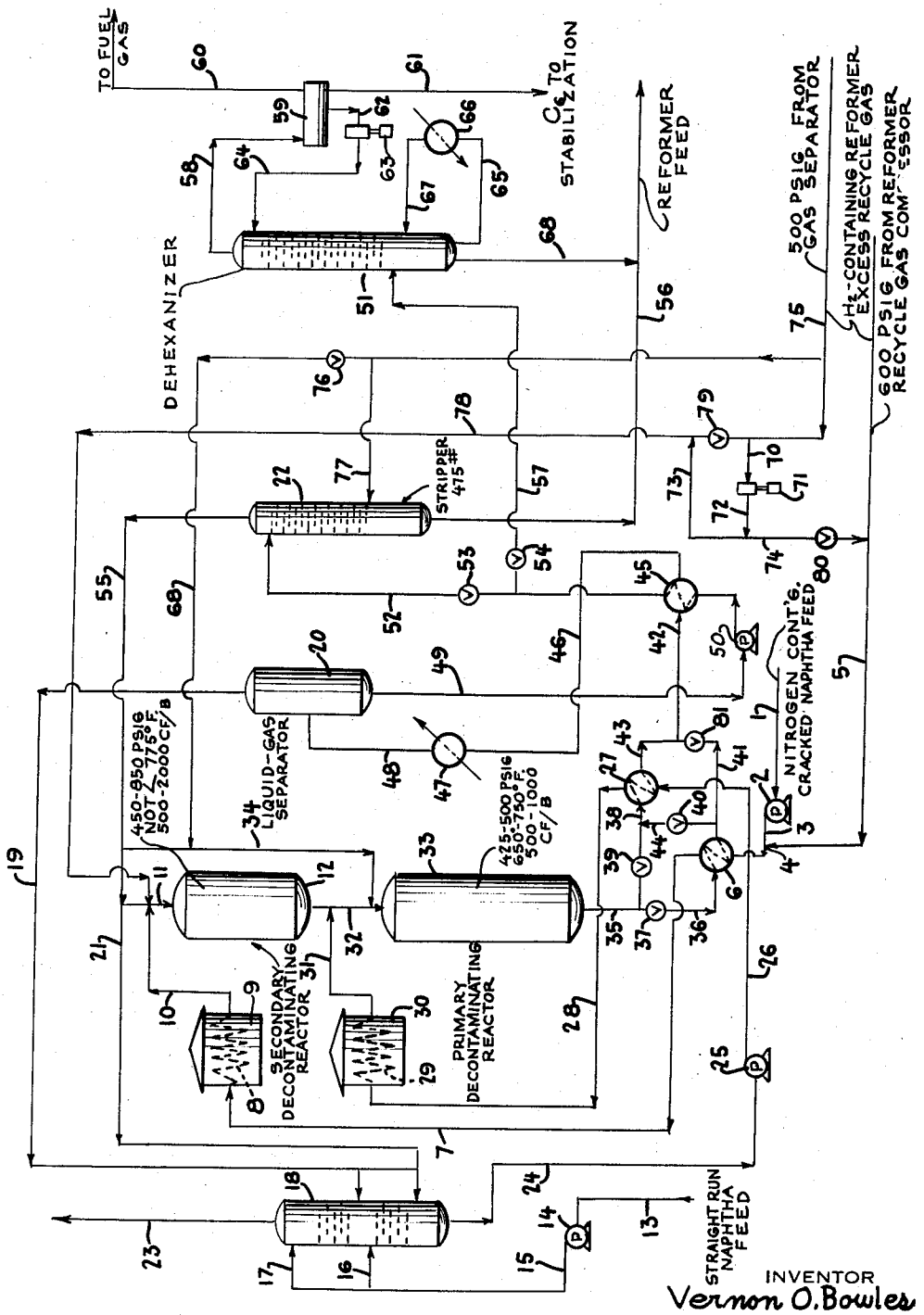
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CASCADED PRETREATER FOR REMOVAL OF NITROGEN

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INVENTOR
Vernon O. Bowles
BY Francis J. Johnston
AGENT

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CASCADED PRETREATER FOR REMOVAL OF NITROGEN

Vernon O. Bowles, Rye, N.Y., assignor to Socony Mobil Oil Company, Inc., a corporation of New York

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The present invention relates to the pretreatment of hydrocarbon mixtures containing nitrogen compounds prior to subjecting said hydrocarbon mixtures to conversion over a nitrogen-sensitive catalyst in the presence of hydrogen and, more particularly, to the pretreatment of hydrocarbon mixtures containing nitrogen compounds before subjecting said hydrocarbon mixtures to conversion over a platinum-type catalyst in the presence of hydrogen.

With the increasing use of platinum-type catalysts and other catalysts which are sensitive to nitrogen and the expanding application of hydrocarbon conversions to stocks which have heretofore not been deemed hydrocarbon mixtures requiring catalytic treatment, deactivation of catalysts suitable for such hydrocarbon conversions as reforming, hydrocracking, and hydrogenating by organic nitrogen compounds has become a problem which in the past had not been of sufficient importance to require consideration or the presence of organic nitrogen compounds in the feed to a hydrocarbon conversion was not recognized as a probable source of operational difficulties. Thus, when designing reforming units consideration was given primarily to the removal of sulfur from the feed. Since most charge stocks were low in the concentration of organic nitrogen compounds no considerable operational difficulties such as rapid deactivation of the catalyst were encountered. Now, however, gasoline components which without reforming previously satisfied the lower gasoline anti-knock requirements of a few years ago must catalytically be reformed to meet the higher anti-knock requirements of present day cars. Whereas, heretofore cracking stocks have not been hydrogenated, consideration is now being given to hydrogenating or hydrogenating and cracking of such stocks to provide improved charge stocks for conventional catalytic cracking or to provide improved charge stocks for catalytic reforming and improved diesel fuels and improved domestic heating fuels. A particularly good example illustrative of the situation and illustrative of the means provided by the present invention for solving the problem is that of the reforming of thermally cracked gasoline components.

Until the anti-knock requirements for motor vehicle gasoline rose to present day levels of about 100 octane (RON+3 cc. TEL) and higher, the octane rating of leaded blends containing thermally cracked gasoline was statisfactory. Consequently, most catalytic reforming units designed and built prior to 1957 were designed to process straight run gasoline. The concentration of organic nitrogen compounds in most straight run gasolines is very low compared to the concentration of organic nitrogen compounds in thermally cracked gasolines. Furthermore, it would appear that the organic nitrogen compounds in straight run gasoline are more readily decomposed than the organic nitrogen compounds present in thermally cracked gasoline. Consequently, when straight run gasoline is subjected to processing under conditions required to remove upwards of 90 percent

of the organic sulfur compounds present in straight run gasoline the concentration of organic nitrogen compounds is reduced to a level at which the on-stream time of platinum-type catalysts is not substantially reduced. However, under the same conditions at which 90 percent or more of the organic sulfur in thermally cracked gasoline is removed, the nitrogen level of the treated thermal gasoline is sufficiently high to markedly affect the on-stream time of reforming units employing nitrogen-sensitive reforming catalysts such as platinum-type catalysts.

The increased severity required to produce satisfactorily denitrogenized stock is illustrated by the following comparisons:

	To Produce Satisfactorily Desulfurized Reformer Charge Stock	To Produce Satisfactorily Denitrogenized Reformer Charge Stock
Pressure, p.s.i.g.	425	425
Temperature, ° F.	675	675
S.c.f. Hydrogen/Bbl. Charge	500	2,000
Space Velocity, v./hr./v.	5	2

To those skilled in the art it is manifest that a decontaminating unit which produces a satisfactorily desulfurized charge stock for a reformer will not necessarily produce a reformer charge stock having a satisfactory nitrogen content. Furthermore, a considerable sacrifice of capacity must be accepted in order to provide the high severity (higher temperature, hydrogen-to-naphtha ratio, lower space velocity) required for adequate nitrogen conversion to volatile hydrogen derivatives thereof.

Heretofore the primary concern of those designing and building units for the reforming of naphtha to produce gasoline of improved anti-knock properties has been the removal of sulfur. Accordingly, many reforming units, especially those wherein a platinum-type catalyst is employed, have been designed with decontaminating units employing process severity sufficient only for decontamination of straight run stock. With the increased demand for motor gasolines of greater and greater anti-knock rating it has become necessary to reform charge stocks which heretofore have not been considered as reformer charge stocks because the anti-knock ratings of the blends containing the fraction were satisfactory without reforming. Typical of these stocks, which under the prior concept of acceptable anti-knock rating were not deemed stocks requiring reforming, is thermally cracked naphtha.

Thermally cracked naphthas have nitrogen contents ranging from about 30 to about 300 parts per million (p.p.m.). Thermally cracked naphthas also contain about 10 to about 40 percent by volume of olefinic hydrocarbons. Consequently, when a naphtha such as thermally cracked naphtha, hereinafter designated thermal naphtha or thermal gasoline, having a high concentration of nitrogen, i.e., in excess of 5 p.p.m., is to be reformed additional hydrogen is necessary to decontaminate the stock having the high nitrogen concentration. Furthermore, it has been discovered recently that the conditions necessary for the reduction of the nitrogen concentration of a reformer charge stock to an innocuous level are more severe than those required to remove 90 percent or more of the sulfur from a reformer charge stock. On the other hand, it is not usual for the volume of naphtha to be reformed having a relatively high nitrogen content to represent only about 20 percent or less of the total volume of naphtha to be reformed. Consequently, it is not economical to subject the entire supply of reformer charge naphtha to the severe conditions necessary to adequately pretreat only one-fifth or less of the supply.

Similarly in hydrocracking a topped crude, or virgin gas oil, or catalytic gas oil the organic nitrogen compounds are concentrated in a relatively minor portion of the charge.

Accordingly, the present invention provides a method of reducing in a separate decontaminating operation the nitrogen concentration of a hydrocarbon fraction having a relatively high nitrogen concentration of about 30 to about 300 p.p.m. to a nitrogen concentration which does not substantially reduce the on-stream time of a hydrocarbon conversion employing a nitrogen-sensitive catalyst, mixing the at least partially decontaminated hydrocarbon fraction with a hydrocarbon fraction having a relatively low nitrogen concentration of about 0 to about 3 p.p.m., hydrodecontaminating the mixture to reduce the concentrations of sulfur and nitrogen to acceptable levels at which the on-stream time of the catalyst is of industrially practical length and the sulfur content of the mixture is not greater than about 5 to about 20 p.p.m., and subjecting the hydrodecontaminated mixture to ultimate conversion at conversion temperature, pressure, hydrogen to feed ratio, and space velocity over a nitrogen-sensitive catalyst.

Thus, for example, the hydrodecontaminated charge stock for a reformer employing a particle-form, solid, platinum-type, reforming catalyst must contain not more than about 1 p.p.m. of nitrogen to maintain an industrially practical on-stream period.

The method of the present invention provides for the application of suitable conditions of temperature, pressure, space velocity and ratio of hydrogen to hydrocarbon mixture to the minor portion of the charge to the ultimate conversion having the relatively high nitrogen concentration in a separate operation with a minimum of equipment in addition to that required to decontaminate the major portion of the charge to the ultimate conversion which requires minimum or no additional gas compression, and has high thermal efficiency.

Since the present invention is basically an invention involving a sequence of operations the description of the invention as applied to hydrodenitrogenizing reformer charge stock is applicable to the hydrodenitrogenizing of other hydrocarbon mixtures hydrodenitrogenized for other ultimate conversions over nitrogen-sensitive catalysts such as hydrocracking topped crudes, gas oils and the like, and hydrogenating or hydrofinishing hydrocarbon mixtures such as kerosines, diesel fuels, jet fuels and the like.

Illustrative of the method of the present invention is the treatment of reformer charge stock comprising a portion having a relatively high concentration of organic nitrogen compounds and a portion having a relatively low concentration of organic nitrogen compounds. For example, the charge to a reformer employing a platinum-type, particle-form, solid, reforming catalyst comprises about 20 percent by volume of thermal naphtha containing about 30 to about 300 p.p.m. of nitrogen and about 80 percent straight run naphtha containing about 0 to about 5 p.p.m. of nitrogen.

The thermal naphtha is pumped at a pressure about 175 p.s.i. higher than the pressure in the hydrodenitrogenizing or secondary reactor, to ensure a pressure differential sufficient to drive the thermal naphtha through a heater, the secondary and primary reactors, heat exchangers and other equipment to the suction side of the pump charging the reformer reactors. Preferably, to overcome or reduce the tendency of the thermal naphtha to foul heater exchanger tubes at least a small quantity, e.g., about 50 to about 100 cubic feet of reformer recycle gas per barrel is injected into the stream of thermal naphtha downstream of the thermal naphtha charge pump and upstream of the thermal naphtha heat exchangers and heater. The preheated naphtha and the aforementioned recycle gas flow to a heater wherein the thermal naphtha is heated to a temperature suitable for the hydrodenitrogenation thereof. From the thermal naphtha heater the thermal naphtha flows to the secondary decontaminating reactor. Between the outlet of the thermal naphtha heater and the inlet of the secondary decontaminating reactor, the portion of the hydrogen-rich reformer recycle gas (containing at least about 70 percent by volume of hydrogen) flowing directly from the reformer gas-liquid separator or from the primary decontaminating circuit or from both, that is required to make up the desired ratio of hydrogen to thermal naphtha charge, is mixed with the thermal naphtha. Alternately, all of the hydrogen-rich gas can be injected into the thermal naphtha stream downstream of the charge pump 25 and upstream of the heat exchangers to more effectively control fouling. The heater outlet temperature is controlled and regulated to maintain an average temperature in the secondary decontaminating reactor of about 650° to about 850° F.

The straight run naphtha flows through an absorber where it is in intimate contact with the gases and vapors from the various gas-liquid separators forming a part of the hydrodecontaminating unit. From the absorber the portion of the reformer charge stock having a low nitrogen content, i.e., in this illustration the straight run naphtha, flows to a heat exchanger where the straight run naphtha is in indirect heat exchange relation with the total effluent from the primary decontaminating reactor. The thus preheated straight run naphtha flows to the straight run naphtha heater wherein the temperature of the straight run naphtha is raised to that required for the reaction in the primary decontaminating reactor. Downstream of the straight run naphtha heater and upstream of the primary decontaminating reactor, the effluent of the secondary decontaminating reactor is mixed with the heated straight run naphtha. The mixture of the effluent of the secondary decontaminating reactor and the heated straight run naphtha flows to the primary decontaminating reactor. Prior to entry of the aforesaid mixture into the primary decontaminating reactor hydrogen-rich reformer recycle gas, preferably, or any other hydrogen-rich gas is mixed with the mixture of the at least partially denitrogenized thermal naphtha and untreated straight run naphtha. Usually, about 500 to about 2000 cubic feet of recycle gas (containing about 70–90 percent by volume of hydrogen) per barrel of total charge stock is mixed with mixture of the at least partially denitrogenized thermal naphtha and the untreated straight run naphtha.

The effluent from the primary decontaminating reactor comprises hydrogen, hydrogen derivatives of contaminants originally present in the naphthas, and C_1+ hydrocarbons. The effluent from the primary decontaminating reactor flows through heat exchangers and a cooler to reduce the temperature of the primary reactor effluent to that at which C_4+ hydrocarbons at least partly separate from hydrogen and the volatile hydrogen derivatives of contaminants.

In the gas-liquid separator hydrogen, C_1 to C_3 hydrocarbons, hydrogen sulfide, ammonia, and other gaseous constituents of the primary effluent at least partly separate from C_4 and heavier hydrocarbons. The uncondensed portion of the primary effluent is vented to the refinery fuel system through an absorber for C_4+ hydrocarbons while the condensate is pumped to a stripper or a dehexanizer where remaining volatile contaminants of the catalytic reformer charge are reduced to a tolerable level.

A preferred means of pretreating a thermal naphtha (relatively high in nitrogen content) in conjunction with a straight run naphtha is illustrated by the highly schematic flowsheet of the drawing.

Thus, thermal naphtha is drawn from a source not shown through pipe 1 by pump 2 and discharged into pipe 3. At some point 4, between pump 2 and thermal

naphtha heat exchanger 6, a small amount (about 50 to about 100 cubic feet per barrel of thermal naphtha) of reformer recycle gas flows from conduit 5 into pipe 3 at a pressure at least equal to that of the thermal naphtha in pipe 3. The mixture of thermal naphtha and hydrogen-containing gas, e.g., reformer recycle gas, flows through pipe 3 to heat exchanger 6 where the mixture is in indirect heat exchange relation with at least a portion of the total effluent flowing from primary decontaminating reactor 33. From heat exchanger 6 the thermal naphtha and hydrogen flow through pipe 7 to coils 8 in heater 9. In heater 9 the thermal naphtha and hydrogen is heated to a temperature suitable for bringing about the hydrogenation of the organic compounds present in the thermal naphtha at the pressure and the hydrogen partial pressure existing in secondary decontaminating reactor 12. For example, at 425 to 850 p.s.i.g. and with 500 to 2000 cubic feet of hydrogen per barrel of thermal naphtha a temperature of about 675 to 775° F. in secondary decontaminating reactor 12 provides satisfactory results.

The heated thermal naphtha flows from coils 8 through pipe 10 to conduit 11 where the thermal naphtha is mixed with the balance of the hydrogen necessary to provide about 500 to about 2000 cubic feet of hydrogen per barrel of thermal naphtha. Alternately, all of the hydrogen required for bringing about the reaction can be admitted through conduit 5 and pipe 3. When the secondary decontaminating reactor is being operated at a pressure of about 450 to about 550 p.s.i.g. the aforesaid additional hydrogen is obtained from the stripper overhead or directly from the gas separator of the reforming unit operating at a pressure in sufficient excess of about 450 to about 550 p.s.i.g. to overcome the back pressure of the intervening piping or from both. When the secondary decontaminating reactor is being operated at a pressure substantially higher than that of the gas separator of the reforming unit, i.e., at pressures greater than about 550 up to about 800 p.s.i.g. the hydrogen for hydrogenating the thermal naphtha in the secondary decontaminating reactor is obtained from the gas separator of the reforming unit and compressed to a pressure in sufficient excess of that of the secondary decontaminating reactor to overcome the back pressure of the intervening piping and equipment.

Thus, when the secondary decontaminating reactor is being operated at a pressure of about 425 p.s.i.g., hydrogen-containing gas, e.g., at least a portion of reformer recycle gas, flows from the reformer gas separator (not shown) through conduit 75 (with valve 76 closed) through pipe 77 to stripper 22 wherein the recycle gas brings about the stripping of the volatile hydrogen derivatives of the contaminants from the primary condensate. The overhead from stripper 22 comprising the aforesaid recycle gas, light hydrocarbons and aforesaid hydrogen derivatives of the contaminants flows through conduit 55 to conduit 11. When additional hydrogen is required recycle gas flows from the reformer gas separator (not shown) through conduit 75 to conduit 78 under control of valve 79 to conduit 11. The additional hydrogen can also be obtained both directly from the reformer gas separator (not shown) and from the stripper. When the additional hydrogen is obtained directly from the reformer recycle gas separator (not shown) but also from the stripper at least a portion of the reformer recycle gas flows from conduit 75 through conduit 77 in the amount necessary to strip the primary condensate of all but tolerable traces of volatile hydrogen derivatives of contaminants in the original feed. From stripper 22 the hydrogen as a part of the overhead from stripper 22 flows through conduit 55 to conduit 11. The balance of the required hydrogen flows from conduit 75 through conduit 78 to conduit 11 under control of valve 79.

When secondary decontaminating reactor 12 is being operated at a pressure in excess of the pressure in the reformer gas separator, e.g., at 600 p.s.i.g. or more, it is necessary to compress the reformer recycle gas to a higher pressure. However, generally it is not desirable to operate the stripper at such higher pressures. Accordingly, reformer recycle gas at the pressure of the reformer gas separator flows as previously described to the stripper 22 and thence through conduits 55 and 21 to absorber 18 while the hydrogen for use in the secondary decontaminating reactor flows from the reformer recycle gas separator (not shown) through conduit 75 to conduit 78 to conduit 70 and the suction side of compressor 71. Compressor 71 compresses the reformer recycle gas to a pressure higher than that of the secondary decontaminating reactor 12 and discharges the recompressed gas into conduit 72. With valve 80 controlling the amount of gas flowing through conduit 74 to conduit 5 (the 50 to 100 cubic feet required in pipe 3 as hereinbefore described) the balance of the recompressed reformer recycle gas (enough to make about 500–2000 c.f./b. of thermal naphtha in secondary decontaminating reactor 12) flows through conduits 73 and 78 to conduit 11 where the compressed reformer recycle gas is mixed with the heated thermal naphtha as described hereinbefore. When desirable all of the hydrogen required in the secondary decontaminating reactor 12 can flow from conduit 75 through conduits 78 and 70 to compressor 71, thence through conduits 72 and 74 under control of valve 80, to conduits 5 and 3.

The mixture of heated thermal naphtha and about 500 to about 2000 cubic feet of hydrogen per barrel of thermal naphtha flows preferably downwardly through secondary decontaminating reactor 12 in intimate contact with a sulfur-and nitrogen-insensitive hydrogenation catalyst such as a mixture of oxides of cobalt and molybdenum supported on alumina.

In secondary decontaminating reactor 12 the nitrogen concentration of the C_4^+ portion of the thremal naphtha is reduced to a concentration such that when mixed with the straight run naphtha and processed further as hereinafter described the nitrogen concentration of the C_4^+ portion of the mixture is not more than about 1 p.p.m. when the mixture is to be reformed over a nitrogen-sensitive platinum-type reforming catalyst. Thus, the feed for the reforming unit in this illustration is about 20 percent thermal naphtha and about 80 percent straight run naphtha and the nitrogen concentration of the thermal naphtha after being processed in the secondary decontaminating reactor is reduced to about 2–20 p.p.m. This at least partially denitrogenized thermal naphtha together with the products of the reactions which take place in secondary decontaminating reactor 12 form the secondary decontaminating reactor effluent. The secondary decontaminating reactor effluent flows from secondary decontaminating reactor 12 through conduit 32. In conduit 32 the secondary decontaminating reactor effluent is mixed with heated straight run naphtha and the additional hydrogen required to provide about 500 to about 1000 cubic feet of hydrogen per barrel of naphtha treated in primary decontaminating reactor 33.

In the primary decontaminating reactor the mixture of partially hydrodecontaminated thermal naphtha and the unprocessed straight run naphtha, the mixture containing not more than about 20 p.p.m. of nitrogen, is contacted with a sulfur- and nitrogen-insensitive catalyst (which can be the same as or different from the catalyst in secondary decontaminating reactor 12 such as a mixture of oxides of cobalt and molybdenum supported on alumina) in the presence of about 500 to about 1000 cubic feet of hydrogen to reduce the nitrogen concentration of the C_4^+ portion of the aforesaid mixture of partially decontaminated and untreated straight run naphtha to not more than about 1 p.p.m.

The straight run naphtha is heated to the reaction temperature required in primary decontaminating reactor 33 as described hereinafter.

Straight run gasoline is drawn from a source not shown through pipe 13 by pump 14 and discharged into pipe 15. The straight run naphtha flows through pipe 15 to a plurality of branches, e.g., two, i.e., pipes 16 and 17 and thence to absorber 18 in which valuable hydrocarbons are absorbed from the gases and heat exchanger fouling precursors such as oxygen are stripped from the naphtha feed. Stripper overhead from stripper 22 gas flowing through conduits 55 and 21 and uncondensed primary decontaminating effluent flowing from gas-liquid separator 20 through conduit 19 are intimately contacted with the straight run naphtha in absorber 18. The straight run naphtha absorbs primarily C_4 and heavier hydrocarbons from the gases while the gas strips oxygen and other heat exchanger fouling materials and water from the naphtha. The absorber residue gases flow from absorber 18 through conduit 23 to plant fuel or other uses while the straight run naphtha leaves absorber 18 through pipe 24.

The straight run naphtha flows through pipe 24 to the suction side of pump 25. Pump 25 discharges the enriched straight run naphtha into pipe 26 at a pressure higher than the pressure in primary decontaminating reactor 33. The naphtha flows through pipe 26 to heat exchanger 27 where the enriched straight run naphtha is in indirect heat exchange relation with a major portion or all of the effluent from the primary decontaminating reactor 33 as hereinafter described. From heat exchanger 27 the enriched straight run naphtha flows through pipe 28 to coil 29 in heater 30.

In heater 30 the preheated, straight run naphtha is heated to a temperature suitable for bringing about desulfurization, e.g., about 700 to about 825° F. From heater 30 the hot, straight run naphtha flows through pipe 31 to conduit 32. As stated hereinbefore, in conduit 32 the hot, straight-run naphtha is mixed with the secondary decontaminating reactor effluent and the amount of hydrogen required to provide with the hydrogen in the secondary decontaminating reactor effluent, about 500 to about 1000 cubic feet of hydrogen per barrel of mixed naphtha flowing into primary decontaminating reactor 33. This hydrogen preferably is drawn from conduit 55 through conduit 34 or from conduit 68 through conduit 34 or from both conduit 55 and conduit 68 through conduit 34.

The mixture of secondary decontaminating reactor effluent, heated straight run naphtha and such additional hydrogen as required flows through conduit 32 into primary decontaminating reactor 33. In primary decontaminating reactor 33 the aforesaid mixture is intimately contacted with a sulfur-insensitive catalyst, e.g., a mixture of cobalt and molybdenum oxides on alumina at a temperature within the range of about 650° F. to about 750° F. In primary decontaminating reactor 33 the sulfur concentration of the mixed naphthas is reduced by conversion to hydrogen sulfide which is rejected in stripper 22 or dehexanizer 51 to a level at which the reforming catalyst is not deactivated to any appreciable extent and the corrosion of the metal parts of the reforming unit is at a practical minimum. In a similar manner nitrogen compounds and other contaminants are hydrogenated to yield volatile hydrogen derivatives of said contaminants which are rejected in stripper 22 or dehexanizer 51.

As illustrated there are at least two paths through which the total effluent, i.e., non-condensible and condensible components, of the primary decontaminating reactor can flow to transfer at least a major portion of the heat in the total effluent from the primary decontaminating reactor to the charge naphthas. Preferably, a minor portion of the total effluent of the primary decontaminating reactor (hereinafter designated primary reactor) is brought into heat exchange relation with the minor portion of the charge naphtha, i.e., the cracked naphtha while the major portion of the total effluent of the primary reactor is brought into heat exchange relation with the balance of the charge naphtha. Alternatively, the entire total effluent of the primary reactor is brought into heat exchange relation with the minor portion of the charge naphtha and then brought into heat exchange relation with the balance of the charge naphtha.

Preferably a minor portion about equivalent to the volume of cracked naphtha flowing through pipe 3 flows through conduit 36 under control of valve 37 to heat exchanger 6 where the minor portion of the total effluent from primary reactor 33 is in indirect heat exchange relation with the cracked naphtha. The balance of the total effluent from the primary reactor flows through conduit 38 under control of valve 39 to heat exchanger 27 where the major portion of the total effluent is in indirect heat exchange relation with the straight run naphtha flowing through pipe 26. With valves 39 and 81 open and valve 40 closed the aforesaid minor portion of the total effluent from primary reactor 33 flows through conduit 41 to conduit 42. The major portion of the total effluent from primary reactor 33 flows from heat exchanger 27 through conduit 43 to conduit 42 where the major portion and the minor portion of the total effluent from the primary reactor 33 mix and flow to heat exchanger 45.

Alternatively, with valve 39 closed and valve 37 open the entire total effluent of primary reactor 33 flows through conduit 36 to heat exchanger 6 where the entire total effluent is in indirect heat exchange relation with the cracked naphtha. With valve 81 closed and valve 40 open the entire total effluent flows from heat exchanger 6 through conduit 44 to conduit 38 and thence to heat exchanger 27 where the entire total effluent from primary reactor 33 is in indirect heat exchange with the straight run naphtha. From heat exchanger 27 the entire total effluent from primary reactor 33 flows through conduits 43 and 42 to heat exchanger 45.

In heat exchanger 45 the entire total effluent of primary reactor 33 is in indirect heat exchange relation with the condensate separated in separator 20 from the total effluent from primary reactor 33 as described hereinafter.

In heat exchanger 45 the primary reactor effluent gives up its heat to the condensate thereby heating the condensate to a temperature at which volatile hydrogen derivaties of contaminants and some hydrocarbons are stripped from the liquid phase at the pressure existing in stripper 22. Alternately, the condensate is heated to a feed temperature suitable for bringing about the separation of hydrogen and hydrogen derivatives of contaminants from the major portion of the condensate at the pressure existing in dehexanizer 51.

From heat exchanger 45 the primary reactor effluent flows through conduit 46 to cooler 47 where it is cooled to a temperature such that at the pressure existing hydrogen, a significant proportion of C_1 to C_4 hydrocarbons and hydrogen derivatives of contaminants are not condensed and a major portion of the C_4+ hydrocarbons are condensed. From cooler 47 the cooled primary reactor effluent flows through conduit 48 to gas-liquid separator 20.

In gas-liquid separator 20 the condensed hydrocarbons are separated from the uncondensed hydrocarbons, hydrogen, and hydrogen derivatives of contaminants. The uncondensed hydrocarbons, hydrogen, hydrogen sulfide, etc., flow from gas-liquid separator 20 through conduit 19 to absorber 18 as described hereinbefore. The condensed hydrocarbons as well as some dissolved light hydrocarbons and hydrogen derivatives of contaminants flow through pipe 49 to the suction side of pump 50. From pump 50 the primary reactor effluent condensate, hereinafter designated primary condensate, flows either to a stripper 22 or to a dehexanizer 51. It is very unusual for a stripper and a dehexanizer to be included in the same pretreating unit. However, for particular local reasons one is often preferred to the other. The flow of primary condensate through a stripper will be described first and

then the alternative flow through a dehexanizer will be described.

The flow of primary condensate is from heat exchanger **45** through pipe **52** (valve **53** open; valve **54** closed) to stripper **22**. In stripper **22** some light hydrocarbons together with residual hydrogen, hydrogen sulfide, and other hydrogen derivatives of contaminants, etc., are taken as overhead through pipe **55** and thence to absorber **18**, or to reactor **12**, or to reactor **33**. To facilitate stripping light hydrocarbons, hydrogen sulfide and other hydrogen derivatives of contaminants from the primary condensate, recycle gas from the gas separator in the reforming unit flowing therefrom through conduit **75** is introduced into stripper **22** through pipe **77**. The C_4+ and heavy hydrocarbons and some dissolved light hydrocarbons form a bottoms fraction in stripper **22**. The bottoms fraction contains only the very small amounts of contaminants tolerable in the reformer charge. The bottoms flow from stripper **22** through pipe **56** to the reformer unit.

When a dehexanizer is used in place of a stripper the primary condensate flows (with valve **53** closed and valve **54** open) through pipe **52** to pipe **57** and thence to dehexanizer **51**. In dehexanizer **51** an overhead of C_6 and lighter hydrocarbons together with hydrogen, hydrogen sulfide, etc. is taken through pipe **58** to accumulator **59**.

From accumulator **59** the hydrogen, hydrogen sulfide, etc., and light hydrocarbons flow through pipe **60** to the refinery fuel system. The C_5 or C_6 and lighter hydrocarbons separated as liquid in accumulator **59** flow through pipe **61** to stabilization and use or to be otherwise processed.

A portion of liquid C_5 or C_6 and lighter hydrocarbons in accumulator **59** flows through pipe **62** to pump **63**. Pump **63** discharges into pipe **64** through which this portion of the liquid hydrocarbons flows to dehexanizer **51** for use as reflux.

The C_7 and heavier hydrocarbons in the primary condensate form a bottoms product a portion of which flows through pipe **65** to heat exchanger or reboiler **66** and then through pipe **67** back to dehexanizer **51** to maintain the required temperature to volatilize the C_8 and lighter hydrocarbons. Any means for maintaining the vaporizing temperature in dehexanizer **51** other than the reboiler described can be used. The balance or the net bottoms of dehexanizer **51** flows through pipe **68** to the reformer feed pump or reformer feed storage.

It will be manifest to those skilled in the art that the foregoing description of the treatment of thermal gasoline and straight run gasoline is illustrative of the treatment of the ultimate feed to a hydocarbon conversion in which treatment a minor portion having a relatively high nitrogen content is processed in a separate or secondary decontaminating reactor under conditions severe enough to reduce the nitrogen content of said minor portion to a level such that when mixed with the major portion of the ultimate feed to said hydrocarbon conversion and the total ultimate feed subjected to hydrodesulfurization conditions usually milder than conditions in the secondary decontaminating reactor the so pretreated ultimate feed has a nitrogen content which does not appreciably decrease the on-stream time of a nitrogen-sensitive catalyst employed in said hydrocarbon conversion.

I claim:

1. The method for the conversion of a hydrocarbon fraction containing at least 30 p.p.m. of nitrogen in the form of organic nitrogen compounds which comprises treating said fraction with hydrogen in the presence of a nitrogen- and sulfur-insensitive solid catalyst in a first reaction zone under hydrodenitrogenizing conditions substantially more severe than required merely of hydrodesulfurization to obtain a first effluent of substantially reduced organic nitrogen compound content, mixing said effluent with a second hydrocarbon fraction having a relatively low concentration of organic nitrogen compounds and containing also impurities in the form of organic sulfur compounds, said second fraction comprisng the major portion of said mixture, treating said mixture with hydrogen in the presence of a nitrogen- and sulfur-insensitive solid catalyst in a second reaction zone under hydrodesulfurization conditions to obtain a second effluent stream comprising C_1+ hydrocarbons and hydrogen derivations of nitrogen and sulfur produced in said treatments, separating said effluent into a pluarlity of fractions, one of said fractions being the C_5+ hydrocarbon fraction of substantially reduced nitrogen content and subjecting said C_5+ hydrocarbon fraction to a conversion in contact with a nitrogen-sensitive solid catalyst.

2. The method as set forth in claim 1 in which the remainder of said separated fractions is recycled to the first and second reaction zones.

3. The method as set forth in claim 1 in which at least a portion of the hydrogen introduced into the first reaction zone is reformer recycle gas.

4. The method as set forth in claim 1 in which the first fraction is a thermal naphtha.

5. The method as set forth in claim 1 in which the first fraction is a thermal naphtha and the said separated C_5+ hydrocarbon fraction contains not more than about 1 p.p.m. of nitrogen.

6. The method as set forth in claim 1 in which the said first fraction is a thermal naphtha, the said second fraction is a straight run naphtha, and the said separated C_5+ hydrocarbon fraction contains not more than about 1 p.p.m. of nitrogen.

7. In the method for reforming in contact with a nitrogen-sensitive solid catalyst a straight run naphtha in admixture with a thermal naphtha which initially contains a relatively high concentration of organic nitrogen compounds equivalent to at least about 30 p.p.m. nitrogen, the improvement which comprises contacting in an auxiliary reaction zone said nitrogen containing thermal naphtha with hydrogen in the presence of a nitrogen-insensitive catalyst under severe hydrodenitrogenizing conditions whereby the content of organic nitrogen compounds within the boiling range of said thermal naphtha is substantially reduced, mixing the effluent from said auxiliary reaction zone with a major proportion of said straight run naphtha, contacting in a primary reaction zone said mixture with hydrogen in the presence of a nitrogen-insensitive solid catalyst under conditions less severe than in said auxiliary reaction zone to obtain a primary reaction zone effluent comprising C_1+ hydrocarbons, hydrogen, and hydrogen compounds of nitrogen and sulfur derived from the organic nitrogen and sulfur compounds present in said thermal naphtha and straight run naphtha, separating said effluent into plurality of fraction including a C_5+ hydrocarbon fraction of substantially reduced nitrogen content and reforming said C_5+ hydrocarbon fraction in contact with a nitrogen-sensitive solid catalyst.

8. The improvement as set forth in claim 7 wherein a minor portion of the primary reaction zone effluent passes in heat exchange relation with the thermal naphtha feed to the auxiliary reaction zone and the major portion of said primary reaction zone effluent passes in heat exchange relation with the straight run naphtha feed to the primary reaction zone.

9. The method of preparing a mixture of cracked naphtha and straight run naphtha adapted for reforming in contact with a nitrogen-sensitive, particle form, solid, catalyst which comprises reacting in the presence of hydrogen a cracked naphtha containing organic nitrogen impurities in an amount of at least 30 p.p.m. nitrogen, in the presence of a nitrogen- and sulfur-insensitive solid hydrogenation catalyst under conditions relatively more severe than required for hydrodesulfurization to obtain a first effluent having a substantially reduced content of organic nitrogen compounds, mixing said first effluent with a straight run naphtha in proportions such that said

straight run naphtha is the major component of the resulting mixture, said straight run naphtha containing impurities in the form of organic sulfur compounds with only a relatively low content of organic nitrogen impurities, treating said mixture with hydrogen in the presence of a nitrogen- and sulfur-insensitive solid hydrogenation catalyst under hydrodesulfurization conditions to obtain a second effluent stream comprising C_1+ hydrocarbons, hydrogen, and hydrogen compounds of nitrogen and sulfur derived from organic nitrogen and organic sulfur impurities originally contained in the said naphthas, and separating from said effluent a reformer feed fraction comprising C_5+ hydrocarbons said fraction having a nitrogen content not in excess of about 1 p.p.m.

10. The method as set forth in claim 7 wherein the nitrogen-insensitive catalyst is a mixture of cobalt and molybdenum oxides supported on alumina and the nitrogen-sensitive solid catalyst is a particle form, platinum-type, reforming catalyst.

References Cited in the file of this patent

UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,937,134 May 17, 1960

Vernon O. Bowles

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 61, for "statisfactory" read -- satisfactory --; column 7, lines 49 and 50, for "deconteaminating" read -- decontaminating --; line 59, after "is" insert -- kept --; column 9, line 71, for "merely of" read -- merely for --; column 10, lines 2 and 3, for "comprisng" read -- comprising--; line 53, for "fraction", first occurrence, read -- fractions --.

Signed and sealed this 4th day of April 1961.

(SEAL)

Attest: ERNEST W. SWIDER

XXXXXXXXXX

Attesting Officer

ARTHUR W. CROCKER

Acting Commissioner of Patents