture to a level range of about 800° F. to about 1,000° F., the heated mixture being introduced into reaction chamber 6 by way of line 5 at a pressure in the range of about 500 to about 4,000 p.s.i.g., and preferably from about 1,000 to about 3,000 p.s.i.g. The design of the internals of reaction chamber 6 are not essential to our invention, and they may be constructed utilizing well-known devices such as disc and donut trays, side-to-side pans, etc. Similarly, in order to assure intimate mixing and contacting of the reactants, a variety of mechanical devices such as spray nozzles, bayonets, distributing grids, etc., may be employed. Residence time, within the reaction chamber depends upon a multitude of considerations. Not the least of these considerations involve temperature, the degree of mixing, catalyst concentration, charge stock characteristics, the degree of conversion and the volumetric ratio of recycle material to fresh feed. In most applications of our invention, the residence time will range from about 30 seconds to about 4 minutes.

The reaction zone effluent is withdrawn through line 7 and, following its use as a heat exchange medium, is introduced thereby into hot separator 8 at a temperature in the range of about 700° to about 900° F. As utilized herein, the phrase "pressure substantially the same as" is intended to indicate that the pressure of a succeeding downstream vessel is the same as that of the upstream vessel, allowing only for the pressure drop normally experienced as a result of fluid flow through the system. The hot separator serves to provide a first principally vaporous phase, withdrawn as an overhead product by way of line 9, containing the lighter components of the cracked product effluent, primarily hydrogen, hydrogen sulfide, ammonia, normally gaseous hydrocarbons and distillable hydrocarbons boiling below a temperature of about 900° F. A first principally liquid phase is withdrawn from hot separator 8 by way of line 14. Hot separator 8 functions in the manner which provides for the greater proportion of catalyst being removed in this normally liquid phase. The first vaporous phase in line 9 is cooled and condensed to a temperature in the range of about 60° to about 140° F., and passes therethrough into cold separator 10. A hydrogen-rich, vaporous phase is withdrawn from cold separator 10 by way of line 2, and recycled therethrough to combine with the charge stock in line 1. The recycled gaseous phase may be treated by any means well known in the art for the purpose of removing hydrogen sulfide and other gaseous components in order to increase the concentration of hydrogen. Makeup of hydrogen, to supplant that consumed in reaction chamber 6, is introduced into the process by way of line 13. The second liquid phase, from cold separator 10, is withdrawn by way of line 11 and introduced into fractionator 12.

Following its use as a heat exchange medium, the liquid phase slurry in line 14, at a temperature in the range of about 500° to about 850° F. is introduced into a separation zone 15. In the drawing, separation zone 15 is illustrated as being a high-pressure slurry clarifier, and functions to concentrate the catalyst particles in a liquid phase being withdrawn by way of line 3, and recycled therethrough to combine with the charge stock and recycle hydrogen in line 1. The quantity of hydrocarbons being recycled by way of line 3 is such that the combined liquid feed ratio, to reaction chamber 6, is in the range of about 1.1 to about 6.0, and preferably from about 1.5 to about 3.0. The normally liquid phase withdrawn as an overhead stream from high-pressure slurry clarifier 15, by way of

line 16, contains from about 0.1 to about 0.4 percent by weight of catalyst particles, and is introduced into fractionator 12, preferably at a locus below that through which the liquid phase in line 11 is introduced. Fractionator 12 functions at conditions of temperature and pressure selected to provide (1) a heptane concentrate in line 19, (2) a light cycle oil concentrate, boiling in the range of about 400° to about 700° F. in line 22 and (3) a catalyst-containing concentrate boiling above a temperature of about 700° F. in line 26. In addition to these specifically designated streams, there is illustrated a typical product recovery including a normally gaseous overhead in line 17, containing butanes and lower boiling normally gaseous products, a pentane/hexane concentrate in line 18 and a heptane-400° F. boiling range fraction in line 21. The catalyst-containing bottom stream in line 26, at a pressure of from atmospheric to about 100 p.s.i.g., continues there-through into a low-pressure slurry clarifier 27 at a temperature of from 600° to about 800° F. In order to facilitate the separation of the catalyst particles in clarifier 27, a portion of the light cycle oil stream is cooled and diverted by way of lines 23 and 25 into the conical section of clarifier 27. Another portion of the light cycle oil continues through line 23, being introduced thereby into high pressure slurry clarifier 15 in the conical section thereof. With respect to high pressure slurry clarifier 15, the hot separator bottoms entering by way of line 14 has a density of approximately 0.6 grams/ml. The catalyst particles settle into the cone of the clarifier where they are taken up by the light cycle oil entering the cone by way of line 23, the mixture being recycled by way of line 3. Since this stream has a density of approximately 0.8 grams/ml., insignificant mixing occurs between the two hydrocarbon streams, and little catalyst is removed from clarifier 15 by way of overhead line 16. Makeup catalyst is introduced into the system by way of line 24 and the light cycle oil recycle in line 23.

A gas oil concentrate is removed from low pressure slurry clarifier 27 by way of line 28. This stream constitutes a product of process, and although not illustrated in the drawing, may be conveniently introduced into a typical vacuum column for the purpose of separating residuum therefrom. A light cycle oil, catalyst-containing stream is withdrawn from low-pressure slurry clarifier 27 by way of line 29, and is introduced therethrough into catalyst separation zone 30. Any suitable means may be utilized to separate solid catalyst particles from the liquid phase hydrocarbons, including filtration, settling tanks, a series of centrifuges, etc. In accordance with our invention, one feature constitutes introducing a portion of the heptane concentrate from line 19 into catalyst separation zone 30. The heptane concentrate is employed to remove residual, soluble hydrocarbons from the catalyst sludge, the heptane-containing stream subsequently being introduced into fractionator 12 by way of line 32 and 11. The catalyst sludge, containing about 2.0 to about 10.0 percent by weight of the catalyst employed, is considered a drag stream and may be treated in any manner which produces a vanadium sulfide for reuse within the process. One such procedure involves burning the sludge in air, thereby producing vanadium pentoxide. This is subsequently reduced with sulfur dioxide, sulfuric acid and water to produce vanadyl sulfate. The procedure then follows the previously described scheme for the preparation of fresh vanadium sulfide.

DESCRIPTION OF A PREFERRED EMBODIMENT

This preferred embodiment will be described in conjunction with a commercially scaled unit processing about 25,000 barrels per day of Laguna reduced crude. In describing the various separations being effected, frequent reference will be made to the accompanying drawing.

The fresh feed charge stock, in an amount of 696 moles/hr., is admixed with 1,540 moles/hr. of a light cycle oil recycle (about 25,000 bbl./day, providing a combined liquid feed ratio of 2.0) containing about 17,378 pounds of vanadium sulfide catalyst. The charge is also admixed with 10,270

moles/hr. of a hydrogen-rich recycle gas stream (about 8,611 moles of hydrogen) and 3,788 moles/hr. of makeup hydrogen (about 3,725 moles of hydrogen). The mixture is heated to a temperature of about 825° F., and enters the reaction chamber 6 at a pressure of about 2,000 p.s.i.g. After its use as a heat exchange medium, the reaction chamber effluent is introduced into a hot separator at a temperature of 830° F. and a pressure of about 1,975 p.s.i.g. Component analyses of the total charge (line 5) and the effluent (line 7), in moles/hr., is presented in table I.

TABLE I
REACTION CHAMBER CHARGE AND EFFLUENT

Component	Line 5	Line 7
Fresh Feed	696	—
Ammonia	—	27
Hydrogen Sulfide	124	332
Hydrogen	12,336	9,223
Methane	1,406	1,658
Ethane	71	177
Propane	43	139
Butanes	13	75
Pentanes	2	2
Pentane-400° F.	—	289
400° F.-650° F.	1,540	2,023
650° F.-1050° F.	—	490
Residuum	—	30
Catalyst	17,378	17,378

In pounds per hour.

The vaporous phase from the hot separator (line 9) is cooled and condensed to a temperature of about 100° F., and is introduced into a cold separator. The cold separator serves to provide 10,270 moles/hr. of a hydrogen-rich recycle gas (line 2) which is admixed with 3,788 moles/hr. of makeup hydrogen, and a normally liquid phase (line 11) which is introduced into a fractionator system. The liquid phase from the hot separator (line 14) is passed into a high-pressure (about 1,950 p.s.i.g.) slurry clarifier at a temperature of about 825° F. A principally liquid phase (line 16) is introduced into the fractionation system. Light cycle oil in an amount of 1,540 moles/hr., containing about 306 lbs./hr. of fresh catalyst, is introduced into the slurry clarifier, at a temperature of 150° F., and recycled (line 3) to combine with the fresh charge stock. Component analyses of the separation effected in the cold separator 10 are presented in the following table II:

TABLE II
COLD SEPARATOR SEPARATION

Component	Line 9	Line 2	Line 11
Ammonia	25	—	—
Hydrogen Sulfide	195	124	71
Hydrogen	8,747	8,611	136
Methane	1,532	1,406	126
Ethane	95	71	24
Propane	86	43	43
Butanes	20	13	42
Pentanes	—	2	—
Pentane-400° F.	235	—	235
237	—	—	—

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400° F.-650° F.	1,239	—	1,239
650° F.-1050° F.	8	—	75
Residuum	Tr.	—	Tr.

*The 25 mols./hr. of ammonia are removed by injecting water into the vaporous phase and supplying cold separator 10 with a dip-leg. This technique is not illustrated in the accompanying drawing.

The separation effected in the high slurry clarifier is presented in table III. The light cycle oil recycle, 1,540 moles/hr. (line 23), introduced into the cone of the clarifier is not listed as part of the feed (line 14).

TABLE III

Component	Line 14	Line 16	Line 3
Ammonia	2	2	—
Hydrogen Sulfide	137	137	—
Hydrogen	476	476	—
Methane	126	126	—
Ethane	82	82	—
Propane	53	53	—
Butanes	20	20	—
Pentane—400° F.	54	54	—
400° F.-650° F.	784	784	1,540
650° F.-1,050° F.	415	415	—
Residuum	30	30	—
Catalyst *	17,378	306	17,378 **

* In pounds per hour.

**Includes 306 lbs./hr. of Fresh Catalyst.

The total charge to fractionator 12 has the composition presented in table IV, inclusive of 10 moles/hr. of heptane introduced into catalyst separation zone 30, and 39 moles/hr. of light cycle oil introduced into clarifier 27.

TABLE IV
FRACTIONATOR FEED COMPOSITION

Component	
Ammonia	2
Hydrogen Sulfide	208
Hydrogen	612
Methane	252
Ethane	106
Propane	96
Butanes	62
Heptanes	10
Pentane—400° F.	289
400° F.-650° F.	2,062
650° F.-1,050° F.	490
Residuum	30

A butane-minus overhead stream, containing about 62 moles/hr. of butane and 454 moles/hr. of C1-C3, is removed from fractionator 12 by way of line 17. The pentane/hexane concentrate, withdrawn by way of line 18, is in an amount of 81 moles/hr. Heptane concentrate is withdrawn by way of line

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19, and 10 moles/hr. thereof is introduced into catalyst separation zone 30, the remainder being diverted via line 20 as part of the heptane-400° F. product in line 21. The total heptane-400° F. product is recovered in an amount of 213 moles/hr. Of the 2,062 moles/hr. of light cycle oil (400°-650° F.) withdrawn from fractionator 12, 1,540 moles are introduced into high-pressure slurry clarifier 15, and 39 moles/hr. are introduced into low-pressure slurry clarifier 27.

The bottoms from fractionator 12, in the amount of 520 moles/hr. containing 306 lbs./hr. of catalyst, are introduced into low-pressure slurry clarifier 27. A gas oil containing stream is removed by way of line 28, and introduced into a vacuum column (not illustrated), from which 30 moles/hr. of residuum are removed (containing about 41 lbs./hr. of catalyst) and 490 moles/hr. of heavy vacuum gas oil are recovered.

The catalyst and light cycle oil are introduced into a centrifuge system utilizing 10 moles/hr. of a heptane wash. Catalyst is recovered in an amount of 265 lbs./hr. and sent to a metal recovery system.

In summation, on the basis of 696 moles/hr. of fresh feed, or 353,775 lbs./hr., the yields of the various recovered streams are: 17,689 lbs./hr. of residuum, or about 5.0 percent by weight; 490 moles/hr. of a heavy vacuum gas oil; 483 moles/hr. of a light cycle oil; 81 moles/hr. of a pentane/hexane concentrate; 62 moles/hr. of a butane concentrate; and, 11,462 lbs./hr. of methane, ethane and propane, or only about 3.2 percent by weight of the fresh feed charge stock.

We claim as our invention:

1. A process for converting an asphaltene-containing hydrocarbonaceous charge stock which comprises the steps of:

- a. forming a reactive slurry of said charge stock, hydrogen and a finely divided catalyst containing at least one metal component from the metals of Groups V-B, VI-B or VIII;
- b. reacting said slurry in a reaction chamber at cracking conditions including a pressure above about 1,000 p.s.i.g. and a temperature above about 800° F.;
- c. separating the resulting cracked product effluent in a first separation zone, at substantially the same pressure and a temperature below about 900° F., to provide a first vaporous phase and a first catalyst-containing liquid phase;
- d. separating said first vaporous phase in a second separation zone, at substantially the same pressure and a lower temperature of from 60° to about 140° F., to provide a second liquid phase and a second vapor phase, recycling at least a portion of the latter to combine with said charge stock and catalyst;
- e. separating said first liquid phase in a third separation zone, at substantially the same pressure and a lower temperature of from 500° to about 850° F., to provide a third liquid phase and a catalyst-containing fourth liquid phase;
- f. separating said second and third liquid phases, in a fourth separation zone at conditions of temperature and pressure to provide a heptane concentrate, a light cycle oil concentrate and a catalyst-containing fifth liquid phase;
- g. separating said fifth liquid phase and at least a portion of said light cycle oil in a fifth separation zone, to provide a sixth liquid phase substantially free from said catalyst and a catalyst-containing seventh liquid phase; and,
- h. removing the catalyst from said seventh liquid phase in a sixth separation zone.

2. The process of claim 1 further characterized in that said catalyst-containing fourth liquid phase is recycled to combine with said charge stock.

3. The process of claim 1 further characterized in that said sixth liquid phase is introduced into said fourth separation zone.

4. The process of claim 1 further characterized in that at least a portion of said heptane concentrate is introduced into said sixth separation zone.

5. The process of claim 1 further characterized in that said catalyst is a sulfide of at least one metal from Groups V-B, VI-B or VIII.

6. The process of claim 5 further characterized in that said catalyst is a vanadium sulfide.

7. The process of claim 1 further characterized in that said cracked product effluent is separated in said first separation zone at a temperature of from 700° to about 900° F.

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