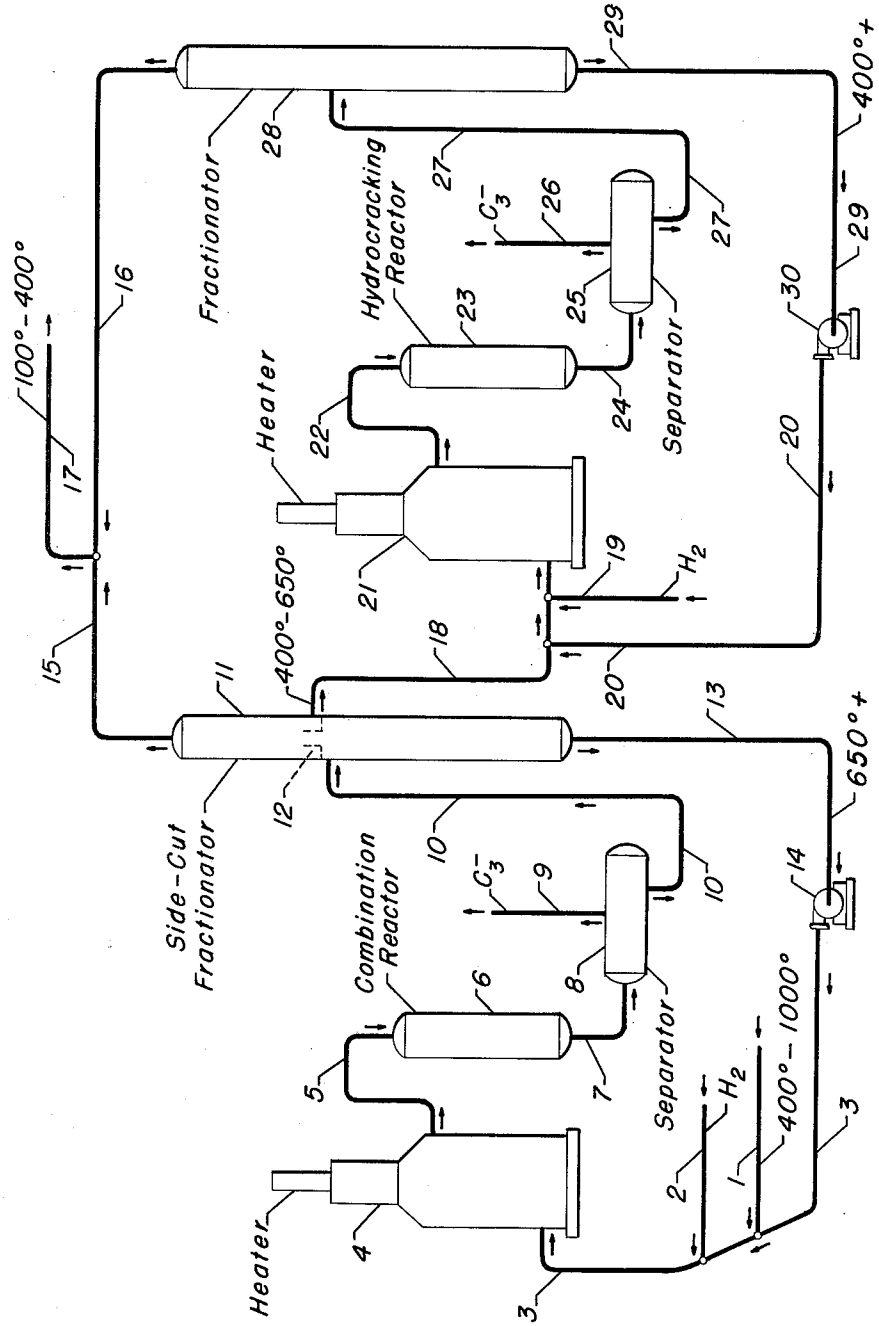
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HYDROCARBON HYROCRACKING PROCESS IN SEVERAL STAGES TO OBTAIN HYDROCARBONS OF REDUCED NITROGEN CONTAINING IMPURITIES

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HYDROCARBON HYDROCRACKING PROCESS IN SEVERAL STAGES TO OBTAIN HYDROCARBONS OF REDUCED NITROGEN CONTAINING IMPURITIES

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The present application is a continuation-in-part of my copending application, Serial Number 248,813 filed December 31, 1962, which application is a continuation-in-part of my copending application, Serial Number 18,742 filed March 30, 1960, all the teachings of which copending applications, now abandoned, are incorporated herein by specific reference thereto.

The present invention relates to a process for the conversion of hydrocarbonaceous material, and, in one embodiment, is directed toward a process for producing low molecular weight hydrocarbons from substantially higher molecular weight hydrocarbons having normal boiling points at temperatures above the gasoline boiling range and contaminated by nitrogenous compounds. The process of the present invention is specifically directed toward a process for producing an aromatic-containing gasoline boiling range hydrocarbon fraction from hydrocarbons boiling at temperatures above the gasoline boiling range, the latter being contaminated by substantial quantities of high-boiling nitrogenous compounds.

Hydrocracking, which is also commonly referred to as "destructive hydrogenation," as distinguished from the simple addition of hydrogen to unsaturated bonds between carbon atoms, effects a definite change in the molecular structure of the hydrocarbons being processed, and may be designated as cracking under hydrogenation conditions such that the lower-boiling products of the cracking reactions are substantially more saturated than when hydrogen, or material supplying the same, is not present. Hydrocracking processes are most commonly employed for the conversion of various coals and tars, and heavy residual oils, for the primary purpose of producing substantial yields of low-boiling saturated products; at least to some extent, intermediates, which are suitable for utilization as domestic fuels, and heavier gas-oil fractions, which find utilization as lubricants, are also produced. Although many of these hydrocracking reactions, or destructive hydrogenation processes, may be, and are, conducted on a thermal basis, the preferred processing technique involves the utilization of a catalytic composite possessing a high degree of hydrocracking activity. In virtually all hydrocracking processes, whether thermal or catalytic, controlled or selective cracking is highly desirable from the standpoint of producing an increased yield of liquid product boiling within the gasoline boiling range, and having improved anti-knock characteristics. In general, the lower molecular weight products possess higher octane ratings, and thus, a hydrocracked product of lower average molecular weight, and consisting essentially of hydrocarbons boiling within the gasoline boiling range is significantly more adaptable as the charge to a catalytic reforming process.

Selective hydrocracking is of particular importance when processing hydrocarbons and mixtures of hydrocarbons which boil at temperatures above the gasoline and middle-distillate boiling range; that is, hydrocarbons and mixtures of hydrocarbons, as well as various hydrocarbon fractions and distillates, having a boiling range indicating an initial boiling point of at least about 650° F. or 700° F., and an end boiling point as high as 1000° F.; or more. Selective hydrocracking of such hydrocarbon fractions results in greater yields of hydrocarbons

boiling within the gasoline and middle-distillate boiling range; that is, hydrocarbons and hydrocarbon fractions boiling below a temperature of about 650° F. to about 700° F. In addition, selective hydrocracking results in a substantially increased yield of a gasoline fraction; that is, those hydrocarbons boiling within the range of from about 100° F. to about 400° F. or 450° F., depending upon the selected end boiling point. Hydrocracking processes must be selective in order to avoid the decomposition of normally liquid hydrocarbons substantially or completely into normally gaseous hydrocarbons. The yield of normally liquid hydrocarbons, boiling within the gasoline boiling range, as a result of the excessive production of normally gaseous hpdrocarbons inherent in non-selective hydrocracking, can be decreased to an extent where the process is not economically feasible. The desired degree of selective hydrocracking involves the splitting of a higher-boiling hydrocarbon molecule into two molecules, both of which are normally liquid hydrocarbons. To a somewhat lesser degree, selective hydrocracking comprises the controlled removal of methyl, ethyl and propyl groups which, in the presence of hydrogen, are converted to methane, ethane, and propane. The removal of the aforesaid radicals is controlled such that not more than one, or possibly two, are removed from a given molecule. For example, in the presence of hydrogen, normal decane may be reduced to two pentane molecules, normal heptane reduced to hexane, nonane to octane or heptane, etc. Conversely, uncontrolled, or non-selective hydrocracking, will result in the decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons; for example, by the continued demthylation of normal heptane to produce seven methyl groups which, in the presence of hydrogen, are converted to seven molecules of methane.

Another disadvantage of non-selective or uncontrolled hydrocracking, is that this type of hydrocracking results in the more rapid formation of larger quantities of coke and other heavy carbonaceous material which becomes deposited upon the catalyst and decreases, or destroys, the activity thereof to catalyze the desired reactions. Such deactivation results in a shorter processing cycle or period, with the necessity of more frequent regeneration of the catalyst, or total replacement thereof with fresh catalyst. Of further significance, in regard to the hydrocracking process, are the aspects of hydrogen production and consumption, and the preservation of aromatic compounds which boil within the gasoline boiling range. Furthermore, rapid deactivation of the catalyst appears to inhibit the hydrogenation activity to the extent that a significant proportion of the gasoline boiling range hymolecular weight components whereby the same is not highly suited for direct processing by catalytic reforming. Investigations have indicated that the presence of hydrogen in the hydrocracking zone tends to decrease the amount of carbonaceous material which ultimately becomes deposited upon the catalyst. Similarly, selective hydrocracking does not tend to effect the substantial hydrogenation, or saturation, of the aromatic compounds boiling within the gasoline boiling range, or the destruction of naphthenic hydrocarbons, or the destructive hydrogenation of low molecular weight straight or branched-chain hydrocarbons into normally gaseous hydrocarbons. Aromatic hydrocarbons, boiling within the gasoline boiling range, possess a relatively high octane blending value, and are, therefore, utilized to great advantage to increase the anti-knock characteristics of gasoline boiling range fractions; a gasoline boiling range fraction rich in naphthenes is a highly desirable charge stock to a catalytic reforming unit. In addition, selective hydrocracking, although inhibiting the saturation of aromatic

compounds, does not result in an excessive quantity of the lower molecular weight, unsaturated hydrocarbons.

Investigations have further indicated that the presence of nitrogen-containing compounds within the hydrocracking feed stock, such as naturally-occurring, organic nitrogenous compounds, examples of which include pyrroles, amines, indoles and other classifications of organic nitrogen-containing compounds, results in the relatively rapid deactivation of the catalytically active metallic component acting as the hydrogenation agent, as well as the solid carrier material which acts as the acidic hydrocracking component of a great variety of hydrocracking catalysts. Such deactivation appears to result from the reaction of the nitrogen-containing compounds with the various catalytic components, the extent of such deactivation increasing as the process continues and as the nitrogen-containing feed stock continues to contaminate the catalyst through contact therewith. Although neutralization appears to be a factor in the deactivation of the catalyst, it is believed that such neutralization occurring when the basicity of the nitrogenous compound reacts with the acidic catalyst, is not the predominant deactivating influence. Rather, the formation of a nitrogen-containing complex with the catalytically active metallic components, whereby the active centers of the catalyst, normally available to the hydrocarbon charge stock, are effectively shielded therefrom, is believed to be the more predominating effect having the greatest influence in regard to catalyst deactivation. Such deactivation is not a simple reversible phenomenon which may be easily rectified by merely heating the catalyst in the presence of hydrogen for the purpose of decomposing such nitrogen-containing complexes.

The primary object of the present invention is to provide a multiple-stage, catalytic hydrocracking process which produces substantially greater yields of hydrocarbons boiling within the gasoline boiling range, without the attendant saturation of aromatic compounds, accompanied by the controlled cracking of the low molecular weight hydrocarbons. A related object is to utilize a catalytic composite which will retain a high degree of hydrocracking activity for a prolonged period of time while processing petroleum hydrocarbon charge stocks containing minimal quantities of residual nitrogenous compounds which otherwise result in comparatively rapid catalytic deactivation.

In a broad embodiment, the present invention relates to a process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling at temperatures above the gasoline boiling range, which comprises reacting said charge stock with hydrogen in a first reaction zone, separating the resultant effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of about 650° F. to about 700° F. and a third fraction containing hydrocarbons and nitrogenous compounds boiling at a temperature above about 650° F.; recycling said third fraction to combine with said hydrogen and charge stock, combining said second fraction with hydrogen and reacting the resultant mixture, at conversion conditions in a second reaction zone, separating the effluent from said second zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F. and recycling said heavy fraction to combine with the aforesaid mixture of said second fraction and hydrogen.

In another embodiment, the present invention involves a process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling at a temperature above the gasoline boiling range, which comprises reacting said charge stock and hydrogen in a first reaction zone with a nitrogen-insensitive catalyst under conditions to convert nitrogenous compounds to ammonia, removing ammonia from the resulting effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of 650° F. to about 700° F. and substantially free from nitrogenous compounds, and a third fraction containing residual nitrogenous compounds and hydrocarbons boiling above a temperature of about 650° F.; recycling said third fraction directly, and without intervening treatment, to combine with said hydrogen and charge stock, admixing said second fraction with hydrogen and reacting the resultant mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst in a second reaction zone, separating the effluent from said second zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to combine with the aforesaid mixture of hydrogen and said second fraction.

A more limited embodiment of the present invention is directed toward a process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling above the gasoline boiling range, which comprises reacting said charge stock and hydrogen in a first reaction zone with a nitrogen-insensitive catalyst comprising from about 6.0% to about 45.0% by weight of molybdenum, calculated as the element, under conditions to convert nitrogenous compounds to ammonia, removing the ammonia from the resultant effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of about 650° F. to about 700° F. and substantially free from nitrogenous compounds, and a third fraction containing residual nitrogenous compounds and hydrocarbons boiling at a temperature above about 650° F.; recycling said third fraction to combine with said hydrogen and charge stock, admixing said second fraction with hydrogen and reacting the resultant mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst comprising from about 2.0% to about 10.0% by weight of nickel and a composite of silica and alumina in a second reaction zone, separating the effluent from said second zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to combine with the aforesaid mixture of hydrogen and said second fraction.

In a specific embodiment, the present invention is directed toward a process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling at a temperature above the gasoline boiling range, and containing from about 1,000 to about 5,000 p.p.m. of nitrogenous compounds, which process comprises reacting said charge stock and hydrogen in a first reaction zone in contact with a nitrogen-insensitive catalyst comprising from about 6.0% to about 45.0% by weight of molybdenum, calculated as the element, under conditions to convert the bulk of said nitrogenous compounds to ammonia, removing the ammonia from the resultant effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of about 650° F. to about 700° F., and substantially free from nitrogenous compounds, and a third fraction boiling at a temperature above about 650° F., thereby concentrating the remainder of said nitrogenous compounds in said third fraction; recycling said third fraction directly and without intervening treatment to said first reaction zone, admixing said second fraction with hydrogen and reacting the resulting mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst com-

prising from about 2.0% to about 10.0% by weight of nickel, calculated as the element, and a composite of silica and alumina in a second reaction zone, separating the effluent from said second reaction zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to said second reaction zone.

The present invention also affords a process for producing hydrocarbons boiling within the gasoline boiling range which comprises reacting hydrogen with hydrocarbons boiling at a temperature in excess of the gasoline boiling range, and in contact with a catalyst comprising a Group VI–B metallic component and a Group VIII metallic component, and a composite of silica and from about 25% to about 65% by weight of alumina, the ratio of said Group VIII metallic component to said Group VI–B metallic component being within the range of from about 0.05:1 to about 5:1, calculated as the elements.

It is believed the method of the present invention may be more clearly illustrated and understood by initially defining several of the terms and phrases as employed within the specification and the appended claims. The term, "hydrocarbons" is intended to connote saturated hydrocarbons, straight-chain and branched-chain hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, naphthenic hydrocarbons, as well as mixtures of various hydrocarbons such as hydrocarbon fractions and/or hydrocarbon distillates. The phrase, "hydrocarbons boiling within the gasoline boiling range," or "gasoline boiling range hydrocarbons" is intended to connote those hydrocarbons boiling at temperatures of from about 100° F. to about 400° F. or 450° F.; that is, hydrocarbon fractions having an initial boiling point of about 100° F., and an end boiling point within the range of about 400° F. to about 450° F. Hydrocarbons, "boiling at a temperature above the gasoline boiling range," is intended to connote, therefore, those hydrocarbons and mixtures of hydrocarbons which possess an initial boiling point above about 400° F. to about 450° F. The term, "middle distillates," or, "light gas oil," refers to those hydrocarbon fractions having an initial boiling point within the range of about 400° F. to about 450° F., and an end boiling point within the range of about 650° F. to about 700° F. Similarly, in regard to both the nitrogen-insensitive catalyst and the nitrogen-sensitive catalyst, the term "metallic component," or "catalytically active metallic component," is intended to encompass those catalytic components which are employed for their hydrocracking activity, or for their propensity for the destructive removal of the nitrogenous compounds, as the case may be, and which components are selected from the metals of Groups VI–B and VIII of the Periodic Table of the Elements, Handbook of Chemistry and Physics, 43rd edition. Thus, the metallic catalytic components are distinguished from those components which are employed as the solid support, or carrier material, or the acidic cracking component. The metallic component of the catalyst of the present invention may comprise mixtures of two or more of such metals, or compounds. Thus, the catalysts employed in the present process may comprise chromium, molybdenum, tungsten, iron, cobalt, nickel, palladium, platinum, ruthenium, rhodium, osmium, iridium, and mixtures of two or more including nickel-molybdenum, nickel-chromium, molybdenum-platinum, cobalt-nickel-molybdenum, molybdenum-palladium, chromium - platinum, chromium - palladium, molybdenum-nickel-palladium, etc. Regardless of the particular catalytically active metallic component, or components, to be utilized, these are composited with a suitable, solid carrier material, which may be either naturally-occurring, or synthetically-prepared. Naturally-occurring carrier material include various aluminum silicates particularly when acid-treated to increase the activity thereof, various alumina-containing clays, sands, earths and the like, while synthetically-prepared cracking catalyst components generally include at least a portion of silica and alumina. Other suitable carrier material components, which may, in particular instances, be combined as an integral portion of the hydrocracking catalyst, include zirconia, magnesia, thoria, boria, titania, etc., the preferred cracking catalyst component comprising a composite of silica and alumina. As hereinafter set forth, the process of the present invention involves two separate, distinct reaction zones, each of which contains a catalyst whose composition depends, at least in part, upon the function to be served within the reaction zone. Therefore, the catalytic composites will be hereafter described in greater detail.

As hereinbefore set forth, the present invention is directed, in one embodiment, toward a process for producing hydrocarbons boiling within the gasoline boiling range, from those hydrocarbons which boil at a temperature above the gasoline boiling range. The process of the present invention encompasses a hydrocracking reaction zone, which, in and of itself, is generally applicable to processing petroleum-derived feed stocks of the middle-distillate boiling range and above. Suitable charge stocks to hydrocracking processes include kerosene fractions, gas-oil fractions, lubricating oil and white oil stocks, cycle stocks, the various high-boiling bottoms recovered from the fractionators generally accompanying catalytic cracking operations, and referred to as heavy recycle stock, fuel oil stocks and other sources of hydrocarbons having a depreciated market demand due to the high boiling points of these hydrocarbons along with the presence of asphalt and other heavy hydrocarbonaceous residues. Generally, all of these sources of feed stocks contain high-boiling, nitrogenous compounds as contaminants. It is very difficult to remove the last few parts per million of nitrogen from the charge stock, prior to subjecting the same to the hydrocracking process. Although the major proportion of such nitrogenous compounds may be removed by many known means, such as a hydrorefining pretreatment in which the feed stock is subjected to the action of a catalyst at reaction conditions, such that the structure of the hydrocarbon components are not substantially altered, but the nitrogenous, organically-bound components are converted into ammonia and the corresponding hydrocarbon residue, the resulting hydrocarbon product effluent will, in all probability, contain a relatively minor amount of nitrogen. Notwithstanding such minor quantities, these organic nitrogen compounds will eventually result in the deactivation of the low-temperature hydrocracking catalysts, such as the Group VI and/or Group VIII metals supported on a solid support or carrier material such as silica-alumina. I have found that the residual nitrogenous compounds, when present in hydrocarbons boiling in excess of the gasoline boiling range, are concentrated in that fraction thereof which contains those hydrocarbons boiling at a temperature beyond the middle-distillate boiling range; that is, the greater proportion of residual nitrogenous compounds is concentrated within that fraction having an initial boiling point of about 650° F. to about 700° F. Through the utilization of the process of the present invention, the greater proportion of the gasoline boiling range hydrocarbons produced therefrom, results from a hydrocracking step imposed upon those hydrocarbons boiling within the middle-distillate boiling range, or having an initial boiling point of about 400° F. to about 450° F. and end boiling point of about 650° F. to about 700° F., and which are substantially free from the contaminating influence of nitrogenous compounds. The present process may be clearly understood through reference to the accompanying drawing which illustrates one embodiment thereof, but which is not intended to be unduly limited thereto. In the drawing, various flow valves, control valves, coolers, condensers, overhead reflux condensers, pumps, compressors, etc., have been

eliminated, or reduced in number as not being essential to a complete understanding of the present process. The utilization of such miscellaneous appurtenances will immediately be recognized by one possessing skill in the art of petroleum processing.

Referring now to the drawing, the hydrocarbon charge stock, contaminated by a substantial quantity of nitrogeneous compounds, on the order of about 1000 to about 5000 parts per million, computed as nitrogen, enters the process through line **1** into line **3**, wherein it is admixed with hydrogen entering via line **2**. Although indicated as having an initial boiling point of 400° F., and an end boiling point of 1000° F., the hydrocarbon charge in line **1** is not intended to be so limited. It is only necessary that such hydrocarbon charge stock consist essentially of those hydrocarbons boiling at a temperature above the gasoline boiling range, or those having an initial boiling point greater than about 400° F. to about 450° F. Accordingly, the hydrocarbon charge stock may consist entirely of a heavy gas oil, or recycle stock, having an initial boiling point of at least about 650° F. and an end boiling point of 1000° F. Or, the hydrocarbon charge stock entering via line **1** may be a kerosene fraction boiling partially within the gasoline boiling range and partially within the middle-distillate boiling range, that is, a boiling range of about 350° F. to about 650° F. The charge stock may be a light cycle oil boiling entirely within the middle-distillate boiling range, or it may be a vacuum gas oil having a boiling range of about 600° F. to about 950° F. The process of the present invention is not strictly limited to a particular hydrocarbon mixture, although especially adaptable to processing those nitrogen-contaminated hydrocarbons boiling substantially entirely at a temperature above the gasoline boiling range. In any event, the mixture of hydrogen and heavy hydrocarbons in line **3**, entering heater **4**, is such that the hydrogen is present in an amount within the range of about 3000 to 8000 standard cubic feet per barrel of hydrocarbon charge. The mixture is raised to a temperature of about 500° F. to about 1000° F. in heater **4**, and is passed through line **5** into combination reactor **6**.

Reactor **6** is maintained under an imposed pressure of about 100 pounds to about 3000 pounds per square inch, and has disposed therein a nitrogen-insensitive catalyst comprising at least about 6.0% by weight of molybdenum, calculated at the element. Under these conditions, and in the presence of the molybdenum-containing catalyst, the organically-bound, nitrogen compounds are separated to form ammonia which is released in a free form from the reaction media. In addition to this rather effective clean-up of the hydrocarbon charge stock, a significant degree of hydrocarbon conversion occurs whereby the heavier molecular weight hydrocarbons, boiling at a temperature of from about 700° F. to about 1000° F., including those hydrocarbons resulting when the nitrogen is separated to form ammonia, are converted to hydrocarbons boiling below about 700° F.; that is, into hydrocarbons boiling within the gasoline and middle-distillate boiling ranges. The conversion reactions are such, however, that very little, if any, light, straight-chain paraffinic hydrocarbons (C_1–C_3) are produced. The total reactor effluent passes through line **7** into separator **8**. Although indicated as a single vessel, the separation means illustrated as separator **8**, may be any suitable system whereby there is produced normally liquid hydrocarbons, indicated as leaving via line **10**, and a separate gaseous phase containing light paraffinic hydrocarbons, ammonia, hydrogen sulfide, carbon dioxide, etc., and as indicated in the drawing, leaving separator **8** via line **9**. Further, this separation zone may provide for the removal of a hydrogen-rich gas stream to be recycled and combined with the hydrogen in line **2**. The normally liquid hydrocarbons are passed through line **10** into side-cut fractionator **11**, containing a center well **12**. Frictionator **11** may be operated at any suitable conditions of pressure and/or temperature, which result in the removal of gasoline boiling range hyrocarbons (butanes to 400° F.) through line **15**, and the removal of the heavier hydrocarbons boiling above a temperature of about 650° F. to about 700° F. through line **13** and pump **14**, being recycled thereby through line **3**. Hydrocarbons boiling within the middle-distillate boiling range, that is, having an initial boiling point of about 400° F. to about 450° F. and an end boiling point of about 650° F. to about 700° F., are withdrawn from fractionator **11** through line **18**.

As hereinafter indicated in a specific embodiment, the middle-distillate boiling range hydrocarbon fraction, leaving fractionator **11** via line **18**, is substantially completely free from nitrogenous compounds. This is true also of the gasoline, or light naphtha fraction leaving via line **15**. The greater proportion, or bulk, of the nitrogenous compounds originally present in the charge stock entering via line **1**, are converted into ammonia and liquid hydorcarbons in reactor **4**. At least a portion of these hydrocarbons will, as a result of the action of the catalytic composite disposed in reactor **4**, undergo further reaction therein to produce lower-boiling liquid hydrocarbons, some of which boil within the gasoline boiling range. The unconverted nitrogenous compounds, entering fractionator **11** through line **10**, have boiling points above about 650° F., or beyond the middle-distillate boiling range, and are concentrated in the heavier fraction leaving through line **13**. These residual nitrogenous compounds are recycled though line **13**, via pump **14** into line **3**, to combine with the fresh charge stock and hydrogen in lines **1** and **2** respectively. In this manner, the nitrogenous compounds are recycled to extinction within the process, ultimately being converted into liquid hydrocarbons and ammonia, the latter being removed from the process via separator **8** and line **9**. It should be further noted that the heavier hydrocarbon fraction in line **13**, following separation from the liquid product effluent in fractionator **11**, is recycled directly, and without additional intervening treatment, to reactor **6** in admixture with the fresh hydrocarbon charge stock and hydrogen. That is, there is no additional separation of this stream, either by physical, or chemical means; the recycled heavy fraction is not subject to further fractionation, adsorption, reaction, etc., prior to entering reactor **6**. This direct recycle further insures against contamination of desired product streams by residual nitrogenous compounds which have been concentrated in this heavier (650° F. +) fraction.

The middle-distillate hydrocarbons in line **18**, containing less than about 10.0 p.p.m. of nitrogen, and preferably less than 3.0 p.p.m., are admixed with hydrogen in line **19**, said hydrogen being utilized in an amount within the range of about 1000 standard cubic feet to about 6000 standard cubic feet per barrel of said hydrocarbons. The resulting mixture enters heater **21** wherein it is raised to the desired temperature within the range of about 500° F. to about 950° F., and at least at a temperature 50° F. less than that temperature of the hydrocarbon-mixture in line **5** entering combination reactor **6**. The heated mixture is passed from heater **21** through line **22** into hydrocracking reactor **23**. Hydrocracking reactor **23** is maintained under an imposed pressure within the range of about 100 to about 3000 pounds per square inch, and has disposed therein a suitable hydrocracking catalyst comprising at least one metallic component selected from the metals of Groups VI–B and VIII of the Periodic Table and a composite of silica and alumina. The effluent from reactor **23** is passed via line **24** into separator **25**. As previously stated with respect to separator **8**, separator **25** merely illustrates a suitable separating zone from which the small quantity of light paraffinic hydrocarbons, produced in hydrocracking reactor **23**, may be removed via line **26**. Normally liquid hydrocarbons, the greater proportion of which are within the gasoline boiling range, are withdrawn from separator **25** through line **27** into frac-

tionator 28. The purpose of fractionator 28 is to separate the hydrocarbons boiling within the gasoline boiling range in line 16, which are combined with the gasoline boiling range hydrocarbons in line 15; the mixture may be withdrawn to storage through line 17. Those hydrocarbons boiling above a temperature of about 400° F. to about 450° F., are withdrawn from fractionator 28 through line 29 and pump 30, being recycled through line 20. The heavier middle-distillate hydrocarbons in line 20 are admixed with the middle-distillate hydrocarbons in line 18, and passed, along with hydrogen from line 19, into heater 21.

From the foregoing description of the embodiment indicated in the accompanying drawing, it is readily ascertained that the present process is a two-stage process for producing hydrocarbons boiling within the gasoline boiling range. The first stage, utilizing combination reactor 6, effects substantially complete destruction of the bulk of nitrogenous compounds contained within the fresh charge stock, consisting essentially of hydrocarbons boiling at a temperature above the gasoline boiling range. In addition, through careful selection of both catalyst and operating conditions, there is effected, in combination reactor 6, a substantial degree of hydrocarbon conversion whereby the heavier hydrocarbons, those boiling above about 700° F., are converted into hydrocarbons boiling below about 700° F., including conversion to both gasoline and middle-distallate hydrocarbons. Since the catalyst in combination reactor 6 is selected for its nitrogen-insensitivity, rapid deactivation of the catalyst, otherwise resulting when hydrocracking nitrogen-contaminated charge stocks, is not experienced.

As hereinbefore set forth, the process of the present invention is particularly directed to the processing of hydrocarbons and mixtures of hydrocarbons boiling above the gasoline boiling range. However, it is most advantageously applied to petroleum-derived feed stocks, particularly those stocks commonly considered as being heavier than middle-distillates. Such stocks include gas oil fractions, heavy vacuum gas oil and cycle stocks, lubricating oils and white oil stocks, as well as the high-boiling bottoms recovered from various catalytic cracking operations. Therefore, although the charge stock to the present process may have an initial boiling point of about 400° F. to about 450° F. and an end boiling point of about 1000° F. or higher, the process is somewhat more advantageous when processing hydrocarbon charge stocks having a significantly higher initial boiling point, that is, of the order of about 650° F. to about 700° F. In further describing the process of the present invention, and the various limitations thereof, the entire process will be divided into its two separate, distinct stages in the interest of simplicity and clarity. The first stage comprises a suitable reaction zone, a separating zone, and a side-cut fractionator, which are utilized in such a manner and under such conditions as to result in the substantially complete removal of nitrogenous compounds from the fresh hydrocarbon charge stock, while producing an aromatic-containing gasoline boiling range hydrocarbon fraction as a product, and a middle-distillate hydrocarbon stream which serves as the charge stock to the second stage of the process, both of which are substantially free from nitrogenous compounds. The heavy hydrocarbon charge stock, for example, a heavy vacuum gas oil, is admixed with hydrogen in an amount of about 3000 standard cubic feet to about 8000 standard cubic feet per barrel of such charge, the mixture being heated to the desired operating temperature, and thereafter passed into the first reaction zone. The precise operating conditions within the first reaction zone will be dependent upon the various physical and/or chemical characteristics of the particular hydrocarbon charge stock being processed. However, in any event, the reactor will be maintained at a temperature of about 500° F. to about 1000° F., and under an imposed pressure within the range of about 100 pounds to about 3000 pounds per square inch. Higher pressures appear to favor the destructive removal of nitrogenous compounds, as well as the conversion of those hydrocarbons boiling at a temperature above about 650° F., and are, therefore, preferred; thus, the particularly preferred pressure will be within the range of about 1000 pounds to about 3000 pounds per square inch. The hydrocarbon charge stock contacts the particular catalyst employed at a liquid hourly space velocity (defined as volumes of liquid charge per hour per volume of catalyst disposed within the reaction zone), within the range of about 0.5 to about 10.0. In those instances where the heavy hydrocarbon charge is contaminated by relatively large quantities of nitrogenous compounds, of the order of about 1000 to about 5000 p.p.m., or more, a lower range of liquid hourly space velocity will be employed, that is, from about 0.5 to about 3.0.

The catalyst disposed within this first reaction zone serves a dual function; that is, the catalyst is non-sensitive to the presence of substantial quantities of nitrogenous compounds, while effecting the destructive removal thereof, and also possesses the activity to promote the conversion of a considerable quantity of those hydrocarbons boiling at a temperature in excess of about 650° F. to about 700° F. I have found that a catalyst comprising comparatively large quantities of molybdenum, calculated as the element, composited with a suitable carrier material such as alumina, is very efficient in carrying out the desired operation. A particularly preferred catalytic composite, for utilization in this first reaction zone, comprises from about 6.0% to about 45.0% by weight of molybdenum, from about 1.0% to about 5.0% by weight of nickel, calculated as the elemental metals, and utilizes alumina as the carrier material. As hereinafter indicated, it is preferred to utilize alumina in the absence of other refractory inorganic oxide material, such as silica, zirconia, magnesia, titania, thoria, boria, etc. Although these refractory inorganic oxides, in specific instances, may be employed in relatively minor quantities with respect to the amount of alumina, they appear to impart additional cracking activity to the catalyst within the first reaction zone, such that the hydrocarbons boiling above about 650° F. are subjected to non-selective cracking whereby an excessive quantity of light paraffinic hydrocarbons are produced therefrom. In addition to minor amounts of nickel, like quantities of cobalt and/or iron may be employed in combination with relatively larger amounts of molybdenum. The catalytic composite may be manufactured in any suitable manner, a particular advantageous method employing impregnating techniques. Thus, where the catalyst is to contain both nickel and molybdenum, the method of preparation involves first forming an aqueous solution of water-soluble compounds of the desired metals, such as nickel nitrate, nickel carbonate, ammonium molybdate, molybdic acid, etc. The alumina particles, serving as the carrier material, are commingled with the aforementioned aqueous solutions, and subsequently dried at a temperature of about 200° F. The dried composite is then oxidized in an oxidizing atmosphere such as air, at an elevated temperature of from about 1100° F. to about 1700° F. for a period of from about 2 to about 8 hours or more. It is understood that the impregnating technique may be effected in any suitable manner: thus, the carrier material may be impregnated first with the molybdenum-containing solution, dried and oxidized, and subsequently impregnated with the nickel-containing solution. On the other hand, the two aqueous solutions may be first intimately commingled with each other, the carrier material subsequently impregnated in a single step. The particular means by which the catalyst, for utilization in the first reaction zone, is prepared, is not considered to be limiting upon the process of the present invention.

The gaseous ammonia, resulting from the destructive removal of nitrogenous compounds, is removed from the total effluent emanating from the first reaction zone,

in any suitable manner. For example, the total effluent may be admixed with water, and thereafter subjected to separation such that the ammonia is adsorbed and removed within the water-phase. In addition to the removal of ammonia, it is desired that what few light paraffinic hydrocarbons, such as methane, ethane and propane, resulting from the rather severe conditions in the first reaction zone, are also removed. Therefore, the separation zone may comprise a low-temperature flash chamber whereby the ammonia and light paraffinic hydrocarbons are removed as a gas phase. Although the bulk of nitrogenous compounds are converted in this first zone, as hereinbefore set forth, the resulting normally liquid hydrocarbons, now boiling within a range of about 100° F. to about 700° F. or higher, will contain some residual nitrogenous compounds. The normally liquid hydrocarbons are, therefore, distilled in a side-cut fractionator under such conditions as will yield a gasoline fraction and a heart-cut having a boiling range of about 400° F. to about 650° F., which heart-cut and gasoline fractions are substantially completely free from nitrogenous compounds. Those hydrocarbons boiling below 400° F., or within the gasoline boiling range, are removed to storage from the upper portion of the fractionator. The now concentrated residual nitrogenous compounds are removed within that hydrocarbon fraction boiling above about 650° F., from the bottom portion of the side-cut fractionator, and are recycled to combine with the original hydrocarbon charge stock. Thus, the first stage of the present process effects the substantially complete removal of nitrogenous compounds, while recycling to extinction those hydrocarbons boiling in excess of about 650° F. to about 700° F. Furthermore, the heavy nitrogenous hydrocarbons are converted into lower molecular weight hydrocarbons from which the nitrogen is more readily removed.

The second-stage of the present process is designed to convert the now substantially nitrogen-free, middle-distillate boiling range hydrocarbons into hydrocarbons which boil within the gasoline boiling range. As hereinbefore stated, the middle-distillate boiling range charge stock to the second reaction zone, designated as the "hydrocracking zone" (reactor **23**) will contain less than 10.0 p.p.m. of nitrogenous compounds, as nitrogen. Under normal operating conditions within the side-cut fractionator, the concentration of nitrogen will be less than 3.0 p.p.m. More advantageous hydrocracking operation within the second reaction zone, will be realized if the side-cut fractionator is operated at conditions which result in a middle-distillate boiling range hydrocarbon mixture containing less than 1.0 p.p.m. of nitrogen. This concept, of concentrating the residual nitrogenous compounds in the heavier-than-middle-distillate fraction, has not previously been recognized, since present-day multi-stage units, in which the second zone is intended for hydrocracking, permit the charge stocks, after hydrorefining, to contain up to 1500 p.p.m. of nitrogen. As hereinafter indicated in a specific example, the present process effects recycle of the heavier fraction when it contains only 40 p.p.m. of nitrogen.

It is to great advantage to utilize certain catalytic composites which are most effective for hydrocracking of the middle-distillate charge stock, although containing a minor quantity of residual nitrogenous compounds, without being detrimentally affected thereby. For example, alumina is a good nitrogen remover when it contains relatively minor quantities of silica (approximately 12% by weight). Likewise, silica is a good hydrocracking catalyst when it contains a relatively small quantity of alumina; however, in and of itself, silica is not a good nitrogen remover. In a like manner, the metallic components of the hydrocracking catalyst will exhibit similar propensities. For example, as indicated in regard to the first reaction zone, molybdenum is a good nitrogen remover, but is not relatively active as a hydrocracking or hydrogenation catalyst. On the other hand, nickel is a good hydrogenation catalyst, but does not possess a relatively high degree of activity in regard to the removal of nitrogenous compounds. Catalytic composites which comprise at least one metallic component selected from Groups VI–B and VIII of the Periodic Table, and a composite of silica and from about 25% to about 65% by weight of alumina, constitute hydrocracking catalysts for use in the second stage of the process of the present invention. These catalysts have a relatively high activity for the conversion of hydrocarbons boiling within the middle-distillate boiling range, which activity is substantially unaffected even by the relatively minor quantities of nitrogen, less than about 3.0 p.p.m., contained within the middle-distillate charge stock, produce a substantially saturated gasoline fraction, and do not effect the hydrogenation of aromatic compounds.

The synthetically-produced solid carrier material, for utilization in the second-stage, may be made in any suitable manner including separate, successive or coprecipitation methods. For example, alumina may be prepared by adding a reagent such as ammonium hydroxide, ammonium carbonate, etc., to a salt of aluminum such as aluminum chloride, aluminum nitrate, aluminum acetate, etc., in an amount to form aluminum hydroxide, which upon drying is converted to alumina. Aluminum chloride is generally preferred as the aluminum salt to be employed, not only for convenience in subsequent washing and filtering procedures, but also it appears to give the best results. The alumina particles may take the form of any desired shape such as spheres, pills, pellets, cakes, extrudates, powder, granules, etc. A particularly preferred form of alumina is the sphere, and these spheres may be continuously manufactured by passing droplets of an alumina hydrosol into an oil bath maintained at an elevated temperature, retaining the droplets in said oil bath until the same set into firm hydrogel spheroids. It is understood that the foregoing description, in regard to the preparation of alumina particles, is equally applicable to the carrier material employed in the manufacture of the catalyst utilized in the first reaction zone.

In a like manner, silica may be prepared in any suitable manner, one method being to commingle water glass and a mineral acid under conditions which precipitate a silica hydrogel. The silica hydrogel is subsequently washed wih water containing a small amount of a suitable electrolyte for the purpose of removing sodium ions. Oxides of other compounds 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 acid to an alkaline salt of the metal, for example, commingling sulfuric acid with sodium aluminate, etc. Usually the inorganic oxide will be washed and filtered, which may be accomplished in the same or separate steps, and may be effected in the presence of an acid or an alkaline material. When it is advantageous to prepare the catalyst 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 stearic acid, polyvinyl alcohol, resin, graphite, etc., and subsequently forming the particles in any suitable pelleting or extrusion apparatus. As hereinbefore stated, the cracking catalyst component comprises at least two refractory inorganic oxides, and such a composite may be prepared in any suitable manner including separate precipitation, successive, or coprecipitation methods. In the separate precipitation method, the oxides are precipitated separately and then mixed, preferably 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, and precipitation of the oxide thereof is effected by the addition of a suitable alkaline or acidic material.

The resulting composite may then be dried and formed into the desired size and/or shape. When the catalyst employed in the second reaction zone comprises silica and alumina, and/or silica, alumina and zirconia, they are preferentially manufactured by commingling an acid such as hydrochloric acid, sulfuric acid, etc., with commercial water glass under conditions to precipitate silica, washing with acidulated water or other means to remove sodium ions, commingling with an aluminum salt such as aluminum chloride, aluminum sulfate, aluminum nitrate, and/or some suitable zirconium salt, etc., and either adding a basic precipitant such as ammonium hydroxide to precipitate alumina and/or zirconia, or forming the desired oxide or oxides by thermal decomposition of the salt as the case may permit. The silica-alumina-zirconia cracking component may be formed by adding the aluminum and/or zirconium salts together or separately. Other cracking components may be prepared in a similar manner, however, not necessarily with equivalent results. The utilization of particular means for the manufacture of the cracking catalyst employed in the second reaction zone is not considered a limiting feature of the process of the present invention.

The catalytically active metallic component, of the catalyst disposed within the second reaction zone, is then composited with the aforementioned cracking component. The active metallic components are generally employed in an amount of from about 0.1% to about 20.0% by weight of the total catalyst. The catalyst comprises at least one metallic component selected from the metals of Groups VI–B and VIII of the Periodic Table, and includes platinum, palladium, rhodium, iridium, nickel, tungsten, and/or molybdenum, and these may be incorporated with the cracking component in any suitable manner. Impregnating techniques, may be advantageously employed by first forming an aqueous solution of a water-soluble compound of the desired metal such as platinum chloride, palladium chloride, nickel nitrate, ammonium molybdate, molybdic acid, chloroplatinic acid, chloropalladic acid, etc., and commingling the solution with the alumina-silica cracking component in a steam drier. In addition to this method, a separate aqueous solution of the metal halide or other metal salt and ammonium hydroxide is added thereto to give the solution a pH between the range of about 5 to about 10. The resulting solution is then commingled with the other cracking component of the catalyst. Other suitable metal-containing solutions or suspensions including the desired metal cyanides, metal hydroxides, metal oxides, metal sulfides, etc. Where these solutions are not water-soluble at the temperature employed, other suitable solvents such as alcohols, ethers, etc., may be utilized.

The final catalytic composite, after all of the catalytic components are present therein, is dried for a period of from about 2 to about 8 hours or more in a steam drier, and subsequently oxidized in an oxygen-containing atmosphere, such as air, at an elevated temperature of about 1100° F. to about 1700° F. for a period of from about 1 to about 8 hours or more. Following this high-temperature oxidation procedure, the catalyst is reduced for a period ranging from about one-half hour to about 1 hour at a temperature within the range of about 700 to about 1000° F., in the presence of hydrogen. Where desired, the catalyst may be reduced in situ, that is, by placing the catalyst within the second reaction zone, and subjecting the same to a hydrogen purge of the system at a temperature of about 600° F.

As hereinbefore set forth, the alumina is present within the solid support in an amount ranging from about 25% to about 65% by weight, while the total metallic components of the final catalyst, employed within the second reaction zone, are present therein within the range of from about 0.1% to about 20.0% by weight of the total catalyst. The Group VI–B metal, such as chromium, molybdenum or tungsten, is usually present within a range of from about 0.5% to about 10.0% by weight of the catalyst. The Group VIII metals, which may be divided into two sub-groups, are present in an amount of from about 0.1% to about 10.0% by weight of the total catalyst. When an iron sub-group metal such as iron, cobalt or nickel, is employed, it is present in an amount of from about 1.0% to about 10.0% by weight, while, if a noble metal such as platinum, palladium, iridium, etc., is employed, it is present in an amount within the range of from about 0.1% to about 5.0% by weight of the total catalyst. When the metallic component of the hydrocracking catalyst consists of both a Group VI–B metal and a Group VIII metal, it will contain metals of the above groups in a weight ratio of from about 0.05:1 to about 5.0:1 of the Group VIII metallic component to the Group VI–B metallic component.

The catalyst employed in the second stage of the process of the present invention, is preferably disposed within the reaction zone as a fixed bed. The substantially nitrogen-free, middle-distillate charge stock, after being combined with hydrogen in an amount of from about 1000 standard cubic feet to about 6000 standard cubic feet per barrel thereof, is raised to a temperature within the range of about 500° F. to about 950° F. Due to the characteristics of the middle-distillate, employed as the charge stock to the second-stage, the operating conditions within the reaction zone are relatively mild. Therefore, the operating temperature at which the catalyst is maintained may be at least about 50° F. less than the temperature employed in the first reaction zone. It is not unusual, in the process of the present invention, to experience a temperature as much as 150° F. lower than that maintained within the first zone. In addition, in view of the nature of the middle-distillate charge stock, there exists the requirement for a lesser quantity of hydrogen within the second reaction zone, and furthermore, the rate of liquid charge may be substantially increased, within the range of from about 1.0 to about 15.0 liquid hourly space velocity. The total effluent from the hydrocracking reaction zone is passed to a suitable separation zone from which a hydrogen-rich gas stream is withdrawn and recycled to supply at least a portion of the hydrogen which is admixed with the middle-distillate charge stock. Where produced, the light paraffinic hydrocarbons, including methane, ethane and propane, are also removed in the separation zone. The normally liquid hydrocarbons, containing butanes and hydrocarbons boiling within the range of about 100° to about 400° or 450° F., are subjected to a fractionation procedure for the purpose of removing any unconverted middle-distillate boiling range hydrocarbons which are recycled to combine with the original hydrocarbon charge entering the second reaction zone. The gasoline boiling range hydrocarbons are removed from the upper portion of the fractionating column and combined with those gasoline boiling range hydrocarbons produced in the first stage of the overall process.

It is understood that the broad scope of the present invention is not to be unduly limited to a particular catalytic composite, or a particular means of manufacturing the same. The utilization of any of the previously mentioned catalytic composites, whether in the first or second reaction zones, at operating conditions which vary within the limits hereinabove set forth, do not necessarily yield results equivalent to those obtained through the utilization of another catalytic composite. An essential feature of the present invention is the separate, distinct two stages in which the overall process is effected. Through the utilization of the process of the present invention, greater concentrations of hydrocarbons boiling within the gasoline and middle-distillate boiling range are produced from those hydrocarbons which boil above the middle-distillate boiling range. Furthermore, greater concentrations of gasoline boiling range hydrocarbons are produced from those middle-distillate boiling range hydrocarbons which have been produced in the first stage of the process. The overall picture results in a substantial reduction in

the quantity of light paraffinic hydrocarbons, such as methane, ethane and propane, otherwise resulting from the non-selective, one-stage hydrocracking of hydrocarbons boiling at a temperature in excess of the gasoline boiling range. An added advantage is the fact that the utilization of the present invention effects a preservation of the aromatic hydrocarbons boiling within the gasoline boiling range, and, as hereinbefore set forth, such aromatic hydrocarbons are valuable as motor fuel blending components. Thus, through the utilization of the process of the present invention, a hydrocarbon charge stock, having a boiling range totally above about 650° F. to 700° F., may be substantially completely converted into hydrocarbons boiling within the gasoline boiling range, notwithstanding the presence of excessive quantities of nitrogenous compounds, without the usual exceedingly high yield loss due to the formation of an excessive quantity of light paraffinic hydrocarbons, and without experiencing rapid deactivation of the catalytic composite employed. The process of the present invention may be effected in any suitable manner, and may comprise either a batch or a continuous-type operation. When utilizing a continuous-type operation, which is the particularly preferred manner of effecting the present invention, the catalyst may be disposed as a fixed bed in a reaction zone, as illustrated in the accompanying drawing, and maintained under the desired operating conditions. The hydrocarbons and hydrogen are admixed and continuously charged to the reaction zones, passing in downward flow through the catalyst, or, where desired, either in upward flow or radial flow. The operation may 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.

The following example is given to further illustrate the process of the present invention, and to indicate the benefits to be afforded through the utilization thereof. It is understood that the example is given for the sole purpose of illustration, and not to limit the generally broad scope and spirit of the appended claims.

Example

This example is given for the purpose of illustrating the process of the present invention as applied to a hydrocarbon fraction boiling entirely beyond the gasoline boiling range, and substantially completely above the middle-distillate boiling range. The charge stock employed was a vacuum gas oil derived from a Wyoming-West Texas crude oil. As indicated in the following Table I, the charge stock had a gravity, ° API at 60° F., of 20.6, an initial boiling point of 590° F., with 95 vol. percent being distilled at a temperature of 990° F.; in addition, the vacuum gas oil was contaminated by total nitrogen in an amount of about 1,300 parts per million.

TABLE I.—VACUUM GAS OIL—PROPERTIES

Gravity, ° API @ 60° F.	20.6
ASTM Distillation, ° F.:	
IBP	590
10%	722
30%	790
50%	835
70%	872
90%	920
95%	990
E.P.	—
Percent @ 400° F.	0
Percent bottoms	2.5
Total nitrogen, p.p.m.	1300

The catalyst employed comprised 2.0% by weight of nickel and 22.5% by weight of molybdenum, calculated as the elements thereof. The catalyst was prepared utilizing a single impregnation technique whereby 100 weight parts of alumina spheres (prepared in accordance with the oil-drop method as detailed in U.S. Patent No. 2,620,314, issued to James Hoekstra), and an impregnating solution containing nickel hydrate hexahydrate (2.4 weight parts of nickel) and molybdic acid (30.0 weight parts of molybdenum). The catalyst was disposed in a reaction zone maintained under an imposed pressure of 1,500 pounds per square inch, and an inlet temperature thereto of 770° F. The liquid change was at a rate of 0.5 liquid hourly space velocity, and was combined with hydrogen in an amount of 6,000 standard cubic feet per barrel. Following a separation procedure to remove ammonia and the light paraffinic hydrocarbons (C_1–C_3), the normally liquid product effluent was fractionated, in a multi-plate distillation column, to yield four individual component fractions. These component fractions were, first a butane-to-180° F. end point fraction, a 180° F.-to-400° F. gasoline fraction, a 400° F.-to-650° F. (middle-distillate) fraction, and a bottoms fraction containing those hydrocarbons and nitrogenous compounds boiling at a temperature above 650° F. In regard to the quantity of residual nitrogenous compounds contained within these fractions, reference is again made to the accompanying drawing. The total normally liquid hydrocarbon effluent, following separation to remove ammonia and the light paraffinic hydrocarbons, that is, the stream indicated in the drawing as being line **10**, contained approximately 18 p.p.m. of total nitrogen. Following fractionation, the total nitrogen content of the 180° F.-to-400° F. fraction was effectively nil, that of the middle-distillate fraction (indicated as line **18** in the drawing) was less than 3.0 p.p.m. of nitrogen, while the hydrocarbon stream, indicated as being recycled through line **13** and pump **14**, contained approximately 40.0 p.p.m. of nitrogen. Other product inspections performed upon the various fractions are indicated in the following table II.

TABLE II.—PRODUCT INSPECTIONS—VACUUM GAS OIL

Fraction [1]	180°–400°	400°–650°	650°+
Volume percent of Total	22.6	47.0	30.0
Gravity, °API	47.8	37.5	37.5
ASTM Distillation, ° F.:			
IBP	240	425	670
10%	280	468	710
30%	312	501	735
50%	320	530	764
90%	359	610	865
E.P	398	653	910
Hydrocarbon Types, Vol. Percent:			
Paraffins	41	----------	----------
Naphthenes	51	----------	----------
Olefins	1	----------	----------
Aromatics	7	----------	----------

[1] Light Paraffins (C_1–C_3) was 2.2% by weight and the C_4–180° F. fraction was 3.0 vol. percent.

To illustrate the second stage of the process of the present invention, those hydrocarbons boiling within the range of 400° F. to 650° F., were charged to a reaction zone containing a catalyst comprising 6.0% by weight of nickel (calculated as the element) and a composite of 75% by weight of silica and 25% by weight of alumina. The silica-alumina carrier material was prepared by diluting 1610 grams of water glass (28% by weight of SiO_2) with 3220 cc. of water, adding thereto 400 cc. of hydrochloric acid, plus an additional 800 cc. of water. The resulting acid-silica hydrosol was then added to 1580 cc. of an aluminum sulfate solution, said solution having a specific gravity of 1.28, and being prepared from iron-free hydrated aluminum sulfate crystals. The resultant alumina-silica hydrosol was then commingled, with vigorous stirring, to 1280 cc. of an aqueous solution of ammonium hydroxide containing 640 cc. of a 28% by weight solution of ammonia. The resulting hydrogel was filtered, reslurried in 8 liters of water, and dried. The dried material was subjected to several washing procedures, with filtering, until the filtrate indicated a negative test for sulfate ions. The sulfate-free composite

was further dried at a temperature of 300° F., ground into a fine powder, and formed into 1/8" x 1/8" cylindrical pills. The pills were subjected to a high-temperature calcination procedure, in an atmosphere of air, for a period of 3 hours at a temperature of 1200° F. An impregnating solution was then prepared by dissolving 60.0 grams of nickel nitrate hexahydrate in water, and further diluting the resulting solution to about 700 milliliters with water. A 200-gram portion of the previously described alumina-silica composite was impregnated with the resulting impregnating solution in a rotating steam drier; the dried catalyst was subsequently calcined at an elevated temperature of 1200° F.

This catalyst was disposed within a reaction zone, as a fixed bed, and maintained under an imposed pressure of 1,500 pounds per square inch. During the processing of the middle-distillate charge stock, the inlet temperature to the reactor was maintained at a temperature of 620° F. The charge stock was introduced to the reaction zone at a rate equivalent to 3.0 liquid hourly space velocity, admixed with hydrogen in an amount of 3000 standard cubic feet per barrel. The total reaction zone effluent was separated to provide a hydrogen-rich gas stream which was recycled to combine with the middle-distillate charge stock. The remaining normally liquid hydrocarbons, including the light paraffinic hydrocarbons (C_1–C_3) was subjected to fractionation in a laboratory, multi-plate distillation column. The results of the fractionation are indicated in Table III.

TABLE III.—MIDDLE-DISTILLATE, VOLUMETRIC YIELDS

Components [1]	Yield, vol. percent
Total butanes	7.9
Pentanes+hexanes	15.3
Heptanes—400° F.	47.2
	70.4
400° F. and heavier	39.5

[1] Light paraffinic hydrocarbons (C_1–C_3) was 0.67% by weight.

The yields are based upon the quantity of middle-distillate being charged, and it is noted that the light paraffinic hydrocarbons resulting therefrom were virtually negligent, being only 0.67% by weight. It is noted that there was a 70.4 volumetric percent yield of hydrocarbons boiling within the gasoline boiling range, including butanes, and 39.5% yield of hydrocarbons boiling in the middle-distillate boiling range. The latter fraction may be readily recycled to combine with the original middle-distillate charge stock, whereby these hydrocarbons are effectively recycled to extinction. In addition, the data of Table III, in conjunction with that presented in Table II, indicates a relatively minor total quantity of light paraffinic hydrocarbon production, less than about 3.0% by weight of the total vacuum gas oil charged. Of greater significance, however, is the fact that there resulted a volumetric increase in both of the reaction zones, taken separately. The total volumetric yield of those hydrocarbon fractions resulting from the first reaction zone, including the 3.0 vol. percent of C_4-to-180° F., was 111.6%. As indicated in Table III, the total volumetric yield was 109.9%.

The embodiment of the process of the present invention illustrated in the foregoing example, clearly indicates the benefits to be afforded through the utilization of the present invention in producing aromatic-containing hydrocarbons boiling within the gasoline boiling range from hydrocarbons boiling in excess of the gasoline boiling range. As indicated in Table II, the 180° F. to 400° F. fraction contained a total of 58.0 volume percent of naphthenes and aromatics. It will be readily ascertained that this fraction is, therefore, extremely well suited as charge to a catalytic reforming unit. Furthermore, the example illustrates the applicability of the present invention when processing heavier hydrocarbon fractions (boiling substantially in excess of the middle-distillate boiling range), which are contaminated by relatively excessive quantities of nitrogenous compounds.

I claim as my invention:

1. A process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling at a temperature above the gasoline boiling range and containing in excess of 1000 parts per million of nitrogenous compounds, which comprises reacting said charge stock and hydrogen in a first reaction zone in contact with a nitrogen-insensivte catalyst under conditions to convert the bulk of said nitrogenous compounds to ammonia, removing the ammonia from the resulting effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of about 650° F. to about 700° F. and substantially free from nitrogenous compounds, and a third fraction boiling above a temperature of about 650° F., thereby concentrating the remainder of said nitrogenous compounds in said third fraction; recycling said third fraction containing the residual nitrogenous compounds to combine with said hydrogen and charge stock, admixing said second fraction with hydrogen and reacting the resultant mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst in a second reaction zone, separating the effluent from said second zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to combine with the aforesaid mixture of hydrogen and said second fraction.

2. The process of claim 1 further characterized in that said nitrogen-insensitive catalyst comprises at least about 6.0% by weight of molybdenum, calculated as the element.

3. The process of claim 1 further characterized in that said nitrogen-sensitive catalyst comprises at least one metallic component selected from the metals of Groups VI–B and VIII of the Periodic Table.

4. The process of claim 3 further characterized in that said nitrogen-sensitive catalyst comprises from about 2.0% to about 10.0% by weight of nickel, calculated as the element, and a composite of silica and alumina.

5. A process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling above the gasoline boiling range and containing in excess of 1000 parts per million of nitrogenous compounds, which comprises reacting said charge stock and hydrogen in a first reaction zone in contact with a nitrogen-insensitive catalyst comprising from about 6.0% to about 45.0% by weight of molybdenum, calculated as the element, under conditions to convert the bulk of said nitrogenous compounds to ammonia, removing the ammonia from the resultant effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400 to about 450° F. a second fraction having an end boiling point of about 650° to about 700° F. and substantially free from nitrogenous compounds, and a third fraction boiling at a temperature above about 650° F., thereby concentrating the remainder of said nitrogenous compounds in said third fraction; recycling said third fraction containing the residual nitrogenous compounds to combine with said hydrogen and charge stock, admixing said second fraction with hydrogen and reacting the resultant mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst comprising from about 2.0% to about 10.0% by weight of nickel and a composite of silica and alumina in a second reaction zone, separating the effluent from said second zone into a light fraction having an end boiling point of

about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to combine with the aforesaid mixture of hydrogen and said second fraction.

6. The process of claim 5 further characterized in that said first reaction zone is maintained under an imposed pressure of from about 100 to about 3,000 pounds per square inch and at a temperature within the range of from about 500° F. to about 1,000° F.

7. The process of claim 5 further characterized in that said second reaction zone is maintained under an imposed pressure of from about 100 to about 3,000 pounds per square inch and at a temperature of at least about 50° F. lower than the temperature at which said first reaction zone is maintained.

8. The process of claim 5 further characterized in that said nitrogen-sensitive catalyst comprises from about 0.1% to about 2.0% by weight of palladium, from about 2.0% to about 10.0% by weight of nickel and a composite of silica and alumina.

9. The process of claim 5 further characterized in that said nitrogen-sensitve catalyst comprises from about 0.1% to about 2.0% by weight of platinum, from about 2.0% to about 10.0% by weight of nickel and a composite of silicia and alumina.

10. A process for producing gasoline boiling range hydrocarbons from a nitrogen-contaminated charge stock boiling at a temperature above the gasoline boiling range, and containing from about 1,000 to about 5,000 p.p.m. of nitrogenous compounds, which comprises reacting said charge stock and hydrogen in a first reaction zone in contact with a nitrogen-insensitive catalyst comprising from about 6.0% to about 45.0% by weight of molybdenum, calculated as the element, under conditions to convert the bulk of said nitrogenous compounds to ammonia, removing the ammonia from the resultant effluent, thereafter separating said effluent into a first fraction having an end boiling point of about 400° F. to about 450° F., a second fraction having an end boiling point of about 650° F. to about 700° F., and substantially free from nitrogenous compounds, and a third fraction boiling at a temperature above about 650° F., thereby concentrating the remainder of said nitrogenous compounds in said third fraction; recycling said third fraction containing the residual nitrogenous compounds directly and without intervening treatment to said first reaction zone, admixing said second fraction with hydrogen and reacting the resultant mixture, at hydrocracking conditions, in contact with a nitrogen-sensitive hydrocracking catalyst comprising from about 2.0% to about 10.0% by weight of nickel, calculated as the element, and a composite of silica and aluminia in a second reaction zone, separating the effluent from said second reaction zone into a light fraction having an end boiling point of about 400° F. to about 450° F. and a heavy fraction containing hydrocarbons boiling above a temperature of about 400° F. to about 450° F., and recycling said heavy fraction to said second reaction zone.

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