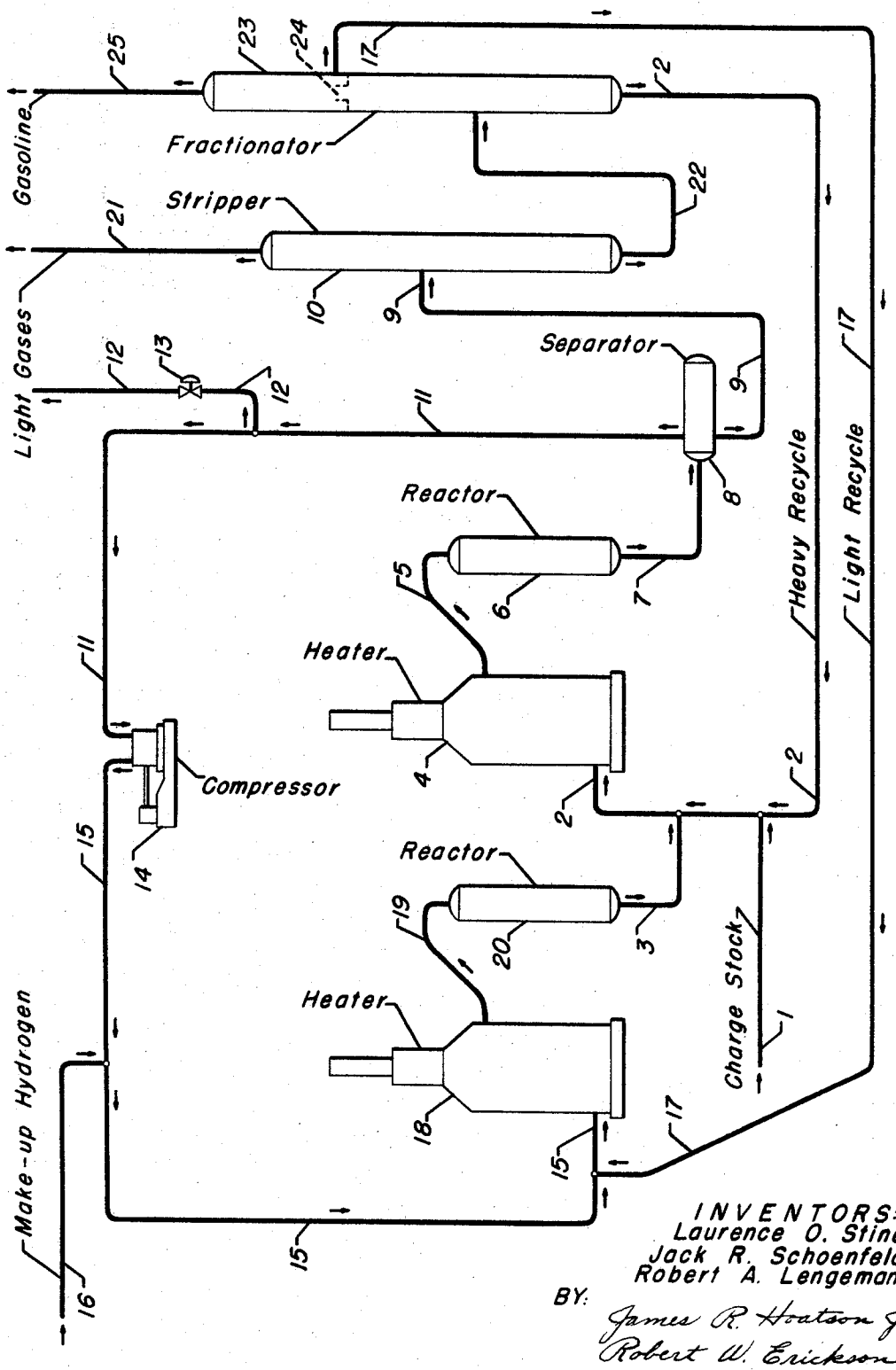
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MULTIPLE-STAGE HYDROCARBON HYDROCRACKING PROCESS

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# MULTIPLE-STAGE HYDROCARBON HYDROCRACKING PROCESS

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## ABSTRACT OF THE DISCLOSURE

A conversion process for producing gasoline boiling range hydrocarbons from distillate material boiling above the gasoline boiling range. The process is conducted in a series of reaction zones, and is particularly intended for use in converting stocks contaminated by the inclusion of nitrogenous and/or sulfurous compounds. Only one fractionation section and recycle gas system is required, and the process affords improved catalyst contact by the reactants.

## BACKGROUND OF INVENTION

The present invention is directed toward multiple-stage hydrocracking of contaminated, heavier-than-gasoline charge stocks—i.e., vacuum gas oils, atmospheric gas oils, etc.—to produce maximum volumetric yields of gasoline boiling range, normally liquid hydrocarbons—i.e., butanes and heavier material boiling up to about 400° F. Hydrocracking, also commonly referred to as "destructive hydrogenation," is distinguished from the simple addition of hydrogen to unsaturated bonds between carbon atoms, since it effects definite changes in the molecular structure of the hydrocarbons being processed. Hydrocracking may, therefore, be designated as cracking under hydrogenation conditions such that the lower-boiling products of the cracking reactions are substantially more saturated than when hydrogen, or material supplying the same, is not present. Although many hydrocracking processes, or destructive hydrogenation processes, are conducted thermally, the preferred processing technique involves the utilization of a catalytic composite possessing a high degree of hydrocracking activity. In virtually all hydrocracking processes, whether thermal or catalytic, controlled or selective cracking is desirable from the standpoint of producing an increased yield of liquid product having improved, advantageous physical and/or chemical characteristics.

Selective hydrocracking is especially important when processing hydrocarbons and mixtures of hydrocarbons which boil at temperatures above the gasoline and/or the middle-distillate boiling range; that is, hydrocarbons and mixtures of hydrocarbons, as well as the various hydrocarbon fractions and distillates, having a boiling range indicating an initial boiling point of from about 650° F. or 700° F., and an end boiling point as high as 1000° F., or more. Selective hydrocracking of such hydrocarbon fractions results in greater yield of hydrocarbons boiling within and below the middle-distillate boiling range. In addition, 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 boiling within the range of about 100° F. to about 400° F. or 450° F. Selective hydrocracking involves the splitting of a higher-boiling hydrocarbon molecule into two molecules, both of which are normally liquid hydrocarbons.

A major disadvantage of nonselective or uncontrolled hydrocracking, is the more rapid formation of increased quantities of coke and other heavy carbonaceous material which becomes deposited upon the catalyst, and decreases, or destroys, the activity thereof to catalyze the desired reactions. Such deactivation results in a shorter acceptable processing cycle or period, with the inherent necessity for more frequent regeneration of the catalyst, or total replacement thereof with fresh catalyst. Of further significance, in regard to a hydrocracking process, are the considerations involving hydrogen production and consumption, and the preservation of aromatic compounds which boil within the gasoline boiling range. The present hydrocracking process does not result in the production of an excessive quantity of the lower molecular weight, unsaturated hydrocarbons.



Investigations have indicated that the presence of nitrogen-containing compounds within the hydrocracking feed stock, such as naturally occurring, organic nitrogenous compounds, examples of which include pyrroles, amines, indoles, results in the relatively rapid deactivation of the catalytically active metallic components acting as the hydrogenation agent, as well as the solid carried material which acts as the acidic hydrocracking component of a great variety of hydrocracking catalysts. Such deactivation appears to result from the reaction of the nitrogen-containing compounds with the various catalytic components to form nitrogen-containing complexes, the extent of such deactivation increasing as the process continues and as the nitrogen-containing feed stock continues to contaminate the catalyst through contact therewith. Furthermore, the deactivation is not a simple reversible phenomenon which may be easily rectified by merely heating the catalyst in the presence of hydrogen for the purpose of decomposing the nitrogen-containing complexes.

## PRIOR ART

While candor compels acknowledgment of the fact that a considerable amount of published literature, including patents, exists in the general area of hydrocracking contaminated charge stocks, there does not appear to be recognition of the process encompassed by our inventive concept. Certainly these prior art processes do not lend themselves to the results obtained by the present process, nor are they enhanced by the many resulting advantages.

Typical of such prior art processes is that described in U.S. Patent No. 3,008,895, wherein a gas oil fraction is initially subjected to hydrorefining (hydrogenation), and the gas oil portion of the product effluent is hydrocracked to gasoline boiling range hydrocarbons. Similarly, another exemplary prior art process is that found in U.S. Patent No. 3,072,560. Here again, a nitrogen-containing light gas oil (350° F. I.B.P to 650° F. E.P.) is denitrified, and the nitrogen-free product effluent subjected to hydrocracking to produce gasoline components.

Significantly, while the prior art processes teach individual reaction zones, each of which is "tailored" for a specific function—e.g., hydrorefining and hydrocracking—there is no appreciation of discharging the entire hydrocracked effluent into the zone designed for hydrorefining. As indicated by the patents briefly described above, it is the hydrorefined effluent which is at least in part the charge to the hydrocracking zone. As a result, a perusal of such prior art reveals more complex separation/fractionation and hydrogen recycle schemes than found herein.

## OBJECTS AND EMBODIMENTS

The primary object of the present invention is to provide a multiple-stage hydrocracking process which produces hydrocarbons boiling within the gasoline boiling range, without the usually attendant uncontrolled cracking of the low molecular weight hydrocarbons, while processing higher boiling petroleum hydrocarbon charge stocks containing nitrogenous compounds. A related ob-

ject is to provide a process having great flexibility in regard to the quality and quantity of the final product produced; that is, for example, to produce 100% gasoline boiling range hydrocarbons, or maximizing the quantity of gasoline while some middle-distillate hydrocarbons are simultaneously produced.

Another object is the simplification of recycle hydrogen systems and separation/fractionation facilities attendant a multiple-stage hydrocracking process.

In one embodiment, our invention encompasses a process for converting a hydrocarbonaceous charge stock boiling above the gasoline boiling range and containing nitrogenous compounds, into lower boiling hydrocarbon products which comprises the steps of: (a) reacting said charge stock and hydrogen in a second of a series of reaction zones in admixture with the product effluent from a first reaction zone in said series; (b) separating the reaction product effluent from said second reaction zone into a hydrogen-rich gaseous phase and a substantially nitrogen-free normally liquid hydrocarbon phase; (c) separating said normally liquid phase into a first fraction having a nominal end boiling point less than about 450° F., a second fraction having a nominal end boiling point of from 650° F. to about 700° F. and a third fraction having a nominal initial boiling point of at least about 650° F.; (d) recycling at least a portion of said third fraction to combine with said charge stock, hydrogen and the product effluent from said first reaction zone, thereby forming the charge to said second reaction zone; and (e) recycling at least a portion of said second fraction in admixture with said hydrogen-rich gaseous phase as the charge to said first reaction zone, and combining the total effluent therefrom with said charge stock as aforesaid.

Other embodiments involve the use of particular operating conditions and catalytic composites, and internal recycle streams. For example, the second fraction, having an end boiling point in the range of about 650° F. to 700° F., is preferably recycled en toto unless market conditions or other economic considerations dictate the withdrawal of a portion of this clean middle-distillate. Likewise, the third, heavier fraction is preferably recycled en toto to the second reaction zone.

Operating conditions include pressures of from 300 to 3000 p.s.i.g. and temperatures in the range of 350° F. to 1000° F., although the two reaction zones, as hereafter specifically set forth, will be maintained under different operating conditions. The catalytic composite in the hydrocracking zone, will generally comprise from 0.1% to about 4.0% by weight of a Group VIII noble metal component, whereas the catalytic composite disposed in the second, or hydrorefining zone, will generally comprise both a Group VI–B metal component and one from the iron-group of Group VIII. Other objects and embodiments will become evident from the following summary of our invention.

## SUMMARY OF INVENTION

The method of the present invention may be more clearly illustrated and understood by initially defining several terms and phrases where employed in the specification and the appended claims. The phrase, "hydrocarbons boiling within the gasoline boiling range," or "gasoline boiling range hydrocarbons," is intended to connote those hydrocarbons boiling at a temperature below about 400° F. or 450° F. and containing butanes. The term "middle-distillates," refers to those hydrocarbon fractions having an initial boiling point within the range of about 400° F. to about 450° F., and an end boiling point within the range of about 650° F. to about 700° F. The term, "metallic component," or "catalytically active metallic component," is intended to encompass those catalytic components which are employed for their hydrocracking activity, or for their propensity for the destructive removal of the nitrogenous compounds, as the case may be, and which components are selected from the metals and compounds of Groups VI–B and VIII of the Periodic Table. In this manner, the metallic catalytic components are distinguished from those components which are employed as the solid support, or carrier material, or the acidic cracking component. As hereinafter set forth in greater detail, the process of the present invention involves the use of two separate, but integrated, stages. Each stage utilizes a distinct catalytic composite different, in most applications of the present invention, from the catalyst employed in the other stage. The preferred catalytic composites will hereinafter be described with reference to the particular stage in which employed, and in regard to the function to be served.

As hereinbefore set forth, one embodiment of the present invention involves a process for producing hydrocarbons which boil within the normal gasoline boiling range, from those hydrocarbons which boil at temperatures above the gasoline boiling range. Suitable charge stocks to the present hydrocracking process include kerosene fractions, gas oil fractions, lubricating oil and white oil stocks, cycle stocks, black oil, the various high-boiling bottoms recovered from the fractionators generally accompanying catalytic cracking operations, and referred to as heavy recycle stock, fuel oil stocks and other sources of hydrocarbons which have a depreciated market demand due to the high boiling points of these hydrocarbons and the presence of various contaminating influences including high-boiling nitrogenous compounds and sulfurous compounds. Through the utilization of the process of the present invention, particularly when processing heavy hydrocarbon charge stocks possessing boiling points above about 650° F. to about 700° F., it is possible to convert substantially all the charge into gasoline boiling range hydrocarbons while simultaneously minimizing the yield of light, normally gaseous paraffins.

## ILLUSTRATED EMBODIMENT

Our invention, as directed toward the multiple-stage hydrocracking of nitrogen-contaminated charge stocks, may be more clearly understood upon reference to the accompanying drawing which illustrates one particular embodiment thereof. In the drawing, various flow valves, control valves, instrumentation and start-up lines, coolers, reflux pots, pumps and/or compressors, etc. have either been eliminated, or reduced in number; only those vessels and connecting lines considered necessary for a complete understanding of the process are shown. The use of miscellaneous appurtenances are well within the purview of one having skill in the art of petroleum processing techniques.

With reference now to the accompanying figure, the charge stock—i.e., a vacuum gas oil—containing a substantial quantity of nitrogenous compounds, on the order of 1000 to 5000 p.p.m. by weight, and sulfurous compounds from 1.0% to as high as 3.0% to 5.0% by weight, enters the process via line **1**. Continuing through line **1**, the charge stock is admixed with a heavy recycle stream in line **2**, the source of which is hereafter set forth, and a hydrocracked product effluent from line **3**, the total mixture continuing through line **2** into heater **4**. As hereinafter indicated, hydrogen is present in the mixture in an amount of about 3,000 to about 15,000 s.c.f./bbl. of fresh charge stock entering via line **1**.

Heater **4** serves to raise the temperature of the mixture to a level within the range of about 500° F. to about 1000° F., the heated mixture continuing through line **5** into reactor **6**. This vessel is herein referred to as a "clean-up reactor since its principal function is the conversion of nitrogenous and sulfurous compounds into ammonia, hydrogen sulfide and hydrocarbons. Through the judicious selection of the catalytic composite disposed therein, a significant amount of conversion of the 400° F.-plus material into gasoline boiling range hydrocarbons is effected. A preferred catalytic composite is one containing both a metallic component from Group VI–B and a metallic component from the iron-group of Group VIII. Reactor **6** is maintained under an imposed pressure of from 300 to 3,000 p.s.i.g., and preferably from 1,000 to about 2,500

p.s.i.g. The quantity of catalyst disposed in reactor **6** is such that the fresh charge stock entering via line **1** passes therethrough at a liquid hourly space velocity within the range of from 0.5 to about 10.0. The total reactor **6** product effluent is removed via line **7** and is introduced into a high pressure, low temperature separator **8**.

Separator **8** is maintained at essentially the same pressure existing at the outlet of reactor **6**, allowing only for the normal pressure drop experienced during fluid flow. The temperature is maintained in the range of 60° F. to 140° F., whereby a normally liquid hydrocarbon stream is recovered via line **9**. A separate gaseous phase is removed through line **11**; this gaseous phase, although rich in hydrogen, contains light paraffinic hydrocarbons, hydrogen sulfide and, in the absence of water injection into line **7**, some ammonia. Where the illustrated flow is modified to provide for water injection, separator **8** is designed to remove sour water containing absorbed ammonia from the system. The gaseous phase in line **11** may be treated by any suitable well-known means to remove hydrogen sulfide and reduce the concentration of gaseous hydrocarbons, in order to increase the hydrogen concentration. In any event, the hydrogen-rich gaseous phase continues to compressor **14**, by which it passes through line **15** into heater **18**. Pressure control is maintained by venting a portion of the gaseous phase through line **12** containing pressure control valve **13**.

The normally liquid phase in line **9** is introduced into stripper **10** wherein light gaseous components including methane, ethane and propane, in addition to residual amounts of hydrogen sulfide, are removed via line **21**. Although designated as a stripper in the drawing, which is the common term applied to this vessel, the separation of light gaseous components can readily be effected by means of a reboiled distillation column. Regardless, a normally liquid hydrocarbon stream, substantially free from nitrogen and sulfur, is passed via line **22** into fractionator **23**. In most applications, this liquid stream will contain some $C_4$-hydrocarbons and virtually all the $C_5$ and heavier material from separator **9**.

Fractionator **23** is maintained at conditions of temperature and pressure such that a gasoline fraction ($C_4$–400° F. end point) is removed as an overhead product via line **25**. A middle-distillate fraction (400° F.–650° F. hydrocarbons), labeled a light recycle in the drawing, is removed through line **17** from a point just above center well **24**. The heavy recycle (650° F.–plus hydrocarbons) are withdrawn as a bottoms product through line **2**. While our invention is most advantageously applied to those situations wherein maximum quantities of gasoline are produced, it must be recognized that periodic economic fluctuations may dictate the withdrawal of a portion of the light recycle stream in line **17**. Preferably, however, in accordance with the illustrated embodiment, the total light recycle stream in line **17** is passed into heater **18** in admixture with both the recycled hydrogen-rich gaseous phase in line **15** and make-up hydrogen being introduced through line **16**. The make-up hydrogen may be introduced from any suitable source, generally in an amount of from 200 to about 2,000 s.c.f./bbl. One such source, well known in the art, is the hydrogen producing catalytic reforming process.

The mixture of light recycle and hydrogen continues through line **15** into heater **18** wherein the temperature is raised to a level in the range of from 350° F. to about 850° F., the heated mixture passing through line **19** into reactor **20**. Reactor **20** is maintained under a pressure of from 300 to 3,000 p.s.i.g., but will, during actual operation, be at a pressure slightly higher than that imposed upon reactor **6**—e.g., about 50 p.s.i.g. greater. The liquid hourly space velocity, through the preferred Group VIII noble metal catalyst, will be in the range of from 1.0 to 15.0. It should be noted that all the hydrogen within the process, that recycled via compressor **14** and the make-up stream being introduced via line **16**, passes through reactors **20** and **6** in series flow. Thus, the concentration of hydrogen, expressed as s.c.f./bbl., in reactor **20** is determined by the quantity of hydrogen stipulated for reactor **6** and the amount consumed in the overall process.

The principal advantages of our invention, stemming from the fact that the total hydrocracked product from the light recycle reactor **20** is admixed with the charge to the clean-up reactor **6**, include maximum hydrogen flow through both reactors, thereby assisting in maintaining "clean" catalyst for an extended period of time. By processing only the light recycle in the reaction zone whose principal function is hydrocracking, catalyst contact is facilitated since the heavy recycle is not present to "mask" the catalyst. Thus, hydrocracking severity can be reduced considerably, with the result that lesser quantities of normally gaseous hydrocarbons are produced. Likewise, since the light recycle reactor effluent is admixed with the heavier feeds, the handling of the latter is facilitated, and catalyst contact is improved.

From the foregoing description of the embodiment presented in the accompanying drawing, it is readily ascertained that the present process is, in effect, a two-stage process for producing hydrocarbons boiling within the gasoline boiling range. Various modifications may be made to the illustrated embodiment by those possessing skill within the art of petroleum processing, and it is not intended that such modifications remove the process from the broad scope and spirit of the appended claims. For example, the separating means shown as separator **8**, may be combined with stripper **10**, whereby a somewhat different flow pattern and apparatus setup results. It is evident, however, that such a flow pattern will merely accomplish the same object resulting from that indicated. An essential feature of the process of the present invention involves the two-stage reactor system, whereby the total liquid effluent from the hydrocracking stage is admixed with the fresh charge and heavy recycle, prior to the introduction thereof into the clean-up zone. In clean-up reactor **6**, substantially complete destruction of nitrogenous compounds, as well as sulfurous compounds, contained within the charge stock is effected. As hereinbefore set forth, through the careful selection of both catalyst and operating conditions, there will be effected, in clean-up reactor **6**, a substantial degree of hydrocarbon conversion whereby the heavier hydrocarbons, boiling above about 650° F., are converted into hydrocarbons boiling below about 650° F., without experiencing a substantial production of the light paraffinic hydrocarbons, methane, ethane, and propane.

As hereinbefore set forth, the process of the present invention is particularly directed to the processing of hydrocarbons and mixtures of hydrocarbons boiling in excess of the gasoline boiling range. However, it is most advantageously applied to petroleum-derived feed stocks, particularly those stocks commonly considered as being heavier than middle-distillate fractions. Such stocks include gas oil fractions, heavy vacuum gas oils, lubricating oils, and white oil stocks, as well as the high-boiling bottoms recovered from various catalytic cracking operations. Therefore, although the charge stock to the present process may have an initial boiling point of about 400° F. to about 450° F. and an end boiling point of about 1000° F., the process affords additional benefits when processing hydrocarbon charge stocks having significantly higher initial boiling points, that is, of the order of about 650° F. to about 700° F.

In further describing the process of the present invention, and the various limitations imposed thereupon, in the interest of simplicity and clarity, each stage will be discussed separately. One stage comprises a reaction zone, the principal function of which is the substantially complete removal of contaminants, a separation zone, and/or a fractionator, and these are utilized in such a manner, and under such conditions as to result in the substantially complete removal of nitrogenous and sulfurous compounds from the hydrocarbon charge stock, while

producing both gasoline and middle-distillate boiling range hydrocarbons. The heavy hydrocarbon charge stock, for example, a heavy vacuum gas oil, having a boiling range of from about 700° F. to about 1000° F., and contaminated by nitrogenous compounds of the order of from about 1000 p.p.m. to about 5000 p.p.m., is admixed with hydrogen in an amount of about 3000 standard cubic feet to about 15,000 standard cubic feet per barrel of such hydrocarbon charge. The mixture is heated to the desired operating temperature, and thereafter passed into a hydrorefining reaction zone, the precise operating conditions of which will be dependent upon the various physical and/or chemical characteristics of the particular hydrocarbon charge being processed. In any event, the reactor will be maintained at a temperature of from about 500° F. to about 1000° F., and under an imposed pressure within the range of about 300 to about 3000 p.s.i.g. Higher pressures appear to favor the destructive removal of nitrogenous compounds, as well as the conversion of those hydrocarbons boiling at a temperature above about 650° F., and are, therefore, preferred; thus, the reaction zone will preferably operate under an imposed pressure within the range of about 1000 to about 3000 p.s.i.g. Where the heavy hydrocarbon charge is contaminated by relatively large quantities of nitrogenous compounds, a lower range of liquid hourly space velocity, that hereinbefore set forth, will be employed, that is, about 0.5 to about 3.0. The catalyst disposed within this reaction zone serves a dual function; that is, the catalyst is nonsensitive to the presence of substantial quantities of both nitrogenous compounds and sulfurous compounds, while at the same time is capable of effecting the destructive removal thereof, and also the conversion of those hydrocarbons boiling at a temperature above about 650° F. to about 700° F. A catalyst comprising comparatively large quantities of molybdenum, calculated as the element, composited with a suitable carrier material, such as alumina, is very efficient in carrying out the desired operation. A particularly preferred catalytic composite comprises from about 4.0% to about 45.0% by weight of molybdenum, and utilizes alumina as the carrier material. Other refractory inorganic oxide material, such as silica, zirconia, magnesia, titania, thoria, boria, etc. may be used in combination therewith. In addition to minor amounts of nickel, from about 0.2% to about 10.0%, like quantities of cobalt and/or iron may be employed in combination wtih the relatively larger amounts of molybdenum. The catalytic composite, for utilization in this reaction zone, may be manufactured in any suitable manner, a particularly advantageous method employing an impregnating technique.

The gaseous ammonia and hydrogen sulfide, resulting from the destructive removal of nitrogenous and sulfurous compounds, are removed from the total reaction zone effluent in any suitable manner. For example, the total effluent may be admixed with water, and thereafter subjected to separation such that the ammonia is absorbed within the water-phase. Or, the total reaction zone effluent may be passed into a separation zone countercurrently to a liquid absorbent whereby the ammonia, hydrogen sulfide, and other gaseous components are effectively removed therefrom. In addition to the removal of hydrogen sulfide and ammonia, it is desired that the light paraffinic hydrocarbons, methane, ethane and propane also be removed from the effluent. Therefore, the separating zone may comprise a low-temperature flash chamber whereby the ammonia and light paraffinic hydrocarbons are removed as a gas phase. These light paraffinic hydrocarbons, along with the normally liquid hydrocarbons, may be passed into a fractionating column, whereby the light paraffinic hydrocarbons are removed from the system; this method has the added advantage of being sufficiently flexible in that the fractionator may function as a debutanizer, depropanizer or dependanizer where such a processing technique is desired. As hereinbefore set forth, regardless of the particular separating means employed, the resulting normally liquid hydrocarbons, boiling within the range from butanes to about 700° F. or higher, will be substantially free from residual nitrogenous and sulfurous compounds. The normally liquid hydrocarbons are, therefore, further distilled in a side-cut fractionator under such conditions as will yield a heart-cut having a boiling range of about 400° F. to about 650° F. Those hydrocarbons boiling below about 400° F., and including aromatic-containing gasoline boiling range hydrocarbons, are removed from the upper portion of the side-cut fractionator, and may be transmitted to storage pending further use either as charge to a catalytic reforming unit, or as gasoline blending components. A hydrocarbon fraction boiling at a temperature above about 650° F., is removed from the bottom portion of the side-cut fractionator.

The bottoms fraction boiling above about 650° F. is herein referred to as "heavy recycle," and is, in fact, recycled in total to combine with the fresh hydrocarbon charge to the reaction zone. Since this material is substantially free from both nitrogen and sulfur, the net effect is a decrease in the concentrations thereof in the total hydrocarbon stream which contacts the catalyst. The heart-cut fraction, boiling from about 400° F. to 650° F., herein referred to as "light recycle," is processed in the second reaction zone in admixture only with the hydrogen flowing through the system. In this manner, the middle-distillate hydrocarbons enjoy more intimate contact with the hydrocracking catalyst for conversion thereof into lower-boiling gasoline components. Furthermore, the operating severity required to effect substantial hydrocracking to gasoline is reduced considerably. Considering the character of the hydrocracking catalyst in this zone, alumina is a good nitrogen remover when it contains relatively minor quantities of silica (approximately 12% by weight). Likewise, silica is a good hydrocracking catalyst when it contains a relatively small quantity of alumina, however, in and of itself, it does not promote effective, acceptable nitrogen removal. In a similar manner, the metallic components of the catalyst disposed within this hydrocracking reaction zone, will exhibit similar propensities. For example, as indicated in regard to the first reaction zone, molybdenum is a good nitrogen remover, but is not relatively active as a hydrocracking or hydrogenation catalyst. Similarly, nickel is a good hydrogenation catalyst, but does not possess a relatively high degree of activity in and of itself, in regard to the removal of nitrogenous compounds. Catalytic composites which comprise at least one metallic component selected from the noble metals of Group VIII of the Periodic Table, constitute preferred hydrocracking catalysts for use in the process of the present invention since they possess a high activity in regard to the conversion of hydrocarbons boiling within the middle-distillate boiling range. Other Group VIII metals, and/or Group VI–B metals may be used in conjunction therewith.

It is preferred that the catalyst within the hydrocracking reaction zone comprise at least two refractory inorganic oxides, and preferably alumina and silica. When silica and alumina are employed in combination, the latter will be present within an amount of from about 10% to about 90% by weight. Excellent results have been achieved through the utilization of the following silica-alumina composites: 88% by weight of silica and 12% by weight of alumina, 75% by weight of silica and 25% by weight of alumina, and 88% by weight of alumina and 12% by weight of silica. The total quantity of metallic components of the catalyst disposed within the second reaction zone, is within the range of from about 0.1% to about 20.0% by weight of the total catalyst. The Group VI–B metal, such as chromium, molybdenum, or tungsten, is usually present within the range of from about 0.5% by weight to about 10.0% by weight of the catalyst. The Group VIII metals, which may be divided into two sub-

groups, are present in an amount of from about 0.1% to about 10.0% by weight of the total catalyst. When an iron subgroup 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 noble metal such as platinum, palladium, iridium, etc., is employed, it is present in an amount within the range of from about 0.1% to about 4.0% by weight of the total catalyst. Suitable catalysts, for utilization within the second reaction zone, include, but are not limited to, the following: 6.0% by weight of nickel and 0.2% by weight of molybdenum; 6.0% by weight of nickel; 0.4% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of palladium; 6.0% by weight of nickel and 0.2% by weight of platinum, etc.

The catalyst employed in the second stage of the process of the present invention is preferably disposed within the reaction zone as a fixed bed. The middle-distillate charge stock, after being combined with hydrogen in an amount as hereinbefore stated, is raised to a temperature within the range of about 350° F. to about 850° F. Due to the characteristics of the middle-distillate, employed as a charge stock to the second stage, the operating conditions within the reaction zone are relatively mild. Therefore, the operating temperature at which the catalyst is maintained within the second reaction zone, may be at least about 50° F. less than the temperature employed in the first reaction zone, and often as much as 150° F. less. In addition, in view of the nature of the charge stock to the hydrocracking zone, the rate of liquid charge thereto may be substantially increased, on the order of about 1.0 to about 15.0 liquid hourly space velocity. The total effluent from the hydrocracking reaction zone is admixed with the incoming fresh charge stock and the heavy, 650° F.–plus recycle stream. The hydrocracked effluent serves to facilitate the handling of the heavier feed, and, more importantly, effects more efficient contact of the heavier components with the catalytic composite.

It is understood that the broad scope of the present invention is not to be unduly limited to a particular catalyst, or a particular means of manufacturing the same. The utilization of any of the previously mentioned catalytic composites, whether in the clean-up or hydrocracking reaction zone, at operating conditions which vary within the limits hereinabove set forth, do not necessarily yield results equivalent to those obtained through the utilization of another catalytic composite, or other operating conditions. An essential feature of the present invention is the separate, distinct integrated two stages in which the overall process is effected, and in which the total hydrocracked effluent is admixed with the fresh charge stock. Through the utilization of the process of the present invention, a greater concentration of hydrocarbons boiling within the gasoline boiling range is produced. Furthermore, greater concentrations of gasoline boiling range hydrocarbons are produced from those middle-distillate boiling range hydrocarbons which result from reactions effected in the first stage of the process. The overall picture results in a substantial reduction in the quantity of light paraffinic hydrocarbons otherwise resulting from the nonselective, one-stage hydrocracking of hydrocarbons boiling at a temperature in excess of the gasoline boiling range. Furthermore, there is no requirement for the removal of mono-, or polynuclear aromatic hydrocarbons from the hydrocarbon charge to the hydrocracking zone. The process of the present invention results in a gasoline boiling range hydrocarbon product substantially free from unsaturated paraffinic hydrocarbons, and is, therefore, extremely well suited as charge stock to a catalytic reforming unit for the purpose of further raising the octane rating thereof. Thus, through the utilization of the process of the present invention, a hydrocarbon charge stock, having a boiling range above about 650° F. to 700° F., may be substantially completely converted into hydrocarbons boiling within the gasoline boiling range, notwithstanding the presence of exceedingly excessive quantities of nitrogenous compounds, without the usual high yield loss due to the formation of an excessive quantity of light paraffinic hydrocarbons and without experiencing the deactivation of the catalytic composite employed.

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

Example

This example is given for the purpose of illustrating the process of the present invention as applied to a hydrocarbon fraction boiling above the gasoline boiling range, and virtually completely above the middle-distillate boiling range. The charge stock employed was a vacuum gas oil obtained from a Wyoming-West Texas crude. As indicated in the following Table I, the charge stock had a gravity, ° API at 60° F., of 20.6, an initial boiling point of 590° F., with 95% by volume being distilled, in accordance with standard ASTM distillation, at a temperature of 990° F.; in addition, the vacuum gas oil was contaminated by total nitrogen in an amount of about 1300 parts per million.

TABLE I.—VACUUM GAS OIL—PROPERTIES

| | |
|---|---|
| Gravity, ° API @ 60° F. | 20.6 |
| ASTM distillation, ° F.: | |
| Initial | 590 |
| 10% | 722 |
| 30% | 790 |
| 50% | 835 |
| 70% | 872 |
| 90% | 920 |
| 95% | 990 |
| End point | |
| Percent @ 400° F. | 0 |
| Percent bottoms | 2.5 |
| Total nitrogen, p.p.m. | 1300 |
| Sulfur, wt. percent | 2.58 |

The catalyst employed in the clean-up reaction zone comprised 2.0% by weight of nickel and 22.5% by weight of molybdenum, calculated as the elements thereof, composited with a carrier of 63.0% alumina and 37.0% silica. The clean-up zone is maintained under an imposed hydrogen pressure of about 1925 p.s.i.g., and the inlet temperature, as measured in the catalyst bed, is 770° F. Based upon a vacuum gas oil charge rate of 7,200 bbl./day, the hydrogen concentration is 10,000 s.c.f./bbl. For convenience, the data hereafter presented are expressed in terms of mols/hr. and/or volume percent where appropriate. References to streams by way of line number connotes the streams as shown in the accompanying drawing.

The liquid charge to the clean-up reaction zone is a mixture of 100.0 mols/hr. of the gas oil charge stock, 65.4 mols/hr. of the hydrocracked effluent in line 3 and 39.0 mols/hr. of the heavy recycle in line 2. Following the removal of light gaseous hydrocarbons, ammonia and hydrogen sulfide, the normally liquid product effluent is fractionated to provide the fractions indicated in the following Table II.

TABLE II

| Fraction: | Mols/hr. |
|---|---|
| $C_4$–180° F. | 30.8 |
| 180° F.–400° F. | 85.4 |
| 400° F.–650° F. | 59.5 |
| 650° F.–plus | 39.0 |

As above set forth, the 39.0 mols/hr. of 650° F.–plus hydrocarbons are recycled to combine with the gas oil

charge stock. The middle-distillate fraction, 59.5 mols/hr. of 400° F.–650° F. hydrocarbons, is passed into the hydrocracking zone in admixture with the recycled hydrogen-rich gaseous phase and approximately 3,200 s.c.f./bbl. of make-up hydrogen to supplant that which is consumed in the process. The hydrocracking reactor is under a pressure of about 2000 p.s.i.g., and the temperature at the inlet to the catalyst bed is controlled at about 700° F. The catalytic composite consists of 2.0% by weight of nickel and 0.4% by weight of palladium combined with a carrier material of 63.0% silica and 37.0% alumina. The quantity of catalyst is such that the liquid hourly space velocity is about 1.5. The total product effluent is admixed with the heavy recycle in line 2 and the gas oil charge in line 1 as hereinbefore set forth.

The overall results are summarized in the following Table III:

TABLE III

| | Stream designation | | |
|---|---|---|---|
| Fraction, mols/hr. | 3 | 5 | 7 |
| $C_4$–180° F. | 14.6 | 14.6 | 30.8 |
| 180° F.–400° F. | 25.0 | 25.0 | 85.4 |
| 400° F.–650° F. | 25.8 | 25.8 | 59.5 |
| 650° F. plus | | 139.0 | 39.0 |

In addition, the hydrogen consumed is 3138 s.c.f./bbl. of gas oil charge stock, and the normally gaseous hydrocarbon production is about 2.8% by weight. It should be noted that the total gasoline fraction, $C_4$–400° F., was 116.2 mols/hr., or an increase of 16.2 mols/hr. as based on fresh feed.

The foregoing specification and example illustrate the method by which the inventive concept is applied, and indicate the benefits afforded through the utilization thereof.

We claim as our invention:

1. A process for hydrocracking a hydrocarbonaceous charge stock boiling above the gasoline boiling range and containing nitrogenous compounds, into lower boiling hydrocarbon products which comprises the steps of:

(a) reacting said charge stock and hydrogen in a second of a series of reaction zones in admixture with the product effluent, including hydrogen, from a first reaction zone in said series;

(b) separating the reaction product effluent from said second reaction zone into a hydrogen-rich gaseous phase and a substantially nitrogen-free normally liquid hydrocarbon phase;

(c) separating said normally liquid phase into a first fraction having a nominal end boiling point less than about 450° F., a second fraction having a nominal end boiling point of from 650° F. to about 700° F. and a third fraction having a nominal initial boiling point of at least about 650° F.;

(d) recycling at least a portion of said third fraction to combine with said charge stock, and the product effluent, including hydrogen, from said first reaction zone, thereby forming the charge to said second reaction zone; and

(e) recycling at least a portion of said second fraction in admixture with said hydrogen-rich gaseous phase as the charge to said first reaction zone, and combining the total effluent, including hydrogen, therefrom with said charge stock as aforesaid.

2. The process of claim 1 further characterized in that said second fraction is recycled in total with said hydrogen-rich gaseous phase as the charge to said first reaction zone.

3. The process of claim 1 further characterized in that said first reaction zone contains a catalytic composite comprising from about 0.1% to about 4.0% by weight of a Group VIII noble metal component and said second reaction zone contains a catalytic composite comprising a Group VI–B metal component and a Group VIII iron-group metal component.

4. The process of claim 1 further characterized in that said first and second reaction zones are maintained under an imposed pressure of about 300 to 3000 p.s.i.g., and at temperatures in the range of 350° F. to 1000° F.

5. The process of claim 1 further characterized in that said third fraction is recycled in total to combine with said charge stock and first reaction zone effluent, including hydrogen.

**References Cited**

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