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MULTIPLE-STAGE HYDROREFINING OF PETROLEUM CRUDE OIL

William K. T. Gleim, Island Lake, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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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 bottoms products, vacuum tower bottoms products, heavy cycle stocks, crude oil residuum, topped crude oils, the hydrocarbonaceous oils extracted from tar sands, etc. The present process is a novel combination of non-catalytic pre-treatment 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 organo-metallic contaminants as well as pentane-insoluble asphaltenic material.

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 90.0% 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; they may exist therein as metal oxides or sulfides, introduced as metallic scale or particles; they may exist in the form of soluble salts of such metals; usually, however, the metallic contaminants are found to exist as organo-metallic compounds of relatively high molecular weight, such as metallic porphyrins and the various derivatives thereof. Where the metallic contaminants are present as oxide or sulfide scale, they may be removed, at least in part, by a relatively simple filtering technique, the water-soluble salt being removed by washing and subsequent dehydration of the crude oil. A considerable quantity of the organo-metallic complexes, however, are linked with asphaltenic material and become concentrated in the residual fractions; other organo-metallic complexes are volatile, oil-soluble and are, therefore, carried over in the 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. Notwithstanding that the concentration of these organo-metallic compounds may be relatively small, for example often less than about 10 p.p.m. (calculated as if the metallic complex existed as the elemental metal), subsequent processing techniques are adversely affected thereby. For example, when a hydrocarbon charge stock containing organo-metallic compounds, such as metal porphyrins, in amounts above about 10.0 p.p.m., is subjected to cat-

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alytic cracking, for the purpose of producing lower-boiling hydrocarbon products, the metals become deposited upon the catalyst, steadily increasing in concentration as the process continues. The composition of cracking catalysts is closely controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity. Such composition is changed drastically as a result of the deposition of the metallic contaminants thereupon, the changed composite resulting, therefore, in changed catalytic characteristics. Such an effect is undesirable since the deposition of the metallic contaminants results in a lesser quantity of normally liquid hydrocarbon products, and produces large quantities of hydrogen and coke, the latter also promoting relatively rapid catalyst deactivation.

Eventually the catalyst must be subjected to elaborate regenerative techniques, or more often be replaced with fresh catalyst. The presence of excessive quantities of organo-metallic complexes adversely affects other processes including catalytic reforming, isomerization, hydrodealkylation, etc. With respect to a process for hydrorefining, or treating of hydrocarbon fractions and/or distillates, 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 highly desirable to produce a hydrocarbon mixture substantially free from asphaltenic material and organo-metallic compounds, and 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 non-metallic 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,

oxygen 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-insoluble products becomes extremely difficult. Thus, in the heavy bottoms from a crude oil vacuum distillation column the polymerized asphaltenes exits as solid material even at ambient temperatures; such a product is generally 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 possessing skill within the art of petroleum refining processes. Heretofore, in the field of catalytic hydrotreating 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 removing 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 processes, in which the oil and hydrogen are passed through the catalyst, are virtually precluded. 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 expanded-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; also, when processing a petroleum crude oil, an indeterminate 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 hydrotreating 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 "hydrotreating," 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 pre-treatment of heavier hydrocarbonaceous material, in combination with a subsequent catalytic hydrotreating 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 hydrotreating 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 hydrotreating 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.

Therefore, in a broad embodiment, the present invention relates to a process for hydrotreating a hydrocarbon charge stock, which process comprises the steps of: (a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide; and, (b) reacting at least a portion of the resulting treated product effluent with hydrogen, in a reaction zone containing a hydrotreating catalytic composite.

Another broad embodiment of the present invention involves a process for hydrotreating a hydrocarbon charge stock boiling at a temperature above the gasoline boiling range, which process comprises the steps of: (a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide; (b) separating 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.

A more limited embodiment of the present invention affords a combinative process for hydrotreating an asphaltene-containing hydrocarbon charge stock boiling at a temperature above the gasoline boiling range, which process comprises the steps of: (a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide, in a treating zone maintained at a temperature within the range of from about 200° C. to about 500° C. and at a pressure of from about 450 to about 5000 p.s.i.g.; (b) separating the thus-treated charge stock to provide a hydrogen sulfide-containing gaseous phase, recycling at least a portion of said gaseous phase to said treating zone; (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 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 450 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 the hydrotreating of petroleum crude oils and the heavier hydrocarbon fractions derived therefrom.

The use of the term "hydrotreating conditions" is intended to encompass those operating conditions of temperature and pressure at which hydrotreating reactions are effected. That is, conditions at which pentane-insoluble asphaltene 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 diolefinic hydrocarbons. Thus, hydrotreating 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. Under the foregoing conditions, the hydrocarbon charge stock is initially treated with a gaseous mixture of hydrogen containing hydrogen sulfide. The composition of the gaseous mixture is such that hydrogen is in the greater concentration, hydrogen sulfide being present therein in an amount within the range of about 5.0% to about 25.0%. Although the pre-treatment 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 hydrogen sulfide is passed. When conducted as a continuous process, it is particularly preferred to introduce the gaseous 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 liquid hydrocarbons.

The thus-treated hydrocarbon charge stock is removed from the non-catalytic, pre-treatment zone, and passed into a suitable high-pressure separator from which a hydrogen sulfide-containing gaseous phase is removed, and recycled at least in part to the pre-treatment zone. It is generally preferred to remove at least a portion of the gaseous phase from the system for the purpose of controlling the pressure within the pre-treatment zone, and to provide a means for controlling the relative concentrations of hydrogen and hydrogen sulfide therein. Similarly, the gaseous mixture emanating from the upper portion of the pre-treatment zone may contain entrained particles of liquid hydrocarbon product, and is, therefore,

preferably subjected to separation, the gaseous portion being combined with the hydrogen and hydrogen sulfide from the above-described high pressure separator. The remaining portion of the treated charge stock is removed from the high-pressure separator, combined with the recovered particles of entrained liquid, the mixture being subjected to suitable separation for the purpose of removing a metal-containing sludge. Suitable separation means involve the utilization 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 quantity originally present. The concentration of organo-metallic contaminants is less than about 10.0 p.p.m. total, and the asphaltene material has been removed to the extent of about 75.0% of the amount included in the fresh hydrocarbon charge stock. Thus, the operating conditions imposed upon the catalytic hydrotreating reaction zone can be significantly less severe than had the pre-treatment procedure been omitted. Prior to entering the reaction zone, to contact the catalytic composite disposed therein, the pre-treated charge is admixed with hydrogen, the latter in 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. The reaction zone is maintained under an imposed pressure of from about 450 to about 5000 p.s.i.g., although pressures within an intermediate range of about 450 to about 3000 p.s.i.g. will suffice. Since the reactions effected within the hydrotreating reaction zone are primarily exothermic, the inlet temperature, or that to which the charge is heated, is less than the temperature within 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 hydrotreating 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.

The total product effluent from the hydrotreating 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 hydrotreating 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 nitrogenous and sulfurous compounds contained within the charge stock. 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, Fischer 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. The carrier material may be formed by any of the numerous techniques which are rather well defined in the prior art relating thereto. Such techniques include the acid-treating of a natural clay, sand or earth, coprecipitation or successive precipitation from hydrosols; these techniques are frequently coupled with one or more activating treatments 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 specified limits by any suitable means, for example, by aging the hydrosol and/or hydrogen under controlled acidic or basic conditions at ambient or elevated temperature, or by gelling the carrier at a critical pH or by treating the carrier with various inorganic or organic reagents. 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.

It is understood that the catalytic composite disposed within the hydrorefining reaction zone may be prepared by any suitable manner which results in a final catalyst possessing the desired catalytic characteristics. Thus, the catalyst may be prepared by initially forming a siliceous refractory inorganic oxide material having the foregoing described characteristics. An alumina-silica composite containing about 63.0% by weight of alumina may be prepared by the well-known coprecipitation of the respective hydrosols. The precipitated material, generally in the form of a hydrogel, is dried at a temperature of about 100° C. and for a time sufficiently long to remove substantially all the physically-held water. The composite is then subjected to a high-temperature calcination technique in an atmosphere of air, for a period of about one hour at a temperature above about 300° C., which technique serves to remove the greater proportion of chemically-bound water. The calcined carrier material may be combined with the catalytically active metallic components through an impregnation technique, whereby solutions of decomposable organo-metallic complexes, or other compounds, of the metals selected from the group of the metals of Groups V-B, VI-B and VIII of the Periodic Table are employed. Suitable organo-metallic compounds include molybdenum blue, molybdenum hexacarbonyl, phosphomolybdic acid, molybdenyl acetylacetonate, nickel acetylacetonate, dinitro diamino palladium, silicomolybdic acid, tungsten hexacarbonyl, phosphotungstic acid, tungsten acetylacetonate, silicotungstic acid, tungsten ethyl xanthate, vanadium carbonyl, vanadyl acetylacetonate, phosphovanadic acid, vanadyl ethyl xanthate, vanadium esters of alcohols, vanadium esters of mercaptans, nickel formate, various other carbonyls, heteropoly acids, beta-diketone complexes, etc. Other compounds suitable for utilization in impregnating the carrier material with the catalytically active metallic components include chloroplatinic acid, chloropalladic acid, nickel nitrate hexahydrate, cobalt nitrate hexahydrate, molybdic acid, ammonium molybdate, etc. In those instances where the particular compound is not water-soluble at the desired impregnation temperature, other solvents may be employed and include alcohols, esters, ketones, aromatic hydrocarbons, etc. The impregnated carrier material is then dried at a temperature less than about 150° C., and preferably within the range of about 100° C. to about 150° C. When the impregnation technique involves the utilization of one or more of the foregoing described organo-metallic complexes, it is preferred that the impregnation and subsequent drying be carried out in a manner such that no decomposition of the organo-metallic complex occurs; in other words, the dry, impregnated carrier material will have distributed therein the decomposable organo-metallic compound. After the catalytic composite, containing the decomposable organo-metallic component, or components, has been placed within the reaction zone, the temperature thereof is increased to a level within the range of about 150° C. to about 310° C. as the hydrocarbon charge stock is introduced into the reaction zone. Thus, the decomposition of the organo-metallic complex selected as a source of the active metallic components,

is effected in situ, and in the presence of the hydrocarbon charge stock being processed.

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, 200 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 granitic particles. A gaseous mixture comprising hydrogen and 10.0% of hydrogen sulfide is introduced into the treatment zone countercurrently to the downwardly flowing hydrocarbon stream, the hydrogen being in a concentration of about 10,000 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 by means of a compressor, and reintroduced into the bottom of the treating zone at a pressure of about 3,000 p.s.i.g. 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-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 asphaltenic sludge is recovered from the centrifugal separator in an amount of about 10.0% by weight, the remaining portion of the treated charge stock being combined with hydrogen in an amount of about 15,000 s.c.f./bbl.

The 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, only 2.0% by weight of pentane-insoluble asphaltenes 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 concentrations of material, the particular charge stock and/or the specific conditions of operation utilized in presenting this example.

Example

The charge stock employed was a vacuum tower bottoms product having a gravity, ° API at 60° F., of 7.1, and containing 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. 204 grams of the vacuum tower bottoms were placed within an 1800 cc., rocker-type autoclave, and initially pressured to 10 atmospheres with hydrogen sulfide. The pressure was raised to 100 atmospheres of hydrogen, and the contents of the vessel slowly heated to a temperature of about 425° C., the final pressure being about 200 atmospheres. The contents of the vessel were allowed to cool and depressured, and separated to provide a normally liquid hydrocarbon product. Upon analysis, the normally liquid hydrocarbons, having a gravity of 30.3° API at 60° F., were found to contain 5.5% by weight of pentane-insoluble asphaltenes, 2727 p.p.m. of nitrogen, 1.7% by weight of sulfur, and less than about 10.0 p.p.m. of both nickel and vanadium, calculated as the elemental metals.

This substantially solid-free treated charge stock is subjected to catalytic hydrorefining in a reaction zone containing a catalytic composite of a spray-dried alumina-silica carrier material comprising about 63.0% by weight of alumina. Prior to the spray drying, a precipitated alumina-silica hydrogel is slurried in methanol and filtered, thus providing a carrier material having an apparent bulk density of about 0.28 gram per cc. An impregnating solution comprising an isopropyl alcohol solution of nickel acetylacetonate and molybdenum acetylacetonate in amounts required to produce a final catalytic composite comprising 2.0% by weight of nickel and 16.0% by weight of molybdenum, calculated as if existing as the elements, is utilized in impregnating the spray-dried carrier material. The thus-impregnated material is dried at a temperature of about 100° C. for a period of about two hours, the drying temperature being controlled such that sudden temperature rises to a level above about 150° C., at which the nickel and molybdenum complexes would decompose, is avoided. The dried catalyst, having a particle size ranging from about 20 to about 150 microns, is disposed as a fixed bed in the hydrorefining reaction zone in an amount of about 220 grams. 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 above about 150° C. When these conditions are reached, the nitrogen stream is admixed with the liquid hydrocarbon charge stock, for the purpose of decomposing the nickel and molybdenum acetylacetonate. The liquid hydrocarbon effluent, during this period of operation in which the nickel and molybdenum acetylacetonate are being decomposed, is recycled to combine with fresh feed, while the gaseous stream from the high-pressure separator is recycled. After a period of about two hours, a hydrogen stream in amount of about 20,000 s.c.f./bbl. replaces the nitrogen, 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 50 p.p.m. of total nitrogen and less than about 0.50% 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 hydrorefining 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 process for hydrorefining a hydrocarbon charge stock which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide; and

(b) reacting at least a portion of the resulting treated product effluent with hydrogen, in a reaction zone containing a hydrorefining catalytic composite.

2. A process for hydrorefining a hydrocarbon charge stock boiling at a temperature above the gasoline boiling range which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide;

(b) separating 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 hydrorefining catalytic composite, and at hydrorefining conditions.

3. A process for hydrorefining a hydrocarbon charge stock boiling at a temperature above the gasoline boiling range which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide at a temperature greater than about 200° C. and under a pressure above about 450 p.s.i.g.;

(b) separating 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 hydrorefining catalytic composite, and at hydrorefining conditions.

4. The process of claim 3 further characterized in that said gaseous mixture comprises hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide.

5. A process for hydrorefining an asphaltene-containing hydrocarbon charge stock boiling at a temperature above the gasoline boiling range which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide, at a temperature of from about 200° C. to about 500° C. and a pressure within the range of from about 450 to about 5000 p.s.i.g.;

(b) separating 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 hydrorefining catalytic composite, at hydrorefining conditions including a temperature above about 200° C. and a pressure above about 450 p.s.i.g.

6. A process for hydrorefining an asphaltene-containing hydrocarbon charge stock boiling at a temperature

above the gasoline boiling range which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide in a treating zone at a temperature of from about 200° C. to about 500° C. and a pressure of from about 450 to about 5000 p.s.i.g.;

(b) separating the treated charge stock to provide a hydrogen sulfide-containing gaseous phase, recycling at least a portion of said gaseous phase to said treating zone;

(c) reacting at least a portion of said product effluent in a reaction zone containing a hydrorefining catalytic composite comprising at least one metallic component selected from the group consisting of the metals of Groups V-B, VI-B and VIII of the Periodic Table, and at hydrorefining conditions including a temperature above about 200° C. and a pressure greater than about 450 p.s.i.g.

7. A process for hydrorefining an asphaltene-containing hydrocarbon charge stock boiling at a temperature above the gasoline boiling range which comprises the steps of:

(a) treating said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide, in a treating zone maintained at a temperature within the range of from about 200° C. to about 500° C. and at a pressure of from about 450 to about 5000 p.s.i.g.

(b) separating the thus treated charge stock to provide a hydrogen sulfide-containing gaseous phase, recycling at least a portion of said gaseous phase to said treating zone;

(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 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 450 to about 5000 p.s.i.g.

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DELBERT E. GANTZ, *Primary Examiner.*

S. P. JONES, *Assistant Examiner.*