

931824



PATENT SPECIFICATION

DRAWINGS ATTACHED

931824

Date of Application and filing Complete Specification: March 19, 1962.

No. 10330/62.

Complete Specification Published: July 17, 1963.

Index at acceptance:—Class 32, E20.

International Classification:—C10g.

COMPLETE SPECIFICATION

Hydrocarbon Oil Hydrofining and Cracking process

I, HAROLD NEWBY, of 47, Lincoln's Inn Fields, London, W.C.2, of English nationality, do hereby declare the invention (which has been communicated to me from abroad by Universal Oil Products Company, a Corporation organised under the Laws of the State of Delaware, United States of America, of 30 Algonquin Road, Des Plaines Illinois, United States of America), for which I pray that a Patent may be granted to me, 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 heavy hydrocarbon oils into lower boiling hydrocarbon products and is more particularly directed to the production of substantially nitrogen-free light oils boiling within the gasoline and middle-distillate boiling ranges from heavy hydrocarbon oils which have a boiling range in excess of the middle-distillate boiling range and are contaminated by substantial quantities of nitrogenous compounds.

In the present process use is made of hydrocracking which effects definite changes in the molecular structure of hydrocarbons. In hydrocracking, cracking is effected under hydrogenation conditions in such a manner that the lower-boiling hydrocarbon products resulting therefrom are substantially more saturated than when hydrogen, or material supplying the same, is not present. As presently practices, hydrocracking processes are most commonly employed for the destructive conversion of various coals, tars and heavy residual oils for the purpose of producing substantial yields of low boiling, saturated products; to some extent, there exists at least partial conversion to intermediates which are suitable for utilization as domestic fuels. In many instances, heavier gas oil fractions, which may find utilization as lubricating material, are also produced. The preferred hydrocracking technique involves the utilization of a catalytic composite possessing a high

[Price 4s. 6d.]

degree of hydrocracking activity. To assure effective catalytic action over an extended period of time, and from the standpoint of producing an increased yield of liquid product having improved physical and/or chemical characteristics, controlled or selective cracking is desirable in virtually all hydrocracking processes. For example, the lower molecular weight products, consisting essentially of those hydrocarbons boiling within the normal gasoline boiling range, usually have a fairly high octane rating and, as such, are particularly suitable for subsequent utilization in catalytic reforming processes to further increase the octane rating. Similarly, controlled or selective hydrocracking results in an increased yield of middle-distillate boiling rate hydrocarbons which are substantially free from high molecular weight unsaturated hydrocarbons.

Selective hydrocracking is of particular importance when processing hydrocarbon mixtures with a boiling range extending to beyond that of the middle-distillate boiling range; this includes various heavy hydrocarbon oils as well as various hydrocarbon oil fractions, and distillate which may have an initial boiling point as low as 200°C. but contain appreciable amounts of hydrocarbons boiling above 415°C. and as high as 540°C. or more. The controlled, or selective hydrocracking of such hydrocarbon mixtures, particularly when they have an initial boiling point above about 340° to 370°C., results in greater yields of hydrocarbons boiling within the gasoline and middle-distillate boiling range, which are those normally liquid hydrocarbon fractions having an end boiling point below about 340° to 370°C. Furthermore, the selective hydrocracking of such heavier hydrocarbon fractions results in a substantially increased yield of gasoline boiling range hydrocarbons, that is, those hydrocarbons and hydrocarbon fractions which boil within the range of from about 38°C. to about 200° or 230°C. Hydrocracking selectivity is necessary for avoiding



Cracking

the decomposition of normally liquid hydrocarbons to any substantial extent into normally gaseous hydrocarbons, the latter being inclusive of methane, ethane and propane.

5 The ultimate volumetric yield of normally liquid hydrocarbons, especially those boiling within the gasoline boiling range, as an inherent result of the excessive production of normally gaseous hydrocarbons, can be decreased to the extent where the process is not economically feasible. Non-selective hydrocracking is distinguished from controlled or selective hydrocracking in that the latter involves the splitting of a higher-boiling hydrocarbon molecule into two hydrocarbon molecules, both of which are normally liquid hydrocarbons. To a somewhat lesser degree, selective hydrocracking involves the controlled removal of methyl, ethyl and propyl groups, which, in the presence of hydrogen, are converted to methane, ethane and propane, the latter being referred to as "light paraffinic hydrocarbons". In selective hydrocracking, the removal of the aforesaid radicals is controlled such that not more than one, or possibly two of such radicals are removed from a given molecule. For example, in the presence of hydrogen, and under selective hydrocracking conditions, normal decane may be reduced to two pentane molecules, normal heptane reduced to hexane, and nonane reduced to octane or heptane, and so forth. Conversely, uncontrolled or non-selective hydrocracking, will result in the decomposition of normally liquid hydrocarbons into the aforesaid normally gaseous hydrocarbons.

Another disadvantage of non-selective or uncontrolled hydrocracking is that such hydrocracking results in a more rapid formation of increased quantities of coke and other heavy carbonaceous material which becomes deposited upon the catalytic composite employed, and decreases, or even destroys, the activity for catalyzing the desired reactions in the desired manner. Such deactivation inherently results in a shorter processing cycle or period, with the attendant necessity of more frequent regeneration of the catalyst, or total replacement thereof with fresh catalyst. Of further significance, in regard to the hydrocracking reaction, are the aspects of hydrogen production and consumption, the preservation of aromatic compounds which boil within the gasoline boiling range, and the production of a liquid product substantially free from low molecular weight, unsaturated hydrocarbons. The deactivation of the catalyst, through the deposition of coke and other heavy carbonaceous material, or other means, appears to inhibit the hydrogenation activity to the extent that a significant proportion of the gasoline boiling range hydrocarbons consists of olefins which are not particularly suitable for subsequent direct processing by catalytic reforming. On the other hand, selective hydrocrack-

ing does not tend to effect substantial hydrogenation, or saturation, of the aromatic hydrocarbons boiling within the gasoline boiling range, or the destructive hydrogenation of low molecular weight, straight or branched-chain hydrocarbons into normally gaseous hydrocarbons.

Investigations have indicated that the relatively rapid deactivation of a hydrocracking catalytic composite and a corresponding rapid loss of selectivity results from the presence of nitrogen-containing compounds within the hydrocracking charge. These nitrogenous compounds, such as naturally-occurring, organic nitrogenous compounds, examples of which include pyrroles, amines, and indoles, result in the deactivation of the catalytically active metallic components, as well as the refractory inorganic oxide carrier material which acts as the acidic component of a great variety of hydrocracking catalysts. Such derivatization appears to result through the reaction of the nitrogenous compounds with the various catalytic components, and the extent of such deactivation steadily increases as nitrogen-containing feed stock continues to contaminate the catalyst through contact therewith. The effect having the greatest influence in regard to catalyst deactivation is believed to be the formation of a nitrogen-containing complex, through inter-reaction with the catalytically active metallic components, whereby the active centers of the catalyst, normally available to the hydrocarbon charge stock, are effectively shielded therefrom. Deactivation of this nature is not believed to be a simple reversible phenomenon which may be easily rectified by merely heating the catalyst in the presence of hydrogen for the purpose of decomposing the nitrogen-containing complexes.

The primary object of the present invention is to provide a process in which substantially greater yields of hydrocarbons boiling within the gasoline and middle-distillate boiling ranges are produced by hydrocracking without the attendant saturation of aromatic compounds, the uncontrolled cracking of the low molecular weight hydrocarbons and rapid deactivation of the hydrocracking catalyst. A related object is to provide a process which permits the utilization of petroleum hydrocarbon charge stock having an initial boiling point as high as about 370° to about 425°C. or more, which charge stocks contain nitrogenous compounds in excessive quantities of the order of about 1000 ppm. to about 5000 ppm. (ppm=parts by weight per million), that are concentrations which result in the rapid deactivation of the catalytic composite employed for promoting selective hydrocracking.

Thus, the present invention relates to a process for converting gasoline-free heavy hydrocarbon oils which contain nitrogenous



not



nitrogenous



shaving

compounds and substantial amounts of hydrocarbons boiling about 415°C. into lower boiling normally liquid hydrocarbon products substantially free from nitrogen, and the process according to this invention comprises cracking a stream of such heavy hydrocarbon oil in a first reaction zone with formation of an intermediate product boiling above the gasoline range and having an end boiling point in the range of from 400° to 435°C., separating this intermediate product in a primary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of the first reaction zone, reacting the intermediate product in a second reaction zone with hydrogen in the presence of a nitrogen-insensitive catalyst having hydrogenating activity with formation of ammonia from nitrogeous compounds, separating ammonia from the normally liquid hydrocarbon effluent of the second reaction zone, thereafter hydrocracking the normally liquid hydrocarbon effluent of the second reaction zone in a third reaction zone in the presence of added hydrogen and a hydrocracking catalyst, separating a hydrocarbon distillate product which is substantially free from nitrogen and has an end boiling point in the range of from 340° to 370°C. in a secondary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of the third reaction zone, returning a stream of the higher boiling components from the secondary fractionation zone to the third reaction zone, and withdrawing the hydrocarbon distillate product from the process.

In a more specific embodiment of the process of the present invention a heavy hydrocarbon oil charge boiling at least largely in the range of from 370° to 540°C. is fractionated into a light charge fraction having an end boiling point in the range of from 400° to 435°C. and into a heavy charge fraction boiling above the light charge fraction, the heavy charge fraction is supplied to the cracking in the first reaction zone, and the light charge fraction is passed together with the intermediate product, upon separation of the latter in the primary fractionation zone, to the second reaction zone. Advantageously the heavy charge fraction is passed to the first reaction zone together with the high boiling components separated from the intermediate product in the primary fractionation zone. Preferably, moreover, substantially all of the high boiling components separated from the hydrocarbon distillate product in the secondary fractionation zone are commingled with the ammonia-free normally liquid hydrocarbon effluent of the second reaction zone and the resultant mixture is supplied to the third reaction zone.

In a preferred embodiment of the process according to the present invention a light charge fraction boiling below 427°C. is separated from the heavy oil charge, the remainder of the heavy oil charge is introduced into the first reaction zone, an intermediate product having an initial boiling point in the range of from 200° to 230°C. and an end boiling point below 427°C. is separated in the primary fractionation zone from the normally liquid hydrocarbon effluent of the first reaction zone and this intermediate product is introduced in commingled state with the light charge fraction into the second reaction zone.

While the conditions of operation in the individual reaction stages of the present three-stage conversion process may be varied considerably, as more fully described below, a typical mode of applying the present process to the conversion of a nitrogen-contaminated heavy hydrocarbon oil having a boiling range of from about 370°C. to about 540°C., into lower boiling hydrocarbon distillate products substantially free from nitrogenous compounds is the following. The heavy hydrocarbon oil charge is initially separated into a light charge fraction containing those hydrocarbons boiling below about 427°C. and a heavy charge fraction having an initial boiling point of about 427°C.; the heavy charge fraction is cracked in a first reaction zone in the presence of a cracking catalyst containing at least one metallic component from the metals of Groups VIA and the iron-group of the Periodic Table, or a mixture thereof. The resultant reaction zone effluent is freed from normally gaseous products and fractionated into an intermediate product boiling up to about 427°C. and a heavier intermediate fraction; the latter is combined with the heavy charge fraction prior to the conversion thereof in the first reaction zone. The intermediate product is combined with the light charge fraction; the resulting mixture substantially boiling below 427°C. is reacted with hydrogen in a second reaction zone in the presence of a catalyst containing from about 4% to about 45% by weight of molybdenum; ammonia and normally gaseous hydrocarbons are removed from the resultant second zone effluent and the entire normally liquid hydrocarbon portion of this effluent is passed along with additional hydrogen into a third reaction zone which is maintained at hydrocracking conditions and contains a catalyst comprising from about 0.01% to about 5.0% by weight of palladium composited with silica and from about 10% to about 90% by weight of alumina; normally gaseous hydrocarbons are removed from the resultant third zone effluent and the normally liquid hydrocarbons of this effluent are separated into a first distillate product fraction having an end boiling point in the range of from 200° to 230°C., a second distillate product fraction having an initial boiling point in the range of from 200° to 230°C. and an end boiling point in the range of from 340° to 370°C., and a third fraction

- boiling above the end boiling point of the second distillate product fraction; at least a portion of the third fraction, or preferably the entire third fraction, is combined with the gas-free normally liquid hydrocarbon portion of the said second reaction zone effluent and with hydrogen prior to conversion in the third reaction zone.

- Various terms and phrases are employed with within the present specification and the appended claims with the meaning herein specifically defined. Thus, the phrase "hydrocarbons boiling within the gasoline boiling range", or "gasoline boiling range hydrocarbons", is intended to connote those hydrocarbons boiling in the range of from about 38°C. to a temperature in the range of from 200° to 230°C. (as determined by Standard ASTM distillation methods). The term, "light paraffinic hydrocarbons" is intended to connote those hydrocarbons containing three or less carbon atoms; that is, methane, ethane and propane. The term "heavy distillate" refers to hydrocarbon fractions which have an initial boiling point in the range of from 300° to 370°C. and an end boiling point in the range of from 400° to 435°C., and more particularly of approximately 427°C. The term "middle-distillate", or "light gas oil", refers to those hydrocarbon fractions which have an initial boiling point substantially within the range of from 200°C. to 230°C. and an end boiling point within the range of from about 340°C. to about 370°C. In regard to the various catalytic composites employed in any one of the three individual reaction zones of the present process, the term, "metallic component", or "catalytically active metallic component", is intended to encompass those components which are employed for their hydrocracking activity, or for their propensity for the destructive removal of nitrogenous compounds, as the case may be. In this manner, the "catalytically active metallic components" are distinguished from those components which are employed as the solid support, or carrier material, or the acidic cracking component. The catalyst used in any one of the three integrated, but separate reaction stages is a distinct catalytic composite, different, in most applications of the present invention, from the catalytic composites employed in any other stages.
- The present invention is particularly directed toward processing heavy hydrocarbon oil change stocks, such as vacuum gas oil fractions, white oil stocks, heavy cycle stocks, fuel oil stocks, reduced crudes, and the like mineral oil-derived high boiling hydrocarbon mixtures, notably those heavy hydrocarbons having an initial boiling point of at least about 340°—370°C. and an end boiling point of about 540°C. or more. Generally, all of these sources of hydrocarbon feed stocks contain high-boiling nitrogenous compounds and sul-

furous compounds as contaminants. Although the major proportion of such nitrogenous compounds may be removed by many known means, such as a hydrorefining pretreatment, it is very difficult, if not virtually impossible, to remove the last few parts per million of nitrogen from such charge stock prior to subject-the same to the hydrocracking reaction. For example, a hydrorefining pretreatment, in which the feed stock is subjected to the action of a catalyst, at reaction conditions, will result in the conversion of the nitrogenous, organically-bound components into ammonia and the corresponding hydrocarbon residue. Although the structure of the hydrocarbon components is not substantially altered, the resulting hydrocarbon charge stock will, in all probability, contain a relatively minor amount of nitrogenous compounds, as compared to the excessive quantity originally present. Notwithstanding such quantities, these organic nitrogen compounds will eventually result in the deactivation of hydrocracking catalyst, and particularly catalysts consisting of metals from Groups VI and VIII of the Periodic Table. For example, a catalyst comprising at least one platinum-group metallic component, impregnated upon a silica-alumina carrier material, is a very effective catalyst for the hydrocracking of gas oils boiling below about 800°F. However, these catalysts are virtually immediately poisoned by either sulfurous or nitrogenous compounds, and particularly by the latter. The contaminants, and particularly organically-bound nitrogenous compounds, are very difficult, if not impossible, to remove from hydrocarbon fractions boiling above about 415° or 425°C., whereas virtually complete removal may be effected from hydrocarbons boiling below these temperatures. Through the utilization of the three-stage process of the present invention, particularly when processing hydrocarbon charge stocks boiling above about 370°C. and up to about 540°C. or more, it is possible to produce high volumetric yields of gasoline boiling range hydrocarbons while simultaneously maximizing the yield of middle-distillate hydrocarbons which are substantially free from nitrogenous compounds. A substantial increase in the overall yield of gasoline boiling range hydrocarbons may then be obtained by further processing nitrogen-free, middle-distillate material simultaneously produced by the present process. The flexibility of the present process permits the withdrawal to storage of the middle-distillate hydrocarbon product for subsequent conversion to gasoline boiling range hydrocarbons when the marketability of the latter so requires.

The present three-stage process may be more clearly understood through reference to the accompanying drawing which illustrates one embodiment thereof. Various flow valves, control valves, coolers, condensers, overhead



5 reflux condensers, pumps, compressors, heaters, knockout pots, and other apparatus details have been omitted, or greatly reduced, as not being essential to the complete understanding of the present process. The utilization of these, and other miscellaneous appurtenances will immediately be recognized by one possessing skill in the art of petroleum processing; it is not intended that such modifications remove the process beyond the scope and spirit of the appended claims. Referring now to the drawing, the hydrocarbon charge stock, contaminated by a substantial quantity of nitrogenous compounds, of the order of about 1000 ppm to about 5000 ppm, and sulfurous compounds as high as about 3.0% to about 5.0% by weight, enters the process through line 1 into the so-called stabilizer or charge separator 2. To illustrate a particularly preferred embodiment of the present invention, the charge stock in line 1 may have an initial boiling point of about 370°C. and an end boiling point of about 540°C., as determined by standard ASTM distillation. However, it is understood that the charge stock may be any of the heavy hydrocarbonaceous material described above; for example, a reduced crude consisting entirely of hydrocarbons boiling at a temperature in excess of 427°C. to 540°C. or more. The total liquid charge stock entering stabilizer 2 is separated into a light charge fraction having an end boiling point of about 427°C., shown as leaving stabilizer 2 via line 3, and a heavy charge fraction having an initial boiling point of about 427°C., indicated as leaving stabilizer 2 via line 4. This heavy charge fraction, is combined with a second heavy fraction containing hydrocarbons boiling in excess of about 427°C., the mixture being passed through heater 6 and line 8 into cracking zone 9. The primary function, to be served by cracking zone 9, is the conversion of those hydrocarbons boiling above a heavy distillate and particularly in excess of a temperature of 427°C. into lower boiling hydrocarbon products. Thus, cracking zone 9 may be a common thermal-cracking reaction zone of the single-coil or double-coil type, in which instance the total liquid charge thereto is raised to the desired thermal cracking temperature in heater 6, prior to entering cracking zone 9 through line 8. In another embodiment, cracking zone 9 may comprise a catalytic hydrocracking unit, in which event the total liquid charge in line 4 is admixed with the requisite quantity of hydrogen entering via line 5, the mixture being raised to the operating temperature in heater 6, passing through line 8 into cracking zone. In this latter instance, cracking zone 9 will contain a suitable hydrocracking catalyst which may be an iron-group metallic component composited with a siliceous carrier material such as alumina and silica. Or, the hydrocracking catalyst may comprise an iron-group metallic component

promoted by a Group VIA metal such as molybdenum, chromium and/or tungsten. The first reaction zone, cracking zone 9, may be, in particular processing schemes, a fluid catalytic cracking unit operating in the absence of added hydrogen. It is understood that the precise conversion means, illustrated in the drawing as cracking zone 9, by which those hydrocarbons boiling at a temperature in excess of about 427°C., are converted to hydrocarbons boiling below about 800°F., is not considered to be a limiting feature of the present invention. It has been found that although the nitrogenous compounds, contaminating the hydrocarbon charge stock entering line 1, are extremely difficult to remove from the heavier hydrocarbons, that is, those hydrocarbons boiling in excess of about 415°C. or 427°C. these nitrogenous compounds are readily susceptible to removal in the second reaction zone of the present process from the hydrocarbons boiling below these temperatures and formed from the higher boiling hydrocarbons in the first reaction zone of the present process. In any event, the total effluent from cracking zone 9 passes through line 10 into separator 11 from which the normally liquid hydrocarbons are removed via line 13 into fractionator 14.

Separator 11 serves to remove light paraffinic hydrocarbons, such as methane, ethane and propane, and other various gaseous components from the total effluent entering through line 10, providing thereby a normally liquid hydrocarbon stream in line 13. The light hydrocarbons are indicated as leaving separator 11 via line 12. Other gaseous components if present, are removed from the normally liquid hydrocarbons in separator 11, and these may include carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, sulfur dioxide, and various oxides of nitrogen. Various modifications may be made to the separating means illustrated by separator 11, involving for example, the use of a suitable absorbent material, whereby to selectively remove the light paraffinic hydrocarbons or the ammonia.

As illustrated, one of the essential features of the present invention is the initial preparation of a stream of normally liquid hydrocarbons boiling below the heavy distillate end boiling point, preferably below about 427°C., and which pass through line 13 into fractionator 14. Fractionator 14 represents the primary fractionation zone of the present process and is maintained under suitable operating conditions, of temperature and pressure, such that the normally liquid hydrocarbons entering via line 13 are separated into a second heavy fraction, containing those unreacted hydrocarbons boiling at a temperature in excess of the heavy distillate end point or 427°C., and a second light fraction constituting the so-called intermediate product of the present process and containing those hydro-

carbons having a heavy distillate end point, preferably an end boiling point of about 427°C. The second heavy fraction is removed from fractionator 14 via line 7 and is combined with the heavy charge fraction in line 4 leaving stabilizer 2. The second light fraction is removed from fractionator 14 via line 15, and is admixed with the light charge fraction leaving stabilizer 2 in line 3. The resulting light fraction mixture is admixed with hydrogen, entering the system via line 16, and the total charge passing through line 3 is raised to the desired operating temperature between about 260°C. and about 540°C., in heater 17. The heated mixture of hydrogen and the light fractions from stabilizer 2 and fractionator 14 are passed via line 18 into clean-up reaction zone 19. Clean-up zone 19 has disposed therein a catalytic composite comprising from about 4% to about 45% by weight of molybdenum, calculated as the element. The reaction zone is maintained under operating conditions such that the normally liquid hydrocarbons leaving said zone will generally contain less than 10.0 ppm. nitrogen, in some cases less than 5 ppm, while a similar reduction in sulfurous compounds contained within the charge stock, the latter now consisting essentially of hydrocarbons boiling below about a temperature of 427°C., is effected. In addition, as hereinafter set forth, through the careful selection of both catalyst and operating conditions, there will be effected, in clean-up zone 19, a substantial degree of hydrocarbon conversion whereby the heavier hydrocarbons, those boiling within the range of from about 340° to 427°C. are converted into hydrocarbons boiling below about 340°C., without experiencing the excessive production of light paraffinic hydrocarbons, methane, ethane and propane. Furthermore, since the catalyst in clean-up zone 19 is selected for its nitrogen-insensitivity, the rapid deactivation of the catalyst, otherwise resulting when hydrocracking such nitrogen-containing charge stocks, is not experienced. The total effluent from reaction zone 19 is passed via line 20 into separator 21.

As described above with reference to separator 11, separator 21 illustrates a separating means whereby the normally liquid hydrocarbons are recovered in line 23 substantially completely free from light paraffinic hydrocarbons and other gaseous material, indicated as leaving separator 21 through line 22. In addition, as a result of the catalyst and operating conditions of clean-up zone 19, substantial quantities of hydrogen sulfide and ammonia are removed in separator 21. The normally liquid hydrocarbons in line 23 enter line 24, are admixed with hydrogen entering the system via line 25, the entire mixture passing into heater 26, and thereafter through line 27 into hydrocracking zone 28. The total charge to hydrocracking zone 28 will be raised

to a temperature in heater 26, within the range of about 232°C. to about 510°C.; that is, the operating temperature of hydrocracking zone 28 will be at least about 28°C. lower than the operating temperature of clean-up zone 19. The total effluent, including butanes, normally liquid hydrocarbons boiling within the range of from about 38°C. to about 427°C., carbon monoxide, carbon dioxide, and light paraffinic hydrocarbons, are passed through line 29 into separator 30. The normally liquid hydrocarbons, including butanes, are removed from separator 30 via line 32, and passed to side-cut fractionator 33 at a point below centerwell. The light paraffinic hydrocarbons entering separator 30 are removed via line 31, and, as hereinbefore described, various other gaseous components are removed therefrom, such that only normally liquid hydrocarbons, but including butanes, are passed into side-cut fractionator 33.

Fractionator 33 represents the secondary fractionation zone of the present process and is maintained at suitable conditions of temperature and pressure whereby the butanes and normally liquid hydrocarbons having an initial boiling point of about 38°C. and an end boiling point of about 204°C. and containing less than 0.1 ppm. of nitrogen, are removed via line 36. A second fraction, containing less than about 5.0 ppm., and usually less than 3.0 ppm., of nitrogen, is removed from a point above centerwell 34, via line 35. This second fraction contains those hydrocarbons boiling within the middle-distillate boiling range, that is, having an initial boiling point of about 204°C. and an end boiling point of about 340°C. A third fraction, containing those unreacted hydrocarbons boiling within the range of from about 30°C. to about 427°C., are passed through line 24, combined, at least in part, with the total normally liquid hydrocarbon effluent in line 23, further admixed with hydrogen in line 25, and recycled to the system through heater 26 and line 27 into hydrocracking zone 28.

From the foregoing description of the embodiment illustrated in the accompanying drawing, it is readily ascertained that the process is, in effect, a three-stage process for producing hydrocarbons boiling within the gasoline boiling range, and simultaneously for producing increased yields of middle-distillate boiling range hydrocarbons, both being of low nitrogen content and the latter being suitable for direct processing to produce additional gasoline boiling range hydrocarbons. In the three-stage reaction zone system of the present invention each stage individually performs a particular function in a particular manner, the combinative effect being the production of gasoline and middle-distillate boiling range hydrocarbons from those hydrocarbons boiling in excess of a temperature of about 370°C., the latter contaminated by sub-



stantial quantities of nitrogenous compounds of the order of about 1000 ppm. to about 5000 ppm.

Although the present process is most advantageously applied to petroleum-derived feed stocks, heavier than middle-distillate fractions, including high-boiling bottoms recovered from various catalytic cracking operations, it is understood that the charge stock to the present three-stage process may have an initial boiling point in the range of from 200° to 230°C., and an end boiling point as high as 540°C. or higher. The process affords greater benefits in the processing of hydrocarbons charge stocks having significantly higher initial boiling points, that is, of the order of at least about 340° or 370°C. In further describing the process of the present invention, and the various limitations imposed thereupon, the process will be divided, in the interest of simplicity, into its three separate, distinctly individual stages.

The first reaction stage is preferably utilized in such a manner, and under such conditions as to bring about the substantially complete conversion of the charge stock into hydrocarbons boiling below the heavy distillate end boiling point or below 427°C. In some cases, however, it may be desirable to withdraw from the process a small portion of the recycle stream of heavy oil passing (through line 7 of the drawing) from the primary fractionation zone back to the first reactor, whereby to prevent buildup of heavy residual material which might interfere with performance of the first stage heater. Although a portion of the charge stock may be converted, in this first stage, to hydrocarbons boiling within the gasoline boiling range, the greater proportion of the charge stock will be converted in this stage to hydrocarbons boiling within the range of from about 200° or 230°C. to about 427°C., the lighter fractions serving as the charge stock to the second stage of the entire process. Briefly, therefore, the heavy hydrocarbons charge stock, for example, a heavy vacuum gas oil having a boiling range of from about 370°C. to about 540°C., or higher, and contaminated by nitrogenous compounds of the order of from about 1000 ppm. to about 5000 ppm., and sulfurous compounds as high as about 3.0% to about 5.0% by weight, is introduced into a stabilizing column for the purpose of removing those hydrocarbons having an end boiling point of about 427°C. The remainder of the vacuum gas oil charge is admixed with hydrogen in an amount of from about 500 to about 1800 standard liters per liter of such hydrocarbon charge, in those instances wherein the first-stage of the process comprises a hydrocracking reaction zone. As hereinbefore set forth, the reaction zone comprising this first-stage may be a thermal-cracking unit of the single-coil or double-coil type or a catalytic cracking unit operating

without added hydrogen. It is preferred, however, in order to avoid the excessive production of light paraffinic hydrocarbons normally resulting from a thermal cracking unit or fluid catalytic cracking unit, to employ catalytic hydrocracking within the first stage of the process. In the latter instance, the mixture of hydrogen and those hydrocarbons boiling above about 427°C., is heated to the desired operating temperature, of from about 260°C. to about 525°C., and thereafter passed into the first reaction zone. The reaction zone will be maintained under an imposed pressure within the range of from about one-third to about 200 atmospheres, and at a temperature within the aforesaid range. The precise operating conditions will be dependent upon the various physical and/or chemical characteristics of the particular heavy hydrocarbon charge being processed, and upon the type of cracking unit employed. Higher pressures appear to favor the destructive conversion of those hydrocarbons boiling in excess of about 425°C., and are, therefore, preferred; thus, the first reaction zone will preferably operate under an imposed pressure within the range of about 7 to about 200 atmospheres. When utilized as a hydrocracking zone, as distinguished from a simple thermal-cracking zone, the first reaction zone will contain a hydrocracking catalyst comprising at least one metallic component from the metals of Groups VIA and the iron-group of the Periodic Table, and mixtures thereof, and preferably the catalyst will comprise one or more of the metals chromium, molybdenum, tungsten, iron, cobalt, and nickel composited with a suitable carrier metal, which may comprise alumina, magnesia, fuller's earth, montmorillonite, keiselguhr, silica, or the like. Preferably, the carrier material will contain substantial quantities of silica. Thus, the hydrocracking catalyst employed in the first reaction zone may typically comprise from about 10% to about 50% by weight of nickel, and a composite of alumina and from about 65% to about 95% by weight of silica. Lesser quantities of the Group VIA metallic components will be employed and will lie within the range of from about 2.0% to about 20.0% by weight thereof. The hydrocarbon charge stock will contact the particular catalyst employed at a liquid hourly space velocity within the range of from about 0.3 to about 10.0, preferably from about 0.3 to about 3.0. Partial conversion of the sulfurous and nitrogenous compounds will occur in the first reaction zone, the resulting ammonia and hydrogen sulfide being suitably separated, along with other gases, from liquid reaction product, as described further above.

The total liquid charge to the second stage of the process, consisting essentially of hydrocarbons boiling below a temperature of about 427°C., is admixed with hydrogen in an amount of from about 180 to about 1400



bottoms



process

standard liters per liter, the mixture is raised to a temperature of from about 260° to about 540°C., and passed at a liquid hourly space velocity of from 0.1 to 10 into the second reaction zone, maintained under an imposed pressure of about 20 to about 200 atmospheres. The preferred second-stage catalyst comprises, as aforesaid, from about 4.0% to about 45.0% by weight of molybdenum, and preferably utilizes alumina as the sole refractory inorganic oxide within the carrier material, although other refractory inorganic oxides, such as silica, zirconia, magnesia, titania, thoria, boria, may be present in relatively minor quantities. Similarly, quantities of nickel, iron and/or cobalt, in concentration from about 0.2% to about 6.0% may be employed.

The charge to the third stage, is passed over the catalyst in admixture with hydrogen in an amount of from about 180 to about 1100 standard liters per liter of total liquid charge, at an imposed pressure preferably within the range of from about 70 to about 200 atmospheres (although lower pressures, within the range of from about 30 to about 100 atmospheres, may be used) at a liquid hourly space velocity with the range of from about 1.0 to about 10.0, and at a temperature usually within the range of about 232° to about 510°C., but which may be as low as 200°C.

The catalyst employed within the third reaction zone comprises a metallic component selected from the metals of Groups VIA and VIII of the Periodic Table or a mixture of two or more of such metals. Preferred individual metals are chromium, molybdenum, tungsten, iron, cobalt, nickel, palladium, platinum, ruthenium, rhodium, osmium, iridium; preferred mixtures include nickel-molybdenum, nickel-chromium, molybdenum-platinum, cobalt-nickel-molybdenum, molybdenum-palladium, chromium-platinum, chromium-palladium and molybdenum-nickel-palladium. The active metallic components are generally employed in an amount of from about 0.01% to about 20.0% by weight of the total catalyst. The Group VIA 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 the catalyst. The Group VIII metals, which may be divided into two sub-groups, are present in an amount of from about 0.01% to about 10.0% by weight of the total catalyst. When an iron sub-group metal, such as iron, cobalt, or nickel, is employed, it is present in an amount of from about 0.2% to about 10.0% by weight, while, if a platinum-group metal such as platinum, palladium, iridium, etc., is employed, it is present in an amount within the range of from about 0.01% to about 5.0% by weight of the total catalyst. Therefore suitable catalysts for utilization within the third reaction zone include, for example, the following: 6.0% by

weight of nickel and 0.2% by weight of molybdenum; 6.0% by weight of nickel and 0.2% by weight of platinum; 0.4% by weight of platinum; 6.0% by weight of nickel and 0.2% by weight of palladium; 0.4% by weight of palladium. When both a Group VIII and a Group VIA metallic component are used, they will be present in a weight ratio, of the Group VIII metal to the Group IV metal, within the range of from about 0.05:1 to about 5.0:1. Preferably the metal or metals will be composited with a support comprising silica and from about 10% to about 90% of alumina. The following combinations, for example, have been found to be effective: 88% silica—12% alumina; 75% silica—25% alumina; 12% silica—88% alumina.

In those instances where the heavy hydrocarbon oil to be processed possesses physical or chemical characteristics which warrant the utilization of a severe hydrocracking reaction zone as the first stage, any suitable acidity-type cracking catalyst may be employed. Generally, suitable hydrocracking catalysts consist essentially of substantially large quantities of chromium, tungsten, molybdenum, nickel, iron, cobalt, and mixtures thereof. For example, kieselguhr, composited with about 10% to about 50% by weight of nickel, and preferably 30% to 50% by weight, is a suitable catalyst for utilization under severe hydrocracking conditions. On the other hand, an acidic carrier material, comprising about 75% by weight of silica and 25% by weight of alumina, may be composited with about 25% to about 50% by weight of chromium and/or tungsten. In accordance with the process of the present invention, it is preferred that the first reaction zone contain a hydrocracking catalyst comprising at least one metallic component from the metals of Group VIA and the iron-group of the Periodic Table, and mixtures thereof. Thus, a preferred catalytic composite of the present invention would comprise a carrier material of silica and alumina composited with about 10% to about 50% by weight of nickel, and promoted by lesser quantities of chromium, tungsten and molybdenum, within the range of about 2% to about 20% by weight.

The catalyst employed within the third stage of the process of the present invention is preferably disposed within the reaction zone as a fixed bed and operating conditions therein are relatively mild. A lesser quantity of hydrogen is required within the third stage, while the rate of liquid charge thereto may be substantially increased, relative to the other stages. The total effluent from the hydrocracking reaction zone may be 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 liquid hydrocarbon charge stock. The success of the

present invention lies in the separate, distinctly integrated three stages within which the overall process is effected. Through utilization of said process, greater concentrations of hydrocarbons boiling within the gasoline and middle-distillate boiling ranges are produced from those hydrocarbons which boil in excess of the middle-distillate boiling range. The quantity of light paraffinic hydrocarbons produced is lower than otherwise results from the non-selective, single-stage hydrocracking of similar heavy hydrocarbonaceous material. The gasoline boiling range hydrocarbon product is substantially free from unsaturated paraffinic hydrocarbons and therefore well suited for catalytic reforming to further increase the octane rating thereof. Moreover, because the middle-distillate product itself is well-suited for further conversion to gasoline-boiling range material, the present process opens the way for transforming a hydrocarbon charge stock having a boiling range of from about 700°F. to about 1000°F. or higher, practically completely into hydrocarbons boiling within the gasoline boiling range, notwithstanding the presence of excessive quantities of nitrogenous and sulfurous compounds.

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.

EXAMPLE.

There was used in this Example a Mid-continent vacuum gas oil, having an initial boiling point of about 316°C. and a 95% distillation point (ASTM Method D-86) of 518°C., the latter indicating an end boiling point of about 538°C. This gas oil thus boiled in excess of the heavy distillate range.

To determine the effect of omitting the first reaction stage of the present process this vacuum gas oil was supplied directly to the second reaction stage of the present process. The gas oil was contaminated by 252 ppm. of nitrogen, and contained 0.35% by weight of sulfur. The catalyst employed in the second reaction zone consisted of an alumina-silica carrier material, comprising 88% by weight of alumina, impregnated with a single impregnating solution containing molybdic acid and nickel nitrate hexahydrate in amounts to yield a final catalyst containing 6.4% by weight of molybdenum and 2.4% by weight of nickel. The catalyst was maintained at a temperature of 399°C. and a pressure of 102 atmospheres. The liquid charge was fed at a rate equivalent to 0.3 liquid hourly space velocity, in the presence of hydrogen in an amount of 800 normal liters per liter of hydrocarbon oil. Under these conditions, the normally liquid hydrocarbon product contained nitrogen in an amount of 21 ppm.

To illustrate the function of the first reaction stage of the present process, another Mid-continent gas oil boiling entirely within the heavy distillate range was taken as representing the intermediate product effluent obtained from the first reaction zone effluent and was processed in the same manner as the above vacuum gas oil, again simulating the second reaction stage of the present process. The second gas oil was contaminated with total nitrogen in an amount of 252 ppm., and total sulfur in an amount of 0.35% by weight. These and other charge stock inspections are given in the following Table I and are compared therein with the product obtained at the conditions of the test.



TABLE I

	Charge	Product
Specific Gravity at 15.6° C.	.862	.82
ASTM, D-86 Distillation, °C.		
Initial Boiling Point	280	—
10%	303	143
30%	321	255
50%	337	308
70%	359	336
90%	387	393
End Point	401	399
% at 204° C.	0	18.4
% at 343° C.	55.0	73.0
Total Nitrogen, ppm.*	252	0.99
Total Sulfur, weight %	0.35	0.022

* ppm. = parts by weight per million parts of oil.

Product Distribution**

Butanes to 82° C., Vol. %	2.7
82° to 204° C., Vol. %	18.8
204° to 343° C., Vol. %	55.7
343° C. and Heavier, Vol. %	27.6
Total Volumetric Yield	104.8

** C₁—C₈ Light Paraffinic Hydrocarbons = 1.80 weight %

The total liquid hydrocarbon effluent, including butanes, had a nitrogen content of slightly less than 1.0 ppm., and a total sulfur content of 0.022 weight %. These data indicate that the nitrogenous and sulfurous compounds are effectively removed in the second reaction stage from the hydrogen fraction boiling within the heavy distillate boiling range, whereas, these compounds, particularly the nitrogenous compounds, are difficult to remove from those hydrocarbon oil fractions which boil in excess of the heavy distillate range. In addition to the rather effective clean-up of the charge to the second reaction zone, regardless whether the intermediate product supplied to this zone is obtained by thermal cracking, by catalytic cracking or by catalytic hydrocracking, there is evidence of a considerable amount of selective hydrocracking taking place in the second reaction zone as shown by the shift in boiling range. The product distribution, as indicated in Table I, was obtained by precise laboratory fractionation in a 30-plate distillation column, and includes the butanes removed along with the light paraffinic hydrocarbons prior to the laboratory distillation. It is significant that the

light paraffinic hydrocarbon yield was less than 2.0% by weight of the total charge, and that the total volumetric yield was in excess of 100%.

The liquid hydrocarbon product obtained from the Mid-continent gas oil in the second test described above was hydrocracked in a manner illustrating the third reaction stage. The catalyst employed in this third reaction stage consisted of a carrier material of 88% by weight of silica and 12% by weight of alumina, impregnated with sufficient palladium chloride to result in a final composite containing 0.4% by weight of palladium. The operating conditions were, a pressure of 102 atmospheres, a temperature of 302°C., a liquid hourly space velocity of 1.0 and a hydrogen rate of 535 normal liters per liter of liquid charge. It should be noted that these operating conditions are comparatively mild with respect to those normally encountered in single-stage hydrocracking process. The product properties, and the product distribution, obtained on the total liquid hydrocarbon effluent resulting from this simulation of the third reaction stage of the present process, are indicated in following Table II.



hydrocarbon

30

35

40

45

50

55



processes

TABLE II

Specific Gravity at 15.6° C.	49.1
ASTM, D-86 Distillation, °C.	
Initial Boiling Point	69
10%	104
30%	152
50%	230
70%	293
90%	343
End Point	365
% at 204° C.	45.0
% at 343° C.	90.0
Product Distribution*	
Butanes to 82° C.	11.8
82° to 204° C.	46.1
204° to 343° C.	40.3
343° C. and Heavier	8.9
Total Volumetric Yield	107.1

* C₁-C₃ Light Paraffinic Hydrocarbons = 1.64 wt. %

- As in the earlier part of this example, the indicated product distribution accounts for those butanes which are removed from the total reaction zone effluent while separating the light paraffinic hydrocarbons therefrom. The product distribution is, however, based upon an overall material balance of 99.9%. It is again significant that the total light paraffinic hydrocarbon yield was less than about 2.0% by weight of the total liquid charge. In addition, the total volumetric yield was significantly in excess of 100%. Of greater significance, is the fact that only 8.9 volume percent of the total liquid charge to the third stage of the present process was unreacted. As indicated in the product distribution, there resulted 57.9% by weight of gasoline boiling range hydrocarbons and 40.3% by volume of middle-distillate boiling range hydrocarbons.

The foregoing example indicates that the three-stage process of the present invention results in exceedingly large volumetric yields of gasoline boiling range hydrocarbons and middle-distillate hydrocarbons while processing heavy hydrocarbon oils severely contaminated by excessive quantities of both nitrogenous and sulfurous compounds.

WHAT I CLAIM IS:—

1. A process for the conversion of a gasoline-free heavy hydrocarbon oil charge containing nitrogenous compounds and hydrocarbons boiling above 415°C. which com-

prises cracking a stream of said heavy oil charge in a first reaction zone with formation of an intermediate product boiling above the gasoline range and having an end boiling point in the range of from 400° to 435°C., separating said intermediate product in a primary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of said first reaction zone, reacting said intermediate product in a second reaction zone with hydrogen in the presence of a nitrogen-insensitive catalyst having hydrogenating activity with formation of ammonia from nitrogenous compounds, separating ammonia from the normally liquid hydrocarbon effluent of said second reaction zone, thereafter hydrocracking the normally liquid hydrocarbon effluent of the second reaction zone in a third reaction zone in the presence of added hydrogen and a hydrocracking catalyst, separating a hydrogen distillate product which is substantially free from nitrogen and has an end boiling point in the range of from 340° to 370°C. in a secondary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of said third reaction zone, returning a stream of said higher boiling components from said secondary fractionation zone to said third reaction zone, and withdrawing said hydrocarbon distillate product from the process.

2. Process as claimed in claim 1 wherein



TABLE II

Specific Gravity at 15.6° C.	49.1
ASTM, D-86 Distillation, °C.	
Initial Boiling Point	69
10%	104
30%	152
50%	230
70%	293
90%	343
End Point	365
% at 204° C.	45.0
% at 343° C.	90.0
Product Distribution*	
Butanes to 82° C.	11.8
82° to 204° C.	46.1
204° to 343° C.	40.3
343° C. and Heavier	8.9
Total Volumetric Yield	107.1

* C₁-C₃ Light Paraffinic Hydrocarbons = 1.64 wt. %

As in the earlier part of this example, the indicated product distribution accounts for those butanes which are removed from the total reaction zone effluent while separating the light paraffinic hydrocarbons therefrom. The product distribution is, however, based upon an overall material balance of 99.9%. It is again significant that the total light paraffinic hydrocarbon yield was less than about 2.0% by weight of the total liquid charge. In addition, the total volumetric yield was significantly in excess of 100%. Of greater significance, is the fact that only 8.9 volume percent of the total liquid charge to the third stage of the present process was unreacted. As indicated in the product distribution, there resulted 57.9% by weight of gasoline boiling range hydrocarbons and 40.3% by volume of middle-distillate boiling range hydrocarbons.

The foregoing example indicates that the three-stage process of the present invention results in exceedingly large volumetric yields of gasoline boiling range hydrocarbons and middle-distillate hydrocarbons while processing heavy hydrocarbon oils severely contaminated by excessive quantities of both nitrogenous and sulfurous compounds.

WHAT I CLAIM IS:—

1. A process for the conversion of a gasoline-free heavy hydrocarbon oil charge containing nitrogenous compounds and hydrocarbons boiling above 415°C. which comprises

cracking a stream of said heavy oil charge in a first reaction zone with formation of an intermediate product boiling above the gasoline range and having an end boiling point in the range of from 400° to 435°C., separating said intermediate product in a primary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of said first reaction zone, reacting said intermediate product in a second reaction zone with hydrogen in the presence of a nitrogen-insensitive catalyst having hydrogenating activity with formation of ammonia from nitrogenous compounds, separating ammonia from the normally liquid hydrocarbon effluent of said second reaction zone, thereafter hydrocracking the normally liquid hydrocarbon effluent of the second reaction zone in a third reaction zone in the presence of added hydrogen and a hydrocracking catalyst, separating a hydrogen distillate product which is substantially free from nitrogen and has an end boiling point in the range of from 340° to 370°C. in a secondary fractionation zone from the higher boiling components of the normally liquid hydrocarbon effluent of said third reaction zone, returning a stream of said higher boiling components from said secondary fractionation zone to said third reaction zone, and withdrawing said hydrocarbon distillate product from the process.

2. Process as claimed in claim 1 wherein

5 a heavy hydrocarbon oil charge boiling at
least largely in the range of from 370° to
540°C. is fractionated into a light charge
fraction having an end boiling point in the
10 range of from 400° to 435°C. and into a
heavy charge fraction boiling above said light
charge fraction, said heavy charge fraction is
supplied to the cracking in the first reaction
zone, and said light charge fraction is passed
together with the intermediate product, upon
separation of the latter in the primary frac-
tionation zone, to the second reaction zone.

15 3. Process as claimed in claim 2 wherein
the higher boiling components separated from
the intermediate product in the primary frac-
tionation zone are supplied together with the
heavy charge fraction to the first reaction
zone.

20 4. Process as claimed in claim 1 or 2 where-
in substantially all of the higher boiling com-
ponents separated in the secondary fractiona-
tion zone are commingled with the ammonia-
free normally liquid hydrocarbon effluent of
the second reaction zone and the resultant
25 mixture is supplied to the third reaction zone.

30 5. Process as claimed in one of the claims
1 to 4 wherein a light charge fraction boil-
ing below 427°C. is separated from the heavy
oil charge, the remainder of said heavy oil
charge is introduced into the first reaction
zone, an intermediate product having an initial
boiling point in the range of from 200° to
230°C. and an end boiling point below 427°C.
35 is separated in the primary fractionation zone
from the normally liquid hydrocarbon effluent
of the first reaction zone and said intermediate
product is introduced in commingled state
with said light charge fraction into the second
reaction zone.

40 6. Process of any of the claims 1 to 5,
wherein said second reaction zone is main-
tained at a temperature within the range of
from 260°C. to 540°C. and said third reac-
tion is maintained at a temperature at least

28°C. lower than the temperature in said
second reaction zone.

7. Process of any of the claims 1 to 6
wherein said first reaction zone contains a
hydrocracking catalyst comprising at least one
metallic component from the metals of Groups
VIA and the iron-group of the Periodic Table,
and mixtures thereof.

8. Process of any of the claims 1 to 7,
wherein the second reaction zone contains a
catalyst comprising alumina, from 4% to 45%
by weight of molybdenum and from 0.2% to
6% by weight of nickel.

9. Process of any of the claims 1 to 8
wherein said third reaction zone contains a
catalyst comprising at least one metallic com-
ponent selected from the metals of Groups
VIA and VIII of the Periodic Table, and
mixtures thereof.

10. Process of claim 9 further characterized
in that said third reaction zone contains a
catalyst comprising a Group VIA and a Group
VIII metallic component, the ratio of said
Group VIII metallic component to said Group
VIA metallic component being within the
range of 0.05:1 to 5.0:1.

11. Process of claim 9 further characterized
in that said third reaction zone contains a
catalyst comprising at least one platinum-
group metallic component composited with
silica and from 10% to 90% by weight of
alumina.

12. Process of claim 11, wherein said third
reaction zone contains a catalyst comprising
from 0.01% to 5.0% by weight of palladium
composited with silica and from 10% to 90%
by weight of alumina.

13. Process for the conversion of a gasoline-
free heavy hydrocarbon oil charge containing
nitrogenous compounds and hydrocarbons boil-
ing above 415°C. substantially as described.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2.
Chartered Patent Agents.

