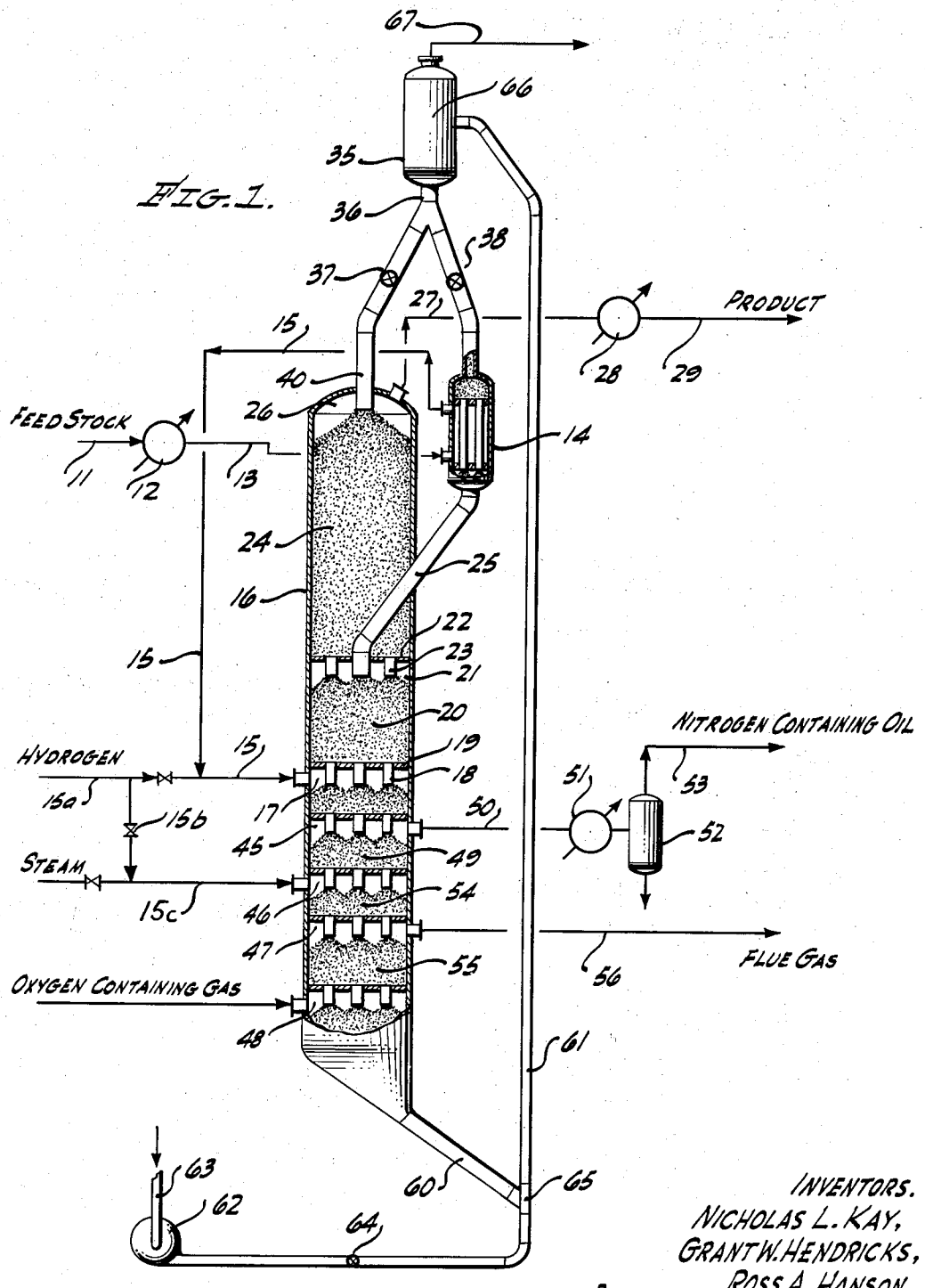
May 1, 1956 N. L. KAY ET AL 2,744,053

HYDROCARBON CONVERSION PROCESS, INCLUDING PRELIMINARY NITROGEN REMOVAL BY ADSORPTION

Filed April 26, 1951 2 Sheets-Sheet 1

FIG. 1.



INVENTORS.
NICHOLAS L. KAY,
GRANT W. HENDRICKS,
ROSS A. HANSON,
BY Ross J. Garofalo
ATTORNEY.

May 1, 1956 N. L. KAY ET AL 2,744,053

HYDROCARBON CONVERSION PROCESS, INCLUDING PRELIMINARY NITROGEN REMOVAL BY ADSORPTION

Filed April 26, 1951 2 Sheets-Sheet 2

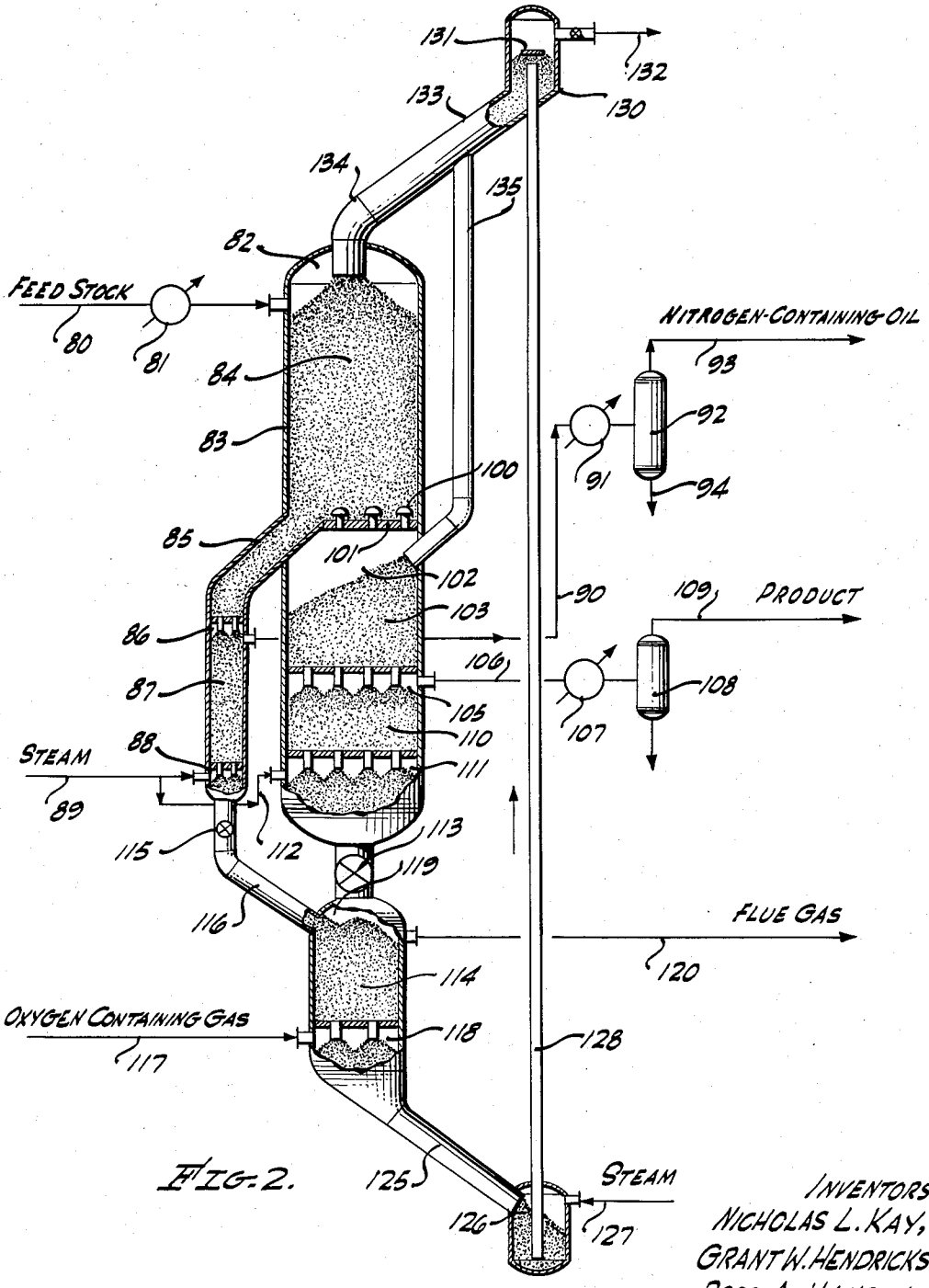


FIG. 2.

INVENTORS.
NICHOLAS L. KAY,
GRANT W. HENDRICKS,
ROSS A. HANSON,
BY Ross J. Garofalo
ATTORNEY.

United States Patent Office 2,744,053 Patented May 1, 1956

2,744,053

HYDROCARBON CONVERSION PROCESS, INCLUDING PRELIMINARY NITROGEN REMOVAL BY ADSORPTION

Nicholas L. Kay, Inglewood, Grant W. Hendricks, Brea, and Ross A. Hanson, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application April 26, 1951, Serial No. 223,062

6 Claims. (Cl. 196—28)

This process relates generally to methods for the conversion of hydrocarbons. More particularly, this invention relates to a process for the removal of nitrogen in a preliminary soprtion zone and a subsequent catalytic treating in a conversion zone wherein the efficiency in the conversion zone is improved as a result of the nitrogen removal.

The presence of nitrogen in refined hydrocarbon products is extremely objectionable. These compounds impart undesirable odors to the products, contribute to increased gum formation and lack of storage stability in the case of gasoline. In the case of hydrocarbon feed stocks for catalytic processes such as cracking, hydrocracking, isomerization, desulfurization, hydrogenation, clay treating and the like, the presence of nitrogen almost invariably contributes to increased rates of catalyst fouling at a given conversion level, decreased activity, and to the formation of less desirable products.

Furthermore, the dearth of high grade refining crudes has necessitated the industrial use of marginal petroleum stocks which contain larger amounts of combined nitrogen than previously employed stocks. Educted shale oils, tar sands oils and the like contain still higher quantities of nitrogen, which oils must be reckoned with in future refining processes.

It has now been found that nitrogen-containing compounds of the relatively lower boiling hydrocarbon stocks such as those boiling below 800° F. are quite readily retained by high surface area catalysts such as are employed in catalytic cracking processes for example.

It is therefore an object of this invention to provide a method for the removal of nitrogen from lower boiling hydrocarbon stocks by sorption on a high surface area catalyst.

It is another object of this invention to treat cracking stocks in two zones wherein the feed stock is first contacted in a relatively cold sorption zone to cause sorption of nitrogen compounds selectively on the catalyst and wherein the nitrogen depleted feed stock is then processed in a relatively hot conversion zone to cause catalytic cracking of the feed stock.

It is another object of this invention to treat gasoline stocks in a relatively cold sorption zone to sorb the nitrogen compounds selectively in the vapor phase and to treat the nitrogen depleted gasoline stock in a second catalytic treating conversion zone wherein the efficiency in the second zone is improved as a result of the nitrogen depletion.

It is another object of this invention to process hydrocarbon stocks boiling below about 800° F. in a nitrogen removal zone and to treat thereafter in a catalytic reaction zone.

It is another object of this invention to improve catalytic processing operations by subjecting the feed stocks to a preliminary nitrogen removal.

It is another object of this invention to produce low nitrogen gasoline and in greater quantities by the cracking or hydrocracking of a relatively nitrogen-free feed stock

wherein the nitrogen has been depleted by sorption on a portion of the catalyst.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly this invention relates to a new method for the catalytic processing of hydrocarbon stocks which contain appreciable quantities of nitrogen compounds and which boil generally in the range up to about 800° F. or less. In the method the nitrogen-containing feed stock is first subjected to a preliminary sorption step in a sorption zone at a relatively low temperature such as at a temperature from 10 to 200° F. above the 90% boiling point of the stock. The non-sorbed portion of the stock generally contains less than about 25% of the original nitrogen compounds and often contains as little as 10% or less of such compounds. The nitrogen-depleted feed stock obtained thereby has been found to be generally superior for subsequent catalytic processing in a conversion zone by virtue of the decreased nitrogen content and possibly due to other factors such as removal of polymers and other gums, removal of peroxides and miscellaneous other catalyst poisoning and fouling materials. Thus the nitrogen-depleted stock gives increased gasoline yields on catalytic cracking and also yields a gasoline of superior quality. Furthermore, the catalytic cracking of a low nitrogen stock lays down less carbon at a given conversion level, gives a higher yield of gasoline per unit of feed stock converted, and gives a higher gasoline to coke ratio which is generally also desirable.

In the treatment of gasoline stocks for the improvement of octane rating, storage stability, desulfurization and the like, past experience has shown that high temperatures such as in the range of 800 to 950° F. are particularly desirable for improving these and other characteristics of the gasoline. It has now been found that such conditions which are most favorable for effecting desulfurization, octane rating increase and the like are most adverse to effecting removal of nitrogen from such gasoline stocks. Thus it has been found that temperatures as low as about 10° to 200° F. above the 90% boiling point of the stock are most favorable for the removal of nitrogen on the catalyst. Furthermore, it has been found that the nitrogen so retained on the catalyst is in a sorbed state and as such is susceptible to desorption in a desorption zone by suitable methods such as heating, vacuum, steam or hydrogen stripping and the like. It has been found that the removal of nitrogen and the general upgrading of the stock is best accomplished by a preliminary low temperature nitrogen removal step which is followed by a high temperature catalytic treating step. Because of the reversibility of the sorption step, it is generally desirable that nitrogen-contaminated catalyst be excluded from the high temperature catalytic treating step. It has been found that a partially carboned catalyst from the high temperature catalytic cracking step is active to some extent for the removal of nitrogen in a low temperature sorption step and may in fact be employed for such processes.

Figure 1 shows one modification of the invention wherein a hot catalyst stream is indirectly exchanged with the cooler feed stock to produce a relatively cold catalyst stream and wherein the heated feed stock is then passed through a cold catalyst contacting sorption zone for the removal of nitrogen and thence through a higher temperature catalytic conversion zone and wherein the feed stock flows countercurrent to the catalyst throughout.

Figure 2 shows another modification of the invention wherein the circulating catalyst stream is split and the relatively cold feed stock is contacted directly with one portion of the hot catalyst so as to cool the catalyst to the

desired sorption temperature for the sorption zone and remove the nitrogen compounds from the vaporized feed stock and wherein the vapors from the sorption zone are then contacted with the second portion of hot catalyst to effect catalytic conversion in the conversion zone.

The hydrocarbon stocks which may be treated by the process of this invention comprise petroleoum distillates, shale oil distillates, hydrogenated coal fractions, tar sand distillates and the like, which boil generally in the range below about 800° F. and which preferably boil below about 700° F. Thus gasolines which boil generally in the range of about 100 to 400° F. and catalytic cracking charge stocks which boil generally in the range of 400 to 700° F. may be processed according to the method of this invention.

In general the nitrogen content of most gasoline stocks is considerably less than that of the corresponding catalytic cracking stocks. Thus gasolines containing between about 0.01% and 0.5% nitrogen by weight or more may be processed and gas oils containing between about 0.1% and 5.0% nitrogen by weight may also be processed.

Catalysts which may be employed for both sorption and catalytic conversion in the method of this invention include the adsorptive oxides such as silica, alumina, zirconia, thoria, magnesia, magnesium hydroxide and the like, or combinations of these oxides either with or without additional metal oxides, sulfides, and like compounds of the relatively heavier metals. It has been found generally that the use of heavier metal oxides and sulfides contributes little to increased sorption if nitrogen compounds and these compounds are not normally employed when they are not necessary in the catalytic treating step.

Catalytic agents which may be employed in the catalysts of this invention, include the oxides, sulfides, or other compounds of heavier metals such as chromium, molybdenum, cobalt, nickel, zinc, iron, lead, beryllium, cadmium, vanadium, manganese, tantalum, tungsten, titanium, platinum, columbium, scandium, thorium, aluminum, uranium, zirconium, tin, copper, etc., or combinations of two or more of such compounds.

Of these catalytic agents those which appear to be most effective and consequently find the greatest usage are the compounds of the heavy metals of atomic No. 22 to 42 including titanium, vanadium, chromium, manganese, iron, cobal, nickel, copper, zinc, yttrium, zirconium, columbium and molybdenum. The oxides of molybdenum, and of cobalt in the presence of molybdenum, have been found to be the preferred catalytic agents for the hydrocracking process of this invention.

The preferred catalyst for the sorption of nitrogen compounds is adsorptive silica and silica containing minor proportions of other oxides such as alumina, magnesia, and the like. Such silicas may be prepared synthetically by precipitation or co-precipitation or they may be prepared by acid treating or other treatment of naturally occurring clays. Commercially available cracking catalysts are predominantly silica in composition and may be employed for nitrogen sorption. A particularly desirable commercially available cracking clay is acid-treated montmorillonite clay and this has been found to be highly suited to nitrogen removal.

The nitrogen sorption step is generally carried out at pressures near atmospheric and at temperatures relatively close to the boiling range of the stock being treated. In certain cases however the gas oil may be treated at slightly elevated pressures and the gasoline may be treated at pressures up to 100 p. s. i., for example.

The liquid hourly space velocity through the sorption zone will generally be in the range of about 0.2 to 10 volumes of liquid feed per volume of catalyst per hour. The ratio by weight of catalyst to oil depends upon the nitrogen content of the oil and the temperature of sorption and is generally in the range of about 0.1 to 20 and preferably in the range of about 0.5 to 10.

The catalytic treating zone following the nitrogen removal zone is generally conducted in a conventional range of operating conditions. Thus in the case of cracking, the temperature is generally in the range of about 800 to 1000° F. and at pressures between about atmospheric and 100 p. s. i., and the space velocity is generally in the range of about 0.2 to 10 volumes of liquid feed per volume of catalyst per hour.

In the case of gasoline treating the temperature is generally in the range of about 750 to 1000° F. and at pressures between about atmospheric and 250 p. s. i. The liquid hourly space velocity is generally in the range of about 0.2 and 20 volumes of liquid feed per volume of catalyst per hour.

Perhaps this invention can best be understood by reference to the drawings.

Referring now more particularly to Figure 1 feed stock is introduced through line **11** and flows through heat exchanger **12** wherein it is partially heated and/or vaporized whence it flows through line **13** to heat exchanger **14** wherein it is exchanged with a hot catalyst stream described hereinafter. In the modification shown, the feed stock enters heat exchanger **14** and passes through the shell against the tubes carrying hot catalyst wherein the vaporization of the feed stock and the heating thereof is completed. Vaporized feed stock discharges from heat exchanger **14** through line **15** and is introduced into catalytic reactor **16** through feed stock engaging zone **17**. Feed stock engaging zone **17** comprises a transverse plate mounted within the tubular shell of reactor **16** and the plate is fitted with a series of downcomers **18** which permit the flow of catalyst downwardly therethrough and the flow of vapors upwardly therethrough. The extension of downcomers **18** below the transverse plate **19** provide a vapor space immediately below the plate which makes up feed engaging zone **17**. The vaporized feed stock passes upwardly through the downcomers and enters sorption zone **20** which is filled with downwardly moving catalyst at a temperature which is preferably somewhat above the boiling range of the feed stock. In sorption zone **20** the vaporized feed stock contacts descending catalysts and the catalyst selectively sorbs the nitrogen compounds from the vaporized feed stock. The non-sorbed feed stock which generally makes up about 95% or more of the original volume of feed stock then passes upwardly through a catalyst distributing zone **21** which is formed by a transverse plate **22** and a series of downcomers **23** which are similar to the previously described feed engaging zone **17**. The non-sorbed vapors pass upwardly through downcomers **23** into catalytic treating zone or conversion zone **24** which is filled with hot descending catalyst at the desired conversion temperature.

Generally the temperature of catalytic treating zone **24** is maintained 100° F. or more above the temperature of sorption zone **20**. This temperature differential is maintained by passing cooled catalyst from previously described exchanger **14** downwardly through line **25** into catalyst mixing zone **21**. In mixing zone **21** hot carboned catalyst from catalytic treating zone **24** is mixed with cooled catalyst from exchanger **14** to form a cool catalyst mixture of the desired sorption temperature. It will be apparent also that the total catalyst flow rate through zone **20** will necessarily be substantially greater than through zone **24**. This provides a higher effective catalyst/oil ratio in sorption zone **20** than in conversion zone **24**.

In catalytic conversion zone **24** the nitrogen-depleted feed stock is caused to undergo desulfurization, octane rating improvement, storage stability improvement, catalytic cracking, hydrocracking, hydrogenation or the like. The converted hydrocarbons from catalytic treating zone **24** pass upwardly to product disengaging zone **26** and

are withdrawn therefrom through line 27. Products in line 27 pass through interchanger 28 and line 29 to product storage not shown or fractionation.

Hot regenerated catalyst in separating vessel 35 is withdrawn through line 36 and is split to flow through either valve 37 or valve 38. Valve 38 controls the flow of hot regenerated catalyst through catalyst interchanger 14 wherein the catalyst is cooled to the desired temperature for admission to the sorption zone.

The hot regenerated catalyst flowing through valve 37 passes through line 40 at the top of reactor 16 and passes into catalytic treating zone 24. The descending catalyst contacts ascending hydrocarbon vapors and effects the catalytic conversion thereof. Hot carboned catalyst from catalytic treating zone 24 descends through catalyst mixing zone 21 wherein it is mixed with colder freshly regenerated catalyst from exchanger 14 flowing through line 25. The mixing of the colder catalyst and the hot carboned catalyst produces a catalyst mixture having the desired sorption temperature in sorption zone 20. The cooled carboned catalyst is generally about 50% as active as fresh uncarboned catalyst for the sorption of nitrogen compounds, i. e. two volumes of carboned catalyst are as active as one volume of fresh catalyst.

In sorption zone 20 the mixture of carboned and uncarboned catalyst containing varying amounts of nitrogen compounds in a sorbed state flows downwardly and successively through nitrogen-oil disengaging zone 45, stripping steam and/or sealing steam engaging zone 46, regeneration gas disengaging zone 47 and oxygen-containing regeneration gas engaging zone 48. The catalyst containing sorbed nitrogen compounds after passing through nitrogen-oil disengaging zone 45 passes through nitrogen-oil stripping zone 49. In nitrogen-oil stripping zone 49 steam admitted through steam engaging zone 46 passes upwardly through the descending catalyst and desorbs the sorbed nitrogen compounds. The mixture of steam and nitrogen-containing oil is withdrawn from nitrogen disengaging zone 45 and flows through line 50 to cooler 51 and separator 52. The less dense oil phase in separator 52 is removed overhead in line 53 whence it passes to nitrogen-oil-containing storage not shown. Condensed steam is discharged from the bottom of separator 52. Heating coils, not shown, may be employed in stripping zone 49 in place of steam injection or concurrently therewith to cause desorption.

The steam-stripped catalyst from stripping zone 49 contains small amounts of residual nitrogen compounds and partly carboned catalyst. This mixture passes through sealing zone 54 and regeneration gas disengaging zone 47 into regeneration zone 55. In regeneration zone 55 oxygen-containing gas introduced in regeneration gas engaging zone 48 passes upwardly through the descending catalyst and combusts residual sorbed nitrogen compounds and miscellaneous carbon, sulfur and nitrogen deposits. Gases from regeneration zone 55 are withdrawn from regeneration gas disengaging zone 47 through discharge line 56.

A small amount of steam in stripping steam engaging zone 46 is permitted to flow downwardly through sealing zone 54 to prevent upflow of regeneration gas which otherwise would contaminate the upper zones. Hot regenerated catalyst from regeneration gas engaging zone 48 passes downwardly through line 60 whence it passes into the catalyst conveyance zone indicated generally by 61.

In the particular catalyst conveyance shown lifting gas such as flue gas, steam, nitrogen or the like is introduced into blower 62 through line 63 whence it passes through valve 64 and enters lifting zone 65. Upwardly moving gas in lifting zone 65 entrains catalyst flowing downwardly in line 60 and transports it upwardly through conveyance zone 61 into the separation zone 66 within the interior of vessel 35. In separation zone 66 the relatively large diameter of the vessel compared to the diameter of conveyance zone 61 causes the catalyst to settle out and collect in the bottom of the vessel. The separated gases are withdrawn from the top of vessel 35 through line 67. The hot regenerated catalyst is then returned through line 36 and valves 37 and 38 as previously described.

In another modification of the invention hydrogen may be introduced into the conversion zone 24 to cause hydrogenation, hydrocracking, hydrodesulfurization and the like, or it may be introduced into the stripping zone 49 to cause hydrogenation of the sorbed nitrogen compounds from the catalyst.

Referring again to Figure 1, hydrogen is introduced through line 15*a* and thence into line 15 whence it flows with the feed to feed engaging zone 17 whence it flows upwardly through the sorption zone 20 and catalytic treating zone 24. Alternatively, or concurrently, the hydrogen passes through valve 15*b* into line 15*c* whence it flows through stripping zone 49 wherein it induces hydrogenation of the sorbed nitrogen compounds to form low boiling nitrogen compounds and hydrocarbons which are withdrawn through line 50.

Referring now more particularly to Figure 2 feed stock is introduced through line 80 whence it flows through exchanger 81 wherein it is heated and partially or completely vaporized whence it passes into feed stock engaging zone 82 which is the vapor space existing at the top of reactor 83. In feed stock engaging zone 82 the feed stock is passed into contact with hot catalyst either by spraying, passing the vapors into contact therewith or the like. The hot catalyst completes the vaporization of the feed stock and maintains the temperature of sorption zone 84 at a suitable sorption temperature which is somewhat above the boiling range of the feed stock. In sorption zone 84 the nitrogen compounds of the feed stock are selectively sorbed on the catalyst and the non-sorbed vapors flow concurrently downwardly with the catalyst.

At the bottom of sorption zone 84 the catalyst containing sorbed nitrogen compounds is withdrawn through line 85 whence it passes through nitrogen oil disengaging zone 86, stripping zone 87 and steam engaging zone 88. Steam is introduced through line 89 into steam engaging zone 88 and passes upwardly through descending catalyst containing sorbed nitrogen compounds in stripping zone 87 wherein the nitrogen compounds are partly or completely removed from the catalyst by stripping. The stripping steam and nitrogen oil is removed from nitrogen oil disengaging zone 86 and passes through line 90 to cooler 91 and thence to separator 92. In separator 92 the condensed lighter oil phase is withdrawn from the tube through line 93 and passed to nitrogen-rich oil storage. Condensed steam is withdrawn from the bottom of separator 92 through line 94.

Vapors from sorption zone 84 pass through vapor disengaging zone 100 which permits the downflow of vapors but prevents the downflow of catalyst therethrough. In one modification such disengaging zone consists of a transverse plate 101 with a series of upwardly projecting tubes which are partially capped at the top. Such tubes permit gases to flow downwardly around the cap and thence downwardly through the tubes while preventing a similar flow of catalyst.

Vapors from disengaging zone 100 pass into vapor engaging zone 102 and thence into catalytic treating zone 103. Catalytic treating zone 103 is supplied with hot fresh catalyst through line 135 which heats the vapors to the desired catalytic treating temperature and maintains catalytic treating zone 103 at the desired reaction temperature.

In catalytic treating zone 103 conversions such as desulfurization, catalytic cracking, clay treating and the like are effected. Carboned catalyst from catalytic treating zone 103 and converted hydrocarbon vapors flow downwardly through product disengaging zone 105. In product disengaging zone 105 the converted hydrocarbon vapors are removed from the carboned catalyst and pass

through line **106** to cooler **107**, separator **108**, whence the product is withdrawn through line **109** and passes to product storage not shown. Carboned catalyst from product disengaging zone **105** passes downwardly through stripping zone **110** and stripping steam engaging zone **111**. Stripping steam introduced into stripping steam engaging zone through line **112** passes upwardly through stripping zone **110** and strips residual hydrocarbons from the carboned catalyst and is removed therewith from product disengaging zone **105**. Stripped carboned catalyst from steam engaging zone **111** passes downwardly through pressuring means **113** which is a star feeder or other suitable device for conveying solids from a low pressure area to a higher pressure area. Solids discharged from star feeder **113** pass to regeneration zone **114**.

Catalyst which has been stripped of sorbed nitrogen compounds and which flows downwardly through steam engaging zone **88** passes through a similar pressuring zone **115** whence it flows through line **116** to regeneration zone **114**.

Oxygen containing gas for regeneration flowing through line **117** passes into regeneration gas engaging zone **118** and flows upwardly through regeneration zone **114** wherein it oxidizes carbonaceous deposits on the catalyst and also oxidizes any residual sorbed nitrogen compounds thereon. Spent regeneration gases are collected at the top of the regeneration zone in regeneration gas disengaging zone **119** and are discharged through line **120**.

In the method of catalyst conveyance shown in Figure 2 a lift line of the so-called "mass flow" type is employed. In this particular modification regenerated catalyst from regeneration gas engaging zone **118** passes through line **125** to vessel **126**. Steam, flue gas, nitrogen or other lifting gas is introduced into the upper part of vessel **126** through line **127** and exerts a downward pressure on the solids causing them to rise within tube **128** which forms the conveyance line. Conveyance line **128** terminates in a relatively wider diameter vessel **130** and a plate **131** is positioned somewhat above the open upper end of conveyance line **128** and inpedes the flow of solids, thereby exerting a back pressure on the solids discharging from line **128**. In vessel **130** the lifting gas is disengaged from the catalyst and is withdrawn through line **132** while the separated solids collect in the bottom of vessel **130** and are withdrawn through line **133**.

The catalyst flow in line **133** splits with part passing into line **134** and the remainder passing into line **135**. Catalyst in line **134** passes into sorption zone **84** wherein a part of the heat content of the catalyst is employed in vaporizing the colder feed stock. The portion of the catalyst flowing through line **135** passes to catalytic treating zone **103**.

It is apparent that the regeneration in this type of apparatus is conducted at a higher pressure than is the sorption and catalytic treating. This differential is created by star feeders **113** and **115** and permits the use of a mass flow-type lift line for conveying the solids. Thus the pressure differential across conveyance line **128** is made possible by the transfer of solids from relatively low pressure zones into high pressure zones. The use of the mass flow lift line in this particular case has the particular advantage in that it permits the regeneration in regeneration zone **114** to be carried out under pressure so as to permit greater rates to regeneration and heat removal of the regenerating catalyst. Furthermore the use of low pressure in the sorption zone permits the use of lower temperatures therein with an improvement in the removal of nitrogen compounds. Thus it is seen that the use of a mass flow lift line offers numerous advantages in the particular process.

Perhaps the process and advantages of this invention can best be understood by reference to the following examples:

EXAMPLE I

One series of experiments was carried out in order to show the adverse effects of nitrogen compounds on catalytic cracking. In the particular series of experiments an East Texas gas oil having the following characteristics was selected for experimentation:

East Texas gas oil—	
Nitrogen, weight per cent	0.02
Sulfur, weight per cent	0.12
Engler distillation (ASTM), °F.:	
Initial	417
10%	483
50%	533
90%	632
Maximum	713

A portion of the foregoing gas oil was blended with quinaldine in an amount sufficient to form a gas oil containing 0.27% nitrogen by weight. Quinaldine has been found to occur in California straight run kerosene (Bailey et al. JACS 52 1239–50 (1950)). The original nitrogen-free gas oil and nitrogen-rich blend were then tested for catalytic cracking under the following conditions:

Temperature, °F	850
Pressure, p. s. i. a	15
Liquid hourly space velocity, by volume	3.0
Catalyst to oil ratio by wt	1.5

The following data compare the results of the catalytic cracking and the distribution of nitrogen between the products for the two cracking runs:

Nitrogen Content of Feed Stock, Wt. Percent	0.02	0.27
Product Gasoline, Vol. Percent of Feed	27.2	10.9
Product Gasoline, Nitrogen Content Wt. Percent	0.001	0.144
Product Gasoline, Octane Rating (F-2)	76	71
Gas Oil Residue, Nitrogen Content, Wt. Percent	0.003	0.221
Conversion, Vol. Percent of Feed	36.9	16.0

The foregoing data show the deleterious effect of the addition of quinaldine in a number of different ways. The volumetric yield of gasoline per pass is decreased from 27.2 to only 10.9 volume per cent while the gasoline which is obtained has a prohibitively high nitrogen content and is of lower octane rating than is obtained in the absence of nitrogen compounds. Thus it is clear that it is highly desirable to remove nitrogen compounds prior to catalytic cracking of gas oils.

Similar results are obtained where a gas oil is subjected to hydrocracking and the deleterious effects are of somewhat similar magnitude.

EXAMPLE II

In another series of experiments the gas oil described in Example I after blending with quinaldine to form a gas oil containing 0.27% nitrogen was subjected to catalytic cracking at a series of temperatures of 750° F. and 950° F. The following results were obtained wherein the reaction conditions were the same as those described in Example I with the exception that the catalyst to oil ratio was 5.0:

Reaction Temperature, ° F	750	950
Product Gasoline:		
Volume Percent of Feed	16.0	20.3
Nitrogen Content, Wt. Percent	0.008	0.070
Gas Oil Residue: Nitrogen Content, Wt. Percent	0.045	0.160
Conversion	29.4	38.3
Nitrogen Retention on Catalyst, percent of total Nitrogen passed over Catalyst during run	90	51

The foregoing data show that the nitrogen content of the hydrocarbons is reduced only slightly at higher temperatures and that by operation at lower temperatures such as 750° F. and particularly at higher catalyst to oil ratios as much as 90% of the nitrogen is removed. Other work shows that when the sorption temperature is lowered

still more that still larger amounts of nitrogen e. g. 95–98% may be sorbed on the catalyst.

EXAMPLE III

In order to show that the same results are obtained with actual catalytic cracking stocks containing nitrogen, a commercially available cracking stock having the following characteristics was subjected to a sorption step:

Nitrogen, wt. per cent	0.186
Sulfur, wt. per cent	1.216
Engler distillation (ASTM), °F.:	
Initial	240
10%	462
50%	628
90%	720
Maximum	725

In the sorption step this gas oil was passed over a commercial cracking catalyst of the acid treated montmorillonite type at a catalyst to oil ratio of 5.0 and at a temperature of 750° F. Under these conditions 82.7% of the nitrogen in the feed stock was retained by the catalyst and only 7.3% remained in the unconverted gas oil which amounted to 46.5 volume per cent of the original charge stock.

It is apparent that the nitrogen compounds of actual catalytic cracking stocks are retained in good yield by low temperature sorption.

EXAMPLE IV

In another series of experiments a gasoline boiling range stock obtained by catalytic cracking of high nitrogen, high sulfur gas oils was obtained which had the following characteristics:

Gravity, °API	51.4
Sulfur, wt. per cent	0.29
Nitrogen, wt. per cent	0.037
Engler distillation (ASTM), °F.:	
Initial	127
10%	163
50%	264
90%	369
Maximum	414

The gasoline was passed over a catalyst which had been partially deactivated by commercial usage in a commercial TCC cracking unit so that its activity was 28 compared to a fresh activity of about 39. The following test conditions were employed:

Pressure, p. s. i. a	15
Liquid hourly space velocity	0.5
Catalyst to oil ratio	1.0

The products obtained thereby were fractionated to obtain a C_5–330° F. cut and a 330 to 400° F. cut. The corresponding fractions from the untreated feed contained 0.019% nitrogen, 0.25% sulfur and 0.088% nitrogen and 0.37% sulfur by weight respectively. The following data were obtained for the sulfur and nitrogen contents of the series of runs:

Nitrogen content

Reaction Temperature, ° F	600	850
C_5–330° F. cut	0.007	0.016
330–400° F. cut	0.029	0.060

Sulfur content

Reaction Temperature, ° F	600	850
C_5–330° F. cut	0.28	0.24
330–400° F. cut	0.32	0.26

It is apparent from the foregoing data that high temperatures favor sulfur removal while low temperatures favor nitrogen removal. Other data show that the use of temperatures below 600° F. results in still further improved nitrogen removal. It is also apparent that the sulfur removal at the 600° F. temperature range is substantially nil. Octane rating is improved at the 850° F. reaction temperature, as is the removal of gums, when these are compared to a reaction temperature of only 600° F.

EXAMPLE V

In another series of experiments a large quantity of denitrogenated gasoline is prepared by the sorption method and is then subjected to desulfurization at a temperature of 900° F. at a liquid hourly space velocity of 1.0 at atmospheric pressure. When the denitrogenated gasoline is compared with the raw gasoline for desulfurization and octane rating increase under these conditions, it is found that the results are considerably more favorable in the case in which the nitrogen is removed by the preliminary adsorption step.

EXAMPLE VI

In another series of experiments the catalyst was coked by desulfurizing low nitrogen gasoline and the coked catalyst was then tested for nitrogen sorption activity. It was found that the nitrogen sorption activity was present in the coked sample of catalyst to the extent of about 50% of that for the uncoked fresh samples. Similarly, favorable results were obtained when catalyst, which had been coked during the cracking of a low nitrogen gas oil, was tested for sorbing nitrogen compounds from gas oil.

It is thus apparent that in its broad application this invention comprises a two-step method for catalytically treating hydrocarbon stocks of the gasoline and kerosene boiling range wherein the material is subjected to a preliminary removal of nitrogen in a sorption zone and is subsequently subjected to catalytic treatment in a catalytic conversion zone. These steps may be carried out in any suitable catalytic processing method such as moving bed, fluidized bed, fixed bed, slurry type media and the like.

In the sorption step the feed stock is separated into a nitrogen rich oil which is sorbed on the catalyst and a nitrogen-lean oil which is non-sorbed by the catalyst. The nitrogen-lean oil is thereafter subjected to treatment in a conversion zone. The nitrogen-rich oil is removed from the catalyst. The methods for removing the nitrogen compounds from the catalyst which have been described hereinabove include hydrogenation, combustion, and/or desorption as in vacuum or by steam stripping, heating and the like. It is apparent however that other methods such as solvent treatment, acid treatment, stripping with other compounds such as alcohols, acids and the like may be similarly employed.

The foregoing disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims.

We claim:

1. A process for the catalytic conversion of a mineral oil distillate boiling below about 700° F. and containing between about 0.01% and 5.0% by weight of nitrogen in the form of organic bases, which comprises flowing a compact bed of granular catalyst through a relatively cool sorption zone, then through a regeneration zone wherein said catalyst is subjected to combustion-regeneration and is reheated to at least the temperature of the hereinafter specified conversion zone, dividing the resulting regenerated catalyst into a first stream and a second stream, flowing said first stream through a cooling zone and then into said sorption zone, flowing said second stream through a relatively hot conversion zone and then into said sorption zone, countercurrently contacting said distillate in vapor phase first with the combined catalyst streams in said sorption zone at a temperature between about 10° and 200° F. above the 90% boiling point of said distillate, a pressure between about atmospheric and 100 p. s. i. g., and at a flow rate controlled to provide a catalyst/oil

ratio between about 0.1 and 20.0 thereby sorbing a major proportion of said nitrogen bases on said catalyst without effecting any substantial degree of conversion, withdrawing nitrogen-lean distillate from said sorption zone, countercurrently contacting said nitrogen-lean distillate with said second catalyst stream in said conversion zone at a temperature between about 750° and 1000° thereby effecting a substantial conversion of said nitrogen-lean distillate, said sorption zone being maintained at a temperature at least 100° F. lower than said conversion zone, said catalyst comprising a major proportion of at least one adsorptive oxide selected from the group consisting of silica, alumina, and natural clays.

2. A process according to claim 1 wherein said regeneration zone is divided into a first, non-oxidizing desorption zone wherein sorbed nitrogen compounds are removed, and a second oxidizing zone wherein coke and heavy residuals are burned from said catalyst.

3. A process according to claim 1 wherein the weight ratio of catalyst to distillate in said sorption zone is between about 0.5 and 10.0.

4. A process according to claim 1 wherein said mineral oil distillate is a gas oil boiling below about 700° F. and containing between about 0.1% and 5.0% of nitrogen in the form of organic bases, and wherein said contacting temperature in said sorption zone is not more than about 750° F., and said conversion is cracking.

5. A process according to claim 1 wherein said mineral oil distillate is a gasoline fraction boiling below about 400° F. and containing between about 0.01% and 0.5% of nitrogen in the form of organic bases, and said conversion is desulfurization.

6. A process according to claim 1 wherein said mineral oil distillate is a gasoline fraction boiling below about 400° F. and containing between about 0.01% and 0.5% of nitrogen in the form of organic bases, and said conversion is reforming to improve the octane rating of said gasoline.

References Cited in the file of this patent

UNITED STATES PATENTS

2,042,298	Davis	May 26, 1936
2,203,470	Pier et al.	June 4, 1940
2,384,315	Kuhl	Sept. 4, 1945
2,414,973	Nelson	Jan. 28, 1947
2,432,644	Alther	Dec. 16, 1947
2,441,572	Hirschler	May 18, 1948
2,507,523	Houdry	May 16, 1950
2,528,586	Ford	Nov. 7, 1950
2,566,353	Mills	Sept. 4, 1951
2,582,415	Claussen	Jan. 15, 1952