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HYDROCARBON SEPARATION PROCESS

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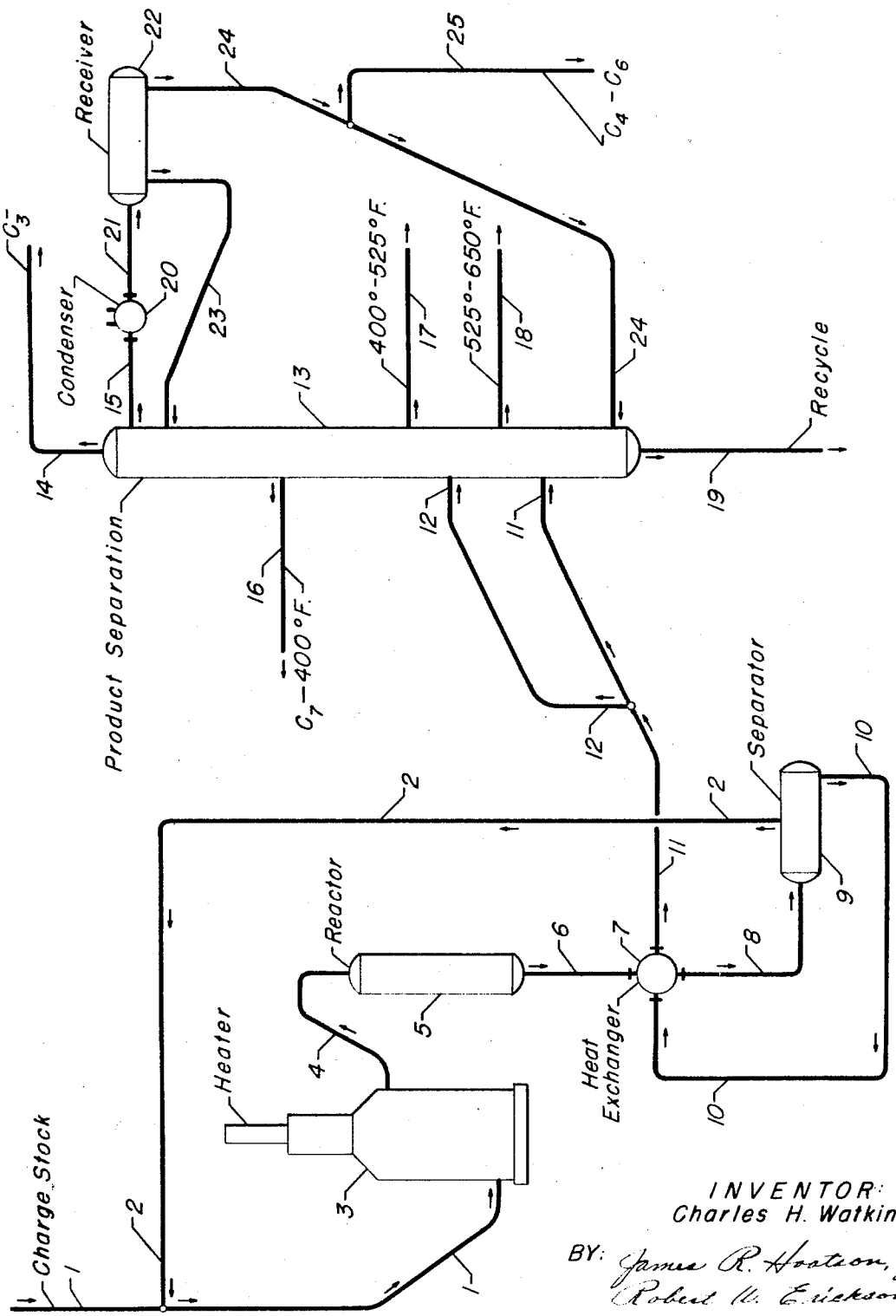

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HYDROCARBON SEPARATION PROCESS

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ABSTRACT OF THE DISCLOSURE

A combination stripping-fractionation technique for the separation of a mixed-phase hydrocarbonaceous material. Applicable especially for the separation and recovery of a hydrocarbon fraction having a predetermined end boiling point, from a hydrocracked product effluent containing hydrocarbons boiling below the initial boiling point of the desired fraction as well as above the predetermined end boiling point. Substantially complete recovery of those hydrocarbons boiling below the predetermined end boiling point is assured, thereby excluding the same from a heavier fraction normally utilized as recycle in combination with fresh charge stock.

Applicability of invention

The inventive concept encompassed by the process herein described, is generally applicable to the separation of mixed-phase hydrocarbonaceous material. Mixed-phase hydrocarbon mixtures are intended to be those containing normally gaseous components including hydrogen and light paraffinic hydrocarbons and butanes, as well as normally liquid hydrocarbons and various hydrocarbons boiling within the gasoline, middle-distillate, kerosene and gas oil boiling ranges. It will be recognized that this particular type of hydrocarbon mixture is characteristic of the product effluent emanating from a hydrocracking process designed to produce lower boiling hydrocarbons. Therefore, the following description of my invention will be directed toward its use in the separation of a mixed-phase, hydrocracked product effluent, wherein the present concept is particularly advantageous.

Hydrocracking, which is also commonly referred to as "destructive hydrogenation," may be designed as cracking under hydrogenation conditions such that the lower-boiling hydrocarbon products, stemming from the cracking reaction, are substantially more saturated than when hydrogen is not present. Hydrocracking processes are most commonly utilized for the conversion of coal oils, tars and various heavy residual oils for the primary purpose of producing substantial yields of lower-boiling saturated products. Although hydrocracking reactions, or destructive hydrogenation processes, may be conducted thermally, a perusal of the prior art indicates that the preferred processing techniques involve the use of a catalytic composite having a high degree of hydrocracking activity. Hydrocracking has assumed a particular degree of importance for the processing of hydrocarbons and mixtures of hydrocarbons having normal boiling points above the middle-distillate boiling range; that is, hydrocarbons and mixtures of hydrocarbons having a boiling range indicating an initial boiling point of from about 550° F. to about 700° F. and an end boiling point which may range as high as 1000° F. or more. These heavier hydrocarbon fractions are converted into lower-boiling hydrocarbon products which may be conveniently referred to as gasoline and middle-distillate fractions. Previous investigation has indicated that the presence of nitrogen-containing compounds within the intended charge stock results in the relatively rapid deactivation

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of the catalytically active metallic components of a great variety of hydrocracking catalysts. Also present in varying degree, in the greater majority of charge stocks intended for hydrocracking, are other "contaminating influences" including sulfurous compounds, organo-metallic complexes, higher molecular weight asphaltics, etc. In order to effect an acceptable, economically feasible hydrocracking process, prior art schemes involve various multiple-stage reaction systems. In these processes, the charge stock is generally initially processed in a first reaction zone under operating conditions which are conducive to hydrorefining reactions resulting in the destructive removal of the nitrogenous compounds and other contaminating influences. The principally liquid-phase portion of the hydrorefined effluent is then generally subjected to hydrocracking in one or more subsequent reaction zones for the purpose of converting the heavier material into lower-boiling hydrocarbon products. The present invention is directed particularly to the separation of the product effluent emanating from the last of such hydrocracking zones.

The intended object of the prior art hydrocracking processes generally resides in the maximum production of a hydrocarbon fraction having a predetermined end boiling point. For example, it may be desired to maximize the production of a kerosene fraction having an initial boiling point of about 400° F. and an end boiling point of about 525° F., from a hydrocarbonaceous charge stock boiling virtually completely beyond the temperature of about 650° F. The product effluent from the last hydrocracking reaction zone is generally introduced into various product separating means including one or more fractionators, distillation columns, flash chambers, etc., whereby the desired fraction is separately recovered, and those hydrocarbons boiling above the predetermined end boiling point (in this case 525° F.) are recycled as a heavy fraction to be combined with the fresh hydrocarbonaceous feed stock.

The improvement induced by the integration of the present invention within such a hydrocracking process, resides in the substantial decrease in the concentration of hydrocarbons boiling below the predetermined end boiling point within the heavy fraction, being recycled. Such lighter hydrocarbons, when recycled with the hydrocarbonaceous charge stock, have the tendency to undergo further cracking to produce the normally gaseous components, methane, ethane and propane. Obviously, this reduces considerably the ultimate yield of the desired fraction which can be obtained from a given quantity of feed stock.

Objects of the embodiments

An object of the present invention is, therefore, to increase the yield of a particularly desired fraction obtainable from a given quantity of hydrocarbonaceous material.

A corollary objective is to reduce the quantity of the desired fraction contained in the heavier material intended to be recycled to the various reaction zones.

Another object of the present invention is to afford an improvement in the present-day methods involved with the hydrocracking of various hydrocarbonaceous charge stocks.

Therefore, a broad embodiment of my invention is directed toward a process for separating a mixed-phase product effluent comprising butanes and normally liquid hydrocarbon components to provide at least one normally liquid fraction having a predetermined end boiling point which process comprises the steps of: (a) introducing said product effluent into product separation means; (b) removing a vaporous fraction, substantially free from

butanes and heavier hydrocarbons, as an overhead product from said separation means; (c) removing a light hydrocarbon fraction, containing butanes, pentanes and hexanes from said separation means; (d) removing a heavier hydrocarbon fraction having said predetermined end boiling point from an intermediate locus of said separation means; (e) introducing at least a portion of said light hydrocarbon fraction into said separation means at a locus below that from which the heavier fraction is removed; and, (f) removing a bottoms fraction from said separating means at a locus below that at which said light hydrocarbon fraction is introduced, said bottoms fraction being substantially free from hydrocarbons boiling below said predetermined end boiling point.

The process, as described in the foregoing embodiment, may be further characterized in that a second portion of said light hydrocarbon fraction is returned to an upper locus of said separation means. Further, that the predetermined end boiling point is a maximum of about 700° F., and generally not below a minimum of 350° F.

As hereinbefore set forth, a specific embodiment of the present invention involves an improvement in a process for hydrocracking heavy hydrocarbonaceous material, into lower-boiling hydrocarbon products in a catalytic reaction zone, in which process the hydrocracked product effluent is separated to provide a principally liquid hydrocarbon fraction having a predetermined end boiling point, and at least a portion of the product effluent boiling above said predetermined boiling point is recycled for further hydrocracking in the catalytic reaction zone, the recycled portion containing hydrocarbons boiling below said predetermined end boiling point.

From the foregoing embodiments, it will be noted that the separation process encompassed by my invention is most advantageously employed as an integral part of a process for the hydrocracking of heavy hydrocarbonaceous material. Other objects and embodiments will become evident from the following description of the embodiment illustrated in the accompanying drawing.

Description of drawing

Before describing my invention with reference to the accompanying drawing, several definitions are believed necessary in order that a clear understanding of the present invention be afforded. The phrase, "hydrocarbons boiling within the gasoline boiling range," or "gasoline boiling range hydrocarbons," is intended to connote those hydrocarbons boiling at temperatures up to about 400° F. or 450° F., including C_5-hydrocarbons and, in some localities C_4-hydrocarbons. However, for the purpose of more clearly defining the component yields of the present process, "gasoline" will allude to a C_5–400° F. hydrocarbon fraction, notwithstanding that commercially-scaled units in various locales will raise or lower the end boiling point as dictated by the then current marketing requirements. Similarly, a "kerosene" fraction may have an initial boiling point in the range of 300° F. to about 400° F. (or the end boiling point of the gasoline fraction), and an end boiling point of from about 500° F. to about 550° F. "Middle-distillate," or "gas oil" fractions will, therefore, have an initial boiling point in the range of from about 500 to about 550° F. and an end boiling point of from 600° F. to about 750° F. Heavier gas oil fractions comprise the remainder of a given product effluent containing those hydrocarbons boiling up to about 1050° F.

With reference now to the drawing, there is indicated, in addition to product separation means, a typical reaction zone system comprising a heater, reactor, heat-exchanger and gas-liquid cold separator. For the purposes of illustration, it will be assumed that this particular reaction system is the last in a series of hydrocracking reaction zones, and that the feed stock entering via line **1** is substantially free from various contaminating influences. In the drawing, various valves, condensers, compressors, instruments, controls, startup lines, etc. have been reduced in number or entirely eliminated as not being essential to an understanding of the inventive concept involved. These, as well as other miscellaneous appurtenances are well within the purview of one skilled in the art of petroleum refining techniques.

The charge stock, entering via line **1**, comprises hydrocarbonaceous material boiling from about 100° F. to about 1050° F., the majority of which boils above a temperature of about 650° F., is admixed with a hydrogen-rich recycle gas stream in line **2**, the mixture continuing through line **1** into heater **3**. The heated mixture passes through line **4** into reactor **5**, the effluent from which is withdrawn via line **6** through heat-exchanger **7**. Following utilization as a heat-exchange medium, the product effluent passes through line **8** into separator **9**. The common practice is, of course, to condense the product effluent in line **8** by means of a cooler, not illustrated in the drawing, prior to introducing the same into separator **9**. A hydrogen-rich recycled gas phase is withdrawn from separator **9** via line **2**, by compressive means not illustrated, to combine with the feed stock in line **1**.

The total charge to hydrocracking reaction zone **5**, via line **4**, is generally heated to a temperature within the range of from about 650° F. to about 850° F. Since the bulk of the reactions being effected in reactor **5** are exothermic, the temperature of the reaction product effluent is higher. Temperature control is maintained such that the maximum temperature within the catalyst bed is about 950° F. Hydrocracking processes are generally conducted at pressures of from about 500 p.s.i.g. to about 3000 p.s.i.g., with pressures above about 1200 p.s.i.g. being most common. The charge stock generally contacts the catalyst at a liquid hourly space velocity of about 0.5 to about 5.0, and the hydrogen concentration is generally maintained within the range of about 5000 to about 50,000 s.c.f./bbl. The catalytic composite usually employed to effect hydrocracking reactions comprises metallic components from the metals of Groups VI–B and VIII of the Periodic Table, as well as compounds thereof. These are generally composited with a suitable refractory inorganic oxide carrier material including alumina, silica, zirconia, magnesia, titania, boria, and mixtures of two or more. It is understood that the foregoing description of the reactor section as indicated in the drawing forms no essential part of my invention, and, therefore, does not limit the scope and spirit as set forth in the appended claims. As hereinbefore stated, the present invention is most advantageously applied to the separation of a hydrocracked product effluent, and the precise means by which such product effluent is obtained is of no consequence.

In any event, a principally normally liquid hydrocarbon phase is withdrawn from separator **9** via line **10** at a temperature in the range of from about 60° F. to about 140° F. As indicated, this temperature is increased by heat-exchange, in heat-exchanger **7**, with the hot product effluent in line **6**. The heated stream continues through line **11** into product separation means **13**. An alternate feed point, line **12**, is supplied so that the hydrocracked product effluent may be introduced into separation means **13** via more than one locus, the choice of which will be dependent upon the predetermined end boiling point of the desired product.

For the purposes of the present illustration, it will be assumed that the hydrocracking process was designed to maximize the production of a middle-distillate boiling range fraction having an initial boiling point of about 525° F. and an end boiling point of about 650° F. This stream is shown as being withdrawn from product separation **13** via line **18**. A principally vaporous phase is withdrawn from product separation **13** as an overhead stream via line **14**, and comprises normally gaseous hydrocarbons

of the character of propane and lighter. Such product separation means as illustrated are generally operated at conditions which minimize the quantity of butanes removed in this overhead fraction.

A gasoline fraction, containing heptanes and hydrocarbons boiling up to an end boiling point of about 400° F., is withdrawn via line **16**; a kerosene fraction boiling in the range of from about 400° F. to about 525° F., is withdrawn via line **17**. In accordance with the present invention, a light hydrocarbon fraction containing principally C_4-hydrocarbons, C_5-hydrocarbons, and C_6-hydrocarbons, is withdrawn from an upper portion of product separation **13** through line **15**. This stream is condensed by way of condenser **20**, and is introduced, via line **21**, into overhead receiver **22**. A reflux stream is withdrawn from overhead receiver **22** via line **23**, and is reintroduced into product separation zone **13** at a locus below that from which the light hydrocarbon stream is withdrawn via line **15**. The amount of reflux is such that the material withdrawn by way of line **15** is substantially free from hydrocarbons heavier than hexane. At least a portion of the condensed light hydrocarbon fraction is withdrawn from receiver **22** by way of line **24**, and is introduced into a lower portion of product separation **13** through a locus below that from which the desired light gas oil fraction (line **18**) is withdrawn.

That portion of the condensed light hydrocarbon phase from receiver **22** not employed as reflux via line **23**, nor introduced into the lower portion of product separation **13** by way of line **24**, is withdrawn as a product stream via line **25**. Since this stream is principally a butane-hexane fraction, it may be blended with C_7–400° F. gasoline fraction which has been withdrawn via line **16**. Those hydrocarbons, having normal boiling points above the predetermined end boiling point of 650° F. (the gas oil fraction withdrawn via line **18**), are withdrawn as a recycle stream from line **19**. It is common practice to utilize this stream in one or more of several ways. It may be recycled in its entirety to the last reaction zone in the series, illustrated as reactor **5**; it may be recycled in total to one of the preceding reaction zones; or, it may be recycled, at least in part to one or more of the reaction zones. Since the processing use of this recycle stream in line **19** is not essential to the present invetnion, it is indicated on the drawing merely as a recycle stream.

The recycle stream in line **19**, normally combined at least in part with the reactor charge in line **1**, is substantially free from normally liquid hydrocarbons boiling below a temperature of 650° F. Since these lighter hydrocarbons are not being exposed to hydrocracking, the volumetric yields of the various product streams, and particularly the light gas oil stream in line **18**, are substantially increased. In conjunction, the vaporous stream in line **14**, consisting primarily of propane and lighter components, is lessened significantly.

In the example which follows, the object is to maximize the production of a jet fuel fraction having an initial boiling point of about 310° F. and an end boiling point of about 525° F., and to concentrate the remainder of the product effluent in a C_7–290° F. light gasoline fraction suitable for subsequent motor fuel blending. Thus, the product separation means **13** incorporates my inventive concept for the purpose of substantially decreasing the quantity of hydrocarbons boiling below a temperature of 525° F. contained in the heavier recycle fraction withdrawn via line **19**.

EXAMPLE

This specific example is presented with frequent reference to the accompanying drawing, and in connection with a commercially-scaled unit designed for maximum production of the above-described jet fuel, from a blend of vacuum tar, reduced crude, atmospheric gas oil, light cycle oil and heavy cycle oil. This charge stock is indicated in the following Table I:

TABLE I.—CHARGE STOCK BLEND

	° API	Bbl./day
Vacuum tar	7.8	2,000
Reduced crude	20.3	3,222
Atmospheric gas oil	40.2	2,279
Light cycle oil	20.8	3,500
Heavy cycle oil	17.0	3,800
Blend	20.4	14,801

The unit processes about 15,000 bbl./day of the blend having a gravity of about 20.4 °API and containing about 1,120 p.p.m. of nitrogen and about 1.05% by weight of sulfur.

Prior to being introduced into hydrocracking reactor **5** via line **1**, the charge stock is subjected to hydrorefining for nitrogen and sulfur removal. The hydrorefining is effected at a pressure of about 3000 p.s.i.g., an inlet catalyst bed temperature of about 675° F. and a liquid hourly space velocity of 0.5. Hydrogen is admixed with the charge stock in an amount of about 10,000 s.c.f./bbl., and hydrogen consumption is about 1010 s.c.f./bbl. Following the removal of a principally vaporous phase from the hydrorefined product effluent, the normally liquid phase is introduced into reactor **5** via line **1**. A component analysis is presented in the following Table II; for convenience, the quantities are given in terms of mols/hr. The charge is in an amount of 28,893.20 mols/hr. (inclusive of recycle which provides a combined feed ratio of about 1.5).

TABLE II: REACTOR CHARGE (Line 1)

Component:	Mols/hr.
Hydrogen	23,564.69
Methane	3,290.86
Ethane	378.31
Propane	235.76
Butanes	200.15
Pentanes	76.04
Hexanes	62.34
C_7–290° F.	95.89
310° F.–525° F.	407.82
525° F.–Plus	581.34

Included in this charge is 247.63 mols/hr., (7,211 bbl./day) of a 525° F.-plus recycle. Reactor **5** contains a catalytic composite of 5.0% by weight of nickel (calculated as the element) and a carrier material of 75.0% silica and 25.0% alumina, the inlet temperature being 755° F., the pressure is about 2,880 p.s.i.g. and the liquid hourly space velocity (on fresh feed) is about 1.57.

The tatal product effluent, at a temperature of about 800° F., is employed as a heat-exchange medium, and enters a high-pressure separator at a temperature of about 300° F. The separator is at a pressure of about 2,780 p.s.i.g. and a temperature of about 115° F. A hydrogen-rich gaseous phase is withdrawn via compressive means, and is recycled in part to combine with the liquid charge to the hydrocracking zone (reactor **5**). The total gaseous phase is 26,506.61 mols/hr., of which about 22,381 mols is hydrogen. The normally liquid phase, at a temperature of about 105° F., is introduced into a reactor effluent heat-exchanger, and the temperature increased to about 325° F., at which temperature the heated stream is fractionated into the desired product streams.

In this particular operation, the product stream being

fractionated has the component analysis shown in the following Table III:

TABLE III: PRODUCT SEPARATOR FEED

Component:	Mols/hr.
Hydrogen	22.42
Methane	34.58
Ethane	35.94
Propane	57.49
Butanes	96.94
Pentanes	62.06
Hexanes	73.08
C_7–290° F.	141.74
310° F.–525° F.	983.50
525° F.–Plus	247.63

In accordnce with the present invention, with reference again to the drawing, about 166.89 mols/hr. of a C_4–C_6 concentrate is withdrawn from overhead receiver **22** by way of line **24**, and is introduced therethrough into the bottom portion of fractionator **13**.

A propane and lighter, normally gaseous phase is withdrawn from line **14**, containing virtually all the hydrogen sulfide, hydrogen, methane, ethane, and propane from the total product stream. A light naphtha (C_4–C_6) concentrate, in an amount of 411.32 mols/hr. (exclusive of reflux), is withdrawn from line **15**, and ultimately condensed in receiver **22**. Of this amount, 244.43 mols/hr. are removed via line **25**.

A recycle stream, in an amount of about 247.63 mols/hr. is withdrawn from fractionator **13**, via line **19**, and contains about 5.20 mols/hr. of C_4–C_6 hydrocarbons, and only a negligible quantity (less than 0.5 mols/hr.) of C_7–525° F. liquid hydrocarbons. In the process wherein there is no light naphtha reflux to the bottom of the product separation zone, via line **19**, design calculations indicate that approximately 10.0% to 15.0% by volume of the recycled material consists of C_7–525° F. hydrocarbons. On the basis of 247.63 mols/hr. of 525° F–plus recycle, there would be a minimum of 24.87 mols/hr. of the desired product streams being subjected to the hydrocracking effected in reactor **5**. Through the use of the present invention, this material is not "lost" by cracking into light paraffinic material, but is recovered either in the C_7–290° F. stream (line **16**), or in the 310° F. to 525° F. jet fuel product (line **17**).

The following Table IV summarizes the product yields and distribution resulting from the 14,801 bbl./day of fresh charge stock:

TABLE IV.—PRODUCT DISTRIBUTION AND YIELDS

Product	° API	Bdl./day
C–C hydrocarbons	83.1	1,185
C–290° F. gasoline	56.3	1,354
310° F.–525° F. jet fuel	43.7	13,438

The foregoing specification and example clearly illustrate the means by which the present invention is integrated into a hydrocarbon separation process, and indicates the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for separating a hydrocracked product effluent comprising butanes and normally liquid hydrocarbon components to provide at least one fraction having a predetermined end boiling point, which process comprises the steps of:

(a) introducing said product effluent into product separation means;

(b) withdrawing a principally vaporous fraction containing propane and lighter hydrocarbons as an overhead product from said separation means;

(c) removing a light hydrocarbon fraction containing principally butanes, pentanes and hexanes from said separation means;

(d) separating a heavier hydrocarbon fraction, having said predetermined end boiling point, from an intermediate locus of said separation means;

(e) introducing at least a portion of said light hydrocarbon fraction into said separation means at a locus below that from which said heavier fraction is removed; and

(f) withdrawing a bottoms fraction from said separating means at a louus below that at which said light hydrocarbon fraction is introduced, said bottoms fraction being substantially free from hydrocarbons boiling below said predetermined end boiling point.

2. The process of claim **1** further characterized in that a second portion of said light hydrocarbon fraction is returned to an upper locus of said separation means.

3. The process of claim **1** further characterized in that said predetermined end boiling point is a maximum of 700° F.

4. In a process for hydrocracking heavy hydrocarbonaceous material into lower-boiling hydrocarbon products, in a catalytic reaction zone, in which process the hydrocracked product effluent is separated to provide a principally normally liquid hydrocarbon fraction having a predetermined end boiling point, and a portion of said product effluent boiling above said predetermined end boiling point is recycled for further hydrocracking in said catalytic reaction zone, in which process the recycled portion contains hydrocarbons boiling below said predetermined end boiling point, the improvement which comprises the steps of:

(a) introducing said product effluent into product separation means;

(b) withdrawing a principally vaporous fraction containing propane and lighter hydrocarbons as an overhead product from said separation means;

(c) removing a light hydrocarbon fraction containing principally butanes, pentanes and hexanes from said separation means;

(d) removing a heavier hydrocarbon fraction, having said predetermined end boiling point, from an intermediate locus of said separation means;

(e) introducing at least a portion of said light hydrocarbon fraction into said separation means at a locus below that from which said heavier fraction is removed; and

(f) removing a bottoms fraction from said separating means at a locus below that at which said light hydrocarbon fraction is introduced, said bottoms fraction being substantially free from hydrocarbons boiling below said predetermined end boiling point, and recycling said bottoms fraction to said catalytic reaction zone.

5. The improvement of claim **4** further characterized in that a second portion of said light hydrocarbon fraction is returned to an upper locus of said separation means.

6. The improvement of claim **4** further characterized in that said predetermined end boiling point is a maximum 700° F.

7. The improvement of claim **4** further characterized in that said predetermined end boiling point is from about 350° F. to about 700° F.

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