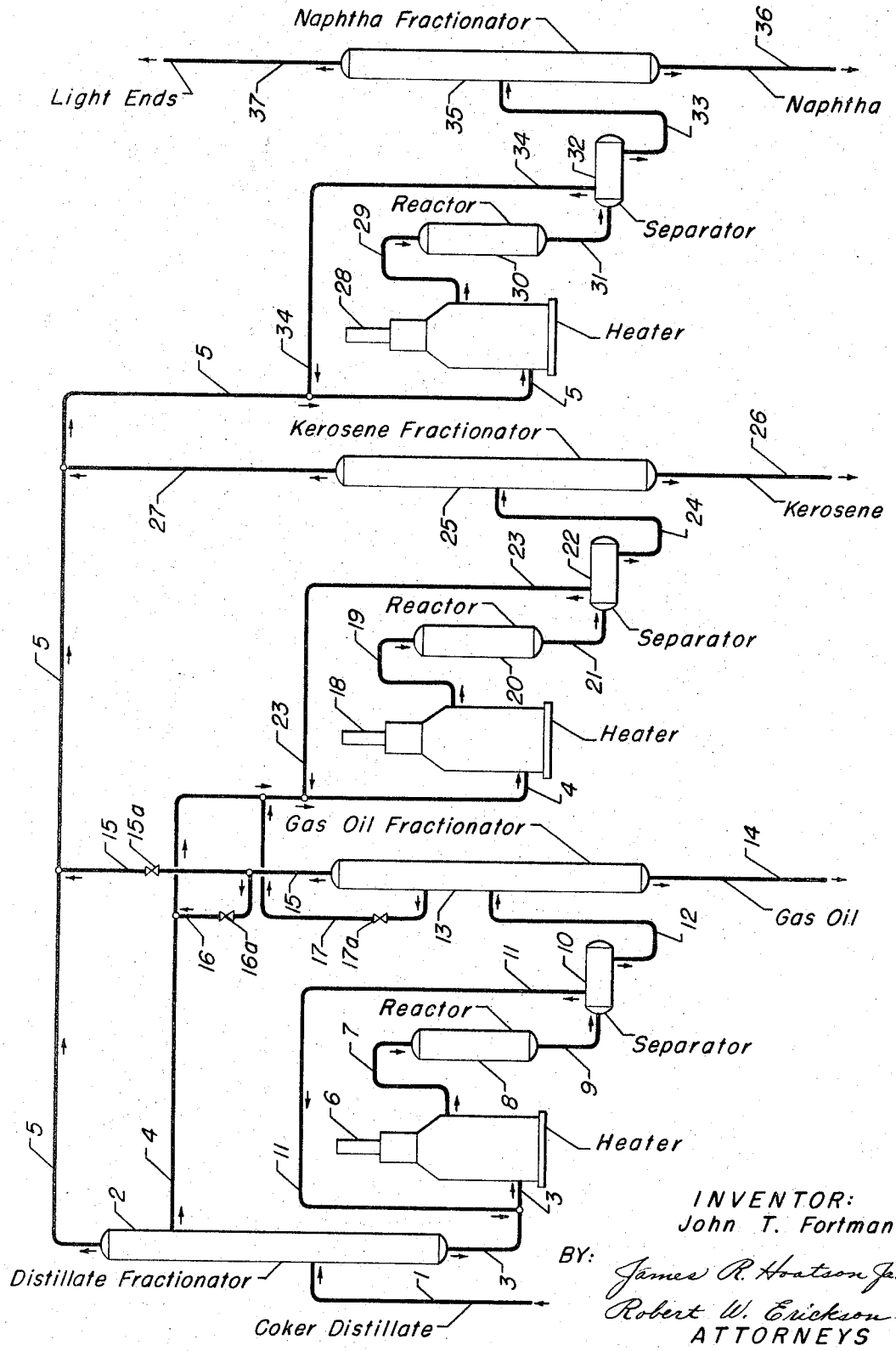
May 2, 1967 J. T. FORTMAN 3,317,419

MULTIPLE-STAGE CASCADE HYDROREFINING OF CONTAMINATED CHARGE STOCKS

Filed June 1, 1964



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United States Patent Office 3,317,419 Patented May 2, 1967

3,317,419

MULTIPLE-STAGE CASCADE HYDROREFINING OF CONTAMINATED CHARGE STOCKS

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Filed June 1, 1964, Ser. No. 371,389
14 Claims. (Cl. 208—97)

In a broad application, the present invention relates to a process for the catalytic hydrorefining of hydrocarbons, mixtures of hydrocarbons, various hydrocarbon fractions and hydrocarbon distillates, for the purpose of removing diverse contaminants therefrom and/or reacting such hydrocarbons to improve the chemical and physical characteristics thereof. More specifically, the process described herein is directed towards the selective hydrorefining of full boiling range hydrocarbon fractions severely contaminated by the inclusion of excessive quantities of nitrogenous and sulfurous compounds, and, in many instances, by the presence of high and low-boiling unsaturated hydrocarbons. The process of the present invention is particularly advantageous in the hydrorefining of contaminated high-boiling hydrocarbon fractions, while simultaneously converting at least a portion of the high-boiling hydrocarbons into lower-boiling hydrocarbon products; through the use of particular operating conditions and techniques, the formation of coke and other heavy carbonaceous material, otherwise resulting from the hydrorefining of such hydrocarbon fractions and/or distillates, is effectively inhibited while achieving the desired end result.

In the present specification and appended claims, the various terms "hydrocarbons," "hydrocarbon fractions," "hydrocarbon distillates," and "hydrocarbon mixtures," are intended to be synonymous, and connote various hydrocarbons and mixtures of hydrocarbons for use as charge to the present process, and which may result from diverse conversion processes, or from the fractionation or initial distillation of various crude oils. Such processes include the catalytic and/or thermal cracking of petroleum, the destructive distillation of wood or coal, coking, shale-oil retorting, etc., and yield various hydrocarbon mixtures which may be advantageously employed as fuels, lubricants, and petro-chemical materials, or as charge stocks in subsequent processes designed for the production of such petroleum products. Such hydrocarbon distillate fractions frequently contain impurities which must necessarily be removed before the distillate fractions are suitable for their intended use, or which, when removed, enhance the value of distillate fractions for further processing. These impurities, or contaminating influences, include sulfurous compounds, nitrogenous compounds, oxygenated compounds, and various metallic contaminants which cause the hydrocarbon distillates to exhibit corrosive tendencies and be unstable, thereby making them less desirable for further utilization as a fuel or lubricant.

Depending upon the intended use of a given hydrocarbon fraction or distillate, various components thereof may be considered as contaminating influences. For example, a naphtha fraction, intended for use as a motor fuel, motor fuel blending component, or as a charge stock to a catalytic reforming unit, is considered to be contaminated by the inclusion therein of mono- and di-olefinic straight and/or branched-chain hydrocarbons. Similarly, the presence of high-boiling unsaturated hydrocarbons in a charge stock intended for conversion into lower-boiling hydrocarbons, is considered a contaminating influence due to the propensity thereof to polymerize and/or copolymerize whereby a more refractory material, much less susceptible to conversion, and more prone

to deactivate catalyst, is formed. In many instances, mono- and polynuclear aromatic hydrocarbons are contaminating influences with respect to a charge stock intended for a cracking process, since the higher the concentration of aromatic hydrocarbons, the more refractory the charge stock, and the higher the required severity of operation; this obviously results in the excessive production of coke and cabonaceous material, as well as excessive quantities of waste gases including light paraffinic hydrocarbons. Similarly, fuel oils containing excessive quantities of aromatic hydrocarbons exhibit poor burning qualities and a low smoke point whereby the products of combustion have a greater tendency to cause severe pollution of the atmosphere.

Probably the most prevalent of the aforementioned impurities is combined sulfur which may exist in the hydrocarbon fraction as a sulfide, mercaptan, or as thiophenic sulfur, etc. Although existing in one or more of these, or other forms, the concentration of the sulfur is generally expressed as if existing as the element thereof. The presence of sulfurous compounds, regardless of the exact boiling range thereof, results in the relatively rapid deactivation of some catalytically active metallic components. The deactivation appears to result from the reaction of the sulfurous compounds with various catalytic components, the extent of such deactivation increasing as the process continues, and the charge stock further contaminates the catalyst through contact therewith. Sulfurous compounds are generally removed by the process of destructive hydrodesulfurization, wherein the sulfur-bearing molecule is treated at an elevated temperature, generally in excess of about 650° F., whereby there occurs a "cracking" of the sulfur-carbon bond which, in the presence of hydrogen, results in the conversion to hydrogen sulfide and a hydrocarbon. The difficulty with which a particular sulfurous compound is thus destructively removed, is generally dependent upon the particular boiling range thereof, the difficulty increasing as the boiling point increases. Similarly, nitrogenous compounds are treated, in the presence of hydrogen, such that there exists a "cracking" of the nitrogen-carbon bond, whereby the nitrogenous compound is converted into ammonia and a hydrocarbon. In general, the conversion, by a suitable hydrorefining process, of the nitrogenous compounds into ammonia and hydrocarbons is more difficult to achieve to an acceptable degree than the conversion of the sulfurous compounds into hydrogen sulfide and hydrocarbons. Furthermore, the presence of high-boiling nitrogenous compounds appears to affect adversely the activity of a particular hydrorefining catalyst with respect to the destructive removal of sulfurous compounds, notwithstanding that the latter reaction is generally more easily achieved.

When existing in some combined form, oxygen offers less of a removal problem than sulfur. Under the operating conditions employed, oxygenated compounds are relatively easily converted to the hydrocarbon counterpart and water, the latter being removed from the hydrocarbon product effluent by any well-known, suitable separation means.

In addition to the above-described contaminants, hydrocarbon distillates resulting from the various conversion processes hereinbefore set forth, contain an appreciable quantity of unsaturated hydrocarbons, including both mono-olefinic and di-olefinic hydrocarbons, and aromatics, including compounds such as styrene, isoprene, dicyclopentadiene, etc. When these highly unsaturated distillates are subjected to hydrorefining for the purpose of removing the sulfurous and nitrogenous compounds, there frequently is encountered the difficulty of effecting the desired degree of reaction due to the formation of coke and other heavy hydrocarbonaceous material. The deposition

of coke and other carbonaceous material appears to be an inherent result of the necessity to effect the destructive removal of sulfurous and nitrogenous compounds at elevated temperatures above about 650° F. Various heaters and miscellaneous appurtenances of the conversion zone experience heavy coking, which appears as a formation of solid, highly carbonaceous material, and results from the thermal reaction of the unstable or coke-forming compounds within the hydrocarbon distillate being charged to the unit. In addition, polymerization and copolymerization of the mono- and di-olefins is effected within the reaction zone, and to the extent that the catalyst disposed therein becomes shielded, by gummy polymerization products, from the hydrocarbon distillate being processed.

As hereinbefore set forth, dependent upon the particular charge stock and/or the intended use of the product to be derived therefrom, mono- and polynuclear aromatics may be considered as contaminating influences. For example, an unrefined gas oil, derived from a topped or reduced crude, and having a boiling range from about 500° F. to about 850° F., contains in excess of about 60.0% by volume of aromatic hydrocarbons, and as such is considered too refractory for use as charge to a catalytic cracking process.

An abundance of hydrocarbon charge stocks, otherwise suitable for subsequent processing, currently exists wherein the same are contaminated through the presence of excessive quantities of all four of the foregoing described contaminating influences. That is, a large volume of hydrocarbon fractions and distillates are available, however, contaminated by the presence of excessive quantities of sulfurous compounds, nitrogenous compounds, mono- and di-olefinic hydrocarbons, and mono- and polynuclear aromatic hydrocarbons. Since the operating conditions required to effect suitable decontamination with respect to a given contaminating influence, are not necessarily those which likewise effect a suitable degree of decontamination with respect to another contaminating influence, it is very difficult to process such charge stocks in a manner which results in an acceptably hydrorefined product effluent. For example, a hydrorefining process which is conducted under conditions of temperature and pressure to produce a substantially saturated product effluent significantly reduced in aromatic content, the liquid yield of such effluent is decreased as a result of the over-production of normally gaseous hydrocarbons, inherently resulting from the undesirable cracking of the lower-boiling components of the hydrocarbon charge stock. Also, as hereinbefore set forth, temperatures which are necessary to produce a substantially sulfur and nitrogen-free product effluent, will generally result in the excessive polymerization and copolymerization of the mono- and di-olefinic hydrocarbons, even prior to entering the reaction zone to contact the catalyst disposed therein.

The object of the present invention is to provide a hydrorefining process particularly adaptable for effecting the decontamination of a hydrocarbon charge stock, boiling at least in part at temperatures above the normal gasoline boiling range, and contaminated by the presence of excessive quantities of nitrogenous and sulfurous compounds, and which may be further contaminated by the inclusion therein of excessive quantities of mono- and di-olefinic hydrocarbons, as well as mono- and polynuclear aromatic hydrocarbons. Another object of the present invention is to permit the processing of a highly contaminated, full boiling range hydrocarbon charge stock to produce a varied and particular product distribution, various desired fractions of such total product meeting relatively rigid specifications with respect to the foregoing described contaminating influences.

The applicability of the present invention, as set forth in the following embodiments thereof, to the production of substantially contaminant-free hydrocarbon products, may be more clearly understood by initially defining several of the terms and phrases employed within the embodiments, the specification, and the appended claims. In those instances where temperatures are given in regard to initial boiling points, boiling ranges and end boiling points it is understood that the temperatures have reference to those which are obtained through the use of standard ASTM Distillation Methods. The term, "hydrocarbons," connotes saturated hydrocarbons, straight-chain and branched-chain hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, naphthenic hydrocarbons, as well as various mixtures thereof including hydrocarbon fractions and/or hydrocarbon distillates. The phrase, "hydrocarbons boiling within the gasoline boiling range," or "gasoline fraction," or "gasoline boiling range hydrocarbons," is intended to connote those normally liquid hydrocarbons boiling at a temperature of from 100° F. to about 400° F. or 450° F.; that is, hydrocarbon fractions having an initial boiling point above about 100° F. and an end boiling point less than about 450° F., which hydrocarbons are generally employed as motor fuels, and which may contain iso- and normal butanes and/or pentanes, as the case may permit. Hydrocarbons "boiling at temperatures above the gasoline boiling range," or, "kerosene fraction," or "middle-distillate hydrocarbons," refers, therefore, to hydrocarbons and hydrocarbon fractions having an initial boiling point of from about 350° F. to about 450° F. and an end boiling point of about 500° F. to about 650° F., which hydrocarbon fractions are generally utilized as fuel oils, jet fuel, kerosene, etc. In some localities, "kerosene" fractions command a greater market value, than a "gasoline" fraction, due to the demand for great volumes of low-boiling fuel for both heat and light. Thus, in these instances, a "kerosene" fraction will have an initial boiling point as low as about 300° F. It is intended that such fractions be included within the broad scope of the present invention. The term, "gas oil," or "hydrocarbons boiling above the middle-distillate boiling range," is intended to describe a hydrocarbon fraction and/or distillate having an initial boiling point of from as low as 400° F. to about 650° F. (generally, these fractions have an initial boiling point of at least about 500° F.), and an end boiling point within the range of about 800° F. to about 950° F., and which hydrocarbons may be employed at least in part as diesel oil, distillate fuel, charge stock to catalytic cracking processes and/or hydrocracking processes, etc.

Similarly, in regard to the catalytic composite employed within the various reaction zones of the process of the present invention, the term, "metallic component," or "catalytically active metallic component," is intended to encompass those catalytic components which are employed for their hydrorefining and/or hydrocracking activity, as well as hydrogenation activity with respect to unsaturated hydrocarbons, as the case may be. In this manner, the catalytically active metallic components are distinguished from those components which are employed primarily as an integral part of the carrier material. As hereinafter set forth in greater detail, the process of the present invention utilizes a catalytic composite consisting of at least four components in particular concentrations.

In a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbon charge stock boiling above the gasoline boiling range and containing a contaminant selected from the group consisting of nitrogenous compounds and sulfurous compounds, which process comprises the steps of: (a) reacting said charge stock and hydrogen at hydrorefining conditions in a first reaction zone containing a hydrorefining catalytic composite; (b) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of from about 500° F. to about 650° F., and a hydrorefined first heavy fraction; (c) combining at least a portion of said first light fraction with a hydrocarbon mixture having an initial boiling point of from about 350° F. to about 450° F. and containing at least one of the aforesaid contaminants, and reacting the resulting mixture with hydrogen at hydrore-

fining conditions in a second reaction zone containing a hydrorefining catalytic composite; (d) separating the normally liquid product effluent from said second reaction zone into a second light fraction, having an end boiling point within the range of from about 350° F. to about 450° F., and a hydrorefined second heavy fraction; (e) combining at least a portion of said second light fraction with a hydrocarbon mixture, having an end boiling point of from about 350° F. to about 450° F. and containing at least one of the aforesaid contaminants, reacting the resulting mixture with hydrogen at hydrorefining conditions in a third reaction zone containing a hydrorefining catalytic composite; and, (f) separating the product effluent from said third reaction zone into a normally gaseous phase and a hydrorefined third heavy fraction.

Another broad embodiment of the present invention encompasses a process for hydrorefining a hydrocarbon charge stock boiling above the gasoline boiling range and containing a contaminant selected from the group consisting of nitrogenous compounds and sulfurous compounds, which process comprises the steps of: (a) separating said charge stock into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of as low as about 400° F. to about 650° F., and a heavy bottoms fraction; (b) reacting said heavy bottoms fraction with hydrogen at hydrorefining conditions in a first reaction zone containing a hydrorefining catalytic composite; (c) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of as low as about 400° F. to about 650° F. and a hydrorefined substantially sulfur-free heavy fraction; (d) combining at least a portion of said first light fraction with the aforesaid kerosene fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions in a second reaction zone containing a hydrorefining catalytic composite; (e) separating the normally liquid product effluent from said second reaction zone into a second light fraction having an end boiling point of from about 350° F. to about 450° F. and a hydrorefined substantially sulfur-free kerosene product; (f) combining at least a portion of said second light fraction with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions in a third reaction zone containing a hydrorefining catalytic composite; and, (g) separating the product effluent from said third reaction zone into a normally gaseous phase and a substantially sulfur and nitrogen-free hydrorefined gasoline product.

A more limited embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock boiling above the gasoline boiling range and containing sulfurous and nitrogenous compounds, which process comprises the steps of: (a) separating said charge stock into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of from about 500° F. to about 650° F., and a heavy bottoms fraction; (b) reacting said heavy bottoms fraction with hydrogen at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons, in a first reaction zone containing a hydrorefining catalytic composite; (c) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of from about 350° F. to about 450° F. and a second light fraction having an end boiling point of from about 500° F. to about 650° F. and a hydrorefined, substantially sulfur-free heavy fraction; (d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons, in a second reaction zone containing a hydrorefining catalytic composite; (e) separating the normally liquid product effluent from said second reaction zone into a third light fraction having an end boiling point of from about 350° F. to about 450° F. and a hydrorefined, substantially sulfur-free kerosene product; (f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbon in a third reaction zone containing a hydrorefined catalytic composite; and, (g) separating the product effluent from said third reaction zone into a normally gaseous phase and a substantially sulfur and nitrogen-free hydrorefined gasoline product.

A more limited embodiment of the present invention affords a process for hydrorefining a full boiling range coker distillate containing sulfurous and nitrogenous compounds, which process comprises the steps of: (a) separating said distillate into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of from about 500° F. to about 650° F., and a heavy bottoms fraction having an initial boiling point of from about 500° F. to about 650° F.; (b) reacting said heavy bottoms fraction with hydrogen present in an amount of about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions including a maximum catalyst temperature within the range of from about 600° F. to about 850° F. and selected to convert sulfurous and nitrogenous compounds to hydrogen sulfide, ammonia and hydrocarbons, in a first reaction zone containing a hydrorefining catalytic composite of alumina, from about 12.0% to about 40.0% by weight of silica, molybdenum and nickel; (c) removing hydrogen sulfide and ammonia from the product effluent from said first reaction zone, separating the remaining normally liquid product into a first light fraction having an end boiling point of from about 350° F. to about 450° F., a second light fraction having an end boiling point of from 500° F. to about 650° F. and a hydrorefined, substantially sulfur-free gas oil fraction; (d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction, reacting the resulting mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions including a maximum catalyst temperature lower than that in said first reaction zone, and selected to convert sulfurous and nitrogenous compounds to hydrogen sulfide, ammonia and hydrocarbons, in a second reaction zone containing a hydrorefining catalytic composite of alumina, from about 10.0% to about 25.0% by weight of silica, molybdenum and nickel; (e) removing hydrogen sulfide and ammonia from the product effluent from said second reaction zone, separating the remaining normally liquid product into a third light fraction having an end boiling point of from about 350° F. to about 450° F. and a hydrorefined, substantially sulfur-free kerosene fraction; (f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions including a maximum catalyst temperature of from about 600° F. to about 850° F. and selected to convert sulfurous and nitrogenous compounds to hydrogen sulfide, ammonia and hydrocarbons, in a third reaction zone containing a hydrorefining catalytic composite of alumina, silica, molybdenum and nickel; and, (g) separating the product effluent from said third reaction zone into a normally gaseous phase containing hydrogen sulfide and ammonia, and a substantially sulfur and nitrogen-free hydrorefined gasoline fraction.

From the foregoing embodiments, it will be noted that the cascade system, encompassed by the present invention, is a multiple-stage process for effecting the hydrorefining

of hydrocarbon charge stocks containing hydrocarbons boiling at temperatures above the normal gasoline boiling range. The particularly preferred charge stocks, for utilization in the cascade system, are those which are referred to as "full boiling range" charge stocks. A full boiling range charge stock is considered to be one which contains a significant percentage of hydrocarbons having boiling points above a temperature of 650° F., a quantity of hydrocarbons boiling within the kerosene, or middle-distillate boiling range, and some hydrocarbons boiling within the normal gasoline boiling range. For example, a full boiling range coker distillate will contain a heavy bottoms fraction having an initial boiling point of about 650° F. in an amount of 26.0 volume percent, a middle-distillate fraction having an initial boiling point of about 450° F. in an amount of about 47.0% by volume and a gasoline fraction having an initial boiling point of from about 100° F. to about 125° F. in an amount of about 37.0% by volume. Thus, full boiling range charge stocks, to which the process of the present invention is particularly adaptable, include, but not by way of strict limitation, various gas oils, a wide variety of coker distillates, deasphalted crude oils, fuel oil stocks, catalytically and thermally-cracked stocks, etc. In accordance with the cascade system, each specific fraction of the charge stock is subjected to selective conditions in a specific reaction zone, after which the desired product is removed, the remainder being combined with another specific fraction for reaction at other selective conditions, and so on until the entire charge stock has been incrementally processed at the most advantageous conditions conducive to the attainment of the desired end result. As hereinafter indicated by specific example, this step-wise processing results in a volumetric yield in excess of 100.0%, and in most instances from about 2.0% to about 15.0% greater than the volume of charge stock processed in a given time interval. The unusual economical advantages of increased volume, while simultaneously producing contaminant-free products, will be readily recognized by those possessing skill within the art of petroleum refining and processing techniques.

Through the utilization of the cascade system of the present invention, a desirable degree of selective hydrocracking is effected in the various stages with the result that the higher molecular weight components of the full boiling range charge stock are converted into lower-boiling, normally liquid hydrocarbon products, without the usual accompanying conversion to light gaseous hydrocarbons. Since the operating conditions within each of the reaction zones are specifically selected in accordance with the physical and chemical characteristics of the charge stock passing therethrough, the degree of hydrocracking effected in a given reaction zone is such that excessive quantities of light, normally gaseous hydrocarbons are not produced at the expense of more valuable liquid hydrocarbon products.

Hydrocracking, or destructive hydrogenation, as distinguished from the addition of hydrogen to unsaturated bonds between carbon atoms (hydrogenation), and the destructive removal of nitrogen and sulfur by splitting the sulfur-carbon and nitrogen-carbon bonds, effects definite changes in the molecular structure of hydrocarbons. Hydrocracking is designated as a cracking under hydrogenation conditions such that lower-boiling products of a more saturated nature result than when hydrogen is not present. Regardless of the degree of hydrocracking intended, and, in the process of the present invention, hydrorefining reactions are of primary concern, in order to assure effective catalytic action over an extended period of time, and from the standpoint of producing the increased yield of liquid product having improved physical and/or chemical characteristics, controlled or selective cracking is desirable. Controlled or selective hydrocracking results in an increased yield of middle-distillate boiling range hydrocarbons which are substantially free from high molecular weight unsaturated hydrocarbons. The necessity for selectivity exists in order to avoid the decomposition of normally liquid hydrocarbons substantially or completely into normally gaseous hydrocarbons, the latter being inclusive of methane, ethane and propane. Hydrocracking reactions which are permitted to run rampant can affect seriously the economic considerations of a given process, particularly in view of the fact that uncontrolled hydrocracking results in a more rapid formation of increased quantities of coke and other heavy carbonaceous material which becomes deposited upon the catalytic composite and decreases, or even destroys, the activity thereof to catalyze the desired reactions in the desired manner.

Selective, or controlled, hydrocracking must also be considered where the primary purpose is to effect an acceptable degree of hydrorefining of the charge stock, and particularly where the greater proportion of such charge stock boils above the normal gasoline boiling range. For example, a full boiling range coker distillate generally contains a significant quantity of aromatic compounds of low molecular weight and boiling within the normal gasoline boiling range. These aromatic compounds are highly desirable as a motor fuel or motor fuel blending component, and it is, therefore, not advantageous to subject these low molecular weight aromatic compounds to hydrocracking, or ring-opening reactions. The cascade system of the present invention permits the higher boiling components of the charge stock to be subjected to the degree of severity required for suitable hydrorefining, without subjecting the low molecular weight aromatic hydrocarbons to undesirable hydrocracking and/or ring-opening reactions. The cascade system for effecting the hydrorefining of a full boiling range hydrocarbon charge stock, further affords flexibility with respect to product distribution, and can be tailored to any desired specifications which may be imposed as a result of considering such items as marketing demands, fluctuations in marketing value of the particular products, other processes which are involved in an integrated refinery operation, etc.

The multiple-stage, cascade hydrorefining process of the present invention may be more clearly understood through reference to the accompanying drawing which illustrates an embodiment thereof. It is not intended, however, to limit unduly the present process to a particular embodiment as indicated in this drawing. Advantages other than those hereinbefore and hereinafter set forth, will become apparent to those cognizant of the techniques involved in petroleum refining operations, upon reference to the drawing and the explanation following. Also, it is recognized that many modifications may be made to the process flow, equipment, operating conditions, etc. depending upon the particular desired end result while processing a given hydrocarbon charge stock. It is not intended that such insignificant modifications remove the present invention beyond the scope and spirit of the appended claims. In the drawing, various flow valves, control valves, coolers, condensers, overhead reflux condensers, reboilers, pumps, compressors, heaters, knockout pots, etc., have been eliminated, or greatly reduced, as not being essential to the complete understanding of the present invention. The utilization of these, and other miscellaneous appurtenances will immediately be recognized by one possessing skill in the art of petroleum processing. It is believed that the illustrative drawing clearly and concisely sets forth the manner in which the present invention is effected. The explanation of the drawing as presented is set forth in more or less general terms in order to present clearly the flexible nature inherent in the cascade system for effecting the hydrorefining process; it is intended that the explanation be supplemented by the specific example hereinafter set forth.

With reference to the drawing, a full boiling range hydrocarbon charge stock, for example a coker distillate,

enters the process through line 1, being subjected to fractionation in distillate fractionator 2. Fractionator 2 is employed for the purpose of separating the coker distillate charge stock into at least three primary fractions, indicated as leaving fractionator 2 via lines 3, 4 and 5. In those instances where the fresh charge stock entering line 1 possesses a boiling range indicating an initial boiling point of about 100° F. to about 125° F. and an end boiling point of from about 800° F. to about 850° F., a gasoline fraction having an end boiling point within the range of about 350° F. to about 450° F. will be removed via line 5; a kerosene fraction having an end boiling point of from about 500° F. to about 650° F. will be removed at some intermediate point in fractionator 2 via line 4; a heavy bottoms fraction, containing that portion of the hydrocarbon charge stock boiling at temperatures above the end boiling point of the kerosene fraction, will be removed via line 3. In many applications of the present invention, the charge stock will have an end boiling point above about 850° F., and/or an initial boiling point of from 130° F. to about 300° F. In such situations, it is generally desirable to remove a naphtha fraction having an end boiling point of about 400° F., a kerosene fraction having an end boiling point of about 650° F. through line 4, a gas oil fraction having an end boiling point of about 850° F. via line 3, which is then located at some point intermediate the charge inlet and bottom withdrawal of fractionator 2 and a heavy bottoms fraction containing that portion of the charge stock boiling above 850° F. In any event, the gas oil fraction, or heavy bottoms in line 3 is passed into heater 6 after being admixed with a hydrogen-rich recycle gas stream in line 11. The mixture of hydrogen in line 11, and gas oil fraction in line 3, is such that the hydrogen concentration is greater than about 1000 s.c.f./bbl., and preferably within the range of about 1000 to about 6000 s.c.f./bbl. of liquid charge. The mixture of hydrogen and hydrocarbons entering heater 6 is raised to the operating temperature required to maintain the maximum temperature of the catalyst disposed in reactor 8 within the range of about 600° F. to about 850° F., and passes through line 7 into reactor 8.

Reactor 8 contains a catalytic composite specifically tailored to effect the hydrorefining of heavier hydrocarbons, while selectively hydrocracking at least a portion into lower-boiling normally liquid hydrocarbon products. Therefore, as hereinafter set forth in greater detail, the catalytic composite in reaction zone 8 comprises a siliceous carrier material containing at least one metallic component selected from Groups VI–B and VIII of the Periodic Table. Reactor 8 is maintained under an imposed pressure of from about 500 to about 5000 p.s.i.g., and preferably at an intermediate level of from about 1000 to about 3000 p.s.i.g.; the liquid hourly space velocity (defined as volumes of liquid hydrocarbon charge per hour per volume of catalyst disposed within the reaction zone) will be within the range of from about 0.25 to about 10.0. The total product effluent is removed from reactor 8 via line 9, and passes into separator 10. Separator 10 is utilized to provide a normally liquid hydrocarbon product and a gaseous phase; the separator is generally maintained under the same pressure as that existing in reactor 8, allowing, obviously, for the inherent pressure drop in the system, and is maintained at a temperature of about 100° F. or less. A hydrogen-rich gaseous phase is withdrawn from separator 10 via line 11 by any suitable compressive means (not illustrated in the drawing), being admixed with the liquid hydrocarbon in line 3 entering heater 6.

Gaseous components other than hydrogen are removed from the normally liquid hydrocarbons in separator 10, including hydrogen sulfide, ammonia, sulfur dioxide, various oxides of nitrogen, and some light paraffinic hydrocarbons, and should be removed from the gas phase prior to the latter being recycled via line 11. Various modifications may be made to the separating means illustrated by separator 10, whereby the overall flow pattern is changed, but the function to be served, as well as the end result, remains the same. As hereinabove set forth, the primary function of separator 10 is to provide a hydrogen-rich recycle gas stream, in line 11, to combine with the hydrocarbons in line 3, and a normally liquid product effluent leaving separator 10 via line 12. Thus, for example, the total gaseous phase illustrated as leaving line 11, may be passed through a suitable absorbent material, whereby the light paraffinic hydrocarbons are recovered substantially free from hydrogen sulfide and ammonia, and the various oxides of nitrogen and sulfur. Similarly, water may be injected into line 9, the mixture entering a suitable liquid-liquid separating zone whereby the ammonia is absorbed in, and removed with the water phase, the light paraffinic hydrocarbons and other gaseous components being removed as indicated by line 11, and the normally liquid hydrocarbons removed via line 12. Various other modifications, in regard to the separating means illustrated by separator 10, as well as those separating means hereinafter described, and illustrated by separators 22 and 32, will be immediately recognized by those possessing skill within the art of petroleum processing.

In any event, the normally liquid portion of the total product effluent from reactor 8 is removed from separator 10 via line 12, and is introduced into gas oil fractionator 13. The primary purpose of fractionator 13 is to provide a hydrorefined, substantially sulfur-free bottoms product, the boiling range of which will depend to a large extent upon the purpose for which this particular product is intended. For example, in one particular embodiment, the bottoms product will have an initial boiling point of about 500° F., and an end boiling point of about 825° F., being a gas oil which is intended for utilization as a charge stock to a catalytic cracking unit. In many applications of the present invention, the bottoms product from fractionator 13 will be intended for utilization as a distillate fuel, in which case the initial boiling point will be as high as about 650° F. As hereinafter indicated by specific example, regardless of its intended use, the gas oil product is substantially sulfur-free, and does not contain that quantity of nitrogenous compounds and aromatic compounds which would detrimentally affect such intended use.

In a particularly preferred embodiment of the present invention, a kerosene fraction, having an initial boiling point within the range of about 350° F. to about 450° F. and an end boiling point of from about 500° F. to about 650° F. is removed from fractionator 13 via line 17 containing valve 17*a*. This fraction is admixed with the original kerosene fraction derived from the hydrocarbon charge stock, leaving distillate fractionator 2 via line 4, the mixture continuing through line 4 into heater 18. The remainder of the liquid product effluent from reactor 8, being a naphtha or gasoline fraction having an end boiling point of from about 350° F. to about 450° F., is removed from fractionator 13 via line 15 containing valve 15*a*. This gasoline fraction is admixed in line 5 with the original gasoline fraction derived from the hydrocarbon charge stock, the mixture being passed into heater 28. In this preferred embodiment, valve 16*a* in line 16 remains closed; however, in another embodiment, depending upon the quantity of gasoline boiling range hydrocarbons originally present in the coker distillate plus those produced in reactor 8, valve 16*a* will be open, valve 15*a* and 17*a* being closed. In this embodiment, that portion of the total product effluent which boils below the desired initial boiling point of the gas oil leaving via line 14, will pass via lines 15 and 16 through valve 16*a* into line 4.

Prior to entering heater 18, the hydrocarbon mixture in line 4 is combined with a hydrogen-rich recycle gas stream in line 23, the concentration of hydrogen being greater than about 1000 s.c.f./bbl., and preferably within the range of from about 1000 to about 6000 s.c.f/bbl. of total liquid in line 4. The mixture is raised to the

operating temperature required to maintain the maximum temperature of the catalyst disposed in reactor **20**, within the range of from 600° F. to about 850° F., and preferably at a temperature less than the operating temperature within the first reaction zone (reactor **8**), leaving heater **18** via line **19**, and passing into reactor **20**. Reactor **20** is maintained at a pressure within the range of from about 500 to about 5000 p.s.i.g., and preferably from about 1000 to about 3000 p.s.i.g. The liquid hourly space velocity, hereinbefore defined, through reactor **20** will be within the range of from about 0.25 to about 10.0, but preferably at a level greater than that experienced in reactor **8**. Although the hydrorefining catalytic composite, disposed in reactor **20**, may be identical to that disposed in reactor **8**, being an alumina-silica carrier material with which is composited at least one metallic component from the metals of Group VI–B anl VIII of the Periodic Table, in many instances the mode of operation is such that the silica content of the catalyst in reactor **20** is less than that of the catalyst disposed in reactor **8**, and lies within the range of from about 10.0% to about 25.0% by weight.

The total product effluent from reactor **20** passes through line **21** into separator **22**, from which a hydrogen-rich recycle gas stream is removed via line **23** to be admixed with the kerosene fraction charge in line **4**. As hereinbefore described with reference to separator **10**, separator **22** is employed to illustrate a separating means whereby the normally liquid hydrocarbon product from reactor **20** is recovered in line **24**, substantially completely free from light paraffinic hydrocarbons and other gaseous material including hydrogen sulfide and ammonia. Similarly, the separating means illustrated by separator **22** may take any form which is suitable for achieving the desired results; that is, treating the normally gaseous phase in line **23** to provide a hydrogen-rich recycle gas stream, and a normally liquid hydrocarbon stream substantially free from light paraffinic hydrocarbons including methane, ethane and propane.

The normally liquid portion of the product effluent from reactor **20** is removed from separator **22** via line **24** and passes into kerosene fractionator **25**. Depending upon the desired end result, the kerosene fraction which is removed from fractionator **25** via line **26** will have an initial boiling point within the range of from 300° F. to about 450° F. and an end boiling point of from 400° F. to about 650° F. The remaining portion of the charge to fractionator **25**, that is, the naphtha or gasoline fraction, is removed via line **27** to combine with the original gasoline fraction in line **5**, the latter also including the gasoline fraction obtained as an overhead product from gas oil fractionator **13**, entering line **5** through line **15** containing valve **15***a*.

The mixture of gasoline boiling range hydrocarbons, having an end boiling point of from about 350° F. to about 450° F., is admixed with a hydrogen-rich recycle gas stream in line **34**, the mixture continuing through line **5** into heater **28**. The temperature of the mixture is increased to the level necessary to maintain a maximum catalyst temperature within the range of from about 600° F. to about 850° F., and passes through line **29** into reactor **30**. Reactor **30** is maintained at a lower pressure than reactors **20** and **8**, within the range of about 500 to about 3000 p.s.i.g., and preferably within the range of from about 700 to about 1500 p.s.i.g. The liquid hourly space velocity, hereinbefore defined, will be within the range of from about 0.25 to about 10.0, and preferably at a level greater than that through reactor **20**. The hydrorefining catalytic composite disposed within reactors **8** and **20**, that is, an alumina-silica carrier material composited with at least one metallic component from the group of metals of Groups VI–B and VIII of the Periodic Table. The total product effluent from reactor **30** passes through line **31** into separator **32**, from which the hydrogen-rich gaseous phase is withdrawn via line **34** to combine with the gasoline fraction in line **5**. The hydrogen-rich recycle gas stream is such that the concentration of hydrogen is greater than 1000 s.c.f./bbl., and preferably within the range of from about 1000 to about 6000 s.c.f./bbl. of liquid charge. The normally liquid portion of the product effluent from reactor **30** is removed from separator **32** via line **33**, and is introduced into naphtha fractionator **35**. Naphtha fractionator **35** may function as a depropanizer, debutanizer, or dependanizer, depending upon the desired boiling range of the hydrorefined product effluent leaving fractionator **35** via line **36**. In those instances where naphtha fractionator **35** functions as a debutanizer, the bottoms gasoline fraction in line **36** will contain pentanes and heavier hydrocarbons up to an end boiling point of about 350° F. to about 450° F. In other instances, depending upon the use for which the naphtha is intended, the overall refinery operation, and other such factors, fractionator **35** may function as a depropanizer such that the iso- and normal butanes are contained in the product naphtha fraction. As hereinafter indicated in a specific example, the product naphtha fraction possesses the physical and chemical characteristics required of a charge stock to a catalytic reforming unit for the purpose of producing large quantities of high quality motor fuel and motor fuel blending components.

From the foregoing description of the embodiments illustrated in the accompanying drawing, it is readily ascertained that the cascade system of the present invention is, in effect, a multiple-stage process for producing hydrocarbon fractions boiling within the gasoline boiling range, the kerosene boiling range, the middle-distillate boiling range and the gas oil boiling range, all of which hydrocarbon fractions are substantially completely free from various contaminating influences, and are, therefore, suitable as charge stocks for direct, subsequent processing, or for immediate use as a particular petroleum product. It is readily ascertained from the foregoing description, that the cascade system of hydrorefining affords the necessary flexibility to permit both moderate and extreme fluctuations in charge stock characteristics, as well as in desired product quality and quantity. Various modifications may be made to the illustrated embodiment to adjust for changes in charge stock and desired product quality; it is not intended that such modifications remove the process from the scope and spirit of the appended claims. For example, as hereinabove stated in regard to separators **10**, **22** and **32**, changes may be made whereby a somewhat different flow pattern and apparatus set up results. It is evident, however, that such a flow pattern will merely accomplish the same object resulting from the flow pattern illustrated within the drawing. An essential feature of the cascade process of the present invention involves the multiple-stage reaction zone system, whereby each stage individually performs a particular function in a particular manner, while processing a particularly given fraction of the full boiling range charge stock, the combinative effect resulting in various hydrocarbon product fractions substantially completely free from the contaminating influence of sulfurous and nitrogenous compounds.

Although the operating conditions of temperature, pressure, hydrogen concentration and liquid hourly space velocity, may be virtually the same in all of the three reaction zones, that is, a maximum catalyst temperature of from about 600° F. to about 850° F., a pressure within the range of about 500 to about 5000 p.s.i.g., a preferred hydrogen concentration of from 1000 to about 6000 s.c.f./bbl. and a liquid hourly space velocity of from about 0.25 to about 10.0, it is significantly more advantageous, in view of the cascade system, to vary the operating conditions in accordance with the characteristics of the charge to a given reaction zone. With reference once again to the accompanying drawing, the charge to reactor **8** may, for example, consist predominantly of gas oil fraction hydrocarbons having an initial boiling point of about 515° F. and an end boiling point of about 825° F. As

contaminating influences, this particular gas oil fraction may contain nitrogenous compounds in an amount as high as about 1500 p.p.m. (as nitrogen), sulfurous compounds in an amount of about 3.3% by weight (as sulfur), and about 60.0% by volume of polynuclear aromatic hydrocarbons. In this instance, the latter is included as a contaminating influence since a "clean" gas oil fraction is generally considered as containing not more than about 30.0% by volume of aromatic compounds when intended either as a distillate fuel or diesel oil, or as the charge stock to a catalytic cracking process. With respect to the concentration of nitrogenous and sulfurous compounds, in a gas oil product, these are necessarily low to avoid the formation of noxious gaseous material upon combustion, and thereby avoid excessive pollution of the atmosphere. Furthermore, nitrogenous compounds interfere with the desired reactions in both catalytic and hydrocracking processes. Therefore, the preferred operating conditions within the gas oil reaction zone (reactor **8**) are a pressure within the range of about 1000 to about 3000 p.s.i.g., a temperature of from about 700° F. to about 800° F., a liquid hourly space velocity of from 0.25 to about 3.0. At these conditions, it is possible to produce a hydrorefined gas oil fraction containing less than about 50 p.p.m. of total nitrogen, approximately 0.01% by weight of sulfur, and about 30.0% by volume of aromatic hydrocarbons.

Similarly, with respect to the kerosene reaction zone, reactor **20**, and processing a charge having an initial boiling point of about 300° F. to about 450° F., the operating severity is of a lesser degree than in the previous reaction zone. Since kerosene product fractions, or light distillates, are normally employed as distillate fuels for heating and lighting, they must also be relatively low in nitrogen and sulfur concentration, but still lower in aromatic concentration, the latter for the purposes of improved burning characteristics in that the greater the concentration of aromatic hydrocarbons, the lower the temperature at which the fuel will result in voluminous quantities of thick, oily smoke. Thus, the operating conditions must necessarily be tailored to produce a kerosene product low in nitrogen, low in sulfur and particularly low in aromatic concentration (15.0% by volume or less). By the same token, operating conditions of a severity which would promote both thermal cracking and hydrocracking of the lower-boiling hydrocarbons must necessarily be avoided in order that the liquid yield of acceptable product is economical. Therefore, although the operating pressure in reactor **20** may be identical to that in reactor **8**, the operating temperature is generally lower and will be within the range of about 600° F. to about 750° F., the liquid hourly space velocity being higher, from about 0.5 to about 5.0.

With respect to the naphtha, or gasoline fraction processed in reactor **30**, the gasoline product effluent must not only be substantially completely free from nitrogenous and sulfurous compounds, but should be substantially free from olefinic and high-olefinic hydrocarbons. Thus, the primary function of gasoline reactor **30** is hydrogenative hydrorefining accompanied by minimum hydrocracking. Therefore, the operating pressure is at a lower level than in the first two reaction zones, being within the range of about 500 to about 1500 p.s.i.g., the operating temperature somewhat higher, and within the range of about 700° F. to about 800° F., whereas the liquid hourly space velocity is higher than in either the first or second reaction zones, within the range of about 1.5 to about 10.0. Under these conditions, a naphtha charge stock having an initial boiling point of about 130° F. and an end boiling point of about 375° F., containing about 105 p.p.m. of nitrogen, 1.6% by weight of sulfur and about 30.0% by volume of olefins, can be processed to yield a hydrorefined gasoline product containing less than about 0.1 p.p.m. of nitrogen, 0.0005% by weight of sulfur and only a trace quantity of olefinic hydrocarbons. Such a charge stock, as will be recognized, is ideally suited for further processing in a catalytic reforming unit. Although at least a portion of the gasoline boiling range aromatics may be hydrogenated to the corresponding naphthenic hydrocarbons in this third reaction zone, such a result is not necessarily detrimental. As hereinbefore set forth, the gasoline product from fractionator **35** is intended as charge to a catalytic reforming process, one of the main reactions of which is the dehydrogenation of naphthenes to the corresponding aromatic hydrocarbons. Thus, a naphtha product fraction containing about 30.0% naphthenes, 8.0% aromatics and 62.0% paraffins is considered a valuable product notwithstanding that up to about 50.0% of the aromatics originally present in the naphtha charge have been hydrogenated to the corresponding naphthenes.

Just as the cascade system of effecting the hydrorefining process permits varying the operating conditions to conform to the characteristics of the charge stock to each zone, the catalytic composite disposed within each reaction zone may be of a composition conducive to producing greater yields of the desired product effluent. On the other hand, the hydrorefining catalytic composite disposed within each of the reaction zones, represented by reactors **8**, **20** and **30**, may possess the same physical characteristics and be of the same chemical composition. Thus, the catalytic composite, for utilization in the cascade system of the process of the present invention will be a composite of a siliceous refractory inorganic oxide carrier material and at least one metallic component selected from the metals and compounds of Groups VI–B and VIII of the Periodic Table. In this regard, a particular catalytic composite, suitable for utilization in all the reaction zones, comprises a carrier material of about 88.0% by weight of alumina and 12.0% by weight of silica. With this siliceous carrier material, there is composited about 11.3% by weight of molybdenum, 4.2% by weight of nickel and a minor amount of cobalt, about 0.05% by weight. Although existing as sulfides, or lower oxides thereof, the catalytically active metallic components are computed as if existing in the form of the elemental metals.

As hereinbefore set forth in the various embodiments of the present invention, the hydrorefining catalytic composite, possessing a finite degree of hydrocracking activity, comprises at least one metallic component selected from the metals and compounds of Groups VI–B and VIII of the Periodic Table. With respect to the use of the term, "Groups VI–B and VIII," reference is made to the Periodic Chart of the Elements, Fischer Scientific Company, 1953. Suitable hydrorefining catalytic composites include, therefore, at least one or more metals or compounds from the group of chromium, molybdenum, tungsten, iron, cobalt, nickel, palladium, platinum, ruthenium, rhodium, osmium, iridium, and mixtures thereof, etc. The total quantity of metallic components, computed as the elemental metals, will be within the range of from about 0.01% to about 30.0% by weight, on the basis of the total composite. The Group VI–B metal, such as chromium, molydbenum, or tungsten, is usually present within the range of from about 10.0% to about 30.0% by weight. The Group VIII metals, which may be conveniently divided into sub-groups, are present in an amount of from about 0.01% to about 10.0% by weight of the total catalyst. When an iron-group metal, such as iron, cobalt, or nickel, is employed, it is present in an amount of from about 0.01% to about 10.0% by weight, while if a platinum-group metal, such as platinum, palladium, iridium osmium, etc., is employed, it is present within an amount within the range of from about 0.01% to 5.0% by weight of the total catalyst. Therefore, suitable catalysts for utilization in the process of the present invention, include, but are not considered to be limited to, the following: 11.3% by weight of molybdenum, 4.2% by weight of nickel and 0.05% by weight of cobalt; 16.0% by weight of molybdenum and 1.8% by weight of nickel; 6.0% by weight of nickel and 0.2% by weight of palladium; 0.4%

by weight of palladium; 0.4% by weight of ruthenium and 11.3% by weight of molybdenum; 0.4% by weight of platinum, etc. As hereinafter indicated, it is preferred to utilize as siliceous carrier material with which is combined from about 10.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 6.0% by weight of nickel. It has been found that this particularly preferred catalytic composite yields the most advantageous results with respect to the greater majority of charge stock types and varied product distributions.

The carrier material for utilization in a hydrorefining catalytic composite of the present process comprises silica and one or more other refractory inorganic oxides including alumina, zirconia, thoria, boria, hafnia, magnesia, strontia, etc., and may be naturally-occurring or synthetically-prepared. When synthetically-prepared, the carrier material may be made in any suitable manner including separate, successive or coprecipitation methods. For example, silica may be prepared by commingling water glass in a mineral acid under such conditions as will precipitate a silica hydrogel. The silica hydrogel is subsequently washed with water containing a small amount of a suitable electrolyte for the purpose of removing residual sodium ions. The oxides of other compounds, when desired, may be prepared by reacting a basic reagent such as ammonium hydroxide, ammonium carbonate, etc., with an acid-salt solution of the metal, as for example, the chloride, sulfate, nitrate, etc., or by adding an acidic reagent to an alkaline salt of a metal such as for example, commingling sulfuric acid with sodium aluminate, etc. When it is advantageous to prepare the carrier material in the form of particles of uniform size and shape, this may be readily accomplished by grinding the partially dried oxide cake, with a suitable lubricant such as steric acid, resin, graphite, polyvinyl alcohol, etc., subsequently forming the particles in any suitable pelleting or extrusion apparatus. The preferred carrier material, for utilization herein, comprises alumina and silica, and such a composite may be prepared by separate precipitation methods, in which the oxides precipitated separately, and then mixed while in the wet state; when successive precipitation methods are employed, the first oxide is precipitated as previously set forth, and the wet slurry, either with or without prior washing, is composited with a salt of the other component. Thus, a precipitated, hydrated silica, substantially alkaline-free is suspended in an aqueous solution of aluminum chloride and/or zirconium chloride following which, precipitated hydrated alumina and precipitated hydrated zirconia are composited upon the silica gel through the addition of an alkaline precipitant such as ammonium hydroxide. The resulting mass of hydrated oxide is water washed, dried and calcined at about 1400° F. Another possible method of manufacturing consists of commingling an acid such as hydrochloric acid with commerical water glass under conditions to precipitate silica, washing the precipitate with the acidulated water or other means to remove sodium ions, and commingling with an aluminum salt such as aluminum chloride and adding ammonium hydroxide to precipitate alumina or forming the desired oxide or oxides through the thermal decomposition of the salt as the case may permit. It is understood that the particular means employed for the manufacture of the catalytic composite is not considered to be a limiting feature of the cascade process of the present invention, and such methods of manufacture are herein presented for the sole purpose of illustration and completeness. The carrier material particles likewise take the form of any desired shape such as spheres, pills, pellets, cakes extrudates, powder, granules, briquettes, etc. A particularly preferred form is the sphere, and shperes may be continuously manufactured by passing droplets of a hydrosol into an oil bath which is maintained at eleveated temperature, retaining the droplets in said oil bath until the same set into firm hydrogel spheriods. This particular method, commonly referred to as the "oil-drop method," is described in detail in U.S. Patent No. 2,620,314, issued to James Hoekstra.

Following the formation of the carrier material, the catalytically active metallic components are composited therewith. The catalytic composite comprises at least one metallic component selected from the metals and compounds of Groups VI–B and VIII of the Periodic Table, and include the platinum-group metals, the iron-group metals, molybdenum, tungsten, and chromium. These components may be incorporated within the alumina-silica carrier material in any suitable manner, although an impregnating technique is particularly convenient, and is preferred. Such a technique involves first forming an aqueous solution of a water-soluble compound of the desired metals such as molybdic acid, platinum chloride, palladium chloride, chloroplatinic acid, ammonium molybdate, nickel nitrate hexahydrate, tungsten chloride, dinitritodiamino platinum, etc., commingling the resulting solution with the alumina-silica in a stream dryer. Where the metallic compound is not water-soluble at the chosen impregnating temperature, other suitable solvents such as alcohols, ethers, etc., may be employed. The final composite, after all the catalytic components are present therein, is dried for a period of from about 2 to about 8 hours or more, and subsequently oxidized or calcined in an atmosphere of air at an elevated temperature within the range of about 1100° F. to about 1700° F., and for a period of from about 1 to about 8 hours or more. Following the high-temperature calcination treatment, the catalyst may be further treated for the purpose of converting the greater proportion of the catalytically active metallic components to a particularly desired form. Thus, the final catalytic composite may contain the active metallic components in the form of oxides, sulfides, as a complex with the alumina and silica or both, or in the most reduced state.

In many instances, the catalytic composite disposed within the first reaction zone (reactor **8** in the drawing) will contain a greater concentration of silica and a lesser concentration of nickel than the catalytic composite disposed in the second and third reaction zones (reactors **20** and **30** in the drawing). For example, where the charge stock to the first reaction zone is predominant in hydrocarbons boiling above a temperature of about 650° F., the catalyst will comprise from about 12.0% to about 40.0% by weight of silica, from about 10.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 4.5% by weight of nickel. Similarly, the charge stock to the second reaction zone consists predominantly of those hydrocarbons boiling within the range of about 400° F. to about 650° F., and the catalyst disposed therein comprises from about 10.0% to about 25.0% by weight of silica, alumina, from about 10.0% to about 30.0% by weight of molybdenum and from about 1.5% to about 6.0% by weight of nickel. In view of the fact that the charge stock to the third reaction zone (reactor **30** in the drawing) comprises essentially gasoline boiling range hydrocarbons, it is preferred to utilize a catalytic composite having a somewhat lesser degree of hydrocracking activity, but a relatively strong activity for effecting hydrorefining reactions, and particularly the hydrogenation of mono- and diolefinic hydrocarbons. Therefore, the catalyst disposed within the third reaction zone will generally comprise alumina, from 10.0% to about 25.0% by weight of silica, 10.0% to about 30.0% by weight of molybdenum and from about 1.5% to about 6.0% by weight of nickel.

When utilizing the continuous-type process flow, which is the particularly preferred manner of effecting the present invention, the various catalytic composites may be disposed in their respective reaction zones as fixed beds, as illustrated in the accompanying drawing, and maintained therein under the desired operating conditions. As illustrated, the charge to each of the reaction zones passes therethrough in downflow; where desired, the internals of

the reaction zones may be designed to permit radial flow through the catalyst bed. The operation may also be effected as a moving-bed type, or a suspensoid-type of operation in which the catalyst and hydrocarbons are passed as a slurry through the reaction zone, or as a combination process of moving-bed, fixed-bed and/or suspensoid-type.

When processing a full boiling range hydrocarbon charge stock, in accordance with the cascade system, complete control is available with respect to the degree of hydrogenation and hydrocracking, and, therefore, highly desirable control in regard to the properties of the intended product fractions. If the entire charge were processed in a single reactor, or in an uninterrupted series, extremely high severity, particularly in terms of pressure, space velocity (lower levels) and hydrogen circulation, would be required in order to meet simultaneously the specifications set upon all the given fractions of the entire product. Extreme operating severity necessarily results in an excessive degree of hydrocracking, whereby large quantities of normally gaseous material are produced at the expense of the more valuable liquid hydrocarbons, and over-hydrogenation whereby a greater quantity of aromatics are saturated than is necessary, in turn increasing hydrogen consumpetion. Of greater importance is the fact that significantly lesser yields of gas oil and kerosene fractions are realized. If the total full boiling range charge stock were to be processed in a single reactor, and at such conditions as to produce a suitable gas oil boiling range specification product, with the resulting kerosene and naphtha fraction in turn charged to a second, in series, reactor, operated to produce a suitable kerosene boiling range specification product, and again followed by a fractionator to produce a naphtha, or gasoline boiling range charge to another reactor system for the production of specific naphtha, many more total barrels of combined feed would be processed than had the cascade system been employed. Furthermore, a significantly greater quantity of catalyst would be required where the process is effected in uninterrupted series flow. It is, therefore, evident that the cascade scheme results in lower initial investment and operating costs, while producing significantly higher yields of normally liquid hydrocarbon product.

The following example is given to further illustrate the cascade system of the process of the present invention, and to indicate the benefits to be afforded through the utilization thereof. It is not intended to limit unduly the present invention to the charge stock, catalyst, operating conditions, product specifications, etc., as set forth. It is understood that the example is given for the sole purpose of illustration, and is not intended to limit the generally broad scope and spirit of the appended claims.

EXAMPLE

In this example, the catalytic composite disposed in all three of the reaction zones was 1/16-inch spherical particles of 88.0% by weight of alumina and 12.0% by weight of silica, containing 0.05% by weight of cobalt (based upon the weight of the finished catalyst). The catalytically active metallic components were added to the cobalt-containing carrier material by commingling molybdic acid (85.0% by weight of molybdic oxide) and nickel nitrate hexahydrate to form the impregnating solution which was intimately commingled with the previously prepared cobalt-containing carrier material. The molybdic acid was utilized in an amount to result in a catalytic composite comprising 11.3% by weight of molybdenum, the nickel nitrate hexahydrate being utilized to result in 4.2% by weight of nickel, computed on the basis of the elemental metals. The impregnated alumina-silica spheres were then dried for a period of about three hours at a temperature of about 300° F., the temperature being increased to 1100° F., and the composite calcined in an atmosphere of air for a period of about one hour at the elevated temperature.

The charge stock was a full boiling range coker distillate having an initial boiling point of about 130° F. and an end boiling point of about 825° F. This distillate was originally derived from a hydrocarbonaceous heavy oil (extracted from Athabaska Oil Sands), when the latter was first processed in a coking unit, and, as such, contained a large quantity of aromatic hydrocarbons boiling above about 500° F. and a high concentration of olefinic hydrocarbons boiling below about 500° F. From this full boiling range coker distillate, it was desired to produce three individual hydrocarbon fractions having particular, specific properties. Specifications required the production of a gas oil fraction having an initial boiling point of about 500° F., and containing less than about 0.1% by weight of sulfur, less than 500 p.p.m. of total nitrogen and a maximum of 30.0% by volume of aromatic hydrocarbons; a kerosene fraction, having a boiling range of from about 375° F. to about 500° F., was required to contain less than about 0.05 weight percent sulfur, less than about 50 p.p.m. of total nitrogen, and less than about 15.0 volume percent aromatic hydrocarbons; the specified product properties were significantly more stringent with respect to a naphtha fraction having an end boiling point of about 375° F., being less than 6.0 p.p.m. of sulfur and less than 1.0 p.p.m. of total nitrogen. With respect to the naphtha fraction, since this particular product was intended for subsequent utilization as the charge stock for a catalytic reforming unit, the concentration of olefinic hydrocarbons therein was required to be substantially "nil."

The full boiling range coker distillate was initially separated by distillation for the purpose of providing the individual raw fractions, each of which was intended for use as charge to a hydrorefining reaction zone. These three initial fractions were, a gas oil fraction, having an initial boiling point of about 515° F. and an end boiling point of about 826° F.; a kerosene fraction having an initial boiling point of about 380° F. and an end boiling point of about 536° F.; a naphtha fraction, or gasoline fraction having an initial boiling point of about 133° F. and an end boiling point of about 368° F. Other significant properties of these three fractions are presented in the following Table I.

TABLE I.—CHARGE STOCK PROPERTIES—INITIAL FRACTIONS

Fraction	Gas Oil	Kerosene	Naphtha
Vol. Percent of Distillate	53.9	20.4	25.7
Gravity, ° API at 60° F	18.3	32.9	54.5
100 ml. ASTM Distillation, ° F.:			
Initial Boiling Point	515	380	133
5%	530	396	168
10%	550	409	188
30%	600	428	236
50%	645	441	272
70%	697	458	297
90%	780	477	342
95%	807	490	357
End Boiling Point	826	536	368
Component Analysis, Vol. Percent:			
Aromatics	62.1	39.2	16.9
Olefins	2.0	14.4	30.8
Paraffins and Naphthenes	35.9	46.4	52.3
Sulfur, Wt. Percent	3.3	2.4	1.6
Total Nitrogen, p.p.m.	1,530	340	105
Bromine Number	18.0	36.0	61.0

The first reaction zone contained 400 cc. of the catalytic composite hereinbefore described, disposed therein in eight individual catalyst beds of 50 cc. each. The reaction zone was maintained at a pressure of about 1500 p.s.i.g. and the inlet temperature thereto controlled such that the maximum catalyst temperature during processing attained a level of 760° F. Hydrogen circulation, by way of compressive means, was in an amount of 3840 s.c.f./bbl., the hydrogen being admixed with the gas oil entering the reaction zone at a rate of 218 cc. per hour. Thus, the liquid hourly space velocity, defined as volumes of liquid

hydrocarbon charge per hour per volume of catalyst disposed within the reaction zone, was 0.54.

Following a suitable interval of stable, lined-out operation, a test period of about 12 hours duration was performed, during which time samples of the product gaseous phase and normally liquid portion of the product effluent were obtained. The normally liquid portion of the product effluent was fractionated in a distillation column at a cut-point of about 500° F. Both the gas oil product, having an initial boiling point of about 505° F. and an end boiling point of about 784° F., and the synthetic kerosene fraction, having an initial boiling point of about 180° F. and an end boiling point of about 492° F., were subjected to analysis to determine the character of the various components, and the concentration of the contaminating influences. Analyses on the gas oil and synthetic kerosene fractions are presented in the following Table II; included in this table is the tabulation of the product distribution of the total reaction zone effluent.

TABLE II.—PRODUCT ANALYSIS AND DISTRIBUTION—GAS OIL

Fraction	Gas Oil Product	Synthetic Kerosene
Gravity, ° API at 60° F	28.6	39.8
100 ml. ASTM Distillation, ° F.:		
Initial Boiling Point	505	180
5%	540	239
10%	550	270
30%	578	352
50%	600	400
70%	650	428
90%	715	452
95%	753	461
End Boiling Point	784	492
Component Analysis, Vol. Percent:		
Aromatics	30.1	32.0
Olefins	1.0	2.5
Paraffins and Naphthenes	68.9	65.5
Sulfur, Wt. Percent	0.0097	0.0001
Total Nitrogen p.p.m.	14.0	0.4
Bromine Number	0.9	2.2

Product distribution, total effluent:	
Hydrogen consumption, s.c.f./bbl.	1262
Light paraffinic hydrocarbons, wt. percent:	
Methane	0.4
Ethane	0.6
Propane	0.8
Liquid yields, vol. percent:	
Total butanes	1.3
Total pentanes	0.2
Hexanes and heavier	102.2
C_5 to 500° F.	23.8
500° F. to end point	78.6

With reference to Table II, it will be noted that the specifications placed upon the gas oil product were achieved. The primary concern was the concentration of aromatics, and this decreased from a level of 62.1 volumetric percent to 30.1 volume percent. Of further significance is the fact that both the gas oil and synthetic kerosene fractions were substantially completely free from the contaminating influence of sulfur and nitrogenous compounds, and the chemical hydrogen consumption was only 1262 s.c.f./bbl., or 1.6% by weight of the raw gas oil charge. There was an incease in liquid yield of about 2.2 volume percent, based upon liquid charge, not including the total butanes and pentanes resulting from the selective hydrocracking of the heavier components. The synthetic kerosene fraction, C_5 to 500° F. end boiling point, was produced in an amount of 23.8 volume percent, while the gas oil product was produced in an amount of 78.6 volumetric percent.

As hereinbefore set forth in a preferred embodiment, the synthetic kerosene fraction resulting from the original gas oil charge would normally be cut at an initial boiling point of about 300° F. to about 450° F., to provide a synthetic naphtha having an end boiling point within this range. That is to say, the total product effluent from the

gas oil reaction zone would be fractionated to provide three individual fractions rather than the two fractions hereinabove described. However, in view of the specified properties on the kerosene and naphtha product fractions, it was expedient in the small pilot plant scale unit to eliminate this extra fractionation step and the accompanying necessary analyses. In a commercial size unit, charging up to as high as about 20,000 barrels per day, particularly where the kerosene fraction had both a higher initial boiling point and end boiling point, the total gas oil product effluent would be fractionated to provide both the synthetic naphtha and synthetic kerosene fractions.

The synthetic kerosene fraction, as produced, was combined with the initial kerosene fraction, the combined kerosene charge having the properties indicated in the following Table III.

TABLE III.—KEROSENE CHARGE AND PRODUCT ANALYSIS

Fraction	Kerosene Charge	Kerosene Product	Synthetic Naphtha
Gravity, ° API at 60° F	35.4	38.5	50.2
100 ml. ASTM Distillation, ° F.:			
Initial Boiling Point	230	378	178
5%	293	397	216
10%	354	408	230
30%	410	424	263
50%	432	434	286
70%	450	447	308
90%	473	472	330
95%	484	483	336
End Boiling Point	510	525	367
Component Analysis, Vol. Percent:			
Aromatics	36.3	15.0	17.2
Olefins	9.6	0	0
Paraffins and Naphthenes	54.1	85.0	82.8
Sulfur, Wt. Percent	1.5	0.0001	0.0001
Total Nitrogen, p.p.m.	204	0.2	1.7
Bromine Number		0.0144	0.0116

Product distribution, total effluent:	
Hydrogen consumption, s.c.f./bbl.	591
Light paraffinic hydrocarbons, wt. percent:	
Methane	<0.05
Ethane	<0.05
Propane	0.1
Liquid yields, vol. percent:	
Total butanes	0.2
Total pentanes	0.4
Hexanes and heavier	100.5
C_5 to 375° F.	20.3
375° F. to end point	80.6

On a volumetric basis, the combined kerosene charge consisted of 60.0% of the initial raw fraction, and about 40.0% of the synthetic kerosene fraction. The combined kerosene charge was admixed with a hydrogen-rich recycle gas stream in an amount of about 4330 s.c.f./bbl., the mixture passing into a second reaction zone maintained at a pressure of about 1500 p.s.i.g. The second reaction zone contained a total of 400 cc. of the catalytic composite hereinbefore described, disposed therein in eight catalyst beds of 50 cc. each; based upon a charge rate of about 391 cc. per hour, the liquid hourly space velocity throughout a 12-hour test period was about 0.98. The inlet temperature to the catalyst bed was maintained at a level such that the maximum catalyst temperature throughout the test period was about 653° F.

The total product effluent from the second reaction zone was separated to provide a gaseous phase and a normally liquid hydrocarbon product. The latter was passed into a distillation column, and fractionated therein to provide a kerosene product having an initial boiling point of about 375° F. and a synthetic naphtha fraction having an end boiling point of about 375° F. Analyses of the two liquid product fractions, as well as the product distribution of the total hydrocarbonaceous effluent, are also given in the foregoing Table III. It will be noted that the specified properties placed upon the kerosene product fraction have been met, and that the product is virtually completely

devoid of sulfurous and nitrogenous compounds. The kerosene product obtained from the 12-hour test period contained about 15.0 volume percent of aromatic hydrocarbons as indicated in Table III. However, it must be stated that the product obtained both before and after the test period, and including that portion obtained during the test period (a total quantity of about 30 gallons), contained 13.8 volume percent aromatics, significantly below the specified quantity. Of further interest, as indicated in Table III, is the fact that the chemical hydrogen consumption was only 591 s.c.f./bbl., or 1.0% by weight of the total kerosene charge. As indicated by the product distribution, on the total liquid effluent, there was an increase in liquid yield of 0.5 volume percent, not counting butanes and pentanes.

The synthetic naphtha was combined with the original raw naphtha fraction, and passed into the third reaction zone containing 100 cc. of the catalytic composite hereinbefore described, disposed in five individual beds of 20 cc. each: The recycle hydrogen rate was 3327 s.c.f./bbl. The reaction zone was maintained at a pressure of about 800 p.s.i.g., the inlet temperature to the catalyst being controlled to result in a maximum catalyst bed temperature of 747° F. Based upon a liquid charge rate of about 243 cc. per hour, the liquid hourly space velocity was 2.43. Analyses of the combined naphtha charge and the normally liquid product effluent are given in the following Table IV.

TABLE IV.—NAPHTHA CHARGE AND PRODUCT ANALYSIS

Fraction	Naphtha Charge	Naphtha Product
Gravity, ° API at 60° F.	52.8	58.3
100 ml. ASTM Distillation, ° F.:		
Initial Boiling Point	124	124
5%	170	167
10%	192	187
30%	243	230
50%	277	265
70%	309	303
90%	343	343
95%	346	360
End Boiling Point	378	388
Component Analysis, Vol. Percent:		
Aromatics	18.6	8.0
Olefins	25.2	Trace
Paraffins and Naphthenes	56.2	92.0
Sulfur, Wt. Percent	1.3	0.0005
Total Nitrogen, p.p.m.	87	0.1
Bromine Number		0.0174

Product distribution, total effluent:	
Hydrogen consumption, s.c.f./bbl.	497
Light paraffinic hydrocarbons, wt. percent:	
Methane	0
Ethane	0.1
Propane	0.2
Liquid yields, vol. percent:	
Total butanes	1.3
Total pentanes	4.1
Hexanes and heavier	97.9
Total pentanes and heavier	102.0

With reference to Table IV, it will be noted that the naphtha product constitutes a highly desirable charge for a subsequent catalytic reforming unit. The liquid consists essentially of aromatics, paraffins and naphthenes, the concentration of olefinic hydrocarbons being in trace quantities only. The contaminating influence of sulfur and nitrogen is virtually non-existent, being 0.0005% by weight and 0.1 p.p.m. respectively. While processing the combined naphtha charge, only 497 s.c.f./bbl. of hydrogen was consumed, and only 0.3% by weight of the charge stock was converted into light paraffinic hydrocarbons generally considered as waste material. Including the butanes and pentanes produced, the liquid yield was 2.0 volume percent greater than the total charge to the third reaction zone.

With reference to the data tabulated in the foregoing Tables I, II, III and IV, several unexpected, extremely beneficial results should be immediately recognized. That these results are unusual is evident when considering the characteristics of the charge stock and the specified properties imposed upon the individual fractions to be derived therefrom. Of prime consideration, economically, is the fact that between about 3.0 and 4.0 volume percent more liquid hydrocarbons are produced than are charged to the overall system; this volumetric increase is of itself unusual in view of the fact that the overall chemical hydrogen consumption, computed on the basis of the total coker distillate, is only slightly higher than 1025 s.c.f./bbl. Furthermore, the weight percent loss to light paraffinic hydrocarbons (methane, ethane and propane) is only about 2.0. As hereinbefore set forth, such results could not be achieved by present-day hydrorefining processes which incorporate in-series reactor systems.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock comprising hydrocarbons boiling above the gasoline boiling range, and containing a contaminant selected from the group consisting of nitrogenous compounds and sulfurous compounds, which process comprises the steps of:

(a) hydrocracking and hydrorefining said charge stock in admixture with hydrogen at a temperature in the range of from about 600° F. to about 850° F. in a first reaction zone containing a hydrorefining catalytic composite;

(b) separating the normally liquid product effluent from said first reaction zone into a first light fraction, having an end boiling point of from about 400° F. to about 650° F. and a heavier fraction;

(c) combining at least a portion of said first light fraction with a hydrocarbon mixture having an initial boiling point of from about 300° F. to about 450° F. and containing at least one of the aforesaid contaminants, and reacting the resulting mixture with hydrogen at a temperature within said range in a second reaction zone containing a hydrorefining catalytic composite and maintained under less severe conversion conditions than said first zone;

(d) separating the normally liquid product effluent from said second reaction zone into a second light fraction, having an end boiling point within the range of from about 300° F. to about 450° F., and a hydrorefined second heavy fraction;

(e) combining at least a portion of said second light fraction with a hydrocarbon mixture, having an end boiling point of from 300° F. to about 450° F. and containing at least one of the aforesaid contaminants, reacting the resulting mixture with hydrogen at a temperature within said range in a third reaction zone containing a hydrorefining catalytic composite and maintained under conditions to effect hydrogenative hydrorefining of said mixture with minimum hydrocracking; and,

(f) separating the product effluent from said third reaction zone into a normally gaseous phase and a hydrorefined third heavy fraction.

2. The process of claim 1 further characterized in that at least a portion of said first light fraction is combined with said second light fraction and a hydrocarbon mixture having an end boiling point of from about 300° F. to about 450° F. prior to reacting the latter with hydrogen in said third reaction zone.

3. A process for hydrorefining a hydrocarbon charge stock comprising hydrocarbons boiling within and above the gasoline boiling range, and containing sulfurous and nitrogenous compounds, which process comprises the steps of:

(a) separating said charge stock into a gasoline fraction having an end boiling point within the range of from about 300° F. to about 450° F., a kerosene fraction having an end boiling point of from 400° F. to about 650° F., and a heavy bottoms fraction;

(b) hydrocracking and hydrorefining said heavy bottoms fraction in admixture with hydrogen at a temperature in the range of from about 600° F. to about 850° F. in a first reaction zone containing a hydrorefining catalytic composite;

(c) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of from about 300° F. to about 450° F. and a second light fraction having an end boiling point of from about 400° F. to about 650° F. and a hydrorefined, substantially sulfur-free heavy fraction;

(d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction and reacting the resulting mixture with hydrogen at a temperature within said range but lower than that maintained in said first zone to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons, in a second reaction zone containing a hydrorefining catalytic composite;

(e) separating the normally liquid product effluent from said second reaction zone into a third light fraction having an end boiling point of from about 300° F. to about 450° F. and a hydrorefined, substantially sulfur-free kerosene product;

(f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen at a temperature within said range in a third reaction zone containing a hydrorefining catalytic composite and maintained under conditions to effect hydrogenative hydrorefining of said mixture with minimum hydrocracking; and,

(g) separating the product effluent from said third reaction zone into a normally gaseous phase and a substantially sulfur and nitrogen-free hydrorefined gasoline product.

4. A process for hydrorefining a hydrocarbon charge stock comprising hydrocarbons boiling within and above the gasoline boiling range, and containing sulfurous and nitrogenous compounds, which process comprises the steps of:

(a) separating said charge stock into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of from about 500° F. to about 650° F., and a heavy bottoms fraction;

(b) hydrocracking and hydrorefining said heavy bottoms fraction in admixture with hydrogen at a temperature in the range of from about 600° F. to about 850° F. in a first reaction zone containing a hydrorefining catalytic composite;

(c) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of from about 350° F. to about 450° F. and a second light fraction having an end boiling point of from about 500° F. to about 650° F. and a hydrorefined, substantially sulfur-free heavy fraction;

(d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons, in a second reaction zone containing a hydrorefining catalytic composite and maintained at a temperature within said range;

(e) separating the normally liquid product effluent from said second reaction zone into a third light fraction having an end boiling point of from about 350° F. to about 450° F. and a hydrorefined, substantially sulfur-free kerosene product;

(f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons in a third reaction zone containing a hydrorefining catalytic composite and maintained at a temperature within said range; and,

(g) separating the product effluent from said third reaction zone into a normally gaseous phase and a substantially sulfur and nitrogen-free hydrorefined gasoline product.

5. The process of claim 4 further characterized in that the conversion conditions include a liquid hourly space velocity within the range of from about 0.25 to about 10.0 in each of said three reaction zones.

6. The process of claim 4 further characterized in that the conversion conditions include a pressure of from about 500 to about 5000 p.s.i.g., in each of said three reaction zones.

7. The process of claim 4 further characterized in that the maximum catalyst temperature in said second reaction zone is less than the maximum catalyst temperature in said first reaction zone.

8. The process of claim 5 further characterized in that the liquid hourly space velocity in said first reaction zone is less than that in said second and third reaction zones, and the liquid hourly space velocity in said second reaction zone is less than that in said third reaction zone.

9. A process for hydrorefining a hydrocarbon charge stock comprising hydrocarbons boiling within and above the gasoline boiling range and containing sulfurous and nitrogenous compounds, which process comprises the steps of:

(a) separating said charge stock into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of from about 500° F. to about 650° F., and a heavy bottoms fraction;

(b) hydrocracking and hydrorefining said heavy fraction in admixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at a temperature in the range of from about 600° F. to about 850° F. in a first reaction zone containing a siliceous hydrorefining catalytic composite;

(c) separating the normally liquid product effluent from said first reaction zone into a first light fraction having an end boiling point of from about 350° F. to about 450° F., a second light fraction having an end boiling point of from about 500° F. to about 650° F. and a hydrorefined, substantially sulfur-free heavy fraction;

(d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction and reacting the resulting mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydrocarbons, in a second reaction zone containing a siliceous hydrorefining catalytic composite and maintained at a temperature within said range;

(e) separating the normally liquid product effluent from said second reaction zone into a third light fraction having an end boiling point of from about 350 to about 450° F. and a hydrorefined, substantially sulfur-free kerosene product;

(f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions selected to convert nitrogenous and sulfurous compounds to ammonia, hydrogen sulfide and hydro-

carbons, in a third reaction zone containing a siliceous hydrorefining catalytic composite and maintained at a temperature within said range; and

(g) separating the product effluent from said third reaction zone into a normally gaseous phase and a substantially sulfur and nitrogen-free hydrorefined gasoline product.

10. The process of claim **9** further characterized in that the catalytic composite in said first, second and third reaction zones is a composite of alumina, silica and at least one metallic component selected from the group of metals of Groups VI–B and VII of the Periodic Table.

11. The process of claim **9** further characterized in that the catalytic composite in said first, second and third reaction zones is a composite of alumina, silica, molybdenum and an iron-group metallic component.

12. The process of claim **11** further characterized in that the catalytic composite in said first, second and third reaction zones is a composite of alumina, silica, from about 10.0% to about 30.0% by weight of molybdenum and from about 1.0% to about 6.0% by weight of nickel, calculated as the elemental metals.

13. The process of claim **12** further characterized in that the catalytic composite in said first reaction zone contains more silica and less nickel than the catalytic composite in said second and third reaction zones.

14. A process for hydrorefining a full boiling range coker distillate containing sulfurous and nitrogenous compounds, which process comprises the steps of:

(a) separating said distillate into a gasoline fraction having an end boiling point within the range of from about 350° F. to about 450° F., a kerosene fraction having an end boiling point of from about 500° F. to about 650° F. and a heavy bottoms fraction having an initial boiling point of from about 500° F. to about 650° F.;

(b) hydrocracking and hydrorefining said heavy bottoms fraction in admixture with hydrogen present in an amount of about 1000 to about 6000 s.c.f./bbl., at a maximum catalyst temperature within the range of from about 600° F. to about 850° F. in a first reaction zone containing a hydrorefining catalytic composite of alumina, from about 12.0% to about 40.0% by weight of silica, molybdenum and nickel;

(c) removing hydrogen sulfide and ammonia from the product effluent from said first reaction zone, separating the remaining normally liquid product into a first light fraction having an end boiling point of from about 350° F. to about 450° F., a second light fraction having an end boiling point of from about 500° F. to about 650° F. and a hydrorefined, substantially sulfur-free gas oil fraction;

(d) combining at least a portion of said second light fraction with the aforesaid kerosene fraction, reacting the result mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions including a maximum catalyst temperature within said range but lower than that in said first reaction zone, and selected to convert sulfurous and nitrogenous compounds to hydrogen sulfide, ammonia and hydrocarbons, in a second reaction zone containing a hydrorefining catalytic composite of alumina, from about 10.0% to about 25.0% by weight of silica, molybdenum and nickel;

(e) removing hydrogen sulfide and ammonia from the product effluent from said second reaction zone, separating the remaining normally liquid product into a third light fraction having an end boiling point of from about 350° F. to about 450° F. and a hydrorefined, substantially sulfur-free kerosene fraction;

(f) combining at least a portion of each of said first and third light fractions with the aforesaid gasoline fraction and reacting the resulting mixture with hydrogen present in an amount of from about 1000 to about 6000 s.c.f./bbl., at hydrorefining conditions including a maximum catalyst temperature of from about 600° F. to about 850° F. and selected to convert sulfurous and nitrogenous compounds to hydrogen sulfide, ammonia and hydrocarbons, in a third reaction zone containing a hydrorefining catalytic composite of alumina, silica, molybdenum and nickel; and,

(g) separating the product effluent from said third reaction zone into a normally gaseous phase containing hydrogen sulfide and ammonia, and a substantially sulfur and nitrogen-free hydrorefined gasoline fraction.

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