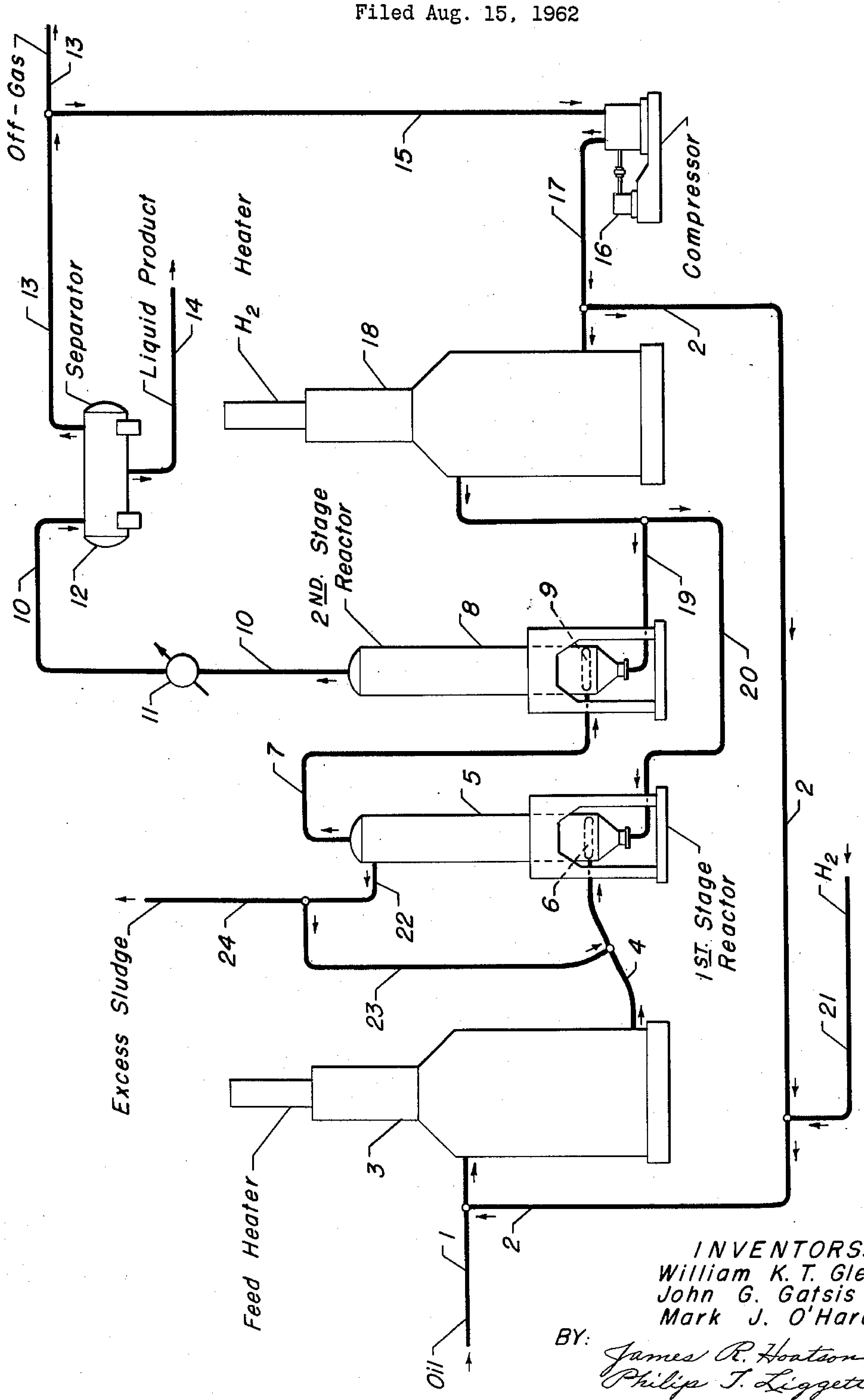
April 27, 1965 W. K. T. GLEIM ETAL 3,180,820

DUAL ZONE HYDROREFINING PROCESS

Filed Aug. 15, 1962



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United States Patent Office

3,180,820
Patented Apr. 27, 1965

3,180,820

DUAL ZONE HYDROREFINING PROCESS

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Filed Aug. 15, 1962, Ser. No. 217,059
20 Claims. (Cl. 208—211)

This invention relates to a process for upgrading heavy hydrocarbon stocks in the presence of hydrogen and a catalyst. More particularly, the present invention is directed to a dual zone catalytic hydrorefining process for effecting the substantial removal of various types of impurities, as hereinafter described, from heavy charge stocks such as crude oil, crude residua and heavy distillates derived therefrom, and for converting such heavy charge stocks to gasoline or middle distillates with minimum gas production.

Crude petroleum oil, topped crude, and other heavy hydrocarbon fractions and/or distillates derived therefrom contain various nonmetallic and metallic impurities. Among the nonmetallic impurities are nitrogen, sulfur and oxygen which exist in heteroatomic compounds and are often present in relatively large quantities. Nitrogen is undesirable because it rapidly poisons various catalysts which may be employed in the conversion of petroleum fractions; in particular, nitrogen must be removed from all catalytic hydrocracking charge stocks. Nitrogen and sulfur are also objectionable because combustion of hydrocarbonaceous fuels containing these impurities releases nitrogen and sulfur oxides which are noxious, corrosive and present a serious problem in the field of air pollution. Sulfur, of course, is deleterious in motor fuels because of odor, gum formation and decreased lead susceptibility.

Another class of undesirable constituents found in crude oil and residual oils is asphaltenes which are nondistillable, oil-insulable, high molecular weight coke precursors containing sulfur, nitrogen, oxygen and metals; they are colloidally dispersed in raw crude oil but when subjected to heat, as in vacuum distillation, the asphaltenes coagulate and or polymerize thereby making their conversion to more valuable oil-soluble products extremely difficult; thus, in the heavy bottoms from a reduced crude vacuum distillation column, the polymerized asphaltenes are solid materials at ambient temperature. Such product is useful only as road asphalt or, when cut back with middle distillates, as low grade fuel and commands a price substantially below that of the raw crude oil itself.

The most common metallic contaminants are nickel and vanadium, although other metals including iron, copper and zinc are often present. These metals may occur as suspended metal oxides or sulfides or water-soluble salts which may be removed, at least in part, by filtration, water-washing, electric desalting, or other fairly simple physical means; mainly however, the metals occur as thermally stable metallo-organic complexes such as metal porphyrins and derivatives thereof. Most of the metallo-organic complexes are associated with the asphaltenes and become concentrated in residual fractions; other metallo-organic complexes are volatile and are therefore carried over in distillate fractions. Reducing the concentration of the metallo-organic complexes is not easily achieved, at least to the extent that the crude oil or other heavy hydrocarbon charge stock may be made suitable for further processing or use. Even though the concentration of these metallo-organic complexes may be relatively small in distillate oils, for example, often less than about 10 p.p.m as the elemental metal, subsequent processing techniques are often adversely affected thereby. For example, when a hydrocarbon charge stock containing metallo-organic compounds, such as metal porphyrins, in excess of about 3.0 p.p.m. calculated as the elemental metal, is subjected to hydrocracking or catalytic cracking for the purpose of producing lower-boiling components, the metals deposit upon the catalyst, the concentration thereof increasing with time. Since vanadium and the Iron Group metals favor dehydrogenation activity at ordinary cracking temperatures, the resulting contaminated hydrocracking or cracking catalyst produces increasingly excessive amounts of coke, hydrogen and light hydrocarbon gases at the expense of more valuable liquid product until eventually the catalyst must be subjected to elaborate regeneration techniques or be replaced with fresh catalyst. The presence of excessive quantities of metallo-organic complexes adversely affects other processes including catalytic reforming, isomerization, hydrodealkylation, etc. Vanadium itself is also objectionable in heavy fuel oils and residual solids used as fuels because vanadium pentoxide formed during combustion is a strong acid at high temperature and will corrode the refractory lining, tube supports and other internal hardware of a fired heater utilizing such fuel.

Heretofore, it has not been considered practicable or economically feasible to catalytically crack or hydrocrack heavy charge stocks containing the aforesaid impurities directly to gasolines and/or middle distillates, because at conventional cracking or hydrocracking temperatures, e.g. above about 750° F. there is excessive production of hydrogen and light hydrocarbon gases, high coke make, and rapid catalyst deactivation due to coke laydown and accumulation of metallic contaminants on the catalyst. When a single hydrotreating step is employed, hydrocarbon conversions are poor as is the removal of nitrogen and sulfur which is favored by higher temperatures. Furthermore, the presence of nitrogen in a catalytic hydrocracking distillate feed stock in excess of about 1 p.p.m. in most cases quickly poisons hydrocracking catalyst at conventional hydrocracking conditions. In consequence, thereof it has been customary refining practice to provide a number of individual feed preparation units for the various distallate streams originating from a crude oil fractionator which are destined to undergo catalytic cracking, hydrocracking, reforming, etc. The feed preparation units are operated under their own specially tailored conditions, and with special catalysts or chemical reagent, so that in an integrated refinery there results extensive duplication of vessels, pumps, exchangers, utility services and manpower.

The present invention provides a simple two-stage hydrorefining process for directly converting a heavy hydrocarbon stock to gasoline and middle distillate boiling range product with minimum gas production, while simultaneously removing to a substantial degree metallic impurities, oil insoluble asphaltenes, nitrogen, oxygen, and sulfur. This invention is founded on the discovery that hydrorefining a heavy hydrocarbon stock in two separate serially connected catalytic zones, each maintained at substantially equal temperatures in the range of 700–850° F., results in a very markedly reduced production of light hydrocarbon gases such as methane, ethane, propane, etc., and superior hydrocarbon conversion and impurities removal, as against a conventional single-stage hydrotreating process providing equivalent residence time and space velocity.

It is, therefore, a broad embodiment of this invention to provide a process for hydrorefining a heavy hydrocarbon oil such as a crude pertoleum oil, vacuum gas oil, or heavy cycle oil, which comprises passing said heavy oil and hydrogen at elevated pressure through a first hydrorefining zone containing a solid hydrogenation catalyst and maintained at a temperature in the range of about 700–850° F., and preferably in the range of about 725–825° F., and then passing the hydrocarbonaceous effluent from said first zone, or at least the higher boiling fraction thereof, together with hydrogen at elevated pressure through a second hydrorefining zone containing a solid hydrogenation catalyst and maintained at substantially the same temperature as said first zone.

A more specific embodiment of this invention relates to a process for hydrorefining a heavy hydrocarbon oil which comprises commingling said oil with a finely divided unsupported catalyst comprising the thermal decomposition product of a thermally decomposable oil-soluble compound of a metal from Groups VB, VIB, and VIII of the Periodic Table, reacting the resulting oil-catalyst mixture with hydrogen at a pressure in excess of about 500 p.s.i.g. in a first hydrorefining zone maintained at a temperature in the range of about 700–850° F., passing at least the higher boiling fraction of the hydrocarbonaceous effluent from said first zone together with hydrogen at a pressure in excess of about 500 p.s.i.g. through a second hydrorefining zone maintained at substantially the same temperature as said first zone and containing a particle-form supported catalyst comprising a metal from Groups VB, VIB, and VIII of the Periodic Table, and recovering from said second zone a hydrorefined product of improved purity and reduced average molecular weight.

This dual zone treatment obviates the need for employing nitrogen-sensitive catalysts and for using a plurality of separate feed preparation units; in its simplest form, all that the present invention requires is two separate serially connected reaction zones, each maintained at substantially the same temperature level. For present purposes, the temperatures in the first and second hydrorefining zones are considered to be substantially equal when they are within about 25° F. apart; the temperature of the first zone may be slightly higher or slightly lower than the temperature of the second zone. The hydrogenation catalyst in the two zones may or may not be of same composition. Under the conditions herein employed, nitrogen deactivation of the catalyst is not encountered and feed stocks containing as much as 3000 p.p.m. of nitrogen may be continuously converted to lower boiling product at sustained high yield for a prolonged period of time. The function of the first or upstream zone is to remove metallic contaminants and to convert oil-insoluble asphaltenes to lower boiling oil-soluble hydrocarbons, while in the second or downstream zone nitrogen, sulfur and oxygen are removed as ammonia, hydrogen sulfide and water respectively. The reactions in the first zone involve predominantly hydrogenation with only minimal cracking as required to convert metallic impurities and asphaltenes; depending on conditions, the reaction in the second zone may involve either predominantly hydrogenation whereby the hydrocarbon charge emerges therefrom substantially unchanged except for impurities removal, or predominantly thermal hydrocracking whereby in addition to removal of nitrogen, sulfur and oxygen the hydrocarbon charge is cracked to yield gasoline, heavy naphtha, kerosene, diesel fuel, and/or fuel oil. By first eliminating metals and converting high molecular weight coke-precursors under hydrogenation conditions in a separate hydrorefining zone, the subsequent thermal hydrocracking proceeds with minimum coke yield and gas production and a correspondingly high liquid product yield.

The heavy hydrocarbon charge may be contacted with the catalyst in the first zone entirely in the liquid phase or as a liquid-vapor mixture; similarly, the effluent from the first zone (or the higher boiling fraction thereof where the first zone effluent is subjected to flash separation or fractionation) may be contacted with the catalyst entirely in the liquid phase or as a liquid-vapor mixture. The catalyst in the first zone may be utilized in the form of a slurry, a finely dispersed suspension, a fixed-fluidized bed, or a moving fluidized bed. The catalyst in the second zone may be utilized in the form of a fixed bed, a finely dispersed suspension, a fixed-fluidized bed, or a moving fluidized bed. As described with greater particularity hereinbelow, the catalysts of both zones may be either unsupported or supported, or the catalyst of one zone may be supported and the catalyst of the other zone unsupported.

Many types of heavy hydrocarbon oils may be treated by means of this invention including full boiling range crude oil, topped or reduced crude oil, atmospheric distillates, heavy cycle oils from thermally or catalytically cracked stock, light and heavy vacuum gas oils, etc. The instant process is particularly well adapted to hydrorefining stocks containing oil-insoluble asphaltenes such as crude oil and crude residua; of these, crude oil is a preferred stock because the oil-insoluble asphaltenes, being in their native environment, are colloidally dispersed and are thus more readily converted to oil-soluble hydrocarbons, whereas the asphaltenes in reduced crude have already been agglomerated to some extent by reason of the reboil temperature of fractionation and are therefore less easily converted. The instant process is also well suited to upgrading distillate stocks containing oil-soluble resins and maltenes as well as other of the above-described metallic and non-metallic contaminants. Generally speaking, higher hydrorefining temperatures are permissible and desirable for lighter charge stocks such as cycle oil than for total crude oil and heavier charge stocks.

The total pressure in both zones should be in excess of about 500 p.s.i.g. with an upper economic limit of about 5000 p.s.i.g., the preferred pressure range being about 1000–3000 p.s.i.g. The hydrogen rate may range from about 5000 to about 300,000 standard cubic feet of hydrogen per barrel of total oil charged, and preferably it is in the range of about 10,000–200,000 standard cubic feet per barrel. The weight hourly space velocity, which is the weight ratio of oil charged to catalyst present in the reaction zone, should be in the range of about 0.25–20 pounds of oil per pound of catalyst per hour. The hydrogen rate and the weight hourly space velocity may or may not be the same in both zones.

The hydrogenation catalyst of the present invention can be broadly characterized as comprising a metallic component having hydrogenation activity which may be employed in an unsupported state or in a supported form wherein it is composited with a refractory inorganic oxide carrier of synthetic or natural origin having a medium-to-high surface area and a well-developed pore structure as is familiar to those skilled in the are of hydrocarbon catalysis. Suitable metallic components having hydrogenation activity include the metals of Groups VB, VIB, and VIII of the Periodic Table; the Periodic Table referred to herein is that contained in the Handbook of Chemistry and Physics, 39th edition, Chemical Rubber Publishing Company (1957–58). Exemplary metallic components include vanadium, niobium, tantalum, molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and compounds thereof. Unsupported hydrogenation catalysts may comprise the elemental metal, oxide, sulfide, or mixed oxides and/or sulfides thereof in varying valence states, or a mixture of two or more such metals or compounds thereof; they may be utilized to advantage in a liquid phase slurry type operation. Unsupported catalysts are most effective when they exist as very finely divided solids uniformly, and preferably colloidally, dispersed in the heavy hydrocarbon charge or reaction zone proper. Such catalysts may be prepared by adding a thermally decomposable, oil-soluble organic compound of the desired metal to the heavy hydrocarbon charge and then decomposing it in situ by the application of heat. Suitable thermally decomposable metallo-organic compounds include molybdenum carbonyl, tungsten carbonyl, nickel carbonyl, molybdyl acetylacetonate, tungstyl acetylacetonate, vanadyl acetylacetonate, vanadium acetylacetonate, nickel acetylacetonate, nickel formate, vanadium xanthate, chromium xanthate, molybdenum xanthate, tungsten xanthate, iron xanthate, and nickel xanthate. Alternatively, the desired metal oxides and/or sulfides may be added to the heavy hydrocarbon charge either directly or by first dissolving them in an appropriate solvent and then commingling the solution with the hydrocarbon charge; suitable metal oxides and sulfides include the oxides and sulfides of molybdenum, vanadium and tungsten and their acid complexes, commonly known as heteropolyacids. Where the hydrocarbon charge is a total crude oil, it will frequently contain a sufficiently high concentration of nickel and vanadium, as porphyrins or other metallo-organic complexes, so that the hydrorefining catalyst it self-generating in situ via the destruction of these complexes and the accumulation of metals in the reaction zone. Hence, only a small amount of fresh catalyst is required to start up the process after which it becomes self-sustaining. Such autogeneration of hydrogenation catalyst is often accompanied by formation of organic sludge resulting from coagulation and polymerization of very high molecular weight coke precursors, which sludge then serves as a carrier for the "unsupported" catalyst; the metal-rich sludge may be recirculated through the reaction zone, or it may be subjected to a simple regeneration treatment and then recycled to the reaction zone, or it may be withdrawn from the reaction zone and passed through a metals recovery unit. When unsupported hydrogenation catalysts are employed, the catalytic concentration of the metallic component or components, computed on the basis of the elemental metal, will range from about 0.5% to about 10% by weight of the total heavy oil charge.

As previously noted, the present invention may also employ supported hydrogenation catalysts which will comprise any one or more of the metallic components discussed above in respect of unsuported catalysts composited with a porous refractory inorganic oxide carrier, suitable carriers include alumina, silica, zirconia, magnesia, titania, thoria, boria, strontia, hafnia, and complexes of two or more oxides such as silica-alumina, silica-zirconia, silica-magnesia, silica-titania, alumina-zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, silica-magnesia-titania, etc. The carrier may comprise additional promoters including combined halogens, particularly fluorine or chlorine, boric acid, phosphoric acid, and boron phosphate. While the supported catalyst may be employed in a slurry operation, or in a fixed or moving bed, it is particularly well adapted to a fluidized bed technique.

The catalytic concentration of the metallic component or components in the supported hydrogenation catalyst, stated here on the basis of the elemental metal, will depend primarily on the particular metal involved; for example, the Group V and Group VI metals are preferably present in an amount within the range of about 1–20% by weight, the iron-group metals in an amount within the range of about 0.2–10%, and the platinum-group metals in an amount within the range of about 0.01–5%.

The supported catalyst may be prepared by any of numerous techniques known to those skilled in the art. The refractory inorganic oxide carrier may be formed by acid-treating a natural clay, co-precipitation or successive precipitation from hydrosols, frequently coupled with one or more activating steps including hot oil aging, steaming, drying, oxidizing, reducing, calcining, etc. The pore structure of the carrier, commonly defined in terms of surface area, pore diameter, and pore volume, may be developed to within specified limits, for example, by aging the hydrosol and/or hydrogel under controlled acidic and/or basic conditions at ambient or elevated temperature, by gelling the hydrosol at a critical pH or by treating the carrier with various inorganic or organic reagents. The catalytically active metallic component or components may be composited with the carrier by impregnating the freshly precipitated or finished carrier with a solution of soluble metal compound or by co-precipitating the metal with the carrier from an aqueous solution thereof. Supported catalysts appropriate for use in the present invention will have a surface area of about 50–700 square meters per gram, a pore diameter of about 20–600 A. units, a pore volume of about 0.10–20 milliliters per gram, and an apparent bulk density of about 0.2–0.80 gram per cubic centimeter. Methods for measuring these physical properties are described in volume I, Catalysis, pp. 37–40, Reinhold Publishing Company (1954). Where the catalyst is to be employed in a liquid phase slurry type operation, catalyst particles should have average diameters ranging from about 0.03 to about 0.30 inch; where the catalyst is to be employed in a fluidized bed operation, the catalyst particles should have diameters ranging from about 5 to about 500 microns. Particle sizes of this latter magnitude may be readily achieved by spray-drying the carrier or by grinding the catalyst in a colloid mill. By way of specific example, a very satisfactory hydrogenation catalyst comprises 2% nickel and 16% molybdenum on an equimolar alumina-silica carrier (63% Al_2O_3/37% SiO_2); another good catalyst comprises 1% nickel and 8% molybdenum on an alumina-silica-boron phosphate carrier containing 68% Al_2O_3, 10% SiO_2, and 22% BPO_4, the general preparation of which is described in United States Patent 2,938,001.

The following examples demonstrate the effectiveness of the dual zone hydrorefining process of this invention and the advantages thereof over a conventional single-stage treatment. It is not intended, however, that the invention be unduly limited to the reactants, catalysts and conditions therein employed.

EXAMPLE I

In this example, a topped Wyoming sour crude oil was subjected to two-stage hydrorefining, wherein the first stage was a continuous process pilot plant employing a fluidized catalyst bed and the second stage, to which the liquid product from the first stage was charged, was a batch-type rocking autoclave utilizing a catalyst-oil slurry. The catalyst in both stages consisted essentially of 2% nickel and 16% molybdenum as oxides, composited with a porous refractory carrier containing 68% alumina, 10% silica and 22% boron phosphate, all of these percentages being by weight; this catalyst was in the form of microspheres having diameters ranging from about 10 to about 150 microns. The topped Wyoming sour crude oil (400° F.+ material removed) had a gravity of 19.5° API and contained 2900 p.p.m. of total nitrogen, 3.05% by weight of sulfur, 8.5% by weight of C_5-insoluble asphaltenes, 21 p.p.m. of nickel and 85 p.p.m. of vanadium. In the first stage treatment, the crude oil was preheated in admixture with hydrogen and thereby partially vaporized, and the resulting mixed phase charge was then passed upwardly through a confined fluidized catalyst bed to which additional fluidizing hydrogen was injected in cocurrent upflow with the hydrocarbon charge. Reaction conditions in the first stage included a temperature of 775° F., a total pressure of 2000 p.s.i.g., a weight hourly space velocity of 0.5 pound of oil per pound of catalyst per hour, and a total hydrogen rate of 50,000 standard cubic feet per barrel of charge. Vaporous effluent was withdrawn from the top of the fluidized solids reactor, condensed by cooling, and separated into gas and liquid fractions in a high pressure separator. The gaseous fraction was returned to the reactor as recycle hydrogen; recycle H_2 purity was maintained above 90 mol percent by withdrawing a slipstream of offgas from the recycle system and adding fresh H_2 from an outside source. The liquid fraction was continuously withdrawn from the high pressure separator as first stage product.

In the second stage treatment, 200 grams of first stage product and 20 grams of catalyst were charged to a high pressure rocking autoclave having a capacity of 1800 milliliters. The autoclave was pressured with hydrogen to 100 atmospheres pressure at room temperature and and then sealed. The autoclave was then heated to reaction temperature and maintained thereat for a period of 2 hours after which it was depressured, the contents removed and the second stage liquid product recovered from the oil-catalyst slurry by centrifugation and filtration. Two runs were made with separate 200 gram aliquots of first stage product: the first (Run A below) was effected at a temperature of 752° F. or slightly below the first stage temperature, and the second (Run B below) at 788° F. or slightly above the first stage temperature.

A comparison of the significant analyses of the topped crude oil charge, first stage product and second stage product is set forth in Table I below:

Table I

	Reaction Temperature, ° F.	° API	Total Nitrogen, p.p.m.	Sulfur, Wt. percent	C_5-Insolubles, Wt. percent	Nickel, p.p.m.	Vanadium, p.p.m.
Charge	----------	19.5	2,900	3.05	8.5	21	85
First Stage Product	775	30.8	1,550	0.62	0.1	0.04	0
Second Stage Product:							
Run A	752	37.5	27	0.03	0.02	0	0
Run B	788	42.8	18	0.02	0.04	0	0

Example II

A total Wyoming sour crude oil was subjected to two-stage hydrorefining, wherein both reaction steps were carried out sequentially in a batch-type rocking autoclave utilizing a catalyst-oil slurry. The catalyst in both steps consisted essentially of 2% nickel and 16% molybdenum, as oxides, composited with a porous refractory carrier containing 63% alumina and 37% silica, all of these percentages being by weight; the particle size of this catalyst was through 60 mesh. The Wyoming sour crude oil had a gravity of 22° API and contained 2700 p.p.m. of total nitrogen, 2.8% by weight of sulfur, 8.3% by weight of C_5-insoluble asphaltenes, 20 p.p.m. of nickel and 80 p.p.m. of vanadium. In the first stage treatment, 300 grams of crude oil and 30 grams of catalyst were charged to a high pressure rocking autoclave having a capacity of 1800 milliliters. The autoclave was pressured with hydrogen to 100 atmospheres pressure at room temperature and then sealed. The autoclave was then heated to a temperature of 752° F. and maintained thereat for a period of 4 hours after which it was depressured, the contents removed and the first stage liquid product recovered from the oil-catalyst slurry by centrifugation and filtration. A 200 gram portion of the first stage liquid product was recharged to the autoclave together with 20 grams of fresh catalyst. The autoclave was pressured with hydrogen to 100 atmospheres pressure at room temperature, sealed, heated to a temperature of 752° F. and maintained thereat for a period of 4 hours after which it was depressured, the contents removed and the second stage liquid product recovered from the oil-catalyst slurry by centrifugation and filtration.

A comparison of the significant analyses of the crude oil charge, first stage product and second stage product is set forth in Table II below:

Table II

	Reaction Temperature, ° F.	° API	Total Nitrogen, p.p.m.	Sulfur, Wt. percent	C_5-Insolubles, Wt. percent	Nickel, p.p.m.	Vanadium, p.p.m.
Charge	----------	22	2,700	2.8	8.3	20	80
First Stage Product	752	31	310	0.22	1.1	2.8	4.4
Second Stage Product	752	39.0	4	0.03	0	0.1	0.5

Example III

The total Wyoming sour crude oil of Example II was subjected to two-stage hydrorefining wherein both reaction steps were carried out sequentially in a batch-type rocking autoclave utilizing a colloidally dispersed unsupported molybdenum catalyst. Six grams of phosphomolybdic acid were dissolved in 100 grams of isopropyl alcohol and this solution was added dropwise to a 500 gram aliquot of the Wyoming sour crude oil, with vigorous stirring and distilling off the alcohol solvent as it was added. Upon complete addition of the solution, the sample was distilled to remove the gasoline fraction, yielding 447 grams of charge stock containing 0.80% by weight of colloidally dispersed molybdenum. 212 grams of the molybdenum-containing charge stock was placed in an 1800 milliliter rocking autoclave, pressured with hydrogen to 100 atmospheres at room temperature, and then sealed. The autoclave was heated to a temperature of 752° F. and maintained thereat for a period of 8 hours after which it was depressured, the contents removed, and the first stage liquid product recovered therefrom by centrifugation and filtration. The foregoing procedure was repeated using a second 223 gram aliquot of the molybdenum-containing charge and the liquid products from both runs were combined to yield charge stock for the second stage treatment.

The second stage reaction was carried out by dissolving 6 grams of phosphomolybdic acid in 75 grams of isopropyl alcohol and adding the solution dropwise to a 250 gram aliquot of the combined first stage products, with vigorous stirring and distilling off the alcohol solvent as it was added. Upon complete addition of the solution, the sample was distilled to remove the gasoline fraction, yielding 211 grams of charge stock containing 1.58% by weight of colloidally dispersed molybdenum. 200 grams of the thus prepared second stage charge stock was placed in the 1800 milliliter rocking autoclave and the autoclave was pressured with hydrogen to 100 atmospheres and then sealed. The autoclave was then heated to a temperature of 752° F. and maintained thereat for a period of 8 hours after which it was depressured, the contents removed and the second stage liquid product recovered therefrom by centrifugation and filtration.

A comparison of the significant analyses of the crude oil charge, first stage product and second stage product is set forth in Table III below:

Table III

	Reaction Temperature, ° F.	° API	Total Nitrogen, p.p.m.	Sulfur, Wt. percent	C_5-Insolubles, Wt. percent	Nickel, p.p.m.	Vanadium, p.p.m.
Charge	----------	22	2,700	2.8	8.3	20	80
Combined First Stage Product	752	30.3	984	0.50	0.32	0.24	2.5
Second Stage Product	752	30.4	322	0.09	0.16	0.03	0.9

The preceding three examples demonstrate that although a single stage treatment is very effective in reducing the concentration of C_5-insoluble asphaltenes and metals, it is much less effective for the removal of nitrogen and sulfur. But by rerunning the product from the first stage, which is now substantially free of asphaltenes and metals, nitrogen and sulfur removal proceeds much more readily and to a degree which could not be approached in a single step. These observations hold true whether the hydrogenation catalyst is supported or unsupported and whether the second zone reaction temperature is slightly higher or lower or exactly equal to the reaction temperature of the first zone. It is evident that the presence of asphaltenes and metals in a heavy oil charge stock materially interferes with reactions relating to hydrogenitrogenation and hydrodesulfurization reactions, but once the asphaltenes and metals are removed, the latter reactions are favorably promoted.

A comparison between Examples I and III shows that rerunning the first stage product in the presence of an unsupported catalyst is somewhat less effective in nitrogen and sulfur removal than when done in the presence of a supported catalyst, yet the unsupported catalyst is very active toward conversion of asphaltenes and removal of metals. It is, therefore, a preferred embodiment of this invention to employ an unsupported catalyst-oil slurry in the first zone and a supported catalyst in the second zone, which latter catalyst may be disposed as a fixed bed, slurry, or fluidized bed.

A continuous process implementing the foregoing principles is illustrated in the accompanying drawing which is a schematic flow diagram of the two-zone process utilizing an unsupported catalyst-sludge complex in the first reaction zone and a fixed-fluidized catalyst bed in the second reaction zone. While this flow scheme represents a preferred specific embodiment, it is not intended that the invention be unduly limited to the particular flow system therein illustrated or to the reactants, catalysts, and processing conditions described below.

Turning now to the drawing, a heavy oil charge is introduced through line 1, mixed with hydrogen from line 2 and passed through feed heater 3 wherein the temperature of the combined feed is raised to within the range of about 700–850° F. The heated mixed phase feed is commingled with recycled catalyst-sludge complex from line 23 and charged via line 4 and feed distributor 6 to the lower portion of first stage reactor 5. Heated recycle hydrogen is also charged to reactor 5 through line 20 and passes in cocurrent upflow with the oil through the first reaction zone. The catalyst in the first stage reactor is a finely divided unsupported catalyst, colloidally dispersed in the oil, which comprises the thermal decomposition product of a thermally decomposable oil-soluble compound of a metal from Gorups VB, VIB, and VIII of the Periodic Table, and more particularly may comprise vanadium, molybdenum, tungsten, nickel, or mixtures of two or more of these metals. There is also formed in the first stage reactor a relatively small quantity of organic sludge resulting from thermal polymerization of the heaviest components of the feed. This organic sludge exists in the form of small particles and preferentially attracts the unsupported catalyst particles so that the concentration of the catalytically active metal is somewhat higher in the sludge than in the total reactor volume generally; in effect, the organic sludge particles provide a quasi-carrier for the unsupported catalytically active metal or metals. When initially starting up this process, a suitable thermally decomposable metallic compound, such as a metal carbonyl, metal acetylacetonate, or metal xanthate, may be continuously or periodically injected into the first stage reactor to build up the metals content in the reaction zone to an operatively actively level, for example, from 0.5% to about 10% by weight of the total heavy oil present in the first stage reactor. After this concentration is reached, the metals natively present in the heavy oil charge, particularly vanadium and nickel, which themselves are bound up in complexes which decompose under the hydrorefining conditions existing within the reaction zone, will serve to maintain the catalytically active metallic concentration at this level, and thereafter further addition of decomposable metal compounds may be discontinued or at least employed only at fairly long intervals. In order to prevent the metal concentration from building up to an excessively high level within the first stage reactor, a slipstream of excess organic sludge-catalyst complex is withdrawn from the upper portion of reactor 5 through line 22 and a fraction thereof is sent to offsite regeneration or metals recovery facilities through line 24 and the balance is returned through line 23 to the reactor inlet; alternatively, line 23 may connect with line 1 upstream from heater 3 so that the soaking section of the heater operates as a catalytic reaction zone. Flow conditions within the first stage reactor are controlled to provide an upper disengaging zone so that the oil-hydrogen mixture leaving reactor 5 through line 7 is substantially free of organic sludge.

The first stage reactor effluent may be charged through line 7 directly to the second stage reactor 8 as illustrated, or, alternatively, the effluent may be first subjected to intermediate fractionation and/or flash separation whereby only the highest boiling fraction of the first stage reactor effluent is charged to the second stage reactor. Reactor 8 contains a fluidized bed of supported catalyst particles, which catalyst comprises a metal from groups VB, VIB, and VIII of the Periodic Table composited with a refractory inorganic oxide carrier, and may be any of those catalysts heretofore discussed in connection with supported hydrogenation catalysts. Thus, for example, the second stage catalyst may comprise about 0.2–10% by weight of nickel and about 1–20% by weight of molybdenum on a porous refractory oxide support comprising alumina and silica, and preferably is in microspherical form having particle diameters in the range of 20–300 microns. The catalyst is maintained in a fluidized state by means of heated fluidizing hydrogen introduced into the lower section of reactor 8 through line 19. The charge to second stage reactor 8 is introduced thereto through feed distributor 9 and passes upwardly through the catalyst bed cocurrently with the fluidizing hydrogen. The fluidizing hydrogen also functions to decrease the partial pressure of the oil vapor within the second stage reactor, to increase vaporization of the oil without raising it to thermal cracking temperature, and to maintain the catalyst bed substantially isothermal so that no vertical temperature gradient exists. The temperature in reactor 8 is maintained within the range of about 700–850° F. and at approximately the same temperature as that in the first stage reactor. Vaporous effluent from reactor 8 is taken overhead through line 10, cooled in condenser 11 and discharged into separator 12. A hydrorefined liquid product of improved purity and reduced average molecular weight is withdrawn from separator 12 through line 14. The gaseous portion of the effluent is withdrawn from separator 12 through line 13, the major portion thereof passing through line 15 to serve as recycle hydrogen, while a small dragstream of impure hydrogen is removed from the system through line 13 and sent to a hydrogen production or gas recovery unit whereby to maintain recycle hydrogen purity at a substantially constant level. The recycle hydrogen is compressed by recycle gas compressor 16 and is then discharged therefrom through line 17 into several parallel paths. A portion of the recycle hydrogen is passed through line 2 and admixed with heavy oil charge in line 1 to suppress thermal cracking in feed heater 3. The balance of the recycle hydrogen is heated in hydrogen heater 18 and then split into two streams, one of which is charged to first stage reactor 5 through line 20 and the other of which is charged to second stage reactor 8 through line 19. Fresh makeup hydrogen from an outside source is introduced to the recycle system through line 21 to maintain system pressure and recycle hydrogen purity.

We claim as our invention:

1. A process for hydrorefining a heavy hydrocarbon oil containing asphaltenes and metallic, nitrogenous and sulfurous contaminants which comprises passing said heavy oil and hydrogen at elevated pressure through a first hydrorefining zone containing a solid hydrogenation catalyst and maintained at a temperature in the range of about 700–850° F. to convert asphaltenes and metallic contaminants, and then passing at least the higher boiling fraction of the hydrocarbonaceous effluent containing nitrogenous and sulfurous contaminants from said first zone together with hydrogen at elevated pressure through a second hydrorefining zone containing a solid hydrogenation catalyst and maintained at substantially the same temperature as said first zone to remove the last-mentioned contaminants.

2. A process for hydrorefining a heavy hydrocarbon oil containing asphaltenes and metallic, nitrogenous and sulfurous contaminants which comprises passing said heavy oil and hydrogen at elevated pressure through a first hydrorefining zone containing a solid hydrogenation catalyst and maintained at a temperature in the range of about 725–825° F. to convert asphaltenes and metallic contaminants, and then passing at least the higher boiling fraction of the hydrocarbonaceous effluent containing nitrogenous and sulfurous contaminants from said first zone together with hydrogen at elevated pressure through a second hydrorefining zone containing a solid hydrogenation catalyst and maintained at substantially the same temperature as said first zone to remove the last-mentioned contaminants.

3. The process of claim 2 further characterized in that said heavy oil is a crude petroleum oil.

4. The process of claim 2 further characterized in that said heavy oil is a vacuum gas oil.

5. The process of claim 2 further characterized in that said heavy oil is a heavy cycle oil.

6. The process of claim 2 further characterized in that the hydrogenation catalyst in said first and second zones comprises a metal from Groups VB, VIB, and VIII of the Periodic Table.

7. The process of claim 6 further characterized in that the hydrogenation catalyst in said first zone comprises the thermal decomposition product of a thermally decomposable oil-soluble compound of a metal from Groups VB, VIB, and VII of the Periodic Table.

8. The process of claim 6 further characterized in that the hydrogenation catalyst in said second zone comprises a refractory inorganic oxide support.

9. A process for hydrorefining a heavy hydrocarbon oil containing asphaltenes and metallic, nitrogenous and sulfurous contaminants which comprises commingling said oil with a finely divided unsupported catalyst comprising the thermal decomposition product of a thermally decomposable oil-soluble compound of a metal from Groups VB, VIB, and VIII of the Periodic Table, reacting the resulting oil-catalyst mixture with hydrogen at a pressure in excess of about 500 p.s.i.g. in a first hydrorefining zone maintained at a temperature in the range of about 700–850° F. to convert asphaltenes and metallic contaminants, passing at least the higher boiling fraction of the hydrocarbonaceous effluent containing nitrogenous and sulfurous contaminants from said first zone together with hydrogen at a pressure in excess of about 500 p.s.i.g. through a second hydrorefining zone maintained at substantially the same temperature as said first zone and containing a particle-form supported catalyst comprising a metal from Groups VB, VIB, and VIII of the Periodic Table to remove the last-mentioned contaminants, and recovering from said second zone a hydrorefined product of improved purity and reduced average molecular weight.

10. The process of claim 9 further characterized in that said thermally decomposable compound is a metal carbonyl.

11. The process of claim 9 further characterized in that said thermally decomposable compound is a metal acetylacetonate.

12. The process of claim 9 further characterized in that said thermally decomposable compound is a metal xanthate.

13. The process of claim 9 further characterized in that said unsupported catalyst comprises vanadium.

14. The process of claim 9 further characterized in that said unsupported catalyst comprises molybdenum.

15. The process of claim 9 further characterized in that said unsupported catalyst comprises tungsten.

16. The process of claim 9 further characterized in that said unsupported catalyst comprises nickel.

17. The process of claim 9 further characterized in that the supported catalyst of said second zone is maintained in a fluidized state.

18. The process of claim 9 further characterized in that the supported catalyst of said second zone comprises nickel.

19. The process of claim 9 further characterized in that the supported catalyst of said second zone comprises molybdenum.

20. The process of claim 9 further characterized in that the supported catalyst of said second zone comprises about 0.2–10% by weight of nickel and about 1–20% by weight of molybdenum, composited with a porous refractory support containing alumina and silica.

References Cited by the Examiner

UNITED STATES PATENTS

2,769,754	11/56	Sweetser et al.	208—210
2,771,401	11/56	Shepherd	208—210
2,878,179	3/59	Hennig	208—210
2,917,448	12/59	Beuther et al.	208—264
2,951,032	8/60	Inwood	208—210

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