

[54] **HYDROTREATING-HYDROCRACKING
PROCESS FOR MANUFACTURING
GASOLINE RANGE HYDROCARBONS**

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[56] **References Cited**

UNITED STATES PATENTS

3,256,178	6/1966	Hass et al.	208/89
3,549,515	12/1970	Brainard et al.	208/89
3,644,197	2/1972	Kelley et al.	208/89

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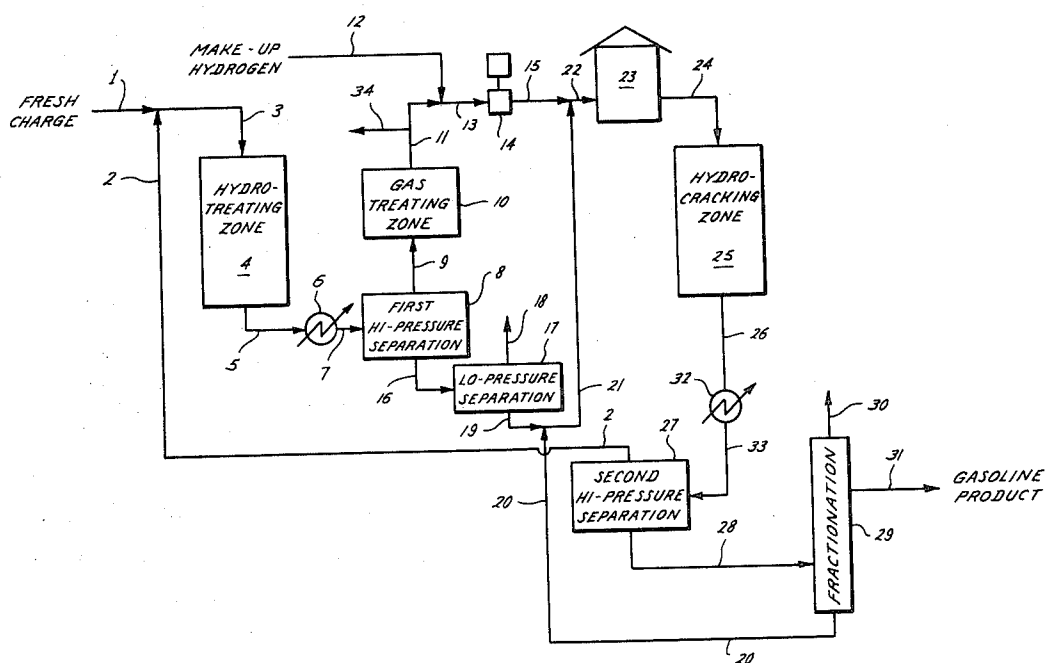
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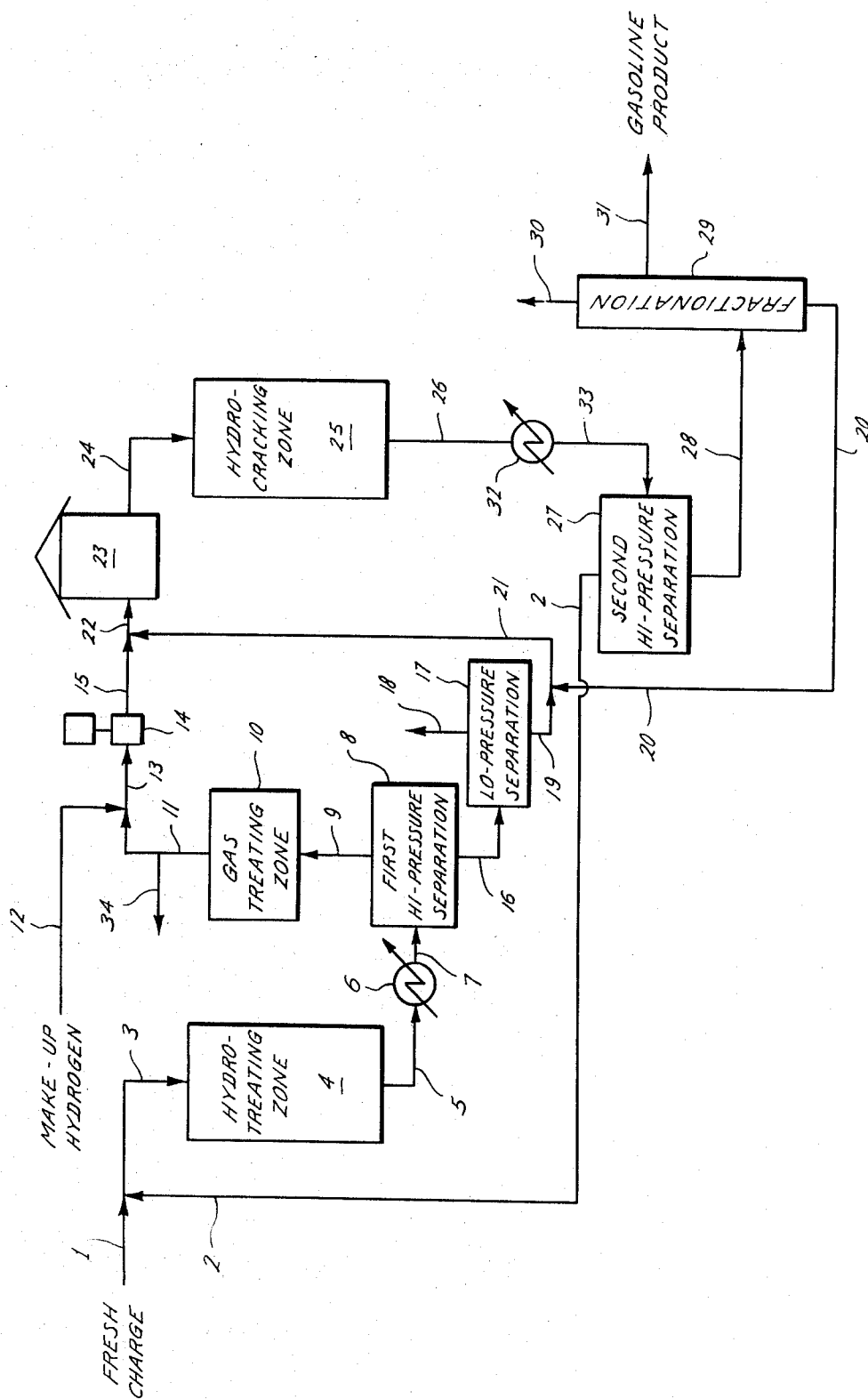
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[57] **ABSTRACT**

A process for converting sulfur and nitrogen containing hydrocarbons boiling in the 400°–1,000° F. range into gasoline range hydrocarbons boiling below about 400° F. which comprises hydrotreating the sulfur and nitrogen containing hydrocarbons to yield a liquid hydrocarbon product containing less than 1 ppm nitrogen, and hydrocracking such hydrotreated hydrocarbon to yield gasoline boiling range product. The hydrotreating reaction is improved by employing pressures in the range of from about 1,200–1,500 psig and hydrogen to hydrocarbon ratios in the range of 10,000–20,000 SCF/B. By operating the hydrocracking reaction at a higher pressure than the hydrotreating reaction only one hydrogen circulation system is required wherein a hydrogen recycle gas is from the hydrocracking reaction effluent is charged to the hydrotreating reaction, wherein a gas stream comprising hydrogen, hydrogen sulfide and ammonia separated from the hydrotreating reaction effluent is treated to remove hydrogen sulfide and ammonia, wherein such treated gas is mixed with make-up hydrogen, compressed and recycled to the hydrocracking reaction.

2 Claims, 1 Drawing Figure





HYDROTREATING-HYDROCRACKING PROCESS FOR MANUFACTURING GASOLINE RANGE HYDROCARBONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the manufacture of gasoline by the process of hydrotreating a sulfur and nitrogen containing petroleum fraction boiling in the range of from about 400° F. to about 1,000° F. and subsequently hydrocracking liquid effluent from the hydrotreating step. In the hydrotreating step, the sulfur and nitrogen compounds contained in the petroleum fraction are converted into hydrogen sulfide and ammonia respectively. The hydrogen sulfide and ammonia are separated from the liquid hydrocarbon portion of the hydrotreating reaction effluent and the liquid hydrocarbon, reduced in sulfur and nitrogen content, is charged to the hydrocracking reaction. In the hydrocracking reaction, hydrocarbons boiling above about 400° F. are hydrocracked into hydrocarbons boiling below about 400° F. A portion of the high boiling hydrocarbons are unconverted in the hydrocracking reaction. The effluent from the hydrocracking reaction is separated into a gasoline product fraction and a fraction boiling above 400° F. The fraction boiling above 400° F. recovered from the hydrocracking reaction is recycled for further conversion to the hydrocracking reaction.

In the hydrotreating reaction, molecular hydrogen is reacted with sulfur and nitrogen compounds to form hydrogen sulfide and ammonia at an elevated temperature and super-atmospheric pressure, in the presence of a hydrotreating catalyst. In the hydrocracking reaction, petroleum hydrocarbons boiling above about 400° F. are converted into hydrocarbons boiling below about 400° F. with molecular hydrogen, at an elevated temperature, a superatmospheric pressure, and in the presence of a hydrocracking catalyst.

2. Prior Art

It is well known to convert hydrocarbons boiling in the range of 400° - 1,000° F. into a gasoline fraction boiling in the range of about 100° - 400° F. by hydrocracking such high boiling hydrocarbon fractions. Hydrocracking operating conditions include temperatures in the range of from 400° - 800° F., pressures of from 500 to 3,000 psig, liquid hourly space velocities (LHSV) of 0.5-15 volumes of oil per hour per volume of catalyst and hydrogen to hydrocarbon ratios of from about 3,000 to 20,000 standard cubic feet of hydrogen per barrel of oil (SCF/B). Hydrocracking reactions are performed in the presence of a hydrocracking catalyst comprising a hydrogenation component and a cracking component. Hydrocracking catalyst employed may comprise a combination of a refractory cracking base with a suitable hydrogenation component. Suitable cracking bases include, for example, mixtures of two or more refractory oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clay, and the like. Additionally, cracking bases comprising partially dehydrated zeolitic crystalline molecular sieves of the X or Y crystal types, having relatively uniform pore diameters of about 8 to 14 angstroms, and comprising silica, alumina, and one or more exchangeable zeolitic cations. It is preferred to employ molecular sieves having a relatively high SiO₂/Al₂O₃ ratio, e.g., between about

2.5 and 6.0. The most active forms of the molecular sieves are those wherein the exchangeable zeolitic cations are hydrogen and/or a divalent metal such as magnesium, calcium or zinc.

The hydrogenation components of the hydrocracking catalyst are compounded with the foregoing cracking bases by methods such as impregnation. The hydrogenation component consists of from about 0.5 percent to about 25 percent of a group VIB or group VIII metal compound such as an oxide or sulfide of chromium, tungsten, cobalt and nickel, the corresponding free metals, or any combination thereof. Alternatively, smaller portions, between about 0.5 and 2 percent, of the metals platinum, palladium, rhodium or iridium or mixtures thereof may be employed as the hydrogenation components. The oxides and sulfides of other transition metals may also be used as hydrogenation catalysts but to less advantage than the foregoing.

Petroleum fractions employed for conversion into gasoline by hydrocracking commonly contain sulfur and/or nitrogen compounds. Such sulfur and nitrogen compounds, when contacted with a hydrocracking catalyst under hydrocracking conditions, have a deleterious effect upon such catalysts. It is known to remove such sulfur and nitrogen compounds by hydrotreating prior to hydrocracking a petroleum fraction. In such a hydrotreating reaction, sulfur and nitrogen contained in the charge petroleum fraction are converted into hydrogen sulfide and ammonia. Effluent from the hydrotreating reaction is treated to remove the hydrogen sulfide and ammonia and a treated hydrocarbon effluent, deficient in sulfur and nitrogen compounds, is then charged to the hydrocracking reaction. By removing such sulfur and nitrogen compounds from the charge petroleum fraction, the hydrocracking reaction may be operated at a lower temperature to obtain a desired degree of conversion into gasoline boiling range hydrocarbons. By removing sulfur and nitrogen compounds which poison the catalyst, lower reaction temperatures may be used which serve to extend the useful life of a hydrocracking catalyst.

The hydrotreating reaction for the conversion of sulfur and nitrogen compounds is performed under operating conditions including temperatures in the range of about 600° - 800° F., pressures of 500 - 3,000 psig, LHSV of 0.5-10 volumes of oil per hour per volume of catalyst (Vo/Hr/Vc), and hydrogen to hydrocarbon ratios of 1,000 - 20,000 (SCF/B). The hydrotreating reaction is performed in the presence of a suitable hydrotreating catalyst. Suitable hydrotreating catalyst include for example, mixtures of the oxides and/or sulfides of the group VI B and/or group VIII metals. Preferably, the hydrotreating catalysts are supported upon a refractory metal oxide carrier such as alumina, silica, titania, and the like. In the hydrotreating reaction, it is preferred to reduce the nitrogen content and the sulfur content of the charge petroleum fraction to low levels in the range of a few parts per million to minimize the effect of such compounds upon the hydrocracking catalysts in the subsequent hydrocracking reaction.

One process scheme known to the prior art comprises hydrotreating a sulfur and nitrogen containing petroleum fraction with a large excess of hydrogen in the presence of a hydrotreating catalyst; passing the total hydrotreating effluent including hydrogen, hydrogen sulfide, ammonia, and hydrocarbons into a hydrocracking zone wherein high boiling hydrocarbons are con-

verted into gasoline boiling range hydrocarbons. In such a process, the hydrogen sulfide and ammonia present in the hydrotreating reaction effluent have an adverse effect upon the hydrocracking catalyst. Such hydrogen sulfide and ammonia poison many hydrocracking catalyst extremely rapidly, making them unsuitable in such a process. Other hydrocracking catalysts, which can withstand the presence of hydrogen sulfide and ammonia, are nevertheless affected by the presence of such compounds and increased operating severities are required to obtain a desired degree of conversion. Increased operating severities in the hydrocracking reaction reduce the period for which a hydrocracking catalyst may be employed before it must be regenerated and increase the rate of production of low molecular weight hydrocarbons in the C₁-C₃ range which are unsuitable for use in gasoline product.

In another process scheme, hydrogen sulfide and ammonia are separated from a hydrotreated petroleum fraction prior to charging such fraction to a hydrocracking reaction. Effluent from a hydrotreating reaction is separated into a gas fraction comprising hydrogen, hydrogen-sulfide and ammonia and a liquid fraction substantially free of hydrogen sulfide and ammonia. At least a portion of the gas fraction is returned to the hydrotreating reaction as recycle hydrogen and the hydrotreated liquid hydrocarbon fraction is charged to a hydrocracking reaction. This process scheme prevents hydrogen sulfide and ammonia from contacting the hydrocracking catalyst. Consequently, less severe operating conditions may be employed in the hydrocracking reaction. This scheme requires separate hydrogen recycle systems for both the hydrotreating reaction and the hydrocracking reaction. The two separate hydrogen recycle systems increase the installation costs and operating expenses for such a process scheme.

The effective life of a hydrocracking catalyst to convert a high boiling petroleum fraction into gasoline range hydrocarbon is increased as the nitrogen content of such petroleum fraction is decreased. The prior art teaches that it is desirable to hydrotreat a petroleum fraction to obtain a hydrocracking reaction charge stock containing less than 25 ppm nitrogen compounds in order to prevent rapid poisoning of the hydrocracking catalyst. As the hydrocracking catalyst is deactivated, the operating temperature must be increased at a constant charge rate to obtain the desired conversion of hydrocracking charge hydrocarbons into gasoline range hydrocarbons. An increased operating temperature increases the coke deposition rate upon hydrocracking catalyst and the period of useful catalyst life is shortened. In the prior art methods, it is necessary to increase the hydrotreating reaction severity with increased catalyst age in order to maintain the nitrogen content of a hydrocracking reaction charge stock within the desired range. Commonly, either the LHSV of the petroleum fraction is decreased or the operating temperature is increased in the hydrotreating reaction. As it is not economical to operate a hydrotreating reaction at a very low LHSV, below about 0.5 Vo/Hr/Vc, generally the operating temperature is increased to improve the conversion of nitrogen compounds in the petroleum fraction being hydrotreated. Such increase in temperature shortens the period of effective catalyst life for the hydrotreating catalyst.

SUMMARY OF THE INVENTION

We have observed that the period of effective catalyst life for a hydrocracking catalyst is substantially increased if the nitrogen content of a petroleum fraction charged to the hydrocracking reaction is maintained below 1 ppm. For petroleum fractions with such low nitrogen content, the hydrocracking reaction temperature may be maintained at a relatively low temperature for an extended time period. The relatively low operating temperatures results in improved yields of gasoline range hydrocarbons as well as longer periods before regeneration of the hydrocracking catalyst is required.

According to the method of the present invention, we have discovered an improvement in the operation of a hydrotreating reaction for the conversion of nitrogen and sulfur compounds contained in a petroleum fraction into ammonia and hydrogen sulfide, wherein such petroleum fractions comprise hydrocarbons boiling in the range of about 400° - 1,000° F. The improvement of our invention comprises operating a hydrotreating reaction wherein the hydrogen to hydrocarbon ratio is maintained in the range of 10,000 - 20,000 SCF/B of hydrocarbon, sufficient to maintain the nitrogen content of the hydrotreated petroleum fraction at one part per million (ppm) or less. By employing the improvement of the present invention, relatively mild hydrotreating operating conditions of temperature, pressure, and LHSV may be employed to obtain the desired low level of nitrogen compounds in the hydrotreated petroleum fraction.

In another embodiment of our invention, an improved process is provided for converting a sulfur and nitrogen containing petroleum fraction boiling in the range of 400° - 1,000° F. into a gasoline fraction boiling in the range 115° - 400° F. The improved process of the present invention comprises hydrotreating a petroleum fraction at a temperature of 600° - 800° F., a hydrogen to hydrocarbon ratio of 10,000 - 20,000 SCF/B, a pressure of 1,200 - 1,500 psig, and a liquid hourly space velocity of 0.5-10. Vo/Hr/Vc; separating the hydrotreater reaction effluent into a gas fraction comprising hydrogen, hydrogen sulfide, and ammonia and a liquid hydrocarbon fraction containing less than 1 ppm nitrogen compounds; scrubbing hydrogen sulfide and ammonia from the hydrotreated gas fraction; charging the scrubbed gas fraction and the hydrotreated liquid fraction to a hydrocracking reaction to convert from about 30 percent to about 75 percent of the hydrotreated liquid fraction into hydrocarbons boiling below 400° F.; separating the hydrocracking reaction effluent into a gas fraction and a liquid fraction; circulating the hydrocracked gas fraction to the hydrotreating reaction; separating the hydrocracked liquid fraction into a gasoline fraction and a fraction boiling above 400° F.; recycling the 400° F.+ fraction to the hydrocracking reaction for further conversion; and recovering the gasoline fraction as product.

By following the improved method of this invention, the period of effective catalyst life for a hydrotreating catalyst is extended by employing relatively low operating temperatures and the period of effective catalyst life for a hydrocracking catalyst is extended by maintaining the nitrogen content of the hydrocracking reaction charge at a concentration less than 1 ppm. Additionally, only one hydrogen recycle gas system is utilized for both the hydrotreating reaction and the hydro-

cracking reaction. By operating the hydrotreating reaction at a pressure somewhat lower than the hydrocracking reaction, it is necessary to employ only one compressor in the hydrogen recycle gas system.

BRIEF DESCRIPTION OF THE DRAWING

The attached drawing is a schematic representation of a process embodying the improvement of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The charge stocks which may be treated according to the method of the present invention include in general any mineral oil fraction having an initial boiling point above the conventional gasoline range, that is above about 400° F. and having an end boiling point of up to about 1,000° F. This includes straight run gas oils, coker distillate gas oils, deasphalted crude oils, catalytic or thermal cracked cycle gas oils and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Such oils may contain up to about 5 weight percent sulfur and up to about 2 weight percent nitrogen.

The hydrotreating reaction contemplated herein is employed to reduce the nitrogen and sulfur content of such charge stocks to low levels, that is to reduce the nitrogen content to 1 ppm or less and the sulfur content by a concomitant amount. Operating conditions include temperatures in the range of 600° – 800° F., pressure of 1,200 – 1,500 psig, LHSV of 0.5 to 10 Vo/Hr/Vc and hydrogen to hydrocarbon ratios in the range of 10,000 – 20,000 SCF/B, such reaction taking place in the presence of a hydrotreating catalyst.

It is contemplated that temperatures in the lower range will be employed at the beginning of a hydrotreating run when the catalyst is fresh and more active and that the temperatures will be incrementally increased up to the maximum as the catalyst ages and activity declines. At temperatures below about 600° F. the rate of conversion of sulfur and nitrogen compounds proceeds too slowly. At temperatures above about 800° F. the rate of coke deposition upon the hydrotreating catalyst increases rapidly, thereby decreasing the activity of the hydrotreating catalyst.

Pressures in the range of 1,200 – 1,500 psig are preferred for the process of the present invention. At pressures below about 1,200 psig the volume of gas passing through the hydrotreating reaction zone increases substantially thereby increasing the linear velocity to a very high value which increases the pressure drop through the reaction zone and which may interfere with the proper contact of the hydrocarbon with the catalyst. Additionally, at low pressures the rate of coke deposition upon the hydrotreating catalyst increases, thereby shortening the period of effective catalyst life. At pressures above about 1,500 psig the hydrocarbon charge stock may not be sufficiently vaporized to obtain the advantages of the present invention.

Liquid hourly space velocities are selected to give the desired degree of sulfur and nitrogen conversion in the hydrotreating reaction zone. At an LHSV below about 0.5 Vo/Hr/Vc the amount of catalyst required to treat a selected amount of hydrocarbon is large and expensive to provide. At an LHSV above about 10 Vo/Hr/Vc the hydrocarbon is not in contact with the catalyst for sufficient time to convert the sulfur and nitrogen com-

pounds. Preferably, an LHSV of from about 0.5 to 3 Vo/Hr/Vc is selected.

We have discovered that in hydrotreating a charge stock boiling in the range of 400° – 1,000° F., the removal of nitrogen and sulfur may be substantially improved by increasing the hydrogen to hydrocarbon ratio while maintaining other operating conditions at set values. We have postulated that by increasing the hydrogen to hydrocarbon ratio the partial pressure of the hydrocarbon is decreased and a substantially larger portion of such hydrocarbon is allowed to vaporize. When treating hydrocarbons boiling in the range 400° – 1,000° F., under hydrotreating conditions, a reaction mixture of hydrogen and hydrocarbon comprises a vapor-liquid mixed phase. We postulate that the liquid hydrocarbon forms a film on the surface and in the pores of the catalyst and that vapor reactants must diffuse across such film to reach the active catalyst sites. Such diffusion may be relatively slow and may be the rate determining step in the hydrotreating reaction. By increasing the hydrogen to hydrocarbon ratio, the partial pressure of the hydrocarbon is decreased which allows additional amounts of hydrocarbon to vaporize. Such vaporization reduces the liquid film thickness on the hydrotreating catalyst. Additionally, by increasing the amount of hydrogen present in the hydrotreating reaction, the linear velocity of reactants through the reaction zone are substantially increased, which also tends to reduce the film thickness upon the hydrotreating catalyst. It has been found that increasing the temperature to increase vaporization of the hydrocarbon is not sufficient to obtain the desired improvement in the hydrotreating reaction. An increase in temperature, without increasing the hydrogen to hydrocarbon ratio at the same pressure, decreases the hydrogen partial pressure. Consequently, the rate of coke deposition increases as the temperature is increased, which shortens the period of effective catalyst life. We have found that by increasing the hydrogen to hydrocarbon ratio the hydrogen partial pressure may be maintained and an increased amount of hydrocarbon may be vaporized at the same temperature and pressure. To obtain the desired increase in hydrotreating reaction efficiency for conversion of sulfur and nitrogen compounds we have found that hydrogen to hydrocarbon ratios above about 10,000 SCF/B must be utilized. Hydrogen to hydrocarbon ratios above about 20,000 SCF/B do not offer a substantial advantage. According to the method of the present invention, the improvement in the efficiency of the hydrotreating reaction continues only until all the hydrocarbon is vaporized. Once all the hydrocarbon is vaporized, no further advantage may be obtained by adding increased amounts of hydrogen.

Catalyst which may be employed in the hydrotreating reaction comprise any suitable hydrotreating catalyst. Examples of such hydrotreating catalysts include metals of group VI B, metals of group VIII, their oxides, their sulfides, and combinations thereof. Preferably such hydrotreating catalysts are supported upon a refractory oxide base such as alumina, silica, titania, and the like.

The hydrocracking reaction within the contemplation of the present invention is for the conversion of hydrocarbons boiling in the range of 400° – 1,000° F. into hydrocarbons boiling below 400° F. We have found that maintaining the nitrogen content of a hydrocarbon charged to the hydrocracking reaction at 1 ppm or less

substantially increases the time period for which the hydrocracking reaction catalyst may be efficiently utilized. Operating conditions for the hydrocracking reaction comprise temperatures in the range of 400° – 800° F., pressures in the range of 500 – 3,000 psig, LHSV in the range of 0.5 – 15 Vo/Hr/Vc, hydrogen to hydrocarbon ratios in the range of 3,000 to 15,000 SCF/B, such reaction taking place in the presence of a hydrocracking catalyst to obtain per pass conversions of hydrocarbons boiling above 400° F. to hydrocarbons boiling below 400° F. of from about 30 percent to about 75 percent. It is known that nitrogen compounds decrease the activity of hydrocracking catalysts thereby requiring increasing temperatures to maintain the desired conversion of hydrocarbon charge. Such increasing temperatures increase the rate at which coke is deposited upon the hydrocracking catalyst, thereby shortening the period for which such hydrocracking catalyst is effective to convert the hydrocarbon into the desired products.

Temperatures in the range of 400° – 800° F. are effective to hydrocrack these selected hydrocarbon charge stocks into the desired gasoline products. It is contemplated that temperatures in the low range will be utilized when the hydrocracking catalyst is fresh and has a high activity and that such temperature will be incrementally increased during a hydrocracking run to maintain the desired degree of conversion. Temperatures below about 400° F. do not allow the hydrocracking reaction to proceed at a sufficient rate. Temperatures above about 800° F. cause substantial cracking of hydrocarbons into very low molecular weight hydrocarbons thereby decreasing the yield of desired gasoline range hydrocarbons.

The liquid hourly space velocity is selected to provide the desired degree of hydrocracking. At LHSV below about 0.5 a large volume of catalyst is required to treat a selected volume of hydrocarbon. At LHSV above about 15 the hydrocarbon is not in contact with the hydrocracking catalyst for sufficient time to obtain a practical degree of conversion. Preferably, the LHSV is maintained from about 1 to 5 volumes of oil per volume of catalyst per hour and the operating temperature is adjusted to provide the desired conversion of hydrocarbon.

In the hydrocracking reaction, the hydrocarbon charge stock is not completely converted into desired products boiling below 400° F. in one pass through the hydrocracking zone. Preferably, about 30 percent to about 75 percent by volume of the hydrocarbon charged to the hydrocracking reaction is converted per pass through the hydrocracking zone. Unconverted hydrocarbon is recovered from the hydrocracking reaction effluent and is recycled to the reaction zone. At conversions below about 30 percent, the rate of hydrocarbon recycle is undesirably large. At conversions above about 75 percent, the severity of the hydrocracking reaction is such that a considerable proportion of the hydrocarbon is converted into hydrocarbons boiling lighter than the gasoline range. As gasoline is the desired product, conversion of hydrocarbon into such low boiling hydrocarbons is undesirable.

Hydrogen to hydrocarbon ratios in the hydrocracking reaction are maintained in the range of from about 3,000 – 15,000 SCF/B such that the recycle gas separated from the hydrocracking reaction effluent is sufficient to provide the desired hydrogen to hydrocarbon

ratio of 10,000 – 20,000 SCF/B in the hydrotreating reaction.

Suitable catalysts for use in the hydrocracking reaction comprise the hydrogenation component and a cracking component. Preferably, the hydrogenation component is supported upon a refractory cracking base. For example, suitable cracking bases include mixtures of two more refractory oxides such as silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, silica-titania, silica-zirconia-titania, acid treated clays, and the like. The preferred cracking bases comprise composites of silica and alumina containing about 50 – 90 percent silica. Additionally, partially dehydrated zeolitic crystalline molecular sieves of the X or Y crystals types, having relatively uniform pore diameters of about 8 to 14 angstroms and comprising silica, alumina, and one or more exchangeable zeolitic cations may also be employed as suitable cracking bases. It is preferred to employ molecular sieves having a relatively high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 2.5 to 6.0. The most active forms of molecular sieves are those wherein the exchangeable zeolitic cations are hydrogen and/or divalent metals such as magnesium, calcium, or zinc. The cracking base may comprise amorphous metal oxides, molecular sieves or mixtures thereof. The hydrogenation components are present upon the cracking base in an amount from about 0.5 to 25 percent. Suitable hydrogenation components are selected from Group VI B metals, Group VIII metals, their oxides, their sulfides, or mixtures thereof. Particularly useful hydrogenation components comprise the oxides or sulfides of chromium, tungsten, cobalt, nickel, or the corresponding free metals or any combination thereof. Alternatively, small proportions, between about 0.5 and 2 percent, of the metals platinum, palladium, rhodium or iridium may be employed. The oxides and sulfides of other transition metals may also be used but to less advantage than the foregoing.

According to the present invention, the desired high hydrogen to hydrocarbon ratio in the range of 10,000 – 20,000 SCF/B is maintained in the hydrotreating zone by circulating a hydrogen containing gas recovered from the hydrocracking reaction effluent to said hydrotreating zone. In order to allow the hydrogen containing gas to pass from the hydrocracking zone to the hydrotreating zone without an intermediate compression step, it is convenient to operate the hydrocracking zone at a higher pressure than the hydrotreating zone. A hydrogen containing gas is recovered from the hydrotreating zone effluent. For the conservation of hydrogen, it is desirable to recycle this gas within the process. However, the hydrogen containing gas recovered from the hydrotreating effluent contains a substantial amount of hydrogen sulfide and ammonia and is at a lower pressure than the operating pressure of the hydrocracking zone. Hydrogen sulfide and ammonia have a deleterious effect upon hydrocracking catalyst, and, in any event, must be removed to maintain the hydrogen concentration in the recirculating gas stream in the range of from about 60 percent to about 100 percent which is required to maintain the desired hydrogen partial pressure in the reaction zones. If a hydrocracking catalyst is employed which has a high tolerance for hydrogen sulfide and ammonia it is possible to control the hydrogen sulfide and ammonia concentration in the recirculating gas stream at a desired value by venting a portion of that gas stream. However, since the major

component of the recirculating gas stream is hydrogen, venting wastes a substantial amount of hydrogen. Therefore, it is preferable to treat the hydrogen containing gas stream recovered from the hydrotreating reaction effluent to remove the hydrogen sulfide and ammonia therefrom. The hydrogen sulfide may be removed by adsorption into an amine solution, reaction with a caustic solution, or by various solid adsorbents such as molecular sieves or activated charcoal. Ammonia may be removed from the gas stream by adsorption into water or upon various solid adsorbents such as molecular sieves or activated charcoal. The hydrogen containing gas stream treated for the removal of hydrogen sulfide and ammonia may contain non-condensable light hydrocarbons which tend to increase in concentration as the process continues. Therefore it may be necessary to vent a small portion of the treated gas stream to maintain the concentration of such light hydrocarbons at a desired low value.

Hydrogen is consumed in both the hydrotreating reaction and the hydrocracking reaction. Therefore, in a continuous process it is necessary to add makeup hydrogen to the recirculating gas stream to replace that consumed in the reactions and that vented from the system. It is not necessary to employ 100 percent pure hydrogen as makeup hydrogen and it is convenient to employ hydrogen streams commonly available in a refinery. Such makeup hydrogen streams should have a purity in the range of 70 to 100 percent hydrogen such that the hydrogen concentration in the recycle gas stream may be maintained at 60 to 100 percent. Since the gas stream recovered from the hydrotreating reaction effluent is at a lower pressure than the operating pressure of the hydrocracking reaction, it is necessary to provide a compression step to transfer the recirculating gas stream from the hydrotreating reaction effluent to the inlet of the hydrocracking reaction.

The liquid hydrocarbon component of the hydrotreating reaction effluent after separation from the gaseous component may still contain appreciable amounts of light hydrocarbons, hydrogen sulfide and ammonia. Such low boiling impurities may be removed from the hydrotreated hydrocarbon by such means as flashing in a low pressure separator, steam stripping, distillation, or other convenient separation means. The hydrotreated hydrocarbon liquid, treated to remove low boiling impurities, is adjusted to the desired reaction inlet temperature of the hydrocracking reaction. The temperature of such hydrocarbons may be adjusted by any convenient heat transfer means such as a fired heater, heat exchanger, etc.

Effluent from the hydrocracking reaction is separated into a hydrogen containing gaseous component and a liquid hydrocarbon component. The hydrogen containing gaseous component is recirculated to the hydrotreating reaction as hereinabove described. The hydrocracked hydrocarbon liquid component is passed to a separation means such as a fractional distillation column, wherein it is separated into a light hydrocarbon fraction, a gasoline fraction, and a heavy hydrocarbon fraction. The light hydrocarbon fraction and gasoline fraction are yielded as products from the process. The heavy hydrocarbon fraction, boiling above about 400° F. represents the unconverted portion of the hydrocarbon charge to the hydrocracking reaction. This heavy hydrocarbon fraction is re-cycled from the separation step to the hydrocracking reaction for conver-

sion into gasoline and lighter hydrocarbon. The gasoline fraction obtained as a product herein is suitable as a charge stock for an octane improving process such as, for example, catalytic reforming.

In order to better describe the present invention reference is now made to the attached drawing. The drawing is a schematic representation of preferred embodiment of the present invention. For the sake of clarity many elements such as pumps, valves, instrumentation, etc. commonly employed in a commercial process but unnecessary to describe the invention herein have been eliminated. Such elements may be conveniently added by those skilled in the art. As stated, the attached drawing represents a preferred embodiment of the present invention and many modifications and alternations within the scope of the present invention will be obvious to those skilled in the art.

In the description of the drawing which follows, liquid flow rates will be expressed in barrels per hour (b/h) and gas flow rates will be expressed in thousands of cubic feet per hour (Mscf/h).

Referring now to the drawing, a delayed coker gas oil having a gravity of 28.8° API, an ASTM distillation range of 338° - 680° F., containing 2,300 ppm total nitrogen, 1.46 weight percent sulfur, 36.2 volume percent aromatics, and 14.5 volume percent olefins is treated according to the process of the present invention to yield a gasoline product boiling in the range of 100° - 400° F. which is suitable for charge stock to a catalytic reforming process. Delayed coker gas oil at a rate of about 100 b/h via line 1 and a recirculating gas stream comprising about 86 percent hydrogen at a rate of about 1,320 Mscf/h via line 2 are mixed in line 3 to form a mixture having a hydrogen to hydrocarbon ratio of about 11,400 SCF/B. From line 3 the mixture passes into a hydrotreating reaction zone 4 at a temperature of about 700° F. wherein the reaction mixture is contacted with a hydrotreating catalyst comprising about 3.2 weight percent NiO and about 15.7 weight percent MoO₃ supported upon an alumina base at an average reaction temperature of about 725° F., an LHSV of about 0.5 Vo/Hr/Vc, and a pressure of 1,500 psig to convert substantially all the nitrogen and sulfur to ammonia and hydrogen sulfide, respectively. From the hydrotreating zone 4 a reaction effluent passes via line 5 to cooler 6 wherein the hydrotreating zone effluent is cooled to a temperature of about 100° F. to condense substantially all the hydrocarbon components boiling above propane. From cooler 6, a cooled effluent comprising a liquid component and a gaseous component passes via line 7 into a first high pressure separator 8 wherein the gaseous component is separated from the liquid component. The gaseous component comprising hydrogen, hydrogen sulfide and ammonia, recovered via line 9, is passed into a gas treater 10 wherein the hydrogen sulfide and ammonia are separated from the hydrogen by adsorption into a water phase and a diethylamine phase. From the gas treater 10, a gas stream comprising hydrogen substantially free of hydrogen sulfide and ammonia at a rate of about 1,224 Mscf/h is recovered via line 11 and mixed with a makeup hydrogen stream comprising about 100 percent hydrogen at a rate of about 250 Mscf/h is recovered via line 12. A bleed gas stream 34, is removed at a rate of about 2,400 SCF/H to remove light hydrocarbons e.g., (C₁-C₂) produced in the process. The gas mixture comprising hydrogen at a pressure of about 1,250 psig is transferred

via line 13 to compressor 14 wherein such gas mixture is compressed to a pressure of about 1,750 psig. From a compressor 14 the compressed gas mixture is recovered via line 15 for recirculation to a hydrocracking reaction as will hereinafter be described.

From the first high pressure separator 8 the liquid component of the hydrotreating reaction effluent is recovered via line 16 and passed to a low pressure separator 17 wherein at a pressure of about 250 psig low boiling components such as hydrogen sulfide, ammonia, some propane and some lighter hydrocarbons are separated from higher boiling components by flashing. The low boiling components comprising hydrogen sulfide, ammonia, and low boiling hydrocarbons are removed from the low pressure separator 17 via line 18. Liquid hydrocarbon component from the low pressure separator, containing less than 1 ppm nitrogen is recovered via line 19 and is mixed with a recycle hydrocarbon component in line 21. The hydrocarbon mixture at a rate of about 212 b/h in line 21 and compressed hydrogen containing gas at a rate of about 1,450 Mscf/h in line 15 are mixed in line 22 and passed into heater 23 wherein the mixture is heated to a temperature of about 635° F., at a pressure of about 1,850 psig. From heater 23 the heated mixture passes via line 24 into hydrocracking zone 25 wherein the mixture is reacted at a temperature of about 650° F., a pressure of about 1,800 psig, a LHSV of about 1.0 Vo/Hr/Vc at a hydrogen to hydrocarbon ratio of about 6,000 SCF/B in the presence of a sulfided hydrocracking catalyst comprising (before sulfiding) 6 weight percent nickel and 19 weight percent tungsten on a silica-alumina base to convert about 50 percent of the hydrocarbon liquids into hydrocarbons boiling below 400° F. A hydrocracking reaction effluent, recovered via line 26, passes into cooler 32 wherein normally liquid hydrocarbons are condensed. Cooler effluent passes via line 33 into a second high pressure separator 27 wherein the cooler effluent is separated into a gas phase and a liquid phase. The second high pressure separator gas phase, comprising hydrogen is recovered via line 22 and passes into line 3 for mixture with additional amounts of delayed coker gas oil as hereinabove described.

The second high pressure liquid phase comprising converted and unconverted hydrocarbons is recovered via line 28 and passes into fractionator 29. In fractionator 29 the liquid phase is separated into a light hydrocarbon component, a gasoline product component, and a recycle hydrocarbon component. The light hydrocarbon component comprising hydrocarbons boiling below about 115° F. is recovered from fractionator 29 at a rate of about 24 b/h via line 30. The gasoline component boiling in the range of about 115° to 400° F. is recovered from fractionator 29 at a rate of about 98 b/h via line 31. The recycle hydrocarbon component comprising hydrocarbons boiling above 400° F. is recovered from fractionator 29 at a rate of about 106 b/h via line 20 and is returned via line 21 for mixture with additional amounts of low pressure separator hydrocarbon as hereinabove described.

By following the process of the present invention, wherein sulfur and nitrogen containing charge stock is treated at a temperature of about 600° F. to about 800° F., a pressure of about 1,200 – 1,500 psig with hydrogen at a hydrogen to hydrocarbon ratio of 10,000 – 20,000 SCF/B in the presence of a hydrotreating catalyst, a hydrocracking charge stock may be obtained.

The hydrocracking reaction charge stock obtained by following the method of this invention contains less than about 1 ppm of nitrogen. By following the method of the present invention the rate of deactivation of both the hydrotreating catalyst and the hydrocracking catalyst is substantially diminished thereby allowing sustained periods of continuous operation of long duration in the range of about 12 to 18 months before the process must be discontinued to allow regeneration of the hydrotreating and hydrocracking catalyst.

By operating the hydrotreating reaction zone at pressures lower than the hydrocracking reaction zone an additional advantage is obtained in that hydrogen containing gas recovered from the second high pressure separator 27 may be circulated directly to the hydrotreating zone 4 without an intermediate compression step, and the hydrogen containing gas recovered from the effluent of the hydrotreating zone 4 may be compressed and returned to hydrocracking zone 25 thereby conserving hydrogen. Only one compression step is required to circulate the hydrogen containing gas through both the hydrocracking zone 25 and the hydrotreating zone 4.

Results analogous to those described in the foregoing description of the drawing are obtained when other hydrocracking catalysts, and operating conditions, other feed stocks, and other hydrotreating catalysts and conditions within the broad purview of the above disclosure are employed. Also modifications and variations of this above described process will occur to those who are skilled in the art. Therefore it is not intended to limit the invention to the details of the specific embodiment described but only to the limitations contained within the spirit and scope of the appended claims.

We claim:

1. In a method for converting a sulfur and nitrogen containing hydrocarbon charge stock boiling in the range of from about 400° F. to about 1,000° F. into a gasoline product boiling in the range of about 100° F. to about 400° F., wherein the hydrocarbon charge stock is treated with molecular hydrogen in the presence of a hydrotreating catalyst to convert sulfur compounds into hydrogen sulfide and nitrogen compounds into ammonia, wherein effluent from the hydrotreating reaction zone is separated into a first hydrocarbon liquid phase and a gas phase comprising hydrogen, hydrogen sulfide, and ammonia, wherein the hydrotreated liquid phase is contacted with molecular hydrogen in the presence of a hydrocracking catalyst to convert hydrocarbons boiling above about 400° F. into hydrocarbons boiling below about 400° F., wherein effluent from the hydrocracking reaction is separated into a gaseous phase comprising hydrogen and a second liquid hydrocarbon phase, wherein the second liquid hydrocarbon phase is separated into a fraction boiling below about 400° F. and a fraction boiling above about 400° F. and wherein the hydrocracked fraction boiling above about 400° F. is recycled to the hydrocracking reaction for conversion into hydrocarbons boiling below 400° F.; the improvement which comprises:

- a. Hydrotreating the hydrocarbon charge at a temperature of from about 600° F. to about 800° F., a pressure of from about 1,200 to about 1,500 psig, a liquid hourly space velocity of from about 0.5 to about 10 volumes of oil per volume of catalyst per hour, and with a hydrogen to hydrocarbon ratio of from about 10,000 to about 20,000 SCF/B;

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- b. separating the hydrotreating reaction effluent into a hydrotreated gas phase comprising hydrogen, hydrogen sulfide, and ammonia and a first liquid hydrocarbon phase containing about 1 ppm or less nitrogen;
- c. treating gas phase from the hydrotreating step for removal of hydrogen sulfide and ammonia therefrom;
- d. compressing treated gas of step (b), comprising hydrogen, to a pressure in the range of about 1,400 psig to about 2,000 psig, above the pressure of hydrotreating step (a);
- e. hydrocracking the hydrotreated liquid phase of step (b) in the presence of the compressed treated gas of step (c) at a pressure in the range of about

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- 1,400 psig to about 2,000 psig;
- f. separating the hydrocracking reaction effluent into a hydrocracked liquid phase and a gas phase comprising hydrogen; and
- g. circulating the gas phase of step (f) for contact with additional hydrocarbon charge in step (a).
2. The method of claim 1 wherein the hydrocracking reaction is performed at a temperature in the range of about 400° F. to about 800° F., at a liquid hourly space velocity of from about 0.5 to about 15 vol. oil/hr./vol. catalyst, and wherein the hydrogen to hydrocarbon ratio is in the range of from about 3,000 to about 15,000 SCF/B.

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