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[54] COMBINATION PROCESS FOR THE CONVERSION OF HYDROCARBONACEOUS BLACK OIL

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[51] **Int. Cl.** **C10g 13/00**
[58] **Field of Search** 208/86, 78, 80, 309

[56] **References Cited**

UNITED STATES PATENTS

2,002,004	5/1935	Gard	208/14
2,606,141	8/1952	Meyer	208/211
2,914,457	11/1959	Beavon	208/79
2,973,313	2/1961	Pevere et al.	208/211
3,227,645	1/1966	Frumkin et al.	208/86

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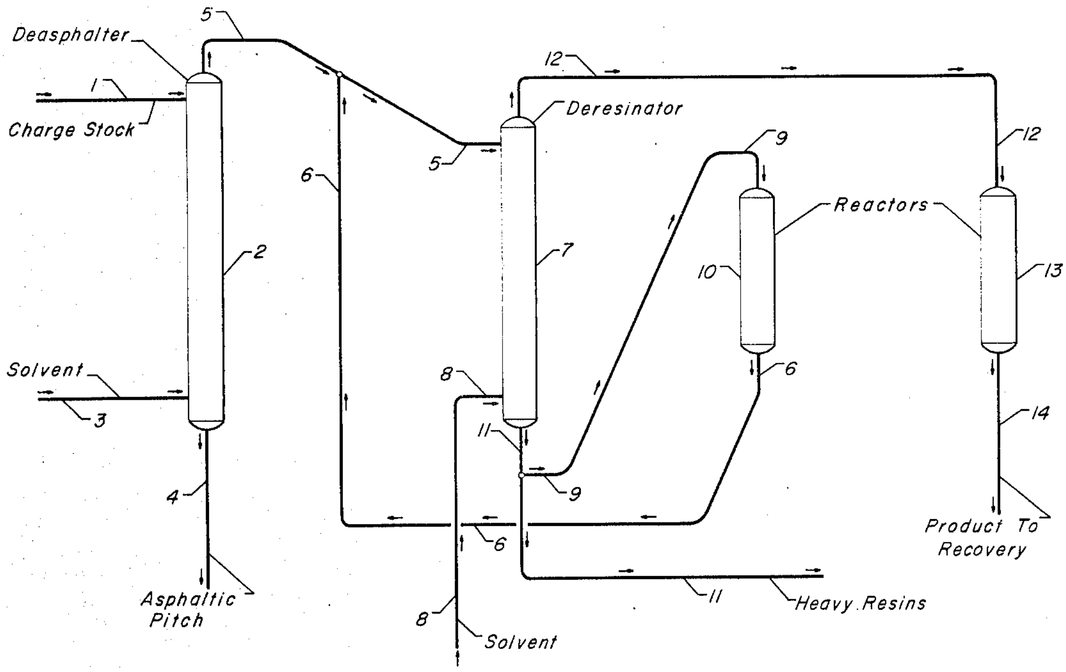
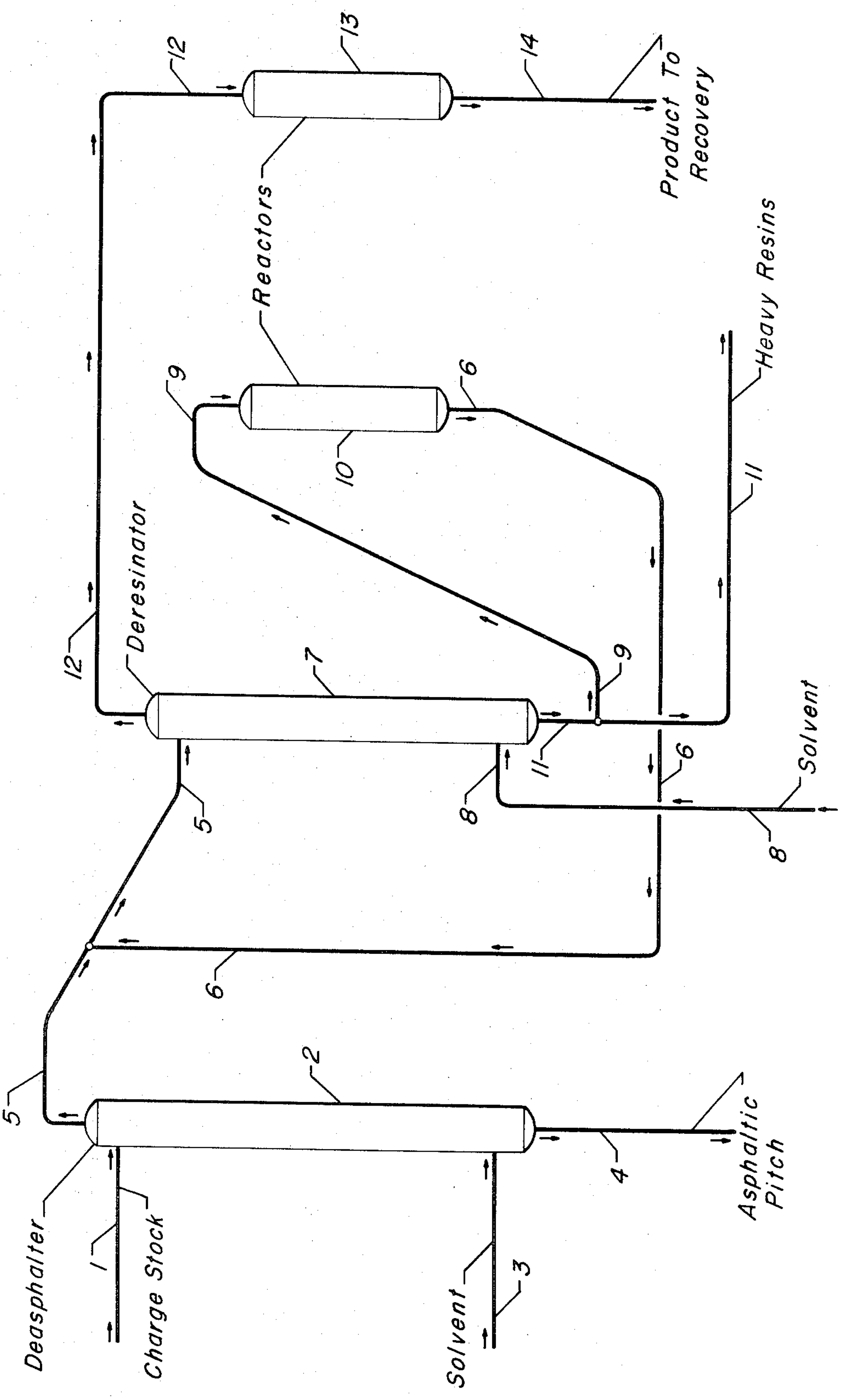
[57] **ABSTRACT**

Maximum conversion of black oil charge stocks to distillable hydrocarbon products is achieved through a combination process involving solvent deasphalting, solvent deresining and multiple-stage hydrocracking.

8 Claims, 1 Drawing Figure




Deasphalter
Charge Stock
1
2
Solvent
3
4
Asphaltic Pitch
5
5
6
6
6
Deresinator
7
8
8
Solvent
9
9
10
11
11
Heavy Resins
12
12
Reactors
13
14
Product To Recovery

COMBINATION PROCESS FOR THE CONVERSION OF HYDROCARBONACEOUS BLACK OIL

APPLICABILITY OF INVENTION

The invention described herein is adaptable to a process for the conversion of sulfurous, heavy carbonaceous material into lower-boiling hydrocarbon products of reduced sulfur concentration. More specifically, the present invention is directed toward processing asphaltene-containing contaminated charge stocks sometimes referred to in the art as "black oils." In particular, the process encompassed by my invention affords the maximum production of desulfurized, distillable hydrocarbons from black oil charge stocks.

Petroleum crude oils, particularly the heavy oils extracted from tar sands, topped or reduced crudes, vacuum residuum, etc., contain high molecular weight sulfurous compounds in exceedingly large quantities. In addition, black oils contain excessive quantities of nitrogenous compounds, high molecular weight organometallic complexes, principally containing nickel and vanadium, and varying quantities of asphaltenic material. An abundant supply of these hydrocarbonaceous charge stocks exists, most of which have a gravity less than about 20.0 °API. Black oils are generally further characterized by a boiling range indicating that 10.0 percent by volume, or more, boils above a temperature of about 1,050°F.

Knowledgeable experts in the various appropriate areas are currently theorizing that a severe energy crisis is soon to be encounterred. For example, those possessing expertise in oil and gas exploration predict that the supply of natural gas, compared to an ever-increasing demand, will soon reach critical low proportions. Several processes are, therefore, presently being proposed which will convert naphtha, via steam reforming and shift methanation, to a methane-rich substitute natural gas. This, in turn, will result in a naphtha shortage for motor fuel production, especially in view of the need to produce voluminous quantities of lead-free gasolines in order to aleviate severe atmospheric pollution. Kerosine fractions, normally utilized as jet fuel for aircraft, will be necessarily converted to naphtha fractions and motor fuels. In short, new technology is required to insure and afford virtually 100.0 percent utilization of petroleum crude oils and the heavy distillates derived therefrom. In the petroleum refining art, this is often referred to as utilization of the "bottom of the barrel." The use of the foregoing described high molecular weight black oils, as the source of more valuable liquid hydrocarbon products, is virtually precluded by present-day refining techniques, especially in view of the high metals and asphaltene content.

The combination process of the present invention is particularly directed toward the catalytic conversion of black oils to produce desulfurized, distillable hydrocarbons, and to effect such conversion in a manner which results in a volumetric yield approaching and/or exceeding 100.0 percent. Specific examples of black oils, illustrative of those to which the present process is applicable, include a vacuum tower bottoms having a gravity of 7.1 °API, and containing 4.05 percent by weight of sulfur and 23.7 percent by weight of asphaltics; a "topped" crude oil, having a gravity of 11.0 °API, and containing 10.1 percent by weight of asphaltics and 5.20 percent by weight of sulfur; and, a vacuum residuum having a gravity of about 8.8 °API, containing 3.0 percent by weight of sulfur and 4,300 ppm. by weight of nitrogen, and having a 20.0 volumetric distillation temperature of about 1,055°F.

OBJECTS AND EMBODIMENTS

An object of the present invention is to provide an economically feasible fixed-bed catalytic process for converting hydrocarbonaceous black oils into distillable hydrocarbons of lower molecular weight and boiling range. A corollary objective is to maximize the production of desulfurized hydrocarbons from a given quantity of an asphaltene-containing black oil.

Another object is to provide a process which affords an extension of the effective, acceptable life of the catalytic composite employed in the conversion reaction zones.

Therefore, the present invention encompasses a process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock, to produce lower-boiling hydrocarbon products, which process comprises the steps of: (a) deasphalting said charge stock with a selective solvent, in a first solvent extraction zone, at extraction conditions selected to provide (i) a solvent-lean asphaltic pitch and (ii) a solvent-rich, deasphalted first liquid phase; (b) deresining at least a portion of said first liquid phase with a selective solvent, in a second solvent extraction zone, at extraction conditions selected to provide (i) a solvent-lean resin concentrate and (ii) a deresined second liquid phase; (c) reacting at least a portion of said resin concentrate with hydrogen, in a first catalytic reaction zone, at hydrocracking conditions selected to convert resins into lower-boiling hydrocarbons; (d) reacting at least a portion of said deresined second liquid phase and at least a portion of the resulting first reaction zone effluent with hydrogen, in a second catalytic reaction zone, at hydrocracking conditions selected to produce lower-boiling hydrocarbon products; and, (e) recovering said lower-boiling hydrocarbon products from the resulting second reaction zone effluent.

Other embodiments of my invention reside in particular operating conditions and techniques, catalytic composites for utilization in the fixed-bed reaction zones, preferred selective solvents, etc. For example, in one such other embodiment, the extraction conditions in said second extraction zone include a higher temperature (10°F. to 200°F. higher) than that in said first extraction zone. In another embodiment, at least a portion of the resulting first reaction zone effluent is introduced into the second solvent extraction zone.

SUMMARY OF INVENTION

Heretofore, when attempting the maximum recovery of desulfurized distillable hydrocarbons from the conversion of heavy hydrocarbonaceous material as hereinbefore described, the principal difficulty encountered involved declining catalyst activity and stability resulting from the lack of a suitable processing technique permitting severe conditions of operation required to convert non-distillables into the lower-boiling products, while simultaneously effecting an acceptable degree of hydrodesulfurization. Catalyst instability, when processing black oil charge stocks in a fixed-bed reaction system, also stems from the presence of the asphaltic material. The asphaltic material consists primarily of high molecular weight, non-distillable coke precursors, insoluble in light hydrocarbons such as pentane or heptane. Generally, the asphaltic material is dispersed within the black oil, and, when subjected to the operating conditions required to effect desulfurization, has the tendency to agglomerate and polymerize, as a result of which the active surfaces of the catalytic composite are effectively shielded from the material being processed. The metallic contaminants, associated with the high-boiling asphaltenic fraction, adversely affect catalyst stability and activity by becoming deposited within the internal catalylically active sites.

Heretofore, when effecting the fixed-bed catalytic processing of hydrocarbonaceous black oils, two principal approaches have been advanced; liquid-phase hydrogenation and vapor-phase hydrocracking. In the former type of process, the charge stock is passed upwardly, in admixture with hydrogen, into a fixed-fluidized catalyst bed, or slurry of subdivided catalyst. This technique is relatively ineffective since the asphaltics are finely dispersed within the charge stock and the probability of effecting simultaneous contact between the catalyst particle, the hydrogen required for the prevention of coke formation and the aspaltic molecule is remote. Additionally, the retention of unconverted asphaltics, suspended in a free liquid-phase oil for an extended period of time, results in additional flocculation and agglomeration. Vapor-phase hydrocracking, which requires a fixed-bed catalytic system, is precluded ue to extreme catalyst deactivation as a result of the deposition of coke thereon and metallic contaminants therein.

The combination process, encompassed by the present inventive concept, utilizes a solvent deasphalting, or solvent extraction zone to precipitate and remove a metal-containing asphaltic concentrate. It must necessarily be acknowledged that the prior art is replete with a wide spectrum of techniques for effecting solvent deasphalting of asphaltene-containing hydrocarbonaceous charge stocks. No attempt is herein made to claim solvent deasphalting other than as an integral element of the present combination process. Any suitable solvent deasphalting technique known in the prior art may be employed, several examples of which are hereinafter described. In the interest of brevity, no attempt will be made to delineate exhaustively the solvent deasphalting art.

Exemplary of such prior art is U.S. Pat. No. 1,948,296 (Class 208–4) in which a separated asphaltic fraction is admixed with a suitable oil and subjected to oxidation to obtain a particular asphalt product. Suitable solvents include light petroleum hydrocarbons such as naphtha, casing-head gasoline, light petroleum fractions comprising propane, n-butane and isobutane, certain alcohols, ether and mixtures thereof, etc.

U.S. Pat. No. 2,002,004 (Class 208–14) involves a 2-stage deasphalting process wherein the second stage completes the precipitation of asphalts which was only partially effected in the first stage. As noted previously, the described solvents include naphtha, casing head gasoline, and liquefied normally gaseous hydrocarbons such as ethane, propane, butanes, and mixtures thereof, etc.

U.S. Pat. No. 2,914,457 (Class 208–79) describes a multiple combination process involving fractionation, vacuum distillation, solvent deasphalting, hydrogenation and catalytic reforming. Again, the suitable liquid deasphalting solvents include liquefied normally gaseous hydrocarbons such as propane, n-butane, isobutane, as well as ethane, ethylene, propylene, n-butylene, isobutylene, pentane, isopentane, and mixtures thereof.

In accordance with the present invention, the deasphalting zone functions to reject an asphaltic pitch and to produce a deasphalted oil containing convertible resins. Significantly, prior art techniques do not distinguish between the asphaltenic material and resins; that is, prior art processes reject resins along with the asphaltic pitch. This is contrary to the present combination process wherein the resin-containing deasphalted oil is subjected to a solvent deresining technique. The solvent-lean resin concentrate is subsequently reacted with hydrogen, in a first catalytic reaction zone at hydrocracking conditions selected to convert resins into lower-boiling hydrocarbons. The deasphalted and deresined oil, preferably in admixture with the lower-boiling hydrocarbons from the conversion of the resin concentrate, is reacted in a second catalytic reaction zone at hydrocracking conditions selected to produce additional lower-boiling hydrocarbons.

In the present specification and the appended claims, the terms, "deasphalting" and "deresining," designate the separate rejection of an asphaltic pitch and a resin concentrate from the black oil charge stock. The precise nature of these two fractions is widely dependent upon the origin of the crude oil and on the extraction conditions employed. In practice, deasphalting generally refers to a one-stage precipitation as applied to an asphalt-containing residuum, whereas deresining refers to a similar treatment conducted on an essentially asphalt-free residuum. Accordingly, deasphalting and deresining apply to the rejection of two contiguous bottoms fractions regardless of their exact nature.

Deasphalting and deresining are carried out under the same general range of operating conditions. However, a preferred technique involves operating the deresining zone at a higher temperature than the deasphalting zone, about 10°F. to about 200°F. higher, in order to recover the resin concentrate with the deasphalted oil, while rejecting an asphaltic pitch. The solvent extraction zones will function at temperatures in the range of about 50°F. to about 600°F., and preferably from about 100°F. to about 400°F.; the pressure will be maintained within the range of about 100 to about 1,000 psig., and preferably from about 200 to about 600 psig. The solvent/oil volumetric ratio will generally be in the range of about 2.0:1.0 to about 30.0:1.0. In accordance with the present invention, the deresining operation will employ a higher temperature and a greater solvent/oil volumetric ratio. For example, in the situation where propane is employed as the selective solvent, deasphalting will be effected at a solvent/oil ratio of 6.0:1.0 and a temperature of 100°F. to 160°F.; the deresining zone will utilize a propane/oil ratio of 10.0:1.0 and a temperature of 140°F. to about 180°F.

The rejected asphaltic pitch has an average molecular weight in the range of 3,000 to 6,000, and will contain 75.8 percent to 90.0 percent by weight of the metallic contaminants originally present in the fresh feed charge stock. The sulfur content will be approximately twice that of the charge stock. The resin concentrate will exhibit a significantly lower average molecular weight, about 1,000 to about 4,000, and will contain a minor proportion of metals; the sulfur content will be about one and one-half times that of the charge stock. The precise operating conditions in the solvent extraction zones will generally depend upon the physical characteristics of the feed stock as well as the selected solvent.

Judicious operating procedure involves the selection of temperature and pressure to maintain the extraction operations in liquid phase. Suitable solvents include those hereinbefore described with respect to prior art deasphalting techniques. Thus, it is contemplated that the solvent will be selected from the group of light hydrocarbons including ethane, methane, propane, butane, isobutane, pentane, isopentane, neopentane, hexane, isohexane, heptane, the mono-olefinic counterparts thereof, etc. Furthermore, the solvent may be a normally liquid naphtha fraction containing hydrocarbons having from about five to about 14 carbon atoms per molecule, and preferably a naphtha distillate having an end boiling point below about 200°F. The solvent-rich, normally liquid phase is introduced into a suitable solvent recovery system, the design and operation of which are thoroughly described in the prior art.

In accordance with the present combination process, therefore, the convertible resin concentrate is processed in a separate reaction zone at conditions selected to convert the same into lower-boiling hydrocarbons. The scheme additionally permits the processing of the deasphalted and deresined oil in the absence of both asphalts and resins and under conditions reflecting greater yields of normally liquid hydrocarbon products. A preferred operating techique involves introducing at least a portion of the converted resin concentrate effluent into the deresining zone for the recovery therein of the lower-boiling products along with the normally liquid deasphalted oil. The mixture is then separately processed in a second hydrocracking and/or hydrotreating reaction zone.

Although the catalytic composites, disposed within the first and second reaction zones, may be of different physical and chemical characteristics in many instances, such is not an essential feature of my invention, and the catalytic composites may, therefore, be identical. Regardless, the catalytic composites utilized in the present combination process comprise metallic components selected from the metals of Groups VI–B and VIII of the Periodic Table, as well as compounds thereof. Thus, in accordance with the *Periodic Table of the Elements*, E. H. Sargent and Company, 1964, suitable metallic components are those selected from the group consisting of chromium, molybdenum, tungsten, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, and platinum. Additionally, recent investigations have indicated that catalytic composites, especially for utilization in the conversion of exceedingly high sulfur content feed stocks, are improved through the incorporation of a zinc, tin and/or bismuth component. The latter three metallic components are more advantageously utilized, in the present invention, as part of the catalytic composite selected to process the resin concentrate.

In the present specification and the appended claims, the utilization of the term "component," when referring to the catalytically active metal, or metals, is intended to encompass the existence of the metal as a compound, such as oxide, sulfide, etc., or in the elemental state. Regardless, the concentrations of metallic components are calculated as if the metal existed within the composite in the elemental state. While neither the precise composition, nor the method of manufacturing the various catalytic composites, is considered essential to my invention, certain aspects are preferred. For example, since the charge stock to the present process is generally of a high-boiling nature, it is preferred that the catalytically active metallic components possess the propensity for effecting hydrocracking reactions while simultaneously promoting the conversion of sulfurous compounds into hydrogen sulfide and hydrocarbons. The concentration of the active metallic component, or components, is primarily depended upon the particular metal as well as the physical and/or chemical characteristics of the charge stocks. For example, the metallic components of Group VI–B are generally present in an amount within the range of about 4.0 percent to about 30.0 percent by weight, the iron-group metals in an amount within the range of about 0.2 percent to about 10.0 percent by weight, whereas the noble metals of Group VIII are preferably present in an amount within the range of about 0.1 percent to about 5.0 percent by weight. In those instances where a zinc, tin and/or bismuth component is employed, the same will generally be present in an amount within the range of about 0.01 percent to about 2.0 percent by weight. All concentrations are computed as if the metallic components existed within the catalytic composite in the elemental state.

The porous carrier material, with which the catalytically active metallic component, or components are combined, comprises a refractory inorganic oxide of the character thoroughly described in the literature. When of the amorphous type, alumina, or alumina in combination with about 10.0 percent to about 10.0 percent to about 90.0 percent by weight of silica is preferred. When processing heavier charge stocks containing a significant quantity of hydrocarbons having normal boiling points above a temperature of about 950°F., and particularly the resin concentrate, it may be appropriate to utilize a carrier material comprising a crystalline aluminosilicate, or zeolitic molecular sieve. In many instances, such a carrier material will be utilized in processing the deasphalted oil admixture with the resin concentrate effluent. Suitable zeolitic material includes mordenite, faujasite, Type A or Type U molecular sieves, etc., and these may be employed in a substantially pure state; however, it is understood that the zeolitic material may be included within an amorphous matrix such as silica, alumina, and mixtures of alumina and silica. It is further contemplated that the catalytic composites may have incorporated therein a halogen component, such component being selected from the group consisting of fluorine, chlorine, iodine, bromine, and mixtures thereof. The halogen component will be composited with the carrier material in such a manner as results in a final catalytic composite containing from about 0.1 percent to about 2.0 percent by weight, again calculated as the element.

A particularly preferred catalytic composite, for utilization in the first reaction zone processing the resin concentrate, is that described in U. S. Pat. No. 3,640,817 (Class 208–59). Briefly, this catalytic composite is described as having more than 50.0 percent of the macropore volume characterized by pores having pore diameters greater than about 1,000 Angstroms. This catalytic composite will contain, in addition to alumina and silica, boron phosphate in the amount of about 5.0 percent to about 30.0 percent by weight.

The metallic components may be incorporated within the catalytic composite in any suitable manner including co-precipitation or cogellation with the carrier material, ion-exchange or impregnation of the carrier material, or during a co-extrusion procedure. Following the incorporation of the metallic components, the catalytic composite is dried and subjected to a high temperature calcination or oxidation technique at a temperature of about 750°F. to about 1,300°F. When a crystalline aluminosilicate is utilized within the carrier material, the upper limit for the calcination technique is preferably about 1,000°F.

With respect to the operating conditions imposed upon the catalytic reaction zones, they are selected primarily to effect the conversion of sulfurous compounds to hydrogen sulfide and hydrocarbons. The second reaction zone will generally function at operating conditions providing a greater severity of operation, although such technique is not necessarily essential. The variance in operating severity between the two reaction zones may be obtained by the adjustment of the pressure, maximum catalyst bed temperature and liquid hourly space velocities. The higher severity operation within the second reaction zone will normally be effected at an increased pressure, an increased maximum catalyst bed temperature and at a somewhat decreased liquid hourly space velocity, or some combination thereof.

With the exceptions as above noted, suitable ranges for the various operating variables will generally be the same for both reaction systems. Thus, the pressure will generally be within the range of about 200 to about 3,000 psig., the hydrogen concentration will be about 500 to about 30,000 scf./Bbl., the maximum catalyst bed temperature will range from about 600°F. to about 900°F. and the liquid hourly space velocity will vary from about 0.25 to about 2.50. In view of the fact that the reactions being effected within both reaction zones are principally exothermic in nature, an increasing temperature gradient will be experienced as the reactants traverse the catalyst bed. Preferred operating techniques dictate that the increased temperature gradient be limited to a maximum of about 100°F., and, in order to control the temperature gradient, it is within the scope of the present invention to employ quench streams, either normally liquid, or normally gaseous, introduced at one or more intermediate loci of the catalyst bed.

Other conditions and preferred operating techniques will be given in conjunction with the following description of the present process. In further describing this combination process, reference will be made to the accompanying drawing which illustrates one specific embodiment. In the drawing, the embodiment is presented by way of a simplified flow diagram in which such details as compressors, pumps, heaters and coolers, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as being non-essential to an understanding of the techniques involved. The use of such miscellaneous appurtenances, to modify the process, is well within the purview of one skilled in the art, and the use thereof will not remove the resulting process from the scope and spirit of the appended claims.

For the purpose of demonstrating the illustrated embodiment, the drawing will be described in connection with the conversion of a vacuum bottoms charge stock in a commerciallyscaled unit. 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 my invention.

DESCRIPTION OF DRAWING

With reference now to the drawing, the illustrated embodiment will be described in conjunction with a commerciallyscaled unit designed to produce a maximum quantity of substantially desulfurized, distillable hydrocarbon products from the vacuum bottoms which has a gravity of about 10.1 °API. Other pertinent properties of the vacuum bottoms charge stock include a sulfur concentration of 3.08 percent by weight, 3,300 ppm. of nitrogen, 186 ppm. by weight of nickel and vanadium and 5.2 percent by weight of heptane-insoluble asphaltic material.

The vacuum bottoms charge stock, in an amount of about 100,000 Bbl./day, is introduced, via line **1**, into deasphalter **2**, wherein it countercurrently contacts a pentane solvent being introduced via line **3**. The solvent to charge stock volumetric ratio is 3.0 and a liquid-phase operation is maintained in deasphalter **2** at a temperature of 295°F. and a pressure of 400 psig. An asphaltic pitch, in an amount of about 14.92 percent by weight is withdrawn as a solvent-lean phase in line **4**, while a deasphalted oil, containing a resin concentrate, is removed via line **5**. The deasphalted oil, having a gravity of about 13.3 °API, and containing 50.0 ppm. by weight of metals, is introduced into deresinator **7** in admixture with a resin concentrate effluent from line **6**, the source of which is hereinafter described. Additional pentane solvent, added to give a volumetric ratio to the deasphalted oil of 6.0, is introduced via line **8**, and the deresinator is maintained at a temperature of 320°F. and a pressure of about 400 psig.

A solvent-lean resin concentrate, in an amount of about 27,000 Bbl./day, is withdrawn by way of line **9**, and introduced thereby into fixed-bed reactor **10**. The resin concentrate is admixed with hydrogen in an amount of about 7,500 scf./Bbl., and the mixture enters reactor **10** at a temperature of 700°F. (the increasing temperature gradient is maintained at 50°F.) and a pressure of about 3,000 psig.; the liquid hourly space velocity, based only a fresh feed exclusive of liquid recycle, is 0.5. Reactor **10** contains a catalytic composite similar to that described in the previously mentioned U.S. Pat. No. 3,640,817 (Class 208–59). In the present instance, the catalyst is a composite of 66.90 percent by weight alumina, 7.90 percent silica, 7.20 percent boron phosphate, 2.0 percent nickel and 16.0 percent by weight of molybdenum. Product yields and component distribution of the resin concentrate product effluent are presented in the following Table I:

In actual practice, that portion of the product effluent, as shown in Table I, boiling below about 650°F. will be removed and recovered prior to recycling the 650°F.-plus remaining portion via line **6** into deresining zone **7**. Heavy,

TABLE I: Resin Concentrate Effluent

Component	Wt.% *	Vol.%	Bbl./day
Ammonia	0.11	—	—
Hydrogen Sulfide	2.41		
Methane	0.49	—	—
Ethane	0.45	—	—
Propane	0.56	—	—

Butanes	0.57	1.05	284
Pentanes	0.44	0.74	200
Hexanes	0.69	1.06	286
Heptane–350°F.	2.89	4.03	1,773
350°F.–550°F.	9.90	12.53	3,383
550°F.–650°F.	9.18	11.03	2,978
650°F.–PLUS	74.02	79.03	21,338

* Includes hydrogen consumption of 1.71%

metal-containing resins are removed, via line **11**, in an amount of about 7.46 percent by weight of the fresh vacuum bottoms feed. The deasphalted oil, inclusive of the 21,338 Bbl./day of the 650°F.-PLUS resin concentrate effluent is removed by way of line **12**, and introduced thereby, in the total amount of 81,338 Bbl./day into reactor **13**.

Reactor **13** contains a catalytic composite of 1.9 percent by weight of nickel and 14.0 percent by weight of molybdenum combined with an amorphous carrier material of 33.0 percent by weight of silica and 67.0 percent by weight of alumina. The charge to reactor **13** has a gravity of 16.9 °API, a sulfur content of 2.01 percent by weight, a nitrogen content of 2,900 ppm. and contains only 3.0 ppm. of metal contaminants. The feed is admixed with about 13,000 scf./Bbl. of hydrogen and contacts the catalyst at a liquid hourly space velocity of 0.35. The maximum catalyst bed temperature is controlled at 775°F., and the pressure is maintained at a level of 3,000 psig. That portion of the normally liquid product effluent boiling above 700°F. is recycled to reactor **13** to provide a combined liquid feed ratio of 1:11. The remainder is sent via line **14** to suitable separation facilities for recovery of various product streams. Yields and component distribution of the effluent from reactor **13** are presented in the following Table II:

TABLE II: Reactor 13 Product Effluent

Component	Wt.% *	Vol.%	Bbl./day
Ammonia	0.35	—	—
Hydrogen Sulfide	2.14	—	—
Methane	0.34	—	—
Ethane	0.55	—	—
Propane	1.11	—	—
Butanes	2.20	3.65	2,969
Pentanes	1.76	2.68	2,180
Hexanes	2.21	3.04	2,473
Heptane–350°F.	13.79	17.34	14,104
350°F.–550°F.	45.80	51.88	42,198
550°F.–700°F.	32.85	36.22	29,461

* Includes hydrogen comsumption of 3.01% by weight

Overall volumetric yields, inclusive of butanes, based upon the 100,000 Bbl./day of fresh vacuum bottoms charge stock, are presented in the following Table III:

TABLE III: Overall Volumetric Yields *

Component	Vol.%	Bbl./day
Butanes	3.25	3,253
Pentanes	2.38	2,380
Hexanes	2.76	Heptane–
Heptane-350°F.	15.88	15,877
350°F.–550°F.	45.58	45,581
550°F.–700°F.	32.44	32,439
TOTALS:	102.30	102,289

* Based upon 100,000 Bbl./day fresh feed

It will be immediately noted that the present combination process produces a 102.3 percent volumetric yield of normally liquid hydrocarbons, based upon the quality of fresh feed charge stock, notwithstanding the by-product production of 14.92 percent of weight of the asphaltic pitch and 7.46 percent by weight of the heavy metallic resins both of which may be used in road asphalt. Analyses indicate that all treams are substantially sulfur-free and that the heptane-350°F. stream, having a gravity of about 55.0 °API, contains 7.0 percent aromatics, 60.0 percent naphthenes and 33.0 percent paraffins. As will be recognized, this constitutes an excellent feed stock for a catalytic reforming unit.

The foregoing illustrates the method of effecting the present invention and indicates the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock, to produce lower-boiling hydrocarbon products, which process comprises the steps of:

a. deasphalting said charge stock with a sensitive solvent, in a first solvent extraction zone, at extraction conditions selected to provide (i) a solvent-lean asphaltic pitch and (ii) a solvent-rich, deasphalted first liquid phase;

b. deresining at least a portion of said first liquid phase with a selective solvent, in a second solvent extraction zone, at extraction conditions selected to provide (i) a solvent-lean resin concentrate and (ii) a deresined second liquid phase;

c. reacting at least a portion of said resin concentrate with hydrogen, in a first catalytic reaction zone, at hydrocracking conditions selected to convert resins into lower-boiling hydrocarbons;

d. reacting at least a portion of said deresined second liquid phase and at least a portion of the resulting first reaction zone effluent with hydrogen, in a second catalytic reaction zone, at hydrocracking conditions selected to produce lower-boiling hydrocarbons; and,

e. recovering said lower-boiling hydrocarbon products from the resulting first and second reaction zone effluents.

2. The process of claim **1** further characterized in that the extraction conditions in said second extraction zone include a higher temperature than that in said first extraction zone.

3. The process of claim **1** further characterized in that the resulting first reaction zone effluent is introduced into said second solvent extraction zone.

4. The process of claim **1** further characterized in that the selective solvents in said first and second extraction zones comprise a light hydrocarbon containing from one to about seven carbon atoms per molecule.

5. The process of claim **1** further characterized that said selective solvents are normally liquid naphtha fractions containing hydrocarbons having from about five to about 14 carbon atoms per molecule.

6. The process of claim **5** further characterized in that said naphtha fractions have end boiling points below about 200°F.

7. The process of claim **1** further characterized in that the hydrocracking conditions, in said first and second reaction zones, include a pressure from about 500 to about 5,000 psig., a hydrogen concentration in the range of about 1,000 to about 30,000 scf./Bbl., a liquid hourly space velocity of from about 0.25 to about 2.50 and a maximum catalyst bed temperature in the range of 600°F. to about 900°F.

8. The process of claim **1** further characterized in that said first and second reaction zones have disposed therein a catalytic composite of a porous carrier material, a Group VI-B metal component and a Group VIII metal component.

* * * * *