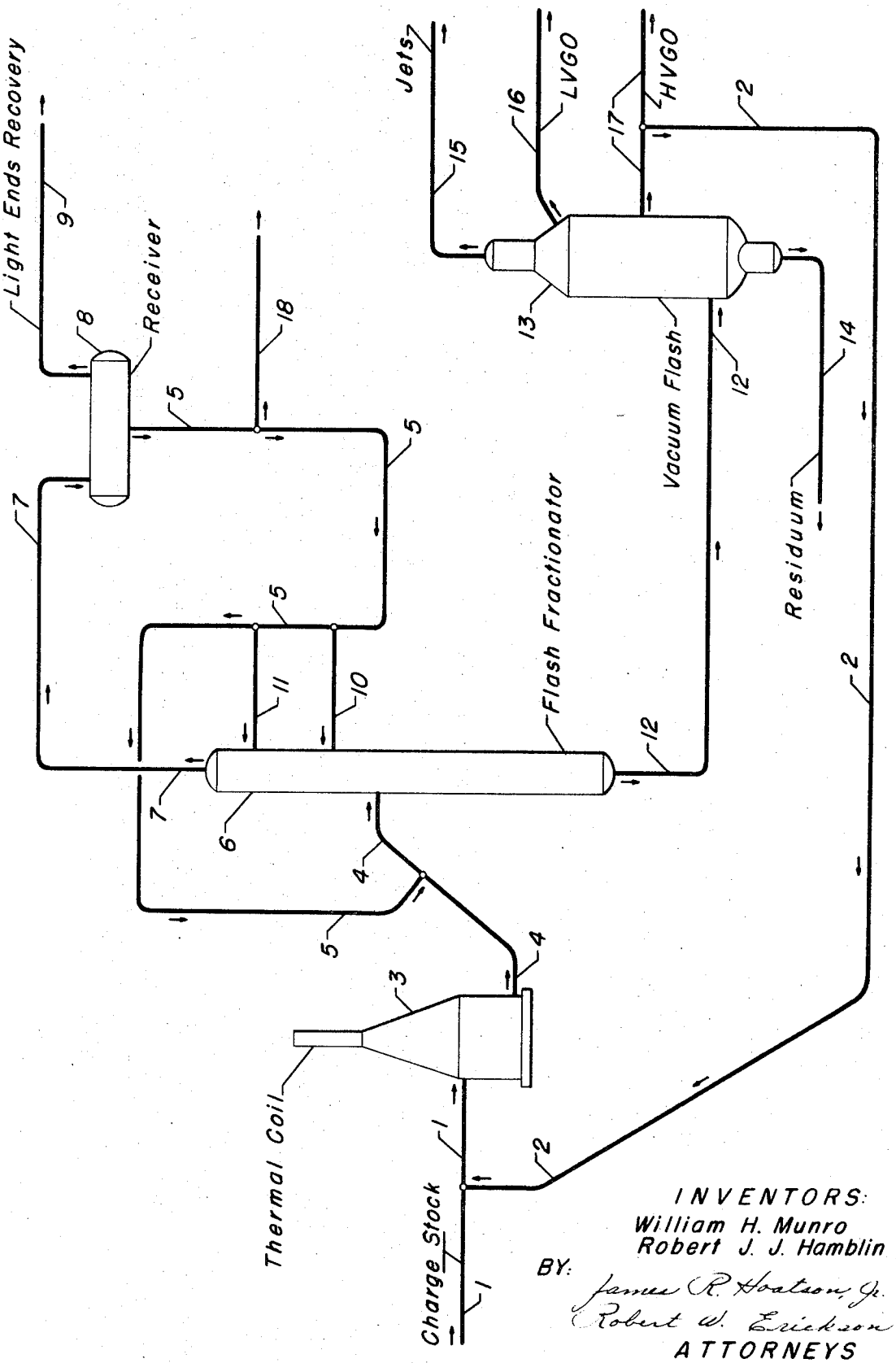
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MIXED-PHASE THERMAL CRACKING PROCESS

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MIXED-PHASE THERMAL CRACKING PROCESS

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ABSTRACT OF THE DISCLOSURE

A process for thermally cracking a mixed-phase hydrocarbonaceous charge stock containing an asphaltic, nondistillable residuum. One such charge stock comprises about 53.0 mol percent propane and lighter, normally gaseous material, and about 17.0 mol percent of asphaltic residuum. The thermal cracking is effected in the presence of a lower-boiling, normally liquid diluent obtained from the thermally cracked product effluent.

APPLICABILITY OF INVENTION

The invention described herein is adaptable to a process for thermally cracking a heavy hydrocarbonaceous charge stock, containing a nondistillable, asphaltic residuum. More specifically, our invention is directed toward a mixed-phase thermal cracking process wherein the charge stock can contain as much as 60.0 mol percent propane and lighter hydrocarbons, and hydrogen, in addition to a nondistillable asphaltic residuum in an amount as high as 25.0 mol percent.

The term "mixed phase," as used herein, denotes a heavy charge stock having dissolved therein substantial amounts of normally gaseous material such as hydrogen and light hydrocarbons.

Such mixed-phase charge stocks, to which the present invention is applicable, generally stem, or are recovered from a prior conversion process such as hydrorefining of heavy hydrocarbonaceous material, conversion of contaminated black oils, reduced crude desulfurization, etc. These conversion processes are conventionally conducted catalytically in a fixed-bed system, and in the presence of hydrogen. The processes are designed to convert contaminated hydrocarbonaceous material into lower-boiling hydrocarbons substantially decreased in the concentration of contaminants. The present invention is most applicable for the thermal cracking of the product effluent from heavier, significantly more contaminated charge stocks commonly referred to as black oils.

Petroleum crude oils, particularly heavy oils extracted from tar sands, topped or reduced crudes, and vacuum residuum, contain high molecular weight sulfurous compounds in exceedingly large quantities, nitrogenous compounds, high molecular weight organo-metallic complexes containing principally nickel and vanadium as the metallic component, and heptane-insoluble asphaltic material. The latter is generally found to be complexed with, or linked to sulfur and, to a certain extent, with metallic contaminants. In this regard, "black oils" differ considerably from heavy gas oils which are not so severely contaminated and which normally do not have as high a boiling range. A black oil can be characterized as a heavy hydrocarbonaceous material of which more than 10.0% (by volume) boils above a temperature of 1050° F., and having a gravity, °API at 60° F., of less than 20.0. Sulfur concentrations are exceedingly high, more than 1.0% by weight, and are often in excess of 3.0% by weight. Conradson Carbon Residue factors exceed 1.0 weight percent, and a great proportion of black oils exhibit a Conradson Carbon Residue factor about 10.0. There exists an abundant supply of such hydrocarbonaceous material, most of which has a gravity less than 10.0 °API at 60° F., and which is characterized by a boiling range indicating that 30.0% or more boils above a temperature of about 1050° F. The utilization of these highly contaminated black oils as a source of more valuable liquid hydrocarbon products is precluded by present-day techniques unless the sulfur and asphaltic content is sharply reduced and a significant proportion of the material can be converted into distillable hydrocarbons.

The process encompassed by the present invention is particularly directed toward the further conversion of the product effluent resulting from the catalytic conversion of black oils into distillable hydrocarbons. Specific examples of the crude oils to which the present scheme is adaptable, include a vacuum tower bottoms product having a gravity of 7.1 °API at 60° F., and containing 4.05% by weight of sulfur and 23.7% by weight of asphalts; a "topped" Middle-east Kuwait crude oil, having a gravity of 11.0 °API and containing 10.1% by weight of asphalts and 5.2% by weight of sulfur; a vacuum residuum having a gravity of 8.8 °API and containing 3.0% sulfur and 4300 p.p.m. (by weight) of nitrogen; vacuum bottoms having a gravity of 5.4 °API, and containing 6.15% sulfur, 233 p.p.m. (by weight) of metals and 12.8% by weight of heptane-insoluble asphaltic material; and, a reduced crude having a gravity of 11.5 °API, and containing 4.2% sulfur, 3400 p.p.m. of nitrogen, 166 p.p.m. of metals and 8.6% by weight of heptane-insolubles.

The primary difficulty being encountered in the processing of hydrocarbonaceous black oils, resides in the lack of an acceptable degree of sulfur stability of the catalytic composite when the charge stock is also characterized by large quantities of asphaltic material. This difficulty arises primarily as a direct consequence of the necessity for conducting the process at an operational severity level such that conversion of nondistillable hydrocarbons, into distillable, normally liquid hydrocarbons, and at least a portion of the asphaltenes simultaneously is effected while sulfurous compounds are being converted into hydrogen sulfide and hydrocarbons.

The asphaltic material, dispersed within the charge stock, has the tendency to agglomerate and polymerize, whereby the conversion thereof to oil-soluble products is virtually precluded. Furthermore, the sulfur-containing polymerized asphaltic complexes become deposited upon the catalytic composite, steadily increasing the rate at which the catalytic composite becomes deactivated. As the metals content of the charge stock increases, the catalyst deactivation rate is further accelerated.

It has been found that an acceptable degree of desulfurization, with respect to the quantity of distillable hydrocarbons produced, can be achieved catalytically at relatively mild operating severities which favor extended effective catalyst life. This has been improved further, with respect to the overall quantity of distillables produced, through the integration of a non-catalytic thermal reaction zone, or coil, with the fixed-bed catalytic system. That is, the fixed-bed product effluent, or more often a portion thereof after separation, is subjected to thermal cracking in order to produce greater yields of lower-boiling distillables, while also converting at least a portion of the unconverted asphaltic residuum into distillables.

The essence of our invention involves a process by which the thermal cracking of the previously-described mixed-phase product effluent is effected. Through the use of our invention, the asphaltic residuum is concentrated, substantially free from distillable hydrocarbons, and greater yields of the latter are produced.

OBJECTS AND EMBODIMENTS

An object of our invention is to provide a process for thermally cracking a mixed-phase hydrocarbonaceous charge stock containing an asphaltic residuum. A corollary objective is to increase the expected yield of distillable hydrocarbons from hydrocarbonaceous charge stocks.

Another object is to provide a process for converting a greater proportion of the asphaltic residuum, contained in the effluent from prior hydrogenative conversion processes, into distillable hydrocarbons.

Therefore, in a broad embodiment, the present invention affords a process for thermally cracking a mixed-phase heavy hydrocarbonaceous charge stock, containing an asphaltic residuum, which process comprises the steps of:

(a) Introducing said charge stock and a lower-boiling, normally liquid diluent into a thermal reaction zone at a temperature above about 650° F.; (b) separating the resulting thermally cracked product effluent, to provide a first liquid phase principally comprising heptane and higher boiling hydrocarbons; (c) further separating said first liquid phase to provide at least a second, normally liquid phase substantially free from asphaltic residuum; and, (d) recycling at least a portion of said second liquid phase to combine with said charge as said lower-boiling diluent.

A more limited embodiment of our invention relates to a process for thermally cracking a mixed-phase heavy hydrocarbonaceous, asphaltic-containing charge stock which comprises the steps: (a) introducing said charge stock and a lower-boiling normally liquid diluent, at a combined feed ratio of from about 1.05:1 to about 4.0:1, into a thermal reaction zone at a temperature above about 650° F.; (b) separating the resulting thermally cracked product effluent, at a lower temperature, to provide a first normally liquid phase and a hydrogen-rich vapor phase; (c) further separating said first liquid phase at a pressure of from subatmospheric to about 100 p.s.i.g., to provide a second liquid phase and to concentrate an asphaltic residuum substantially free from distillable hydrocarbons; (d) recycling at least a portion of said second liquid phase, as said lower-boiling diluent, to combine with said charge stock; (e) condensing said hydrogen-rich phase at a temperature of from 60° F. to about 140° F., to provide a third liquid phase; and, (f) combining at least a portion of said third liquid phase with said thermally cracked product effluent.

SUMMARY OF INVENTION

The thermal cracking process encompassed by the present invention generally utilizes, as the charge thereto, a hydrogenated product effluent from a prior conversion process. As a consequence of preferred processing techniques integrated into these processes, the total product effluent is generally separated to provide a hydrogen-rich gaseous phase, for recycle to the catalytic conversion zone, and a principally liquid phase containing dissolved hydrogen and an asphaltic residuum. Thus, the majority of the applications of our invention will utilize, as the charge to the thermal coil, at least a portion of the total product effluent not utilized as recycle to the original catalytic conversion zone.

That portion of the product effluent, hereinafter referred to as charge stock, introduced into the thermal reaction zone, or coil, is generally at a temperature of from 700° F. to about 850° F. and a pressure in the range of about 1,000 p.s.i.g. to about 4,000 p.s.i.g. The pressure is usually reduced, prior to entering the thermal reaction coil, by means of a pressure reducing valve. The pressure level, to which the charge to the thermal cracking zone, is reduced, is dependent upon a variety of factors and preferred processing techniques. For example, pressure control may be facilitated by monitoring

the pressure under which the following flash fractionator functions. Certainly, the inlet pressure must be sufficient to afford flow of material through the reaction coil. The inlet pressure also depends, to a certain degree, on the physical and chemical characteristics of the charge stock, and possibly more so on the ultimate desired product quantity and quality. For most situations, the inlet pressure of the thermal coil will be at least about 25 p.s.i.g., with the upper limit being the pressure at which the previously converted product effluent is introduced into the present process. In any event, the inlet pressure will generally be in the range of 25 p.s.i.g. to about 4000 p.s.i.g., and preferably at least about 100 p.s.i.g. An intentional reduction in pressure will result in a decrease in temperature; however, it is preferred that the charge to the thermal coil be introduced thereto at a temperature not lower than 650° F. The thermally-cracked product effluent, at a higher temperature and lower pressure, is quenched to a lower temperature in the manner, and to the degree hereinafter set forth.

The thus-cooled cracked product effluent is separated, preferably in a flash fractionator having one or more distillation trays in the upper portion thereof, to provide a liquid phase relatively low in normally gaseous components and primarily comprising butane and heavier normally liquid hydrocarbons, including the unconverted asphaltic residuum. A hydrogen-rich vapor phase is removed from the flash zone, at a temperature below about 850° F., and is further separated, in a cold receiver, at substantially the same pressure, but at a lower temperature of about 60° F. to about 140° F. The temperature of the material leaving the upper portion of the flash zone, or from the rectifying zone, is maintained in the range of 750° F. to 850° F. in order to insure that no part of the asphaltic residuum is "carried over" into the cold receiver. The function of the cold receiver is to concentrate the normally gaseous components in a principally vaporous phase which can be sent to a light ends recovery system, along with other similarly constituted refinery streams, and to provide a principally liquid phase.

At least a portion of the liquid phase from the cold receiver is employed to quench the thermally cracked product effluent to a lower temperature, and to control the flash fractionator temperature profile to provide a top temperature less than 850° F., as hereinbefore set forth. Portions of this quench stream can also be introduced at intermediate loci of the fractionation zone, especially located above one or more of the distillation trays in the upper rectifying zone.

A bottoms, normally liquid stream is withdrawn from the fractionator and introduced into a separation zone. Although the separation can be effected at pressures up to about 100 p.s.i.g., the make-up of this stream indicates that vacuum separation, at pressures of about 20–60 mm. of Hg, absolute, is the preferred technique. A typical stream comprises about 2.6 mol. percent hexanes and lighter normally liquid hydrocarbons, and normally gaseous hydrocarbons; about 2.5 mol percent of heptanes and hydrocarbons having normal boiling points up to about 320° F.; and, about 95.0 mol percent of 320° F.-plus hydrocarbons, including the asphaltic residuum. A light vacuum gas oil (LVGO), boiling from about 320° F. to 750° F., and a heavy vacuum gas oil (HVGO), containing 750° F.-plus distillables, are removed as product streams. The material boiling below about 320° F. is removed by way of the vacuum jets. As hereinafter set forth, in the description of the drawing, a preferred technique is to withdraw a slop-wax cut, 980° F.-plus, for use as recycled diluent for the charge to the thermal cracking zone. Where a particular desired product distribution demands, a portion of the HVGO may be used as part of the diluent with the slop-wax cut. In any event, the diluent will be employed in an amount such that the combined liquid feed ratio

to the thermal cracking coil is about 1.05:1 to about 4.0:1.

Other conditions, as well as preferred processing techniques, will be given in conjunction with the following description of the present process. Reference will be made to the accompanying figure which illustrate one specific embodiment.

DESCRIPTION OF THE DRAWING

In the drawing, the embodiment is illustrated by means of a simplified flow diagram in which details such as pressure reducing valves, pumps, heaters, instrumentation and controls, heat-exchange and/or heat recovery circuits, valving, start-up lines and similar hardware have been omitted since they are not essential to an understanding of the techniques involved. The use of these, and other miscellaneous appurtenances, to modify the process as illustrated, are well within the purview of those skilled in the art of petroleum processing techniques. Similarly, it is 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 our invention, the scope of which is defined by the appended claims.

By way of further demonstrating the illustrated embodiment, the drawing will be described in connection with the conversion and desulfurization of a vacuum column bottoms product having a gravity of about 6.0 °API, and containing about 5.5% by weight of sulfur. This vacuum column bottoms product is intended for conversion into maximum distillable hydrocarbons having a sulfur concentration less than about 1.0% by weight.

The vacuum bottoms is initially subjected to desulfurization and hydrogenation in a fixed-bed catalytic reaction zone. The product effluent is separated, at a pressure of about 3,000 p.s.i.g. and a temperature of about 775° F., to provide a hydrogen-rich gaseous phase, at least a portion of which is employed as recycle to the catalytic reaction zone. The principally liquid phase from this initial separation serves as the charge stock to the present process.

With reference now to the drawing, based upon a commercially-scaled unit having a capacity of about 11,500 bbl./day, the liquid phase charge stock enters the process through line **1** in the amount of 10,350 bbl./day (about 623 mols/hr.), at a temperature of about 775° F. and a pressure of about 3,000 p.s.i.g. A recycled, lower-boiling diluent, in an amount of 5,150 bbl./day, the source of which is hereafter described, is admixed therewith, following pressure reduction (combined liquid feed ratio of 1.5:1) by way of line **2**. The mixture continues through line **1** into thermal coil **3** at a temperature of about 770° F. and a pressure of about 250 p.s.i.g. A component analysis of the 10,350 bbl./day of charge in line **1**, is presented in the following Table I, in terms of mols/hr., for convenience:

TABLE I

Fresh charge to thermal coil

Component:	Mols/hr.
Nitrogen	2.49
Hydrogen	237.35
Hydrogen sulfide	36.80
Methane	42.17
Ethane	10.22
Propane	5.78
Butanes	2.82
Pentanes	1.25
Hexanes	1.72
C_7–320° F.	4.32
320° F.–520° F.	15.17
520° F.–650° F.	22.95
650° F.–750° F.	30.71
750° F.–980° F.	90.72
980° F.-plus (distillable)	12.51
Residuum (non-distillable)	106.41

The thermally-cracked product effluent, at a temperature of about 930° F. and a pressure of about 100 p.s.i.g., passes through line **4**, is quenched with 187.11 mols/hr. of a condensed liquid from line **5**, the source of which is hereafter set forth, and the mixture continues through line **4** into flash fractionator **6**. In this particular operation, the quench liquid in line **5** is employed in an amount such that the temperature of the overhead fraction, removed by way of line **7**, is at a temperature of about 800° F.; the pressure of this stream, as it enters receiver **8** is slightly less than 100 p.s.i.g. as a result of the normally experienced pressure drop due to fluid flow through the system. The component analyses of the thermally-cracked effluent stream, and that of the quench liquid in line **5**, are presented in the following Table II:

TABLE II.—CRACKED EFFLUENT AND QUENCH LIQUID

	Effluent	Quench
Component, mols/hr.:		
Nitrogen	2.49	----------
Hydrogen	246.12	0.62
Hydrogen sulfide	45.30	3.66
Methane	76.04	1.22
Ethane	34.05	2.01
Propane	40.89	6.17
Butanes	26.65	8.21
Pentanes	12.60	6.06
Hexanes	20.31	11.96
C_7–320° F	68.88	44.82
320° F.–520° F	90.46	55.53
520° F.–650° F	47.40	13.51
650° F.–750° F	38.28	12.51
750° F.–980° F	88.89	10.89
980° F.-plus (distillable)	15.66	----------
Residuum (non-distillable)	59.08	----------

The sum of the two streams constitutes, of course, the total charge to flash fractionator **6** by way of line **4**.

The overhead fraction, withdrawn from flash fractionator **6** by way of line **7**, is introduced into receiver **8** at a pressure of about 100 p.s.i.g. and a temperature of 120° F. A hydrogen-rich vaporous phase is withdrawn from line **9** and conveniently subjected to a light ends recovery system in admixture with other similarly constituted refinery streams. A principally liquid phase is withdrawn by way of line **5** and, as hereinbefore set forth, a portion continues through line **5** as quench of the hot thermally cracked effluent. The net liquid, being the remainder after quench, is withdrawn from receiver **8** through line **18**. Where temperature control and/or the composition of the thermally cracked effluent so dictates, portions of the quench liquid in line **5** may be introduced into flash fractionator **6** through one or more lines, and preferably in the upper section, or rectifying zone, thereof; this technique is indicated as being accomplished by way of lines **10** and **11**.

A principally liquid phase is withdrawn from flash fractionator **6** through line **12**, and is introduced therethrough into vacuum column **13** at a temperature of about 750° F. and a pressure of about 25 mm. of Hg, absolute. The vacuum jets function via line **15**, removing the lighter material from the charge in line **12**. A light vacuum gas oil, having a nominal boiling range of from about 320° F. to about 750° F., is withdrawn by way of line **16**, and a heavy vacuum gas oil, comprising the 750° F-plus distillable hydrocarbons, is removed through line **17**, a portion of which is diverted through line **2** to serve as recycle diluent as hereinbefore set forth. The asphaltic residuum, substantially free from distillable hydrocarbons, is withdrawn through line **14**. As hereinbefore stated, although not so illustrated in the drawing, a third stream is preferably withdrawn from vacuum flash column **13**, for recycle by way of line **2** to combine with the charge stock. Generally, this third stream, commonly referred to as "slop-wax," comprises those distillable hydrocarbons boiling at 980° F. and above. Complete recycle of this stream to the thermal coil results in greater yields of clean, more valuable gas oils.

Component analyses of the streams resulting from the separation being effected in flash fractionator 6 are presented in the following Table III:

TABLE III.—FLASH FRACTIONATOR STREAM ANALYSES

Line Number	12	7
Component, mols/hr.:		
Nitrogen		2.49
Hydrogen	1.35	245.39
Hydrogen sulfide	0.36	48.60
Methane	0.44	76.82
Ethane	0.50	35.56
Propane	0.72	46.34
Butanes	0.65	34.21
Pentanes	0.47	18.19
Hexanes	0.99	31.28
C_7-320° F.	4.03	109.67
320° F.-520° F.	12.99	133.00
520° F.-650° F.	14.63	46.28
650° F.-750° F.	20.84	29.95
750° F.-980° F.	73.71	26.07
980° F.-plus (distillable)	15.66	
Residuum (non-distillable)	59.08	

With respect to the illustrative embodiment, the LVGO in line **16**, 320° F. to 750° F., is an amount of about 48.46 mols/hr., and the HVGO in line **17**, 750° F.-plus distillables, exclusive of the amount of slop-wax recycled as diluent, is about 73.71 mols/hr. The asphaltic residuum is, obviously, the 59.08 mols/hr. shown in Table III.

The separation being effected in receiver **8**, exclusive of the quench liquid which continues through line **5**, is indicated in the following Table IV:

TABLE IV.—COLD RECEIVER STREAM ANALYSES

Line Number	9	18
Component, mols/hr.:		
Nitrogen	2.49	
Hydrogen	243.93	0.84
Hydrogen sulfide	39.86	5.08
Methane	73.92	1.68
Ethane	30.77	2.78
Propane	31.58	8.59
Butanes	14.55	11.45
Pentanes	3.71	8.42
Hexanes	2.67	16.65
C_7-320° F.	1.37	63.48
320° F.-520° F.	0.06	77.41
520° F.-650° F.		32.77
650° F.-750° F.		17.44
750° F.-980° F.		15.18
980° F.-plus (distillable)		
Residuum (non-distillable)		

An overall product distribution, exclusive of the foregoing quench and recycle streams, but inclusive of the material subject to recovery from the vacuum jets (line **15**) and the light ends recovery system, is presented in the following Table V:

TABLE V

Overall product distribution

Component:	Mols/hr.
Methane	76.04
Ethane	34.05
Propane	40.89
Butanes	26.65
Pentanes–320° F.	101.79
320° F.–750° F.	176.15
750° F.-plus (distillable)	104.55
Residuum	59.08

The foregoing specification, and especially the example integrated into the drawing, indicates the method by which our invention is effected, and clearly illustrates the benefits afforded through the utilization thereof. It should be particularly noted that the asphaltic residuum has been reduced from 106.41 mols/hr. to 59.08 mols/hr.

We claim as our invention:

1. A process for thermally cracking a heavy hydrocarbonaceous asphaltic-containing charge stock containing a substantial amount of hydrogen which comprises the steps:

(a) introducing said charge stock and a lower-boiling, normally liquid diluent, at a combined feed ratio of from about 1.05:1 to about 4.0:1, into a thermal reaction zone at a temperature above about 650° F.;

(b) separating the resulting thermally cracked product effluent, at a lower temperature, to provide a first normally liquid phase and a hydrogen-rich phase;

(c) further separating said first liquid phase at a pressure of from subatmospheric to about 100 p.s.i.g., to provide a second liquid phase and to concentrate an asphaltic residuum substantially free from distillable hydrocarbons,

(d) recycling at least a portion of said second liquid phase, as said lower-boiling diluent, to combine with said charge stock;

(e) condensing said hydrogen-rich phase at a temperature of from 60° F. to about 140° F., to provide a third liquid phase; and,

(f) combining at least a portion of said third liquid phase with said thermally cracked product effluent.

2. The process of claim **1** further characterized in that said hydrogen-rich phase from said fractionation zone is at a temperature below about 850° F.

3. A process for thermally cracking a heavy hydrocarbonaceous asphaltic-containing charge stock containing a substantial amount of hydrogen which comprises the steps:

(a) introducing said charge stock into a thermal reaction zone at a temperature above about 650° F.;

(b) separating the resulting thermally cracked product effluent in a flash fractionation zone, at a lower temperature, to provide a hydrogen-rich overhead stream and a normally liquid bottoms stream;

(c) further separating said bottoms stream at a pressure of from subatmospheric to about 100 p.s.i.g. to provide a distillate fraction which is lower boiling than said charge stock, and a bottoms fraction comprising asphaltic residuum substantially free from distillable hydrocarbons; and

(d) condensing said overhead stream and combining at least a portion of the resulting condensate with said thermally cracked product effluent.

4. The process of claim **3** further characterized in that at least a portion of said distillate fraction is recycled to combine with said charge stock.

5. The process of claim **4** further characterized in that said distillate fraction is recycled in an amount to provide a combined feed ratio to said thermal reaction zone above about 1.05:1.

References Cited

UNITED STATES PATENTS

1,932,174	10/1933	Gaus et al.	208—89
2,526,966	10/1950	Oberfell et al.	208—89
2,756,186	7/1956	Owen et al.	208—102
2,900,327	8/1959	Beuther	208—106
3,027,317	3/1962	Reeg et al.	208—89
3,371,029	2/1968	Weiland	208—102
3,402,122	9/1968	Atwater et al.	208—102

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