

1

3,453,206

**MULTIPLE-STAGE HYDROREFINING OF
PETROLEUM CRUDE OIL**

John G. Gatsis, Des Plaines, Ill., assignor to Universal
Oil Products Company, Des Plaines, Ill., a corporation
of Delaware

No Drawing. Filed June 24, 1966, Ser. No. 560,071

Int. Cl. C10m 31/08, 23/00

U.S. Cl. 208—210

4 Claims

ABSTRACT OF THE DISCLOSURE

Plural stage hydrorefining of a heavy hydrocarbon charge stock whereby the charge is treated in a first reaction zone with a mixture of H_2 and H_2O at a temperature above the critical temperature of water and in the absence of catalyst. The first zone liquid product is reacted with hydrogen in a second reaction zone in the presence of catalyst at hydrorefining conditions.

The invention described herein is adaptable to a process for the hydrorefining of heavy hydrocarbon fractions and/or distillates for the purpose of eliminating or reducing the concentration of various contaminants contained therein. More specifically, the present invention is directed toward a combination process for hydrorefining petroleum crude oils, atmospheric tower bottoms products, vacuum tower bottoms products, heavy cycle stocks, crude oil residuum, topped crude oils, the heavy hydrocarbonaceous oils extracted from tar sands, etc. The present process is a novel combination of non-catalytic pretreatment and catalytic hydrorefining, and is especially advantageous in treating petroleum crude oils and topped, or reduced crude oils severely contaminated by the inclusion therein of excessive quantities of pentane-insoluble asphaltenic material as well as high molecular weight sulfurous compounds.

Petroleum crude oils, and the heavier hydrocarbon fractions and/or distillates obtained therefrom, particularly heavy vacuum gas oils, oils extracted from tar sands, and topped or reduced crudes, contain nitrogenous and sulfurous compounds in exceedingly large quantities. In addition, such heavy hydrocarbon fractions contain excessive quantities of organo-metallic contaminants; causing detrimental effects with respect to various catalytic composites utilized in a multitude of processes to which the heavy hydrocarbon fraction may be subjected. Crude hydrocarbon oils originally extracted from a variety of tar sands, contain an added contaminant in the form of an ash in an amount of about 2.0% by weight, the composition of which being about 99.0% silica. Of the metallic contaminants, those containing nickel and vanadium are most common, although other metals including iron, copper, lead, zinc, etc., are often present. These metallic contaminants, as well as others, may be present within the hydrocarbonaceous material in a variety of forms; usually, however, they are found to exist as organo-metallic compounds of relatively high molecular weight, including metallic porphyrins and various derivatives thereof. A considerable quantity of the organo-metallic complexes are linked with asphaltenic material and contain sulfur. These become concentrated in the residual fractions; other organo-metallic complexes are volatile, oil-soluble and are, therefore, carried over with a distillate fraction. A considerable reduction in the concentration of the organo-metallic complexes is not easily achieved, and to the extent that the crude oil, reduced crude oil, or other heavy hydrocarbon charge stock becomes suitable for further processing. With respect to a process for hydrorefining,

2

or treating of such hydrocarbon mixtures, the presence of exceedingly large quantities of asphaltenic material and organo-metallic compounds interferes considerably with the activity of the catalyst with respect to the destructive removal of the nitrogenous, sulfurous and oxygenated compounds, which function is normally the easiest for the catalytic composite to perform to an acceptable degree. Therefore, it is very desirable to produce a hydrocarbon mixture substantially free from asphaltenic material and organo-metallic compounds, which mixture is substantially reduced with respect to nitrogen and sulfur concentration.

Crude oils and other heavy hydrocarbon fractions contain greater quantities of sulfurous and nitrogenous compounds than are generally found in lighter hydrocarbon fractions such as gasoline, kerosene, light middle-distillates, etc. For example, a Wyoming sour crude oil, having a gravity of about 23.2° API at 60° F., contains about 2.8% by weight of sulfur and approximately 2700 p.p.m. of total nitrogen, calculated as the elements thereof, in addition to 18 p.p.m. of nickel and 71 p.p.m. of vanadium. Similarly, a vacuum tower bottoms product, having a gravity, ° API at 60° F., of 7.1, contains 4.05% by weight of sulfur, 6060 p.p.m. of nitrogen, 46 p.p.m. of nickel and 195 p.p.m. of vanadium. Of the nonmetallic impurities, nitrogen is probably most undesirable because it effectively poisons various catalytic composites which may be employed in the conversion of petroleum fractions; in particular, nitrogen and nitrogenous compounds are recognized as effective hydrocracking suppressors. Therefore, it is particularly necessary that nitrogenous compounds be removed substantially completely from all catalytic hydrocracking charge stocks. Nitrogenous and sulfurous compounds are further objectionable because combustion of fuels containing these impurities results in the release of nitrogen and sulfur oxides which are noxious, corrosive and present a serious problem with respect to pollution of the atmosphere. With respect to motor fuels, sulfur is particularly objectionable because of odor, gum and varnish formation, and significantly decreased lead susceptibility.

In addition to the foregoing described contaminating influences, crude oils and other heavy hydrocarbon fractions contain excessive quantities of high molecular weight, pentane-insoluble asphaltenic material. For example, the Wyoming sour crude described above consists of about 8.3% by weight of pentane-insoluble asphaltenes, whereas the vacuum tower bottoms product contains as much as 23.7% by weight of pentane-insoluble asphaltenes. These are non-distillable, oil-insoluble coke precursors which may be complexed with sulfur, nitrogen and various metals. Generally, the asphaltenic material is found to be colloiddally dispersed within the crude oil, and when subjected to heat, as in a vacuum distillation process, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult. Thus, in the heavy bottoms from a crude oil vacuum distillation column the polymerized asphaltenes exist as solid material useful only as road asphalt, or as an extremely low grade fuel when cut with distillate hydrocarbons such as kerosene, light gas oil, etc.

The necessity for the removal of the foregoing contaminating influences is well known to those aware of petroleum refining processes and techniques. Heretofore, in the field of catalytic hydrorefining two principal approaches have been advanced: liquid-phase hydrogenation and vapor-phase hydrocracking. In the former type of process, the oil is passed upwardly in liquid phase, and in admixture with hydrogen, into a fixed-bed or slurry of sub-divided catalyst; although perhaps effective in remov-

ing at least a portion of the oil-soluble organo-metallic complexes, this type process is relatively ineffective with respect to oil-insoluble asphaltenes which are colloiddally dispersed within the charge, with the consequence that the probability of effecting simultaneous contact between the catalyst particle and asphaltenic molecule is remote. Furthermore, since the hydrogenation reaction zone is generally maintained at an elevated temperature, the retention of unconverted asphaltenes, suspended in a free liquid phase oil for an extended period of time, will result in flocculation making conversion thereof substantially more difficult. The rate of diffusion of the oil-insoluble asphaltenes is substantially lower than of dissolved molecules of the same molecular size; for this reason, the fixed-bed catalytic processes, in which the oil and hydrogen are passed through the catalyst, are extremely difficult. The asphaltenes, being neither volatile nor dissolved in the crude, are unable to move to the catalytically active sites, the latter being obviously immovable. Furthermore, the efficiency of hydrogen to oil contact obtainable by bubbling hydrogen through an extensive liquid body is relatively low. On the other hand, vapor phase hydrocracking is carried out either with a fixed-bed or expended-bed system at temperatures substantially above about 950° F.; while this technique obviates to a certain extent the drawbacks of liquid-phase hydrogenation, it is not suited to treating crude and heavy hydrocarbon fractions due to the non-volatility of the asphaltenes which favors a high production of coke and carbonaceous material, with the result that the catalytic composite succumbs to relatively rapid deactivation; this requires high capacity catalyst regeneration equipment in order to implement the process on a continuous basis.

Selective hydrocracking of a full boiling range heavy hydrocarbon charge stock is not easily obtained, excessive amounts of light gases are produced at the expense of the more valuable normally liquid hydrocarbon product; minimum quantity of cracked gasoline production is unavoidable, and such a result is not desirable where the object is to maximize the production of middle and heavy distillates such as jet fuel, diesel oil, furnace oils, and gas oils.

The object of the present invention is to provide a hydrorefining process for effecting the removal of various contaminating influences from heavier hydrocarbonaceous material, and particularly petroleum crude oil and crude tower bottoms product. The term "hydrorefining," as employed herein, connotes the treatment, in an atmosphere of hydrogen, of a hydrocarbon fraction or distillate for the purpose of eliminating and/or reducing the concentration of the various contaminating influences previously described. The present invention encompasses a non-catalytic technique which affords unusual advantages in the pretreatment of heavier hydrocarbonaceous material, in combination with a subsequent catalytic hydrorefining system. The present combinative process yields a liquid hydrocarbon product which is more suitable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing contaminants. The present process is particularly advantageous for effecting the conversion of the organo-metallic contaminants without significant product yield loss while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbon products. The present invention affords the utilization of a fixed-bed hydrorefining process, which, as hereinbefore set forth, has not been considered feasible due to the deposition of coke and other gummy carbonaceous material. The difficulties encountered in a fixed-bed catalytic process are at least partially solved by a fixed-fluidized process, in which the catalytic composite is disposed within a confined reaction zone, being maintained, however, in a fluidized state by exceedingly large quantities of a fast-flowing hydrogen-containing gas stream. Difficulties attendant the fixed-fluidized type process reside in the difficulty of removing the catalyst from

the reaction zone for regeneration purposes, a large loss of catalyst, removed from the reaction zone with the hydrocarbon product effluent, the relatively large quantities of catalyst necessary to effect proper contact between the asphaltenic material and active catalyst sites, etc. The combinative process of the present invention encompasses the use of a particularly preferred hydrorefining catalyst utilizing a refractory inorganic oxide carrier material, which catalyst permits effecting the process in a fixed-bed unit without incurring the deposition of exceedingly large quantities of coke and other heavy hydrocarbonaceous material.

A broad embodiment of the present invention encompasses, therefore, a process for hydrorefining a hydrocarbon charge stock boiling above the gasoline boiling range which comprises the steps of: (a) treating said charge stock, in the absence of a catalytic composite, with a mixture of hydrogen and water at a temperature above the critical temperature of water; and, (b) reacting at least a portion of the remaining liquid product effluent with hydrogen and water in a reaction zone containing a hydrorefining catalytic composite, and at hydrorefining conditions.

A more limited embodiment of the present invention affords a combinative process for hydrorefining an asphaltene-containing hydrocarbon charge stock boiling above the gasoline boiling range, and contaminated by sulfurous compounds, which process comprises the steps of: (a) treating said charge stock, in the absence of a catalytic composite, with a mixture of hydrogen and from about 2.0% to about 30.0% by weight of water, in a treating zone maintained at a temperature above the critical temperature of water, having an upper limit of about 500° C. and at a pressure of from about 1000 to about 5000 p.s.i.g.; (b) separating the thus-treated charge stock to remove a hydrogen sulfide-containing gaseous phase; (c) separating the remainder of said treated product effluent to provide a substantially solid-free liquid hydrocarbon product; and, (d) reacting at least a portion of said liquid hydrocarbon product with hydrogen and water in a reaction zone containing a siliceous hydrorefining catalytic composite comprising at least one metallic component selected from the group of metals of Groups V-B, VI-B and VIII of the Periodic Table, and at hydrorefining conditions including a temperature of from about 200° C. to about 500° C. and a pressure of from about 1000 to about 5000 p.s.i.g.

From the foregoing embodiments, it will be noted that the combinative process encompassed by the present invention involves the non-catalytic treatment of hydrocarbons boiling at a temperature above the normal gasoline boiling range. Thus, the process of the present invention is adaptable to the decontamination of various hydrocarbon mixtures, fractions and/or distillates containing substantial concentrations of hydrocarbons boiling at a temperature above about 425° F. However, it is not intended to limit the process of the present invention to hydrocarbon charge stocks essentially devoid of hydrocarbons boiling within the gasoline boiling range. As hereinbefore set forth, the present invention is particularly adaptable to hydrorefining of petroleum crude oils and the heavier hydrocarbon fractions derived therefrom.

The use of the term "hydrorefining conditions" is intended to encompass those operating conditions of temperature and pressure at which hydrorefining reactions are effected. That is, conditions at which pentane-insoluble asphaltenic material is converted into pentane-soluble liquid hydrocarbon products, nitrogenous compounds are converted into ammonia and hydrocarbons, and sulfurous compounds are converted into hydrogen sulfide and hydrocarbons, which reactions are accompanied by the destructive removal of organo-metallic compounds and the substantially complete saturation of the mono- and di-olefinic hydrocarbons. Thus, hydrorefining conditions are intended to include temperatures above about 200° C.,

with an upper limit of about 500° C., and pressures greater than about 450 p.s.i.g., having an upper limit of about 5000 p.s.i.g., and preferably a lower limit of 1000 p.s.i.g. Under the foregoing conditions, the hydrocarbon charge stock is initially treated with a mixture of hydrogen and water, with the water concentration being in an amount within the range of about 2.0% to about 30.0%, based upon the weight of the charge stock. Although the pretreatment technique of the present combination process may be conducted in a batch-wise fashion, it readily lends itself to continuous processing in an enclosed vessel through which the mixture of hydrocarbon charge stock, hydrogen and water is passed. When conducted as a continuous process, it is particularly preferred to introduce the hydrogen-water mixture into the vessel countercurrently to the flow of charge stock therethrough, the latter passing through the vessel in downward flow. The internals of the vessel may be constructed in any suitable manner capable of providing the required intimate contact between the liquid charge stock and the gaseous mixture. In many instances it may be desirable to provide the reaction zone with a packed bed of inert material such as particles of granite, porcelain, berl saddles, sand, aluminum and other metal turnings, etc. Although not considered an essential feature of the present invention, the flow rate of the charge stock and gaseous mixture are such that hydrogen is present in an amount within the range of about 1000 to about 100,000 s.c.f./bbl. of hydrocarbon charge stock. The pretreatment zone, into which the charge stock and mixture of hydrogen and water is introduced, is maintained under an imposed pressure greater than 450 p.s.i.g., and preferably at an elevated pressure within the range of 1000 to about 5000 p.s.i.g. The temperature in the treating zone is above the critical temperature of water, and generally up to about 500° C. The mixture of hydrogen and water is such that the latter is in an amount of from about 2.0% to about 30.0% by weight of the hydrocarbon charge stock.

The thus-treated hydrocarbon charge stock, now of reduced asphaltene and metal content, is removed from the non-catalytic pretreatment zone, and passed into a suitable high pressure separator from which a gaseous phase containing hydrogen, ammonia and hydrogen sulfide is removed. This phase is further treated for the purpose of removing the hydrogen sulfide and ammonia from the process system prior to recycling the hydrogen to the pretreatment zone. Such hydrogen sulfide results primarily from the conversion of the sulfur-containing high molecular weight asphaltenes and organo-metallic complexes into pentane-soluble liquid hydrocarbons of lower molecular weight. The ammonia obviously results from the conversion of nitrogenous compounds into hydrocarbons.

Similarly, the gaseous mixture emanating from the upper portion of the pre-treatment zone will contain some entrained particles of valuable liquid hydrocarbon product, and is separated to recover these entrained particles for admixture with the liquid portion of the treated charge being removed from the high-pressure separator. This mixture is then further separated for the purpose of removing a metal-containing sludge consisting in part of the unconverted asphaltenes (approximately 10.0% of those asphaltenes originally present in the hydrocarbon charge). Suitable separation means include the use of settling tanks, centrifugal separators, or combinations thereof, whereby there is produced a substantially solid-free, normally liquid hydrocarbon product.

The substantially solid-free normally liquid hydrocarbon product from the pre-treatment zone is reduced in nitrogen and sulfur concentration to less than about 50.0% of that quality originally present. The concentration of organo-metallic contaminants is less than about 10.0 p.p.m. total, and the asphaltenic material has been removed to the extent of about 90.0% of the amount included in the original hydrocarbon charge stock. Thus, the operating

conditions imposed upon the catalytic hydrorefining reaction zone can be significantly less severe than had the pre-treatment procedure been omitted. Prior to entering the hydrorefining reaction zone, to contact the catalytic composite disposed therein, the pre-treated charge is admixed with hydrogen, the latter in an amount of from about 1000 to about 100,000 s.c.f./bbl., the mixture of hydrocarbon and hydrogen being heated to the desired operating temperature. Since the reactions effected within the hydrorefining reaction zone are primarily exothermic, the inlet temperature, or that to which the charge is heated, is less than the average temperature of the catalyst particles disposed within the reaction zone. Thus, the mixture is heated to a level such that the maximum catalyst temperature is within the range of from about 200° C. to about 500° C. Since a lower level of severity is permitted within the fixed-bed reaction zone, the preferred maximum catalyst temperature is intermediate, and within the range of about 385° C. to about 450° C. At these operating conditions, thermal cracking is inhibited and suppressed to the extent that the loss of liquid hydrocarbon product to gaseous waste material is significantly decreased, as is the deposition of coke and other heavy hydrocarbonaceous material. As hereinbefore set forth, hydrogen is employed in admixture with the charge stock in an amount of from about 1000 to about 100,000 s.c.f./bbl. The hydrogen-containing gas stream, herein sometimes designated as "recycle hydrogen," since it is conveniently recycled externally of the hydrorefining zone, fulfills a number of various functions: it serves as a hydrogenating agent, a heat carrier, and particularly a means for stripping converted material from the catalytic composite, thereby creating still more catalytically active sites available for the incoming, unconverted hydrocarbon charge stock. The liquid hourly space velocity, herein defined as the volumes of hydrocarbon charge per hour per volume of catalyst disposed within the reaction zone, will be at least partially dependent upon the physical and chemical characteristics of the charge stock; however, the liquid hourly space velocity will normally lie within the range of from about 0.5 to about 10.0, and preferably from about 0.5 to about 3.0. Although not essential to the present combinative process, water, in an amount of from 2.0% to 30.0% by weight of the liquid charge to the catalytic hydrorefining zone, may be admixed with the hydrogen stream. This procedure has advantage where the desired result is to maximize the gasoline boiling range hydrocarbons in the product, as distinguished from those situations where the process is designed to maximize the production of middle-distillate hydrocarbons.

The total product effluent from the hydrorefining reaction zone is passed into a high-pressure separator maintained at about room temperature. Normally liquid hydrocarbons are recovered from the separator while the hydrogen-rich gaseous phase is returned to the hydrorefining zone in admixture with additional external hydrogen required to replenish and compensate for the net hydrogen consumption which may range from about 200 to about 3000 s.c.f./bbl. of liquid charge, the precise amount being dependent upon the characteristics of the charge stock. The recycle hydrogen-rich gas stream may be treated by any suitable means for the purpose of effecting the removal of ammonia and hydrogen sulfide resulting from the conversion of the residual nitrogenous and sulfurous compounds. Furthermore, the normally liquid hydrocarbon product, removed from the high-pressure separator, may be introduced into a stripping or fractionating column, or otherwise suitably treated for the purpose of removing dissolved normally gaseous hydrocarbons, including methane, ethane and propane, and additional hydrogen sulfide and ammonia.

The catalytic composite disposed within the hydrorefining reaction zone can be characterized as comprising a metallic component having hydrogenation activity, which component is composited with a refractory inorganic oxide

carrier material of either synthetic or natural origin, which carrier material has a medium to high surface area and a well-developed pore structure. The precise composition and method of manufacturing the carrier material is not considered to be an essential feature of the present invention, although the preferred carrier material, in order to have the most advantageous pore structure, will have an apparent bulk density less than about 0.40 gram per cc., and preferably within the range of from about 0.10 to about 0.30 gram per cc. Suitable metallic components having hydrogenation activity are those selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table, as indicated in the Periodic Chart of the Elements, Fisher Scientific Company (1953). Thus, the catalytic composite may comprise one or more metallic components from the group of vanadium, niobium, tantalum, molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium, and mixtures thereof. The concentration of the catalytically active metallic component, or components, is primarily dependent upon the particular metal as well as the characteristics of the charge stock. For example, the metallic components of Groups V-B and VI-B are preferably present in an amount within the range of about 1.0% to about 20.0% by weight, the iron-group metals in an amount within the range of about 0.2% to about 10.0% by weight, whereas the platinum-group metals are preferably present in an amount within the range of about 0.1% to about 5.0% by weight, all of which are calculated as if the components existed within the finished catalytic composite as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, and mixtures of two or more including 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-alumina-boria, etc. It is preferred to utilize a carrier material containing at least a portion of silica, and preferably a composite of alumina and silica with alumina being in the greater proportion. By way of specific examples, a satisfactory carrier material may comprise equimolar quantities of alumina and silica, or 63.0% by weight of alumina and 37.0% by weight of silica, or a carrier of 68.0% by weight of alumina, 10.0% by weight of alumina, 10.0% by weight of silica and 22.0% by weight of boron phosphate. An absorptive hydrogenation catalyst, adaptable for utilization in the process of the present invention, will comprise a carrier material having a surface area of about 50 to about 700 square meters per gram, and a pore diameter of about 20 to about 300 angstroms, a pore volume of about 0.10 to about 0.80 milliliter per gram and an apparent bulk density within the range of from about 0.10 to about 0.40 gram per cc.

Briefly, one particularly preferred embodiment of the present invention is effected by heating an atmospheric tower bottoms product to a temperature of about 425° C. This atmospheric tower bottoms product consists essentially of hydrocarbonaceous material boiling at temperatures above about 800° F., and indicates a gravity, ° API at 60° F., of about 6.9. The charge stock is contaminated by the presence of about 7000 p.p.m. of nitrogen, 6.0% by weight of sulfur, 20 p.p.m. of both nickel and vanadium, and consists of 25.0% by weight of pentane-insoluble asphaltenes. The charge stock is passed into the upper portion of a non-catalytic treating zone, and passes downwardly therethrough in contact with a bed of inert granite particles. A gaseous mixture comprising hydrogen and 20.0% by weight of water, based upon the charge, is introduced into the treatment zone countercurrently to the downwardly flowing hydrocarbon stream, the hydrogen being in a concentration of about 20,000 s.c.f./bbl.

The gaseous mixture is removed from the uppermost portion of the treatment zone into a suitable liquid-gas separator in which any entrained liquid particles are collected, the gaseous phase being withdrawn and reintroduced into the bottom of the treating zone at a pressure of about 3,000 p.s.i.g., after removal of hydrogen sulfide and ammonia. The hydrocarbon stream emanating from the bottom of the treating zone passes into a high-pressure separator maintained at about 3,000 p.s.i.g. and about room temperature. A hydrogen sulfide and ammonia-containing gas stream is vented from the separator by means of pressure control, normally liquid hydrocarbons being removed on liquid level control, the latter being combined with the recovered entrained liquids and passed into a centrifugal separator. A metal-containing asphaltene sludge is recovered from the centrifugal separator, the remaining portion of the treated charge stock being combined with hydrogen in an amount of about 15,000 s.c.f./bbl.

The thus-treated charge stock indicates a gravity, ° API at 60° F., of 23.7, and is contaminated by the presence of 3,000 p.p.m. of nitrogen, about 2.5% by weight of sulfur, contains only 10.0% of those pentane-insoluble asphaltenes originally present and less than about 10 p.p.m. of total metals. The mixture of hydrogen and substantially solid-free liquid hydrocarbon is raised to a temperature of 400° C. and passes into a hydrorefining reaction zone containing a catalyst comprising 2.0% by weight of nickel and 16.0% by weight of molybdenum, calculated as the elements thereof, and an alumina-silica carrier material containing 37.0% by weight of silica. The total product effluent from the catalyst-containing reaction zone passes into a high-pressure separator from which the normally liquid hydrocarbon product is withdrawn into a low-pressure fractionation column. The normally gaseous phase from the high-pressure separator is treated to remove ammonia, hydrogen sulfide and light paraffinic hydrocarbons, the remainder being compressed to a level of about 3,000 p.s.i.g., and combined with additional treated hydrocarbon charge. Following the removal of pentanes and lighter hydrocarbons, the final product effluent indicates a gravity of about 36.5° API at 60° F., and contains less than about 100 p.p.m. of nitrogen, less than 0.5% by weight of sulfur, less than 0.1% of pentane-insoluble asphaltenes and substantially no nickel and vanadium organo-metallic compounds.

The following example is given to illustrate the present invention, and to indicate the unexpected effectiveness thereof in hydrorefining a petroleum crude oil fraction to remove the various contaminating influences hereinbefore described. It is not intended to limit the present invention to the particular method employed, the concentration of material, the particular charge stock and/or the specific conditions of operation utilized in presenting this example.

EXAMPLE

The charge stock employed is a vacuum tower bottoms product having a gravity, ° API at 60° F., of 7.1, the analysis of which indicates 23.7% by weight of pentane-insoluble asphaltenes, 6060 p.p.m. of nitrogen, 4.05% by weight of sulfur, 46 p.p.m. of nickel and 195 p.p.m. of vanadium. The charge stock, in an amount of 200 cc./hr., is passed downwardly through a ¾-inch (nominal diameter) stainless-steel tube equipped with an external heater controlling the inlet temperature at about 425° C. The tube is packed with stainless-steel turnings to provide intimate contact of the tower bottoms with a countercurrently flowing once-through hydrogen stream containing 15.0% by weight of water, based upon the hydrocarbon feed, in an amount of 10,000 s.c.f./bbl. The gaseous overhead stream is passed through a condenser/separator from which entrained normally liquid hydrocarbons are removed and combined with the bottoms product effluent, the mixture passing into a high-pressure separator. A hydrogen-rich gaseous phase, containing hydrogen sulfide, ammonia and

some light hydrocarbons in addition to carbon oxides, is removed from the separator, and the liquid hydrocarbons subjected to centrifugal separation to remove a metal-containing sludge and produce a substantially solid-free liquid. In this bench-scale operation, the hydrogen-rich phase is not treated to remove the components other than hydrogen; obviously, in a commercial size operation such would not be the case.

Upon analysis, the solid-free liquid product, having a gravity of 18.7° API @ 60° F., indicates about 2600 p.p.m. of nitrogen, 1.8% by weight of sulfur and less than 10.0 p.p.m. of metallic porphyrins, as elemental vanadium and nickel. The asphaltene content is such that 88.0% of those asphaltenic compounds originally present have been converted into pentane-soluble hydrocarbons. This treated material is subjected to hydrotreating in a reaction zone containing a catalyst of 2.0% by weight of nickel and 16.0% by weight of molybdenum on an alumina-silica carrier material. The pressure within the zone is increased to a level of about 3,000 p.s.i.g., utilizing a stream of nitrogen having been heated to a temperature of about 375° C. When these conditions are stabilized, the nitrogen stream is replaced with a hydrogen stream in an amount of about 20,000 s.c.f./bbl., while the temperature is increased to a level of about 400° C., the liquid hourly space velocity of the hydrocarbon charge stream being 1.0. The normally liquid product effluent from the high-pressure separator, upon analysis and removal of pentanes and lighter normally liquid hydrocarbons, indicates less than 0.5% of pentane-insoluble asphaltenic material, less than 0.5 p.p.m. of organo-metallic compounds (calculated as elemental metals), less than about 30 p.p.m. of total nitrogen and less than about 0.30% by weight of sulfur, the gravity, ° API, being within the range of from about 33.0 to about 36.5.

The foregoing example and specification clearly indicate the method by which the combinative process of the present invention effects the hydrotreating of heavy hydrocarbonaceous material. The benefits afforded petroleum refining operations and techniques will be readily ascertained by those possessing skill in the art relating thereto.

I claim as my invention:

1. A combination process for hydrotreating an asphaltene-containing hydrocarbon charge stock boiling above the gasoline boiling range which comprises the steps of:

- (a) treating said charge stock, in the absence of a catalyst, with a mixture of hydrogen and from about 2.0% to about 30.0% by weight of water, based upon said charge stock, at a temperature above the critical temperature of water, having an upper limit of about 500° C., and a pressure above about 1000 p.s.i.g.;
- (b) removing asphaltenic sludge from the effluent of step (a); and
- (c) reacting at least a portion of the remaining liquid product effluent with hydrogen in a reaction zone

containing a hydrotreating catalytic composite, and at hydrotreating conditions.

2. A combination process for hydrotreating a sulfur-containing hydrocarbon charge stock boiling above the gasoline boiling range which comprises the steps of:

- (a) treating said charge stock, in the absence of a catalyst, with a mixture of hydrogen and from about 2.0% to about 30.0% by weight of water, based upon said charge stock, at a temperature above the critical temperature of water, having an upper limit of about 500° C. and a pressure above about 1000 p.s.i.g.;
- (b) removing hydrogen sulfide from the resulting treated product effluent; and,
- (c) reacting at least a portion of the remaining liquid product effluent with hydrogen in a reaction zone containing a hydrotreating catalytic composite, and at hydrotreating conditions.

3. The process of claim 2 further characterized in that said hydrotreating conditions of step (c) include a pressure above about 1,000 p.s.i.g. and a temperature below about 500° C.

4. A combination process for hydrotreating an asphaltene-containing hydrocarbon charge stock boiling above the gasoline boiling range and contaminated by sulfurous compounds, which comprises the steps of:

- (a) treating said charge stock, in the absence of a catalyst, with a mixture of hydrogen and from about 2.0% to about 30.0% by weight of water, based upon said charge stock, in a treating zone maintained at a temperature above the critical temperature of water, having an upper limit of about 500° C. and at a pressure of from about 1000 to about 5000 p.s.i.g.;
- (b) removing hydrogen sulfide from the thus treated charge stock;
- (c) removing asphaltenic sludge from the remainder of said treated product effluent to provide a substantially solid-free liquid hydrocarbon product; and,
- (d) reacting at least a portion of said liquid hydrocarbon product with hydrogen and water in a reaction zone containing a siliceous hydrotreating catalytic composite comprising at least one metallic component selected from the group of metals of Groups V-B, VI-B, and VIII of the Periodic Table, and at hydrotreating conditions including a temperature of from about 200° C. to about 500° C. and a pressure of from about 1000 to about 5000 p.s.i.g.

References Cited

UNITED STATES PATENTS

3,017,345	1/1962	Eastman et al.	208—210
3,173,853	3/1965	Peralta	208—89
3,271,302	9/1966	Gleim	208—210
3,362,901	1/1968	Szepe et al.	208—210

DELBERT E. GANTZ, *Primary Examiner*.