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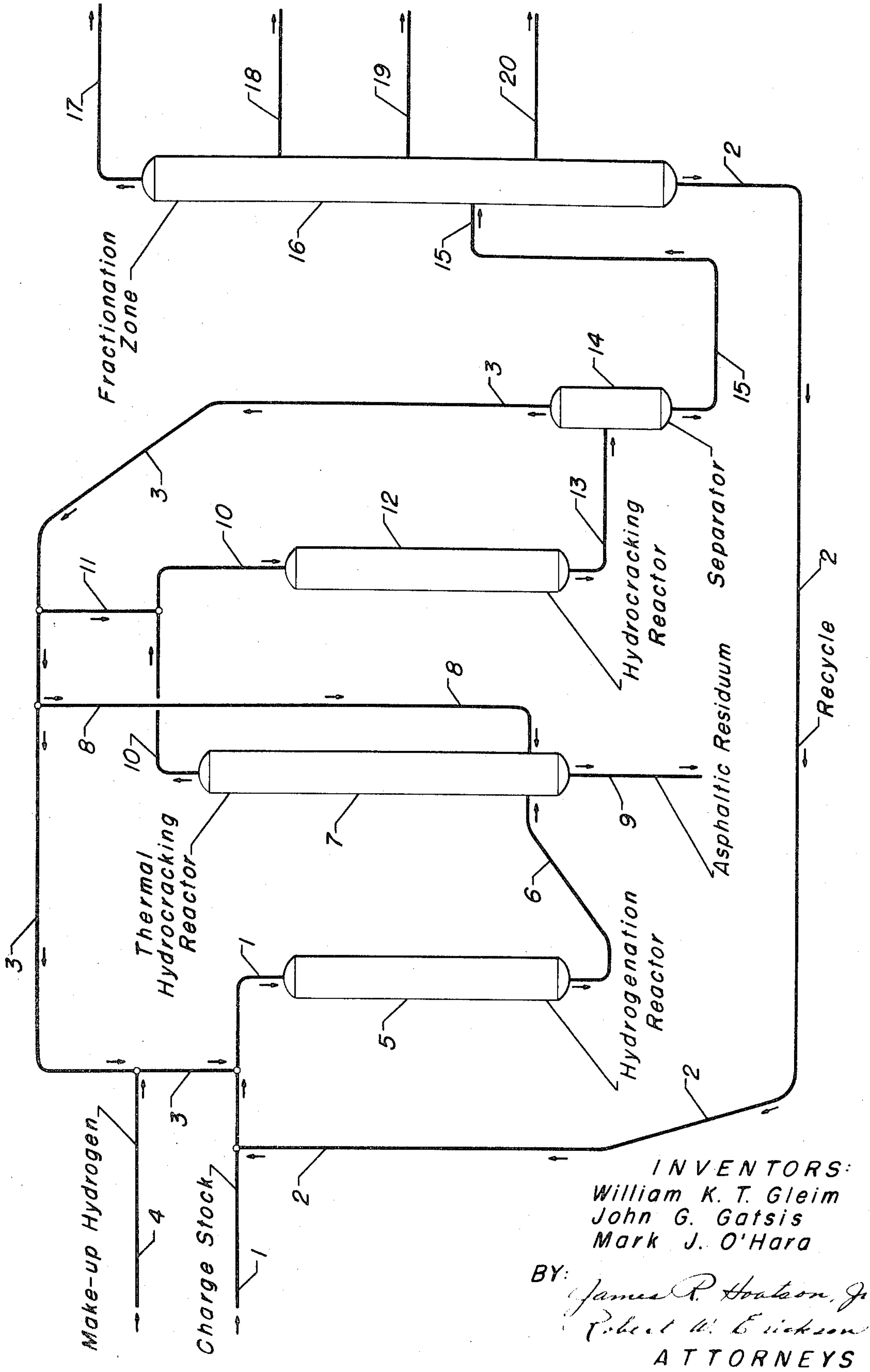

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COMBINATION PROCESS FOR BLACK OIL CONVERSION

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ABSTRACT OF THE DISCLOSURE

A hydrocarbonaceous black oil is converted into lower-boiling hydrocarbon products in a combination process involving catalytic hydrogenation, non-catalytic hydrogenative thermal cracking and catalytic hydrocracking.

APPLICABILITY OF INVENTION

The combination process herein described is adaptable to the conversion of asphaltic hydrocarbonaceous charge stocks which are commonly referred to in the art as "black oils." Such asphaltenic material includes full boiling range crude oil, "topped" crude oil, vacuum and atmospheric tower bottoms products, tar sands oil, coal oil extract, shale oil extract, etc. A black oil is characterized in the petroleum refining art as a heavy carbonaceous material of which more than about 10.0% by volume boils above a temperature of about 1050° F. This high-boiling fraction is often referred to as being non-distillable—i.e. would thermally crack at 1050° F. during distillation. Additionally, black oils are known to contain excessive quantities of nitrogenous and sulfurous compounds, the latter often in quantities as high as 5.0% by weight, calculated as elemental sulfur. Organometallic complexes, principally comprising nickel and vanadium, often found linked to high molecular weight sulfurous compounds, constitute another contaminating influence.

It is generally conceded that the presence of both the high-boiling asphaltenes and metallic components precludes fixed-bed catalytic processing in view of the rapid catalyst activity decline rate resulting from coke and metal deposition. Further acknowledged is the fact that the ever-increasing need for voluminous quantities of lower-boiling hydrocarbons—i.e. naphtha, kerosene, fuel oil, etc.—virtually demands conversion of the heavier material to the greatest possible extent, even to the conversion of the so-called "bottom of the barrel." Regardless of the overall scheme selected to achieve maximum conversion of high-boilers, a fixed-bed catalytic unit or process will necessarily be an integral part. Obviously, therefore, there exists the necessity for such a scheme to include means for effecting the removal of those substances having deleterious effects with respect to the catalyst disposed in the fixed-bed unit. Our invention is intended to provide such a scheme by way of a particular combination process which involves (1) pre-hydrogenation, (2) hydrogenative thermal cracking and (3) fixed-bed catalytic hydrocracking.

OBJECTS AND EMBODIMENTS

A principal object of our invention is to provide a process for the conversion of heavy hydrocarbonaceous charge stocks commonly referred to in the art as "black oils." A corollary objective is to produce maximum quantities of naphtha fractions, kerosene and low pour point, low viscosity fuel and diesel oil, all of which are significantly reduced in sulfur concentration.

Another object is to effect an extension of the period of acceptable, economical catalyst life while desulfurizing and converting hydrocarbonaceous black oils.

Therefore, in a broad embodiment, our invention is directed toward a combination process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock into lower-boiling hydrocarbons which comprises the steps of: (a) reacting said charge stock with hydrogen, in a catalytic hydrogenation reaction zone, at hydrogenating conditions including a maximum catalyst bed temperature in the range of 600° F. to about 750° F.; (b) further reacting the resulting hydrogenated effluent, in a non-catalytic thermal reaction zone, at thermal cracking conditions including an elevated temperature in the range of 800° F. to 950° F.; (c) reacting at least a portion of the resulting normally liquid, thermally-cracked effluent, in a catalytic hydrocracking reaction zone, at hydrocracking conditions including a maximum catalyst bed temperature in the range of 700° F. to about 900° F.; and, (d) separating the resulting hydrocracked effluent to provide a hydrogen-rich vaporous phase and to recover lower-boiling hydrocarbon products.

Other embodiments of our invention, as hereinafter set forth in greater detail, reside primarily in preferred ranges of operating variables and in various processing techniques. For example, one such embodiment involves introducing the hydrogenated effluent into a lower locus of the non-catalytic thermal reaction zone, withdrawing the normally liquid, thermally-cracked effluent through an upper locus and withdrawing an unreacted asphaltic, metal-containing residuum through a lower locus.

Other objects and additional embodiments of our invention will become evident from the following, more detailed description of the process encompassed thereby.

SUMMARY OF INVENTION

As hereinbefore set forth, the principal function served by the present invention is the production of maximum quantities of distillable hydrocarbons, including gasoline, kerosene, fuel oil of low pour point and low viscosity and diesel fuel, all of which have been substantially reduced in sulfur concentration. Thus, our invention affords significant advantages in the production of fuel oils for use in relatively cold climates where pour point and viscosity become critically important, and especially where the charge stock is itself highly viscous. Another distinct advantage resides in the available flexibility with respect to the product distribution of gasoline, kerosene and fuel oil fractions. Of paramount importance is the extension of the period of time during which the fixed-bed catalytic composite functions in an acceptable manner.

The present combination process is founded upon recognition of the character of the non-distillable portion of the hydrocarbonaceous black oil. This fraction, boiling about a temperature of about 1050° F., contains the greater proportion of metallic contaminants and consists principally of resins, asphaltenes and extremely high molecular weight polynuclear aromatic derivatives. Such material is virtually immune to conversion in a non-catalytic process, and, if anything, tends to polymerize and otherwise agglomerate, with equipment fouling being the most predominant detrimental effect. Current methods for processing black oils involve such ancient techniques as deasphalting, coking, etc., all of which suffer from ultimate yield loss with respect to lower-boiling products. In accordance with our invention, the black oil is first subjected to catalytic hydrogenation at conditions which do not foster extensive cracking reactions. Essential in this regard is a maximum catalyst bed temperature in the range of 600° F. to about 750° F., and preferably in the narrower range of 650° F. to 700° F. The reaction zone will be maintained under an imposed hydrogen pressure of 500 to 5,000 p.s.i.g., although a pressure from 1,000 to 3,000 p.s.ig. may be suitably employed.

For effecting the hydrogenation of the hydrogen-poor resins, asphalts and polynuclears, the catalytic composite should be one which does not have the capability to adsorb asphaltenes and metals. Such a catalyst is one virtually devoid of macropores; that is, one having a relatively high apparent bulk density of from 0.55 to about 0.85, and utilizes a carrier material of alumina and/or alumina-silica, with silica in an amount of from 0% to 25.0% by weight. The catalyst contains at least one metallic component from Groups VI–B and the iron-group. The Group VI–B metal, chromium, tungsten or molybdenum, is generally present in an amount of 4.0% to 30.0% by weight, whereas lesser amounts of the iron-group, cobalt, iron and nickel, in the range of 1.0% to 10.0% by weight, are suitable. A particularly preferred composite comprises nickel and molybdenum combined with 88.0% by weight alumina and 12.0% by weight of silica.

The charge stock, in admixture with hydrogen in an amount of from 1,000 to 30,000 s.c.f./bbl. of hydrogen, is preferably passed downflow through the hydrogenating catalyst bed at a liquid hourly space velocity (defined as volumes of normally liquid charge, exclusive of recycle, per hour, per volume of catalyst disposed in the reaction zone) of from 0.5 to about 3.0. The effluent from the hydrogenation reaction zone, preferably in total, is, without substantial change in pressure, introduced into a thermal reaction chamber maintained at an elevated temperature in the range of 800° F. to 950° F. A narrower, intermediate temperature from 825° F. to 875° F. is preferred. Based upon the volume of this thermal reaction chamber, the liquid hourly space velocity is 0.5 to about 2.0. The non-distillables, including asphaltenes, resins and organo-metallic contaminants are more susceptible to hydrogenative thermal cracking as a result of the pre-hydrogenation treatment hereinabove described.

A preferred processing technique involves introducing the hydrogenated effluent into a lower portion of the reaction chamber and withdrawing the thermally-cracked effluent through a locus in the upper portion thereof. Unreacted asphaltenes and resins settle to the bottom of the reaction chamber, and are removed therefrom as a metal-containing asphaltic residuum. The cracked product effluent, removed as an overhead product, is introduced into a fixed-bed catalytic hydrocracking reaction zone, again without a substantial change in pressure. The use of the term, "pressure substantially the same as," is intended to connote that the pressure under which a downstream vessel is maintained, is substantially the same as the pressure imposed upon an upstream vessel, allowing only for the normal pressure drop experienced as a result of the flow of fluids throught the system.

Although the hydrocracking catalyst may be identical to the hydrogenation catalyst, in most applications of the present process it will be distinctly different in character. For example, the hydrocracking catalyst may contain from 0.1% to about 2.0% by weight of a Group VIII noble metal component, including platinum, palladium, osmium, ruthenium, iridium and rhodium. Likewise, the carrier material will generally contain a greater concentration of silica, with respect to the alumina, and in many instances, will comprise a crystalline aluminosilicate such as faujasite, mordenite, Type A or Type U molecular sieves, etc. One preferred carrier material contains, in addition to alumina and silica, from about 2.0% to about 30.0% by weight of boron phosphate. The principal functions of the hydrocracking catalyst are to desulfurize the thermally-cracked effluent and to hydrocrack the same into distillable hydrocarbons. The maximum catalyst bed temperature is in the range of about 700° F. to about 900° F., and preferably in the range of 750° F. to 850° F.

Since the reactions being effected are principally exothermic in nature, an increasing temperature gradient will be experienced as the charge stock and hydrogen traverse the catalyst bed, with the highest temperature being recorded at the outlet of the catalyst. The temperature gradient should not be permitted to exceed about 100° F., and conventional quench streams, liquid and/or vaporous, may be utilized, at various loci, to control the increasing temperature gradient at the desired level. Hydrocracking reactions are generally affected at a liquid hourly space velocity of 0.5 to 3.0.

Following its use as a heat-exchange medium, and additional cooling, to reduce the temperature to a level of 60° F. to about 140° F., the hydrocracked product effluent is introduced into a high-pressure cold separator. A hydrogen-rich vaporous phase is withdrawn and at least in part recycled, by way of compressive means, to combine with the fresh feed charge stock to the hydrogenation reaction zone. This vaporous phase may be treated, by any of the methods well known in the art, for the removal of hydrogen sulfide and normally gaseous components including methane, ethane and propane, in order to increase the hydrogen purity. Control of the operating pressure throughout the system is facilitated when the focal point for pressure is the cold separator. In a preferred embodiment, at least a portion of the enriched recycle gas is introduced into each of the hydrogenation, thermal cracking and hydrocracking reaction zones. Make-up hydrogen, to supplant that which is chemically consumed in the overall process and that removed through dissolution in liquid product streams, may be introduced at any suitable location; preferably, the make-up hydrogen is combined with the fresh charge to the hydrogenating reaction zone.

The condensed, normally liquid portion of the hydrocracked product effluent is removed from the cold separator and introduced into suitable distillation/fractionation facilities from which the desired product slate is recovered. That portion of the product which boils above the end point of the desired product may be recycled as a diluent to the hydrogenating reaction zone, for further conversion in the hydrocracking reaction zone, or to both reaction zones in part. When so recycled, the combined liquid feed ratio, defined as total volumes of liquid feed per volume of fresh feed charge stock will be maintained in the range of 1.1 to 6.0.

One embodiment of our invention is illustrated in the accompanying drawing. This embodiment is presented by way of a simplified flow diagram in which miscellaneous details such as compressors, pumps, heaters, instrumentation and controls, heat-exchange and/or heat-recovery circuits, start-up lines and similar hardware have been omitted since they are superfluous to an understanding of the present combination process. Utilization of these appurtenances, to modify the illustrated flow, are well within the purview of those having skill in the petroleum refining arts. Similarly, it is understood that the charge stock, operating conditions, catalyst compositions, 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.

DESCRIPTION OF DRAWING

In further summarizing our invention, reference will be made to the accompanying drawing which will be described in conjunction with a commercially-scaled unit designed to process about 23,000 bbl./day of an atmospheric column bottoms product. The desired product slate includes the maximum production of a 550° F.-plus fuel oil fraction containing less than 0.5% by weight of sulfur. This charge stock has a gravity of about 13.7° API, and contains 2.66% by weight of sulfur, 4,500 p.p.m. by weight of nitrogen, 4.0% by weight of heptane-insoluble asphaltenes and 284 p.p.m. of vanadium and nickel, calculated as the elements. The charge stock enters the process by way of line **1**, is admixed with about 7,000 bbl./day of a recycled diluent from line **2** and about 6,000 s.c.f./bbl. of hydrogen in line **3**. The latter includes about 900 s.c.f./bbl. of make-up hydrogen being introduced through line **4**.

The resulting mixture continues through line **1** into hydrogenation reactor **5** at a pressure of about 2,150 p.s.i.g. and a temperature selected to maintain the maximum catalyst bed temperature at a level of 675° F. A catalytic composite of 2.0% by weight of nickel and 16.0% of molybdenum, combined with an amorphous carrier material of 88.0% by weight of alumina and 12.0% by weight is silica, is disposed in reactor **5** in an amount which results in a liquid hourly space velocity of about 1.0. The total product effluent is withdrawn through line **6** and introduced therethrough into the lower portion of thermal cracking chamber **7** at a pressure of about 2,100 p.s.i.g. and a temperature of about 900° F. Also introduced into reactor **7** is about 1,000 s.c.f./bbl. of hydrogen via line **8**.

A metal-containing, unreacted asphaltic residuum is removed by way of line **9**; this may be sent to a suitable separation zone for the recovery of entrained distillables. Distillable hydrocarbons, including some hydrogen sulfide and normally gaseous hydrocarbons are withdrawn as an overhead through line **10** and, after the addition of about 1,000 s.c.f./bbl. of hydrogen from line **11**, are introduced thereby into hydrocracking reactor **12** at a pressure of 2,075 p.s.i.g. and a catalyst bed inlet temperature of 720° F. The hydrocracking catalyst is a composite of 68.0% by weight of alumina, 10.0% by weight of silica and 22.0% by weight of boron phosphate with which is combined about 3.0% by weight of nickel and 12.0% by weight of tungsten. Were the desired end result the maximum production of gasoline boiling range hydrocarbons, the catalyst in reactor **12** would be a faujasitic carrier material containing about 5.0% by weight of nickel. The catalyst is utilized in an amount which results in a liquid hourly space velocity of about 1.1, and the maximum catalyst bed temperature is maintained at 780° F.

The hydrocracked product effluent is utilized as a heat-exchange medium and introduced by way of line **13** into cold separator **14** at a temperature of about 100° F. A hydrogen-rich gaseous phase is withdrawn at a pressure of about 2,025 p.s.i.g. and recycled via compressive means through line **3**; as herein above set forth, a portion of the hydrogen is diverted through lines **11** and **8** to the hydrocracking reactor and the thermal cracking chamber, respectively. The normally liquid portion of the hydrocracked effluent is removed from separator **14** by way of line **15**, and introduced thereby into fractionation zone **16**. Although illustrated as a single vessel, it is understood that the final product separation may be effected in any manner which yields the desired product slate. In this instance, butanes and lighter constituents are removed as an overhead stream in line **17**, a pentane-340° F. naphtha fraction is withdrawn through line **18**, a 340° F.–550° F. kerosene cut through line **19** and the desired fuel oil, 550° F.–950° F., through line **20**. Material boiling above 950° F. is recycled through line **2** to combined with the fresh charge in line **1**.

Product distribution and component yields are presented in the following Table I:

TABLE I.—PRODUCT YIELD AND DISTRIBUTION

Component	Wt. percent	Vol. percent
Ammonia	0.17	
Hydrogen sulfide	1.61	
Methane	0.25	
Ethane	0.32	
Propane	0.54	
Butane		1.87
Pentane-340° F		8.41
304° F.-550° F		9.83
550° F.-950° F		75.50
Asphaltic residuum		16.05

Through the use of the present combination process, the overall volumetric yield, inclusive of butanes and exclusive of the asphaltic residuum, is 95.61%. In the absence of the pre-hydrogenation treatment, the volumetric yield is approximately 78.81% and the amount of asphaltic residuum increases to about 24.05%.

Pertinent properties of the various product streams are presented in the following Table II:

TABLE II.—PRODUCT PROPERTIES

Product	C_5-340° F.	340° F.–550° F.	550° F.–950° F.
Gravity, °API	64.0	41.3	25.8
Sulfur, wt. percent	0.01	0.05	0.10

The asphaltic residuum, following removal of the entrained distillables, has a gravity of —3.0° API, and contains 3.90% by weight of sulfur.

The foregoing specification indicates the method by which the present combination is effected and the benefits to be afforded through the utilization thereof.

We claim as our invention:

1. A process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock into lower-boiling hydrocarbon products which comprise the steps of:

(a) reacting said charge stock with hydrogen, in a catalytic hydrogenation reaction zone, at hydrogenating conditions including a maximum catalyst bed temperature in the range of 600° F. to about 750° F.;

(b) further reacting the resulting hydrogenated effluent, in a non-catalytic thermal reaction zone, at thermal cracking conditions including an elevated temperature in the range of 800° F. t o 950° F.;

(c) reacting at least a portion of the resulting normally liquid, thermally-cracked effluent, in a catalytic hydrocracking reaction zone, at hydrocracking conditions including a maximum catalyst bed temperature in the range of 700° F. to 900° F.; and,

(d) separating the resulting hydrocracked effluent to provide a hydrogen-rich vaporous phase and to recover lower-boiling hydrocarbon products.

2. The process of claim **1** further characterized in that at least a portion of said vaporous phase is introduced into said hydrogenation reaction zone.

3. The process of claim **1** further characterized in that at least a portion of said vaporous phase is introduced into said thermal reaction zone.

4. The process of claim **1** further characterized in that at least a portion of said vaporous phase is introduced into said hydrocracking reaction zone.

5. The process of claim **1** further characterized in that said hydrogenated effluent is introduced into a lower locus of said non-catalytic reaction zone, said normally liquid, thermally-cracked effluent is withdrawn through an upper locus of said zone and an unreacted asphaltic residuum is withdrawn throuhg a lower locus thereof.

6. The process of claim **1** further characterized in that said hydrocracked effluent is separated at a temperature in the range of 60° F. to 140° F.

7. The process of claim **1** further characterized in that said hydrogenation zone, said thermal reaction zone and said hydrocracking reaction zone are maintained at substantially the same pressure in the range of 500 to 5,000 p.s.i.g.

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