

939,200



PATENT SPECIFICATION

DRAWINGS ATTACHED

939,200

Date of Application and filing Complete Specification: Nov. 8, 1961.

No. 39936/61.

Application made in United States of America (No. 68263) on Nov. 9, 1960.

Complete Specification Published: Oct. 9, 1963.

© Crown Copyright 1963.

Index at acceptance:—Class 32, E20.

International Classification:—C10g.

COMPLETE SPECIFICATION

Process for Catalytic Hydrocracking of High Boiling Hydrocarbon Oils

We, UNIVERSAL OIL PRODUCTS COMPANY, a corporation organised 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 single-stage process for the conversion of high boiling hydrocarbon oils into more valuable lower-boiling hydrocarbon products by catalytic hydrocracking. More specifically, the present invention is directed to a catalytic hydrocracking process for the production of hydrocarbons boiling within the normal gasoline boiling range, while maximizing the production of hydrocarbons boiling within the middle-distillate boiling range, utilizing as starting materials a hydrocarbon oil boiling at temperatures in excess of the gasoline and middle-distillate boiling ranges. The process of the present invention is particularly adaptable to the conversion of heavy hydrocarbon oils contaminated through the inclusion of sulfurous and nitrogenous compounds in significant quantities.

Hydrocracking, also commonly referred to as "destructive hydrogenation", or "catalytic cracking in the presence of hydrogen", effects a definite change in the molecular structure of the hydrocarbons being processed, and may be designated as cracking under hydrogenation conditions such that the lower-boiling products of the conversion reactions are substantially more saturated than when hydrogen is not present. Hydrocracking processes are most commonly employed for the conversion of a wide variety of coal tars and heavy residual hydrocarbon oils, for the purpose of producing lower-boiling, saturated products; to some extent such products

include intermediate fractions suitable for utilization as domestic fuels, and heavier gas-oil fractions suitable as lubricants. The preferred processing technique involves the utilization of a catalytic composite having a high degree of selective hydrocracking activity. The use of a catalytic composite in the hydrocracking process affords a measure of control by which the cracking reactions being effected become more selective from the standpoint of producing an increased yield of normally liquid product having improved chemical and physical characteristics. Of great significance to a catalytic hydrocracking process is the achievement of effective catalytic action over an extended period of time.

Selective hydrocracking is of particular importance when processing hydrocarbons and mixtures of hydrocarbons having normal boiling points at temperatures in excess of the gasoline and middle-distillate boiling ranges; that is, hydrocarbons and various mixtures of hydrocarbons, as well as hydrocarbon fractions and distillates which boil entirely or at least predominantly in a boiling range extending from an initial boiling point in the range of from about 343° to about 371° C. to an end boiling point as high as 538° C. or more. Through the exercise of control over the selective hydrocracking of such heavier hydrocarbon fractions, it becomes possible to produce a substantially increased yield of middle-distillate boiling range hydrocarbons; that is, those hydrocarbons and hydrocarbon fractions having a boiling range indicated by an initial boiling point of about 204° to 232° C. and an end boiling point of about 343° to 371° C. Selectivity is required in order to avoid the usually experienced, excessive decomposition of normally liquid gasoline and middle-distillate boiling range hydrocarbons into normally gaseous hydrocarbons, the latter generally considered to be waste products. As a result of the excessive production of

[Price 4s. 6d.]

normally gaseous hydrocarbons, inherent in uncontrolled or non-selective hydrocracking, the volumetric yield of valuable normally liquid hydrocarbons is readily decreased to the extent that the process is not economically feasible. In illustration, it might be said that desired selective hydrocracking involves the splitting of a higher-boiling hydrocarbon molecule into two molecules, both of which are normally liquid hydrocarbons boiling within the gasoline and middle-distillate boiling ranges. Selective hydrocracking minimizes the removal of methyl, ethyl and propyl groups, which, in the presence of hydrogen, are converted to methane, ethane and propane, these hydrocarbons being usually referred to as "light paraffinic hydrocarbons". The production of the aforesaid radicals is controlled in order to produce acceptable yields of normally liquid hydrocarbons. Uncontrolled or non-selective catalytic hydrocracking, moreover, results in rapid formation of coke and other heavy hydrocarbonaceous material, which becomes deposited upon the catalyst and decreases, or destroys, the activity thereof to catalyze the desired reactions in the desired controlled manner. A shorter processing cycle results, accompanied by the inherent necessity of more frequent regeneration of catalyst, or of total replacement thereof with fresh catalyst. Furthermore, the deactivation of the catalyst appears to inhibit the hydrogenation activity thereof to the extent that a significant proportion of the gasoline and middle-distillate boiling range products consists of unsaturated hydrocarbons, so that these products are not especially suitable for immediate utilization, or for subsequent direct processing by catalytic reforming.

Investigations have further indicated that the presence of nitrogen-containing compounds, and sulfur-containing compounds within the hydrocracking charge stock, regardless of the exact boiling range thereof, ordinarily results in the relatively rapid deactivation of the catalytically active metallic components, as well as the solid carrier material which serves as the acidic-hydrocracking component. The deactivation of the catalyst appears to result from the reaction of nitrogenous and sulfurous compounds with the various catalytic components, the extent of such deactivation increasing as the process continues, and as the charge stock further contaminates the catalyst through contact therewith. It appears that the deactivation, resulting from the presence of excessive quantities of nitrogenous and sulfurous compounds, is not a simple reversible phenomenon, which may be easily rectified by the relatively simple expediency of heating the catalyst in a suitable atmosphere for the purpose of decomposing the nitrogen-contain-

ing complexes, or by overcoming the adverse effect of the sulfurous compounds.

A primary object of the present invention is to provide a catalytic hydrocracking process which results in substantially greater yields of hydrocarbons boiling within the middle-distillate boiling range, while processing petroleum hydrocarbon charge stocks boiling in excess of the middle-distillate boiling range. A related object is to provide a process utilizing a particular catalytic composite which permits the use of a hydrocarbon charge stock containing relatively excessive quantities of residual nitrogenous and sulfurous compounds which otherwise tend to effect the rapid deactivation of the catalytic composite. Through the utilization of the selective hydrocracking process of the present invention, a hydrocarbon charge stock, consisting entirely of hydrocarbons boiling in excess of the middle-distillate boiling range, is converted in virtual 100.0% yield by weight, into hydrocarbons boiling within the gasoline and middle-distillate boiling ranges. An advantage of the process of the present invention is the inherent flexibility in regard to the quality and quantity of the final product produced; that is, for example, the production of substantial yields of gasoline boiling range hydrocarbons while simultaneously maximizing the quantity of middle-distillate hydrocarbons produced. Furthermore, the process of the present invention makes possible the simultaneous production of gasoline boiling range hydrocarbons, kerosene fractions suitable as jet fuel blending components, and middle-distillate hydrocarbon fractions, all of which are substantially completely free from sulfurous and nitrogenous compounds.

In accordance with the present invention a hydrocarbon oil charge boiling entirely or at least predominantly above 343° C. and containing nitrogenous and sulfurous hydrocarbon derivatives is converted practically completely into lower boiling normally liquid hydrocarbons substantially free from nitrogen and sulfur by contacting a mixture of said hydrocarbon oil and recirculated heavy oil in a reaction zone in the presence of from 35.6 to 178 normal cubic meters of hydrogen per hectoliter of normally liquid hydrocarbons at a temperature in the range of from 316° to 454° C. and a pressure of from 54.5 to 204 atmospheres with a catalyst in which a catalytic composite of from 20% to 50% by weight of silica and from 50% to 80% by weight of alumina contains in excess of 10% and not more than 30% by weight of molybdenum and from 1% to 6% by weight of nickel (said molybdenum and nickel being calculated as the elements and based upon the weight of said alumina-silica composite) at a space velocity of at least 0.5 liquid



extent

5 volumes of the normally liquid hydrocarbons per hour per volume of said catalyst, separating hydrogen sulfide and ammonia from the effluent of the reaction zone and also separating a hydrogen-rich gas from said effluent, thereafter separating the normally liquid hydrocarbons of said effluent by fractionation into gasoline- and middle distillate fractions and into a higher boiling oil fraction having an initial boiling point in the range of from 10 343° to 371° C., and returning said higher boiling oil fraction as said recirculated heavy oil to said reaction zone.

15 In a more specific embodiment of the process according to the present invention ammonia and hydrogen sulfide and the hydrogen-rich gas are first separated from the effluent of the reaction zone, the hydrogen-rich gas is recirculated together with fresh 20 hydrogen to the reaction zone, the remaining reaction zone effluent is freed from light paraffinic hydrocarbons, the resulting normally liquid hydrocarbon stream is passed into a first fractionation zone and therein is separated into an overhead hydrocarbon stream containing hexanes and lower-boiling hydrocarbons, an intermediate hydrocarbon mixture boiling in the gasoline boiling range and a bottoms fraction consisting of those hydrocarbons boiling in excess of said intermediate 30 mixture, this bottoms fraction is passed into a second fractionation zone, a hydrocarbon fraction boiling within the middle-distillate boiling range and having an end boiling point in the range of from 343° to about 371° C. is recovered as distillate from the second fractionation zone, and the hydrocarbons boiling in excess of the middle-distillate boiling range are withdrawn from the second fractionation zone and supplied 40 together with the hydrocarbon oil charge and hydrogen to the reaction zone. Preferably the ratio of total liquid hydrocarbon charge to the reaction zone to the fresh hydrocarbon oil charge is maintained between 1.0 and 3.0 and the total liquid hydrocarbon charge is passed through the reaction zone at a space velocity of not more than 2 volumes per hour per volume of catalyst.

50 The applicability of the present invention to the production of lower-boiling hydrocarbon products from the heavy hydrocarbon oil charge may be more clearly understood by initially defining several of the terms and 55 phrases employed within the specification and the appended claims. In those instances where temperatures are given in regard to initial boiling points, boiling ranges, and end boiling points, it is understood that the temperatures have reference to those which are obtained through the use of standard ASTM distillation methods (methods of the American Society for Testing Materials). The term "hydrocarbons", except when specifically 60 qualified, refers generally to saturated hydro-

carbons, straight-chain and branched-chain hydrocarbons, unsaturated hydrocarbons, aromatic hydrocarbons, naphthenic hydrocarbons, as well as various mixtures of hydrocarbons such as hydrocarbon fractions and/or hydrocarbon distillates. The phrase "hydrocarbons boiling within the gasoline boiling range", or "gasoline boiling range hydrocarbons", is intended to connote those hydrocarbons which boil within the range of from 48° C. to 204° to 232° C.; this includes those hydrocarbon fractions which boil within the range extending from 48° C. to an end boiling point within the range of from 204° to 232° C., which are generally employed as motor fuels, and which may, or may not, contain iso- and normal butanes, and/or pentanes. Hydrocarbons "boiling at a temperature in excess of the gasoline boiling range" is intended to connote therefore, those hydrocarbons and mixtures of hydrocarbons which possess an initial boiling point in excess of about 204° C. to about 232° C. The term "middle-distillate" refers to those hydrocarbon fractions having an initial boiling point within the range of from about 204° C. to about 232° C. and an end boiling point within the range of from about 343° C. to about 371° C. The process of the present invention possesses the inherent flexibility to produce a kerosene fraction in addition to middle-distillate and gasoline boiling range fractions. The term "kerosene fraction" is intended to connote those hydrocarbons boiling within the range of from about 204° C. to about 260° C. Similarly, in regard to the catalytic composite employed within the reaction zone of the present invention, the term "metallic component", or "catalytically active metallic component", is intended to encompass those catalytic components which are employed for their hydrocracking activity, as well as the propensity for the destructive removal of the nitrogenous and sulfurous compounds as the case may be. In this manner, the catalytically active metallic components are distinguished from those components which are employed in the acidic cracking component used as the carrier material. As hereinafter set forth in greater 115 detail, the process of the present invention utilizes a catalytic composite consisting of at least four components in particular concentrations. This catalytic composite is one of the essential features of the present invention, and will be hereinafter described with reference to the reaction zone and in regard to the function to be served.

120 In addition to the foregoing definitions, the use of the term "gasoline fraction" is intended to include also a hydrocarbon fraction having an end boiling point of about 177° C. Similarly, the term "kerosene fraction" is designed to encompass a hydrocarbon fraction having an initial boiling point within the range of 130

about 177° C. to about 232° C., and an end boiling point up to about 260° C.

Regardless of the precise composition of the catalytic composite, it is prepared through the utilization of a suitable carrier material, which may be either naturally-occurring or synthetically-prepared. Suitable naturally-occurring carrier materials include various aluminum silicates, particularly when acid-treated to increase the activity thereof, while synthetically-prepared cracking catalyst components are selected from the refractory inorganic oxides including at least both silica and alumina. Other suitable refractory inorganic oxides which may be combined as an integral portion of the hydrocracking catalyst, in particular instances, and for the purpose of imparting certain desired characteristics to the catalyst, include zirconia, magnesia, titania, thoria and boria. The preferred cracking catalyst component is a composite of silica and alumina.

As hereinbefore set forth, the process of the present invention is particularly directed toward the conversion of hydrocarbons and mixtures of hydrocarbons boiling in excess of the gasoline and middle-distillate boiling ranges. It is most advantageously applied to petroleum-derived feed stocks, particularly those stocks commonly considered as being heavy gas oil fractions, heavy vacuum gas oils, lubricating oils, black and white oil stocks, and is easily adaptable to the processing of the high-boiling bottoms recovered from various catalytic cracking operations. Therefore, although the charge stock of 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, on the order of about 343° C. to about 371° C. Generally, all of the sources of feed stock contain high-boiling nitrogenous compounds and sulfurous compounds as contaminants; the nitrogenous compounds are generally present in quantities as high as about 1000 ppm to about 8000 ppm ("ppm" signifies parts per million parts by weight). Although the major proportion of such nitrogenous and sulfurous compounds may be removed by various refining treatments, whereby the structure of the hydrocarbon components is not substantially altered, but the nitrogenous, organic bound components are converted into ammonia and the corresponding hydrocarbon residue, it is very difficult to remove the last few parts of nitrogen prior to subjecting the charge stock to the hydrocracking process. Through the utilization of the process and the catalyst of the present invention, charge stocks may be subjected to conversion notwithstanding the fact that they are contaminated by sulfurous

compounds in an amount as high as about 8.0% by weight of sulfur, and nitrogenous compounds in amount as high as 8000 ppm of nitrogen.

The present invention may be more clearly understood through reference to the accompanying drawing which illustrates one particular embodiment thereof. It is not intended, however, that the process of the present invention be unduly limited to the particular embodiment so illustrated. In the drawing, various auxiliary equipment such as flow valves, control valves, coolers, condensers, overhead reflux condensers, pumps, compressors, and knock-out pots, have either been eliminated, or greatly reduced as not being essential to the complete understanding of the present process. The utilization of such miscellaneous appurtenances will immediately be recognized by one possessing skill within the art of petroleum processing. Referring now to the drawing, the hydrocarbon charge stock, contaminated by a substantial quantity of nitrogenous compounds on the order of about 1000 ppm. to about 8000 ppm. and sulfurous compounds as high as about 2.0% to about 8.0% by weight, enters the process through line 1 wherein it is admixed with make-up hydrogen (that is, fresh hydrogen supplied from outside the process) in line 2, a hydrogen-rich recycled gas in line 3, and hydrocarbons boiling in excess of about 343° C. in line 4, the source of which is later described. In some instances, it may be preferable not to heat the recycled hydrogen in line 3 with the hydrocarbon charge in line 1; in such a case, the recycled hydrogen will be commingled with the heated charge in line 6. The mixture of hydrogen and heavy hydrocarbons in line 1 is passed through heater 5 and line 6 into reactor 7. The mixture entering heater 5 via line 1 is such that hydrogen is present therein in an amount within the range of from 35.6 to 178 normal cubic meters per hectoliter of liquid hydrocarbons. The temperature of the mixture is raised to a level within the range of from 316° C. to 454° C., and is passed from heater 5 through line 6 into reactor 7 containing a catalyst containing the four components alumina, silica, molybdenum and nickel. Reactor 7 is maintained under an imposed pressure within the range of from 54.5 to 204 atmospheres, and the liquid hydrocarbon charge stock contacts the catalyst at a liquid hourly space velocity (defined as volume of liquid charge per hour per volume of catalyst disposed within the reaction zone), within the range of from about 0.5 to about 2.0. This liquid hourly space velocity is calculated on the basis of the total liquid hydrocarbon charge, or combined feed to reactor 7. The combined feed ratio, that is, the total liquid hydrocarbon charge to the fresh hydrocarbon charge, will generally be between 1.0 and 3.0.

Under the foregoing conditions, and in the presence of the high molybdenum-containing catalyst, the organically-bound nitrogenous 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 mercaptans and thiophenes, are converted into hydrogen sulfide and the corresponding sulfur-free hydrocarbon counterpart. In addition to this effective clean-up of the hydrocarbon charge stock, whereby the nitrogenous and sulfurous compounds are converted into hydrogen sulfide and ammonia, a significant degree of hydrocarbon conversion occurs whereby the heavier molecular weight hydrocarbons, boiling at a temperature in excess of about 343° C. are converted via highly selective cracking reactions virtually completely into hydrocarbons boiling below about 343° C. It is significant that the conversion reactions effected in reactor 7 are such that very little, if any, light (normally gaseous) paraffinic hydrocarbons are produced; for the most part, the conversion reactions produce hydrocarbons boiling within the middle-distillate boiling range of from about 204° C. to about 343° C., accompanied by the production of about 25.0% by volume of gasoline boiling range hydrocarbons.

The total reaction zone effluent is passed via line 8 into separator 9, and is a mixture of normally liquid hydrocarbons including butanes, light paraffinic hydrocarbons (such as methane, ethane, and propane), hydrogen sulfide, ammonia, and hydrogen. Therefore, although indicated as a single vessel, the separation zone illustrated by separator 9 may be any suitable separation means whereby there is produced a stream of normally liquid hydrocarbons (containing butanes and some light paraffinic hydrocarbons) indicated in the drawing as leaving separator 9 via line 12, and a separate gaseous phase containing some light paraffinic hydrocarbons, ammonia, hydrogen sulfide, hydrogen, and other gaseous components such as carbon dioxide, and as illustrated in the drawing, leaving separator 9 via line 10. For example, water may be injected into line 8 being admixed therein with the total reactor effluent and thereafter subjected to separation such that ammonia is absorbed and removed within the water-phase while the hydrogen sulfide and other gaseous components are removed in a gaseous phase and the normally liquid hydrocarbons are separately recovered through line 12. On the other hand, the total reaction zone effluent may be passed into a separations zone counter-currently to a liquid absorbent whereby the ammonia, hydrogen sulfide, and various gaseous components other than hydrogen are effectively removed therefrom. Still another modification would involve separately treating the gaseous phase in line 10 to remove the

ammonia, hydrogen sulfide, carbon dioxide, and light paraffinic hydrocarbons, so as to recover therefrom a substantially pure hydrogen recycle gas stream. This hydrogen recycle gas stream is raised to the operating pressure within the range of from 54.5 to 204 atmospheres by compressor 11, and is passed through line 3 to combine with the mixture of hydrocarbon charge in line 1.

The normally liquid hydrocarbons, containing some butanes, pass from separator 9 through line 12 into debutanizer 13. Debutanizer 13 functions to separate those paraffinic hydrocarbons containing four or less carbon atoms, which hydrocarbons are removed via line 14, generally being employed as fuel gas. In those instances where it is desired to recover the iso- and normal butanes, debutanizer 13 may be operated so as to function as a depropanizer, in which case the C₄ hydrocarbons will be removed from the bottom of the fractionator via line 15 along with the normally liquid hydrocarbons containing pentanes and heavier hydrocarbons. In any event, the normally liquid hydrocarbons are passed into a fractionating column 16 herein called "splitter" which contains an upper center well 17 and a lower center well 18, the charge to the splitter entering at a point intermediate the center wells. Hydrocarbons containing five and six carbon atoms, and in some instances the iso- and normal butanes, are recovered through line 19, and may be directly employed as jet fuel blending components, motor fuel blending components, or may be employed as charge to an isomerization process for the purpose of increasing the octane rating thereof. Gasoline boiling range hydrocarbons are removed above center well 17 via line 23 and consist essentially of heptanes and heavier hydrocarbons boiling up to a temperature of about 204° C. This gasoline boiling range fraction is substantially completely free from nitrogenous and sulfurous compounds and is readily adaptable as charge to a catalytic reforming unit for the purpose of increasing the octane rating thereof. Where economic considerations demand, a kerosene portion of middle-distillate boiling range hydrocarbons may be removed above center well 18 via line 24 containing valve 25. This kerosene fraction will generally have a boiling range of from about 204° C. to about 260° C. Under certain operating conditions, valve 25 may be closed and the gasoline boiling range hydrocarbons in line 23 withdrawn to contain those hydrocarbons boiling up to about 232° C., in which case those hydrocarbons which boil above 232° C. will be removed from splitter 16 via line 20. As illustrated in the drawing, those middle-distillate boiling range hydrocarbons passing through line 20 are fractionately redistilled in rerun column 21

70

75

80

85

90

95

100

105

110

115

120

125

130



to provide a middle-distillate fraction which is removed via line 22. Those hydrocarbons boiling in excess of the middle-distillate boiling range, or in excess of a temperature in the range of from about 343° C. to about 371° C. are removed from rerun column 21 via line 4 and are recycled to commingle with the fresh hydrocarbon charge and hydrogen in line 1. As hereinbefore stated, the heavier hydrocarbons are admixed with the fresh hydrocarbon charge in an amount to yield a combined feed ratio of between 1.0 and 3.0. Where desired splitter 16 and rerun column 21 may be combined into a single vessel wherein the middle-distillate fraction is withdrawn as an intermediate stream.

In the present process both the gasoline and middle-distillate hydrocarbon streams are produced substantially free from contamination by nitrogenous and sulfurous compounds. The gasoline boiling range hydrocarbons are, therefore, extremely well suited for immediate direct processing by way of catalytic reforming, and the middle distillate hydrocarbons are adapted for utilization as a light lubricating or fuel oil. As hereinbefore stated, a kerosene fraction boiling up to about a temperature of 260° C., and substantially free from contaminating nitrogenous and sulfurous compounds may be produced, and may be immediately employed as a jet fuel blending component.

Various modifications may be made to the illustrated embodiment by those possessing skill within the art of petroleum processing, without departing from the invention as defined by the appended claims. For example, the separating means indicated by separator 9 may be combined with debutanizer 13, whereby a somewhat different flow pattern and apparatus results. It is evident, however, that such a flow pattern will merely accomplish the same object resulting from the indicated flow pattern.

The catalyst containing alumina, silica, molybdenum and nickel for utilization in the present process may be manufactured by any suitable means; a particularly convenient method involves the utilization of impregnating techniques. The impregnating method of preparation involves initially forming an aqueous solution of water-soluble compounds of nickel and molybdenum, such as nickel nitrate, nickel carbonate, ammonium molybdate and molybdic acid. Where the compound of either molybdenum and/or nickel is not water-soluble at the temperature employed during the impregnating technique, other suitable solvents such as ammoniacal solutions, alcohols and ethers, may be employed. In any event, the alumina-silica carrier material particles are commingled with the aforementioned aqueous solutions, and subsequently are dried at a temperature of about 93° C. The dried composite is thereafter

subjected to high temperature calcination in an atmosphere of air, at a temperature of from about 593° C. to about 927° C. The alumina-silica carrier material may be impregnated first with the molybdenum-containing solution, subsequently dried and calcined, and thereafter impregnated with the nickel-containing solution. On the other hand, the two solutions may be first commingled with each other, the carrier material being then impregnated in a single step. The particular means which are chosen for the preparation of the catalyst is not considered to be a limitation upon the process of the present invention. Likewise, the molybdenum and nickel, after being composited with the alumina-silica carrier material, may be caused to exist therein in any desired form, and either as the element or as some compound thereof. Thus, the calcined composite may be further treated for the purpose of providing a catalyst in which the molybdenum and nickel exist as sulfides, nitrates, oxides, sulfates, or in their most reduced state. For the purposes of defining the present invention, the concentrations of molybdenum and nickel, as stated in the specification and the appended claims, refer to the concentrations calculated as the elements thereof, and are based upon the weight of the alumina-silica carrier material.

The carrier material preferred in the catalyst for use in the present process may be synthetically prepared in any suitable manner including, separate, successive, or coprecipitation methods. For example, an alumina-silica carrier material, comprising from 20.0% to 50.0% by weight of silica, may be prepared by the method wherein the oxides are precipitated separately and then mixed, preferably in the wet state; when a method of successive precipitations is employed, the first oxide is precipitated, and the wet slurry, either with or without prior washing, is composited with a salt of the other component. Precipitation of the oxide thereof 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 size and/or shape. A preferred means of manufacture comprises commingling an acid such as hydrochloric acid with commercial water glass under conditions to precipitate silica, washing the resulting precipitate with acidulated water or other means to remove sodium ions, commingling the slurry with an aluminum salt such as aluminum chloride, and either adding a basic precipitant such as ammonium hydroxide to precipitate alumina, or forming the desired oxide or oxides by the thermal decomposition of the salt as the case may permit.

The catalytic composite utilized in the hydrocracking reaction zone of the present



- invention, which composite is specifically designed to be relatively immune to the deactivating influence of sulfurous compounds, and especially insensitive to nitrogen, contains at least the four components alumina, silica, molybdenum, and nickel. With respect to the composite of alumina and silica, the alumina is present in an amount of from 50.0% to 80.0%, and at least as great as silica which is present in an amount of from 20.0% to 50.0%. The molybdenum component is present in an amount in excess of 10.0% and up to 30%, calculated as the element and based upon the weight of the alumina-silica composite. The nickel is present in an amount less than the molybdenum, and within the range of from 1.0% to 6.0% by weight of the alumina-silica composite.
- The following example is given for the purpose of further illustration, and to indicate the benefits afforded through the utilization of the process of the present invention.
- The catalyst employed within the example comprised 2.42% by weight of nickel, 18.9% by weight of molybdenum, 27.7% by weight of silica, the remainder thereof being alumina. The catalyst was prepared by initially, separately preparing alumina and silica hydrosols.
- The alumina-containing hydrosol was prepared from aluminum metal and hydrochloric acid, and resulted in an aluminum chloride hydrosol containing 13.74% by weight of aluminum and having a 1.20 aluminum to chloride weight ratio. The silica hydrosol was prepared by adding dilute water glass to dilute hydrochloric acid, the mixture being combined with the alumina hydrosol in an amount to yield a final carrier material containing about 31.0% by weight of silica and 69.0% by weight of alumina. The silica hydrosol was combined with the alumina hydrosol, and urea was added thereto to effect 200% neutralization of the total chloride in the mixture, and sufficient hexamethylenetetramine was added to effect 30% neutralization of the mixture. The resulting combined hydrosol was formed into 1.6 mm spherical particles in accordance with the "oil-drop" method as set forth in U.S. Patent No. 2,620,314 issued to James Hoekstra. The spheres were dried at a temperature of about 121° C. and then calcined for a period of two hours at a temperature of 677° C. The apparent bulk density of the spherical silica-alumina particles was about 0.41 grams per cc.
- The impregnation of the spherical silica-alumina particles was made by commingling nickel nitrate hexahydrate and molybdenum as molybdic acid in an ammoniacal solution in a ratio of 12.0 grams of nickel and 100.0 grams of molybdenum per liter of silica-alumina particles. The impregnated material was dried and then calcined for one hour at a temperature of 593° C. in an atmosphere of air. The calcined catalyst, having an apparent bulk density of 0.60 grams per cc, comprised 2.42% by weight of nickel, 18.9% by weight of molybdenum and 27.7% by weight of silica, in addition to the alumina, and about 1.5% by weight of volatile matter.

EXAMPLE

The charge stock employed in this example was a Farmer's Union vacuum gas oil having a gravity of 0.9242 at 15.6° C. The charge stock boiled within the range from 257° C. to 510° C.; other charge stock properties are given in the following Table I:

TABLE I

100 ml ASTM Distillation, °C.	
Initial Boiling Point	257
5%	307
10%	331
30%	379
50%	408
70%	439
90%	478
95%	492
End Boiling Point	510
Contaminants	
Sulfur, wt. %	2.60
Nitrogen, ppm.	1200

The vacuum gas oil was passed into a reaction zone containing the four-component catalyst described above. The reaction zone was maintained at a pressure of 102 atmospheres and a temperature of 399° C.; the liquid hourly space velocity was 1.0, based upon the combined feed to the reaction zone, in the presence of 106.8 normal cubic meters of hydrogen per hectoliter of this combined feed. The product distribution, and ultimate yields are given in the following Table II. The total reaction zone effluent was separated to remove hydrogen sulfide and ammonia and to provide a hydrogen rich recycle gas stream, a light paraffinic gas from which the iso- and normal butanes were subsequently recovered,

and a normally liquid hydrocarbon phase. The latter was then subjected to fractionation to recover a pentane-hexane fraction, a heptane to 204° C. gasoline fraction, a 204° C. to 343° C. middle-distillate fraction, and those hydrocarbons which boiled in excess of 343° C. and which were recycled to commingle with the fresh charge to the reaction zone. The recycle of the heavy hydrocarbons, boiling in excess of 343° C. resulted in a combined feed ratio of from 1.2 to 1.5 over the entire period of the operation. Additional calculations indicated that a total of about 33.82 normal cubic meters of hydrogen were consumed for each hectoliter of liquid hydrocarbon charge to the reaction zone.

TABLE II
Hydrocarbon Product Distribution and Yields

Component	Wt. %	Vol. %
Methane	0.5	—
Ethane	0.5	—
Propane	1.0	—
Total Light Paraffins	2.0	—
Butanes	1.2	1.9
Total Gaseous Hydrocarbons	3.2	—
Pentanes	1.2	1.8
Hexanes	1.7	2.3
Total C ₅ —C ₆ Fraction	2.9	4.1
Heptanes — 204° C. Gasoline	21.9	25.9
204°— 343° C. Middle-Distillate	72.3	78.5
Total Debutanized Liquid Yield	—	108.5

As indicated in Table II, the process of the present invention resulted in a total liquid volume yield of 108.5% exclusive of the iso- and normal butanes. Of this total quantity, the pentane-hexane fraction, which may be employed as a jet fuel blending component, amounted to about 4.1% by volume. Middle-distillate hydrocarbons boiling within the range of from 204° C. to 343° C., were produced in an amount of 78.5% by volume; the heptane to 204° C., gasoline fraction was recovered in an amount of about 25.9% by volume. Probably the most significant factor appearing in Table II is the volume percent yield of marketable hydrocarbons, while ex-

periencing a virtually insignificant, negligible yield loss to light paraffinic hydrocarbons of only 2.0% by weight, based upon fresh charge to the reaction zone. The gasoline fraction indicated a composition of 5.0% aromatics, 45.0% naphthenes and 50.0% paraffins, an excellent charge for use in a catalytic reforming process. The pentane/hexane fraction indicated an octane rating, F-1+3.0 cc. TEL of 91.

The foregoing example and specification indicate clearly the process of the present invention and the benefits to be afforded by the utilization thereof. It has been shown that the present process effects virtually complete

conversion of severely contaminated heavy hydrocarbonaceous material into valuable lower-boiling products, accompanied by a negligible yield loss to light paraffinic hydrocarbons.

5

WHAT WE CLAIM IS:—

1. Process for converting a high boiling hydrocarbon oil into more valuable lower boiling hydrocarbon products in the presence of added hydrogen and a hydrocracking catalyst characterized in that a hydrocarbon oil charge at least predominantly boiling above 343° C. and containing nitrogenous and sulfurcus hydrocarbon derivatives is converted in high weight yield into lower boiling normally liquid hydrocarbons substantially free from nitrogen and sulfur by contacting a mixture of said hydrocarbon oil and recirculated heavy oil in a reaction zone in the presence of from 35.6 to 178 normal cubic meters of hydrogen per hectoliter of normally liquid hydrocarbons at a temperature in the range of from 316° to 454° C. and a pressure of from 54.5 to 204 atmospheres with a catalyst in which a catalytic composite of from 20% to 50% by weight of silica and from 50% to 80% by weight of alumina contains in excess of 10% and not more than 30% by weight of molybdenum and from 1% to 6% by weight of nickel (said molybdenum and nickel being present as the elements or compounds thereof and amounts thereof being calculated as the elements and based upon the weight of said alumina-silica composite) at a space velocity of at least 0.5 liquid volumes of the normally liquid hydrocarbons per hour per volume of said catalyst, separating hydrogen sulfide and ammonia from the effluent of the reaction zone and also separating a hydrogen-rich gas from said effluent, thereafter separating the normally liquid hydrocarbons of said effluent by fractionation into gasoline- and middle-distillate fractions and into a higher boiling oil fraction having an initial boiling point in the range of from 343° to 371° C., and returning said higher boiling oil fraction as said recirculated heavy oil to said reaction zone.

2. Process according to claim 1, characterized thereby that the ratio of total liquid

hydrocarbon charge to the reaction zone to the fresh hydrocarbon oil charge is maintained between 1.0 and 3.0 and the total liquid hydrocarbon charge is passed through the reaction zone at a space velocity of not more than 2 volumes per hour per volume of catalyst present in said reaction zone.

55

3. Process according to claim 1 or 2, characterized thereby that the hydrogen and the mixture of the hydrocarbon oils are brought into contact in the reaction zone with the catalyst after the latter has been calcined at a temperature of at least 593° C.

60

4. Process according to one of the claims 1 to 3, characterized thereby that ammonia and hydrogen sulfide and the hydrogen-rich gas are first separated from the effluent of the reaction zone, the hydrogen-rich gas is recirculated together with fresh hydrogen to the reaction zone, the remaining reaction zone effluent is freed from normally gaseous paraffinic hydrocarbons, the resultant normally liquid hydrocarbon stream is passed into a first fractionation zone and therein is separated into an overhead hydrocarbon stream containing hexanes and lower boiling hydrocarbons, an intermediate hydrocarbon mixture boiling in the gasoline boiling range and a bottoms fraction consisting of hydrocarbons boiling in excess of said intermediate mixture, said bottoms fraction is passed into a second fractionation zone, a hydrocarbon fraction boiling within the middle-distillate boiling range and having an end boiling point in the range of from 343° to 371° C. is recovered as distillate from said second fractionation zone, and the hydrocarbons boiling in excess of said middle-distillate and boiling point are withdrawn from said second fractionation zone and supplied together with the fresh hydrocarbon oil charge to the reaction zone.

65

70

75

80

85

90

5. The process for converting a high boiling hydrocarbon oil into more valuable lower boiling hydrocarbon products as claimed in claim 1 and substantially as described with reference to the accompanying drawing.

95

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

J.L.C.

conversion of severely contaminated heavy hydrocarbonaceous material into valuable lower-boiling products, accompanied by a negligible yield loss to light paraffinic hydrocarbons.

WHAT WE CLAIM IS:—

1. Process for converting a high boiling hydrocarbon oil into more valuable lower boiling hydrocarbon products in the presence of added hydrogen and a hydrocracking catalyst characterized in that a hydrocarbon oil charge at least predominantly boiling above 343° C. and containing nitrogenous and sulfurous hydrocarbon derivatives is converted in high weight yield into lower boiling normally liquid hydrocarbons substantially free from nitrogen and sulfur by contacting a mixture of said hydrocarbon oil and recirculated heavy oil in a reaction zone in the presence of from 35.6 to 178 normal cubic meters of hydrogen per hectoliter of normally liquid hydrocarbons at a temperature in the range of from 316° to 454° C. and a pressure of from 54.5 to 204 atmospheres with a catalyst in which a catalytic composite of from 20% to 50% by weight of silica and from 50% to 80% by weight of alumina contains in excess of 10% and not more than 30% by weight of molybdenum and from 1% to 6% by weight of nickel (said molybdenum and nickel being present as the elements or compounds thereof and amounts thereof being calculated as the elements and based upon the weight of said alumina-silica composite) at a space velocity of at least 0.5 liquid volumes of the normally liquid hydrocarbons per hour per volume of said catalyst, separating hydrogen sulfide and ammonia from the effluent of the reaction zone and also separating a hydrogen-rich gas from said effluent, thereafter separating the normally liquid hydrocarbons of said effluent by fractionation into gasoline- and middle-distillate fractions and into a higher boiling oil fraction having an initial boiling point in the range of from 343° to 371° C., and returning said higher boiling oil fraction as said recirculated heavy oil to said reaction zone.

2. Process according to claim 1, characterized thereby that the ratio of total liquid

hydrocarbon charge to the reaction zone to the fresh hydrocarbon oil charge is maintained between 1.0 and 3.0 and the total liquid hydrocarbon charge is passed through the reaction zone at a space velocity of not more than 2 volumes per hour per volume of catalyst present in said reaction zone.

3. Process according to claim 1 or 2, characterized thereby that the hydrogen and the mixture of the hydrocarbon oils are brought into contact in the reaction zone with the catalyst after the latter has been calcined at a temperature of at least 593° C.

4. Process according to one of the claims 1 to 3, characterized thereby that ammonia and hydrogen sulfide and the hydrogen-rich gas are first separated from the effluent of the reaction zone, the hydrogen-rich gas is recirculated together with fresh hydrogen to the reaction zone, the remaining reaction zone effluent is freed from normally gaseous paraffinic hydrocarbons, the resultant normally liquid hydrocarbon stream is passed into a first fractionation zone and therein is separated into an overhead hydrocarbon stream containing hexanes and lower boiling hydrocarbons, an intermediate hydrocarbon mixture boiling in the gasoline boiling range and a bottoms fraction consisting of hydrocarbons boiling in excess of said intermediate mixture, said bottoms fraction is passed into a second fractionation zone, a hydrocarbon fraction boiling within the middle-distillate boiling range and having an end boiling point in the range of from 343° to 371° C. is recovered as distillate from said second fractionation zone, and the hydrocarbons boiling in excess of said middle-distillate and boiling point are withdrawn from said second fractionation zone and supplied together with the fresh hydrocarbon oil charge to the reaction zone.

5. The process for converting a high boiling hydrocarbon oil into more valuable lower boiling hydrocarbon products as claimed in claim 1 and substantially as described with reference to the accompanying drawing.

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

