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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

Hydrocracking Process

We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of No. 30 Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the conversion of nitrogen-containing hydrocarbons into lower boiling hydrocarbon products, and particularly a process for producing hydrocarbons boiling within the gasoline boiling range from hydrocarbons which boil largely in excess of the gasoline boiling range and which are contaminated by substantial quantities of 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 definite changes in the molecular structure of the hydrocarbons being processed. Therefore, hydrocracking 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, tars and heavy residual oils for the purpose of producing substantial yields of low boiling saturated products, intermediates which are suitable for utilization as domestic fuels, and heavier gas-oil fractions which find utilization as domestic fuels, and heavier gas-oil fractions which find utilization as suitable lubricants. Although many of these hydrocracking reactions may

be conducted on a thermal basis, the preferred processing technique involves the utilization of a catalytic composite possessing a high degree of hydrocracking activity. However, in virtually all hydrocracking processes, whether thermal or catalytic, controlled or selective cracking is desirable from the standpoint of producing an increased yield of liquid product having improved anti-knock characteristics, and to assure effective catalytic action over an extended period of time. In general, the lower molecular weight hydrocarbons which boil within the gasoline range possess higher octane ratings, and a hydrocracked product of lower average molecular weight will therefore usually have a higher octane rating.

Selective hydrocracking is of particular importance when processing hydrocarbons and mixtures of hydrocarbons which boil at a temperature in excess of the gasoline and middle-distillate boiling range; that is, hydrocarbons and mixtures of hydrocarbons, having an initial boiling point of from about 343° to 371°C., and an end boiling point of 538°C. or higher. Selective hydrocracking of such hydrocarbon fractions results in greater yields of hydrocarbons boiling within the gasoline and middle-distillate boiling range; that is, below about 343° to about 371°C., as well as substantially increased yields of gasoline hydrocarbons, that is, those boiling within the range of from about 38° up to about 204° or 232°C., and containing iso- and normal butane. Hydrocracking processes must be selective in order to avoid excessive decomposition of normally liquid gasoline hydrocarbons into normally gaseous hydrocarbons, because otherwise the yield of gasoline produced can be decreased to the extent where the process is not economically feasible. Desired selective hydrocracking involves the splitting of a higher-boiling hy-

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drocarbon molecule into two molecules, both of which are normally liquid hydrocarbons. Also, in selective hydrocracking the removal of methyl, ethyl and propyl groups, which, in the presence of hydrogen, are converted to the so-called "light paraffinic hydrocarbons" namely methane, ethane and propane, is controlled such that preferably not more than one, or possibly two, of such radicals 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 and nonane to octane or heptane. On the other hand, uncontrolled, or non-selective hydrocracking, will result in the decomposition of normally liquid hydrocarbons into normally gaseous hydrocarbons, as for example, the conversion of normal heptane into seven molecules of methane.

Another disadvantage of non-selective hydrocracking is the more rapid formation of coke and other heavy carbonaceous material which deposit upon the catalyst and decrease the activity thereof for the desired reactions, thereby shortening the processing cycle and necessitating more frequent regeneration of the catalyst, or early replacement thereof with fresh catalyst. The deactivation of the catalyst also appears to inhibit the hydrogenation activity to the extent that a significant proportion of the gasoline boiling range hydrocarbon fraction consists of unsaturated hydrocarbons, whereby the same is not highly suited for direct processing by catalytic reforming. Selective hydrocracking does not tend to effect substantial hydrogenation, or saturation, of the aromatic compounds, which possess a high octane blending value, and are, therefore, utilized to great advantage to increase the anti-knock characteristics of gasoline boiling range fractions.

Nitrogen-containing compounds within the hydrocracking feed stock, such as pyroles, amines, indoles, and other classifications of organic nitrogenous compounds, result in the relatively rapid deactivation of the catalytically active metallic components 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 by the formation of complexes of nitrogen and components of the catalyst. Such deactivation is not a simple reversible phenomenon since it cannot be 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 hydrocracking process which increases substantially the yield of hydrocarbons boiling within the gasoline boiling range and attains an effectively controlled hydrocracking by avoidance of the disadvantages ordinarily arising from nitrogenous contaminants and uncontrolled cracking.

The process for the catalytic hydrocracking of hydrocarbons in accordance with the present invention comprises reacting a stream of a hydrocarbon oil charge boiling at least predominantly above 204°C. and containing nitrogenous compounds in a first reaction zone with hydrogen in the presence of a nitrogen-insensitive hydrorefining catalyst with formation of ammonia from the nitrogenous compounds, removing the ammonia from the effluent of said first reaction zone, then separating from said effluent a light normally liquid fraction having an end boiling point of from 204° to 232°C. and also separating from said effluent a heavier fraction containing effluent components boiling between the end boiling point of said light fraction and 343°C.; reacting a stream of said heavier fraction in a second reaction zone with hydrogen in the presence of a nitrogen-sensitive hydrocracking catalyst, and commingling at least the normally liquid portion of the effluent of said second reaction zone with the normally liquid portion of the effluent of said first reaction zone prior to the separation of said light fraction therefrom.

In a specific embodiment of the invention the mixture of the total normally liquid components of the effluents from the first reaction zone and the second reaction zone is separated into a first fraction having an end boiling point of from 204° to 232°C., a second fraction having an end boiling point of from 343° to 371°C. and a third fraction containing those hydrocarbons of said mixture which boil above said second fraction, a stream of said second fraction is reacted with hydrogen in the second reaction zone, and at least a portion of the third fraction is subjected together with the hydrocarbon charge stream to the reaction with hydrogen in the first reaction zone. In this embodiment, a portion of said third fraction may be commingled, if so desired, with the stream of said second fraction passing to the second reaction zone.

The nitrogen-insensitive catalyst employed in the first reaction zone preferably contains between 4.0% and 45.0% by weight of molybdenum and between 0.2 and 10.0% by weight of nickel on a support consisting at least largely of alumina, the amount of nickel being smaller than the amount of molybdenum in the catalyst, and the support containing advantageously up to 12% by weight of silica. The nitrogen-sensitive catalyst used in the second reaction zone generally

comprises at least one metallic component selected from the metals of Groups VI-A and VIII of the Periodic Table and mixtures thereof on a support which is in itself a cracking catalyst. This nitrogen-sensitive catalyst preferably contains between 0.5 and 10% by weight of nickel or between 0.1 and 5.0% by weight of a platinum group metal on a support consisting of from 88 to 75% by weight of silica and from 12 to 25% by weight of alumina.

In the operation of the process of this invention, it is preferred that the first and second reaction zones be maintained under a pressure of about 68 to about 204 atmospheres and that the first reaction zone be maintained at a temperature substantially within the range of from 260° to 538°C., while the second reaction zone is maintained at a temperature substantially within the range of from 260° to 510°C. and advantageously from 28°C. to 83°C. lower than the temperature within the first reaction zone.

The present process may be more clearly understood through reference to the accompanying diagrammatic drawing which illustrates one embodiment thereof. In the drawing, various flow valves, control valves, coolers, condensers, overhead reflux condensers, pumps, compressors, knockout pots, and miscellaneous appurtenances have been omitted since they are not essential to the complete understanding of the present process and their utilization in the present operation will immediately be recognized by those familiar with the art of petroleum processing. Referring now to the drawing, the hydrocarbon charge stock, contaminated by a substantial quantity of nitrogenous compounds, such as about 1000 to about 5000 ppm. (= parts by weight per million parts), and sulfurous compounds as high as 3.0% by weight, enters the process through line 1 into line 3, wherein it is admixed with hydrogen entering via line 2. Although the hydrocarbon charge may have a boiling range from an initial boiling point of 343°C., to an end boiling point of 538°C. or more, the hydrocarbon charge in line 1 is not intended to be limited to this boiling range. Accordingly, the hydrocarbon charge stock may consist entirely of a heavy vacuum gas oil, or recycle stock, having the indicated boiling range, or the hydrocarbon charge stock may be a kerosine fraction boiling partially within the gasoline boiling range and largely within the middle-distillate boiling range; that is, a hydrocarbon charge having a boiling range of from about 177°C. to about 288°C. or 316°C. The terms "middle-distillate" and "light gas oil" refer to those hydrocarbon fractions having an initial boiling point within the range of about 204° to about 232°C., and an end boiling point within the range of from about 343° to about

371°C. 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 from about 316°C. to about 510°C. The process of the present invention is especially adaptable to the processing of those nitrogen-contaminated hydrocarbons boiling substantially entirely in excess of the middle-distillate 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 178 to about 1425 normal liters per liter of such liquid hydrocarbon charge. The mixture is raised to a temperature of about 260°C. to about 538°C. in heater 4, and is passed through line 5 into clean-up reactor 6. Clean-up reactor 6 is maintained under an imposed pressure of from about 6.8 to about 204 atmospheres and has disposed therein, in one embodiment, a nitrogen-insensitive catalyst containing at least about 4.0% by weight of molybdenum, calculated as the element thereof. The hydrocarbon charge stock will contact the particular catalyst employed at a liquid hourly space velocity (defined as volumes of liquid charge per hour per volume of catalyst within the reaction zone), within the range of from about 0.5 to about 10.0. Under these conditions, and in the presence of the molybdenum-containing catalyst, the organically-bound, nitrogen compounds are separated at the nitrogen-hydrogen bonds to form ammonia which is released in a free form from the reaction media. Furthermore, any sulfurous compounds, such as for example mercaptans and thiophenes, are converted into hydrogen sulfide and the corresponding sulfur-free hydrocarbon. In addition to this effective clean-up of the hydrocarbon charge stock, a significant degree of hydrocarbon conversion occurs whereby the heavier hydrocarbons, boiling at a temperature of from about 371°C. to about 538°C., are converted, via highly selective cracking reactions into hydrocarbons boiling below about 371°C. The conversion reactions are such that very little, if any, light, straight-chain paraffinic hydrocarbons are produced. The total reactor effluent is removed from clean-up reactor 6 through line 7 into separator 8.

Although indicated as a single vessel, the separation device illustrated by separator 8 may be any suitable means for separating the normally liquid hydrocarbons, which are indicated in the drawing as being removed from separator 8 via line 10, from a separate gaseous phase which may contain, for example, light paraffinic hydrocarbons, ammonia, hydrogen sulfide, and carbon dioxide, and, which is illustrated in the drawing as leaving separator 8 via line 9. For example,

water may be injected into line 7, being admixed therein with the total reactor effluent, and thereafter subjected to separation such that the ammonia is adsorbed and removed within the water-phase, while the hydrogen sulfide and light paraffinic hydrocarbons are removed in a gaseous phase and the normally liquid hydrocarbons are separately recovered through line 10.

The normally liquid hydrocarbons in line 10 are admixed with the effluent from hydrocracking reactor 26, or at least with the total amount of the normally liquid components of this effluent, as hereinafter described, in line 11 and pass therewith into fractionator 12. Fractionator 12 is operated at any suitable conditions of pressure and/or temperature which result in the removal of light paraffinic hydrocarbons (C_1 to C_4) through the line 13, the heavier, normally liquid hydrocarbons, including butanes, being removed from fractionator 12 through line 14 into side-cut fractionator 15. Fractionator 15 contains a center well 16 below which the hydrocarbons enter via line 14. Fractionator 15 is operated under conditions of temperature and pressure such that the gasoline boiling range hydrocarbons, including butanes, are removed through line 17, containing less than 1.0 ppm. of the aforesaid nitrogenous compounds. Hydrocarbons boiling within the middle-distillate boiling range, containing less than 5.0 ppm. of nitrogen, are removed via line 21 from a point above center well 16. Any residual nitrogenous compounds, entering fractionator 15 via line 14, are removed therefrom with the hydrocarbons having a boiling range in excess of about 343° to 371°C. , through line 18. It has been found that the residual nitrogenous compounds are largely contained in the heavy fraction boiling above the middle-distillate boiling range. The middle-distillate boiling range hydrocarbons in line 21 are, at least in part, passed through line 24, containing valve 25, into heater 29. This stream of middle-distillate hydrocarbons may be admixed with the heavier hydrocarbons from fractionator 15 via lines 18 and 20, and is further admixed with hydrogen entering through line 31. If so desired, a portion of the middle-distillate boiling range hydrocarbons may be removed to storage through line 22 containing valve 23.

In those instances where the residual nitrogenous compound concentration in the heavier hydrocarbons leaving line 18 is greater than about 5.0 parts per million, it is not desired to subject the same to conversion in hydrocracking reactor 26, and in such case these hydrocarbons are preferably removed from line 18 to line 3 through valve 19, to combine with the original hydrocarbon charge in line 1 and the hydrogen in line 2.

In this latter method, the hydrocarbons boil-

ing at a temperature in excess of about 343°C. or 371°C. may be recycled to extinction within the process.

In any event, the hydrogen entering through line 31, and combining with the hydrocarbons in line 24, is an amount of from about 178 to about 1070 normal liters per liter of these liquid hydrocarbons. The resulting mixture enters heater 29 wherein it is raised to the desired temperature, within the range of about 260°C. to about 510°C. , and usually at least 28°C. lower than the temperature of the total charge passing through the line 5 to reactor 6. The heated mixture from heater 29 is passed through line 30 into hydrocracking reactor 26. This reaction zone is maintained under an imposed pressure within the range of from about 6.8 to about 204 atmospheres, and has disposed therein, a suitable hydrocracking catalyst which differs from the catalyst in reaction zone 6 by being nitrogen-sensitive and which contains at least one metallic component selected from the metals of Groups VI-A and VIII of the Periodic Table, and mixtures thereof. The hydrocarbon charge is passed from heater 29 through line 30 into hydrocracking reactor 26 at a liquid hourly space velocity within the range of from about 1.0 to about 15.0.

It is preferred that the total effluent from hydrocracking reactor 26 is passed through line 27 containing pump 28, into the line 11 and then is commingled with the normally liquid hydrocarbons in line 10, thereafter passing through line 11 into fractionator 12. Where desired, however, normally gaseous components may first be separated from the effluent from hydrocracking reactor 26, as described further below, and in such case at least the normally liquid components of the effluent from hydrocracking reactor 26 are passed to line 11.

From the foregoing description of the embodiment illustrated in the accompanying drawing, it is readily seen that the present process is, in effect, a two-stage process for producing hydrocarbons boiling within the gasoline boiling range, with built-in flexibility for the purpose of producing increased yields of middle-distillate boiling range hydrocarbons. Various modifications may be made to the illustrated embodiment without departing from the invention. For example, the separating means encompassed within separator 8, may be combined with fractionator 12, 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 indicated flow pattern. An essential feature of the process of the present invention involves the two-stage reactor system, whereby the liquid effluent streams from each individual stage, or reaction zone, are

combined and then subjected to the separation as embodied within fractionator 12 and side-cut fractionator 15. The first stage, utilizing clean-up reactor 6, effects substantially complete destruction of the nitrogenous compounds, as well as sulfurous compounds, contained within the charge stock consisting entirely or at least largely of hydrocarbons boiling in excess of the gasoline boiling range. Through the careful selection of both catalyst and operating conditions, there will be effected, in clean-up reactor 6, a substantial degree of conversion whereby the heavier hydrocarbons, notably those boiling above about 371°C., are converted into lower boiling hydrocarbons without experiencing a substantial production of the light paraffinic hydrocarbons, methane, ethane, and propane. Since the catalyst in clean-up reactor 6 is selected for its nitrogen-insensitivity, the rapid deactivation of such catalyst, otherwise resulting when hydrocracking such nitrogen-containing charge stocks, is not experienced.

The process of the present invention is most advantageously applied to feed stocks which are derived from petroleum; particularly those stocks commonly considered as being heavier than middle-distillate fractions. Such stocks include gas oil fractions, heavy vacuum gas oils, 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 204°C. to about 232°C. and an end boiling point of about 538°C. or higher, the process affords additional benefits when processing hydrocarbon charge stocks having significantly higher initial boiling points, that is, of the order of about 343°C. to about 371°C.

In further describing the process of the present invention, and the various limitations imposed thereupon, 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/or a fractionator, and these are utilized in such a manner, and under such conditions as to result in the substantially complete removal of nitrogenous and sulfurous compounds from the hydrocarbon charge stock, while producing both gasoline boiling range hydrocarbons as a product, and middle-distillate hydrocarbons which serve as the greater proportion of the charge stock to the second stage of the entire process. The heavy hydrocarbon charge stock contaminated by nitrogenous compounds after admixture with the hydrogen and heating to the desired operating temperature, is contacted with the nitrogen insensitive catalyst in the first reaction zone, the precise operating conditions of which will

be dependent upon the various physical and chemical characteristics of the particular hydrocarbon charge being processed. In any event, the reactor will be maintained at a temperature substantially in the range of from 260°C. to 538°C. and under an imposed pressure generally within the range of from 6.8 to 204 atmospheres. High pressures in this range appear to favor the destructive removal of nitrogenous compounds, as well as the conversion of those hydrocarbons boiling at a temperature in excess of about 371°C. and are, therefore, preferred; thus, the first reaction zone is preferably operated under an imposed pressure within the range of from about 68 to about 204 atmospheres. While the hydrocarbon charge stock will contact the particular catalyst employed at a liquid hourly space velocity generally within the range of about 0.5 to about 10.0, a lower range of liquid hourly space velocity will be employed, that is, about 0.5 to about 3.0, in those instances where the heavy hydrocarbon charge is contaminated by relatively large quantities of nitrogenous compounds. 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 both nitrogenous compounds and sulfurous compounds, while at the same time it is capable of effecting both the destructive removal thereof and also the conversion of those hydrocarbons boiling at a temperature in excess of about 343°C. or 371°C. 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 in this first reaction stage. A particularly preferred catalytic composite, for utilization in this first reaction zone, comprises from about 4.0% to about 45.0% by weight of molybdenum, and utilizes alumina as the carrier material. It is preferred to utilize alumina in the absence of other refractory inorganic oxide material, such as silica, zirconia, magnesia, titania, thorina and boria. Although these refractory inorganic oxides may be employed in relatively minor quantities, with respect to the amount of alumina, preferably not more than about 12% by weight of the composite with the alumina, they appear in some cases to impart excessive cracking activity to the catalyst within the first reaction zone, such that those hydrocarbons boiling in excess of about 343°C. or 371°C. would be subjected to non-selective cracking with production of an excessive quantity of light paraffinic hydrocarbons. Minor amounts of nickel, namely from about 0.2% to about 10.0%, or like quantities of cobalt and/or iron may be employed in combination with the relatively larger amounts of

molybdenum.

The catalytic composite, for utilization in the first reaction zone, may be manufactured in any suitable manner, a particularly advantageous method employing an impregnating technique. 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 for example as nickel nitrate or nickel carbonate, and ammonia molybdate or molybdic acid. The alumina particles, serving as the carrier material, are commingled with the aqueous solutions, and subsequently are dried at a temperature of about 93°C. The dried composite is then subsequently oxidized in an oxidizing atmosphere such as air, at an elevated temperature of from about 593°C. to about 927°C., and for a period of from about 2 to about 8 hours or more.

The gaseous ammonia and hydrogen sulfide, resulting from the destructive removal of nitrogenous and sulfurous compounds in the first reaction stage are removed from the total reaction zone effluent in any suitable manner. For example, the total effluent may be admixed with water, and thereafter subjected to separation such that the ammonia is absorbed within the water-phase. Or, the total reaction zone effluent may be passed into a separation zone countercurrently to a liquid absorbent whereby the ammonia, hydrogen sulfide, and other gaseous components are effectively removed therefrom. In addition to the removal of hydrogen sulfide and ammonia, it is desired that the small amount of light paraffinic hydrocarbons, methane, ethane and propane, resulting from the rather severe conditions in the first reaction zone, is also removed from the effluent. Therefore, the separating zone may comprise a low-temperature flash chamber whereby the ammonia and light paraffinic hydrocarbons are removed as a gas phase. As illustrated in the drawing, these light paraffinic hydrocarbons, along with the normally liquid hydrocarbons, may be passed into a fractionating column, whereby the light paraffinic hydrocarbons are removed from the system. This latter method has the added advantage of being sufficiently flexible to function as a debutanizer or depentanizer where such a processing technique is desired. Furthermore, this method permits the simultaneous fractionation of the effluent from hydrocracking reactor 26 to remove the light paraffinic hydrocarbons therefrom after the removal of ammonia from the effluent from the first stage of the process.

Regardless of the particular separating means employed, the resulting normally liquid hydrocarbons, now boiling within the range of about 38°C. to about 371°C. or higher, and containing butanes, will contain

some residual nitrogenous compounds. The normally liquid hydrocarbons are, therefore, further distilled using a side-cut fractionator under such conditions as will yield a heart-cut boiling within the range of from about 204°C. to about 343°C., which heart-cut fraction is substantially completely free of nitrogenous compounds. Those hydrocarbons which boil below about 204°C. and which include the gasoline boiling range hydrocarbons produced in the second-stage of the present process, are removed from the upper portion of the side-cut fractionator, and may be transmitted to storage pending further use either as charge to a catalytic reforming unit, or as gasoline blending components. The minor quantity of residual nitrogenous compounds is removed in that hydrocarbon fraction boiling above about 343°C., from the bottom portion of the side-cut fractionator.

The second stage of the present process is designed to convert the now nitrogen-free middle-distillate boiling range hydrocarbons, together, if so desired, with at least a portion of the hydrocarbon stream boiling in excess of about 343°C. to about 371°C., into hydrocarbons which boil within the gasoline boiling range. While it has been stated above that the middle-distillate boiling range charge stock for the second-stage reaction zone 26 contains less than about 5.0 parts per million of nitrogenous compounds, it is preferred that the fractionation system be operated at conditions which result in a middle-distillate boiling range hydrocarbon mixture containing less than about 1 part per million of nitrogen, and still more preferably, less than about 0.3 ppm. of nitrogen. In any event, when the hydrocarbons boiling above about 343°C. to 371°C. contain sufficient residual nitrogenous compounds to result, upon their supply to the second-stage reaction stage, in a total nitrogen concentration entering hydrocracking reactor 26, in excess of 5.0 ppm., these hydrocarbons will be recycled through valve 19 and line 3 to combine with the original hydrocarbon charge, for the purpose of removing the excessive quantity of nitrogenous compounds. In such a situation, for the purpose of maintaining virtually steady-state operation within the hydrocracking reactor 26, a greater proportion of middle-distillate will be processed through this reaction zone.

In view of the fact that the total hydrocarbon charge to the second reaction zone may contain up to about 5.0 ppm. of nitrogen, it is to great advantage to utilize certain catalytic composites therein which are most effective for the mild hydrocracking of the middle-distillate charge stock containing these residual nitrogenous compounds, but are not detrimentally affected thereby. As an illustration, alumina is a good nitrogen

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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, is not a good nitrogen remover. In a similar manner, the metallic components of the catalyst disposed within the second reaction zone 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 and of itself, in regard to the removal of nitrogenous compounds. Catalytic composites which comprise at least one metallic component selected from Groups VI-A and VIII of the Periodic Table including 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 and molybdenum-nickel-palladium, and a composite of silica and from about 10% to about 90% by weight of alumina, constitute hydrocracking catalysts, for use in the second stage of the process of the present invention, which have a relatively high activity in regard to 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 5.0 parts per million.

The synthetically-produced solid carrier material, for utilization in the catalyst of the second stage, which carrier material also possesses hydrocracking propensities, 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 or ammonium carbonate, to a salt of aluminum such as aluminum chloride, aluminum nitrate, or aluminum acetate, in an amount to form aluminum hydroxide. 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 resulting precipitate is, upon drying, converted to alumina. The alumina particles may take the form of any desired shape such as spheres, pills, or extrudates. 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; this particular method, commonly known as the oil-drop method, is described in detail in U.S. Patent No. 2,620,314, issued to James Hoekstra. It is understood that the foregoing description, in regard to the preparation of alumina particles, is applicable to the preparation of the carrier material employed in the manufacture of the catalytic composite which is utilized in the first reaction zone. In 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 with water containing a small amount of suitable electrolyte for the purpose of removing sodium ions. Other refractory oxide components may be prepared in a manner analogous to that outlined above with reference to the alumina.

The cracking catalyst component of the catalyst for the second reaction stage of the present process comprises at least two refractory inorganic oxides, and such a composite may be prepared in any suitable manner including, separate, 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 in the manner set forth above, and wet slurry, either with or without prior washing, is composited with a salt of the other component. Precipitation of the oxide of the latter is effected by the addition of a suitable alkaline or acidic material to the resulting slurry. The composite which results may then be dried and formed into the desired shape and/or size. 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 or sulfuric acid, with commercial water glass under conditions to precipitate silica, washing the precipitate with acidulated water or other means to remove sodium ions, commingling with an aluminum salt such as aluminum chloride, and/or some suitable zirconium salt, and either adding a basic precipitant such as ammonium hydroxide to precipitate alumina and/or zirconia, or forming the desired oxide or oxides through the 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.

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 and 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 for example platinum chloride, palladium chloride, nickel nitrate, ammonia molybdate, molybdic acid, chloroplatinic acid, or chloropalladic acid, and commingling the solution with the cracking component in a steam drier. Other suitable metal-containing solutions which may be employed are colloidal solutions or suspensions of the desired metal cyanides, metal hydroxides, metal oxides, or metal sulfides. Where these solutions are not water-soluble at the temperature employed, other suitable solvents such as alcohols or ethers, 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, and subsequently oxidized in an oxidizing atmosphere such as air, at an elevated temperature of from about 593°C. to about 927°C. and 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 $\frac{1}{2}$ hour to about 1 hour at a temperature within the range of from about 371°C. to about 538°C., and 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 an imposed hydrogen purge of the system at a temperature of about 316°C.

As hereinbefore set forth, it is preferred that the catalyst within the second reaction zone comprises at least two refractory inorganic oxides, preferably alumina and silica. When silica and alumina are employed in combination, the latter will be present generally with an amount of from about 10% to about 90% by weight. As shown in the examples below, excellent results have been achieved through the utilization of the composites of 88% by weight of silica and 12% by weight of alumina, and of 75% by weight of silica and 25% by weight of alumina, in the catalyst of the second reaction stage, and through the utilization of a composite of 88% by weight of alumina and 12% by weight of silica in the catalyst of the first reaction stage. While the total quantity of metallic components of the catalyst disposed within the second reaction zone is within the range of from about 0.1% to about 20.0% by weight of the total

catalyst, the Group VI-A metal, such as chromium, molybdenum, or tungsten, is usually present within the range of from about 0.5% to about 10.0% by weight of this catalyst. When an iron sub-group metal of Group VIII such as iron, cobalt, or nickel, is employed, in this catalyst, it is present in an amount of from about 0.2% to about 10.0% by weight, while, if a noble metal such as for example platinum, palladium, or iridium, is employed, it is present in an amount within the range of from about 0.1% to about 5.0% and preferably between 0.1% and 2.0% by weight of the total catalyst. When the metallic component of the catalyst of the second stage consists of both a Group VI-A 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-A metallic component. Examples of metal components in particularly suitable catalysts for utilization within the second reaction zone are the following: 6.0% by weight of nickel and 0.2% by weight of molybdenum; 6.0% by weight of nickel; 0.4% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of platinum.

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. Due to the characteristics of the charge to the second reaction stage, the operating conditions within the reaction zone are relatively mild. Therefore, the operating temperature at which the catalyst is maintained within the second reaction zone, may be at least about 28°C. less than the temperature employed in the first reaction zone. It is not unusual, in the process of the present invention, to operate the second reaction zone at a temperature which is as much as 83°C. lower than the temperature within the first reaction zone. In addition, in view of the nature of the charge to the second reaction zone, the rate of liquid charge thereto may be substantially larger than that of the charge to the first reaction zone and is usually in the range of from about 1.0 to about 15.0 liquid hourly space velocity. The total effluent from the second reaction zone, may be passed to a suitable high-pressure, low-temperature 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 liquid hydrocarbon charge stock. The normally liquid hydrocarbons, containing the light paraffinic hydrocarbons (C_1 to C_4) and butanes, are combined with the normally liquid hydrocarbons resulting from the separating means employed within the first reaction stage to thereafter remove therefrom those

hydrocarbons boiling within the gasoline boiling range.

An essential feature of the present invention is the system of the two distinct integrated stages in which the overall process is effected. Through the utilization of the process of the present invention, greater concentration of hydrocarbons boiling within the gasoline and middle-distillate boiling range are produced from those hydrocarbons which boil in excess of 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 effect is a substantial reduction in the quantity of light paraffinic hydrocarbons 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 which boil within the gasoline boiling range and are valuable as motor fuel blending components. Furthermore, the process of the present invention results in a gasoline boiling range hydrocarbon product substantially free from unsaturated hydrocarbons, and is, therefore, suited as charge stock to a catalytic reforming unit for the purpose of further raising the octane rating thereof. Thus, through the utilization of the process of the present invention, a hydrocarbon charge stock, having a boiling range in excess of about 343°C. to 371°C., may be substantially completely converted into hydrocarbons boiling within the gasoline boiling range, notwithstanding the presence of exceedingly large quantities of nitrogenous compounds, and without the usual high yield loss due to the formation of an excessive quantity of light paraffinic hydrocarbons and also without experiencing the catalyst deactivation encountered in a single-stage hydrocracking treatment of such oils as are used as charge in the present process.

When effecting the present process in a continuous manner, it is preferred to utilize each catalyst as a fixed bed in the respective reaction zone, as illustrated in the accompanying drawing. The mixtures of hydrocarbons and hydrogen are continuously charged to the reaction zones and passed in downward flow through the catalyst, or, where desired, they are passed either in upward flow or radial-flow through the respective reaction zones. Alternatively, 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 respective reaction zone.

The following examples are given to fur-

ther illustrate the process of the present invention, and to indicate the benefits to be afforded through the utilization thereof.

EXAMPLE I

This example illustrates the process of the present invention as applied to a hydrocarbon charge boiling entirely above the gasoline boiling range, and almost completely in excess of the middle-distillate boiling range. The charge was a vacuum gas oil obtained from a Wyoming-West Texas crude and had the properties shown in the following Table I in which the distillation data are those determined by the ASTM method.

TABLE I
VACUUM GAS OIL—PROPERTIES
Specific Gravity at 15.6°C. 0.9393

Distillation, °C.		
Initial Boiling Point	310	
10%	383	85
30%	421	
50%	446	
70%	467	
90%	493	
95%	532	90
% at 204°C.	0	
% Bottoms	2.5	
Total Nitrogen, ppm.	1300	
Sulfur, Weight %	2.58	
The catalyst employed in the first reaction zone 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 impregnating technique involving 100 parts of alumina spheres (prepared in accordance with the oil-drop method as described in U.S. Patent No. 2,620,314, issued to James Hoekstra), and a single impregnating solution containing nickel nitrate 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 102 atmospheres, and an inlet temperature thereto of 410°C. The liquid charge was treated at a rate of 0.5 liquid hourly space velocity, and was combined with hydrogen in an amount of 1068 normal liters per liter of the oil charge. Following a separation, to remove ammonia, hydrogen sulfide and the light paraffinic hydrocarbons (C ₁ to C ₃), the normally liquid product effluent of the reaction zone was fractionated in a multi-plate distillation column to yield four fractions. These fractions were, (1) a butane to 82°C. fraction, (2) a 82°C. to 204°C. fraction, (3) a 204°C. to 343°C. (middle-distillate) fraction, and (4) a bottoms fraction containing those hydrocarbons boiling at a temperature in excess of 343°C. 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 efflu-		
		130

ent, following separation to remove the ammonia and light paraffinic hydrocarbons, that is, the stream indicated in the drawing as passing through line 14, contained approximately 18 parts per million of total nitrogen. Following fractionation, in side-cut fractionator 15, the total nitrogen content of the gasoline boiling range hydrocarbons, those having an end point of about 204°C., was effectively nil, that of the middle-distillate fraction, indicated in line 21 of the drawing, contained less than 3.0 parts per million nitrogen, while the hydrocarbon stream, indicated as being in line 18, contained approximately 40 parts per million of nitrogen. It should be noted that a portion of the latter stream, which contains the hydrocarbons boiling above about 343°C., may be combined with the middle-distillate fraction employed as the oil charge to the second reaction stage of the present process, at least to the extent that the nitrogenous compound content of the resultant oil charge does not exceed about 5.0 parts per million. Other product inspections performed upon the various fractions are indicated in the following Table II.

TABLE II
INSPECTION OF PRODUCTS FROM
VACUUM GAS OIL

Fraction*, °C. range	83°-204°	204°-343°	343°+
Volume % of Total	22.6	47.0	39.0
Specific Gravity, at 15.6°C.	0.7892	0.8373	0.8373
ASTM Distilla- tion, °C.			
Initial			
Boiling Point	116	219	354
10%	138	242	377
30%	156	261	391
50%	160	277	407
90%	182	321	463
End Point	203	345	488
Hydrocarbon- Type Anal- ysis, Vol. %			
Paraffins	41	—	—
Naphthenes	51	—	—
Olefins	1	—	—
Aromatics	7	—	—

* Light Paraffinic Hydrocarbons (C₁ to C₃)
Yield was 2.2% by weight, and the C₄-83°
C. fraction was 3.0 vol. %.

To illustrate the second stage of the process of the present invention, those hydrocarbons boiling within the range of 204°C. to 343°C., 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 composite was prepared by diluting

1610 grams of water glass (28% by weight of SiO₂) 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, having a specific gravity of 1.28, and prepared from iron-free, hydrated aluminum sulfate crystals. The resultant alumina-silica hydrosol was then commingled, with vigorous stirring, with 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 149°C., ground into a fine powder, and formed into 3.2 mm × 3.2 mm cylindrical pills. The pills were subjected to a high-temperature calcination procedure, in an atmosphere of air for a period of 3 hours and a temperature of 649°C. 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 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 649°C. This catalyst was disposed within the reaction zone, as a fixed-bed, and maintained under an imposed pressure of 102 atmospheres. During the processing of the middle-distillate charge stock, the inlet temperature to the reactor was maintained at a level of 327°C. The charge stock was introduced to the reaction zone at a rate equivalent to 3.0 liquid hourly space velocity, and was admixed with hydrogen in an amount of 534 normal liters per liter of the oil charge. 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 liquid hydrocarbons, including the light paraffinic hydrocarbons (C₁ to C₃) were subjected to fractionation in a laboratory, multi-plate distillation column, the results of which fractionation are indicated in Table III.

TABLE III
VOLUMETRIC YIELDS FROM
MIDDLE-DISTILLATE

Components*	Vol. % Yield
Total Butanes	7.9
Pentanes & Hexanes	15.3
Heptanes to 204°C.	47.2
204°C. and Heavier	39.5
* Light Paraffinic Hydrocarbons (C ₁ to C ₃)	
Yield was 0.67% by weight.	

The yields indicated in Table III 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 of the total charge. It is further noted that there was a 70.4% by volume yield of hydrocarbons boiling within the gasoline boiling range and inclusive of the 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.

EXAMPLE II

This example illustrates the applicability of the present process to a hydrocarbon fraction boiling partially within the gasoline boiling range, the greater proportion of which boils within the middle-distillate boiling range. The charge stock was an East Texas kerosine having the properties shown in the following Table IV:

TABLE IV
EAST TEXAS KEROSINE—
PROPERTIES

Specific Gravity at 15.6°C.	0.8189
ASTM distillation, °C.	
Initial Boiling Point	186
10%	211
30%	222
50%	230
70%	241
90%	258
End Point	283
% at 204°C.	5.0
% Bottoms	0.8
Total Nitrogen, ppm	3.6
Sulfur, weight %	0.036
Hydrocarbon Types, Vol. %	
Paraffins	82.8
Naphthenes	
Olefins	
Aromatics	16.8

The kerosene fraction was passed into a first or clean-up reaction zone maintained at a pressure of 54.2 atmospheres and an inlet temperature of 371°C. The charge was admixed with hydrogen in an amount of 178 normal liters per liter of oil, and contacted the catalyst disposed within the reaction zone at a liquid hourly space velocity of 5.0. The catalyst employed in the clean-up reaction zone consisted of 3.2 mm × 3.2 mm cylindrical alumina pills which had been impregnated, utilizing a single impregnating solution, with 2.0% by weight of cobalt and 6.0% by weight of molybdenum, calculated as the elements thereof. Hydrogen sulfide, ammonia, and hydrogen were removed from the total reactor effluent in a high-pressure separator, the hydrogen being recycled to combine with the hydrogen admixed with the kerosine fraction prior to the introduction

thereof into the clean-up reaction zone. The remainder of the reaction zone effluent was passed into a fractionator wherein the light paraffinic hydrocarbons, methane, ethane, and propane, were removed and a stream of normally liquid hydrocarbons containing butanes and heavier components was obtained. This stream was then subjected to further fractionation to provide a butane fraction, a C₃-hydrocarbon fraction having an end point of 46°C., a C₄-hydrocarbon fraction (46°C. to 82°C.), a 82°C.-204°C. fraction, and those hydrocarbons boiling in excess of 204°C.

The fraction boiling above 204°C. was then admixed with hydrogen in an amount of 534 normal liters per liter of this oil fraction, and passed at a liquid hourly space velocity of 1.0 into a second or hydrocracking reaction zone maintained at a pressure of 102 atmospheres and at a temperature of about 302°C. The catalyst disposed within this hydrocracking reaction zone comprised 0.4% by weight of palladium composited with a cracking component consisting of 88% by weight of silica and 12% by weight of alumina. The total reaction zone effluent, from the hydrocracking reactor, was combined with the effluent from the first reaction zone following the removal of ammonia therefrom, and prior to the separation of the light paraffinic hydrocarbons (C₁ to C₃). Various product inspections, and a portion of the resulting yields are given in the following Table V.

TABLE V
INSPECTION OF PRODUCTS FROM
KEROSINE CHARGE

Fraction, °C. range	82°-204°	204° +
Specific Gravity at 15.6°C.	0.7678	0.7901
ASTM Distillation, °C.		
Initial Boiling Point	99	213
10%	109	218
30%	117	221
50%	126	225
70%	142	231
90%	168	246
95%	178	254
End Point	191	274
Hydrocarbon Type Analysis, vol. %		
Paraffins	37	—
Olefins	NIL	—
Naphthenes	46	—
Aromatics	17	—
Octane Ratings		
F-1 Clear	63.9	—
F-1, + 3 cc. TEL.	83.1	—

The portion of the liquid product boiling up to 82°C. consisted of 33.3% by weight of butanes, 34.2% by weight of C₄ to 46°C., and 32.6% by weight of C₄ hydrocarbons (46° to 82°C.) The octane rating of the debutanized fraction to an end point of 82°C. was 82.4 F-1 Clear, and 96.3 F-1 + 3 cc.

TEL.

The gasoline boiling range fraction boiling from 82°C. to 204°C. was obtained in an amount of 53% by volume, based upon the total charge to the first reaction zone. The characteristics of this fraction, as indicated in Table V, are such that this fraction is ideally suited for subsequent processing in a catalytic reforming process for the purpose of increasing the octane ratings, or anti-knock characteristics thereof. It should be noted that the fraction is substantially completely free from olefinic hydrocarbons, and contains 17% by volume of aromatic hydrocarbons and 46% by volume of naphthenic hydrocarbons.

EXAMPLE III

This example illustrates the applicability of the present process to the utilization of various light cycle oils, boiling entirely at a temperature in excess of the gasoline boiling range, and partially in excess of the middle-distillate boiling range. Two individual charge stocks were separately processed in accordance with the method described in Example II; one charge stock was an Oklahoma light cycle oil having a boiling range of from 232°C. to 315°C., and the other was a Leduc light cycle oil having a boiling range of 231°C. to 352°C. Other properties of these light cycle oils are given in the followings Table VI.

TABLE VI
OKLAHOMA AND LEDUC LIGHT
CYCLE OILS—PROPERTIES

	Oklahoma	Leduc
Specific Gravity at 15.6°C.	0.8849	0.8990
ASTM Distillation, °C.		
Initial Boiling Point	232	231
10%	251	257
30%	261	277
50%	270	291
70%	280	307
90%	293	327
End Point	315	352
% at 204°C.	0	0
% Bottoms	1.0	1.5
Total Nitrogen, ppm.	285	345
Sulfur, weight %	0.70	0.69
Hydrocarbon Type Analysis, vol. %		
Paraffins	50.7	43.4
Naphthenes		
Olefins	3.7	5.4
Aromatics	45.6	51.2

In regard to the Oklahoma light cycle oil, the catalyst employed in the first or clean-up reaction zone comprised 2.4% by weight of nickel, 6.4% by weight of molybdenum, and a composite consisting of 88% by weight of alumina and 12% by weight of silica. The second or hydrocracking reaction zone contained a catalyst consisting of 0.4% by weight of palladium on a composite of 88% by weight of silica and 12% by weight of alumina. The clean-up reaction zone was

maintained at a pressure of 102 atmospheres, an inlet temperature of 399°C., and the charge stock contacted the catalyst at a liquid hourly space velocity of 1.0. The light cycle oil was admixed with hydrogen in an amount of 356 normal liters per liter of oil, prior to entering the first reaction zone. The second or hydrocracking reaction zone was maintained at a pressure of 102 atmospheres, and an inlet temperature of about 315°C., and the charge to this zone contacted the catalyst at a liquid hourly space velocity of 1.0 after being combined with hydrogen in an amount of 534 normal liters per liter of oil. The foregoing operating conditions, on both reaction zones, were also employed when processing the Leduc light cycle oil.

Inspection data of various products obtained from the Oklahoma light cycle oil appear in the following Table VII.

TABLE VII
INSPECTION OF PRODUCTS FROM
OKLAHOMA LIGHT CYCLE OIL

Fraction, °C. range	82°-204°	204° +
Specific Gravity at 15.6°C.	0.7861	0.8222
ASTM Distillation, °C.		
Initial Boiling Point	91	213
10%	108	229
30%	120	241
50%	133	254
70%	151	270
90%	178	292
End Point	211	317
Hydrocarbon Type Analysis, vol. %		
Paraffins	18	—
Olefins	NIL	—
Naphthenes	63	—
Aromatics	19	—
Octane Ratings		
F-1 Clear	70.7	—
F-1 + 3 cc. TEL	86.5	—

The product fraction boiling up to 82°C. contained 33.3% by weight butanes, 35.5% by weight C₅ hydrocarbons to 46°C. and 31.2% by weight of C₆ and heavier hydrocarbons (46° to 82°C.).

The benefits afforded through the utilization of the present invention are readily ascertained from the data given in Table VII. The gasoline fraction of 82°-204°C. boiling range having a specific gravity of 0.7861 at 15.6°C. is extremely well suited for utilization as charge to a subsequent catalytic reforming process. Of special significance is the fact that this gasoline fraction contained a total of 82% by volume of aromatic precursors in the form of naphthenes and aromatics, substantially no olefinic hydrocarbons, and only 18% by volume of paraffinic hydrocarbons. In addition, this particular fraction exhibited a relatively high octane rating, even in the absence of further processing.

The operations described in the foregoing examples were repeated on the several

charge stocks in order to obtain the relation of product distribution to severity of operation. To obtain such a relationship, the severity of the operation was indicated by varying percentages of conversion to hydrocarbons boiling below 204°C. The following Table VIII indicates the product distribution summary, for the kerosine, light cycle oils and vacuum gas oil, as determined at a severity of operation which resulted in 60% by volume conversion to hydrocarbons boiling below 204°C., and without liquid recycle within the process.

TABLE VIII
PRODUCT DISTRIBUTION SUMMARY

Charge Stock	E. Texas Kerosine	Okla.-Leduc Cycle Oil	Wyo.-Tex. Cycle Oil	Vac. Gas Oil
Product Distribution				
C ₁ to C ₄ , weight %	1.0	1.7	1.0	0.9
C ₄ to 82°C., vol. %	16	19	15	23
82°-204°C., vol. %	53	57	64	58
204°C. and Heavier, vol. %	40	40	40	40
Total C ₁ + Yield, vol. %	109	116	119	121

It is immediately noted that, in all four situations, the production of the light paraffinic hydrocarbons was extremely low, in no instance amounting to more than 2.0% by weight of the total charge to the process. Of greater significance, is the fact that in all instances, there was indicated a volumetric gain in regard to the total yield of butanes and heavier hydrocarbons. In the case of the East Texas kerosine fraction, the total yield of butanes and heavier hydrocarbons, including those boiling above 204°C., was 109.9 volumetric percent. The highest volumetric increase was experienced when processing the heavy vacuum gas oil, and amounted to 121%. Thus, the applicability of the process of the present invention, while processing those charge stocks boiling in excess of the gasoline boiling range, is readily ascertained. That the present invention offers particular advantages when processing the heavier hydrocarbon feed stocks, as indicated by the Wyoming-West Texas vacuum gas oil, is clearly indicated.

WHAT WE CLAIM IS:—

1. Process for the catalytic hydrocracking of hydrocarbons which comprises reacting a stream of hydrocarbon oil charge boiling at least predominantly above 204°C. and containing nitrogenous compounds in a first reaction zone with hydrogen in the presence of a nitrogen-insensitive hydrorefining catalyst

with formation of ammonia from said nitrogenous compounds, removing the ammonia from the effluent of said first reaction zone, then separating from said effluent a light normally liquid fraction having an end boiling point of from 204° to 232°C. and also separating from said effluent a heavier fraction containing effluent components boiling between the end boiling point of said light fraction and 343°C., reacting a stream of said heavier fraction in a second reaction zone with hydrogen in the presence of a nitrogen-sensitive hydrocracking catalyst, and commingling at least the normally liquid portion of the effluent of said second reaction zone with the normally liquid portion of the effluent of said first reaction zone prior to the separation of said light fraction therefrom.

2. Process according to claim 1, characterized in that the mixture of the normally liquid components of the effluents from the first reaction zone and the second reaction zone is separated into a first fraction having an end boiling point of from 204° to 232°C., a second fraction having an end boiling point of from 343° to 371°C., and a third fraction containing those hydrocarbons of said mixture which boil above said second fraction, a stream of said second fraction is reacted with hydrogen in the presence of the nitrogen-sensitive catalyst in said second reaction zone, and at least a portion of said third fraction is subjected together with the hydrocarbon oil charge to the reaction with hydrogen in the presence of the nitrogen-insensitive catalyst in the first reaction zone.

3. Process according to claim 2, characterized in that a portion of the third fraction is commingled with the stream of the second fraction being supplied to the second reaction zone contains less than 5 parts by weight of nitrogen per million parts by weight of said mixture and all of the remaining portion of said third fraction is commingled with the hydrocarbon oil charge being introduced into the first reaction zone.

4. Process according to one of the claims 1 to 3 characterized in that the hydrocarbon oil charge is contacted with the nitrogen-insensitive catalyst in the first reaction zone at a space velocity of from 0.5 to 10 volumes, measured as liquid, per hour per volume of catalyst together with from 178 to 1425 normal liters of hydrogen per liter of oil, measured as liquid, and at a temperature in the range of from 260° to 538°C. and a pressure of from 68 to 204 atmospheres, and the hydrocarbon stream introduced into the second reaction zone is contacted with the nitrogen-sensitive catalyst therein at a space velocity of from 1 to 15 volumes, measured as liquid, per hour per volume of catalyst together with from 178 to 1070 normal liters of hydrogen per liter of oil, measured as liquid, and at a temperature in the range of from 260°

charge stocks in order to obtain the relation of product distribution to severity of operation. To obtain such a relationship, the severity of the operation was indicated by varying percentages of conversion to hydrocarbons boiling below 204°C. The following Table VIII indicates the product distribution summary, for the kerosine, light cycle oils and vacuum gas oil, as determined at a severity of operation which resulted in 60% by volume conversion to hydrocarbons boiling below 204°C., and without liquid recycle within the process.

TABLE VIII
PRODUCT DISTRIBUTION SUMMARY

Charge Stock	E. Texas Kerosine	Okla-homa Cycle Oil	Wyo.-Leduc Cycle Oil	W.Tex. Vac. Gas Oil
Product Distribution				
C ₁ to C ₄ weight %	1.0	1.7	1.0	0.9
C ₄ to 82°C. vol. %	16	19	15	23
82°-204°C. vol. %	53	57	64	58
204°C. and Heavier, vol. %	40	40	40	40
Total C ₄ + Yield, vol. %	109	116	119	121

It is immediately noted that, in all four situations, the production of the light paraffinic hydrocarbons was extremely low, in no instance amounting to more than 2.0% by weight of the total charge to the process. Of greater significance, is the fact that in all instances, there was indicated a volumetric gain in regard to the total yield of butanes and heavier hydrocarbons. In the case of the East Texas kerosine fraction, the total yield of butanes and heavier hydrocarbons, including those boiling above 204°C., was 109.9 volumetric percent. The highest volumetric increase was experienced when processing the heavy vacuum gas oil, and amounted to 121%. Thus, the applicability of the process of the present invention, while processing those charge stocks boiling in excess of the gasoline boiling range, is readily ascertained. That the present invention offers particular advantages when processing the heavier hydrocarbon feed stocks, as indicated by the Wyoming-West Texas vacuum gas oil, is clearly indicated.

WHAT WE CLAIM IS:—

1. Process for the catalytic hydrocracking of hydrocarbons which comprises reacting a stream of hydrocarbon oil charge boiling at least predominantly above 204°C. and containing nitrogenous compounds in a first reaction zone with hydrogen in the presence of a nitrogen-insensitive hydrorefining catalyst

with formation of ammonia from said nitrogenous compounds, removing the ammonia from the effluent of said first reaction zone, then separating from said effluent a light normally liquid fraction having an end boiling point of from 204° to 232°C. and also separating from said effluent a heavier fraction containing effluent components boiling between the end boiling point of said light fraction and 343°C., reacting a stream of said heavier fraction in a second reaction zone with hydrogen in the presence of a nitrogen-sensitive hydrocracking catalyst, and commingling at least the normally liquid portion of the effluent of said second reaction zone with the normally liquid portion of the effluent of said first reaction zone prior to the separation of said light fraction therefrom.

2. Process according to claim 1, characterized in that the mixture of the normally liquid components of the effluents from the first reaction zone and the second reaction zone is separated into a first fraction having an end boiling point of from 204° to 232°C., a second fraction having an end boiling point of from 343° to 371°C., and a third fraction containing those hydrocarbons of said mixture which boil above said second fraction, a stream of said second fraction is reacted with hydrogen in the presence of the nitrogen-sensitive catalyst in said second reaction zone, and at least a portion of said third fraction is subjected together with the hydrocarbon oil charge to the reaction with hydrogen in the presence of the nitrogen-insensitive catalyst in the first reaction zone.

3. Process according to claim 2, characterized in that a portion of the third fraction is commingled with the stream of the second fraction being supplied to the second reaction zone contains less than 5 parts by weight of nitrogen per million parts by weight of said mixture and all of the remaining portion of said third fraction is commingled with the hydrocarbon oil charge being introduced into the first reaction zone.

4. Process according to one of the claims 1 to 3 characterized in that the hydrocarbon oil charge is contacted with the nitrogen-insensitive catalyst in the first reaction zone at a space velocity of from 0.5 to 10 volumes, measured as liquid, per hour per volume of catalyst together with from 178 to 1425 normal liters of hydrogen per liter of oil, measured as liquid, and at a temperature in the range of from 260° to 538°C. and a pressure of from 68 to 204 atmospheres, and the hydrocarbon stream introduced into the second reaction zone is contacted with the nitrogen-sensitive catalyst therein at a space velocity of from 1 to 15 volumes, measured as liquid, per hour per volume of catalyst together with from 178 to 1070 normal liters of hydrogen per liter of oil, measured as liquid, and at a temperature in the range of from 260°



to 510°C. and a pressure of from 68 to 204 atmospheres.

5. Process according to claim 4, characterized in that the reaction of the hydrocarbons with hydrogen is effected in the second reaction zone at a higher space velocity than in the first reaction zone and at a temperature which is from 28° to 83°C. lower than the temperature maintained in said first reaction zone.

6. Process according to one of the claims 1 to 4, characterized in that the reaction in the first reaction zone is effected in the presence of a catalyst which contains between 4.0 and 45.0% by weight of molybdenum and between 0.2 and 10.0% by weight of metal of the group of nickel and cobalt on a support consisting at least predominantly of alumina and containing not more than 12% by weight of silica.

7. Process according to one of the claims 1 to 6, characterized in that the reaction in the second reaction zone is effected in the presence of a catalyst which contains between 0.5 and 10% by weight of nickel on a synthetically produced support consisting predominantly of silica and from 12 to 25% by weight of alumina.

8. Process according to claim 7, characterized in that the catalyst contains approximately 6% by weight of nickel on a support consisting substantially of 75% by weight of silica and 25% by weight of alumina.

9. Process according to one of the claims 1 to 6, characterized in that the reaction in the second reaction zone is effected in the presence of a catalyst which contains between 0.1 and 5.0% by weight of a platinum group metal on a support consisting predominantly of silica and containing from 12

to 25% by weight of alumina.

10. Process according to claim 9, characterized in that the catalyst contains between 0.1 and 2.0% of palladium on a support consisting substantially of 88% by weight of silica and 12% by weight of alumina.

11. Process according to one of the claims 1 to 10, characterized in that a hydrocarbon oil charge boiling between 204° and 538°C. and containing a substantial amount of nitrogenous contaminants is contacted in the presence of the hydrogen with the nitrogen-insensitive catalyst in the first reaction zone at a space velocity of from 0.5 to 3 volumes of oil, measured as liquid, per hour per volume of catalyst, a fraction having an initial boiling point in the range of from 204° to 232°C., an end boiling point of not less than 343°C., and a nitrogen content of less than 1 part by weight per million parts by weight of said fraction is separated from the mixture of the normally liquid components of the two reaction zone effluents, and a stream of said fraction is supplied as the hydrocarbon charge stream to the second reaction zone at a space velocity which is higher than that employed in the first reaction zone and is greater than one volume of oil, measured as liquid, per hour per volume of the nitrogen-sensitive catalyst in said second reaction zone.

12. The hydrocracking process substantially as described with reference to the accompanying drawing.

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