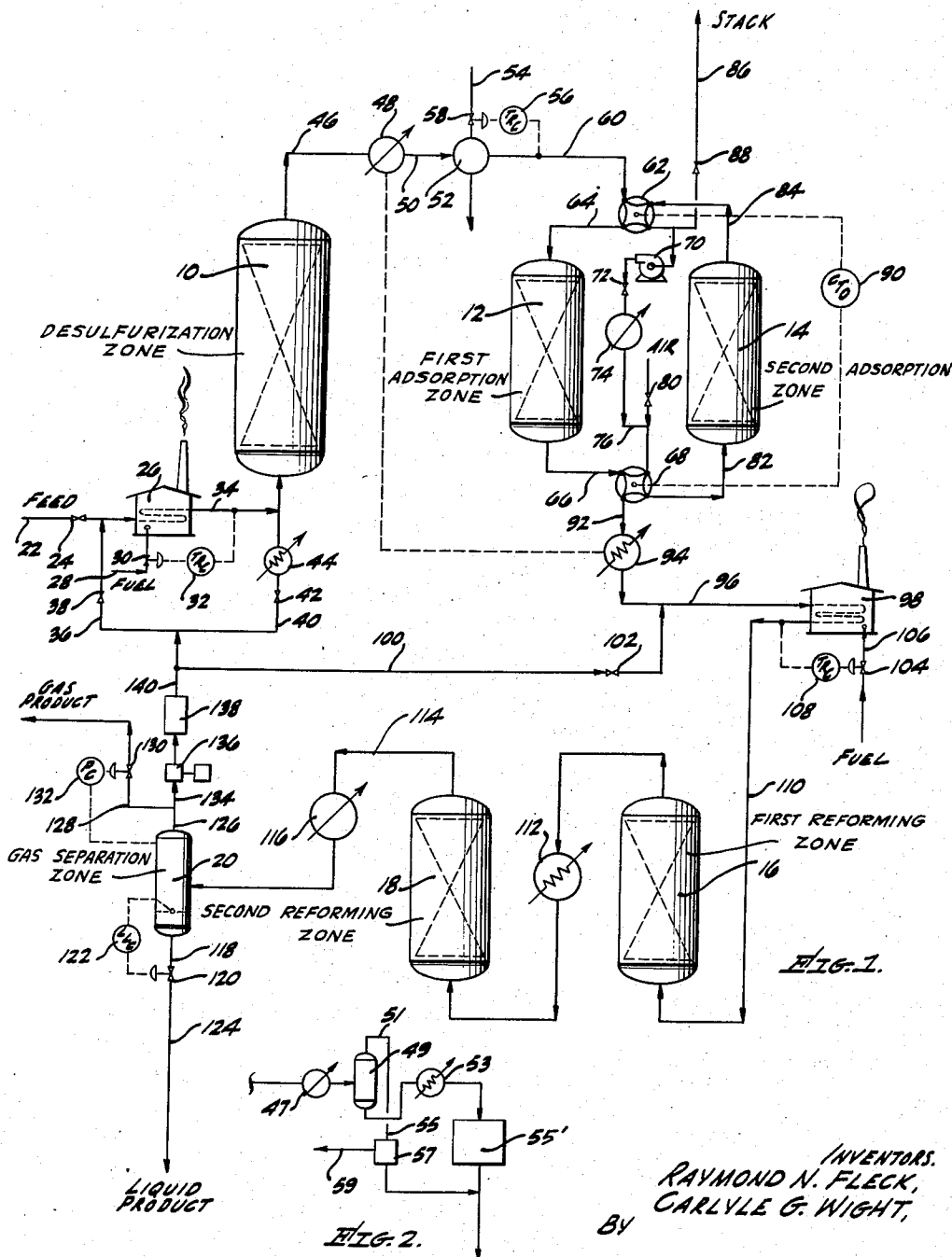


Feb. 16, 1960

R. N. FLECK ET AL
HYDROCARBON REFINING AND CONVERSION PROCESS
INCLUDING REMOVAL OF ORGANIC NITROGEN
COMPOUNDS WITH AZEOLITE
Filed Nov. 26, 1956

2,925,375



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**HYDROCARBON REFINING AND CONVERSION
PROCESS INCLUDING REMOVAL OF ORGANIC
NITROGEN COMPOUNDS WITH AZEOLITE**

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Application November 26, 1956, Serial No. 624,387

14 Claims. (Cl. 208—89)

This invention relates to the refining and conversion of hydrocarbons and particularly to an improved process for refining gasoline boiling range materials of low antiknock rating and conversion of such materials by catalytic refining and dehydroaromatization to produce increased quantities of high antiknock rating fuels suitable for use as premium automotive and aviation fuels.

Modern premium automotive and aviation gasoline fuels are used in very high compression engines where ordinarily an antiknock rating of 98 to 100 is the minimum tolerable value. These fuels are frequently a blend of alkylate, being a mixture of a highly branched C_7 to C_9 paraffin hydrocarbons, together with an aromatic blending stock forming the fuel to which is added the usual few milliliters of tetraethyllead. The aromatic blending stock is nearly always produced by dehydrogenation of naphthene hydrocarbons. The naphthenes often are produced by paraffin dehydrocyclization reactions and a catalyst which increases the rate of reaction is nearly always employed. Such processes and the products which are produced thereby are known to be detrimentally affected by the presence of hydrocarbon derivatives of sulfur and nitrogen in the feedstock and therefore frequently the raw hydrocarbon feed is subjected to a catalytic desulfurization and denitrogenation treatment to minimize these problems.

Considerable quantities of such premium fuels are presently being produced from low grade gasoline boiling range naphthas by first catalytically desulfurizing the feedstock in the presence of hydrogen. This removes substantially all of the hydrocarbon derivatives of sulfur and the major portion of the hydrocarbon derivatives of nitrogen. The thus treated material is then catalytically dehydroaromatized to produce the aromatic blending stock of high antiknock rating. This degree of desulfurization is obtained using a cobalt molybdate catalyst and at conditions hereinafter more fully described. It has been found however that although most of the nitrogen compounds are removed, a significant residual quantity remains which still has an adverse effect upon the subsequent catalytic dehydroaromatization step, commonly referred to as reforming. The adverse results are most pronounced when the reforming catalyst comprises a platinum catalyst, particularly a halide (commonly fluoride or chloride, or both) promoted platinum reforming catalyst supported on an alumina base and in which alkyl halides are added to the feed to maintain the catalyst activity. The nitrogen compounds appear to react with the catalyst or with the alkyl halides or both to precipitate ammonium halide in the system. This causes mechanical difficulties, and can cause catalyst deactivation.

It has been determined that these residual quantities of hydrocarbon derivatives of nitrogen can be removed only by raising the desulfurization pressure to extremely high values, namely of the order of 5,000 to 15,000 p.s.i. and above. Such operating pressures in the desulfurization of hydrocarbons on a commercial basis are at the present time at least practically impossible.

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The present invention is directed to an improved process of the type discussed above for the desulfurization, denitrogenation, and aromatization of gasoline in which a substantially complete removal of hydrocarbon derivatives of nitrogen is obtained without the necessity of these extremely high superatmospheric pressures.

It is a primary object thereof of this invention to provide an improved process for the refining and conversion of gasoline.

It is a further object of this invention to provide a combined process for the catalytic desulfurization and denitrogenation of low grade gasoline streams followed by the catalytic reforming of the thus treated material including an intermediate step which completely removes residual quantities of hydrocarbon compounds of nitrogen from the feedstock to the reforming step.

It is a specific object of this invention to provide, in the desulfurization and reforming process referred to above, an intermediate adsorptive treatment of the feedstock to the reforming zone with a particular solid contact material so as to effect a substantially complete elimination of residual hydrocarbon compounds of nitrogen.

Other objects and advantages of the present invention will become more apparent to those skilled in the art as the description and illustration thereof proceed.

Briefly the present invention comprises an improved combination process for the production of high quality premium or aviation grade gasoline fuels having high antiknock ratings from hydrocarbon naphthas heavily contaminated with hydrocarbon derivatives of sulfur and nitrogen. The combination process includes three essential steps; namely a catalytic desulfurization and denitrogenation step in which hydrogen is consumed in the reaction, an adsorptive step in which residual hydrocarbon compounds of nitrogen are removed, and a catalytic reforming or dehydroaromatization step in which hydrogen is produced.

In the first step the gasoline boiling range feedstock is contacted in the presence of hydrogen with a desulfurization and denitrogenation catalyst whereby substantially all of the hydrocarbon derivatives of sulfur and the great majority of the hydrocarbon derivatives of nitrogen are decomposed catalytically. The products of these reactions are hydrogenated fragments of the sulfur or nitrogen compounds together with ammonia, and hydrogen sulfide. The resulting substantially sulfur-free gasoline is then cooled from the desulfurization temperature substantially to its dew point.

In the second process step, the thus cooled stream is then contacted with a granular solid zeolitic metalloaluminosilicate activated by partial dehydration and which has pores open to adsorption which are at least 7 Å. in diameter, and which preferably are of the order of 7 Å. to 13 Å. in diameter, or more. These materials exert extremely high preferential adsorptive forces for the minor amount of residual hydrocarbon derivatives of nitrogen present in the desulfurization effluent vapor even in the presence of hydrocarbons of the same boiling range. The effluent from this adsorption step is substantially free of hydrocarbon derivatives of nitrogen, or if any traces remain they are of such minor magnitude that they exert no measurable adverse effect upon the subsequent catalytic reforming step.

In the third step of the process the adsorption effluent containing substantially no hydrocarbon derivatives of sulfur and nitrogen is reheated to hydrocarbon reforming conditions and is contacted with a reforming catalyst. The dehydrogenation reactions convert naphthene hydrocarbons into aromatic hydrocarbons. In some cases, particularly where cobalt molybdate is used as the reforming catalyst, these naphthenes are at least in part produced simultaneously with the reforming reaction by dehydro-

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cyclization of paraffin hydrocarbons. The effluent from the catalytic reforming step is cooled and partially condensed and the gas rich in hydrogen produced during the reforming step is recirculated to the desulfurization and denitrogenation step together with fresh feed. This hydrogen is consumed in the desulfurization and denitrogenation reactions. The recycle hydrogen stream may be purified if desired to remove accumulations of hydrogen sulfide, ammonia, water vapor, low molecular weight hydrocarbons, and the like.

In the first or catalytic desulfurization and denitrogenation step of this process it is preferred to employ a cobalt molybdate catalyst supported on a silica stabilized activated alumina carrier. The cobalt molybdate catalyst may analyze between about 7% and 22% by weight of total cobalt oxide and molybdenum trioxide. The molecular ratio of cobalt oxide to molybdenum trioxide is in the range from about 0.2 to about 5.0 mols per mol. One preferred form of cobalt molybdate catalyst analyzes about 3% by weight cobalt oxide and 9% by weight molybdenum trioxide. The total cobalt and molybdenum oxide analysis in this catalyst is 12% and the molecular ratio is 0.64. Proper temperatures for effecting the desulfurization and denitrogenation lie between about 575° F. and about 900° F., preferred operating temperatures lying between about 700° F. and 850° F. The operating pressure may be varied widely between about 50 and 5,000 p.s.i.g. and is preferably operated between about 300 and 1,000 p.s.i.g. at a value which is substantially the same or slightly higher than the operating pressure used in the catalytic reforming step. The liquid hourly space velocity measured in liquid volumes of feed per volume of catalyst per hour may be varied between about 0.1 and about 10, but preferably is in the range of from 1.5 to 6.5. A hydrogen recycle gas analyzing between about 35% by volume and about 95% by volume of hydrogen is recirculated through the catalytic desulfurization zone at a rate of about 50 and 10,000 s.c.f./b. (standard cubic feet per barrel) of feed. Preferred hydrogen to feed ratios lie between about 1,000 and about 5,000 s.c.f./b. In the preferred operating conditions indicated above a low grade sulfur and nitrogen contaminated gasoline can be treated to produce an effluent gasoline having a substantially zero sulfur analysis and analyzing of the order of 100 to 300 parts per million of nitrogen, from a feed gasoline analyzing about 0.55% by weight of sulfur and about 0.27% by weight of nitrogen.

In the second or intermediate step of the process of this invention, the desulfurized and partially denitrogenated gasoline effluent produced from the catalytic desulfurization and denitrogenation step is passed through contact with a static or moving bed, or a fluidized body, of a natural or synthetic zeolitic metallo alumino silicate having pores of at least 7 Å. so as to remove residual traces of hydrocarbon derivatives of nitrogen. This contact is effected at substantially the same pressure as those employed in the desulfurization and reforming steps and at a temperature which is just above the dew point of the mixture of gasoline and hydrogen recycle gas. With lower ratios of hydrogen recycle gas, or where the recycle gas is separated prior to this step, this temperature approaches about 400° F. With higher recycle gas ratios this temperature may drop as low as about 275° F. Temperatures as high as the desulfurization temperature may be employed if desired although the adsorptive capacity of the specific adsorbent hereinafter defined is somewhat reduced.

It has been found that the specific zeolitic adsorbent employed in the present invention may not be substituted with the other known granular solid adsorbents such as silica gel, activated aluminum oxide, activated charcoal, and the like. At these operating temperatures the adsorption capacity of these materials is reduced to substantially zero, and there appears to be no particular affinity for nitrogen compound adsorption. With the pre-

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ferred adsorbent, however, it is found that the very high selective adsorption capacity for hydrocarbon derivatives of nitrogen is substantially unaffected at these temperatures.

The adsorbent employed in the process of this invention is a solid granular material having a mesh size range between about 2 and 100 mesh or smaller and preferably between about 4 and about 30 mesh for static or moving solids bed contact. It is used in the form of a dense compact bed of material through which the desulfurization effluent stream passes in the vapor phase. The process may employ the adsorbent in the form of a single static bed of material in which case the process is only semi-continuous. Preferably a plurality of two or more static beds of adsorbent is employed with appropriate remotely operable valving so that the feed stream is passed through one or more of the contacting vessels in a set while the regeneration gas stream passes through one or more of the other vessels in the set. In this case, the feed and product flows are continuous. In another modification, a moving solids bed may be employed. Here the flow of feed is maintained continuously through a first contacting or adsorption zone, and the flow of regeneration gas is maintained continuously through a second contacting or regeneration zone. The granular adsorbent is recirculated successively through these two zones. With the smaller sized mesh ranges of adsorbent, e.g. with powdered solids, the material may be fluidized in and by the fluid streams contacting it. The compact bed modifications are preferred since a greater number of theoretical and actual contact stages are more readily obtained in smaller and simpler equipment.

The present invention may not be carried out with the commonly available solid granular adsorbents as indicated above. It has been found that particular adsorbents which are highly efficient and preferred in the adsorptive denitrogenation step of the present invention are the natural or synthetic crystalline partially dehydrated metallo alumino silicates. The composition of one typical synthetic zeolite having a pore size of about 13 Å. is $5\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$. Another composition has pore sizes of 10 Å. They may be prepared by heating stoichiometric quantities of alumina and silica and excess caustic under pressure. The excess is washed out. Other desired metal ions may then be introduced by ion exchange. Part of the sodium in this material can be ion exchanged with concentrated salt solutions at super-atmospheric pressure and temperatures of 150–300° C. to introduce other metal ions. Certain naturally occurring minerals, such as chabazite, analcite, gmelinite, and the like, can be heated to dehydrate the molecule partially and obtain an activated zeolitic adsorbent similar in adsorption properties to the manufactured materials. These natural and synthetic materials are all zeolites and their sodium and calcium derivatives are very stable solids which apparently have "pores" available for adsorption which are quite uniform in size. Other derivatives have different sized "pores." The 10 Å. and 13 Å. metallo alumino silicate, and others with pore diameters above 7 Å. exert preferential adsorptive forces for hydrocarbon-nitrogen compounds in great preference to the hydrocarbons of the same boiling range.

In the process of this invention the solid contact material utilized for the adsorptive denitrogenation of the desulfurization effluent appears to be deactivated only very slowly. Ultimately in a long continued process the material may require regeneration due to the accumulation on the material of traces of very high molecular weight hydrocarbonaceous materials present in the feed stream. Since the temperature at which the feed contact occurs is approximately 400° F. and thus is relatively low, little if any chemical reaction ordinarily occurs in contact with the material. The accumulated deactivating materials may be removed from the metallo alumino silicate by heating to temperatures of the order of those

customarily employed in the oxidative regeneration of spent hydrocarbon conversion catalysts and passing a dilute oxygen-containing stream in contact therewith. Regeneration may also be effected by stripping with steam followed by contact at this temperature with an anhydrous gas.

In the third or catalytic reforming step of the process of this invention the desulfurized and denitrogenated gasoline is passed in the vapor phase through a reforming catalyst which may be molybdenum trioxide, chromium oxide, cobalt molybdate, or the noble metals. An excellent catalyst is one containing between about 0.01 and about 10% by weight of platinum and preferably between about 0.1 and 0.5% by weight of platinum. The catalyst is promoted by inclusion of a minor amount of a halide such as chloride or fluoride or both in the alumina carrier. With any of the known reforming catalysts the processing conditions may be as follows: The liquid hourly space velocity in this step may be varied between about 0.1 and 10, but preferably is about 1.0. A recycle gas containing hydrogen is also maintained flowing through the catalytic reforming zone. The quantity of such recycle gas ranges from about 50 to 10,000, but preferably is between about 1,000 and 5,000 s.c.f./b. The operating pressure may be between about 5 and about 500 p.s.i.g., and a pressure of about 300 p.s.i.g. is preferred. Suitable temperatures may be between about 800° F. and about 1050° F. Under the preferred operating conditions of the reforming step a reformed gasoline is produced substantially free of sulfur and nitrogen and which has an antiknock rating of the order of 100+(F-1+3 ml. TEL).

The process of this invention and the various modifications and applications thereof, as well as several forms of the apparatus in which the process may be effected, will be more readily understood by reference to the accompanying drawings in which:

Figure 1 is a schematic flow diagram of the process of this invention for refining and conversion of low grade gasolines, and

Figure 2 is a modification of the flow from the desulfurization to the adsorption steps.

Referring now more particularly to Figure 1, the essential elements of apparatus in which are effected the essential steps of the process of this invention include catalytic desulfurization zone 10, first and second adsorption zones 12 and 14, first and second catalytic reforming zones 16 and 18, and product-recycle gas separator zone 20. The process flow sheet will be described below in conjunction with a specific example of this invention applied to the refining and reforming of a low grade gasoline boiling range naphtha having the following properties:

TABLE I

Process feedstock

Boiling range, ° F.	120-440
Gravity, ° API	46.8
Sulfur, wt. percent	1.21
Nitrogen, p.p.m.	260
Knock ratings:	
F-1 clear	63.5
F-1+3 ml. TEL	71.0

The feed gasoline is introduced through line 22 at a rate of 5,000 barrels a day controlled by valve 24 and is heated and vaporized in vaporizer 26 to a temperature of about 750° F. Heater 26 is provided with fuel through line 28 controlled by valve 30 at a rate which is varied by means of temperature controller 32 in response to the temperature of vapor passing from furnace 26 through line 34 into catalytic refining zone 10. If desired, all or a portion of the hydrogen-containing recycle gas may be combined with the feed by passing it through line 36 controlled by valve 38 into the inlet to furnace 26, or it may be introduced through line 40 at a rate controlled by

valve 42 through hydrogen preheater 44 into admixture with the heated and vaporized feed flowing through line 34. The total hydrogen recycle rate is 10,000 M s.c.f. per day, or about 2,000 s.c.f./b.

The combined naphtha vapor and hydrogen recycle gas mixture passes at a pressure of about 500 p.s.i.g. and at a temperature of 750° F. through catalytic refining zone 10. This zone contains a static bed of cobalt molybdate catalyst analyzing 3% cobalt oxide and 9% molybdenum trioxide on a silica stabilized alumina carrier. The liquid hourly space velocity is about 4.0. During this contact under these conditions better than 99.5% of the hydrocarbon derivatives of sulfur in the feedstock is converted to hydrogen sulfide and hydrogenated hydrocarbon fragments. About 96.3% of the hydrocarbon derivatives of nitrogen are removed. The inspection of the product is given below in Table II.

TABLE II

Refining zone effluent analysis

Boiling range, ° F.	120-440
Gravity, ° API	50.5
Sulfur, wt. percent	0.0005
Nitrogen, p.p.m.	9.7
Knock ratings:	
F-1 clear	40
F-1+3 ml. TEL	66

This effluent from the catalytic refining zone 10 passes through line 46 into heat exchanger 48 in which the effluent is partially cooled and heat is recovered in reheating other process streams such as the feed to the catalytic reforming zone. The partially cooled effluent flows through line 50 through cooler 52 through which sufficient coolant is passed by means of line 54 in order to cool the effluent further to a temperature just above its dew point. This control is effected by means of temperature controller 56 and valve 58. The sulfur-free and substantially nitrogen-free effluent then flows through line 60, four-way control valve 62, and line 64 into and through first adsorber 12. Here is maintained a static bed of metallo alumino silicate adsorbent of 13 A. pore size. The liquid hourly space velocity of the stream passing through adsorber 12 is between about 5 and 10 volumes of liquid hydrocarbon per volume of adsorbent per hour. During this contact all residual traces of hydrocarbon derivatives of nitrogen present in the stream are removed by the adsorbent, and the nitrogen and sulfur-free effluent continues through line 66, four-way control valve 68, and is sent through means subsequently described to the catalytic reforming zone.

If desired, the modification in Figure 2 may be used. Here the desulfurization effluent is condensed in cooler 47, passed to separator 49 in which the noncondensed recycle and other gases are separated from the condensate through line 51. The condensate is revaporized and heated to a temperature somewhat above its end or dew point in vaporizer 53 and passed through contact with the adsorbent in zone 55'. The gas thus by-passes the adsorption step through line 55, and is introduced into the adsorption effluent for passage through the catalytic reforming zone. This brings the nitrogen compound concentration to a maximum and increases the amount thereof which can be adsorbed on the zeolitic silicate. If desired, the gas may be purified in treating zone 57 to raise the hydrogen concentration by removal of ammonia, hydrogen sulfide, and light hydrocarbon gases through line 59.

The 13 A. silicate adsorbent present in second adsorber 14 is shown being regenerated at temperatures ranging between about 900° F. and about 1100° F. by circulating therethrough a stream of flue gas in which is mixed between about 0.1% and about 10% by volume of oxygen. By this means the residual adsorbed hydrocarbon derivatives of nitrogen present on the adsorbent are

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burned forming combustion products which are removed from the system. Flue gas passes by means of recycle blower 70 at a rate controlled by valve 72 through regeneration cooler 74 in which the exothermic heat of combustion is dissipated. The cooled gas, at a temperature of about 750° F., continues through line 76, is mixed with air introduced through line 78 at a rate controlled by valve 80 forming a fresh regeneration gas. This gas passes through four-way control valve 68 and line 82 through secondary adsorber 14 in which the nitrogen compounds are burned and the adsorbent is regenerated. Hot flue gases at a temperature of about 1050° F. are discharged through line 84 and pass through four-way control valve 62 for division into two streams. One stream is recirculated as stated by means of blower 70 and the other stream is vented to the atmosphere through a stack by means of line 86 at a rate controlled by valve 88.

Four-way control valves 62 and 68 are operated remotely by means of cycle timer operator 90. This operator serves to reverse the settings of valves 62 and 68 periodically thereby alternating the contact of the 13 A. silicate adsorbent therein with the refining zone effluent and the regeneration gas as described.

The composition of the effluent from the adsorption zone and the feedstock to the catalytic reforming zone is given in Table III. The gravity, knock rating, and boiling range are substantially the same as noted in Table II.

TABLE III

Refining zone feedstock

Sulfur, wt. percent	0.0005
Nitrogen, p.p.m.	0.5

The adsorption effluent flows therefrom through line 92 through exchanger 94 through line 96 into reforming zone preheater 98. If desired, an added quantity of recycle hydrogen may be introduced through line 100 at a rate controlled by valve 102. By means of exchanger 94 and vapor reheater 98 the nitrogen-free hydrocarbon and hydrogen stream is reheated to reforming temperatures of the order of 910° F. This is controlled by means of valve 104 in fuel line 106 which is actuated by temperature controller 108. The reheated hydrocarbon and hydrogen stream flows through line 110 successively through first reforming zone 16, intermediate reheating zone 112, second reforming zone 18 and is discharged therefrom through line 114 through product cooler and condenser 116 into recycle gas-liquid product separator 20. First reforming zone 16 is maintained at an average reaction temperature of about 910° F. The effluent therefrom is cooled by means of endothermic dehydroaromatization reactions to a temperature of about 890° F. Interheater 112 reheats this effluent to about 915° F. for reaction in second catalytic reforming zone 18. The effluent from this zone is similarly cooled from this reaction temperature by these endothermic reactions and is removed therefrom at a temperature of about 900° F.

In separator 20 the reformed liquid product is removed through line 118 at a rate of about 4365 barrels per day controlled by valve 120 and liquid level controller 122. It is sent to production or further processing facilities not shown by means of line 124. The properties of this product are listed below in Table IV.

TABLE IV

Liquid product properties

Boiling range, °F.	124-424
Gravity, °API	43.7
Sulfur, wt. percent	0.00
Nitrogen, p.p.m.	0.2
Knock rating (F-1+3 ml. TEL)	101

A hydrogen-containing recycle gas is removed from the upper portion of separator 20 through line 126. The gas analyzes approximately 75% hydrogen and also contains light hydrocarbon gases together with water vapor,

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ammonia, and hydrogen sulfide if these have not been removed immediately after the desulfurization step. Depending upon the quantity of hydrogen and sulfur compounds present in the feed to the catalytic refining zone and the extent of dehydrogenation which takes place in the catalytic reforming zone, a net production of hydrogen may be involved in the process. In this case excess gas is bled from the system through line 128 at a rate controlled by valve 130 and pressure controller 132. If there is a net consumption of hydrogen, makeup hydrogen must be added to the system to maintain the pressure of operation and in this instance such makeup hydrogen is added through line 128 in the reverse direction.

The remaining quantity of gas flows through line 134 into recycle gas compressor 136 and from there through gas purification zone 138 in which hydrogen sulfide and ammonia, if not previously removed, are removed from the recycle gas. This is done in order to maintain the hydrogen concentration as high as possible in the recycle gas. Any of the many well known ways for removing ammonia and hydrogen sulfide from hydrogen and hydrocarbon-containing gases may be used. For example, the ammonia may be removed by washing with water or with dilute acids, hydrogen sulfide may be removed by washing with oil or water, or with monoethanolamine or diethanolamine, or the like. If desired, all or a portion of these contaminants may be removed. If desired, all or a portion of the hydrogen contaminants may also be removed. This may be done in any of the well known manners such as by oil absorption, adsorption on a solid adsorbent, low temperature distillation, and the like. The recycle gas is then passed through line 140 for recirculation in the process.

In order to illustrate in the foregoing process the effect of allowing the residual 10 p.p.m. of hydrocarbon compounds of nitrogen to remain in the feed to the catalytic reforming zone, the effluent from the catalytic refining zone 10 was by-passed around the adsorption zones 12 and 14 and sent directly to the catalytic reforming zone. Operating conditions were otherwise identical to those given in the foregoing example. The reformed product had the following properties:

TABLE V

Product analysis

Boiling range, ° F.	124-424
Gravity, ° API	43.7
Sulfur, wt. percent	0.0005
Nitrogen, p.p.m.	5.0
Knock rating (F-1+3 ml. TEL)	92

Ammonium halide deposits in the system under these conditions and deactivates the catalyst.

It is apparent that the removal of this relatively minor amount of hydrocarbon derivatives of nitrogen has effected a substantial improvement in the quality of the liquid product raising the knock rating about 9 points.

Although the process of this invention has been described above in detail by reference to a preliminary catalytic desulfurization and denitrogenation step and a subsequent catalytic dehydroaromatization step, the present invention is applicable in the treatment of hydrocarbon feedstocks to treat for complete nitrogen removal in the feedstock to such other catalytic conversions and refining processes which are adversely affected by the presence of such materials. For example, the catalytic reforming step described above may be substituted with a catalytic isomerization step, a catalytic cracking step, or the like. In each of these catalytic conversion processes the feed-stock is very desirably pretreated for the removal of hydrocarbon derivatives of sulfur. This is accomplished in catalytic desulfurization zone 10. Also each of these processes is very detrimentally affected by the presence of hydrocarbon derivatives of nitrogen. As indicated above, only the most extreme superatmospheric

pressures will remove catalytically all of these nitrogenous materials in the catalytic reforming and accordingly the intermediate adsorption step using the zeolitic adsorbents with pores of 7 Å. and over is used. In each of these cases the quantity and quality of the effluent from the subsequent conversion zone is markedly improved by the removal of all of these contaminants.

A particular embodiment of the present invention has been hereinabove described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be made by those skilled in this particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

We claim:

1. In a process wherein a normally liquid hydrocarbon mixture which is contaminated with normally incident organic sulfur and organic nitrogen compounds of substantially the same boiling range is (1) subjected to a catalytic desulfurization treatment in a desulfurization zone to produce a hydrocarbon effluent which is substantially free of organic sulfur compounds but contains small amounts of organic nitrogen compounds, and (2) said effluent is subjected to a catalytic conversion treatment in a conversion zone to produce a process product of improved qualities, said catalytic conversion treatment being one which is adversely affected by the presence of said small amounts of organic nitrogen compounds, the improvement which consists in contacting said effluent in the vapor phase with a partially dehydrated zeolitic metallo alumino silicate having pores of substantially uniform diameter greater than 7 Å. in an adsorption zone prior to subjecting said effluent to said catalytic conversion treatment.

2. A process according to claim 1 wherein the said catalytic conversion treatment comprises catalytic dehydroaromatization.

3. A process according to claim 1 wherein the said zeolitic silicate has a composition corresponding substantially to $5\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$ and has pores of substantially uniform diameter of about 13 Å.

4. A process according to claim 2 in combination with the steps of cooling and partially condensing the said effluent; separating the non-condensed gases from the condensate; revaporizing the condensate; introducing the revaporized condensate substantially free of non-condensable components into contact with said zeolitic silicate, and combining the non-condensed gases with the effluent from said adsorption zone for introduction into said conversion zone.

5. A process according to claim 1 in combination with the step of passing a hydrogen-containing gas with said hydrocarbon mixture through said desulfurization, adsorption, and conversion zones, separating said gas from the upgraded process product, and recirculating at least part of said gas into said desulfurization zone for passage therethrough in admixture with said hydrocarbon.

6. A process according to claim 1 in combination with the step of cooling the desulfurization zone effluent to just above the dew point thereof for contact with said metallo alumino silicate, and reheating the effluent from said adsorption zone prior to introduction to said conversion zone.

7. A process for upgrading hydrocarbon mixtures boiling in the gasoline range and contaminated with normally incident organic sulfur and nitrogen compounds which comprises passing said mixture through a desulfurization zone in the presence of hydrogen and a desulfurization catalyst while controlling the desulfurization conditions therein at temperatures between about 575° F. and about 900° F., pressures between about 50 p.s.i.g. and about 5000 p.s.i.g., liquid hourly space velocities between about

0.1 and 10.0 volumes of liquid feed per volume of catalyst per hour, and hydrogen recycle rates between about 50 s.c.f. and 10,000 s.c.f./b. of hydrocarbon, to produce a first hydrocarbon effluent substantially free of organic sulfur compounds but containing small amounts of organic nitrogen compounds passing said first effluent in the vapor phase through an adsorption zone in contact with a partially dehydrated zeolitic metallo alumino silicate adsorbent having pores of substantially uniform diameter of at least 7 Å. to produce a second hydrocarbon effluent substantially free of organic nitrogen compounds; passing said second hydrocarbon effluent through a reforming zone in the presence of hydrogen and a dehydroaromatization catalyst while controlling the reforming conditions therein at temperatures between about 800° F. and about 1050° F., pressures between about 5 and about 500 p.s.i.g., liquid hourly space velocities between about 0.1 and about 10.0 volumes of liquid hydrocarbon per volume of catalyst per hour, and hydrogen recycle rates between about 50 and about 10,000 s.c.f./b. of feed; cooling and partially condensing the effluent from said reforming zone; separating the condensate gasoline as the process product from the noncondensed gases; and recirculating at least part of said gas to said desulfurization zone.

8. A process according to claim 7 wherein said desulfurization catalyst comprises cobalt molybdate and contains between about 7% and 22% by weight total cobalt oxide and molybdenum trioxide, and in which the molecular ratio of cobalt oxide to molybdenum trioxide is between about 0.2 and 5.0 mols per mol.

9. A process according to claim 7 wherein said dehydroaromatization catalysts comprises between 0.01 and 10.0% by weight of a noble metal promoted by a halide.

10. A process according to claim 7 in combination with the step of periodically regenerating said metallo alumino silicate by contacting it with an oxygen-containing gas to burn adsorbed organic nitrogen compounds therefrom.

11. A process according to claim 7 in combination with the steps of cooling and partially condensing said first hydrocarbon effluent; separating the condensate from the noncondensed gases; revaporizing said condensate and introducing it into said adsorption zone; and passing said noncondensed gases into mixture with said second hydrocarbon effluent for introduction therewith into said reforming zone.

12. A process according to claim 11 in combination with the step of raising the hydrogen concentration in said noncondensed gases by removal therefrom of gases other than hydrogen.

13. A process according to claim 7 in combination with the step of controlling the temperature of the fluids passing through said adsorption zone at values slightly above the dew point thereof.

14. A process according to claim 7 wherein said zeolitic silicate has a composition corresponding substantially to $5\text{Na}_2\text{O} \cdot 6\text{Al}_2\text{O}_3 \cdot 15\text{SiO}_2$ and has pores of substantially uniform diameter of about 13 Å.

References Cited in the file of this patent

UNITED STATES PATENTS

2,717,230	Murray et al. -----	Sept. 6, 1955
2,758,064	Haensel -----	Aug. 7, 1956
2,763,603	Skinner -----	Sept. 18, 1956
2,882,244	Milton -----	Apr. 14, 1959

OTHER REFERENCES

- Linde: "Physical Properties of Molecular Sieves,"
 70 Form 9947-A, Union Carbide Bulletin.
 "Selective Adsorption with Zeolites," Chemical and Engineering News, volume 32, Nov. 29, 1954, page 3786.